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CHEMICAL MODIFICATION OF WOOD SUBSTANCE

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PROCEEDINGS

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–Research potential for strengthening
the competitiveness of wood

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1. Introduction

The chemical and physical properties of a material are, for the most part, a result of the chemistry of the components in the material. If we desire to change the properties of that material, we commonly manipulate the chemistry of the components. In the case of a polymer blend in, for example, a textile, we modify, substitute or eliminate one or more of the polymers in the composite in order to improve the properties. While we practice this in textiles (i.e. wrinkle resistance, permanent press, color fastness, fire retardancy, and stain resistance) we do not apply the same thinking to wood. Wood is, however, a three-dimensional polymeric composite made up of cellulose, hemicelluloses, and lignin. These polymers make up the cell wall and are responsible for most of the chemical and physical properties exhibited by wood.

Wood is a preferred building material because it is economical, renewable, widely available, strong, aesthetically pleasing, and low in process energy. It has, however, several disadvantageous properties such as biodegradability, flammability, changing dimensions with varying moisture contents, and degradability due to ultraviolet light, acids, and bases. These properties of wood are all the result of chemical reactions involving degradative environmental agents. Because all of these degradative effects are chemical in nature, it should be possible to eliminate or greatly reduce the rate of degradation by changing the basic chemistry of the cell wall polymers.

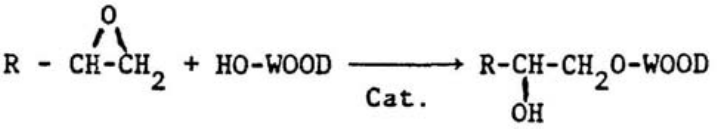
By chemically modifying the carbohydrate polymers (cellulose and hemicelluloses), for example, the highly specific biological enzymatic reactions involved in biodegradation cannot take place because the chemical configuration and molecular conformation of the substrate has been altered. Modifying the cell wall polymers to make them more hydrophobic or bulking them with bonded chemicals would reduce the tendency of wood to swell and shrink with changes in moisture content.

2. Chemical Modification

In developing the basic techniques, solid wood was used, and various chemical reaction systems were studied looking for reagents that would react quickly with hydroxyl groups on cellulose, hemicellulose, and lignin. The optimumchemical reaction system is one capable of reacting with wood hydroxyls under neutral or mildly alkaline conditions at temperatures below 120°C. The chemical system should be simple and capable of swelling the wood structure to facilitate penetration. The complete molecule should react quickly with wood components yielding stable chemical bonds, and the treated wood must still possess the desirable properties of untreated wood while improving one or more undesirable properties.

Several chemical systems have been explored for chemical modification of wood (1). Three classes of reactive chemicals were studied in this work: expoxides (2), isocyanates (3), and anhydrides (4). Reactions of these with wood are fast and complete, and stable chemical bonds are formed. The systems swell wood and penetrate well.

Epoxides:



Isocyanates: $$R\text{-}N{=}C{=}O + HO\text{-}WOOD \xrightarrow[\text{Cat.}]{} R\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}WOOD$$

Anhydrides: $$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R + HO\text{-}WOOD \longrightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}WOOD + R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OH$$

3. Reactions on Solid Wood

The results on solid wood for these three reaction systems showed that at 17-25 weight percent gain of bonded chemical:

1. Reaction had taken place in the cell wall.
2. 70-75 percent dimensional stability was achieved.
3. Less than 3 percent of weight was lost in laboratory test with both brown- and white-rot fungi.
4. Less than 5 percent of weight was lost in laboratory termite tests.
5. Were resistant to degrade by marine organisms for 9 years in ocean exposure.
6. Most of the lignin hydroxyl groups were reacted while only a small portion of the hydroxyl group in the carbohydrate fraction was substituted.
7. Both heartwood and sapwood reacted about equally for many softwoods and hardwoods.

