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Surface Modification of Wood Using Nitric Acid

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Surface modification of wood flakes by oxidation with nitric acid has been investigated at three different moisture contents of wood, and two different concentrations of the oxidant. It is shown that a significant number of the acid groups generated are chemically linked to wood. Increasing moisture content in wood has the effect of local dilution of the nitric acid oxidant while reduction in moisture content of wood during drying makes potential oxidation sites less accessible. Thus, two different regimes of oxidation, one of more accessible, and another, of less accessible, sites are observed. The nature of the generated acid is established as carboxylic, which is capable of undergoing a coupling reaction with 2-(1-aziridiny)ethyl methacrylate. The catalysis of *in situ* polymerization of furfuryl alcohol by bound acid has also been shown to occur.

INTRODUCTION

Although the use of wood has been known since antiquity, its application in the specialty areas has been surpassed by that of the newer types of composite materials, mostly synthetic, whose operational properties can be tailored to meet performance requirements. Obviously, for wood to be an effective competitor, there needs to be ways of modifying the wood to give desirable properties in use. In the case of wood, one such method of manipulating the wood properties is by chemically introducing polymers into the wood giving a wood-polymer product with a resultant complementary blend of polymer and wood properties.

Although this approach has been tried in the case of lumber^{1,2} the method has eluded application in realizing the concept of the total utilization of the

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tree. Thus, this mode of property modification has not been tried extensively in particleboard and related products whose large surface area should offer ample reaction sites for the chemically introduced polymer.

A still further concern is the type and source of adhesive to be used for the wood-polymer adherend. Presently, most of the wood adhesives are derived from petrochemical intermediates whose availability and pricing are uncertain. Clearly, new adhesive systems based on readily available and, preferably, easily renewable resources should be found.

This paper collectively addresses the above concerns. It stems from the observation of Johns *et al.*³ that treatment of wood with nitric acid improves the wet strength of particleboards; and, in an effort to gain a better understanding of the nitric acid treatment, it continues the application of the new analytical techniques developed in our laboratory for the determination of soluble and insoluble acid components in many species of wood.⁴ Thus, wood flakes have been surface-modified using nitric acid, an oxidant, and the resulting product has been shown to catalyze the polymerization of furfuryl alcohol, a biomass-derived adhesive component. In addition, the oxidized wood has been shown to react with an aziridiny coupling agent whose use is known to promote adhesion.⁵

EXPERIMENTAL

Nitric acid spray treatment

Early experiments on treating of wood by nitric acid were conducted by spraying two-kilogram quantities of Douglas-fir (*Pseudotsuga menziesii*) Pallman wood flakes with 50% nitric acid. The weight of nitric acid sprayed was adjusted to be 1.5% of the weight of wood sprayed. From the known weight and strength of acid sprayed, the exact amount of nitric acid applied in milliequivalents per gram of wood could be calculated.

Total soluble acids

The amount of soluble acids in wood was determined by titration of aqueous extracts of wood with alkali. The extraction procedure, standardized after extensive experimentation, was as follows. Twenty-five-gram sample of treated or untreated wood, as the case may be, was weighed out into a beaker, and 200 ml distilled water added to it. The sample was filtered by decantation through a Whatman #40 filter paper into a 1-liter volumetric flask. More distilled water (300 ml) was added to the wood in the beaker and left to soak for 24 h. Following decantation again, the wood in the beaker was washed

repeatedly with 175-ml quantities of distilled water and filtered. The filtrate and washings collected in the volumetric flask were made up to the 1-litre mark. Aliquots of this extract were used for titration against standard sodium hydroxide solution.

The total amount of soluble and insoluble acids in wood was determined by using a decinormal sodium acetate solution in the extraction procedure described above, following the initial rinsing with 200 ml water. As discussed later, sodium acetate liberates an equivalent amount of acetic acid by reaction with insoluble acid groups chemically bonded to wood.⁴ Titration of the sodium acetate extract thus gives total soluble and insoluble acids in wood. Subtraction of soluble acids obtained by aqueous extraction gave the insoluble acid content of wood.

