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STABLE AND DURABLE WOOD BUILDING MATERIALS BASED ON MOLECULAR LEVEL CHEMICAL MODIFICATION

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ABSTRACT

Wood is referred to as a material but in the true material sciences definition, a material is uniform, predictable, continuous, and reproducible. No two pieces of wood are the same even if they came from the same tree and the same board. Wood is better described as a composite and, more accurately, as a porous three-dimensional, hydroscopic, viscoelastic, anisotropic bio-polymer composite composed of an interconnecting matrix of cellulose, hemicelluloses, and lignin with minor amounts of inorganic elements and organic extractives. So, even solid wood is a composite. The characteristics we deal with at the solid wood level (swelling/shrinking, biological attack, and strength) are derived from the properties at the cell wall matrix and polymer level. Moisture sorption and desorption in the cell wall polymers results in dimensional instability and changing mechanical properties. Many different types of microorganisms recognize wood as a food source and are able to break it down resulting in both weight and strength losses. One technology that has now been commercialized to achieve high levels of stability, durability, and improved wet mechanical properties is acetylation: a reaction between the hydroxyl groups in the wood cell wall polymers and acetic anhydride. While all woods contain a low level of acetyl groups, increasing this acetyl content changes the properties and, thereby, the performance of the reacted wood. When a substantial number of the accessible hydroxyl groups are acetylated consistently across the entire cell wall, the wood reaches its highest level of stability and durability.

Keywords: chemical modification, durable, hemicellulose, molecular level, performance, properties, shrinking, stable, strength, swelling, wood.

1 INTRODUCTION

Wood is composed of approximately 50% cellulose, 25% hemicellulose, and 25% lignin with minor amounts of organic extractives and inorganics and is designed to perform, in nature, in a wet environment. Nature is programmed to recycle wood in a timely way through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations. In simple terms, nature builds wood from carbon dioxide and water and has all the tools to recycle it back to the starting chemicals using five basic chemistries [oxidation, reduction, dehydration, hydrolysis, and free radical reactions]. We harvest a green tree and convert it into dry products, and nature, with its arsenal of degrading chemistries, starts to reclaim it at its first opportunity [1].

We learned 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. The codes and standards for woods use are written based on the diverse nature of wood and the properties and performance of wood in use.

2 MOISTURE

The number one enemy of wood is moisture both indoors and outdoors. Sorption and desorption of moisture results in swelling/shrinking, cracking, coating failure, and surface degradation. Combine moisture with microorganisms and it results in mold growth and decay. Combine moisture with ultraviolet energy and it results in surface erosion, checking, and

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color changes. The key to improving stability and durability is to control the amount of moisture in the cell wall. Keeping the cell wall dry in a moist environment is critical.

Although wood is a porous material (60%–70% void volume), its permeability or flow of water is extremely variable. This is due to the highly anisotropic arrangement of the component cells and to the variable condition of the microscopic channels between cells. Wood is much more permeable in the longitudinal direction than in the radial or tangential directions.

According to the Dent sorption theory, water is added to the cell wall polymers in monolayers [2]. Figure 1 shows the mechanism of water molecules adding to the wood cell wall. The hemicelluloses are the most hydroscopic polymers in the cell wall as shown in Fig. 2. These polymers are also very accessible to moisture and so may be the first site for moisture sorption. Water molecules enter the cell wall and start hydrogen bonding with accessible hydroxyl groups. Moisture is sorbed either as primary water molecules or secondary water molecules. Moisture opens the cell structure by "unzipping" hydrophilic polymer chains [3] until the cell wall is fully saturated with bonded water. Hydrogen bonds between hydroxyl groups on and between hemicelluloses, cellulose, and lignin are constantly changing. As moisture is added to the cell wall, wood volume increases nearly proportionally to the volume of water added [4, 5]. Swelling of the wood continues until the cell matrix reaches the fiber saturation point (FSP), and water, beyond the FSP, is free water in the void structure and does not contribute to further swelling. This process is reversible, and wood shrinks as it loses moisture below the FSP.

When we measure cell wall moisture, we usually record it at a defined relative humidity and designate it as the equilibrium moisture content or EMC. This is an average moisture

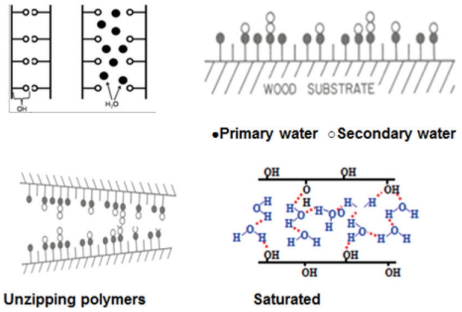

Figure 1: Moisture sorption in the cell wall and cell.

