

# SURFACE ACTIVATION TREATMENT OF WOOD AND ITS EFFECT ON THE GEL TIME OF PHENOL-FORMALDEHYDE RESIN<sup>1</sup>

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## ABSTRACT

Surface activation treatment of wood using hydrogen peroxide, nitric acid, and sodium hydroxide was examined to assess its effect on the gel time of phenol-formaldehyde resin. Four wood species comprising both hardwoods and softwoods, two treatment levels, and two treatment conditions (activation and activation followed by drying) were examined in the study. The effect of surface activation on the gel time of phenol-formaldehyde resin varies for a particular surface activator according to treatment level and treatment condition. Surface activated treated wood decreases the gel time of phenol-formaldehyde resin with hydrogen peroxide treatment having the greatest effect followed by nitric acid and sodium hydroxide treatments.

*Keywords:* Gel time, phenol-formaldehyde resin, surface activation, southern pine, red maple, red oak, sweetgum.

## INTRODUCTION

The nonconventional bonding of wood through surface activation has received a great deal of attention over the past 15 years (Zavarin 1984). In most instances, surface activation has been accomplished through the use of various oxidizing agents, such as hydrogen peroxide (Philippou et al. 1982), nitric acid (Johns et al. 1978), and recently, sodium hydroxide (Young et al. 1985), in combination with polymeric gap filling materials. Many of the nonconventional bonding studies were initiated during the "energy crisis," and most of the gap filling materials used in the various bonding processes were based upon chemicals obtained from renewable resources such as lignin and furfuryl alcohol. Although the use of polymeric gap fillers derived from renewable resources is highly desirable from utilization considerations, the costs involved in the production of wood panels

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using such bonding systems limit their commercial application at the present time.

Only a small amount of work has been reported using surface activation in combination with conventional synthetic resins as a gap filler, but such an approach may offer advantages over present bonding systems. Direct comparisons could be made among the various surface activation treatments effect on bond quality without regard to gap filler type. In the past, this was not possible because different gap fillers were used with different surface activators. Furthermore, a reduction in the use of phenol-formaldehyde resin may be possible through the use of surface activation.

The current study was initiated, therefore, to examine the surface activation of wood and its effect on the gel time of phenol-formaldehyde resin. Although the gel time of a resin is not the actual cure time, it is typically considered as a relative measure of the rate of bond formation in fiberboard (Albritton and Short 1979) and is commonly used as a screening or quality control procedure for resins during manufacture or product analysis. The determination of the gel point of thermo-setting compounds is critical in evaluating the relative measure of polymerization of such materials, the impact of variables on that rate, shelf life, and other characteristics (Sunshine Instruments 1986). The gel point is usually characterized by a sudden pronounced increase in the viscosity of the material.

The effect of extractives from pressure-refined hardwood fiber on the gel time of urea-formaldehyde (UF) resin was studied by Albritton and Short (1979), and Slay et al. (1980). Their results showed that gel time of UF resin is affected by the addition of small amounts of extractives from pressure-refined wood, with ethanol-soluble extractives reducing gel time to a greater extent than water-soluble extractives. It was demonstrated that a substantial amount of extractives are both water- and ethanol-soluble, and that the gel time of the resin-extractive mixture increases exponentially as its pH increases.

The effect of pH and buffering capacity of various woods on the gel time of UF resin was studied by Johns and Niazi (1980). They found that gel time of a UF resin was directly correlated with acid-buffering capacity for both hardwood and softwood aqueous extracts, such that a decrease in either pH or an increase in acid equivalent decreased the gel time of UF resin for both hardwoods and softwoods. In a similar study (Subramanian et al. 1983), the effect of bound acids in wood on the gel time of UF resins was examined. Bound acid was found to be better correlated to gel time than soluble acid.

Subramanian et al. (1982) studied nitric acid oxidation of wood by monitoring the amount of soluble and bound acids formed as the result of treatment. It was found that nitric acid oxidation of wood resulted in the formation of carboxylic acid covalently bonded to the wood. These acid groups were capable of reaction with coupling agents such as 2-(1-aziridinyl) ethyl methacrylate (AEM), and also catalyzing the *in situ* polymerization of furfuryl alcohol.