The acid contents of treated wood samples were thus measured after different periods, following acid spray, varying from 2 to 8 h. In subsequent series of experiments, conducted for studying the kinetics of reaction, a different procedure was followed. Treatment with nitric acid was carried out by allowing nitric acid to percolate through 2-gram samples of wood flakes (0.38 mm thick), placed in a filtering funnel, for varying periods of time (up to 32 h), after which the flakes were washed with water (4 × 40 ml, residence time > 0.3 h) to remove unreacted nitric acid. The wood flakes were then soaked overnight in water to remove any residual free nitric acid. The amount of insoluble (chemically bonded) acid groups was then determined by sodium acetate extraction, followed by alkali titration of the extract.

End points in neutralization were determined by plotting $\Delta\text{pH}/\Delta V$ *v.* volume obtained from pH-titration curves. A blank titration was conducted with 200 ml of water, for aqueous extracts, and with 200 ml sodium acetate decinormal solution, for sodium acetate extracts.

Reactions of treated wood

For reaction with 2-(1-aziridinyl)ethyl methacrylate (AEM, Polysciences, Inc., Warrington, PA), wood flakes were added to AEM solution (10 volume percent) in an appropriate solvent (water, MeOH or acetone) and left to stand overnight. The unreacted AEM was removed by washing repeatedly with MeOH followed by acetone, and finally soaking overnight in acetone. The nitrogen content of wood samples was then determined by elemental analysis.

The polymerization of furfuryl alcohol was studied by adding redistilled furfuryl alcohol (25 ml) to the fresh batch of oxidized wood (about 1g) and then monitoring the time taken for the color to change from straw yellow to dark brown. In a more quantitative manner, the polymerization taking place was monitored by following the flow times of the furfuryl alcohol, measured in an Ostwald viscometer, as a function of reaction time.

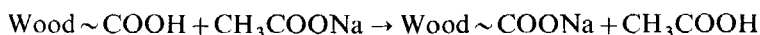
RESULTS AND DISCUSSION

Oxidation of wood can be expected to result in a change of the wood surface. The new surface formed may offer means of controlling the bond performances of wood. The factors influencing this oxidation and the possible uses to which the resultant oxidized wood can be put are discussed below.

A. Nitric acid oxidation

Untreated wood was first analyzed for soluble acids by water extraction and titration of the aqueous extract with sodium hydroxide. In addition, it was recognized that wood may contain acidic functional groups chemically bonded to it. A chemical method was therefore developed to determine this chemically bonded or insoluble fraction of acid groups, which will be referred to as "bound acid" in this paper.

The method depends on the reaction of the insoluble acids, say carboxylic acids, with sodium acetate to liberate an equivalent amount of acetic acid as shown below :



It should be noted that the conditions of extraction are mild ; sodium acetate is close to neutral, and the extraction is done at room temperature. It can be expected therefore, that this process of liberation of acetic acid, in an amount equivalent to bound acid present in wood, does not involve the generation of new acid groups during the extraction procedure.

The extraction procedures described in the experimental section were arrived at after optimization with respect to volume of reagents, time, etc. It was found that repeated washings were necessary for complete extraction of the acid. Even though the breaks in the pH-titration curve were not very sharp, it was easy to determine the end points by plotting $\Delta\text{pH}/\Delta V$ v. volume (V).