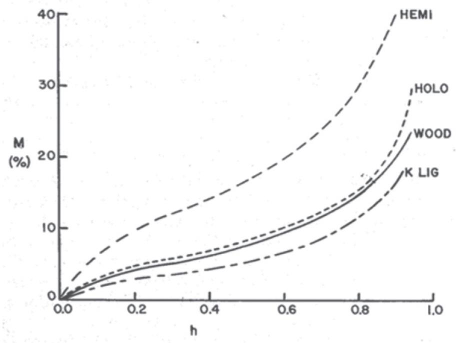

Figure 2: Sorption Isotherms for wood and cell wall polymers.

Table 1: SPC and EMC of cell wall wood and cell wall polymers at 65% RH and 90% RH.

Cell Wall Polymer	SMC 65% RH, 27C	SMC 90% RH, 27C
Hemicellulose	22	38
Lignin	7	16
Cellulose	5	12
	EMC	EMC
WholeWood	11	21

content of all cell wall polymers but does not tell us the specific moisture content of each individual polymer. We need to know the moisture content of each polymer at a given relative humidity to know how much moisture is present and where the moisture is. Table 1 shows the EMC for whole wood and the specific moisture content (SMC) of each cell wall polymer measured at 65% and 90% RH. The data show that hemicelluloses have a much higher specific moisture content as compared to cellulose or lignin at both RH values.

Jakes *et al.* [6] have reported that the glass transition temperature for hemicelluloses at 65% RH is 25°C. This means that at room temperature and 65% RH, the hemicelluloses are softened and moisture is starting to percolate into the hemicellulose interconnecting matrix.

Wood is degraded biologically because organisms have the ability to break down the wood structure into digestible units. While the brown-rot fungi accounts only for about 6% of the total fungal population, it is the most damage causing fungi, especially in softwoods. There are many theories on the mechanism of the attack of brown-rot fungi on softwoods. Many researchers have tried to explain the mechanism as consisting of one or two steps. However, it is too simple and the actual mechanism involves many steps. Theoretically, the first step may be a favorable environment. Fungi need an environment that is conducive to their survival: temperature, moisture, pH, and toxicity. The fungi cannot colonize if the temperature is too high or too low, if the wood is too wet or too dry, or if the pH is too high or too low. And, if there are toxic chemicals in the wood, the fungi cannot survive. If the environment is favorable, the fungal attack starts. It may start with some type of substrate recognition but it is observed that the pH of the wood starts to drop as the fungus colonizes. The hyphae of a brown-rot fungus must detect a source of nutrition in the wood it has come into contact with in order to survive. The first attack is thought to be by oxidation and rearrangement of lignin by an enzymatic reaction. No lignin is lost at this point but it is known to be somewhat oxidized and condensed. At this stage, the fungus is undergoing gene expression to start the production of cellulosic enzymes. [7–9].

Since the result of brown-rot degradation is mainly a loss of cell wall carbohydrate polymers, it is logical to assume that the first degrading reaction is an enzymatic attack on some very easily hydrolyzable carbohydrate sugar that is probably located in the side chain of an accessible hemicellulose structure. The hypha grows in the inside of a cell wall so it is in contact with the S_3 layer that is rich in lignin. The products of this attack provide the energy to proceed to Fenton chemistry. The first enzyme reaction then leads to the generation of a peroxide/ferrous ion and a hydroxyl radical chemical system [10] that depolymerizes the structural polysaccharides in the cell wall matrix resulting in strength losses [11]. The hemicelluloses and the cellulose polymers start to degrade and major strength losses are observed. As this Fenton chemistry progresses, new enzyme reaction take place in other accessible regions of the cell wall polysaccharides resulting in significant weight losses. Very little lignin is lost in the final stages of attack where the majority of wood weight is lost.

In each of these theoretical steps, moisture is involved. Moisture is part of the porous surface: it is required for the production of oxalate and its movement in Fenton chemistry [$Fe{+}{+} + H_2O_2 + H{+} = Fe{+}{+}{+} + \bullet OH$ (hydroxyl radical) $+ H_2O$], necessary at a glyosidic bond for hydrolysis, required for enzyme activity and, finally, required to move soluble sugars. All of this is wet chemistry and the question is how much moisture is required, where does it come from and where is it located in the cell wall?

