

Bond formation by wood surface reactions: Part III — Parameters affecting the bond strength of solid wood panels

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Abstract

Parameters such as press conditions, activating reagent, wood species, and bridging material were investigated to determine their effects on the shear strength of bonded solid wood panels. Panels with good dry shear strength were produced at moderate temperatures and pressures with a long closed press time. The type of activating reagent and the species of wood bonded had an important effect on the final strength properties. Sugar maple (*Acer saccharum* Marsh.) activated with aqueous nitric acid yielded the highest and most consistent dry shear strength values. However, prolonged nitric acid activation degraded the wood substrate.

Anatomical features of the wood played an important role in the final strength properties. The softwood species exhibited extensive crushing of the earlywood which created an uneven wavy surface with very poor bonding properties. The ring-porous hardwood examined also showed similar crushing of the vessel elements which resulted in lowering of the shear strength. Bridging materials such as diacids, diamines, and aromatic compounds enhanced the strength properties of the bonded panels. An aqueous solution of tannin in combination with nitric acid activation produced a panel with good wet and dry shear strengths.

The concept of forming a bonded wood product by chemically activating or altering the wood surface prior to bonding has been extensively studied in the last 10 years (5,9,15,23,29). In this process the wood surface is treated with chemical reagents, usually an oxidizing reagent or acid, to modify the functional groups present on the surface. These newly formed, more reactive functional groups are capable of reacting directly with

functional groups on another wood surface or with a difunctional cross-linking agent to connect the two activated wood surfaces. Cross-linking agents which have been investigated include diamines and diacids as well as molecules capable of undergoing condensation reactions such as mixtures of furfuryl alcohol and phenols, tannins, or lignosulfonates.

This article will briefly review some of the changes that take place on the wood surface, along with a more extensive review of previous work on wood surface bonding. An extended review is necessary because much of the research has not been published or is found in patent or foreign literature. Finally, some new results of bonding solid wood with this technique will be presented.

Literature review

Changes on the wood surface

The different chemical reagents that have been used to modify the wood surface include nitric acid and nitrogen oxides, hydrogen peroxide with iron catalyst, peroxyacetic acid, and periodate. All of these systems are capable of oxidizing wood hydroxyl groups to carbonyl or carboxyl groups in aqueous solutions. To confirm that these reagents were also capable of oxidizing wood surfaces, infrared spectroscopy (8,18,23) and electron spectroscopy for chemical analysis (ESCA) (29) have been used to examine treated wood surfaces. These two techniques measure chemical properties by different means and thus provide an independent confirmation of changes on the wood surface.

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The spectral results, some of which were presented in Parts I and II of this series of publications (18, 29), showed that the solid wood surface was extensively oxidized by treatment with nitric acid, hydrogen peroxide, or periodate. The ESCA results showed that nitric acid pretreatment yielded a surface which was especially rich in carboxyl groups. These studies clearly established that treatment of the wood surface with nitric acid, hydrogen peroxide, or periodate resulted in an oxidized wood surface.

Additional previous work

The concept of treating a wood surface to improve adhesion was mentioned as early as 1939 (27). This patent states that oxidants were used in conjunction with heat to yield a "nonhygroscopic" product. Incorporation of an adhesive was preferred, but a product of "significant" strength was claimed without the adhesive.

Two patents (6, 7) by Emerson described a process whereby particles were pretreated with nitric acid before being bonded with furfural mixed with either urea or "waste lignin liquor from a sulfite pulp." Based on Emerson's work, a plant owned by Kroehler Manufacturing Co. started producing "Cultured Wood" in 1960 (28). The product was a medium-density fiberboard in which the fibers had undergone a nitric acid pretreatment before being bonded with furfural under heat and pressure. It should be noted that furfural undergoes acid-catalyzed condensation reactions and does not require surface activation to act as an adhesive.