It can be seen from Table I that untreated Douglas-fir contains 7.4

TABLE I
Soluble and insoluble acids in Douglas-fir, after being sprayed with HNO_3 (1.5%)

	Elapsed time, hours	Soluble acids, m.eq./100 g wood	Insoluble acids, m.eq./100 g wood
Untreated wood		2.30	7.41
Nitric acid, sprayed	0.00	23.7	—
Treated wood	0.33	21.7	8.50
Treated wood	1.00	21.7	8.50
Treated wood	6.00	21.5	8.55
Treated wood	25.00	21.7	8.02
Treated wood	174.00	23.7	8.16

milliequivalents (m.eq.) of insoluble, *i.e.*, bound acid, per 100 g wood. The increase in bound acid content after spraying with 23 m.eq. of nitric acid per 100 g wood is only about 1 m.eq. This could mean that, under the conditions of the experiment, oxidation by sprayed nitric acid is not facile. In agreement with this observation is the fact that the amount of soluble acid remains constant over a period of time up to 170 h after spraying. The concentration of bound acid in wood also remains unchanged during this treatment time.

In studying the formation of bound acids in more detail, a different procedure was therefore adopted for the oxidation step. In this series of experiments, nitric acid of different concentrations was allowed to percolate through wood of various moisture contents. The dependence of bound acid concentration on treatment time is presented in Figure 1 for three wood specimens of different moisture content. It can be seen that in all cases the reaction proceeds quickly before reaching a plateau region; this region is reached fastest by wood of the highest moisture content. Thus oven-dried (OD) wood reaches a plateau concentration after 1.5 h whereas wood at 6.5% moisture content does so at an earlier time of 0.7 h. Such a trend would be expected since the reaction will be highly dependent on the permeation of nitric acid through the flakes, and since the diffusion of nitric acid into the

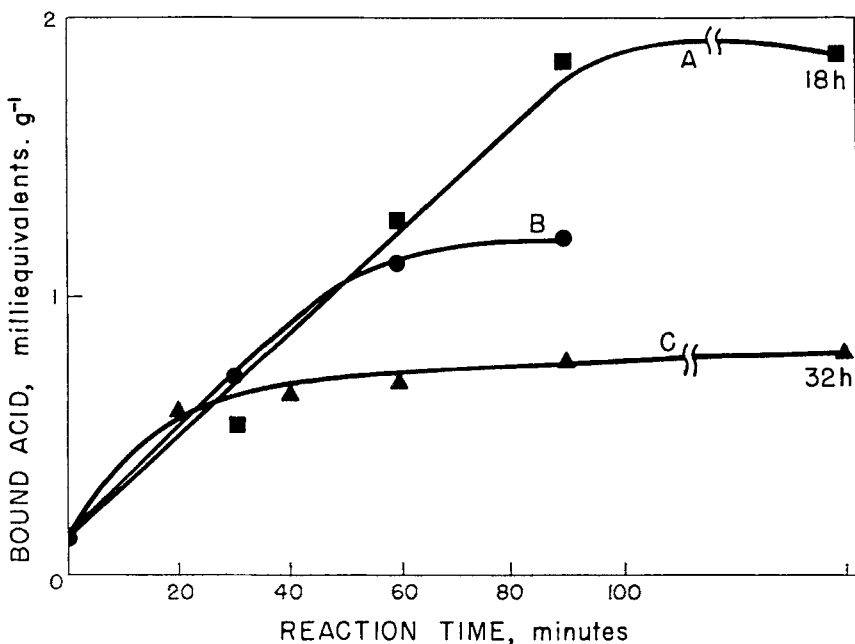


FIGURE 1 Formation of bound acid by nitric acid oxidation of wood with various moisture contents; oven dried (A), 3.0% (B) and 6.5% (C).

wood structure would be greatly facilitated at higher wood moisture contents. In pulp and paper manufacture, it has been observed that dry chips are difficult to penetrate with liquids due to blockage by air pockets. Furthermore, the collapsible nature of wood, particularly through its cellulose and hemicellulose components, is evident during the drying of wood blocks. Though it is difficult to gage the extent to which these mechanisms could occur in thin wood flakes, it is clear, from the results of Figure 1, that the permeation and reaction of nitric acid in wood increase with initial moisture content of the flakes. It is noteworthy that these differences are observed even in a reaction conducted in an aqueous medium.

