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Surface Tension of Phenol-Formaldehyde Wood Adhesives

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Pinus taeda L.

Schlüsselwörter (Sachgebiete)
Oberflächenspannung
Phenolharz
Phenol
Formaldehyd
Natriumhydroxid
Adhäsion
Wasserstoffbindung
Methylolgehalt
Rohdichte
Härtung
Sperrholz
Pitch pine

Surface Tension of Phenol-Formaldehyde Wood Adhesives

Summary

Thirty-six phenol (P) formaldehyde (F) resins were formulated to complete a factorial arrangement: three NaOH/P molar ratios (0.4, 0.7, and 1.0), three solids contents (37, 40, and 43 percent), and four F/P molar ratios (1.6, 1.9, 2.2, and 2.5).

Surface tension ranged from 68.4 to 79.9 dynes/cm. and was affected most by NaOH/P ratio, next by F/P molar ratio, and least by solids content. On the average, surface tension increased as NaOH/P and F/P ratios increased. At NaOH/P ratio of 0.4 surface tension increased as solids content increased, but at ratios of 0.7 and 1.0 this relationship was reversed.

The relationship between surface tension and bond quality in loblolly pine plywood was curvilinear. Increases in surface tension caused difficulty in obtaining spontaneous spreading of the glue. Resins with high surface tension tended to form impervious skins while curing and made inferior bonds.

Oberflächenspannung von Phenol-Formaldehyd-Kunstharzbindemitteln

Zusammenfassung

Es wurden 36 verschiedene Kunstharz-Kombinationen aus Phenol (P) — Formaldehyd (F) gemäß Betriebsbedingungen hergestellt und geprüft: drei NaOH/P Mol Verhältnisse (0,4; 0,7 und 1,0), drei Festharzgehalte (37, 40 und 43%) und vier F/P Mol Verhältnisse (1,6; 1,9; 2,2 und 2,5). Die Oberflächenspannung lag zwischen 68,4 und 79,9 dyn/cm und wurde am meisten durch das NaOH/P Verhältnis, weniger stark durch das F/P Verhältnis und am wenigsten durch den Festharzgehalt beeinflußt. Im Durchschnitt wuchs die Oberflächenspannung mit zunehmenden NaOH/P und F/P Verhältnissen. Bei einem NaOH/P Verhältnis von 0,4 wuchs die Oberflächenspannung mit steigendem Festharzgehalt, bei Verhältnissen von 0,7 und 1,0 war diese Beziehung jedoch umgekehrt.

Die Beziehung zwischen Oberflächenspannung und Verleimungsgüte war bei Pitch pine Sperrholz kurvilinear. Bei wachsender Oberflächenspannung ergaben sich Schwierigkeiten bei der spontanen Leimausbreitung. Harze mit großer Oberflächenspannung neigten dazu, undurchdringliche Häute während des Härtevorgangs auszubilden und ergaben schlechte Verleimungen.

Although the surface tension of a liquid adhesive affects surface pressure, spreading coefficient, and work of adhesion, few studies have been made on wood glues. Horioka et al. (1958) and Herczeg (1965) briefly mentioned strengths of urea resins whose surface tensions had been modified by addition of surfactants. More recently, in a study examining the relations between basic properties of phenolic resins and wood adhesion, the present author (1971) correlated surface tensions with bond quality in southern pine (loblolly pine, *Pinus taeda* L.) plywood. The results prompted further examination of the data in an effort to develop criteria for controlling both formulation and performance of resin adhesives. This paper reports the effects of various resin formulation factors on surface tension and, in turn, on bond quality.

Procedure

Resin preparation. All resins were prepared in the laboratory; formulation variables were:

Molar ratio of sodium hydroxide to phenol (NaOH/P) — 0.4, 0.7, and 1.0.
Molar ratio of formaldehyde to phenol (F/P) — 1.6, 1.9, 2.2, and 2.5.
Concentration of reaction mixture (percentage of weight of pure sodium hydroxide, phenol, and formaldehyde) — 37, 40, and 43.