Hydrogen peroxide was used in combination with phenol-formaldehyde, urea-formaldehyde, and tannin-formaldehyde resin-adhesives to decrease resin cure time in fiberboard, particleboard, and plywood (Chapman and Jenkin 1986). Their results showed that panel pressing times could be reduced by 30%, and in some cases better resin cure permitted a reduction in binder level.

In this study, we address fundamental aspects of the effect of surface activation

treatment of wood on the gel time of phenol-formaldehyde resins. The results of this study should provide basic information regarding the gel characteristics of resin-surface activated wood, and the efficacy of such an adhesive system.

#### PROCEDURE

Southern pine (*Pinus taeda*), red maple (*Acer rubrum*), southern red oak (*Quercus falcata*), and sweetgum (*Liquidambar styraciflua*) were obtained from the Auburn University Experimental forest. The wood bolts were debarked, broken up, and Wiley-milled through a one-eighth-inch screen followed by air drying. To have consistent-sized particles for surface activation treatments, the particles were sieved in a particle classifier, and the particles passing through a 9-mesh Tyler screen and held on a 20-mesh Tyler screen (-9 +20) were used in the study.

The surface activation treatments examined were hydrogen peroxide, nitric acid, and, sodium hydroxide. The amounts of the surface activating agents added to the particles were established, based on levels applied to wood surfaces in previous studies. The levels reported in the literature for flakes were 2% of 50% hydrogen peroxide (Philippou et al. 1982) and 1.5% of 40% nitric acid (Johns et al. 1978), and for shear block specimens 2% of 3 N sodium hydroxide (Young et al. 1985) based on the oven-dry weight of wood. Since the material used in this study had to be more finely divided to fit in gel time tubes, the level of surface activating agent added was modified to account for the increase in surface area. The surface area of wood flakes was determined using the relationship described by Moslemi (1974), in which

$$\text{surface area} = \frac{24}{t \times g}$$

where

g = wood density

t = flake thickness (0.025")

The surface area per unit weight of wood for the -9 +20 Tyler fraction was assumed to be similar to the surface area per unit weight for -9 +20 Tyler mesh Douglas-fir particles (94.5 sq. ft/lb) reported by Maloney (1970). The ratio of surface area per unit weight for the flakes and -9 +20 Tyler mesh particles was calculated, and the ratio value was multiplied by the treatment level used for the wood surfaces reported in the literature (Philippou et al. 1982; Johns et al. 1978; and Young et al. 1985) to determine the required amount of surface activating agent based on the oven-dry weight of wood for the -9 +20 Tyler mesh particles (Table 1). The increase in surface area/wood weight for the -9 +20 Tyler mesh particles was between three and four times that of wood flakes.

The surface activation treatments were run in duplicate. Surface activation was accomplished by spraying the activating agent using a glass atomizer on approximately 25 g of the wood particles contained in a 1,000-ml Erlenmeyer flask. The particles were sprayed using intermittent bursts of spray followed by agitation of the particles in the flasks to facilitate even distribution of the surface activation agent. Two levels of surface activation were examined (Table 1) and gel times were measured for treated particles in the wet condition and treated particles dried in an oven at 103 C for 30 minutes. Separate samples were prepared for each

TABLE 1. Values used in determining treatment levels for surface activation (SA) of wood particles.

Species	Specific <sup>a</sup> gravity	Density (lb/cu ft)	Surface area ratio	Amount of SA agent applied <sup>b</sup> %					
				50%		40%		3 N	NaOH
				H <sub>2</sub> O <sub>2</sub>		HNO <sub>3</sub>			
Level		Level		Level		Level			
				One	Two	One	Two	One	Two
Pine	0.49	30.6	3.0	6.0	12.0	4.5	9.0	6.0	12.0
Red maple	0.59	36.8	3.6	7.2	14.4	5.4	10.8	7.2	14.4
Red oak	0.62	38.7	3.8	7.6	15.2	5.7	11.4	7.6	15.2
Sweetgum	0.50	31.2	3.1	6.2	12.4	4.7	9.4	6.2	12.4

<sup>a</sup> Determined by the maximum moisture content method (Stamm 1964).