In addition, Figure 1 shows that the final level of bound acid generated is highest in oven-dried wood, while wood at higher moisture contents (3.0 and 6.5) contains increasingly lower acid concentrations. We attribute this behavior to localized dilution of the nitric acid at the reaction sites. Obviously, the diluting effect, which depends upon the presence of tightly bound water in wood, will increase with increasing moisture content of wood. In the same manner, at a constant wood moisture content, concentrated acid solutions will then be expected to produce a higher level of bound acid than dilute acid. Indeed, this has been shown (Figure 2) to be the case. Thus, the use of 50%

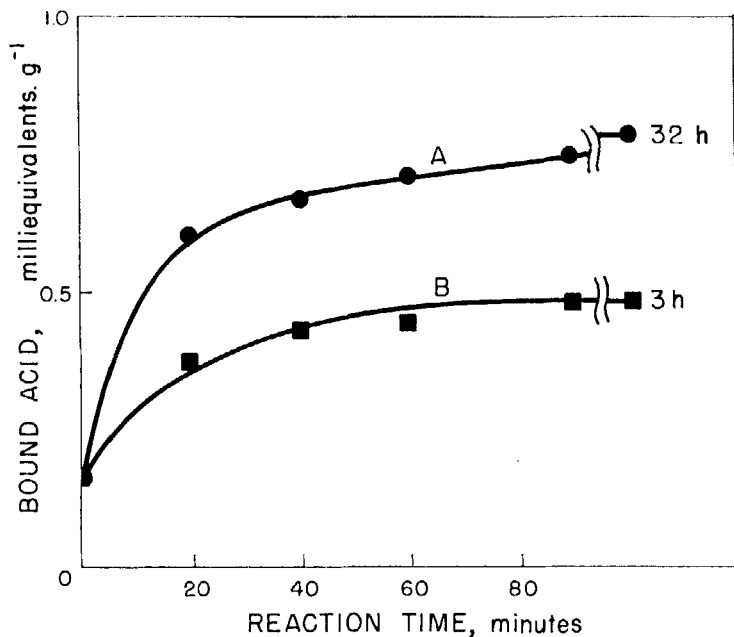


FIGURE 2 Time-reaction profile of wood bound acid formation using 50% (Curve A) and 25% (Curve B) nitric acid. Wood moisture content : 6.5%.

nitric acid solution resulted in a correspondingly higher plateau value than when a less concentrated (25%) nitric acid solution was used as oxidant.

An insight into the influence of diffusion on the reaction between wood and nitric acid can be realized by following the build-up of bound acid with reaction time. Figure 3 shows one such typical plot of $\log \frac{a}{a-x}$ v. t , where a is the maximum concentration of bound acid formed, and x is the concentration at time t . It is characterized by the presence of two intersecting lines; the point of intersection divides the plot into two reaction regimes. Below the intersection point, we have the reaction of the easily accessible sites, mostly surface sites. Beyond the intersection point, there is the retarded reaction of the less easily accessible reaction sites.