There are three major concerns in the chemical modification of solid wood. One is the need for dry wood to minimize reagent hydrolysis. Drying wood to less than 3 percent moisture is very expensive and can cause damage to the structure because of drying defects. The second concern is the problem of penetration of the reacting chemical into and chemical recovery from solid wood that is greater than 1 to 2 cm thick. The third concern is the complexity of many modifying systems that have been devised. Multicomponent systems create problems in chemical recovery. These concerns, along with the great potential seen in the growing future in reconstituted wood products, led to a new research program starting in 1981 on chemical modification of wood particles.

4. Reactions on Reconstituted WoodProducts

The greatest single application of the technology developed in wood modification is in reconstituted products in which standard operating procedures call for near-dry wood materials and small particle size for good chemical penetration and chemical recovery. Chemical modification could greatly improve the properties of reconstituted products, Dimensional instability, for example, especially in the thickness direction, is a greater problem in reconstituted wood products such as flakeboards, particleboards, and fiberboard than it is in solid wood products. In these products, not only normal swelling occurs (reversible swelling) but also swelling caused by the release of residual compressive stresses imparted to the board during the pressing process (irreversible swelling). Chemical modification could also result in biological resistance in reconstituted products based on substrate blocking

rather than toxicity which could have a very great environmental advantage to present broad spectra wood preservation techno logy.

5. New Modification Procedure Developed

The experimental results from the epoxide, isocyanate, and anhydride studies showed that while epoxides and isocyanates have many advantages over other reaction systems, they tend to use toxic, flammable, and expensive chemicals which, in some cases, give inconsistent reaction weight gains. The anhydride systems, especially acetic anhydride, are more consistent and much less toxic, flammable, and expensive. All of the procedures, however, to acetylate wood developed over the years have been complicated reaction schemes using catalyst and/or organic cosolvent and have required a long reaction time. Because of the complexities of the reaction/recovery systems and the length of reaction time, these acetylation schemes have not gone beyond laboratory technology.

We set out to develop a new acetylation procedure that would (a) eliminate both catalyst and organic cosolvent, (b) reduce the reaction time necessary to achieve a level of acetylation that will give a high degree of dimensional stabilization and biological resistance to the resulting boards, and (c) shorten and simplify the chemical recovery after reaction.

A new procedure was developed (5) in which southern pine and aspen flakes were acetylated with acetic anhydride alone without cosolvent or catalyst by a simple dip procedure. The procedure calls for dipping the flakes in acetic anhydride containing a small amount of acetic acid to facilitate swelling for 1 minute. The flakes are drained for 3 minutes and placed in a closed container at 120°C. No pressure is applied and little is developed during the reaction. After the reaction is complete, unreacted acetic anhydride and byproduct acetic acid are quickly recovered in a short vacuum cycle.

The new procedure greatly shortens reaction time and simplifies chemical recovery. Acetylation weight gains of 15 to 20 percent can be achieved with southern pine flakes in 1 to 3 hours (fig. 1). Reaction time is even shorter when the procedure is applied to whole wood fiber.

6. Properties of Acetylated Flakeboards

Southern pine flakes acetylated by the simplified dip procedure show greatly reduced fiber saturation point (table 1) and boards made from these flakes had a lower equilibrium moisture content (table 2). The rate of swelling in liquid water is significantly reduced in southern pine flakeboards made from acetylated flakes as compared to control boards (fig. 2). Thickness swelling in repeated water/ovendrying tests is greatly reduced in southern pine flakeboards made from acetylated flakes (fig. 3). The same trend is observed in 30 to 90 percent relative humidity cycle tests (fig. 4).

In standard laboratory soil block tests, southern pine flakeboards made from acetylated flakes were resistant to attack by the brown-rot fungus *Gloephyllum trabeum* above about 15 weight percent gain (table 3). Acetylated pine flakeboard also resisted attack by brown-, white-, and soft-rot fungi as well as tunneling bacteria in fungal cellar tests (table 4) and showed good resistance to termite attack (table 5).

7. Summary and Future Need

Chemical modifying wood cell wall polymers changes the basic properties of the wood. With the growing markets for reconstituted wood products, the technology developed for solid wood was applied to these products. A new procedure was developed to acetylate flakes that greatly reduced reaction the and simplified the total system. Flakeboards made from acetylated flakes from the new procedure absorbed much less water, both in liquid and vapor tests, swelled at a lower rate and to a lower extent than did control boards. Acetylated flakeboards also showed greatly improved resistance to tunneling bacteria and brown-, white-, and soft-rot fungi and termites.

