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DIMENSIONAL STABILITY AND FUNGAL DURABILITY OF ACETYLATED WOOD

The reaction of wood to acetic anhydride greatly reduces moisture sorption and improves the dimensional stability of the wood due to the esterification of the accessible hydroxyl groups in the cell wall, reducing hydrogen bonding with water and bulking the cell wall back to its green volume. The sorption of both primary and secondary water are reduced. Dimensional stability is not 100% since the water molecule is smaller than the acetyl group, therefore water can access hydroxyl sites even when the wood is fully acetylated. The equilibrium moisture content is reduced in a linear relationship to the level of acetyl content. This means that the reduction in moisture content is not dependent on where the acetylation reaction takes place in the cell wall. Resistance to fungal attack increases as the level of acetylation increases. Resistance to attack by white-rot fungus occurs at a much lower level of acetylation (7-10%) than that to brown-rot fungal attack (17-19%). The cell wall moisture content may be too low at high levels of acetylation to support fungal attack, therefore initial colonization does not take place.

Keywords: Acetylation, dimensional stability, fungal resistance, moisture sorption, equilibrium moisture content

Introduction

As fossil resources become increasingly expensive, alternatives are being sought that are not based on diminishing fossil resources. If a transition is to be made from a fossil-based economy to a bio-based economy, major changes have to take place in technology, codes and standards, and, perhaps more importantly, in the way society thinks and acts.

Wood has been used since the first humans walked the earth for fuel, shelter, weapons, tools and for decoration. It is considered easy to work, and is renewable, sustainable and widely available. For the most part, it has been used without modification. Solid timber 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. Humans have learned to

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use wood accepting that it changes dimensions with changing moisture content, can be decomposed by a wide variety of organisms, burns and is degraded by ultraviolet energy.

With an increased awareness of the fragility of the environment and the need for durability in wood products, new technologies have been developed to increase the service life of wood materials without the use of toxic chemicals. Issues of sustainability, carbon sequestration and performance converge in this search for new technologies to improve stability and durability.

Chemical modification using acetic anhydride is an environmentally friendly method of wood stabilization and protection. This technology has been studied for many years and is now commercially available.

Acetylation

All woods contain acetyl groups: softwoods – 0.5-1.7%, and hardwoods – 2-4.5%, therefore adding more acetyl groups introduces chemical groups that already exist in the wood. The acetylation of wood was first performed in Germany by Fuchs [Fuchs 1928], using acetic anhydride and sulfuric acid as a catalyst. Fuchs found an acetyl weight gain of over 40%, which meant that in the process he decrystallized the cellulose. He used the reaction to isolate lignin from pine wood. In the same year, Horn acetylated beech wood to remove hemicelluloses in a similar lignin isolation procedure [Horn 1928]. Tarkow first demonstrated that acetylated balsa was resistant to decay [Tarkow 1945]. Tarkow was also the first to describe the use of acetylation to stabilize wood in order to prevent it from swelling in water [Tarkow 1946].

While laboratory acetylation of wood has been practised for nearly a century, the commercialization of acetylated wood has been met with several challenges. The Koppers Company may have made the first earnest, albeit short-lived, attempt at entry into the commercial acetylated wood market in the 1960s. This was followed by efforts in Russia and Japan (Diaken) in the 1970s and 1980s. In the late 1980s and early 1990s, A-Cell Acetyl Cellulosics AB, in Sweden, were granted a number of patents and built two pilot plants: one for solid wood, using microwave technology, and one for acetylating fibers. Accsys Technologies, which had acquired technologies developed earlier at Stichting Hout Research (the Netherlands) and Scion (New Zealand), launched trial quantities of Accoya®, an acetylated *Pinus radiata*, onto the market and began full commercial scale production in Arnhem, the Netherlands. This was followed in 2012 by Eastman Chemical Company introducing Perennial Wood™ using acetylated southern pine produced at its pilot facility in Kingsport, Tennessee, although production was stopped in 2014 [Rowell 2012].

