

EFFECT OF pH AND BUFFERING CAPACITY OF WOOD ON THE GELATION TIME OF UREA-FORMALDEHYDE RESIN¹

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ABSTRACT

The pH and buffering capacity for water extract of the heartwood and sapwood of ten hardwoods and nine softwoods were determined. pH values ranged from 4.00 to 5.86 for hardwood and 4.02 to 5.82 for softwood. The gelation time for a urea-formaldehyde resin as affected by wood flour for each wood was determined. Analysis shows that a strong correlation between gel time of wood flour and either pH or acid buffering capacity of water extract exists.

Keywords: pH, buffering capacity, hardwoods, softwoods, urea-formaldehyde resin, gelation time.

INTRODUCTION AND REVIEW OF LITERATURE

Knowledge of the pH and buffering capacity of wood is fundamental to the efficient use of wood in many gluing and coating processes where the glue or coating is pH-sensitive. For example, a urea-formaldehyde (UF) resin is acid-catalyzed and cannot be used to an optimum state-of-cure in a low acid environment.

Various methods for determining pH of wood have been proposed in an attempt to correspond to the conditions to which the wood will be exposed in use. For air-dry wood (5 to 20% MC), Campbell and Bryant (1941) proposed that pH of wood “. . . is numerically equal to that of a solution containing free hydrogen ions, which when added to it under the conditions stated, undergoes neither a net loss nor gain of hydrogen ions.” A series of unbuffered solutions of acids and bases of different pH are prepared and samples of wood are immersed. The solution whose pH does not change by immersion of wood as measured by a glass electrode is taken to represent the true pH of the wood. The drawback of this method is that a large number of solutions have to be prepared approximating pH value of wood.

¹ We wish to thank Joe Dede at Georgia-Pacific Corporation, Albany, Oregon, for providing the urea-formaldehyde resin and staffs of the University of Minnesota College of Forestry, Virginia Polytechnic Institute, and Weyerhaeuser Company for assistance in obtaining the wood specimens used for this experiment.

Ingruber (1958) used the method of Campbell and Bryant but with only a few different unbuffered solutions of varied pH. By plotting the values on a graph of pH change vs. original pH, he found the point at which no change in pH occurred.

Stamm (1961) compared the above two methods with the method of measuring pH on the surface of moistened wood itself using flat-headed glass electrodes. However, he reported erratic pH readings with the contact method unless great care was taken. Stamm concluded that the three methods gave comparable results and that simple extraction using comminuted wood and water in the ratio of 1:6 gave satisfactory pH values if the extract solution is sufficiently buffered, as with most woods.

Gray (1958) used a 1:3 ratio of wood sawdust to water and measured pH by a spear-type glass electrode and wick-type reference electrode. This ratio of wood-to-water was used to represent the most drastic conditions to which metal fittings are likely to be exposed. Gray attempted to correlate pH of wood to the corrosion of iron nails and concluded that the higher acidity of some woods accelerates the corrosion of iron under moist conditions.

In general, wood species range in pH from 3.0 to 5.5 (Stamm 1964). The knowledge of pH and buffering capacity of wood is an important consideration to a better understanding of the wood gluing processes (Maloney 1977; Foster 1967). Extreme values of wood pH have been reported to be troublesome for achieving good adhesive bonds. For example, the rate of cure of UF resin is retarded by Indian alkaline timber Quirpo and the bond is adversely affected (Narayanamurti 1957). Gluing of English oak gives low strength with resorcinol or resorcinol/phenol glue but excellent strength with UF resin. However, when the surface of wood is washed with dilute solutions of sodium acetate, excellent adhesion with both resorcinol and resorcinol/phenol adhesives is obtained. The acidity of oak (pH 3.7) is believed to seriously prolong the gelation and curing of relatively unbuffered resorcinol glue at room temperature (Rayner 1965). Thus, the wood pH may change the pH of adhesive at the interface and modify the curing of glue.

Although UF is the most commonly used wood glue for the particleboard industry, no published work is available in correlating pH and buffering capacity of aqueous wood extract to the gelation time of this acid curing adhesive. It is the purpose of the present study to find out if such a correlation can be established.

