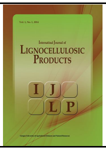

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INVITED PAPER

Acetylation of wood – A review

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Abstract

Wood is 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. Some, but not all, of the cell wall polymer hydroxyl groups are accessible to moisture and these accessible hydroxyls form hydrogen bonds with water. As the water layers build up, the cell wall expands to accommodate the water resulting in an increase in wood/water volume up to the fiber saturation point. Increased moisture levels also offer a large variety of micro-organisms the opportunity to colonize and begin the process of decay. If these accessible hydroxyl groups are chemically substituted with a larger and more hydrophobic chemical groups, the bonded chemical can expand the cell wall until it reaches its elastic limit. And if the hydrophobic nature of substituted groups sufficiently reduces the cell wall moisture levels, the wood will no longer support the colonization of micro-organisms. This modified wood then achieves a high level of dimensional stability and durability. One technology that has now been commercialized to achieve these properties is *acetylation*: a reaction between the hydroxyl groups on the wood cell wall polymers with acetic anhydride. While all woods contain a low level of acetyl groups, increasing this acetyl content changes the properties and 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 dimensional stability and durability.

***Keywords*:** Acetylation, Acetic anhydride, Brown-rot, Chemical modification, Decay resistance, Dimensional stability, Equilibrium moisture content, Fiber saturation point, Hardwoods, Mechanisms, Softwoods, Stiffness, Strength, Water soak, White-rot.

1. Introduction

As fossil resources become increasingly expensive, we are looking for alternatives that are not based on our diminishing fossil resources. If we are make a transition 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 we think and act.

Wood has been used by humans since the first humans walked the earth. They used it for fuel, shelter, weapons, tools and for decoration. They found it easy to work, renewable, sustainable and available. 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 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. Wood has mainly been used as a construction material because it is widely available, renewable, sustainable and cheap. The average person does not consider wood as a high performance material.

Wood changes dimensions 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, non-crystalline cellulose, lignin, and surface of crystalline cellulose also play major roles. Moisture swells the cell wall, and the fiber expands until the cell wall 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 expansion. This process is reversible, and the fiber shrinks as it loses moisture below the FSP.

Wood is degraded biologically because organisms recognize the carbohydrate polymers (mainly the hemicelluloses) in the cell wall and have very specific enzyme systems capable of hydrolyzing these polymers into digestible units. Biodegradation of the cell wall matrix and the high molecular weight cellulose weakens the fiber cell. Strength is lost as the cell wall polymers and matrix undergoes degradation through oxidation, hydrolysis, and dehydration reactions.

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 lignin acts as an adhesive in the cell walls, holding the cellulose fibers together. The surface becomes richer in cellulose content as the lignin degrades. In comparison to lignin, cellulose is much less susceptible to ultraviolet light degradation. After the lignin has been degraded, the poorly bonded carbohydrate-rich fibers erode easily from the surface, which exposes new lignin to 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.

Wood burns because the cell wall polymers undergo pyrolysis reactions with increasing temperature to give off volatile, flammable gases. The gases are ignited by some external source and combust. The hemicelluloses and cellulose polymers are degraded by heat much before the lignin. The lignin component contributes to char formation, and the charred layer helps insulate the composite from further thermal degradation.

We have 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. We accept these degrading chemistries and design and build around them. Our codes and standards are written with the knowledge of these chemistries. But, what if wood did not swell and shrink with changing moisture, what if it didn’t decay or degrade by pyrolysis reactions or by ultra violet energy.

If we could change the chemistry of the wood cell wall, we could make a new bioarchitecture other than what Nature gives us with greatly improved performance properties. We could design the wood properties we wanted. We have discovered that if you change the chemistry of wood, you change it properties and that leads to a change in performance. From this foundation, the science of chemical modification of wood was born.

While there are many early references to reacting chemicals with wood, the term *“chemical modification of wood”* was first used in 1946 by Tarkow (Tarkow, 1945). 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 (Hill, 2006; Hon, 1996; Jahn, 1947; Kumar, 1994; Rowell, 1975; Rowell, 1983; Rowell, 2013). 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, di-functional aldehydes, chloral, phthaldehydic acid, dimethyl sulfate, alkyl chlorides, β-propiolactone, acrylonitrile, epoxides, such as, ethylene, propylene, and butylene oxide, and di-functional epoxides.

Most of the research in chemical modification of wood has been focused on improving dimensional instability and resistance to biological degradation. And of all of the chemistries published on the chemical modification of wood, the reaction of wood with acetic anhydride (*acetylation*) has been studied the most and is now commercial.

2. Acetylation of Wood

The *acetylation* of wood was first performed in Germany by Fuchs in 1928 using acetic anhydride and sulfuric acid as a catalyst (Fuchs, 1928). Fuchs found an acetyl weight gain of over 40 percent, which meant that he decrystalized the cellulose in the process. 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). Also in 1928, Suida and Titsch acetylated powdered beech and pine using pyridine or dimethylaniline as a catalyst to yield an acetyl weight gain of 30 to 35 percent after 15 to 35 days at 100°C (Suida and Titsch, 1929).