The effects of a number of different oxidizing systems on wood and the individual wood components were studied by Stofko (23). These systems included hydrogen peroxide with transition metal catalysts at various pH's as well as sodium hydroxide and sulfuric acid. A boiling-water-resistant product was formed from wood fibers and lignin but under different reaction conditions. Physical tests were used to conclude that "oxidative coupling produces significantly higher bonding strengths" than either acid or alkaline reactions through repolymerization of oxidation degradation products. It should be noted that extreme pressing conditions of 1,200 psi and temperatures up to 340°F were used. Under these conditions, it is reasonable to expect plastic flow of lignin to effect some bonding without the addition of chemical reagents.

Two patents (4, 25) were also issued to different researchers at the University of California-Berkeley. Both dealt with the formation of a bonded wood product following an oxidative treatment. One patent (4) also diagrams a process by which wood particles can be reacted. The particles were oxidized with nitric acid or oxides of nitrogen and several bridging materials were incorporated into the mixture before pressing. The second patent (25) specifies several combinations of oxidizing reagents, including hydrogen peroxide and sodium chlorate with various catalysts. These oxidants were used to treat veneer panels which were bonded without any bridging materials. Both of these patents claimed that a product of moderate strength was formed. The products were also claimed to have some water-resistant properties. Exceptional dimensional stability

was noted for particleboard activated with nitric acid and nitrogen oxides (4).

Similar concepts with a different approach were used by Antonie et al. (2) to bond spruce particles without an adhesive. Here a thermal pretreatment was used to oxidize the wood substrate and generate organic acids. These acids were reported to degrade parts of the wood substrate into resinous products that were sensitive to condensation reactions. The final result of these reactions was an improvement in swelling resistance and "hygroscopicity properties" of the boards.

Nitric acid and nitrogen oxides were used by Collett as an oxidative pretreatment for particleboard (5). Surface activation was reported to occur by nitration followed by heat initiated oxidation of wood hydroxyl groups. Diamines and diols were then used to create amide or ester linkages between wood surfaces. One diamine, 1, 6-hexamethylene diamine, was reported to promote the formation of a water-resistant product. Alkaline extraction prior to bonding led to reduced strength values. This was thought to be due to the removal of low molecular-weight degradation products that were capable of in situ esterification reactions. From his results, Collett concluded that oxidation was responsible for the in situ polymerization of ligno-cellulosic fibers.

In separate work by Schorning et al. (20, 21), 1,6-hexamethylene diamine, in combination with polyvinylchloride or epichlorohydrin, was used as a particleboard binder. When this mixture was used under alkaline conditions and in combination with microcrystalline cellulose, strength values comparable to those of phenolic controls were reported. Lignin was noted to be of particular importance for bond formation. In their second publication (21), these authors reported a bonding system using maleic anhydride and polyvinyl alcohol at an acidic pH. While particleboard could be made between room temperature and 140°C, none of the boards made under acidic conditions showed good water-resistant properties.

Diacids in conjunction with an acid catalyst were used by Pohlman (17) to form in situ ester linkages in particleboard. Maleic and succinic anhydride and maleic acid were used as cross-linking agents with hydrochloric acid the best catalyst. Based on tests of the physical properties of the particleboards and extraction data, the bond strength was attributed to covalent and hydrogen bonds.

Phillippou used oxidants such as hydrogen peroxide, peroxyacetic acid, nitric acid, and potassium ferricyanide to pretreat chips that were then cross-linked with furfuryl alcohol or mixtures of furfuryl alcohol with various phenolic compounds (14). Most of the different combinations of activators and cross-linking agents provided a water-resistant product with remarkable dimensional stability. Differential scanning calorimetry (DSC) was used to show that the furfuryl alcohol-ammonium lignosulfonate mixture cured differently if it was catalyzed by heat alone, or by hydrogen peroxide or maleic acid in conjunction with heat. Lignin was found to be the most reactive wood component and seemed to be susceptible to the formation of covalent bonds with the cross-linking mixture. It

was concluded that the furfuryl alcohol-ammonium lignosulfonate mixture, preceded by surface activation, bonded to the wood surface by a graft polymerization mechanism rather than a conventional condensation reaction.