PROCEDURE

To achieve the objective, the following determinations were made:

1. pH of aqueous wood extract.
2. Buffering capacity of aqueous wood extract for a pH range of 3-7.
3. Gelation time of unbuffered urea-formaldehyde resins as affected by the several wood species.

Air-dried heart- or sapwood of a variety of species was isolated (Table 1), Wiley-milled through a coarse screen ($\frac{1}{8}$ -inch mesh), and stored in polyethylene bags until used. No classification of the wood meal was made. The aqueous wood extract was prepared by refluxing 25 g of dry wood material in 250 g of distilled water for 20 min. After refluxing, the mixtures were filtered through Whatman

TABLE 1. pH, acid buffering capacity, and gelation time of hardwood and softwood species.

Species	SW/HW ¹ /MIX	pH ²	Acid ³ - buffering capacity	Gel time ³ (minutes)
Hardwoods				
1. White oak (<i>Quercus alba</i> L.)	SW	4.56	0.182	12.13
	HW	4.00	0.435	5.92
2. Aspen (<i>Populus</i> spp.)	MIX*	4.30	0.204	11.70
	Wet Wood	4.35	0.154	11.92
3. Red alder (<i>Alnus rubra</i> Bong.)	HW	4.66	0.081	11.38
4. Yellow poplar (<i>Liriodendron tulipifera</i> L.)	SW	4.75	0.103	15.50
	HW	4.79	0.053	12.50
5. Hickory (<i>Carya</i> spp.)	SW	4.97	0.105	15.00
	HW	5.63	0.049	25.00
6. Sweet gum (<i>Liquidambar styraciflua</i> L.)	MIX	5.01	0.082	18.25
7. Blackgum (<i>Nyssa sylvatica</i> Marsh.)	SW	5.13	0.079	21.50
	HW	5.86	0.019	34.75
8. Red maple (<i>Acer rubrum</i> L.)	SW	5.40	0.037	20.50
	HW	5.45	0.024	18.50
9. Red oak (<i>Quercus rubra</i> L.)	SW	5.04	0.100	19.18
	HW	5.66	0.009	19.00
10. White birch (<i>Betula papyrifera</i> Marsh.)	SW	5.54	0.014	21.75
	HW	5.51	0.079	22.50
Softwoods				
11. Douglas-fir (<i>Pseudotsuga menziesii</i> Mirb.) Franco	SW	4.76	0.065	14.00
	HW	4.02	0.277	7.75
12. White pine (<i>Pinus strobus</i> L.)	SW	4.15	0.227	9.25
	HW	4.90	0.039	12.50
13. Red pine (<i>Pinus resinosa</i> Ait.)	SW	4.50	0.125	10.25
	HW	4.46	0.155	9.50
14. Southern pine (<i>Pinus</i> spp.)	MIX	4.66	0.065	12.08
15. Jack pine (<i>Pinus banksiana</i> Lamb)	SW	4.70	0.074	14.26
	HW	4.94	0.050	12.50
16. White spruce (<i>Picea glauca</i> Moench) Voss	MIX	4.96	0.022	15.35
17. White fir (<i>Abies concolor</i> Gord. and Glend.)	SW	5.25	0.022	16.38
18. Tamarack (<i>Larix laricina</i> (DuRoi) K. Koch)	SW	5.17	0.027	18.33
	HW	5.18	0.044	18.75
19. Northern white cedar (<i>Thuja occidentalis</i> L.)	SW	5.82	0.009	22.75
	HW	4.97	0.051	12.13

¹ SW = Sapwood; HW = Heartwood; MIX = Mixture of sapwood and heartwood (used when precise separation of heartwood and sapwood was not possible).

² Average of four values, based on two extract replications.

³ Average of two values, based on two extract replications.

* Isolated as an obviously discolored zone of wood near pith.

#1 filter paper with an aspirator vacuum. The mixtures were cooled to room temperature before titrating.

