Holistic Approach to Wood Protection

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Abstract

When untreated wood is exposed to adverse outdoor conditions, nature has a series of chemistries to degrade it to its original building blocks of carbon dioxide and water. Fungi, termites, heat, moisture, ultraviolet (UV) energy, and chemicals take their toll on the performance properties of wood. We tend to study each of these degradation chemistries as individual events but, in fact, they are all connected by five basic chemistries: hydrolysis, oxidation, dehydration, reduction, and free radical cleavage. If we look more broadly at the commonalities involved in these chemistries, we can take a more holistic approach to the protection of wood through chemical modification. For example, simple acetylation of wood results in a lowering of the equilibrium moisture content and increases dimensional stability. The mechanism is simple bulking of the cell wall to near its elastic limit and substituting a less hydrophilic group on the hydroxyl groups in the cell wall polymers. This same chemistry increases biological resistance. The resistance to biological attack is probably due to lowering the moisture content of the cell wall below that needed for biological activity and may be, in part, due to a change in conformation and configuration of the substrate. If the bonded chemical contained a halogen, for example, the reacted wood would not only have the improved properties listed above but would also increase resistance to thermal degradation. If the bonded chemical contained a free radical scavenger, resistance to UV radiation could be improved. All of these improvements in performance can be achieved using one chemical reaction system interfering with hydrolysis, oxidation, reduction, dehydration, and free radical chemistries.

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Introduction

When wood is used in outdoor exposures, several types of degradations occur. Moisture causes wood to swell and shrink depending on the amount of moisture present. The wood will be attacked by both micro- and macro-organisms depending on the type of organisms present in the immediate vicinity of the wood. Ultraviolet (UV) radiation will degrade the surface of the wood depending on the intensity of the radiation and the amount of rain that will wash away the degraded surface polymers. Wood will be degraded by heat, and if the temperature is high enough and there is a source of ignition, the wood will bum. All of these degradations are based on one of five chemistries: hydrolysis, oxidation, dehydration, reduction, and free radical cleavage (Rowell 2005a).

A more holistic view of wood protection can be approached by at least two different avenues. One is by considering the chemistries involved in each type of desired protection and the other is to look at each separate chemistry as it applies to each type of desired protection. In the former case, we would consider the degradation due to, for example, hydrolysis and then oxidation, and dehydration, etc. In the latter case, we would consider the type of degradation and then consider all of the chemistries involved in that type of degradation. In this case, we would consider, for example, attack by microorganisms and look at the chemistries involved in biological attack, i.e., hydrolysis, oxidation, and free radical cleavage.

For this paper, I have chosen to approach protection by degradation type and describe the chemistries involved and possible chemical modifications that would interfere or stop that type of chemistry from occurring (Rowell 2005b).

Protection from Moisture

Dimensional changes in wood with changing moisture contents (MC) is one of the biggest reasons wood is not used in applications where dimensional stability is a critical issue. The dashboard of an expensive car, for example, may look like wood but, in fact, it is plastic made to look like wood. If wood were used in this application, the changes in dimensions with changing MC would result in expansion beyond or shrinkage below the tolerances allowed. Changes in dimensions in furniture results in loose joints in the dry seasons of the year. Using wet lumber in home construction results in warpage, nail failure, and other defects in the final house. It is clear that if wood could be dimensionally stabilized inexpensively, wood would have a much greater application.

The chemistries in the degradation due to moisture is mainly hydrolysis. Hydrogen bonds are formed and broken between water molecules and cell wall hydroxyl groups with the varying MC. Glycosidic bonds are hydrolyzed between carbohydrate groups mainly in the hemicelluloses.

To reduce accessibility of water to a glycosidic bond for hydrolysis, wood can be made more hydrophobic and/or bond a chemical to the hydroxyl groups to interfere with hydrogen bonding.