Acetylation is a single-addition reaction, which means that one acetyl group is on one hydroxyl group with no polymerization:

$$\underset{}{\text{WOOD–OH}} + \underset{\text{Acetic anhydride}}{\text{CH}_3\text{–C(=O)–O–C(C=O)–CH}_3} \rightarrow \underset{\text{Acetylated wood}}{\text{WOOD–O–C(=O)–CH}_3} + \underset{\text{Acetic acid}}{\text{CH}_3\text{–C(=O)-OH}}$$

Thus, all the weight gain in acetyl can be directly converted into the units of hydroxyl groups blocked. This is not true for a reaction where polymer chains are formed (epoxides and isocyanates, for example). In these cases, the weight gain cannot be converted into units of blocked hydroxyl groups.

Isolated lignin reacts faster with acetic anhydride than hemicelluloses and holocellulose [Kumar and Agarwal 1983, Rowell et al. 1994] Kumar and Agawal reported that at an acetyl weight percent gain of 13.5, 86.4% of the lignin was acetylated, 21.6% of the hemicelluloses and 9.3% of the cellulose. Reacting wood at 120°C with acetic anhydride and no catalyst, at an acetyl weight gain of 16 to 19%, theoretically approximately 90% of the lignin is esterified, and 25% of the holocellulose [Rowell 1982]. It is assumed that 100% of the hemicellulose hydroxyl groups are substituted and no cellulose hydroxyl substituted. There may be a small number of hydroxyls esterified on the surface hydroxyls in the amorphous regions of the cellulose. This conclusion is based on the observation that pure cotton cellulose cloth can be used to hold wood fiber and no weight gain is observed in the cotton cloth after several acetylation reactions.

Moisture and dimensional stability

It is important to understand how moisture enters the wood and how it moves within the wood. 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. Due to this anisotropy, longitudinal flow paths are of major importance in the wetting of wood exposed to the weather [Miller and Boxall 1984]. Moisture enters wood in one of two ways: by capillary action as liquid water in the end grain or as moisture from the surrounding atmosphere. It is the end grain capillary uptake of liquid water that causes problems in the corners of windows and doors. Since wood is hygroscopic, it attracts moisture which bonds to the cell wall polymers through hydrogen bonding [Rowell 1984].

As moisture is added to the cell wall, wood volume increases nearly proportionally to the volume of water added [Tiemann 1944; Stamm 1964]. Swelling of the wood continues until the cell 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.

According to the Dent sorption theory, water is added to the cell wall polymers in mono-layers [Dent 1977]. Figure 1 shows the mechanism of water molecules adding to the wood cell wall. In figure 1A, water molecules enter the

cell wall and start hydrogen bonding with accessible hydroxyl groups. Figure 1B shows the "unzipping" of hydrophilic polymer chains [Caulfield 1978]. Figure 1C shows the sorption of primary water ● molecules and secondary water ○ molecules, while figure 1D illustrates the fully hydrogen bonded water in the cell wall. Hydrogen bonds between hydroxyl groups on and between hemicelluloses, cellulose and lignin are constantly changing.