All pH and buffering capacities measurements were made with a Fischer Accumat pH meter, Model 310 after the technique of Lambuth (1967). Prior to each

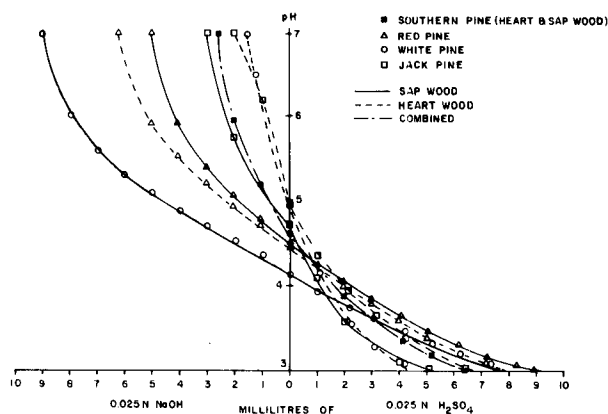


FIG. 1. The pH, acid, and base buffering potential for selected pines.

titration, the pH meter was calibrated with standardized buffer solution to a pH of either 4 or 7, depending on the buffering capacity measurement to be made. After calibration, exactly 50 ml of wood extract solution was pipetted into a 150-ml beaker, the pH of the extract solution noted, and then titrated to a pH of either 3 or 7 with nominal 0.025 N NaOH or H_2SO_4 solutions. The pH of the constantly stirred solutions was noted after each incremental ml of acid or base. The acid buffering capacity or acid equivalent is defined by Lambuth (1967) as the number of ml of NaOH solution required to raise the starting pH of the wood extract to a pH of 7.0 times the normality of the base solution. Similarly, alkaline buffering capacity determinations utilized the H_2SO_4 solution with the comparable calculation. Total buffering capacity is merely the sum of these two values.

An unbuffered urea-formaldehyde resin was obtained from Georgia-Pacific Corporation, Albany, Oregon. Experimentally it was determined that a gel time of 25.7 min resulted when 5 drops of 0.5% NH_4Cl solution were added to 4 ml of the resin in a 13- × 100-mm test tube, and the test tube immersed in boiling water and stirred with a stainless steel wire. Gelation time is defined as that point when the adhesive or adhesive-wood mixture suddenly loses its fluidity; it becomes a solid. Gelation time as affected by various wood species was found by mixing 0.7 grams of wood meal (O.D. wood basis), 5 drops of 0.5% NH_4Cl , and 4 ml of the resin in the test tube and heating in boiling water with constant stirring.

STATISTICAL CONSIDERATIONS

All initial pH readings are the average of four measurements, while buffering capacity and gelation times are the means of two determinations. A total of thirty-three samples of sapwood and heartwood (ten hardwood and nine softwood) were obtained from the species noted in Table 1. In cases where heartwood and sapwood were not readily separated, representation samples from the total wood cross-section were used.

Linear regression and correlation analysis were completed on the following combinations for hardwoods, softwoods and combined hardwoods/softwoods.

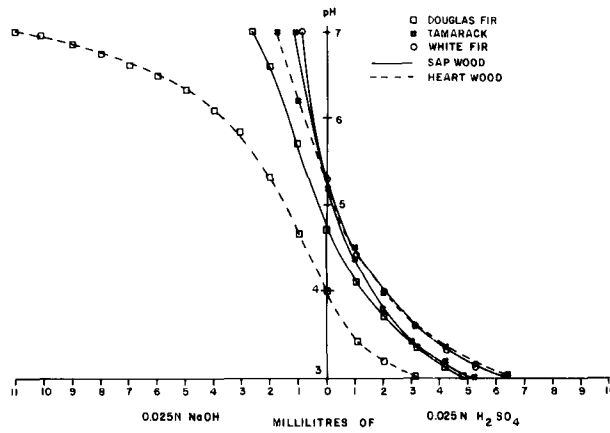


FIG. 2. The pH, acid, and base buffering potential for Douglas-fir, western larch (tamarack), and white fir.

- gelation time vs. pH
- gelation time vs. acid equivalent
- gelation time vs. base equivalent
- gelation time vs. total buffering capacity

In addition, nonlinear analysis was completed for gelation time vs. acid equivalent for hardwoods, softwoods, and combined data.