More recently, peroxyacetic acid was used by Johns and Nguyen (9) to bond solid wood panels without the benefit of any gap-filling materials. The peroxyacetic acid was generated by mixing acetic acid and hydrogen peroxide with a mineral acid catalyst. Variables that led to higher concentrations of peroxyacetic acid, such as higher concentrations of hydrogen peroxide or more mineral acid, increased shear strengths, both wet and dry. The extreme variability of the shear strengths was attributed to the lack of gap-filling capabilities of the system. Although not stated directly by the authors, it seems likely that the more concentrated the peroxyacetic acid, the more oxidized the wood surface and the higher the shear strength of the bonded panel.

Several other researchers (10, 11, 12, 15, 24) have examined the possibility of bonding particles with furfuryl alcohol-lignin mixtures or with furfuryl alcohol alone, following hydrogen peroxide or nitric acid activation. A review of these studies is left to a subsequent article (12) since the bridging material more closely resembles a three-dimensional condensation adhesive with an acid catalyst than an intermediate difunctional linkage.

The studies mentioned above clearly indicated that surface treatments can promote a bonded wood product and that oxidation often occurs as a result of the surface treatment. However, none of the studies showed a direct cause and effect relationship between oxidation and bond formation, nor did the results show that covalent bonds were indisputably present. The purpose of the present study was to demonstrate a more direct correlation of surface treatment and bond strength.

Materials and methods

Five different wood species were used in this study: three hardwoods – sugar maple [*Acer saccharum* (Marsh.)], yellow birch [*Betula alleghaniensis* Britton], and northern red oak [*Quercus rubra* L.], and two softwoods – Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco.], and longleaf pine [*Pinus palustris* Mill.]. Samples were selected from lumber according to ASTM Standard D-905 (1) and conditioned to give an equilibrium moisture content of 8 percent. The sample panels measured 0.8 by 12.7 by 17.8 cm with the face to be bonded finished on a special jointer to give a smooth surface. Two such panels were bonded with the grain parallel. The panel size allowed nine modified shear blocks (26) to be cut from each panel and the edges to be discarded. All chemical reagents were obtained from commercial sources. The concentrations and solvents for the activating agents and bridging materials are shown in Table 1.

A set of three bonded panels was made to study the effects of the bonding parameters, species, and activating reagents. These panels were bonded with 8 g of 40 percent nitric acid at 100°C and 2 MPa for 1 hour. Many replications were necessary due to the highly variable nature of the samples bonded without a

TABLE 1. – *Chemicals used for bonding studies.*

Material	Concentration when applied
Nitric acid	40% aqueous solution
Sulfuric acid	30% aqueous solution
Hydrogen peroxide	30% aqueous solution
Potassium periodate	0.3 M aqueous solution
Potassium persulfate	0.3 M aqueous solution
Urea	3.5 M aqueous solution
Hexamethylene diamine	3.5 M aqueous solution
Maleic anhydride	3.5 M solution in acetone
Phthalic anhydride	3.5 M solution in acetone
Vanillin	3.5 M solution in 95% ethyl alcohol
Benzoic acid	3.5 M solution in 95% ethyl alcohol
Phenol	3.5 M aqueous solution
Resorcinol	3.5 M aqueous solution
Wattle tannin	1.0 M aqueous solution

bridging material. For the analysis of the different bridging materials, two panels were produced with 6 g of the appropriate bridging material added immediately before pressing. These panels were pressed at 170°C and 2 MPa for 30 minutes. The open assembly time (O.A.) was defined as the time at room temperature between the application of the surface activating reagent and the time the panels were put in the press. Both the surface activating reagents and the chemical bridging materials were applied as solutions with a hand-held atomizer.

