

Production of Dimensionally Stable and Decay Resistant Wood Components Based on Acetylation

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Theme 1 Durability of Materials
T12 Wood and wood components

ABSTRACT

Wood is a renewable, biodegradable and sustainable composite of cellulose, hemicelluloses, lignin, extractives and inorganics in a three-dimensional matrix. Nature is programmed to recycle it, in a timely way, back into its basic building blocks of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations. The properties of wood are the result of the chemistry of its cell wall components and the matrix they are in. If the chemistry is changed at the molecular level, the properties change and performance changes. Based on performance requirements of wood, chemical modifications can be carried out to change properties and performance. Dimensional stability, resistance to decay fungi and destructive insects, as well as other positive performance improvements can be greatly increased by reacting wood with acetic anhydride (acetylation) resulting in a new generation of value added wood-based products that perform very well in adverse environments.

KEYWORDS

Chemical modification, acetylation, dimensional stability, decay resistance, mechanical properties,

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1. INTRODUCTION

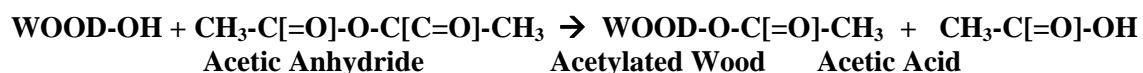
Wood changes dimension with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding. The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, noncrystalline cellulose, lignin, and surface of crystalline cellulose also play roles. Moisture swells the cell wall which expands until it is saturated with water (fiber saturation point, FSP). Beyond this saturation point, moisture exists as free water in the void structure and does not contribute to further swelling. This process is reversible, and the fiber shrinks as it loses moisture below the FSP. Wood exposed to moisture frequently is not at equilibrium, having wetter areas and drier areas within the same board. This exacerbates the moisture problem resulting in differential swelling followed by cracking and/or compression set. Over the long term, wood undergoes cyclic swelling and shrinking as moisture levels change resulting in more severe moisture effects than those encountered under steady moisture conditions.

Wood is degraded biologically based on an organisms' ability to recognize a potential food source mainly in the carbohydrate polymers [primarily the hemicelluloses] in the cell wall and having both non-specific chemical and highly specific enzyme systems capable of hydrolyzing these polymers into digestible units. Biodegradation of both the matrix and the high molecular weight cellulose weakens the fiber cell wall. Strength is lost as the matrix and cellulose polymer undergoes degradation through oxidation, hydrolysis, and dehydration reactions. As degradation continues, removal of cell wall content results in weight loss. All of these biological reactions take place in a high humidity condition.

Wood exposed outdoors undergoes photochemical degradation caused by ultraviolet radiation. This degradation takes place primarily in the lignin component, which is responsible for the characteristic color changes. The surface becomes richer in carbohydrate polymer content as the lignin degrades. In comparison to lignin, carbohydrate polymers are much less susceptible to ultraviolet degradation. After the lignin has been degraded, the poorly bonded carbohydrate-rich fiber surface easily erodes which exposes new lignin to undergo further degradative reactions. In time, this "weathering" process causes the surface of the composite to become rough and can account for a significant loss in surface fibers.

2. CHEMICAL MODIFICATION

Chemical modification of wood has been used to improve performance properties of wood. Many chemical reaction systems have been published for the modification of wood, however, the reaction of wood with acetic anhydride has been the most studied. The reaction with acetic anhydride with wood results in esterification of the accessible hydroxyl groups in the cell wall with the formation of byproduct acetic acid [Hill, 2006, Rowell 1983, 1984, 2005, 2006]. The byproduct acid must be removed from the product as the human nose is quite sensitive to the smell of acetic acid. While this is easily done in the case of wood particles and fiber, it is somewhat difficult to do in solid wood.



Acetylation is a single-site reaction that means that one acetyl group is on one hydroxyl group with no polymerization. This means that all of the weight gain in acetyl can be directly converted into units of hydroxyl groups blocked.

All woods naturally contain acetyl groups. In general, softwood have an acetyl content between 0.5 to 1.5% and more durable hardwoods between 2 to 4.5%.

3. HISTORY OF WOOD ACETYLATION

The acetylation of wood was first done in Germany in 1928 by Fuchs using acetic anhydride and sulfuric acid as a catalyst. He found an acetyl weight gain of over 40% which meant that he decrystallized 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. In 1929, Suda and Titsch acetylated powdered beech and pine using pyridine or dimethylaniline as a catalyst and got 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 first described the use of wood acetylation to stabilize wood from swelling in water. Since the 1940's, many laboratories around the world have looked at acetylation of many different types of woods and agricultural resources.