Significance of correlation coefficients, regression analysis, and differences between mean gelation times was tested (Steele and Torrie 1960).

RESULTS AND DISCUSSION

The data for pH and buffering capacity are graphed in Figs. 1 through 6. In this study, initial pH values ranged from 4.00 to 5.86 for hardwoods and from

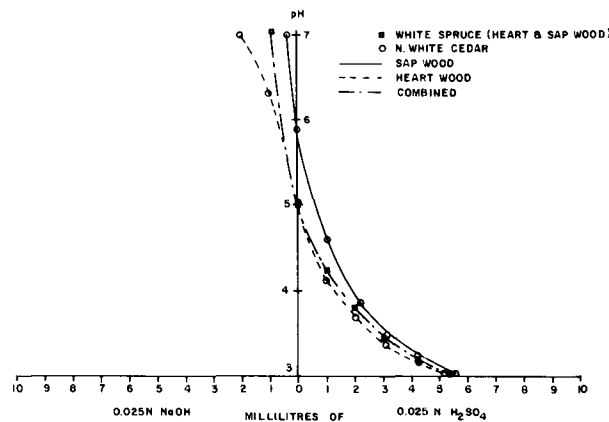


FIG. 3. The pH, acid, and base buffering potential for white spruce and northern white cedar.

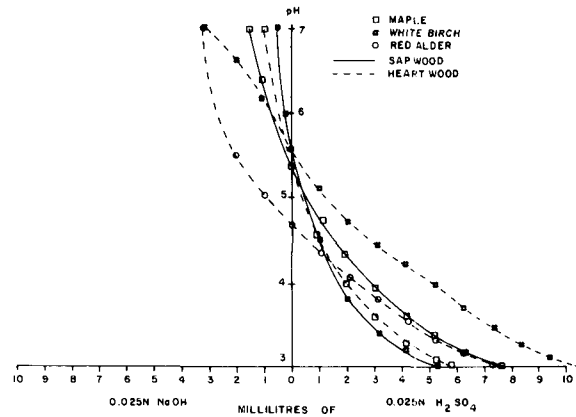


FIG. 4. The pH, acid, and base buffering potential for maple, white birch, and red alder.

4.02 to 5.82 for softwoods (Table 1). The difference between sapwood and heartwood pH values was not consistent, as was also reported by Gray (1958). In hardwoods, two species (white oak and white birch) gave higher values of pH for sapwood, while five species (yellow poplar, hickory, black gum, southern pine, and jack pine) gave higher pH values for heartwood. It was not possible to compare these pH values with those in the literature because of lack of identical combinations except for one comparison in the case of Douglas-fir. Our method gave slightly higher pH values for Douglas-fir than those reported by Crawford (1968) (4.76 vs. 4.61 for sapwood and 4.02 vs. 3.94 for heartwood). It was not practical within the scope of this experiment to seek possible chemical reasons for the differences between heartwood and sapwood of the same species.

Figures 1 through 6 show that acid equivalent, base equivalent, and total buffering capacity of aqueous extracts of various wood species and those of sapwood and heartwood within the species vary considerably. No similar information is available to compare these with the results of others.

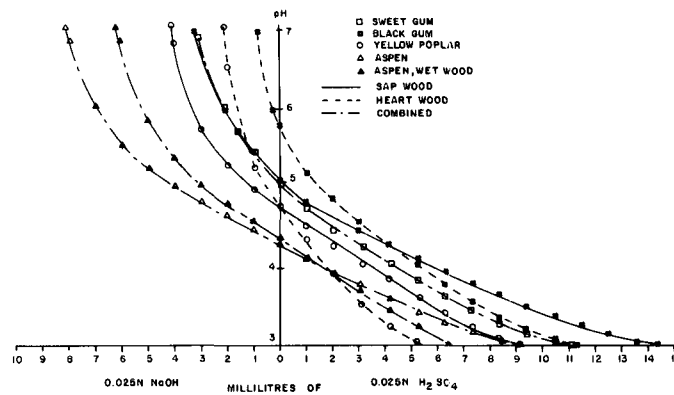


FIG. 5. The pH, acid, and base buffering potential for selected hardwoods.