Thus, 36 resins were formulated. As each was replicated, 72 batches were prepared. The methods of resin preparation have been described in a previous paper (Hse 1971).

Surface tension measurement. The surface tension of each resin was measured with a Du Nouy ring suspended from the fixed crosshead of an Instron testing machine set at maximum sensitivity (10 g full scale). Resin in a beaker was supported on the moving crosshead of the machine. Upward movement of the crosshead positioned the beaker at the starting point, i. e., the suspended ring was immersed in the resin. The crosshead was then lowered at a speed of 0.25 cm per minute, and pull on the Du Nouy ring was recorded continuously. The maximum pull observed (at the instant of rupture of the ring from the resin surface) permitted calculation of surface tension from a calibration curve that had been established by evaluating 11 liquids of known surface tension (Fig. 1). All measurements were in a room maintained at 25°C and a relative humidity of 50 percent.

Evaluation of glue bond quality. Glue bond quality was measured by evaluating wet shear strenght and percentage of wood failure in plywood specimens subjected to the vacuum-pressure cycle for exterior glue lines (PS-1-66), and by measurement of delamination after 3 months of exterior exposure.

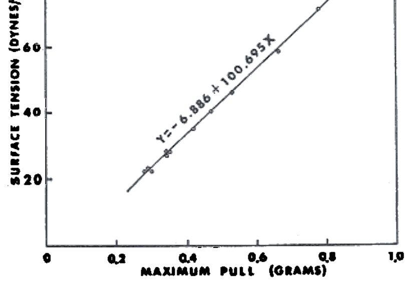

Fig. 1. Relationship between maximum pull on Du Nouy ring and liquid surface tension

Table 1

Surface tension of phenol-formaldehyde resins related to glue bond quality in three-ply, $^3/_8$-inch southern pine plywood

Molar ratio NaOH/P and resin solids content (percent)1)	Molar ratio1) F/P	Surface tension	Shear strength	Wood failure	Delamination
		Dynes/cm	kg/cm^2	Percent	
0.4 mole NaOH/P					
37	1.6	69.8	18.7	76	39
37	1.9	70.2	20.3	75	14
37	2.2	68.9	18.2	79	34
37	2.5	71.9	20.1	71	46
40	1.6	70.3	21.5	60	29
40	1.9	71.5	20.4	82	27
40	2.2	70.8	19.6	75	17
40	2.5	70.6	18.7	78	28
43	1.6	71.1	21.3	69	11
43	1.9	71.3	20.3	75	15
43	2.2	71.7	18.8	76	42
43	2.5	72.7	19.2	64	45
0.7 mole NaOH/P					
37	1.6	76.3	10.8	30	14
37	1.9	76.2	11.2	38	57
37	2.2	77.7	10.5	30	53
37	2.5	79.1	12.4	27	50
40	1.6	76.2	17.2	50	49
40	1.9	75.5	17.4	66	54
40	2.2	77.1	13.8	51	52
40	2.5	78.1	14.9	48	48
43	1.6	76.4	17.3	61	35
43	1.9	75.3	18.1	63	24
43	2.2	77.4	18.5	66	44
43	2.5	76.4	16.7	54	49
1.0 mole NaOH/P					
37	1.6	76.5	17.9	50	58
37	1.9	78.3	11.8	25	50
37	2.2	79.1	11.0	28	39
37	2.5	79.2	11.2	21	64
40	1.6	76.9	15.2	50	53
40	1.9	77.9	15.7	65	53
40	2.2	78.0	15.4	58	54
40	2.5	78.4	17.7	55	66
43	1.6	77.3	17.1	62	42
43	1.9	77.1	16.4	45	38
43	2.2	76.7	18.4	58	48
43	2.5	75.6	17.3	57	38

1) F means formaldehyde; P means phenol

The exposure specimens measured 1.3 cm square and were made of two cross-laminated plys of all earlywood or all latewood. Methods of gluing and of measuring percentage of delamination were similar to those reported by Hse in 1968. General gluing conditions were:

Spread: 365 g per m^2 of double glue line.
Closed assembly time: 20 minutes.
Hot press temperature: 140°C.
Hot press time: 6½ minutes.
Specific pressure: 12 kg per cm^2.