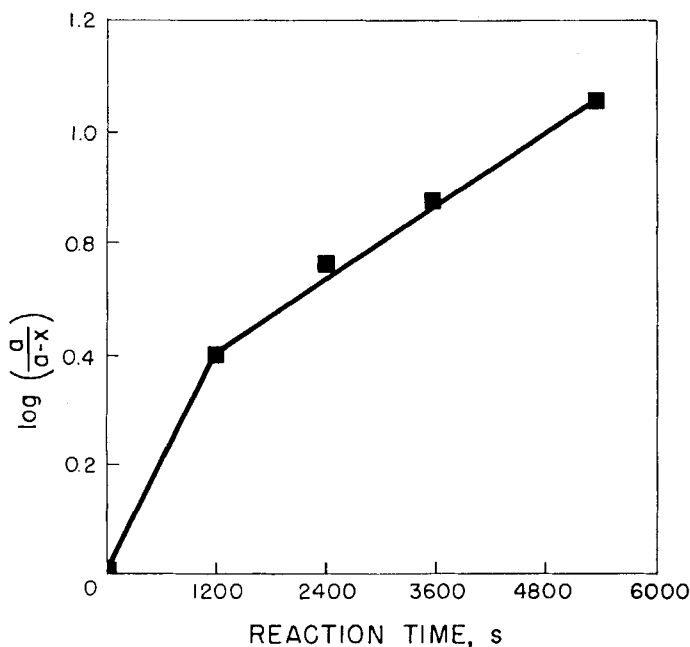
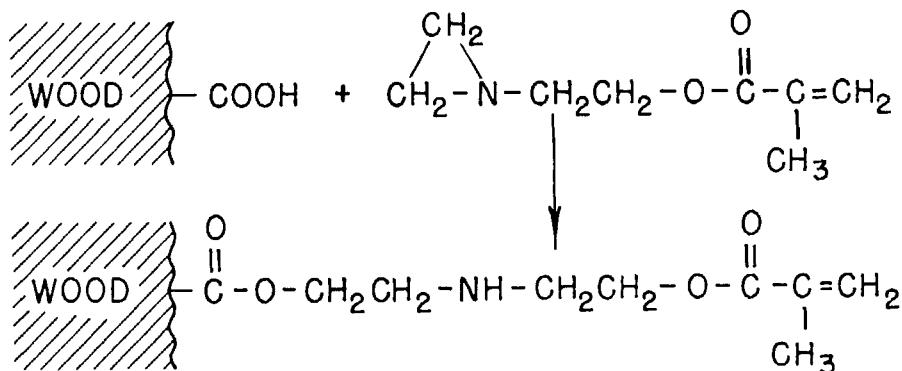


FIGURE 3 Bound acid formation on wood using 25% HNO_3 ; concentration ' a ' at $t \infty$ and ' x ' at $t < t \infty$.

B. Coupling with AEM

In itself, the oxidation reaction provides a means of surface modification. However, a still better modification was attempted by reacting the oxidized wood with AEM (Scheme 1), a coupling agent known to promote adhesion.⁵



SCHEME 1. Reaction between bound wood acid and 2(1-aziridinyl)ethyl methacrylate (AEM).

If carboxylic acid groups are present in oxidized wood, the expected reaction⁶ with the aziridinyl group of AEM can be depicted as in Scheme 1. As a consequence of this reaction, the nitrogen content of the oxidized wood should increase after reaction with AEM. Table II summarizes the uptake of AEM by the oxidized wood measured as a function of the nitrogen content of wood. It should be noted that the nitrogen content is not lost even after Soxhlet extraction, thereby indicating that the AEM moiety is not just occluded but is covalently bonded to wood. Confirming this conclusion, is the fact that unoxidized wood does not show evidence of reaction with AEM; its nitrogen content shows little increase after AEM treatment.

Both methanol and water may appear to be suitable solvents for this reaction as reflected in increase of nitrogen content (Table II). However, it was observed that after standing for only a very short time, the aqueous solutions

TABLE II
Reaction of oxidized wood with AEM

Solvent	N, %	
	1	2 ^a
MeOH	6.23	6.40
Acetone	4.98	5.29
Water	6.22	^c
Unoxidized wood ^b	0.12	^c

^a After Soxhlet extraction with acetone for 48 h.

^b Reaction with neat AEM, no solvent.

^c Not determined.

of AEM turned milky, a process which is due to the polymerization of AEM through the aziridinyl group.⁶ In view of this, water is not a suitable solvent for this treatment, whereas methanol should be preferred as solvent.