3 PROPERTIES AND PERFORMANCE

As was stated before, the performances we deal with at the solid wood level (swelling/shrinking, biological attack, and strength) are derived from the properties at the cell wall matrix and polymer level (Fig. 3). Swelling/shrinking, rotting, weathering, burning, and strength properties are all a result of the properties at the molecular level. If we want to change performance, it is best done at the molecular level.

The properties of any resource are, for the most part, a result of the chemistry of the resource. If you change the chemistry, you change properties, and if you change properties, you change performance. Stable and durable properties of wood can be changed by changing the chemistry at the molecular level through a process known as acetylation. All woods contain acetyl groups: softwoods–0.5%–1.7%, and hardwoods–2%–4.5%. Increasing the cell wall acetyl level changes properties and performance in proportion to the level of bonded acetyl. Wood that has been acetylated to an acetyl level above about 18% has very high dimensional stability, decay resistance has greatly improved coating performance and wet strength and stiffness, and is commercially available as a solid material or as a composite [12, 13].

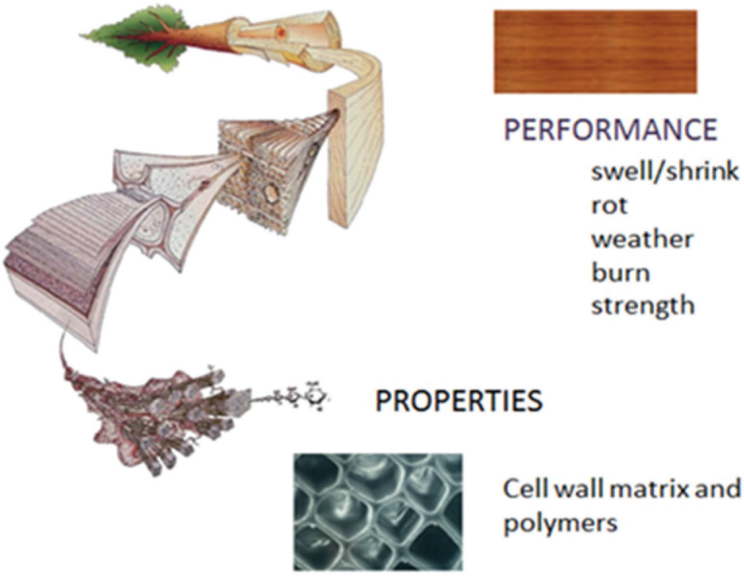

Figure 3: Performance and properties of wood.

$$\text{WOOD-OH} + CH_3C(=O)\text{-O-}C(=O)\text{-}CH_3 \quad \text{WOOD-O-}C(=O)\text{-}CH_3 + CH_3C(=O)\text{-OH}$$

Acetic anhydride Acetylated wood Acetic acid

Figure 4: Reaction of acetic anhydride with wood.

4 ACETYLATION PROCESS

The hydroxyl groups of the wood cell wall polymers react with acetic anhydride, resulting in stable, covalently bonded ester groups [12]. Acetylation is a single-addition reaction, which means that one acetyl group is on one hydroxyl group with no polymerization (Fig. 4). Thus, all the weight gain in the acetyl group can be directly converted into units of hydroxyl groups blocked. For each hydroxyl that is acetylated, there is a mole of acetic acid released as a by-product. The elasticity of the cell wall is not exceeded and the acetylated wood is back to the wood's original green volume, which is the mechanism of dimensional stability described later.

Wood acetylation can trace its history to the late 1920s when it was used to isolate both lignin and hemicelluloses [12]. The first patent was in 1930 in Austria. In 1945, Tarkow [14] acetylated balsa for decay resistance and in 1946, [15] Tarkow, Stamm, and Erickson showed that acetylated wood was dimensionally stabile. So, we have known that acetylated wood was stable and durable for over 70 years.

5 PROPERTIES OF ACETYLATED WOOD

As the level of acetylation goes up, the equilibrium moisture content decreases (Table 2). The bonded acetyl groups are less hygroscopic than the unreacted hydroxyls. More evidence of the increase in hydrophobicity of acetylated wood is obtained from contact angle measurements. Using the Wilhelmy method for acetylated scots pine sapwood at 20% weight gain the contact angle was found to be 81.5 while the control was 59.7 [16]. Also, as the acetyl weight goes up, the wood increases in volume (Table 3). The weight of added acetyl is equal to the increase in wood volume.