<sup>b</sup> Percentage based on the oven-dry weight of wood.

treatment. Gel time measurements were made at 100 C using a Sunshine gel tester. Ten grams of PF resin (Cascophen PB-10) were mixed with 0.5 gram of untreated wood or surface activated wood particles. For each treatment, the gel time measurements were duplicated. Gel time measurements of neat resin were made throughout the study as a control measure and the neat resin gel time varied from 18.86 to 20.16 minutes.

#### Statistical analyses

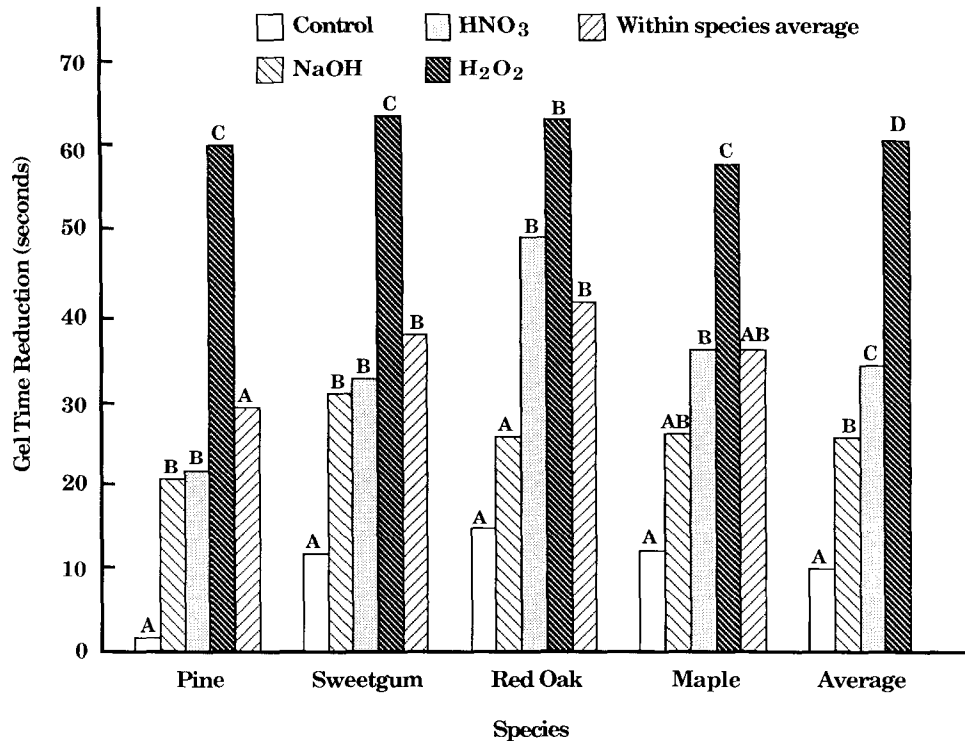
The surface activation treatment effects on gel time and wood species were analyzed using the Statistical Analysis System (SAS) (SAS User's Guide. SAS Inst., Cary, N.C.) programming package. Since PF resin constantly advances, thus changing neat resin gel time, the actual variable used to assess the effect of surface activation treatments on gel time in the statistical analyses was the difference between the wood particle gel times and the neat resin gel time for a particular day and is denoted in the figures as gel time reduction. The General Linear Models (GLM) procedure was used to determine differences among the data. Significant effects ( $P < 0.05$ ) between treatment variables were further characterized by the Duncan's Multiple Range test.

#### RESULTS AND DISCUSSION

The effect of the surface activating agents on the gel time of phenol-formaldehyde resin for each species and the average across all species is shown in Fig. 1. The values include both the wet and dry conditions, and the high and low levels of treatment. The control produced the slowest gel times, while the hydrogen peroxide gave the fastest. The nitric acid and sodium hydroxide treatments resulted in intermediate gel times for all species except red oak, for which the hydrogen peroxide and nitric acid treatments were not found to differ significantly.