There are still problems to overcome before commercialization of chemically modified reconstituted products will be realized. We are working to develop a continuous acetylation process with greatly improved chemical recovery and recycling. The final economic evaluation will be when all reaction mass balance data is complete.

Since the acetylated wood is so hydrophobic, standard water soluble adhesives do not produce the strongest bond. Other adhesives including isocyanates, are presently under investigation. Long term stability of acetyl groups to high humid conditions and pH ranges are also under investigation as well as thermal properties, corrosivity, and mechanical properties.

Other chemical reaction systems are also under investigation. This research will hopefully result in the most efficient/economic procedure to chemically modify wood.

Chemical modification of ligno-cellulosic material is a complex subject requiring many scientific disciplines. Because of this (and because of the interest in chemical modification from many scientists around the world) an international team has been formed to research various aspects of the total problem. Research is presently being conducted in Sweden, Denmark, France, Germany, Poland, Switzerland, Wales, Canada, Japan, China, New Zealand, and several locations in the United States. It is hoped that this effort will lead to an efficient/economic process to chemically modify ligno-cellulosic materials with improved dimensions stability, water repellancy, biological resistance, fire resistance, and ultraviolet resistance.

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Table 1.--Fiber saturation point of dip acetylated southern pine flakes

Weight percent gain	Fiber saturation point
	Pct
0	45
6	24
10.4	16
21.6	10

Table 2.--Equilibrium moisture content of southern pine flakeboards made from dip acetylated flakes. (6 pct phenol-formaldehyde adhesive, 27°C)

Weight percent gain	Equalibrium moisture content at			
	30 percent relative humidity	65 percent relative humidity	80 percent relative humidity	90 percent relative humidity
0	4.5	10.3	14.5	20.1
6	3.3	7.9	11.8	16.7
10.4	2.7	6.9	10.3	14.9
21.6	2.1	5.1	9.0	13.1

Table 3.--Average weight loss for southern pine flakeboards made from dip acetylated flakes exposed for 12 weeks to Gloeophyllum trabeum (6 percent phenol-formaldehyde)[1]

Weight percent gain	Average weight loss				
	Nonleached	Threshold weight percent gain	Leached[2]	Threshold weight percent gain	Weight loss[3]
0	15.1		34.3		2.3
6.0	4.3		29.3		2.2
14.8	0		0.8		1.8
18.4	0		0		1.6
		10.4		15.3	

[1]In standard ASTM test D 1413-76 (1981).
[2]After 2 weeks' water leaching.
[3]Due to leaching.

Table 4.--Perfomance of southern pine flake-boards made from dip acetylated flakes exposed to white-, brown-, and soft-rot fungi and tunneling bacteria in fungal cellar tests (6 percent phenol-formaldehyde)

Weight percent gain	Rating after (months)					
	2	4	6	8	10	12
0	S/2	S/3	S/4	--	--	--
6.0	S/0	S/0	S/2	S/3	S/4	--
10.4	0	S/0	S/1	S/2	S/2	S/3
14.8	0	0	S/0	S/0	S/1	S/l
18.4	0	0	0	0	0	0

[1]Rating system: 0 = no attack; 1 = slight attack; 2 = moderate attack; 3 = heavy attack; 4 = destroyed; S = swollen.

Table 5.--Weight loss and termite survival after 4 weeks on southern pine flakeboards made from control and dip acetylated flakes

Weight percent gain	Weight loss	Final termite biomass[2]
	- - - - (g) - - - - -	
0	0.23	0.83
10.4	0.09	0.67
17.8	0.06	0.75
21.6	0.05	0.65

[1]Average of 3 specimens.
[2]Starting weight, 1 g.