As the level of bonded acetyl goes up, resistance to attack by both brown- and white-rot fungi decreases. Table 4 shows the results of an ASTM standard 12-week soil block test using the brown-rot fungus *Gloeophyllum trabeum* or the white-rot fungus *Trametes versicolor*. At an acetyl weight gain of only 6%, the weight loss is almost cut in half in both the brown- and white-rot fungal tests. At an acetyl level of about 10%, weight loss due to brown-rot attack is cut to less than 7% and white-rot to less than 3%. At an acetyl level of about 15%, weight loss due to brown-rot attack is less than 4% and white-rot is within experimental error for zero. Complete protection against brown-rot fungus is achieved at an acetyl level of about 18%.

The relationship between EMC and decay resistance is not linear or proportional (Fig. 5) [17, 18]. At an EMC under about 13%, the weight loss due to attack by a brown-rot fungi is less than 5%. The reported EMC where no attack occurs is about 8% [12]. This data shows that the first hydroxyls to react have the most impact on reducing EMC and increasing decay resistance. It has been shown that the lignin phenolic hydroxyl groups are the first to react with acetic anhydride in wood followed by the hemicelluloses [19]. The hydroxyls on lignin are almost completely substituted at a weight gain approximately 20% acetyl [20] while only about 25% of the hydroxyls are substituted on the hemicelluloses.

Table 2: Equilibrium moisture content of pine at different levels of acetyl weight gain.

Weight Percent	Equilibrium Moisture Content at 27°C		
Gain	30%RH	65%RH	90%RH
0	5.8	12.0	21.7
6.0	4.1	9.2	17.5
10.4	3.3	7.5	14.4
14.8	2.8	6.0	11.6
18.4	2.3	5.0	9.2
20.4	2.4	4.3	8.4
22.9	1.9	3.6	4.8

Table 3: Change in volume in wood from oven dry to acetylated.

Green	OD	Change	Ac	OD	Change
Vol (cm^3)	Vol (cm^3)	Vol (%)	(%)	(cm^3)	(%)
38.84	34.90	−10.1	22.8	38.84	+10.1

Table 4: Weight loss in an ASTM standard test using a brown- and a white-rot fungus. [12 week soil block ASTM D 2017-71 test - Brown-rot fungus = *Gloephyllum trabeum*, White-rot fungus = *Trametes versicolor*].

Acetyl	Weight Loss After 12 Weeks	
Weight Gain (%)	Brown-rot Fungus (%)	White-rot Fungus (%)
0	61.3	7.8
6.0	34.6	4.2
10.4	6.7	2.6
14.8	3.4	<2
17.8	<2	<2

At 65% RH, the SMC of the hemicelluloses are close to the level needed to support fungal colonization. At 90% RH, the hemicelluloses SMC are well above the moisture level needed to support fungal colonization.

In earlier research, control and acetylated wood at several WPGs were put in a fungal cellar in Sweden [12]. Table 5 shows the results of a three year test of control and acetylated wood in the fugal cellar. What is interesting is that there is no attack on the wood until swelling is observed indicating that moisture is required before attack can take place.

Figure 6 shows electron micrographs of control and acetylated pine. The control sample before the test (a) and the control after the 12 week test with a brown-rot fungus Figure 6b and 6c. The control sample after test is almost completely covered with fungal hypha (Fig. 6b) with a destroyed cell wall (Fig. 6c). The acetylated sample shows a few hypha growing on the inner cell wall but no weight loss is detected. Note that the hypha are growing on the S_3 layer of the inner cell wall.

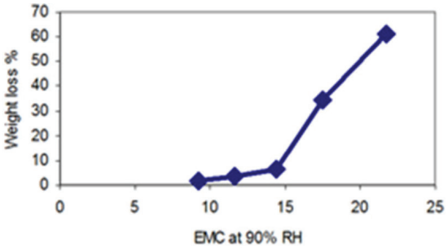

Figure 5: Relationship between EMC and weight loss due to attack by a brown-rot fungus.

Table 5: Control and acetylated wood in a fungal cellar in Sweden.

Rating at intervals[a]								
WPG	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.	12 mo.	24 mo.	36mo.
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
17.9	0	0	0	0	0	0	0	0

[a] Nonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria. Rating system: 0 = no attack; 1 = slight attack; 2 = moderate attack; 3 = heavy attack; 4 = destroyed; S = swollen.

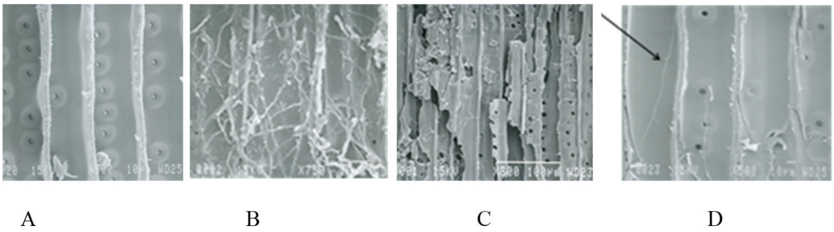

Figure 6: Electron micrographs of pine control before test, (a), (b), and (c) control after 12 weeks with a brown-rot fungus, and acetylated (d) after the 12 week test.