In a comparison of species that included all treatments, pine had a significantly lower gel time reduction than the other species, but also had the lowest surface area per weight of wood particles (Table 1). This result indicates that the amount of treated surface area may have an effect on the gel characteristics of the resin. In addition, red oak exhibited faster gel times in the dry condition as compared to the wet condition. No other species differences were detected with treatment condition.

The behavior of the surface activating agents in the wet and dry conditions, and when applied at both levels, is described in Fig. 2. These results, which do



Values with the same capital letter are not significantly different at  $P < 0.05$ .

FIG. 1. The effect of surface activation on the gel time of phenol-formaldehyde resin for individual species and average across species.

not separate species, show that hydrogen peroxide significantly reduced gel time in all instances except when the wood was dried after application of the surface activators. In this instance, no statistical difference was found between the nitric acid and hydrogen peroxide treatments. Furthermore, increasing the nitric acid level was found to increase the reduction in gel time, while the higher amounts of both sodium hydroxide and hydrogen peroxide negatively affected the gel time reduction.

The difference between the nitric acid and hydrogen peroxide treatments is even more apparent upon examination of the interaction between treatment levels and conditions for all species. These data, illustrated in Fig. 3, show that nitric acid reduces gel time to a significantly greater extent than hydrogen peroxide for the level 2 dry treatment. Based on Fig. 3, it is apparent that the effect of hydrogen peroxide on gel time reduction was decreased by heating. This is perhaps due to evaporation which would diminish the amount of hydrogen peroxide present in the gel time experiment. Similarly, it has been reported that evaporation of hydrogen peroxide occurs during thermal analysis (Nguyen et al. 1980).

The improvement in performance of the nitric acid treatment as a result of drying and increased application rate may be caused by an increase in the reaction of nitric acid with the wood surface, thus producing a greater number of functional groups that may react with the phenol-formaldehyde resin during the gel time