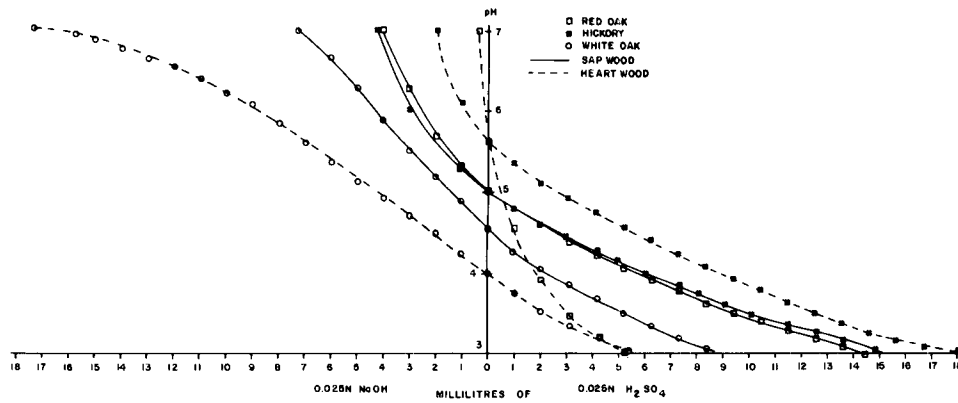


FIG. 6. The pH, acid, and base buffering potential for selected hardwoods.

Figures 7 and 8 give the gelation time of UF resin as a function of pH and acid equivalent, respectively, for hardwoods, softwoods, and combined data. A highly significant linear correlation was found for each of these cases (Table 2).

Statistically, there is no difference between the slopes of the lines of gelation time vs. pH for hardwoods and softwoods at the 5% level (Fig. 7). In other words, increase in pH and acid equivalent of hardwoods and softwoods have the same corresponding effect on gelation time.

Curiously, the data in Figs. 7 and 8 show that the hardwoods gelled more slowly than the softwoods at the same pH and acid-equivalent values. The exact

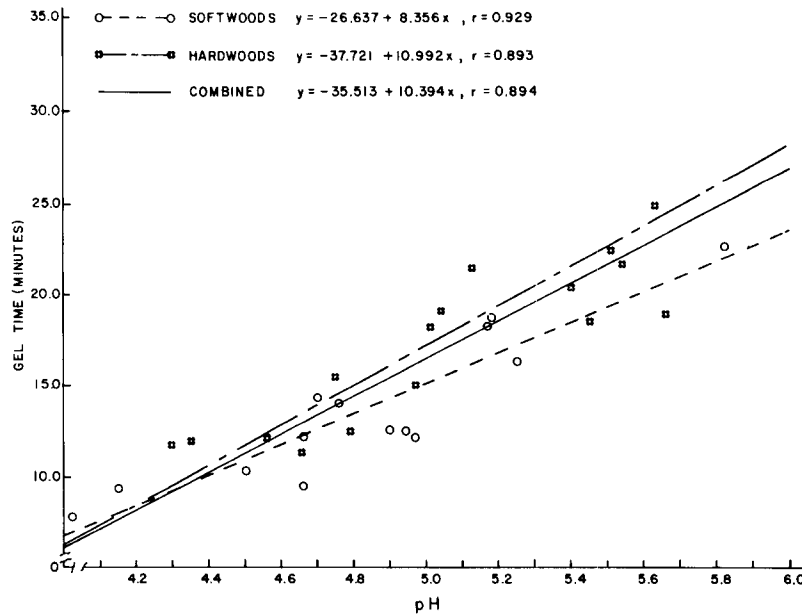


FIG. 7. The relationship between the pH and wood extracts and the gel time of a urea-formaldehyde resin as affected by wood meal of the same species.