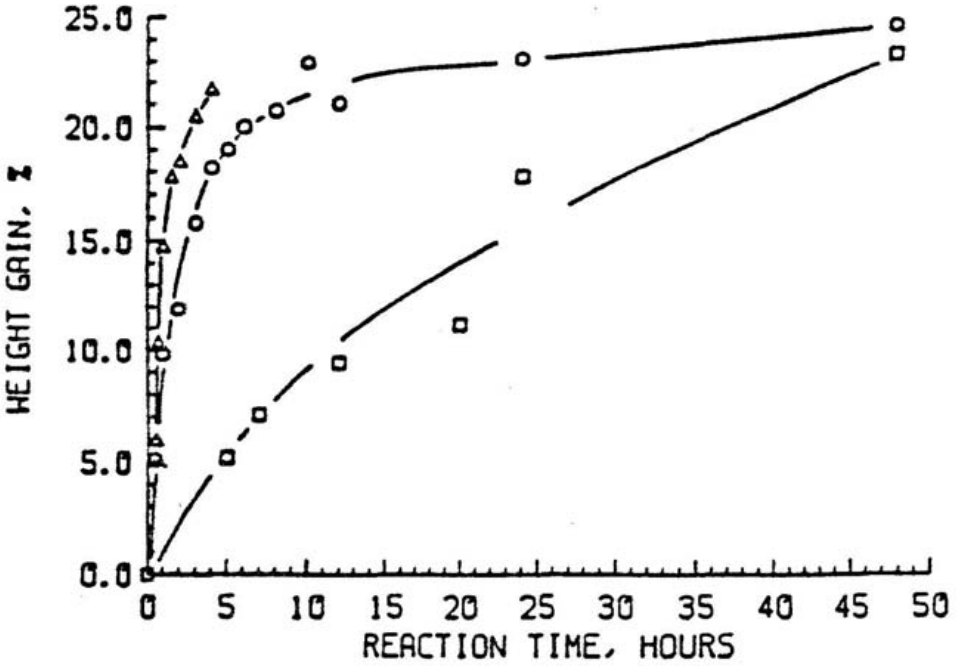

Figure 1.--Weight gain versus reaction time for southern pine flakes acetylated by various procedures. □ Vapor phase treatment, 0 refluxing actic anhydride/xylene , Δ dip procedure.

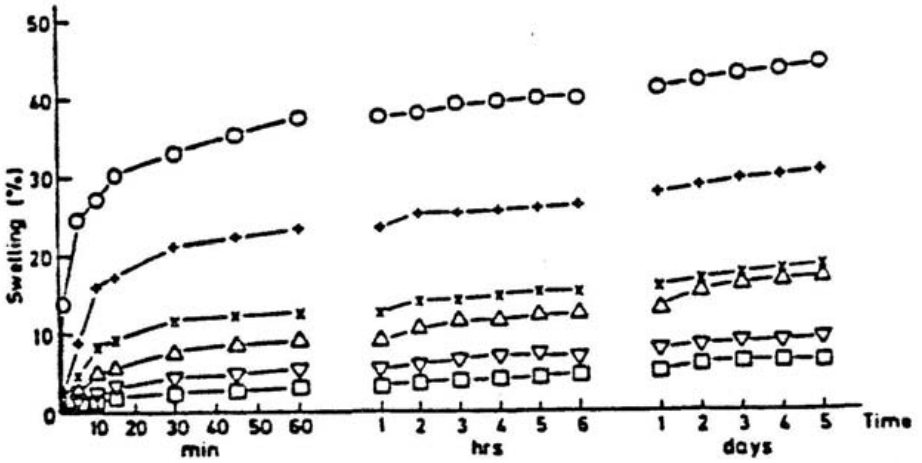

Figure 2.--Rate of swelling in liquid water of southern pine flakeboard made from dip acetylated flakes. 0 Control, + 6.0 WPG, X 10.4 WPG, Δ 14.8 WPG, ∇ 18.4 WPG, □ 21.1 WPG. (ML85 5495)

