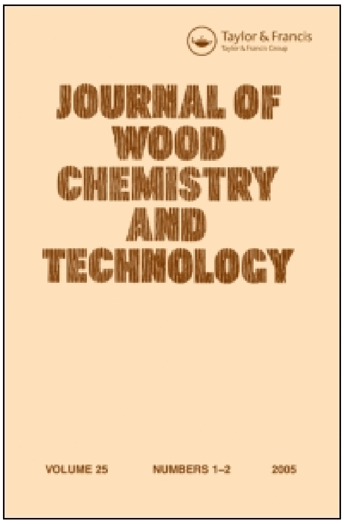

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Applicability of Oxidative Systems to Initiate Grafting on and Bonding of Wood

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APPLICABILITY OF OXIDATIVE SYSTEMS TO INITIATE GRAFTING ON AND BONDING OF WOOD

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ABSTRACT

Graft polymerization techniques were applied to induce bonding in wood composites. Wood surfaces were activated with an oxidant such as hydrogen peroxide, nitric acid, peracetic acid, potassium ferricyanide or sodium dichromate. The activated wood surfaces were then chemically crosslinked with polymerizing materials such as furfuryl alcohol, ammonium lignosulfonate, mixtures of lignosulfonate with furfuryl alcohol, with formaldehyde or with maleic acid. The wood composites were pressed using conventional manufacturing conditions. The strength and water resistance properties of the wood composites were suitable for exterior structural applications. The various methods proposed to induce chemical bonding of wood are briefly reviewed.

INTRODUCTION

Bonding wood on an industrial scale presently is based on synthetic adhesives such as urea- and phenol-formaldehyde resins. These adhesives are manufactured from natural gas or petrochemicals, hence finding alternate ways of bonding wood is desirable.

The conventional bonding process involves application of an adhesive and solidification of the adhesive between the surfaces to be bonded. The strength and durability of the bonding is directly related to the nature and type of bonds which are formed between adhesive and substrate, and of bonds formed within the adhesive film. The formation of adhesive bonds has been ascribed to mechanical interlocking, van der Waals forces, electrostatic forces, hydrogen bonding and covalent bonding.[1] Secondary forces are sufficient to impart strength to a bonded joint, while chemical or covalent bonds appear to be important to the durability of the joint.[2] The energy of van der Waals forces is of the same order of magnitude as that of hydrogen bonds, while both are several dozen times less than the energy of chemical bonds.[1] Furthermore, depending on the affinity of substrate and adhesive for each other and for water, water can displace adsorbed adhesives held by secondary forces but not adhesives held by chemical bonds.

The relative importance of covalent bonds to the strength and durability of a bonded wood joint becomes more evident if we consider the behavior of wood when exposed to water or to loading of long duration. Wood shrinks and swells very little along the fiber direction in which anhydro-glucose units are held by covalent bonds within cellulosic chains, but swells and shrinks about 20-80 times more in the other directions in which cellulosic molecules are largely held by secondary forces, primarily by hydrogen bonds. The strength of wood is also several times higher in the fiber direction than in the others and decreases with increasing amounts of adsorbed water. The resistance of the bonding to the deteriorating action of water is of primary importance to the utilization of composite wood products, particularly in structural applications.

The chemical nature of wood and the ability of the wood components to undergo chemical modification and reactions with other chemicals offer possibilities of bonding through formation of chemical links. Interfiber crosslinking with formaldehyde,[3] esterification reactions,[4] and grafting of polymers on pulps,[5] have long been known to modify the physicochemical properties of wood and improve interfiber bonding of paper.

Recently, oxidative techniques have been proposed to develop bonding by direct coupling of wood surfaces. Stofko and Zavarin[6] reported bonding through treatment of wood with a wide variety of oxidizing agents including peroxides, chromates, nitrates, nitrites, ferric compounds and hypochlorites. When such chemicals are mixed with wood flour or wood fibers and pressed under heat, they produce wood composites which are strong and resistant to boiling water.[7] Johns and Nguyen[8] applied the same technique of oxidative bonding to laminates of wood. However, presumably because this process does not use a gap-filler, particleboards resistant to boiling water could only be made at very high densities of 1.2-1.3 g/cc,[7,9] and laminate panels bonded only at points of intimate contact.[8]

Another type of chemical bonding involves chemical oxidation of wood and crosslinking with difunctional monomers. Collett[10] preoxidized wood flakes and fibers with nitrogen oxides or nitric acid to create carboxylic groups on the surface of wood. He then used diamines or dialcohols under pressure and heat to crosslink the activated wood surfaces. The process resulted in excellent bonding. Since this system also lacks true gap-filling properties, particleboards resistant to boiling water were only made at densities higher than 0.9 g/cc. Similar results in particleboards at densities above 0.9 g/cc have been obtained by crosslinking reactive sites of wood with maleic or succinic anhydrides.[11]

Shorning and co-workers[12,13] using dialcohols, diamines or maleic and succinic anhydride either alone or in combination with polyvinyl chlorides and polyvinyl alcohols, respectively, investigated chemical crosslinking of wood without preactivation. The process develops particleboards of medium density (0.75-0.85 g/cc) with good mechanical properties but of low resistance to cold water.