With practice, the amount of material applied to each surface could be controlled within 25 percent. All panels were pressed immediately following the application of the bridging material. The modified shear blocks were tested according to ASTM Standard D-905 (1). All of the shear blocks made under the same conditions were considered as a group and the statistical parameters calculated accordingly (22). Practically all the samples failed at the modified wood surface or bondline. Therefore, wood failure data is not available for this type of study.

Results

Preliminary experiments

Several preliminary experiments were conducted to establish bonding conditions that would give reproducible results. These experiments were a cursory look at the parameters relevant to the formation of a bonded product and no effort was made to maximize the various interactions. The parameters that were investigated included press temperature and pressure, the amount of nitric acid applied as a surface activating agent, and the orientation of the bonding surface (tangential or radial). All of these panels were treated with 40 percent aqueous nitric acid.

The press temperature not only affects the rates of any chemical reactions but it also affects the flow of the different components and hence may influence contact between the two surfaces. A series of panels was made at different closed press time and temperature combinations. While there were some anomalous data points, a definite trend was observed. At a constant closed-press time, as the temperature increased, so did the bond strength until a point, after which the strength decreased.

TABLE 2. - The effect of pressure on the dry shear strength of nitric acid treated hard maple.

Press pressure MPa	Dry shear strength	
	Mean MPa	Standard error MPa
1.0	8.96	1.07
2.0	13.81	0.56
3.5	11.97	1.05

Bonding conditions: 8 g of 4% nitric acid, 4-hr. open assembly time, 1 hr. in the press at 100°C; 27 specimens tested.

TABLE 3. - The effect of grain orientation on the dry shear strength of nitric acid treated hard maple.

Bonded surface	Dry shear strength	
	Mean MPa	Standard error MPa
Tangential	9.33	0.70
Radial	13.81	0.56

Bonding conditions: 8 g of 40% nitric acid, 4-hr. open assembly time, 1 hr. in the press at 100°C and 2 MPa pressure; 27 specimens tested.

Three different press pressures were also investigated to determine the effect on dry shear strength. The results (Table 2) showed that the pressure had a dramatic effect on dry shear strength. At the highest pressure, 3.5 MPa, there was visible crushing of the vessels and fiber lumen and flow at the bondline. The dense latewood bands resisted crushing better than the earlywood which gave a wavy texture to the samples. These broad latewood bands, which are prominent on the tangential surfaces, tend to bridge one another and reduce the area of intimate contact. There was also crushing, on a microscopic scale, at the lower pressures. Both lignin and hemicellulose are also known to become more plastic and flow at an elevated temperature (19). Thus, the anatomical features of the wood contributed to the results given in Tables 2 and 3.

The orientation of the bonded surface (tangential or radial) could have several effects. Wood is an anisotropic material that has different dimensional characteristics in different directions. The dense latewood bands are more prominent on the tangential surface. The results (Table 3) showed that activation of the radial surfaces led to significantly higher shear strengths.

A 40 percent nitric acid solution was used in this study based on encouraging results in previous work (5). By minimizing the amount of applied acid, it was hoped that dimensional changes and surface degradation could be minimized. As shown in Figure 1, the more nitric acid applied to the wood surface, the higher the dry shear strength. The decline in strength above 8 g of applied acid was probably due to excessive surface degradation caused by the applied nitric acid.

The effects of temperature and amount of applied reagent appeared to be more directly related to chemical changes at the wood surface. Dry shear strength increased with temperature up to a maximum. The decline in shear strength at higher temperatures appeared to be due to degradation of the substrate

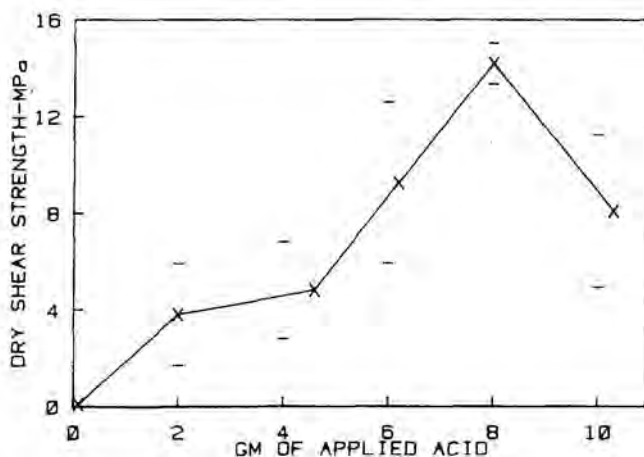


Figure 1. - Effect of differing amounts of applied 40 percent nitric acid on the dry shear strength for sugar maple with a 2-hour open assembly time (bonded at 100°C and 2 MPa for 1 hour).