From all of the preceding data it is clear that no fungal attack takes place until the wood swells indicating that moisture is required for fungal attack. Acetylation to a level of about 20% reduces the cell wall moisture content below that required for attack. It may be important to know where the acetyl groups are bonded in the cell wall but there is no easy way to find that out. Lignin acetylation may be more important than we have previously thought in that lignin is modified by the fungus in one of the early steps in the degradation process. Moisture is required for the production of oxalate and its movement and in Fenton chemistry. Moisture is also needed for gene expression and enzyme activity and the movement of soluble sugars. It is also possible that acetylation changes the conformation and configuration of the substrate so the specific enzyme reactions cannot take place. The acetyl groups may block micropores so enzyme penetration cannot take place.

Table 6: Strength and stiffness properties of control and acetylated pine.

Sample	Dry Strength MOR N/mm^2	Wet Strength MOR N/mm^2	Dry Stiffness MOE N/mm^2	Wet Stiffness MOE N/mm^2	EMC 65% RH
Radiata Pine	63.6	39.4	10,540	6760	12
Acetylated Radiata Pine	64.4	58.0	10,602	9690	4

6 STRENGTH AND STIFFNESS PROPERTIES

Dry and wet strength and stiffness properties of acetylated pine are shown in Table 6. Modulus of rupture and modulus of elasticity are about the same for dry control and for acetylated wood with the acetylated vales slightly higher than for dry control. The real difference between control and acetylated pine are in the values for wet modulus. Control pine strength is greatly decreased upon wetting while the acetylated pine retains much of its dry strength. Wet stiffness is greatly decreased upon wetting in the control pine while the acetylated pine retains much of its dry stiffness.

7 COATING PERFORMANCE

Various research groups have been studying the effect of acetylation on coating performance with field tests [21]. This group carried out a 13-year-old outdoor exposure test in Sweden according to EN 927-3 of acetylated Scots pine finished with alkyd and acrylic film-forming coating systems. Acetylated Scots pine panels, finished with the acrylic coating system (alkyd primer + acrylic topcoat), are still in good shape after 13 years exposure, whereas the corresponding control panels from unmodified Scots pine needed repainting after five years (Fig. 7).

This significant improvement of film-forming coating performance on acetylated wood was also reported by others based on an outdoor exposure test with acetylated Scots pine

Figure 7: Control coated panel (left) after 5 years and acetylated panel (right) after 13 years.

Figure 8: Some examples of using acetylated wood in construction.

panels in the Netherlands [22, 23]. A significant improvement of the performance was found for the tested alkyd coating system. It was concluded that the intrinsic quality of the coating itself has become the main factor affecting the durability of coatings on acetylated wood. With an acrylic opaque white coating the condition of the coating after 9.5 years without any maintenance was still good. If a coating system is adapted to be used on acetylated wood and the application is done in the appropriate way, it is expected that the maintenance frequency can be once every 10 years or even lower.

8 ACETYLATED BUILDING MATERIALS

Acetylated wood has been used in housing construction now for over 10 years. The following figures are just a few examples of construction done using acetylated wood in Europe (Fig. 8). Builders using acetylated wood say that acetylated wood seems to be more brittle but this is because it is performing as very dry wood.

9 CONCLUSIONS

Wood acetylated to approximately 20% acetyl weight gain shows a large reduction in cell wall moisture content due to the bonding of a much less hygroscopic acetyl group replacing a hydroxyl group. The increase in dimensional stability is due to the cell wall bulking of the dry bonded acetyl groups and bulking the cell wall back to its original green volume. Since the elastic limit of the cell is not exceeded during the acetylation process, no structural damage to the cell wall is done. The mechanism of fungal resistance due to acetylation is not clear but moisture is critical and the moisture content and accessibility to moisture of the acetylated cell wall may be too low to support fungal activity. Although there is little difference in dry strength and stillness in control and acetylated pine, there are major differences in wet strength and stiffness with the acetylated pine, which retains much of its dry strength and stiffness.

Acetylation of wood results in a product that is more consistent, uniform, predictable, and reproducible converting a biocomposite to a biomaterial. The acetylated wood is reusable, recyclable, and burnable.

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