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Chemical modification of wood: A short review

ROGER M. ROWELL

United States Department of Agriculture, Forest Products Laboratory, and University of Wisconsin, WI, USA

Abstract

For most markets for wood, it is used without any treatments or modifications. When wood is used in adverse environments, it may be treated with chemicals to help prevent decay, improve water resistance, reduce the effects of ultraviolet radiation or increase fire retardancy. Many of these treatments involve the use of toxic or corrosive chemicals that can harm the environment. Chemical modification of wood provides an alternative by providing protection against water, decay, UV and thermal degradations by bonding chemicals to the cell wall polymers that do not leach out. Dimensional stability and decay resistance are two major properties that can be greatly improved by simple reactions with acetic anhydride.

Keywords: *Acetic anhydride, acetylation, chemical modification, decay, dimensional stability, equilibrium moisture content, fungal cellar, fungi.*

Introduction

Wood has been used as a construction material since the beginning of human existence. For the most part, it has been used without modification. Solid timbers and lumber were treated for decay and fire resistance as recorded in ancient accounts. However, most applications for wood today have little treatment other than a coating or finish. We have learnt to use wood accepting that it changes dimensions with changing moisture content, decomposes by a wide variety of organisms, burns, and is degraded by ultraviolet energy. Wood has mainly been used as a construction material because it is widely available, renewable and cheap. The average person does not consider wood as a high performance material.

In ancient Africa, natives hardened wood spears by placing a sharpened straight wooden stick in the bottom of glowing coals following by pounding the burnt end with a rock, and repeating this process many times until the end was sharp and hard. It would be many hundreds of years before we understood that pyrolysis of hemicelluloses produces furan resins which, when combined with carbon and compressed, result in an extremely hard composite.

The ancient Egyptians used dry-to-wet wooden wedges to split giant granite obelisks from the side of a quarry long before we discovered the tremendous swelling pressure that is exerted when wood swells. The Bible records a message to Noah to build an ark using a wood known to resist decay, long before we understood how micro-organisms recognized wood as a food source. Finally, the Vikings burned the outsides of their ships to make them water resistant and flame resistant without knowing anything about hydrophobicity or the insulating properties of char.

Correlating studies of the chemistry of wood with observations of performance, it became clear that cell wall chemistry and properties were, for the most part, responsible for the observed performance. These early observations led researchers to connect chemistry and performance.

Combining all the art and science of wood recorded from ancient times to the present, we have discovered that if you change the chemistry of wood, you change its properties, and that leads to a change in performance. From this foundation, the science of chemical modification of wood was born.

Whilst there are many early references to reacting chemicals with wood, the term "chemical modification of wood" was first used in 1946 by Tarkow.

Correspondence: Roger M. Rowell, Project Leader and Professor, USDA, FS, Forest Products Laboratory and University of Wisconsin, One Gifford Pinchot Dr., Madison, WI 53705, USA. E-mail: rmrowell@wisc.edu or rmrowell@fs.fed.us

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Chemical modification of wood is defined as covalently bonding a chemical group to some reactive part of the cell wall polymers.

Many chemical reaction systems have been published for the modification of wood, and these systems have been reviewed in the literature several times in the past (Jahn, 1947; Rowell, 1975, 1983, 1991, 2005; Kumar, 1994; Hon, 1996). These chemicals include anhydrides such as, acetic, butyric, phthalic, succinic, maleic, propionic and butyric anhydride, acid chlorides, ketene carboxylic acids, many different types of isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, phthaldehydic acid, dimethyl sulphate, alkyl chlorides, β-propiolactone, acrylonitrile, epoxides, such as, ethylene, propylene, and butylene oxide, and difunctional epoxides.

The bulk of the research into the chemical modification of wood has been focused on improving dimensional stability. Resistance to biological degradation is a by-product of lowering the equilibrium moisture content of the cell wall below the moisture level needed for the organism to attack wood. There has also been a small amount of research to bond fire retardants and chemicals to reduce degradation due to ultraviolet radiation to wood.