surface. Acid degradation of the substrate also appeared to be responsible for the low strength values of samples activated with an excess of acid. The extensive degradation of the wood substrate was quite evident upon microscopic examination. A detailed review of the microscopic results was presented elsewhere (13).

Species effects

Five different species of wood were bonded by treatment with nitric acid. The resulting dry shear strengths are shown in Figure 2. The two softwoods, Douglas-fir and longleaf pine, performed very poorly, while one hardwood, red oak, gave moderate strength values. Sugar maple panels yielded high strength values, especially at short O.A. Yellow birch samples showed a constant increase in shear strengths with increased O.A.

Again, the differences in shear strengths can be explained by anatomical differences between the species. Penetration of the softwoods by the nitric acid was dramatically affected by the earlywood-latewood transitions. The latewood bands were not readily penetrated and tended to bridge one another. This led to a wavy surface, poor contact between the two activated surfaces, and low strength values. The large red oak vessels were preferentially crushed during pressing. The crushing led to a wavy and uneven surface but there were still some areas of good contact, as indicated by the moderate strength values.

Sugar maple and yellow birch are both diffuse porous hardwoods with a moderate number of vessels. However, the vessels in sugar maple are generally smaller than those in yellow birch. The penetration of nitric acid into both of these woods was relatively uniform and the surfaces of the failed samples were smooth. It is possible that the differences in vessel size were enough to introduce slight variations of contact between the surfaces. As mentioned before, bonding by this method is extraordinarily sensitive to surface

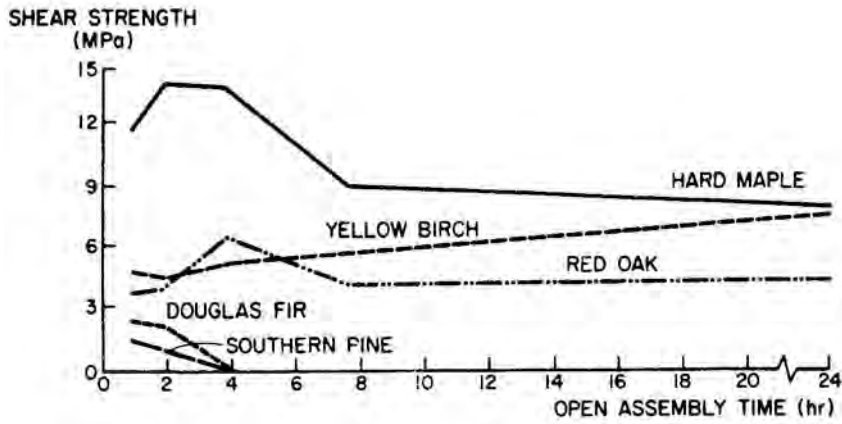


Figure 2. - Dry shear strengths of different species of wood activated with 40 percent nitric acid (bonded at 100°C and 2 MPa for 1 hour).

contact. Thus the sugar maple, with better surface contact, would be expected to yield higher strength shear samples.

Activating reagent effects

Five different chemicals were tested as wood surface activators. The predominant reactions between wood and each reagent can be very roughly separated into different categories (Table 4). It was hoped that a single type of reaction, i.e., oxidation, might be found to be responsible for the formation of bond between treated wood surfaces. The results from the evaluation of the reagent effects are shown in Figure 3.