As well as providing a means of surface modification, the ready room temperature reaction between the aziridinyl functional group and carboxylic acids⁶ provides chemical proof of the formation of carboxylic acid groups in wood on reaction with nitric acid. Both oxidation and hydrolysis of ester groups are likely mechanisms for the formation of carboxylic acids. The pendant vinyl group of the chemically-bonded AEM, and the new secondary amine group generated by opening of the aziridinyl ring by carboxylic acid, provide new sites for reaction with binder resins for bonding of wood particles.

C. Furfuryl alcohol polymerization

Furfuryl alcohol is a good penetrant, and is also a component of adhesive binders for wood particles. It is also well known that dimensional stabilization of wood can be achieved by impregnating wood with chemicals and polymerizing them *in situ* with suitable catalysts.⁷ Thus Stamm^{7,8} has used water soluble monomers, including furfuryl alcohol, to effect dimensional stabilization.

It was therefore of interest to see if the carboxylic acid groups generated in oxidized wood could initiate *in situ* polymerization of furfuryl alcohol. A slow but definite change of color was observed from straw yellow to dark brown, when oxidized wood, washed free of adhering acid, was left in contact with furfuryl alcohol. This rate and type of color change was about the same as observed when acetic acid was added to furfuryl alcohol; with nitric acid, the color change was very much faster. On the other hand, with unoxidized wood there was no noticeable color change. Since acetic and nitric acid are known catalysts for furfuryl alcohol polymerization, the qualitative tests described above are indication of the initiation of furfuryl alcohol polymerization by bound acid generated in wood. This observation was supported by increase in viscosity of the polymerizing furfuryl alcohol which was followed by the measured flow times in an Ostwald viscometer (Figure 4).

The advantages deriving from the catalysis of *in situ* polymerization of furfuryl alcohol are noteworthy. The polymerization taking place in the interior of wood flakes would have the effect of reinforcing the wood flakes and also reducing its water sorption, both of which can be expected to improve composite board properties.⁷ In actual practice the catalytic activity of the wood acids will, of course, be augmented by that of the free nitric acid present on the surface. The consequences of the *in situ* polymerization of furfuryl alcohol in oxidized wood are now under detailed investigation.

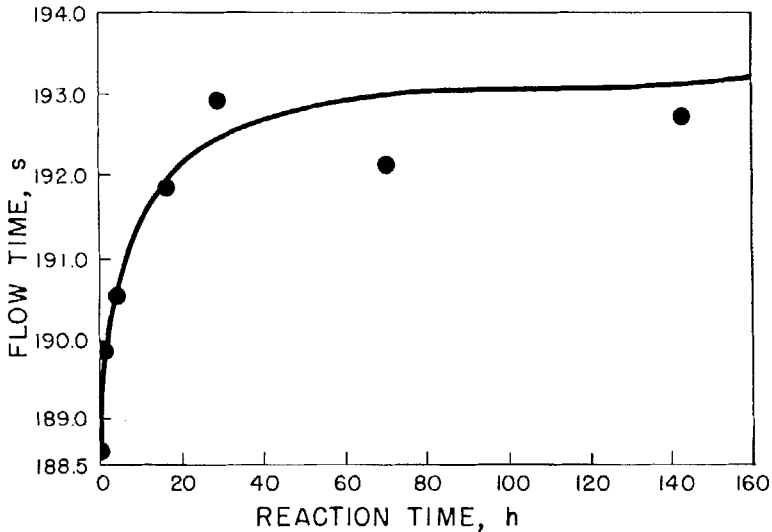


FIGURE 4 Furfuryl alcohol polymerization by the bound wood acid at 25°C, indicated by changes in capillary flow time of furfuryl alcohol with reaction time.

SUMMARY

Nitric acid oxidation of wood results in the formation of carboxylic acid covalently bonded to wood. These acid groups are capable of reaction with coupling agents such as 2-(1-aziridinyl)ethyl methacrylate, and also catalyze the *in situ* polymerization of furfuryl alcohol.

Acknowledgement

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