Many simple bulking chemistries are known. The simplest and most controlable is reaction of wood withacetic anhydride. The reaction with acetic anhydride results in esterification of the accessible hydroxyl groups in the cell wall with the formation of by product acetic acid

$$\underset{}{\text{WOOD-OH}} + \underset{\text{Acetic Anhydride}}{CH_3\text{–C(=O)-O-C(C=O)–}CH_3} \rightarrow$$

$$\underset{\text{Acetylated Wood}}{\text{WOOD–O-C(=O)–}CH_3} + \underset{\text{Acetic Acid}}{CH_3\text{–C(=O)-OH}}$$

Table 1 shows the reduction in the fiber saturation point (FSP) of pine and aspen as a result of acetylation. As the level of bonded acetyl groups increases, the FSP decreases showing that the bonded acetyl group is less hydrophilic than the hydroxyl group it substituted.

Table 2 shows the effect of acetylation of the equilibrium moisture content (EMC) of pine. As the level of cell wall bonded acetyl groups goes up, EMC goes down.

Table 3 shows the stability of the bonded acetyl groups in pine and aspen flakes. After forty-one 3-month cycles of 90 percent relative humidity (RH) to 30 percent RH or 30 percent RH to 90 percent RH, there is very little loss of bonded acetyl groups showing how stable the acetyl groups are in the cell wall.

Table 4 shows the dimensional stability of acetylated pine in repeated water soaking and oven-drying tests. This also demonstrates the stability of the acetyl groups in wood. It also shows the effect of bulking the cell wall by the acetyl groups to bring the wood back to near its green volume. Anti-shrink efficiency (ASE) values of over 80 percent are achieved for solid wood and 90 percent for medium density fiberboards made using acetylated fibers.

Table 1. – *FSP for acetylated pine and aspen.*

Weight percent gain	Pine	Aspen
	(%)	
0	45	46
6	24	--
8.7	--	29
10.4	16	--
13.0	--	20
17.6	--	15
18.4	14	--
21.1	10	--

Table 2. – *EMC of control and acetylated pine.*

		EMC at 27°C		
Chemical	WPG[a]	30% RH	65% RH	90% RH
Control	0	5.8	12.0	21.7
Acetic anhydride	20.4	2.4	4.3	8.4

[a] WPG = weight percent gain.

Table 3. – *Stability of acetyl groups in pine and aspen flakes after cyclic exposure between 90% RH and 30% RH. Each cycle is 3 months long.*

	Acetyl content (%) after cycle (number)				
Wood	0	13	21	33	41
Pine	18.6	18.2	16.2	18.0	16.5
Aspen	17.9	18.1	17.1	17.8	17.1

Table 4. – *Repeated anti-shrink efficiency of chemically modified solid pine.*

WPG[a]	ASE_1	ASE_2	ASE_3	ASE_4	Weight loss after ttest
Acetic anyhydride					
20.5	83.2	81.4	80.9	78.4	< 2

[a] WPG = weight percent gam.

Micro-Organism Protection

There are two theories on how chemical modification prevents attack by microorganism. One is that chemical modification lowers the cell wall MC below that needed for microorganisms to attack. The second is that chemical modification changes the molecular conformation and configuration of the substrates such that the enzymes cannot recognize the wood components as a food source.

Based on the data previously presented and the data in **Tables 5 to 7,** it would appear that excluding moisture from the cell wall is the dominate mechanism for the effectiveness of chemical modification to give resistance to attack by microorganisms. This means that the chemical modification is preventing moisture from hydrolyzing glycosidic bonds in the carbohydrate polymers.

Table 5 shows the resistance of acetylated wood to attack by brown- and white-rot fungi. The brown-rot fungus *Gloeophyllum trabeum* and the white-rot fungus *Trametes versicolor* were used in this standard ASTM 12-week test. **Table 6** shows the results of control and acetylated pine in a fungal cellar containing brown-, white-, and soft-rot fungi and tunneling bacteria. It is clear from the results presented in **Table 6** that no attack occurs until the specimens swell. The specimens with an average level of acetylation of about 7 percent shows swelling at 2 months and the decay is observed a month later. For the specimens at about 12 percent, swelling is recorded at 4 months followed by decay at **5** months. The specimens at about 14 percent do not show any swelling until 6 months and then, the first signs of decay are observed 6 months later. The specimens above about 16 weight percent gain (WPG) did not swell during the 144 month test and no decay was observed. This is more evidence that restricting moisture is the key to controlling fungal and bacteria attack.