Nimz, et al.[14] reported on the use of hydrogen peroxide in mixtures with potassium ferricyanide and pulping residues to chemically bond medium density particleboard. This process also develops particleboard with good mechanical properties but no resistance to cold water. Better results were obtained in particleboards bonded with lignosulfonates as crosslinking material, when the wood flakes were pretreated with sulfuric acid.[15,16]

Oxidation treatment of wood surfaces prior to bonding with adhesives has long been known as a technique to improve bonding and durability of wood composites. As early as 1939, Tischer[17] reported on the use of oxidizing agents such as potassium and sodium dichromates or nitric acid to improve water resistance of plywood bonded with an animal hide glue. Bryant[18] studied pretreatment of wood with chrome complexes to improve bonding with synthetic resins. Kim and Goring[19] reported that surface treatment of wood with corona-discharge improves gluability and bond strength of composites bonded with thermoplastic polymers. Chow[20] treated veneer surfaces with boric acid and borax to enhance adhesive bonding of wood with phenol and urea resins. Black and co-workers[21,22,23] reported treatments of wood surfaces with inorganic salts such as chromic acid and many of its salts or complexes to enhance adhesion to wood and durability of coatings, paints and stains. With reference to the mechanism of increasing adhesion strength and durability of paints, Black and Mraz[20] note "... all these inorganic chemicals being strong oxidizers probably cause chemical bonding of paint to wood by creating reactive sites or by crosslinking the paint to wood."

The work of the above researchers shows that bonding of wood by covalent bonds is possible. The work of Stofko[7] and Collett[10] has shown that chemical bonding of wood is also possible without the need of "waterproof" synthetic adhesives. Direct coupling of active sites on wood surfaces or crosslinking of such sites with difunctional monomers requires, however, that the wood surfaces come into close contact with separation not larger than a few angstroms. Due to the natural roughness of wood, formation of strong and waterproof bonding by the above methods requires pressing at high pressures, which results in wood composites of high densities. What is probably needed to overcome the roughness of wood and develop strong chemical bonding of wood composites at practical densities, is a macromolecule varying in molecular length that would chemically bridge active sites on the surfaces to be bonded at longer distances. Figure 1 shows how graft polymerization techniques offer such a possibility.

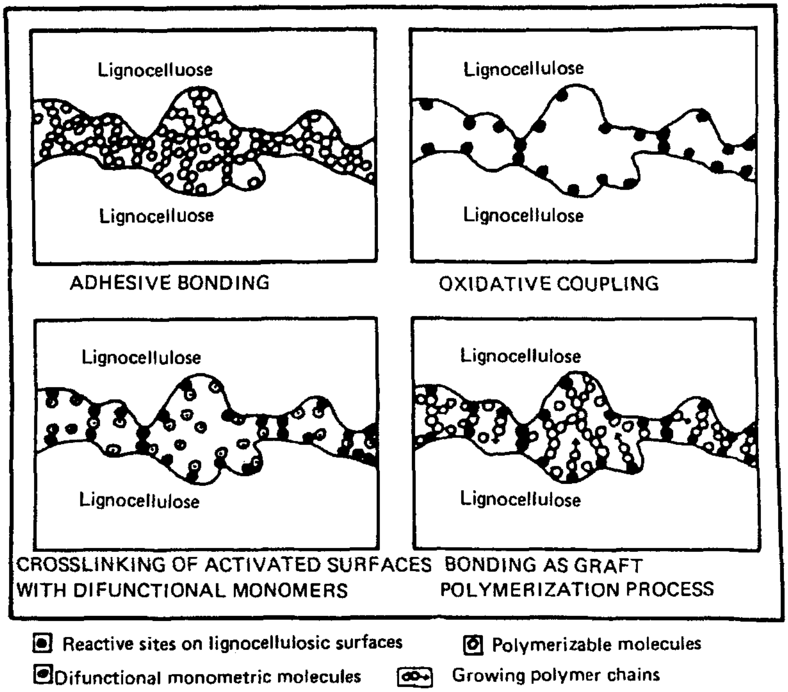

Figure 1. Idealized interfaces of lignocellulosic products bonded by various types of processes. The figure illustrates the gap-filling advantages of graft-polymerization.

Bonding of wood by a graft polymerization process involves chemical activation of wood and introduction of polymerizable chemicals between activated surfaces. These chemicals should be capable of reacting chemically with active sites on wood and then polymerize to growing chains until they meet and react with active sites on adjacent surfaces or polymer chains initiated from those surfaces.

This study was undertaken to investigate the applicability of graft polymerization techniques as outlined above to chemically bond wood.