In 1945, Tarkow first demonstrated that acetylated balsa was resistant to decay (Tarkow, 1945). Tarkow also was first to described the use of wood *acetylation* to stabilize wood from swelling in water (Tarkow, 1946, Tarkow et al., 1946). The first patent on wood *acetylation* was filed by Suida in Austria in 1930 (Suida, 1930). Nearly two decades later in 1947, Stamm and Tarkow filed a patent on the *acetylation* of wood and boards using pyridine as a catalyst (Stamm, and Tarkow, 1947). In 1961, the Koppers Company published a technical bulletin on the *acetylation* of wood using no catalyst but an organic co-solvent.

In 1973, Rowell started a research program on chemical modification that included new ideas for wood *acetylation* (Rowell, 1975). Several new ideas for wood *acetylation* were developed in this program depending on the size of the wood to be acetylated. For fiber, flakes, chips and wood up to about 3 cm in thickness, uncatalyzed hot acetic anhydride with a small amount of acetic acid was used. Wood does not float in acetic anhydride so the fiber, flakes or chips can be removed from the bottom of soaking container by a screw or belt for continuous removal of the saturated wood. Technology was also developed to use a minimal amount of anhydride based on the over dry weight of the wood to reduce the energy required to heat the reaction mixture. For wood thicker than about 3 cm, the wood is first soaked in a vacuum/pressure process with cold anhydride to saturate the wood and then heated. If this is not done, as the reaction starts on the outside of the thick wood, the by-product acetic acid builds up and will either slow the reaction or stop it (Rowell, 1986).

In 1977 in Russia, Otlesnov and Nikitina came close to commercializing *acetylation* but the process was discontinued, presumably because it was not cost effective. In the late 1980s in Japan, Daiken started commercial production of acetylated wood for flooring called alpha-wood. Also in the late 1980's and early 1990's, ACell, in Sweden, were granted many 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*, into the market and began full commercial scale production in Arnhem, the Netherlands. This was followed in 2012 with Eastman Chemical Company introducing Perennial Wood™ using acetylated southern pine produced at its pilot facility in Kingsport, Tennessee. In 2014, Eastman stopped the production of Perennial Wood™.

The reaction of acetic anhydride with wood results in esterification of the accessible hydroxyl groups in the cell wall, with the formation of by-product acetic acid. The by-product acid must be removed to low levels from the product as the human nose is quite sensitive to the odor of acetic acid.

3. Chemistry

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

$$\textbf{WOOD-OH} + (\mathbf{CH_3CO})_2\mathbf{O} \rightarrow \textbf{WOOD-O-COCH}_\mathbf{3} + \mathbf{CH_3COOH}$$

acetic anhydride acetylated wood acetic acid

Thus, all the weight gain in acetyl can be directly converted into 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. Table 1 shows that when green wood is dried, it shrinks about 10% in volume (Rowell, 2006). When that wood is acetylated to about 20 weight percent gain (WPG), the new dry modified volume has increased about 10% and the wood is now approximately the same size as it was when green (Table 1).

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

Green Volume (cm^2)	Oven dry Volume (cm^2)	Change (%)	Ac (%)	Ac Volume (cm2)	Change (%)
38.84	34.90	-10.1	22.8	38.84	+10.1

Acetylation has also been done using ketene gas (Tarkow, 1945; Karlson and Svalbe, 1972; Karlson and Svalbe, 1977; Rowell et al., 1986). In this case, esterification of the cell wall hydroxyl groups takes place but there is no formation of byproduct acetic acid. While this is interesting chemistry and eliminates a byproduct, it has been shown that reactions

$$\textbf{WOOD-OH} + \mathbf{CH_2{=}C{=}O} \rightarrow \textbf{WOOD-O-COCH}_\mathbf{3}$$

ketene acetylated wood

with ketene gas results in poor penetration of reactive chemical and it has been shown that the rate of the reaction is determined by the rate of diffusion of the vapor into the wood. Since the rate of diffusion into a porous solid varies inversely with the square of its thickness, reaction of wood with ketene has been restricted to a maximum wood thickness of about 3 mm if the reaction is to be carried out in a reasonable length of time. The properties of the reacted wood are less desirable than those of wood reacted with acetic anhydride (Rowell et al., 1986b).

Through the years, many catalysts have been tried for *acetylation*, both with liquid and vapor systems. These include zinc chloride, urea-ammonium sulphate, dimethylformamide, sodium acetate, magnesium persulfate, trifluoroacetic acid, boron trifluoride, and γ-rays. In the early 1980's, the technology changed to using a controlled and limited amount of acetic anhydride, no catalyst or cosolvent; a small amount of acetic acid; and a reaction temperature of between 120 and 130 °C for solid wood (after soaking in cold anhydride) and 120 to l65 °C for fibers, particles, chips, veneer and thin solid wood (Rowell et al., 1986a). The rate-controlling step in the chemical modification of solid wood is the rate of penetration of the reagent into the cell wall.