In spite of the vast amount of research on chemical modification of wood, and, more specifically, on the acetylation of wood, commercialization has not come easily. The first patent on the acetylation of wood was filed by Suida in Austria in 1930. Later, in 1947, Stamm and Tarkow filed a patent on the acetylation of wood and boards using pyridine as a catalyst. In 1961, the Koppers Company published a technical bulletin on the acetylation of wood using no catalysis but with an organic cosolvent [Goldstein et al. 1961, Dreher et al. 1964]. In 1977, in Russia, Otlesnov and Nikitina came close to commercialization but the process was discontinued presumably because it was not cost-effective. In the late 1980's, Daiken, in Japan, started a small commercial production of acetylated wood for flooring called alpha-wood that is still in production today.

There is one large commercial-scale production facility of acetylated wood today. It is produced by TitanWood in The Netherlands [www.titanwood.com] at an expanding 30,000 m³ pa plant capable of acetylating lumber up to 100mm thick. Their technology is being used to build additional facilities with capacities in excess of 100,000 m³pa each.

5. PRODUCTION OF ACETYLATED WOOD

In large scale production of acetylated wood, lumber is stickered and placed in a high pressure vessel using advanced handling equipment for efficiency. Acetic anhydride is introduced into the vessel and the temperature raised to the reaction temperature. Pressure is applied as needed. After the reaction is complete, the excess anhydride is recycled and the by-product acetic acid is processed back into anhydride. The acetylated wood is then dried, removed from the vessel and stored until shipment. The entire process has minimal by-products which have ready end-uses and is environmentally benign. When combined with the use of sustainable grown wood from certified sources as input, acetylated woods provide and improved building material that address a range of environmental factors.

6. PROPERTIES OF ACETYLATED WOOD

The properties presented in this paper are mainly a combination of results on southern yellow pine, aspen, radiata pine, poplar, beach and birch, demonstrating that wood acetylation properties apply to a range of species.

6.1 Volume Changes

Table 1 shows the increase in volume of pine after reaction with acetic anhydride and the calculated volume of chemical added to the cell wall after re-drying the wood. Since the volume increase due to reactions with acetic anhydride is equal to the calculated volume of chemical added, this shows that the reaction has taken place in the cell wall and not in the void spaces of the wood.

Table 1. Changes in pine volume and volume of chemical added as a result of chemical reactions.

WPG ¹	Increase in wood volume ²	Calculated volume of added chemical ³
17.5	3.0	2.9
22.8	3.9	4.0

¹ Weight Percent Gain ² Difference in oven-dry volume between reacted and non-reacted wood.

³ Density used in volume calculations: acetic anhydride 1.049

There is a change in color due to acetylation. Light colored woods tend to darken slightly while dark colored woods become slightly lighter.

6.2 Acetyl Stability

Table 2 shows the stability of acetyl groups in southern yellow pine and aspen to cyclic exposure to 90% and 30% relative humidity [RH] [Rowell et al. 1992]. Each cycle represents exposure for three months at 30% RH and then three months at 90% RH. Within experimental error, there is no loss of acetyl over 41 cycles of humidity changes.

Table 2. Stability of acetyl groups in southern yellow pine and aspen flakes after cyclic exposure between 90% relative humidity [RH] and 30% RH.

Wood	Acetyl content [%] after cycle [number]				
	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

This data was collected starting in 1992 and this experiment has continued to this day. After more than 20 years of cycling these samples from 30 to 90% RH, analysis shows that there is still no loss of acetyl resulting from humidity cycling and thus other benefits reviewed below are likely to, or have been proven in separate field tests, to be ongoing as well.

6.3 Moisture Properties and Dimensional Stability

By replacing some of the hydroxyl groups on the cell wall polymers with bonded acetyl groups, the hygroscopicity of the wood material is reduced. Table 3 shows the fiber saturation point for acetylated southern yellow pine and aspen. As the level of acetylation increases the fiber saturation point decreases in both the soft and hard wood.

Table 3. Fiber saturation point for acetylated southern yellow pine and aspen.

WPG	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	--

Figure 1 shows the sorption isotherm of control Pine and acetylated Pine. The lower curves are for the acetylated pine shows much lower moisture content at a given relative humidity as compared to non-acetylated pine.

Figure 1. Sorption isotherm of control and acetylated pine.