RESULTS AND DISCUSSION

The Role of Surface Activators

It was assumed as a starting point that treatment of wood with oxidants will create reactive sites on the surface for formation of chemical bonds with the polymerizable chemicals. Table 1 shows that hydrogen peroxide was necessary to develop

TABLE 1

The Role of H_2O_2 in Developing Bonding of Particleboard*

H_2O_2 % (on O.D. wood)	Polymerizable Chemicals		Density (g/cc)	I.B. kPa	2-hour Boil	
	A	B			T.S.(%)	W.A.(%)
0	FA	—	0.75	0	—	—
2	FA	—	0.74	641	32.5	66.8
0	FAR	—	0.74	255	fail	fail
2	FAR	—	0.74	876	41.1	89.7
0	NH_4LS	—	0.74	0	—	—
2	NH_4LS	—	0.74	200	fail	fail
0	NH_4LS	MA**	0.75	0	—	—
2	NH_4LS	MA**	0.75	483	63.8	105.3
0	NH_4LS	CH_2O	0.75	0	—	—
2	NH_4LS	CH_2O	0.72	607	37.5	78.8
0	NH_4LS	FA	0.75	90	fail	fail
2	NH_4LS	FA	0.72	765	18.1	56.9
2	NH_4LS	FA**	0.76	724	18.3	46.5
0	PH	FA	0.70	0	—	—
2	PH	FA	0.74	483	35.2	74.5

*Particleboard made from white fir particles.

**$FeCl_3$ was used as catalyst. In all other boards maleic acid was used.

FA = furfuryl alcohol FAR = furfuryl alcohol resin
NH_4LS = lignosulfonate MA = maleic anhydride
CH_2O = formaldehyde PH = phenol

T.S. % = thickness swell W.A. % = water absorption particleboard resistant to boiling water. Only furfuryl alcohol resin from the seven polymerizable chemicals used, developed some adhesive bonding without hydrogen peroxide, but the internal bond was low and the boards failed in a few minutes when exposed to boiling water.

The role of hydrogen peroxide in developing water resistant bonding is also shown in Table 2. Wood failures of plywood and shear strengths of laminated panels, made with hydrogen peroxide as surface activator and a mixture of ammonium lignosulfonate and furfuryl alcohol, are comparable with those obtained with phenolic resins.[8]

Table 3 shows the effectiveness of other surface activators in developing bonding of particleboard. With the exception of sodium dichromate all surface activators developed bonding

TABLE 2

The Role of H_2O_2 in the Bonding of Laminated Panels

Type of Panel	H_2O_2 g/m^2	Polymerizable Chemicals A	Polymerizable Chemicals B	Wood Failure (%) Dry	Wood Failure (%) Wet	Shear Strength kPa Dry	Shear Strength kPa Wet
Plywood	0	NH_4LS	FA	93	28		
Plywood	0.14	NH_4LS	FA	100	83		
Laminated	0	NH_4LS	FA			6460	1550
Laminated	0.14	NH_4LS	FA			7826	3620
Plywood	0.19	NH_4LS	FAR	100	95		
Laminated	0.19	NH_4LS	FAR			11310	4480

NH_4LS = lignosulfonate FA = furfuryl alcohol

FAR = furfuryl alcohol resin

TABLE 3

The Effect of Various Surface Activators in the Bonding of Particleboard*

Surface Activator	Polymerizable Chemicals A	Polymerizable Chemicals B	Density (g/cc)	I.B. kPa	2-hour Boil T.S. (%)	2-hour Boil W.A. (%)
Hydrogen peroxide	NH_4LS	FA	0.72	765	18.1	56.9
Peroxyacetic acid	NH_4LS	FA	0.73	834	35.3	60.3
Nitric acid	NH_4LS	FA	0.72	565	23.8	57.0
Potassium ferricyanide	NH_4LS	FA	0.75	600	54.3	94.2
Sodium dichromate	NH_4LS	FA	0.74	234	fail	fail
Hydrogen peroxide	NH_4LS	CH_2O	0.72	607	37.5	78.8
Peroxyacetic acid	NH_4LS	CH_2O	0.74	862	57.7	107.9
Potassium ferricyanide	NH_4LS	CH_2O	0.73	207	fail	fail
Hydrogen peroxide	FAR		0.74	876	41.1	89.7
Peroxyacetic acid	FAR		0.70	938	33.7	84.2

*Particleboard made from white fir particles.
NH_4LS = lignosulfonate CH_2O = formaldehyde   FA = furfuryl alcohol
FAR = furfuryl alcohol resin
T.S. % = thickness swell   W.A. % = water absorption

resistant to boiling water when used with the mixture of ammonium lignosulfonate-furfuryl alcohol. Potassium ferricyanide, however, was ineffective when used with the mixture lignosulfonate-formaldehyde. Hydrogen peroxide and nitric acid appear to be the most effective in developing "waterproof" bonding.