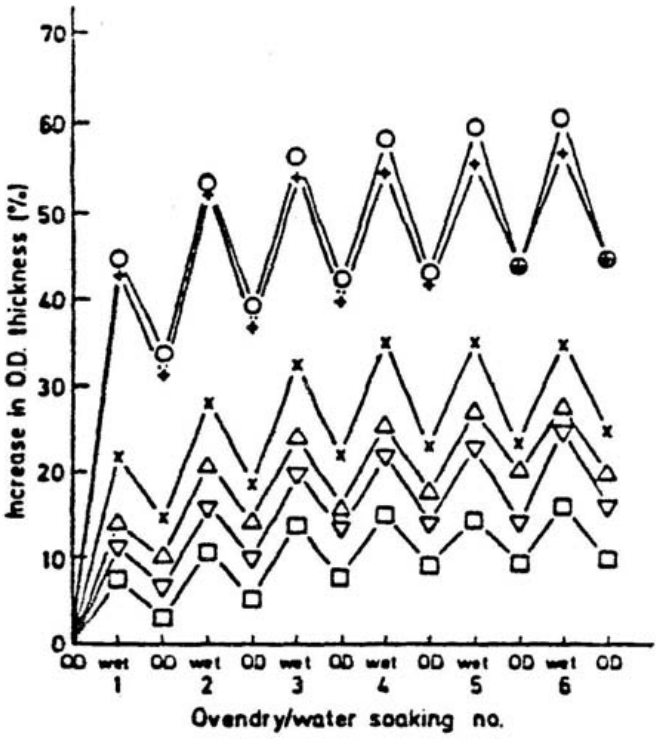

Figure 3.--Change in thickness in repeated water swelling test of southern pine flakeboard made from dip acetylated flakes. O Control, + 6.0 WPG, X 10.4 WPG, Δ 14.8 WPG, ▽ 18.4 WPG, □ 21.1 WPG.

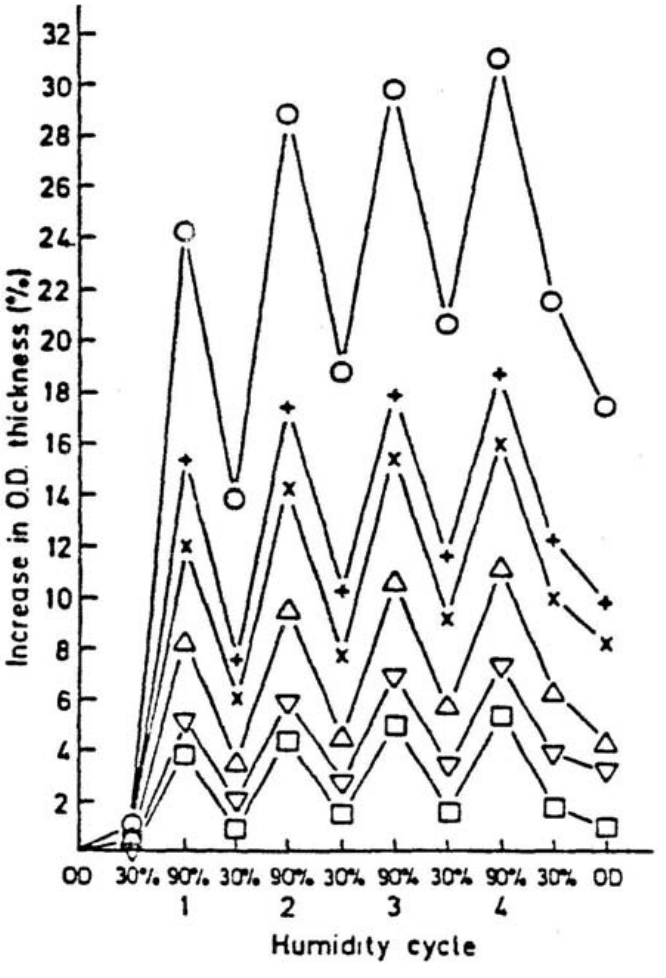

Figure 4.--Changes in thickness at 30 and 90 percent relative humidity of southern pine flakeboard made from dip acetylated flakes (27°C). O Control, + 6.0 WPG, X 10.4 WPG, Δ 14.8 WPG, ▽ 18.4 WPG, □ 21.1 WPG.