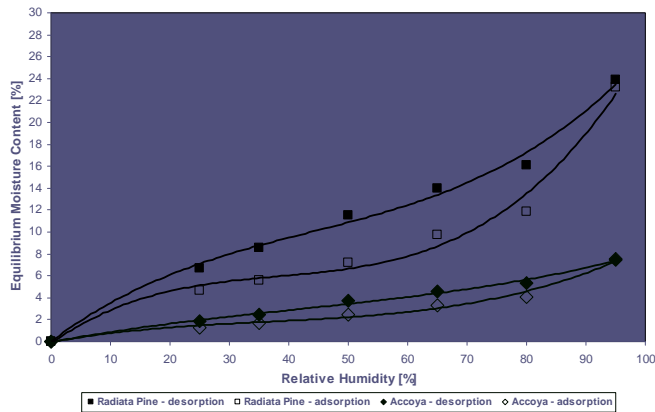


Table 4 shows the equilibrium moisture content [EMC] of control and acetylated pine and aspen at several levels of acetylation and three levels of relative humidities. In all cases, as the level of chemical weight gain increases, the EMC of the resulting wood goes down.

Table 4. Equilibrium moisture content of acetylated SYP, aspen and radiata pine.

Specimen	WPG	Equilibrium Moisture Content at 27 °C		
		30%RH	65%RH	90%RH
Southern Yellow Pine	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
Aspen	0	4.9	11.1	21.5
	7.3	3.2	7.8	15.0
	11.5	2.7	6.9	12.9
	14.2	2.3	5.9	11.4
	17.9	1.6	4.8	9.4
Radiata Pine	0	5.1	11.9	22.2
	15	2.3	5.4	10.6
	20	2.2	4.1	8.7

Dimensional stability is recorded as antishrink efficiency [ASE] [Stamm 1964]. It is calculated as:

$$S = \frac{V_2 - V_1}{V_1} \times 100 \quad [S = \text{Swelling coefficient}; V_1 = \text{Volume dry}; V_2 = \text{Volume wet}]$$

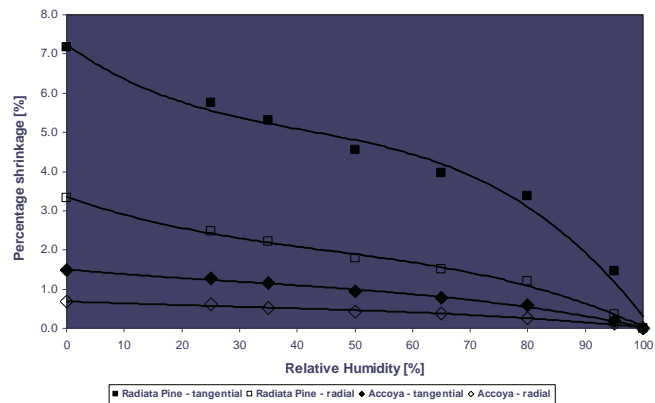
$$ASE = \frac{S_2 - S_1}{S_1} \times 100 \quad [S_2 = \text{Acetylated}; S_1 = \text{Control}]$$

Table 5. Dimensional stability of acetylated southern pine.

WPG	ASE
10	35
15	55
17	63
20	72

Figure 2 shows the reduction in swelling in control and acetylated pine. The un-acetylated pine shows much greater shrinkage especially in the tangential direction as compared to acetylated pine. Less shrinkage is observed in the radial direction.

Figure 2. Reduction in shrinkage in radiata pine.



6.4 Resistance to Biological Attack

6.4.1 Fungi

Various types of solid wood, particleboards and flakeboards made from acetylated wood have been tested for resistance to several different types of organisms [Imamura et al. 1987, Rowell et al. 1987, 1989, 1997, Beckers et al. 1994, Militz 1991, Wang et al. 2002].

Acetylated radiata has been tested against several types of decay fungi in an European Union standard [EN 113] decay test using the brown rot fungus *Gloeophyllum trabeum* and white rot fungus *Coriolus versicolor*. Table 6 shows the resistance at several levels of acetylation to attack by brown- and white rot fungi. As the level of acetylation goes up, the resistance to attack goes up.

Table 6. Resistance of southern yellow pine against fungi.