The surface activators used in this study are more or less strong oxidants. Hydrogen peroxide in the presence of metal ions, carboxylic acids or at high temperatures decomposes into hydroxyl ions (HO^-), hydroxyl radicals ($H\dot{O}$), superoxyl radicals ($H\dot{O}_2$) and oxygen.[24] This chemical reactivity of hydrogen peroxide has been used to modify the properties of wood in a number of ways. Hydrogen peroxide has been used as an effective pulping or bleaching agent for wood,[25] as initiator in grafting various polymers onto cellulose and wood pulps,[5,26] and more recently as initiator of direct chemical bonding between wood surfaces.[6,7] Peroxyacetic acid, being a stronger oxidant than hydrogen peroxide, has also been used as an effective bleaching agent,[27] as grafting initiator[26,28] and as a bonding agent of wood.[8] The oxidative properties of nitric acid were used in pulping wood,[29] in chemically modifying the surface of wood and in making it reactive for bonding with difunctional monomers.[10] Potassium ferricyanide and sodium dichromate have been used as initiators for oxidative coupling of phenolic compounds and grafting of polymers onto lignocellulosic fibers.[29,30] From the above information it is reasonable to assume that the above oxidants chemically modify the surface of wood and provide active sites for grafting of polymer chains.

The Role of Polymerizing Chemicals

In selecting the chemicals for this study from the large number of available polymerizing chemicals the following requirements were set forth: first, the chemicals should be capable of homo- or copolymerization to form long polymer chains and possess at least one functional group for reacting with the components of wood; second, the chemicals should come from the class of natural renewable materials.

Table 1 shows that six of the seven systems of polymerizing materials developed water resistant bonding when used with hydrogen peroxide. Furfuryl alcohol as a monomer appears to develop better water resistance than its resin. The latter develops better internal bonding. Furfuryl alcohol appears also to develop better bonding than its mixture with the monomeric phenol. Ammonium lignosulfonate, in contrast to its mixtures with maleic anhydride, with formaldehyde or with furfuryl alcohol, failed to develop adequate bonding. It is interesting though that the mixture, consisting of seven parts of ammonium lignosulfonate and three parts of furfuryl alcohol, developed better water resistance than all the other chemical systems. Table 2 shows that the mixture lignosulfonate-furfuryl alcohol develops better bonding with all surface activators.

The relative performance in bonding of furfuryl alcohol and of lignosulfonate when used alone in comparison to their mixture is interesting. Furfuryl alcohol, a small molecule, is capable of reacting through condensation with lignin, through etherification with cellulose and lignin, and through esterification with oxidized wood. It is also capable of homo- and copolymerization via condensation, ionic or free radical addition reactions.[31] Thus, furfuryl alcohol appears to have better chances than any of the other chemicals in reacting with oxidized wood and in forming homo- or copolymeric chains. Lignosulfonates being large molecules and capable of copolymerizing with furfuryl alcohol appear to be important in forming long chains which are necessary to bridge distances between wood surfaces.

It should be noticed that lignosulfonates, due to their polymeric structure and to a rather small number of reactive sites on their structure, are not capable of forming highly crosslinked adhesive films when condensed with furfuryl alcohol, with formaldehyde or with maleic anhydride, at least under the conditions used in this study. Also, the presence of sulfonic groups on their structure will render any polymerization products of lignosulfonates with the above chemicals soluble in water if their polymeric chains are not chemically anchored on the wood surfaces. The resistance to boiling water of the boards made using surface activation suggests that polymer chains of the above chemicals react and form chemical bonds with the activated wood.

Effect of Surface Proximity

The results in Table 4 and Figures 2-5 show the ability of the hydrogen peroxide-ammonium lignosulfonate/furfuryl alcohol system to bond particleboard at various densities.

Table 4 shows properties of Douglas-fir particleboards made with two levels of hydrogen peroxide application at five densities. All boards exhibit strength and water resistance properties suitable for exterior structural application. Increasing the board density from 0.58 g/cc to 0.80 g/cc improves all properties. Use of 3% hydrogen peroxide results in better bonding than use of 1.5% hydrogen peroxide at all densities. Figures 2, 3, 4 and 5 illustrate this effect of board density in internal bond, MOR, and MOE, thickness swelling and water absorption in the 2-hour boiling test and in the 24-hour water soak test, respectively.

Analogous improvements in strength properties with board density have been found in conventionally bonded particleboard.[32] The improvement in thickness swelling and water absorption of our boards with density is, however, in sharp contrast to the behavior of particleboard bonded with conventional adhesives.[32] In conventional particleboard the higher the density the faster and greater the "springback", and the more wood substance the more thickness swelling and water absorption. The boards made with the grafting process do not obey this rule.