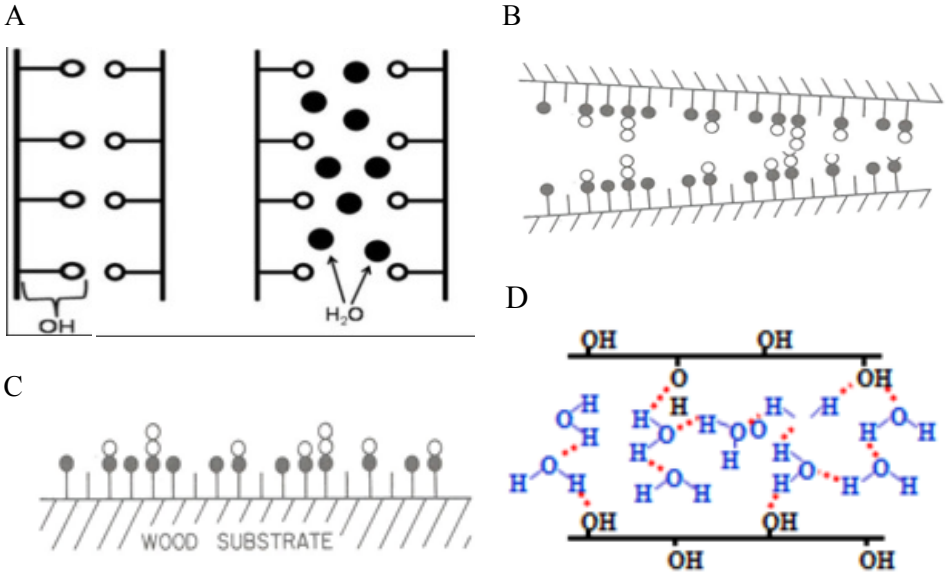

Fig. 1. Models of water added to the wood cell wall: A – Water molecules entering the wood cell wall, B – water molecules unzipping hydrophylic polymer chains, C – water bonding to the cell wall either as primary water ● or secondary water ○, D – fully hydrated cell wall at the fiber saturation point

Materials and methods

Freshly cut Scotch Pine (*Pinus sylvestris* L.) sapwood was cut into boards measuring 2.5 cm thick and dried. The test samples were cut from this wood as follows: for the acetylation reaction: 2.5 × 5 × 25 cm (radial × tangential × longitudinal); to test equilibrium moisture content and water swelling: 1 × 3 × 0.5 cm (radial × tangential × longitudinal); for the ASTM soil block test: 2.5 × 2.5 × 2.5 cm (radial × tangential × longitudinal); for the fungal cellar: 1 × 2 × 5 cm (radial × tangential × longitudinal); and for the in-ground tests: 2.5 × 3 × 30 cm (radial × tangential × longitudinal).

Acetylation was carried out in a 1 liter glass reactor using 5% acetic acid in acetic anhydride at reflux for 4 hours. The volume and oven dry weight of each sample was recorded before the reaction. After the reaction was complete, the modified wood was placed in a vacuum desiccator in water, a vacuum was

drawn for 30 minutes, then released, and finally the water was discarded and fresh water was added. This process was repeated 3 times to remove excess acetic anhydride and the by-product, acetic acid. The samples were then oven dried overnight at 105°C. The weight and volume of each sample was recorded and the acetyl weight percent gain (WPG) and change in volume were calculated.

The oven-dried and weighed control and acetylated samples were placed in humidity rooms that were controlled at 30, 65 and 90% relative humidity at 27°C. After 30 days, the samples were weighed again and the equilibrium moisture content determined.

Swelling in liquid water was carried out by placing the oven-dried and measured control and acetylated samples in water at room temperature. The swelling was measured using a flatbed micrometer until no further swelling was observed. The swelling coefficients and antishrink efficiencies were then calculated.

The control and acetylated samples were placed for testing in a soil block according to the ASTM standard D-2017-71 using the brown-rot fungus *G. trabeum* or the white-rot fungus *T. versicolor*. The test was run for 12 weeks and the weight loss was recorded.

The control and acetylated samples were measured and placed in a fungal cellar where the soil contained brown-, white-, and soft-rot fungi and tunneling bacteria. The samples were pulled at 2, 3, 4, 5, 6, 12, 24 and 36 months and rated for decay.

The control and acetylated samples were placed in the ground in three different places in Sweden in three different soil types: compost, sandy and forest soils. The samples were pulled after 300 days and rated for decay.

Results and discussion

Table 1 shows the change in the volume of the wood from green to dry to acetylated. The elastic limit of the cell wall was not exceeded and the bulked acetylated wood returned to the wood's original green volume. From green volume to dry resulted in a loss of approximately 10% in wood volume, while acetylation brought the wood volume back to that of the original green wood.