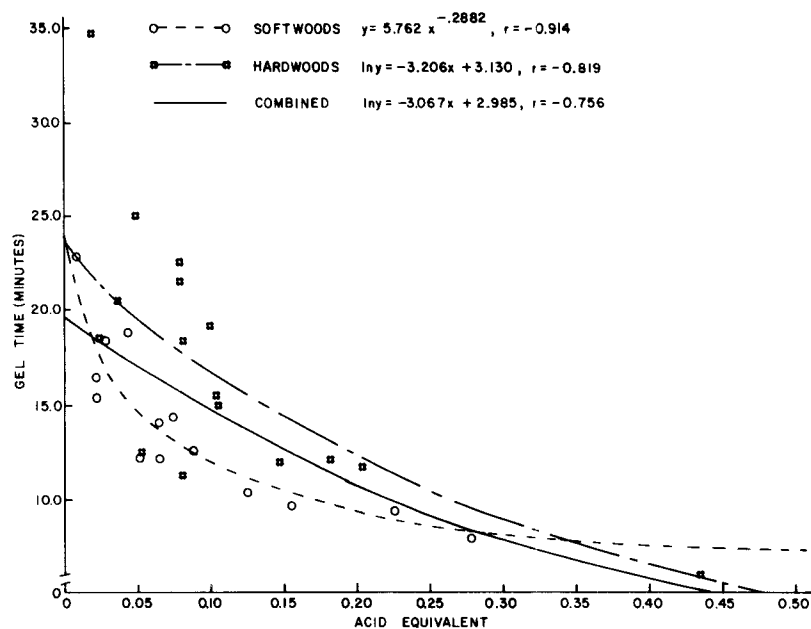


FIG. 8. The relationship between the acid equivalent of wood extracts and the gel time of a urea-formaldehyde resin as affected by wood meal of the same species.

reason for this is not known but is probably related to the experimental technique used for wood extraction and hence, pH and acid-equivalent values as compared to the technique used for the gelation time.

The pH and the acid-equivalent values of wood extract were determined in a closed system with the probability of no volatile acid(s) loss, while gelation time was measured in an open system, and any volatile acids were capable of escape. Modification of the gelation technique to a closed system is not direct in that constant stirring is required. Thus, wood-extract pH and the buffering capacity values were not necessarily representative of the values for the gelation time process.

TABLE 2. Summary of statistical tests for correlation of gelation time vs. pH, acid equivalent, base equivalent, and total buffering capacity of various wood species.

Species	Gel time vs. pH	Gel time vs. acid equivalent	Gel time vs. base equivalent	Gel time vs. total buffering capacity
Combined hardwoods and softwoods	** $r = 0.894$	** $r = 0.756$	* $r = 0.427$	ns $r = -0.191$
Hardwoods	** $r = 0.893$	** $r = 0.819$	ns $r = 0.421$	ns $r = -0.248$
Softwoods	** $r = 0.929$	** $r = 0.914$	ns $r = 0.193$	** $r = -0.738$

Remarks: ns = statistically not significant at 5% level

* = statistically significant at 5% level but not significant at 1% level

** = statistically significant at 1% level.

A higher rate of acid liberation from hardwoods (oak and birch) as compared to softwoods (Douglas-fir and Parana pine) has been reported by Packman (1960); higher rate of acid liberation and thus loss in the open system is consistent with our results—that is, hardwood species when compared to softwood species have a longer gelation time because of the loss of acid associated with the procedure used for measuring the gelation time.

Table 2 shows that base equivalent and total buffering capacity are not significantly related to the gelation time. The one exception seems to be the relationship of total buffering capacity vs. gel time for softwoods. This may very well be related to the very strong correlation of pH and acid equivalents for hardwoods.

The best fit equations are provided in Figs. 7 and 8 for future reference.

CONCLUSIONS

1. A pH range of 4.00 to 5.86 for hardwoods and 4.02 to 5.82 for softwoods was found.
2. Gelation time of a urea-formaldehyde resin was directly correlated to the pH and inversely correlated with acid-buffering capacity for both hardwood and softwood aqueous extracts.
3. An increase in either pH or acid equivalent has the same effect on the gelation times for UF resins when in contact with either hardwood or softwood aqueous extracts.

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