Results and Discussion

Table 1 summarizes surface tension, shear strength, percentage of wood failure, and percentage of delamination for each combination of factors. Surface tension ranged from 68.4 to 80.0 dynes/cm. By analysis of variance, it differed significantly with changes in NaOH/P and F/P ratios but not with changes in resin solid content.

Surface tension increased substantially (from 70.9 to 76.8 dynes/cm) with a change of NaOH/P ratio from 0.4 to 0.7; thereafter it increased slightly (from 76.8 to 77.6 dynes/cm) with a change of NaOH/P ratio from 0.7 to 1.0. The rapid increase between ratios of 0.4 and 0.7 is important in considering resin formulation; i. e., a small increase in NaOH/P ratio may change surface tension sufficiently to alter glue bond formation.

On the average, surface tension increased consistently as F/P ratio increased. However, the range of values was small: surface tension rose from 74.6 to 75.8 dynes/cm as F/P ratio changed from 1.6 to 2.5.

The NaOH/P ratio interacted with resin solids content. At NaOH/P ratio of 0.4, surface tension was positively correlated (0.05 level) with solids content;

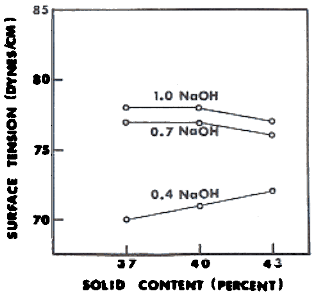

Fig. 2. Interactions of surface tension with molar ratio of sodium hydroxide to phenol and with solids content

at NaOH/P ratios of 0.7 and 1.0, the correlation was negative (Fig. 2).

The reaction of phenol and formaldehyde under alkaline conditions involves the addition of methylol groups at the position of the benzene ring ortho and para to its phenolic hydroxyl group, together with a condensation reaction between methylol groups of one molecule and the ring hydrogen or methylol groups of another phenolic molecule. Several studies have shown that the NaOH/P and F/P ratios are important in affecting the extent to which these two reactions take place (Sprung 1941; Debing et al. 1952; Freeman and Lewis 1954). The methylol content and length of molecular chain of the resins — and therefore the surface tension — may differ according to the extent of these reactions.

In the study, the resins were prepared to have identical final viscosities; it is therefore unlikely that molecular chain lengths differed sufficiently to affect surface tensions. Methylol groups, on the other hand, provide active sites for intermolecular interaction (i. e., hydrogen bonding), and by the principle of additivity of intermolecular forces at surfaces (Fowkes 1962) such bonds might affect surface tension. Phenolic hydroxyl groups in the resin system might be expected to have a similar effect; the phenolic OH, however, is not considered to be a factor controlling surface tension, since it is not directly involved in either the addition or condensation reaction of phenolic resins.

This reasoning led to the conclusion that methylol content largely determined observed differences in surface tension. Therefore, methylol content of uncured resin was measured with an infrared spectrophotometer, by method of Vasishth et al. (1968). The ratio obtained by dividing the absorbance of the methylol group at 1010 cm^{-1} by the absorbance of the phenolic OH band at 1210 cm^{-1} was taken as a quantitative estimation of the methylol content. Additionally, an attempt was made to evaluate the probability of methylol-group bond formation in the intermolecular interaction. Direct experimental measurement of this probability factor is difficult. Because intermolecular forces act at short distances, the compactness of the polymer chain may chiefly determine the factor of bond probability. Specific gravity of the resins was used as an index positively correlated with compactness, i. e., the greater the specific gravity, the greater the compactness and probability factor of molecular interaction.