Table 5. – *Resistance of acetylated pine against brown- and white-rot fungi.*

		Weight loss after 12 weeks (%)	
Chemical	WPG[a]	Brown-rot fungus	White-rot fungus
Control	0	61.3	7.8
Aceticanhydride	17.8	1.7	1.1

[a] WPG = weight percent gain.

Though somewhat redundant, **Table 7** combines all of the data on moisture and fungal resistance as a function of the level of bonded cell wall acetyl groups. For pine, resistance to fungal attack is achieved at a WPG of approximately 14 to 15 percent.

UV Radiation Protection

Bonding a simple group to the cell wall hydroxyl groups can decrease moisture sorption, improve dimensional stability, and reduce or stop attack by fungi and tunneling bacteria. If the bonded chemical contains structures that can reflect, adsorb UV energy, or stabilize free radicals, the reacted wood would be more stable to UV degradation. The chemistries involved in the UV degradation of wood are oxidation, hydrolysis, and free radical depolymerization.

Table 6. – *Fungal cellar tests of aspen flakeboards made from control and acetylated flakes.* [a,b]

Weight	Rating at interval (months)[C]									
percent gain	2	3	4	5	6	12	24	36	72	144
0	S/2	S/3	S/3	S/3	S/4	--	--	--	--	--
7.3	S/0	S/1	S/1	S/2	S/3	S/4	--	--	--	--
11.5	0	0	S/0	S/1	S/2	S/3	S/4	--	--	--
13.6	0	0	0	0	S/0	S/1	S/2	S/4	--	--
16.3	0	0	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0	0	0

[a] Nonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria.
[b] Flakeboards bonded with 5% phenol-formaldehyde adhesive.
[c] Rating system: 0 = no attack 1 = slight attack 2 = moderate attack 3 = heavy attack 4 = destroyed S = swollen.

Table 7. – *WPG, FSP, EMC, ASE, and weight loss attack by brown- and white-rot fungi of control and acetylated pine.*

Weight		EMC at 27°C			Anti-shrink	Weight loss after 12 weeks	
percent gain	FSP	30%RH	65%RH	90%RH	efficiency	Brown-rot fungus	White-rot fungus
				(%)			
0	45	5.8	12.0	21.7	--	61.3	7.8
6.0	24	4.1	9.2	17.5	12.5	37.6	5.1
10.4	16	3.3	7.5	14.4	37.4	8.7	3.3
14.8	--	2.8	6.0	11.6	63.4	3.0	< 2
18.4	14	2.3	5.0	9.2	79.2	< 2	< 2
20.4	10	2.4	4.3	8.4	85.4	< 2	< 2

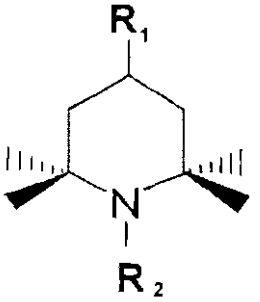

Figure 1. – *Characteristic structure of hindered amine UV stabilizer*

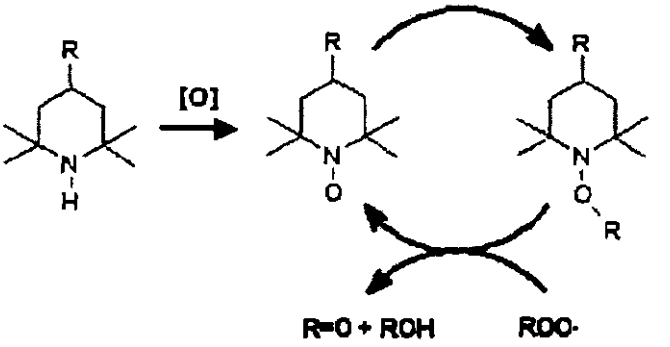

Figure 2. – *Mechanism of UV* stabilization.