Dimensional stability

The mechanism of this performance enhancing modification is the reaction of a small chemical to an hydroxyl group on one or all of the cell wall polymers. The bulking of the cell wall with the reacted chemical brings the wood back nearly to its green volume so additional moisture can only swell the wood to the elastic limit of the cell wall. However, since all reacted chemicals used so far are larger than the water molecule, some swelling always takes place. The hydrophylicity of the wood is also changed during the modification with the reacting chemical interfering with normal hydrogen bonding.

Table 1 shows the effect of bonding epoxides, formaldehyde and acetic anhydride on the equilibrium moisture content of pine. Propylene and butylene oxides and acetic anhydride lower the EMC by bulking the cell wall and increasing the hydrophobicity of the cell wall, whilst formaldehyde functions as a cross-link agent holding cell wall polymers together.

Table 2 shows the dimensional stability expressed as anti-shrink efficiency (ASE) of several chemical modifications on solid pine. The highest value is obtained with reactions with acrylonitrile. However, Table 3 shows that the reactions with acrylonitrile do not form stable chemical bonds. Table 2 also shows that butylene oxide is more effective in improving dimensional stability than propylene oxide. The difference is probably due to increased hydrophobicity resulting from reactions with butylene oxide as compared to propylene oxide. In the reactions of epoxides with wood, a new hydroxyl group is formed after the oxirane reacts with a cell wall hydroxyl group. Reactions using pine with acetic anhydride result in a consistent ASE value after several water soak-drying tests. ASE values obtained on wood composites such as flakeboard and fibreboard are much higher than on solid wood. Values of up to 90% compared to control boards have been obtained using acetylated flakes and fibres in the production of these boards.

Biological resistance

As the moisture content is reduced due to chemical modification, biological resistance increases. Table 4 shows the resistance to brown- and white-rot fungi from several types of chemical modification. Whilst the control sample showed over 60% weight loss due to brown-rot attack, and almost 8% weight loss due to white-rot fungi, all of the modification chemistries resulted in a reduction in fungal attack. Consistent with the results obtained in the moisture tests, propylene oxide was not as effective as butylene oxide. Propylene oxide does not reduce the cell wall moisture content low enough to inhibit complete fungal resistance.

The effects of moisture on control and acetylated flakeboards in a fungal test are clearly shown in Table 5. The fungal cellar used in these experiments

Table 1. Equilibrium moisture content of control and chemically modified pine

		Equilibrium Moisture Content at 27 °C		
Chemical	WPG	35% RH	60% RH	85% RH
Control	0.0	5.0	8.5	16.4
Propylene Oxide	21.9	3.9	6.1	13.1
Butylene Oxide	18.7	3.5	5.7	10.7
Formaldehyde	3.9	3.0	4.2	6.2
Acetic Anhydride	20.4	2.4	4.3	8.4

Table 2. Antishrink efficiency (ASE) of chemically modified solid pine.

Chemical	WPG	ASE
Control	0.0	–
Propylene Oxide	29.2	62.0
Butylene Oxide	27.0	74.3
Acetic Anhydride	22.5	70.3
Methyl Isocyanate	26.0	69.7
Acrylonitrile		
NH_4OH*	26.1	80.9
NaOH*	25.7	48.3

* Catalyst.

contained brown-, white-, and soft-rot fungi, and tunnelling bacteria. Control blocks were destroyed in less than 6 months whilst flakeboards made from acetylated furnish above 16 WPG showed no attack after 1 year (Nilsson et al., 1988; Rowell et al., 1988). These data show that no attack occurs until swelling of the wood occurs (Rowell et al., 1988). This fungal cellar test was continued for an additional 5 years, with no attack at 17.9 WPG, which provides additional evidence that the moisture content of the cell wall is critical to fungal attack (Ibach & Rowell, 2000; Ibach et al., 2000).