In polymer science, the degree of swelling of a three-dimensional polymer in various solvents measures the degree of crosslinking density of the polymeric network.[33] The lower the swelling of the polymer the higher the degree of its crosslinking, i.e., the polymeric chains in the network are held close together by a larger number of chemical bonds (links). This information could be used to explain the swelling behavior of our particleboards. If we accept the model that grafted chains of various lengths are formed at the interface and they are involved in the

Table 4. Effect of Board Density on Properties of Particleboard

							Water Soak Test							
					2-hour Boil Test		Thickness Swelling %				Water Absorption %			
H_2O_2 %	Density g/cc	I.B. kPa	MOR MPa	MOE GPa	T.S. %	W.A. %	1 day	2 days	4 days	7 days	1 day	2 days	4 days	7 days
1.5	0.58	220	22.07	4.27	107.4	130.8	51.6	54.8	56.6	60.6	106.2	115.6	125.3	129.3
1.5	0.62	440	23.68	4.72	83.7	109.9	31.0	32.4	34.4	35.0	80.7	88.5	97.3	101.3
1.5	0.68	614	28.31	5.19	60.8	97.4	23.0	27.1	28.2	29.4	62.9	70.9	78.8	80.5
1.5	0.74	814	29.52	5.55	31.0	70.9	10.8	13.5	16.4	18.2	39.2	47.2	54.6	57.2
1.5	0.78	862	31.46	5.78	11.4	31.4	5.7	8.8	11.1	12.3	30.0	36.6	43.2	45.2
3.0	0.58	503	21.00	4.32	84.3	116.1	33.1	35.5	36.3	37.6	92.1	100.2	108.8	110.9
3.0	0.64	703	23.74	5.07	46.7	86.6	17.8	20.8	22.1	23.6	59.4	70.3	78.7	80.9
3.0	0.68	834	26.53	5.68	30.2	69.2	11.5	15.2	16.9	18.3	45.7	54.5	63.0	65.9
3.0	0.74	896	25.15	5.79	14.6	44.7	5.8	7.8	9.0	10.0	28.2	33.6	40.0	43.1
3.0	0.80	924	26.13	6.02	5.8	14.6	3.4	4.8	5.8	7.3	18.4	22.7	29.7	33.7

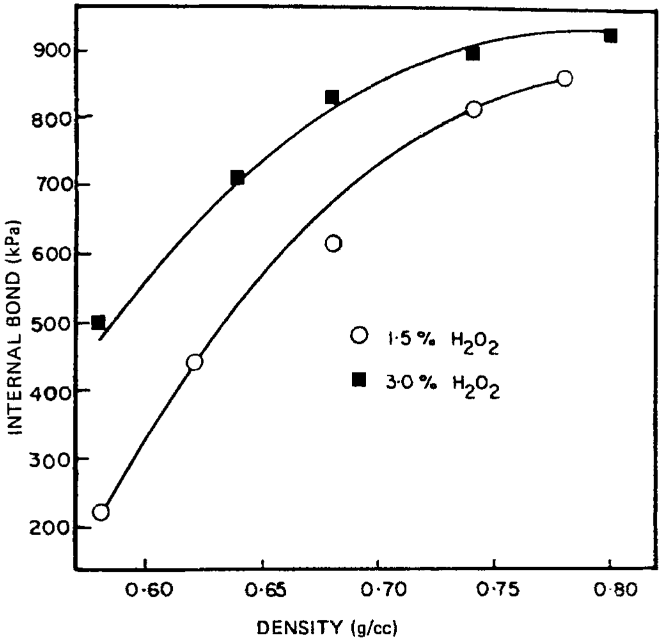

Figure 2. Effect of board density on internal bonding of particleboard.

bonding of wood, then more linkages become effective at higher board densities (due to the shorter distances between surfaces being bonded). Furthermore, if we accept resistance to boiling water as a measure of the number of chemical linkages between wood surfaces, then it appears that wood, at least in particleboard, is bonded by a continuous network of covalent bonds. The cross-linking density of this network increases as the distance of the surfaces being bonded becomes shorter and as the number of reactive sites on the surfaces (amount of oxidant) increases.

Grafting of Wood Particles

The ability of wood to undergo grafting with a number of polymers has been demonstrated by many researchers.[5,26,28,34,35]

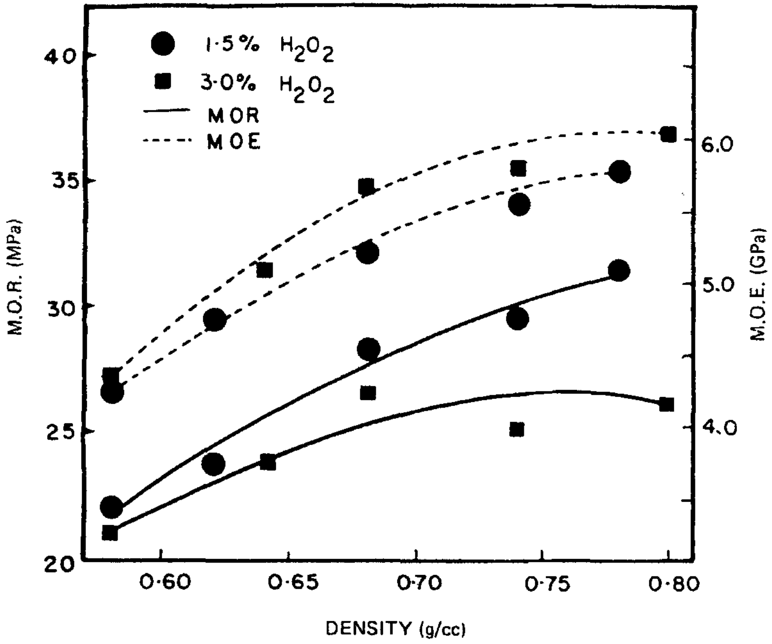

Figure 3. Effect of board density on MOR and MOE of particleboard.