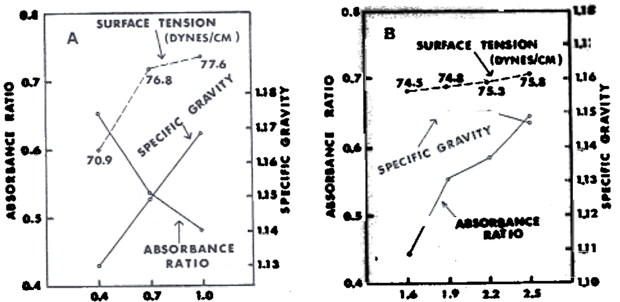

Fig. 3. Surface tension, absorbance ratio, and specific gravity as related to NaOH/P ratio (A) and F/P ratio (B). The absorbance ratio is the infrared absorbance of the methylol band at 1010 cm^{-1} divided by absorbance of the phenolic hydroxyl band at 1210 cm^{-1}

As Figure 3A indicates, methylol content — measured as absorbance ratio 1010/1210 — decreased as NaOH/P ratio increased. The result appears contradictory to what might have been expected, considering that surface tension of the resin increased as NaOH/P ratio increased. However, the resins with low methylol contents also had high specific gravities. Probably the combined effects of methylol content with probability factor of molecular association — as indicated by specific gravity — caused the observed results.

Figure 3B shows that methylol content increased as F/P ratio increased. Specific gravity was not significantly related to F/P ratio. Therefore, as expected, the surface tension increased as the methylol content of the resin increased.

Relationships between surface tension and glue bond quality were analyzed by multiple regression. Curvilinear regressions proved significant (0.01 level) between surface tension and the bond quality evaluators of shear strenght, wood failure, and delamination (Fig. 4).

The best equations for shear strength (kg/cm^2) and percentage of wood failure were:

Shear strength = $-233.9358 + 7.4727\gamma - 0.0547\gamma^2$

Percent of wood failure = $-1{,}585.47 + 48.28\gamma - 0.35\gamma^2$

where

γ = surface tension in dynes/cm.

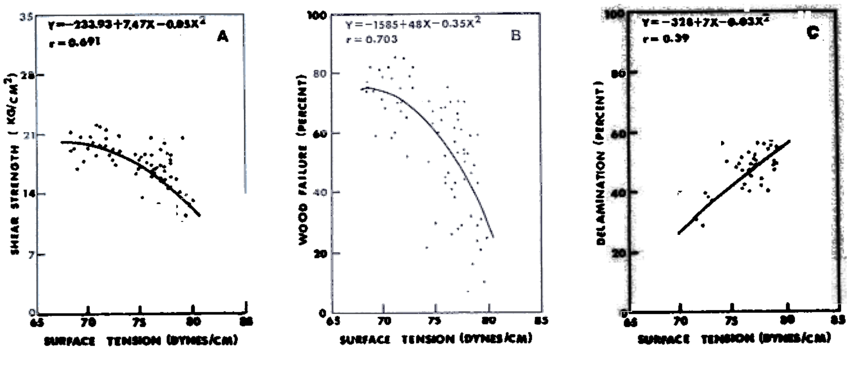

Fig. 4. Relationships of surface tension to shear strength (A), percentage wood failure (B), and percentage delamination (C)

The equations accounted for 49 and 48 percent of the total variation with standard errors of 2.51 kg/cm^2 for shear strength and 13.69 percent for wood failure.

The best equation for delamintation accounted for 30 percent of the variation with standard error of 14.81 percent:

$$\text{Percent of delamination} = -328.15 + 7.06\gamma - 0.03\gamma^2.$$

The decline in bond quality with increases in surface tension may be due at least in part to the greater difficulty of obtaining spontaneous spreading of the glue. The hot press would reduce surface tensions below those reported in Table 1, but perhaps not sufficiently to achieve optimum spread before curing took place.

Observations on a cure plate maintained at 140° C indicated that resins having high surface tension tended to form an impervious skin during the early stages of cure. Further contraction then took place inside the skin, creating voids that would weaken the bond if they formed between veneers (Hse 1971). It also seemed possible that the skin prolonged curing.

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