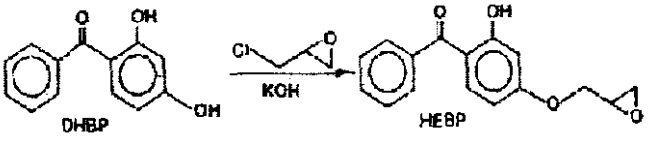

Figure 3. – *Synthesis of HEBP from DHBP*

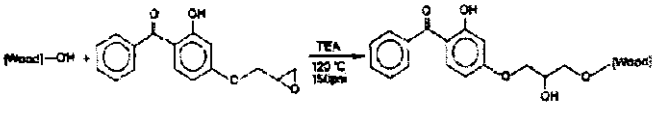

Figure 4. – *Bonding of HEBP to wood.*

Lignin adsorbs UV energy and free radicals are formed that are stabilized in the lignin molecule. The free radicals can migrate deep into the lignin structure but mainly degrade the surface layers of lignin. After the lignin is degraded, rain hitting the exterior wood washes out the degraded lignin and the cellulose and hemicelluloses polymers are also lost since the lignin is the encrusting agent holding the cell wall polymers together.

Hindered amines are known to stabilize materials against UV degradation (Fig. 1). This class of chemicals do not adsorb UV radiation but act by scavenging radical intermediates formed in the oxidation of wood, mainly in the lignin (www.cibasc.com).

Figure 2 shows the mechanism of UV stabilization using a hindered amine (www.cibasc.com). Other amines that are used as UV stabilizers include benzopheonone, benzotriazole, and hydroxyphenyl triazine (www.cibasc.com, Faoro 2005).

DHBP (2,4-dihydroxybenzophenone) has been reacted with epichlorohydrin to give a para-substituted oxirane HEBP [2-hydroxy-4-(2,3-epoxypropoxy) benzophenone] (Fig. 3). Bonding this epoxide to western red cedar slowed the erosion rate due to UV degradation as shown in weatherometer tests (Williams 1983).

Thermal Protection

The chemistries involved with thermal degradation are oxidation, hydrolysis, dehydration, and free radical cleavage. If the bonded chemical contains elements that can promote the formation of more char and lower the temperature of thermal degradation or help trap free radicals in the flame, the reacted wood would be more fire retardant.

Chemicals that increase char formation and lower the temperature where thermal degradation starts include phenolics, nitrogen/phosphorus, boron, and acid salts. Halogens, such as bromine, act as free radical traps in the flame.

Fire retardants have been bonded to wood (Rowell et al. 1984, Ellis et al. 1987, Ellis and Rowell 1989). Wood can be reacted with phenolic-type compounds but this type of char increasing chemical usually results in more smoke. Wood has been reacted with chlorophosphates (Ellis et al. 1987) and isocyanate phosphonates (Ellis and Rowell 1989).

Figure 5 shows a thermogram of unmodified and modified wood. Unmodified wood is more thermally stable than fire-retardant reacted wood and does not start to degrade until about 275° to 280°C with a maximum rate of degradation in the range of 325° to 340°C with very little residual char. The fire-retardant reacted wood starts to thermally degrade at a lower temperature than unmodified wood in the range of 200° to 220°C. The maximum rate of degradation in the range of 260° to 270°C with a much higher level of residual char.

Conclusions

Simple reactive chemicals that have easy access to cell wall hydroxyl groups and bond to the cell wall polymers provide protection from hydrolysis by water, increase water repellency by increasing hydrophobicity, and increase dimensional stability by bulking the cell wall. The same simple system also prevents hydrolysis and oxidation by microorganisms by restricting water from a glycosidic bond and by changing the configuration and

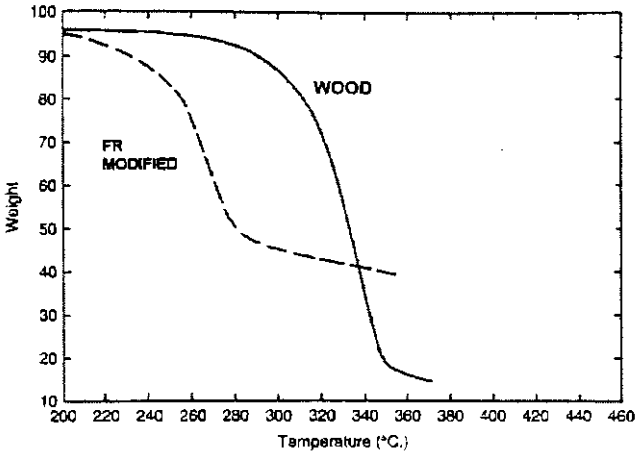

Figure 5. – *Thermogravimetric analysis of wood and fire. retardant reacted wood.*

conformation of the cell wall polymers in such a way as to make them unrecognizable to the enzyme systems of the microorganisms.