These results show that sugar maple activated with three reagents, nitric acid, sulfuric acid, and potassium periodate, produced boards with comparable moderate strength values. Samples activated with hydrogen peroxide and potassium persulfate gave significantly lower dry shear strengths. The highest strength panels

TABLE 4. - Prominent reactions of selected activating reagents.

Treatment	Oxidation	Acid condensation	Free radical generation
Nitric acid (40%)	X	X	-
Sulfuric acid (30%)	-	X	-
Hydrogen peroxide (30%)	X	-	X
Potassium persulfate (0.3 M.)	X	-	X
Potassium periodate (0.3 M.)	X	-	-

were induced by nitric acid activation with an O.A. of 2 or 4 hours.

Sulfuric acid activated samples yielded consistent shear strengths which were not affected by O.A. The potassium periodate gave highly variable results that were not consistently affected by O.A. The two strongest oxidants (hydrogen peroxide and potassium persulfate), which were also capable of free radical generation,

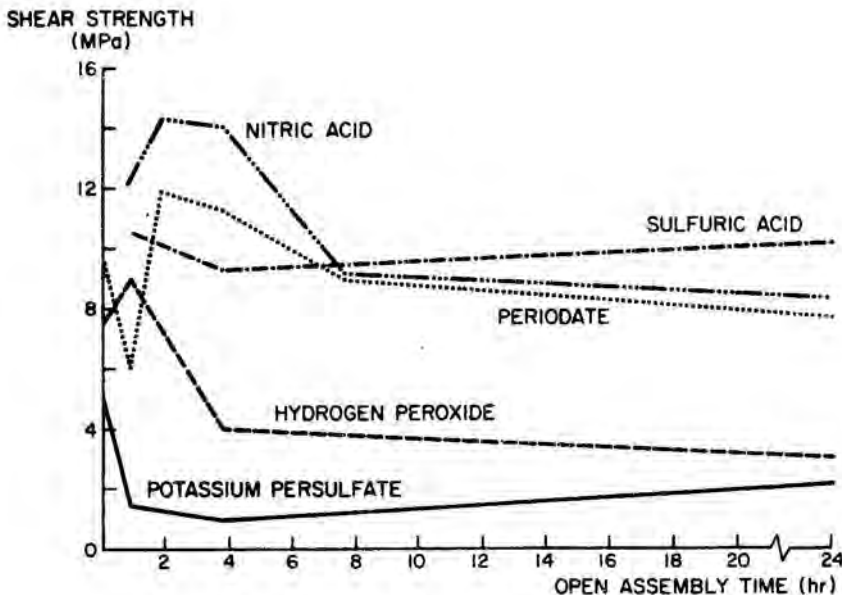


Figure 3. - Dry shear strengths of sugar maple activated with different reagents (bonded at 100°C and 2 MPa for 1 hour).

produced panels with low bond strengths regardless of the O.A.

Wood removed from the surfaces of failed samples and examined with infrared spectroscopy showed that oxidation and condensation reactions did take place, in approximate accordance with Table 4. The pH of failed samples was determined with a surface electrode and no relationship was found between pH and shear strength.

Nitric acid and sulfuric acid are capable of undergoing a wide variety of reactions with the wood components. Hydrolysis and dehydration of polysaccharides to furans with subsequent condensation could lead to the formation of a high strength bond. The infrared spectra and the light color of the failed samples indicated that oxidation was the predominant reaction of the periodate-treated samples. Based on the low strengths of the hydrogen peroxide and potassium persulfate samples, it appears that free radical reactions do not strongly contribute to bond formation. It is also doubtful that oxidation alone is sufficient for the formation of a high strength bond.

These results indicate that a single type of reaction, i.e., oxidation, is not solely responsible for the formation of a bonded product. It seems likely that bonds can be formed through several different mechanisms, and that formation of high strength bonds requires a combination of several different reactions (5, 14, 15, 23, 29).