The results shown in Figure 6 clearly illustrate that ammonium lignosulfonate, furfuryl alcohol or a mixture of these chemicals graft effectively on wood. The mixture ammonium lignosulfonate-furfuryl alcohol gave the highest "percent graft" and the lignosulfonate the lowest. The results match bonding of particleboard (Tables 1 and 4).

The "percent graft" of the above chemicals increases with increasing peroxide concentration. The increase in grafting is most significant at low peroxide concentrations. The extent of grafting appears to depend also on time. The "percent graft" of the mixture lignosulfonate-furfuryl alcohol was about 30% higher with 2-1/2 hour than with 1-1/2 hour heating. The dependence of the extent of grafting of polymers on cellulose, lignin and wood

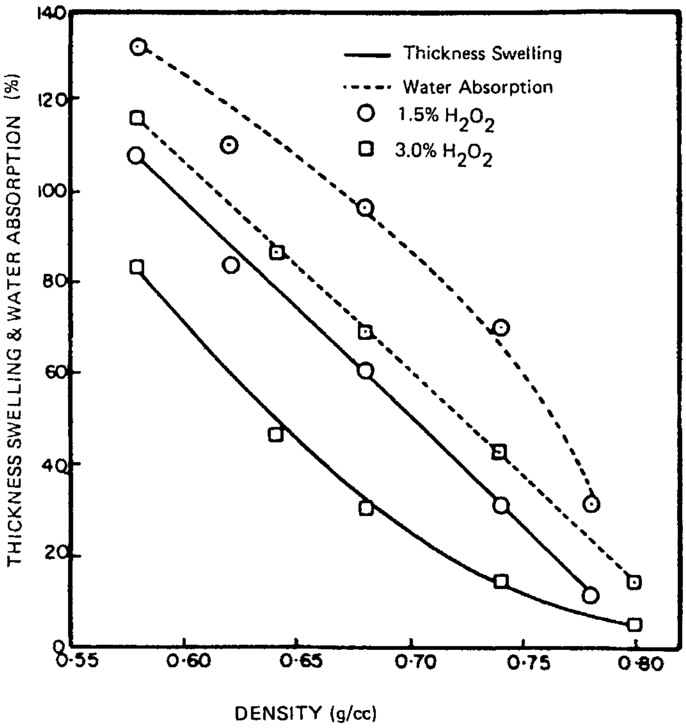

Figure 4. Effect of board density on thickness swelling and water absorption of particleboard after 2-hour boiling.

pulps upon the concentration of grafting initiator and time has been reported by many researchers.[5,26,28,34,35] These researchers have also found that wood exhibits a certain ability to initiate grafting in the absence of an initiator. Oxidation of or formation of free radicals on wood during heating of the wood-polymerizable chemicals mixture in the presence of air could account for the relatively high "percent graft" in the absence of peroxide shown in Figure 6.

The presence of ungrafted-insoluble polymeric products on the treated wood was considered and tested. For this purpose the

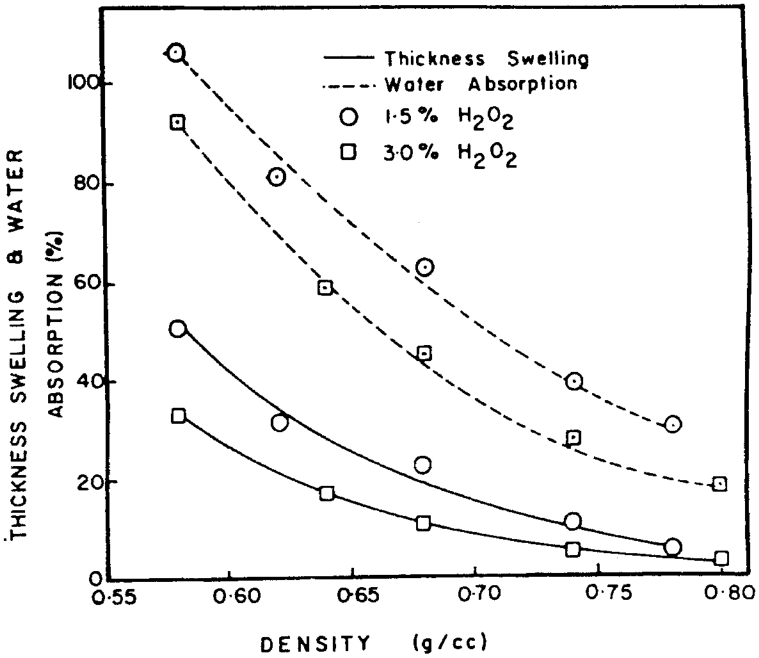

Figure 5. Effect of board density on thickness swelling and water absorption of particleboard after 24-hour water soaking.