Acetylated solid wood and flakeboards have been subjected to in-ground tests (Hadi et al., 1996; Rowell et al., 1997; Larsson-Brelid et al., 2000) throughout the world. In the United States, Sweden, and New Zealand, specimens showed little or no attack after 10 years of exposure. In Indonesia, specimens failed in less than 3 years (Hadi et al., 1996), mainly as a result of termite attack. In Sweden, acetylated pine at a WPG of 21.2 has been outperforming wood treated with copper chromium arsenic at 10·3 kg/m^3 after 8 years of exposure (Larsson-Brelid et al., 2000).

Acetylated wood has also shown resistance to attack by termites (Rowell et al., 1988) and marine organisms (Johnson & Rowell, 1988; Larson-Brelid et al., 2000).

Acetylation

Of all of the chemical modification procedures that have been studied over the years, acetylation, using acetic anhydride, has been the most studied and has given the most consistent results (Rowell in press). Acetylation of wood is already practiced on a commercial basis in Japan and may soon be so in the United States, Sweden, Denmark, Holland, England, and New Zealand: see Figure 1 showing two state-of-the-art pilot plants located in Sweden for acetylation of solid wood and wood fibres. Whilst many of the modification chemistries are effective in improving dimensional stability and biological resistance, acetylation remains the reaction of choice partly due to its controllability, cost and the global availability of acetic anhydride.

The acetylation of wood was first performed in Germany in 1928 by Fuchs, using acetic anhydride and sulphuric acid as a catalyst (Fuchs, 1928). Fuchs found an acetyl weight gain of over 40%, which meant that he de-crystallized the cellulose in the process. He used the reaction to isolate lignin from pine wood. In the same year, Horn (1928) and Suida and Titsh (1928) acetylated beech wood to remove hemicelluloses in a similar lignin isolation procedure. A year later, Suida and Titsch (1929) acetylated powdered beech and pine using pyridine or dimethylaniline as a catalyst to yield an acetyl weight gain of 30% to 35% after 15 to 35 days at 100°C. In 1945, Tarkow first demonstrated that acetylated balsa was resistant to decay (Tarkow, 1945). In 1946, Tarkow, Stamm and Erickson (Tarkow, 1946; Tarkow et al., 1946) first described the use of wood acetylation to stabilize wood from swelling in water. Since the 1940s, many laboratories around the world have looked at acetylation of many different types of woods and agricultural resources.

Through the years, many catalysts have been tried for the acetylation of wood both with liquid and vapour systems. The most common acetylation procedure used today, however, is acetic anhydride containing a small amount of acetic acid without a

Table 3. Repeated antishrink efficiency (ASE) (Dry-Wet cycles) of chemically modified solid pine.

Chemical	WPG	ASE_1	ASE_2	ASE_3	ASE_4	Weight Loss After Test
Propylene Oxide	29.2	62.0	43.8	50.9	50.3	5.7
Butylene Oxide	26.7	74.3	55.6	59.7	48.1	4.6
Acetic Anhydride	22.5	70.3	71.4	70.6	69.2	<0.2
Methyl Isocyanate	26.0	69.7	62.8	65.0	60.7	4.3
Acrylonitrile						
NH_4OH*	26.1	80.9	0.0	0.0	0.0	22.6
NaOH*	25.7	48.3	0.0	0.0	0.0	14.7

* Catalyst.

Table 4. Resistance of chemically modified pine against brown- and white-rot fungi.

		Weight Loss After 12 Weeks	
Chemical	WPG	Brown-rot Fungus (%)	White-rot Fungus (%)
Control	0.0	61.3	7.8
Propylene Oxide	25.3	14.2	1.7
Butylene Oxide	22.1	2.7	0.8
Methyl Isocyanate	20.4	2.8	0.7
Acetic Anhydride	17.8	1.7	1.1
Formaldehyde	5.2	2.9	0.9
β-Propiolacetone	25.7	1.7	1.5
Acrylonitrile	25.2	1.9	1.9

Table 5. Fungal cellar tests of aspen flakeboards made from control and acetylated flakes[1,2].