Table 1. Change in volume of wood from green to dry to acetylated

Green vol cm^3	OD Vol cm^3	Change %	Ac WPG	OD Vol cm^3	Change %
38.84	34.90	-10.1	22.8	38.84	+10.1

The equilibrium moisture content (EMC) reduced as the level of acetyl weight gain increased. Table 2 shows the reduction in EMC as a function of acetyl weight gain.

Table 2. Equilibrium moisture content of acetylated pine [Rowell 2012]

Percent Gain	Weight EMC at 27°C		
	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

Figure 2 shows the sorption/desorption isotherms for the control and two levels of acetylation. The curves for the acetylated samples were lower than the control but there was still a separation (hysteresis) in the adsorption/desorption curves. The differences in the acetylation curves were larger due to the slower adsorption than desorption.

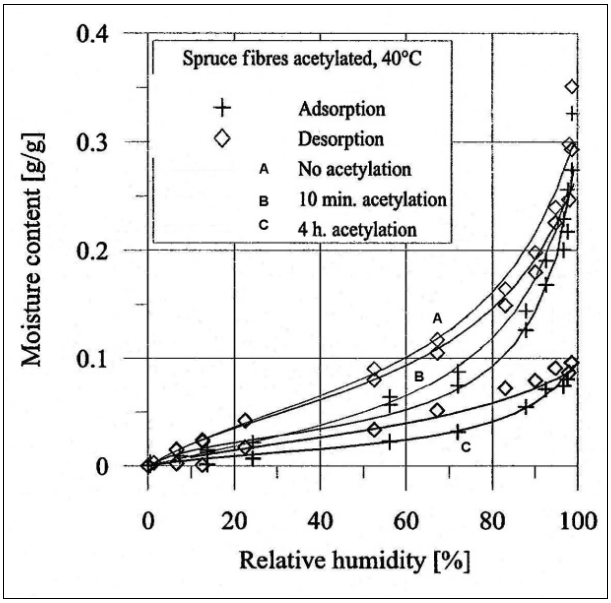

Fig 2. Sorption/desorption curves for control and two levels of acetylated spruce fiber [Rowell 2012]

Table 3 shows the dimensional stability resulting from the acetylation of solid pine wood and for a fiberboard made from acetylated pine fiber.

Table 3. Dimensional stability of acetylated wood (solid wood, 21.6 WPG, fiber 22.7 WPG, 24 hour water-soak)

	EMC	S	ASE
Solid Pine			
Control	21.7	13.8	–
Acetylated	8.4	4.2	81.3
Pine Fiberboard (5% phenolic resin)			
Control	20.2	21.3	–
Acetylated	3.4	2.1	90.1

S – swelling coefficient, ASE – antishrink efficiency [Rowell 2012].

Over the years, several mechanisms have been put forward to explain the resistance provided by acetylated wood to brown-rot fungal attack. The earliest ideas centered around the modification of the conformation and configuration of the substrate such that the specific enzymatic attack could not take place [Stamm and Baechler 1960; Takahashi et al. 1989a, b]. Another theory is based on the bulking effect of the covalently bonded acetyl group [Foster 1988; Foster et al. 1997]. Another was advanced that the mechanism was based on the physical blocking of the cell wall micropores so that enzyme penetration cannot take place [Hill 2001, 2006; Papadopoulos and Hill 2002; Hill et al. 2005]. Highley et al. [1994] showed that the smallest enzyme of a brown-rot fungi is too large to penetrate the cell wall. The average size of a cellulitic enzyme is ca 5 nm and the smallest pore size in wood is < 3.8 nm. Mohebby speculated that there are very small regions in the cell wall that are not acetyated due to the size of the acetate group but which are accessible to free radicals produced by the fungus [Mohebby 2003].