mixtures of lignosulfonate-furfuryl alcohol and hydrogen peroxide at 0.625% and 12.5% concentrations were heated at 80°C for 2-1/2 hours in the absence of wood. The resulting materials were completely soluble in hot water. This finding suggested that insoluble polymers were not formed and that the solvents used (hot water, ethanol) for the extraction of the grafted wood solubilized and removed all ungrafted chemicals.

The dark-brown color of the treated wood served also as an indication of grafting. The color of the grafted wood became darker as the peroxide concentration in the grafting specimens increased.

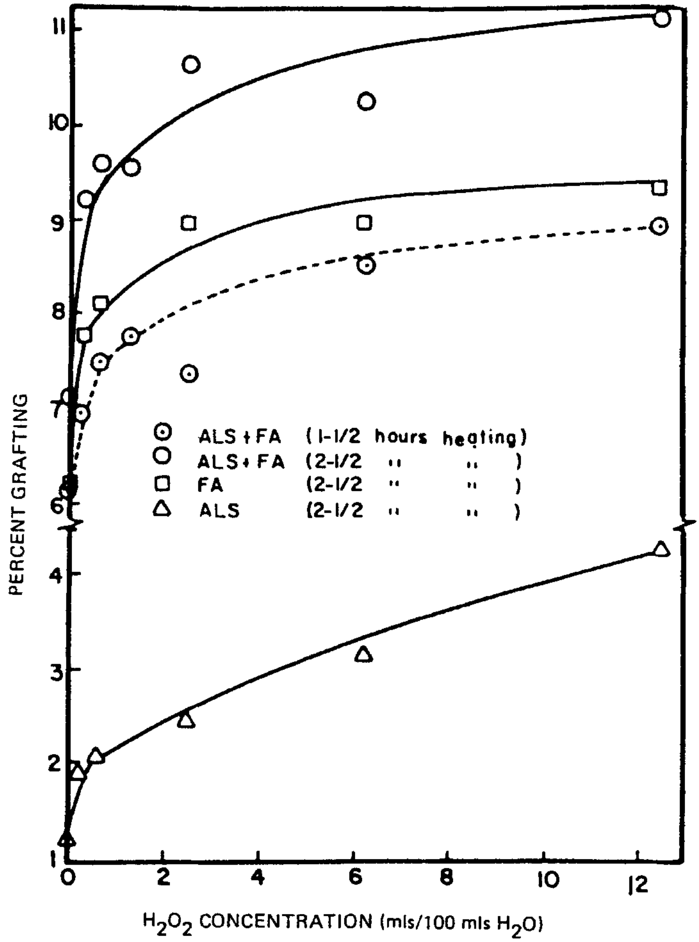

Figure 6. Grafting of ammonium lignosulfonate (ALS), furfuryl alcohol (FA) and ammonium lignosulfonate-furfuryl alcohol mixture (ALS+FA) on wood particles.

EXPERIMENTAL

Chemicals

Water solutions of hydrogen peroxide, peroxyacetic acid, nitric acid, potassium ferricyanide, and sodium dichromate were used as surface activators. Furfuryl alcohol, ammonium lignosulfonate (Orzan A, Crown Zellerbach Corp.) in combination with furfuryl alcohol, with formaldehyde or with maleic anhydride, and phenol in combination with furfuryl alcohol were used as polymerizable chemicals. Furfuryl alcohol was used either as a monomer or a resin manufactured according to U.S. Patent 3,130,165. Maleic acid was used in small amounts to catalyze the polymerization reactions and decomposition of peroxides. In addition, ferric chloride was also used as a catalyst in a few experiments.

Substrates

Particleboard and laminated panels were used in this study as vehicles for studying the bonding system. White fir (*Abies concolor*) and coast Douglas-fir (*Pseudotsuga menziesii* var *menziesii*) flake type particles of about 0.63 mm in thickness were used as particleboard furnish at a moisture content of about 4%. Douglas-fir (3.17 mm) veneer and Douglas-fir (6.35 mm) sawn and planed boards at a moisture of about 4% were used to make 3-ply plywood and parallel laminated panels, respectively.

Preparation of Chemicals and Wood Composites

All the surface activators, with the exception of potassium ferricyanide, were sprayed directly on the substrates just before application of the polymerizable chemicals. Potassium ferricyanide (30% water solution) was applied mixed with the other chemicals. Hydrogen peroxide was used as a 50% water solution. In the case of peroxyacetic acid three parts of 50% H_2O_2 and one part of glacial acetic acid were mixed and sprayed. Sodium dichromate and nitric acid were used as 30% and 20% water solutions, respectively.