	Rating at intervals (Months)[3]									
WPG	2	3	4	5	6	12	24	36	72	144
0.0	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

[1] Nonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria.

[2] Flakeboards bonded with 5% phenol-formaldehyde adhesive.

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

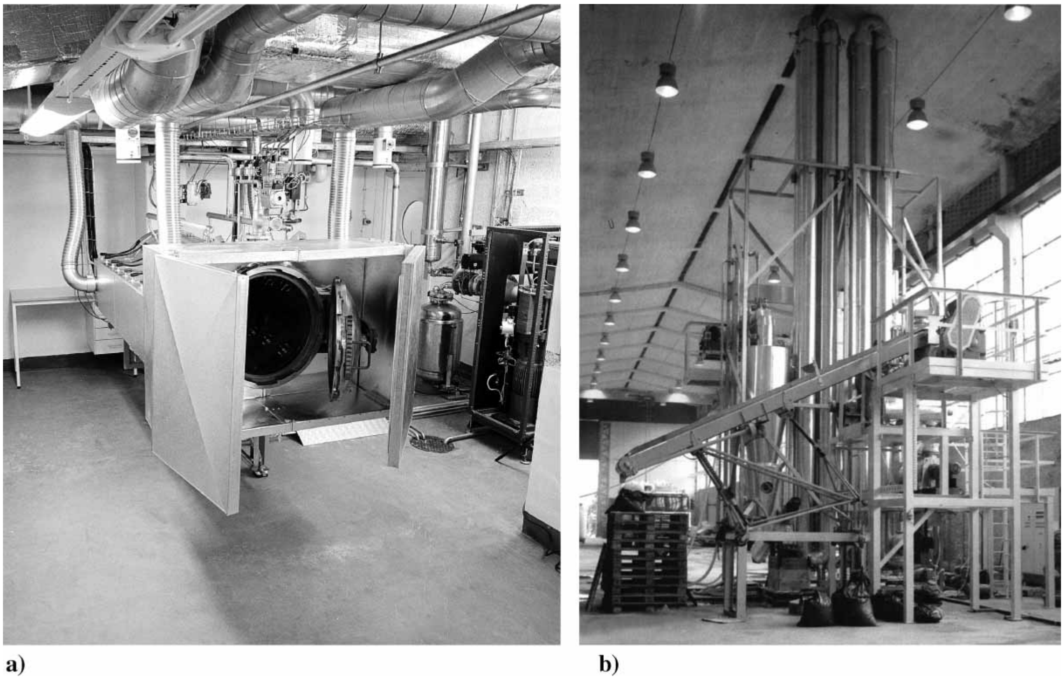
a) b)

Figure 1. State-of-the-art pilot plants for acetylation of solid wood (a) and wood fibres (b).

catalyst. For solid wood, a vacuum is applied to the wood before the anhydride is introduced, and after the reaction is complete, followed by a drying step. For flakes, particles, or fibre, no vacuum or pressure is applied and the reaction is carried out in a rotating reactor to ensure the material is completely exposed to the chemicals. Heat is applied by using either microwaves or conventional heating.

Holistic approach to chemical modification

When untreated wood is exposed to adverse conditions, nature has a series of chemistries to degrade it back to its original building blocks of carbon dioxide and water. Micro-organisms, termites, heat, moisture, ultraviolet 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. 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 have increased resistance to thermal degradation. If the bonded chemical contained a free radical scavenger, resistance to ultraviolet radiation could be improved. All these improvements in performance could be obtained from one chemical reaction system interfering with hydrolysis, oxidation, reduction, dehydration and free radical chemistries.

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