As the level of bonded acetyl increased, resistance to decay increased to both brown- and white-rot fungi (tab. 4). There was a significant decrease in fungal attack at an acetyl level of approximately 10%, which means that many of the hydroxyl groups that are required for a fungi to recognize wood as a food source were modified. As the acetyl level reached 15%, the attack by white-rot fungi stopped and very little attack occurred by the brown-rot fungi. At an acetyl level of ca 18%, there was no attack by either the brown- or white-rot fungi.

A possible key to fungal resistance can be seen in table 5. Control and particleboards made from different levels of increasing acetyl content were placed in a fungal cellar in Uppsala, Sweden [Nilsson et al. 1988]. The samples were evaluated at different times, up to 36 months, to determine the level of attack and to measure sample thickness. The first sample check was done at 2 months and already the control had swollen and there was moderate fungal attack. At the same inspection time, the acetylated sample at 7.3 weight percent gain (WPG) was swollen but there was no evidence of fungal attack. By

6 months, the control samples were badly swollen and destroyed as a result of fungal attack.

Table 4. Resistance of acetylated pine to decay fungi in ASTM D-2017-71 soil block test[1] (brown-rot – *G. trabeum*; white-rot – *T. versicolor*)

Acetyl weight gain (%)	Weight loss after 12 weeks	
	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

[1]ASTM D 1413 – American Society for Testing and Materials, ASTM – standard method of testing wood preservatives using laboratory soil-block cultures (1976) [Rowell 2012].

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

WPG Rating at intervals (months)[3]								
0	2	3	4	5	6	12	24	36
7.3	S/2	S/3	S/3	S/3	S/4	–	–	–
11.5	S/0	S/1	S/1	S/2	S/3	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

[1]Non-sterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria.
[2]Flakeboards bonded with 5 percent phenol-formaldehyde adhesive.
[3]Rating system: 0 – no attack, 1 – slight attack, 2 – moderate attack, 3 – heavy attack, 4 – destroyed, S – swollen [Rowell 2012].

At 3 months, the acetylated sample at 7.3% showed the first signs of fungal attack and was still swollen. This sample continued to be attacked and was destroyed at 12 months. At 4 months, the sample at 11.5% was swollen but no fungal attack was noted. After one more month, this sample showed the first signs of fungal attack. This trend, of a sample first showing swelling before any fungal attack, led to the conclusion that swelling must take place before any fungal attack occurs. This shows the importance of cell wall moisture before fungal attack can take place.

Figure 3 shows the control sample (A) before the 12 week soil bottle test using a brown-rot fungi (see tab. 4). After 12 weeks, the control sample was covered with fungal mycelium (B) and the cell wall was destroyed. After the same length of time in the same experiment, the sample acetyylated to 19 WPG showed no weight loss but there was evidence of mycelium growth (fig. 4).

There is a fungal hyphe visible on the radial wall of the acetylated sample and it is growing on the S_3 layer of the cell wall (arrow in fig. 4). This shows that the acetyated wood was not toxic to the fungus, rather that the fungus could not recognize it as a food source.