Ammonium lignosulfonate, supplied in powder form, was dissolved in water to 55% solids for use in particleboard and 68% solids for use in plywood and laminates. Lignosulfonate/formaldehyde and lignosulfonate/ maleic anhydride were used in a ratio of 9:1, and lignosulfonate/furfuryl alcohol and phenol/furfuryl alcohol in a ratio of 7:3 on a solids weight basis. The amount of polymerizable chemicals applied to substrates was kept constant at 7% solids (based on o.d. wood) for particleboard, and 1.39 g/m^2 for plywood and laminates. The polymerizable chemicals were sprayed on the particles or brushed on veneer and laminates immediately after the application of the surface activators.

Particleboards made with H_2O_2-furfuryl alcohol resin, H_2O_2-phenolfurfuryl alcohol and all boards employing peroxyacetic acid were 21.6 x 21.6 x 1.11 cm in size, made in duplicate, and were pressed at 149°C for 8 minutes. All other boards, in duplicate for each experiment, were 35.6 x 45.7 x 1.27 cm in size and pressed at 177°C for 7 minutes. Target density of the boards was 0.75 g/cc. In one experiment designed to assess the effect of density, the density varied from 0.55 to 0.80 g/cc. In density determinations mass was expressed on oven-dry basis and volume at the 6-8% moisture content; the difference between o.d. and 6.8% moisture content volumes was negligibly small (0.2-0.8%). Plywood and laminates (in duplicate) were 30.5 x 30.5 cm and were made by pressing at 177°C for 5 minutes using 1240-1381 kPa pressure.

Testing

Particleboard was tested for internal bond (4 specimens per board), MOR and MOE (one specimen per board) and thickness swelling and water absorption in a 24-hour water soak and 2 hours of boiling water (2 specimens per board) according to ASTM D1037-72a. The small (21.6 x 21.6 x 1.11 cm) boards were only tested for internal bond and resistance to 2-hour boiling. The plywood was tested for dry and wet (vacuum-pressure soak) wood failure as outlined in PS1-74 and the laminates for dry and wet (vacuum pressure soak) shear strength in comparison loading according to ASTM D-905. Four specimens for the dry and four specimens for the wet properties were tested from each panel.

Grafting Experiment

White fir wood was passed through a micro-Wiley mill and screened to obtain 60-80 mesh particles. This material was placed in test tubes, about 1.5 g in each followed by 20 mls of hydrogen peroxide varying in concentration from 0 to 12.5%, and 10 g (solids) of polymerizable chemicals, in that order. Furfuryl alcohol, ammonium lignosulfonate or mixtures of 7 parts of ammonium lignosulfonate and 3 parts of furfuryl alcohol were used as polymerizable chemicals. The mixtures in the test tubes were heated at 80°C for 1-1/2 or 2-1/2 hours. After cooling to room temperature the content of the tubes was filtered using glass crucibles of coarse porosity, washed with hot water and then extracted. The extraction sequence included 4 hours hot water, 24 hours ethyl alcohol and 2 hours hot water. After the extraction the material was oven dried at 105°C for 16 hours. Control specimens of wood with varying H_2O_2 concentration in the absence of polymerizable materials were subjected to the same conditions. Duplicate tests for each experiment were made.

The "initial mass" of wood and the oven dry mass of grafted wood were determined. The percent average mass increase was defined as "percent graft". "Initial mass" is defined as the mass of wood-hydrogen peroxide specimens after treatment. The following formulas were used to calculate the initial mass and percent graft.

$$\text{mass loss}^{36}\ \% = \frac{\text{wood mass} - (\text{O.D. } H_2O_2 \text{ treated wood mass})}{\text{wood mass}} \times 100$$

$$\text{initial mass} = \text{wood mass} - \left(\frac{\text{wood mass} \times \text{mass loss }\%}{100}\right)$$

$$\%\ \text{graft} = \frac{\text{O.D. grafted wood mass} - \text{initial mass}}{\text{initial mass}} \times 100$$

CONCLUSIONS

1. Bonding through formation of chemical bonds between wood surfaces is possible. Graft polymerization techniques offer a viable means of achieving such bonding in wood composites for practical applications.
2. Hydrogen peroxide, nitric acid, and peroxyacetic acid modify the surface of wood and make it receptive to chemical reaction with polymerizing chemicals.

3. Lignosulfonates and furfuryl alcohol in the presence of the above oxidants graft on wood and provide effective chemical bridges between wood surfaces. This results in strong and water resistant bonding of rough wood surfaces or of wood composites of medium densities.
4. The bonding achieved using the above process is at least comparable to that of phenolic adhesives in terms of strength and water resistance. The bonding appears to take place under press conditions similar to those currently used in industry.

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36. Mass loss includes moisture, extractives, and any other losses resulting from the treatment.

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