WPG	Weight Loss After EN 113 test	
	Brown-rot Fungus	White-rot Fungus
[%]	[%]	[%]
0	58.8	7.3
6	32.7	4.1
10	6.3	2.2
15	2.7	<2
20	<2	<2

Another test for fungal and bacterial resistance that has been done on acetylated composites is with brown-, white-, and soft-rot fungi and tunneling bacteria in a fungal cellar. Control blocks were destroyed in less than 6 months while samples made from acetylated wood above 16 WPG showed no attack after 1 year. [Nilsson et al. 1988, Rowell et al. 1988]. This data shows 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. This is more evidence that the moisture content of the cell wall is critical before attack can take place [Ibach and Rowell 2000, Ibach et al. 2000].

In-ground tests have also been done on acetylated solid wood and flakeboards [Rowell et al. 1997, Larsson Brelid et al. 2000]. Specimens have been tested in the United States, Sweden, and New Zealand. The specimens in test in Mississippi are showing little or no attack after 10 years.

Acetylated fiberboards in three in-ground locations in Gulf Port, Mississippi show no attack after 14 years. Recent results show that acetylated pine at a WPG of 21.2 is outperforming CCA [copper-chromium-arsenic] at 10.3 kg/m³ after 8 years in test in Sweden [Larsson Brelid et al. 2000].

Table 7. Data on control and acetylated stakes in Gulf Port, Mississippi test plot.

WPG	Rating at [years]									
	1	2	3	4	5	6	8	10	12	14
0	3	4	--							
20	0	0	0	0	0	0	0	0	0	0

Rating system 4 = Destroyed, 3 = Badly attacked, 2 = Some attack, 1 = Evidence of attack, 0 = No attack.

6.5 Other Properties

6.5.1 Strength

Table 8 shows the bending stiffness [MOE] and bending strength of [MOR] of acetylated radiata pine. The table shows strength properties are retained even after of acetylation.

Table 8. Bending stiffness [MOE] and bending strength of [MOR] of control and acetylated radiata pine.

Specimen	Density	Moisture	MOE	MOR
	[Kg/m ³]	[%]	[N/mm ²]	[N/mm ²]
Radiata Pine	417	12.2	9664	43
Acetylated Radiata Pine	492	5.2	8788	39

6.5.2 Hardness

Table 9 shows the Janka hardness of acetylated and control radiata pine. Acetylated radiata is much harder in all directions as compared to unacetylated pine but this is partly due to the lower moisture content of compared to unacetylated radiata pine.

Table 9. Janka hardness of samples according to ASTM D143

Specimen	Density	Moisture Content	Janka hardness ASTM D143		
			Radial	Tangential	End Grain
	[Kg/m ³]	[%]	[N]	[N]	[N]
Radiata Pine	479	12.1	2750	2748	3637
Acetylated Radiata	521	4.2	4046	4187	6595

6.5.3 Machinability

In general, acetylated wood has the same machining properties [sawing, planing, drilling, routing] as unacetylated wood. Gluing and coating properties are also similar to unacetylated wood using the present industrial gluing and coating systems. Due to the dimensional stability of wood acetylated to its core, coatings typical have a life of 2-3 times that of control samples. The surface of acetylated wood after planing is smoother than unacetylated wood resulting in less sanding before coating application.

7. PRODUCTS IN TEST AND APPLICATION

Acetylated wood has been in commercial use for several years. As an early test acetylated poplar was placed in test in the walls of one of the canals in The Netherlands [Figure 4 (left)]. After 13 years it was removed and determined to have minimal damage due to UV or biological degradation Figure 4 (right).

Figure 4. Acetylated poplar in test in a canal [left] and the sample after 13 years [right].



Leading applications of acetylated wood include use in windows doors, siding, decking, and exterior load-bearing glulam beams for buildings, bridges and other structures. Acetylated pine is now being used by many manufacturers for windows and doors [Figure 5] in the European market.

Figure 5. Examples of acetylated wood applications



Acetylated wood has also been successfully tested for use in load-bearing glulam structural beams for multiple purposes. As an example, two 40 meter long heavy road traffic bridges are currently under construction in Sneek, Netherlands due for completion in 2009. All beams have been produced for the projects. This following extensive testing for the application by leading independent institutes. Laminated beams up to 1080 x 1400 mm were produced. Superior strength-to-weight, durability, dimensional stability and low maintenance costs were cited as reasons for selection.

8. CONCLUSIONS

Acetylation of both softwoods and hardwoods gives a product which has a very high degree of dimensional stability and durability. Strength properties and hardness are not reduced.

This technology provides an environmentally safe method of protecting sustainable common woods to give a new generation of value-added products with increased stability and durability without the use of toxic chemicals. This method can take stress off of endangered tropical hard wood species that have been the traditional means of meeting durability requirements.

9. REFERENCES

All referenced used in this paper can be found in the following books.

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