It should also be noted that none of the activating reagents generated a water-resistant product. This was surprising because some of the acid-condensation reactions of lignin and polymerization of carbohydrate degradation products (furans) should lead to water-resistant bonds. Condensation type reactions generally yield strong carbon-carbon bonds rather than the more labile ether and ester linkages. The absence of water-resistant linkages was probably due to poor contact between the two surfaces. This also inhibits the formation of other linkages. Wood is a rough substrate and large areas of intimate contact are uncommon. Even though softening and flow are promoted by the heat and pressure, it is probable that surface roughness was too great to allow the transfer and wetting required for the formation of strong bonds. One method of obtaining contact and hence higher shear strengths is through the use of bridging (gap-filling) materials.

Bridging materials

Two classes of bridging materials were selected based on previous success with the bonding of wood particles (5,17,20). Diacids and diamines were reported to form ester and amide linkages, respectively, with the activated wood surfaces. Both types of linkages should be resistant to moisture. The dry shear strengths for samples bonded with the different bridging materials are shown in Figure 4.

Neither urea nor phthalic anhydride promoted a high bond strength. The shear strengths for bonded samples which contained these compounds were lower than panels bonded with nitric acid alone. The addition of maleic anhydride and 1,6-hexamethylene diamine promoted higher shear strengths than the nitric acid activation alone. However, only maleic anhydride had residual strength after a vacuum-pressure soak (Table

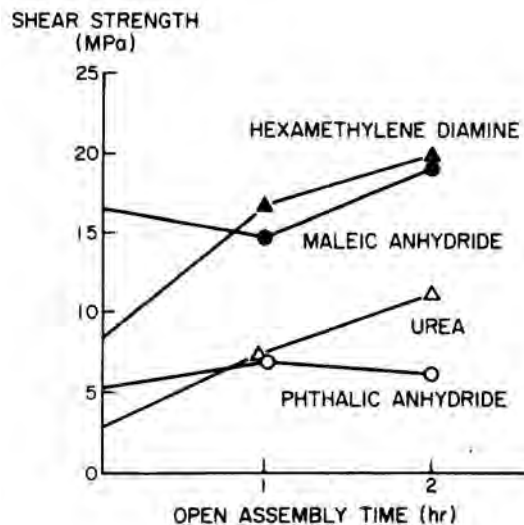


Figure 4. - Dry shear strengths of sugar maple panels activated with 40 percent nitric acid and bonded with various diamine and diacid cross-linking agents (pressed at 170°C, 2 MPa for 30 minutes). Values for controls are listed in Table 5.

5). Thus, if amide linkages were formed, they were not numerous enough to resist the internal stresses generated by the shear block as it adsorbed moisture. Maleic anhydride could have formed ester linkages, although maleic anhydride is a relatively small molecule and would not be capable of bridging large gaps between the wood surfaces.

Previous work (5, 18, 23) has shown lignin to be an important component in the formation of a bonded product by surface activation. Thus, several lignin degradation model compounds and aromatic molecules were tested as additives to surface activated samples. The dry shear strengths are shown in Figure 5 and the wet shear strengths in Table 5. With the exception of vanillin, all of the compounds promoted higher dry and wet strengths than samples activated with nitric acid alone.

Tannin, a natural polymer extract of black wattle (*Acacia mearnsii*), is typified by the (+) catechin chemical structure (16). This large molecule gave the best strength values, both wet and dry, of any of the compounds tested. Because of the large size and reactive sites, tannin appears to be well suited for bridging gaps between two activated surfaces. Tannins may also polymerize to form a polymer in situ under acidic conditions. Resorcinol and phenol are too small to connect two wood surfaces directly but would also be capable of forming an adhesive in situ. Compounds with aromatic rings would be capable of condensing with aldehyde groups on the wood surface or with any of the aldehydes, including formaldehyde, that are known degradation products of nitric acid-treated wood (3). Thus, an individual molecule could connect two surfaces directly, which is unlikely based on their small size, or form a condensation polymer that could be terminated at the opposite activated wood surfaces.