Hinder amines are effective in preventing hydrolysis, oxidation, and free radical cleavage resulting from the interaction of wood with UV radiation. And, phenolics, halogen containing chemicals, nitrogen/phosphorus containing chemicals, boron containing chemicals, and metal salts increase the fire retardancy of wood.

Perhaps the ultimate chemical modification, from a more holistic approach, is a reactive isocyanate or epoxide substituted halogen containing hindered amine (Fig. 6). The final result might be a single chemical reaction that prevents the degradation of wood by water, microorganisms, UV energy, and high temperatures.

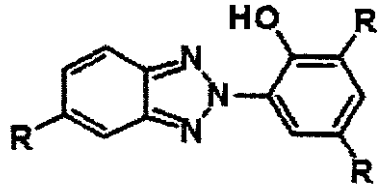

Figure 6. – *Possible structure of a modified benzotriazole.*

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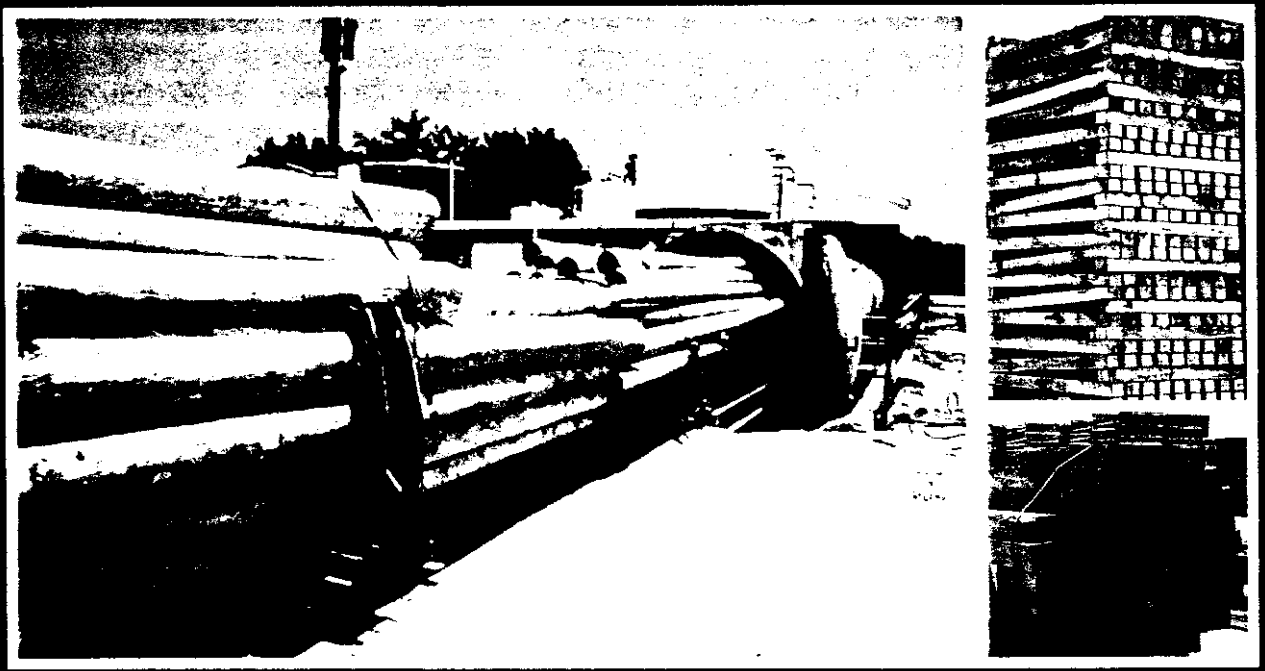

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