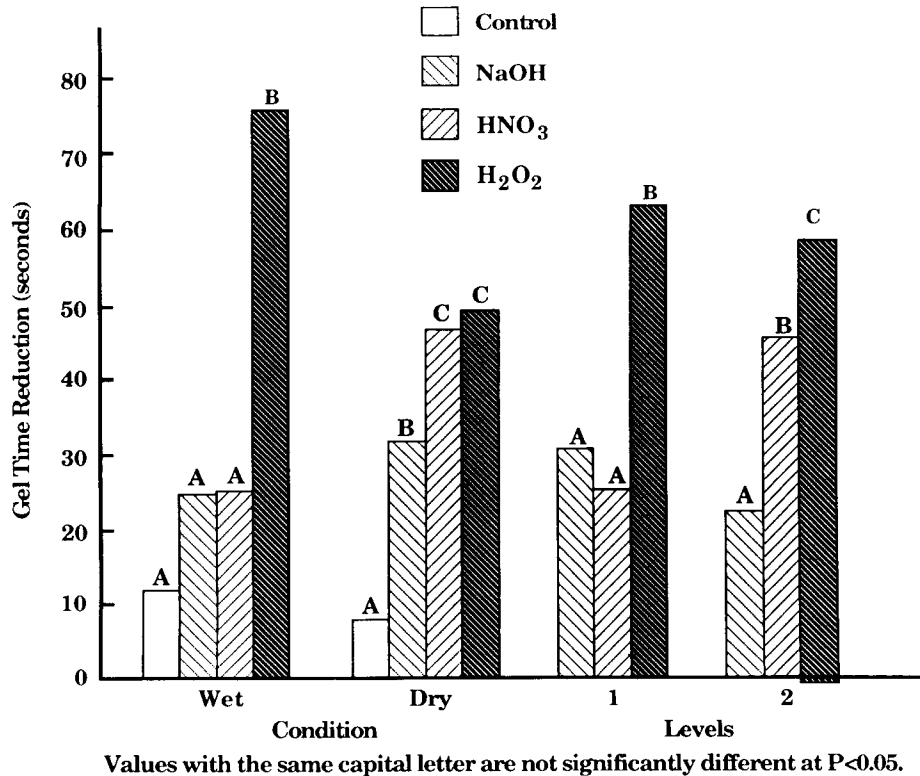
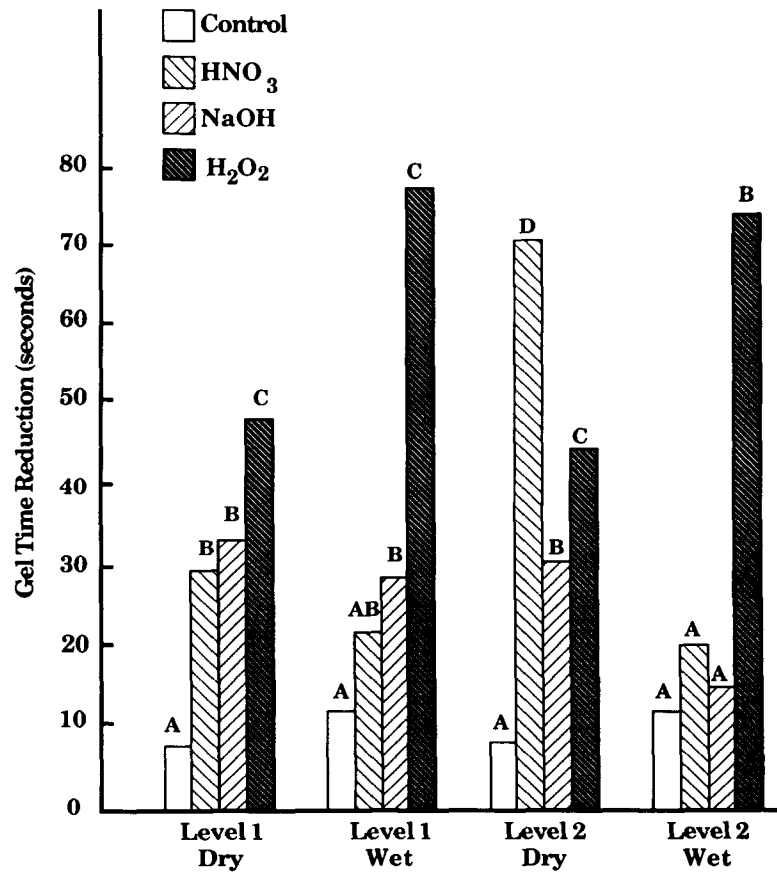


FIG. 2. The effect of surface activation treatment condition and treatment level on the gel time of phenol-formaldehyde resin.

experiment. This is supported by the work of Rammon et al. (1982) who found that nitric acid oxidation of wood at 100 C produced a greater degree of hydrolysis and oxidation of the wood components than wood treated at ambient temperature.

The specific trend, with respect to the condition of the wood and level of surface activation treatment, is substantiated by the significant reduction in gel time across all species and surface activators, by drying and treating at the higher activation level. This and the preceding information suggest that different conditions may be required for the most efficient application of an individual surface activating agent.

While this study has indicated that hydrogen peroxide is, in general, the most effective surface activating agent in reducing gel time, it may be important to note that under certain conditions, nitric acid may perform as well or better. Since nitric acid is much less expensive, this may be an important economic consideration as these methods continue to be developed. Furthermore, it may be possible to reduce pressing times and/or phenol-formaldehyde resin levels in the production of wood composite panels using a surface activation bonding system. Future research should be directed at determining the effect of surface activation on adhesive bond quality in composite panels bonded with phenol-formaldehyde resin.



Values with the same capital letter are not significantly different at  $P < 0.05$ .

FIG. 3. The effect of surface activation on the gel time of phenol-formaldehyde resin within levels and conditions.

#### CONCLUSIONS

1. The effect of surface activation on the gel time of phenol-formaldehyde resin will vary according to sample treatment for a particular surface activator with treatment conditioning and level of treatment having the most noticeable effects on the gel time of PF resin.
2. Surface activation of wood decreases the gel time of phenol-formaldehyde resin with increasing amounts of effect from sodium hydroxide, nitric acid, and hydrogen peroxide.

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