TABLE 5. - Dry and wet (after a vacuum-pressure soak) shear strength for boards bonded with different chemical agents.

Chemical bridging agent	Open assembly time ^a (hr.)	Dry shear	Wet shear
		(Mpa)	(MPa)
Urea	C ^b	7.22	0
	0	3.13	0
	1	6.72	0
	2	11.25	2.28
Hexamethylene diamine	C	13.82	0
	0	8.71	0
	1	16.55	0
	2	19.47	1.74
Maleic anhydride	C	8.73	1.10
	0	16.34	4.67
	1	14.41	4.88
	2	18.64	3.21
Phthalic anhydride	C	0	0
	0	5.32	0
	1	6.73	0
	2	6.20	0
Vanillin	C	7.40	0
	0	6.72	0
	1	9.01	0
	2	5.50	0
Benzoic acid	C	9.30	0
	0	14.35	5.12
	1	16.39	3.69
	2	16.07	3.37
Phenol	C	8.36	0
	0	14.00	0
	1	11.40	2.43
	2	14.14	1.12
Resorcinol	C	11.86	0
	0	17.66	1.80
	1	17.80	5.00
	2	13.74	4.15
Tannin	C	10.94	2.03
	0	19.07	9.19
	1	16.49	8.64
	2	18.45	8.64

^aOpen assembly time is the length of time after the acid treatment and before the addition of the chemical bridging agent.

^bC - Control; the chemical bridging agent was added to a sample which had no acid pretreatment.

Conclusions

The results from this study demonstrate that solid wood panels can be bonded by activating the wood surface. The shear strength of the product was highly dependent on the surface activating reagent and species of wood. Sugar maple (*Acer saccharum* Marsh.) activated with 40 percent nitric acid provided the highest and most reproducible shear strengths. However, substantial degradation of the wood structure resulted from the nitric acid activation and subsequent pressing. Press conditions had a profound effect on the resulting dry shear strength. Anatomical features of the wood, such as density differences between earlywood and latewood and the number and size of vessel elements, also had a dramatic effect on the resulting shear properties although good dry shear strengths were obtained. None of the various combinations of wood

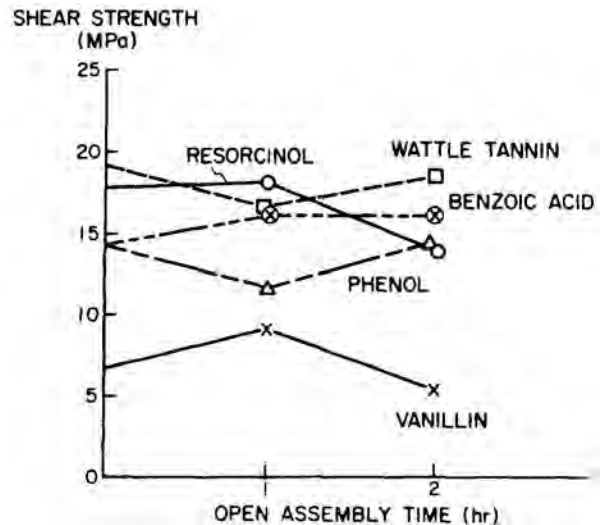


Figure 5. - Dry shear strengths of sugar maple panels activated with 40 percent nitric acid and bonded with various phenolic cross-linking agents (pressed at 170°C, 2 MPa for 30 minutes). Values for controls are listed in Table 5.

species and surface activating reagents yielded a water-resistant sample. Instrumental analysis of the samples indicated that no single mechanism, i.e., oxidation, was responsible for the formation of a high strength bond.

Several different bridging materials were applied to the activated wood surface prior to pressing to improve strength properties. Diacids and diamines in several cases improved the dry shear strengths, but did little to improve the wet strength values. Several lignin degradation model compounds and other aromatic compounds were also used as bridging materials. Benzoic acid, resorcinol, and tannin all improved the dry and wet strengths. The addition of tannin provided shear strengths comparable to that achieved with phenolic type adhesives.

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