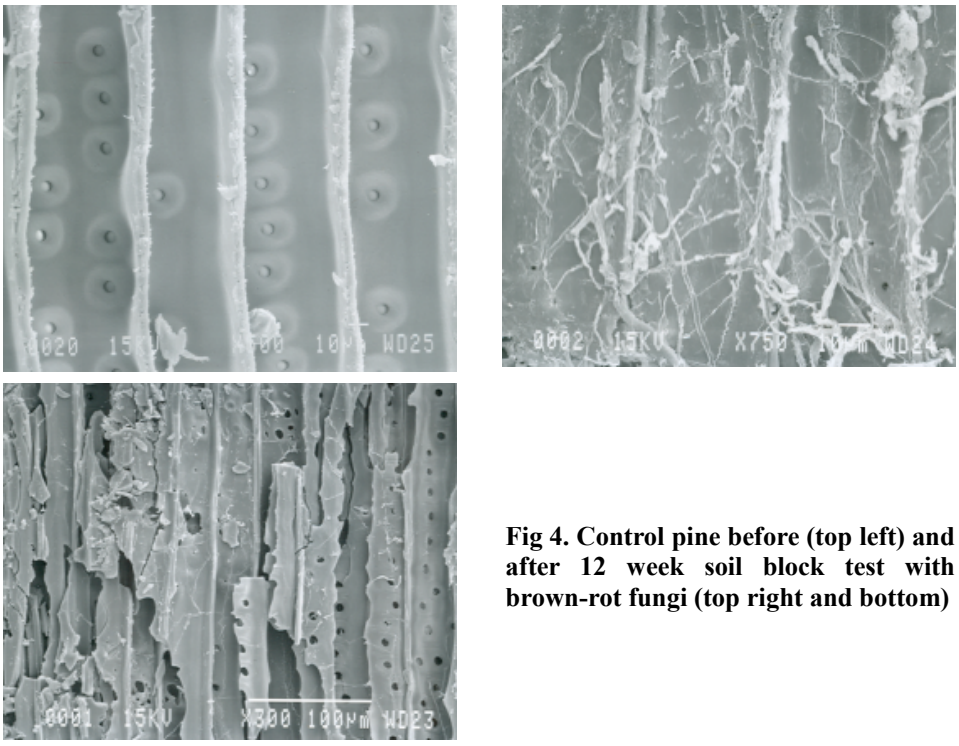

Fig 4. Control pine before (top left) and after 12 week soil block test with brown-rot fungi (top right and bottom)

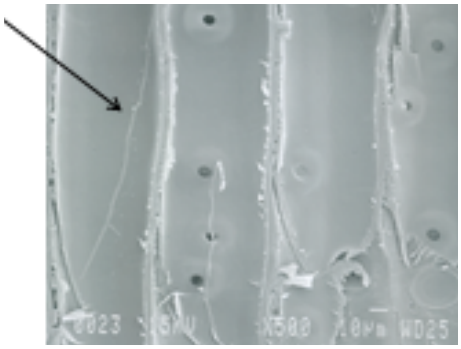

Fig 5. Acetylated pine after 12 week soil block test with brown-rot fungi

Table 6 shows the results of acetylated wood after 300 days in three different types of soil. The compost soil had mainly brown-rot fungi, the sandy soil had mainly soft-rot fungi, while the forest soil had mainly white-rot and soft-rot fungi.

Table 6. Results of in-ground tests on control and acetylated pine [Rowell 2012]

Sample	Weight Loss in:		
	compost	sandy soil	forest soil
Control	74 ±9	50 ±16	27 ±24
Acetylated	1 ±0	1 ±0	0

Table 7 shows the loss of carbohydrates in the wood fiber. The non--acetylated fiber lost 85.8% carbohydrate with major weight loss in all sugars except the galatans. The acetylated sample at 15% acetyl showed only 13.2% total carbohydrate loss, no loss of cellulose (glucans) but major losses of arabans and rhamnans. In addition, there was no loss of lignin in these experiments.

Table 7. Carbohydrate analysis after brown-rot degradation of wood fiber

WPG	Wt loss %	Total carbo lost %	Ar lost %	Gal lost %	Rha lost %	Glu lost %	Xyl lost %	Man lost %
0	51.7	85.8	87.9	71.9	90.0	83.8	90.6	92.5
15	1.4	13.2	89.0	55.2	70.0	0	38.3	42.0

A – Arabans, Ga – Galatans, Rh – Rhamans, Gl – Glucans, Xy – Xylans, Man – Mannans.

Conclusions

Reductions in the moisture sorption in acetylated wood are due to the substitution of hydroxyl groups with acetyl groups. Increased dimensional stability in acetylated wood is due to the bulking of the cell wall with acetyl groups back to its original green dimension so that the cell wall cannot expand very much more because the elastic limit has not been exceeded. The decay resistance of acetylated wood may be due to the lowering of the cell wall moisture content below that needed to support fungal colonization, therefore the initial enzymatic attack does not take place.

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