In the reaction of liquid acetic anhydride with wood, at an acetyl weight percent gain of about 4, there is more bonded acetyl in the S_2 layer than in the middle lamella. At a WPG of about 10, acetyl is equally distributed throughout the S_2 layer and middle lamella. At a WPG over 20, there is a slightly higher concentration of acetyl in the middle lamella than in the rest of the cell wall. These results were found using chloroacetic anhydride and following the fate of the chlorine by energy-dispersive x-ray analysis (Rowell et al. 1991a).

Questions have been raised about the long-term stability of the acetate group in wood. Table 2 shows the stability of acetyl groups in pine an aspen flakes to cyclic exposure to 30 and 90% relative humidity (RH) (3 months at 30% RH, followed by 3 months at 90% RH). Within experimental error, no loss of acetyl occurred over 41 cycles. This experiment has been ongoing for more than 20 years; results continue to show little or no loss of acetyl from humidity cycling (Rowell et al., 1992).

Table 2. Stability of acetyl groups in pine and aspen flakes after cyclic exposure between 90% and 30% relative humidity (RH).

	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

The mass balance in the *acetylation* reaction shows that all the acetic anhydride going into the *acetylation* of hardwood and softwood could be accounted for as increased acetyl content in the wood, acetic acid resulting from hydrolysis by moisture in the wood, or as unreacted acetic anhydride. The consumption of acetic anhydride can be calculated stoichiometrically based on the degree of *acetylation* and the moisture concentration (MC) of the wood (Rowell et al., 1990).

Table 3 shows the distribution of acetyl groups in southern yellow pine reacted with acetic anhydride to three levels of WPG at 120 °C. Assuming that part of the cellulose is not accessible due to its crystallinity and the fact that cellulose did not react as seen in Figure 1, at a WPG of 23.6, all of the theoretical hydroxyl groups on lignin are acetylated (assuming approximately 1 hydroxyl group per C-9 unit) and over 60% of the hemicellulose hydroxyls are acetylated (Rowell, 1982).

Table 3. Distribution of acetyl group in southern yellow pine.

WPG	Total Accessibility*	Limited Accessibility**	Degree of Substitution in Lignin
8.5	0.12	0.28	0.78
18.5	0.19	0.46	1.10
23.6	0.26	0.63	1.15

*Assuming accessibility of all cell wall hydroxyl groups.

**Assuming 100% accessibility of hemicelluloses and lignin hydroxyl groups but no accessibility of cellulose hydroxyl groups.

Figure 1 shows the rate and extent of each isolated cell wall polymer in the wood along with whole wood. Reacting wood with acetic anhydride reacts first with the more acidic phenolic hydroxyl on lignin but the bulk of the bonded acetyl is on the hemicelluloses (Rowell et al., 1991a).

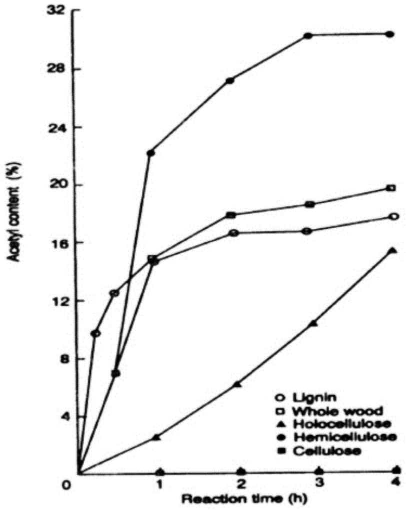

Figure 1. Reaction of acetic anhydride with isolated cell wall polymers and whole wood.

4. Properties of Acetylated Wood

4.1. Moisture and water sorption

The replacement of some hydroxyl groups on the cell wall polymers with bonded acetyl groups reduces the hygroscopicity of wood. One measurement of level of this change is the reduction in fiber saturation point. Table 4 shows the fiber saturation point for acetylated pine and aspen. As the level of *acetylation* increases, the fiber saturation point decreases, in both softwood and hardwood [Rowell, 2005; Dickerson et al., 2012).

Acetylation reduces the fiber saturation point (FSP) as seen in Table 4. The FSP is lowered more in softwoods as compared to hardwoods at similar acetyl contents.

Table 4. Fiber saturation point (FSP) for acetylated pine and aspen.

WPG	Pine (%)	Aspen (%)
0	45	46
6	24	---
8.7	---	29
10.4	16	---
13	---	20
17.6	---	15
18.4	14	---
21.1	10	---

Table 5 shows the equilibrium moisture content (EMC) of control and acetylated pine and aspen at several levels of *acetylation* and three levels of RH. In all cases, as the level of chemical weight gain increases, EMC is reduced in the modified wood. Figure 2 shows the sorption/desorption isotherm for acetylated and control spruce fiber (Stromdahl, 2000). The 10 minute *acetylation* curve represents a WPG of 13.2 and the 4 hour curve represents a WPG of 19.2. The untreated spruce reaches an adsorption/desorption maximum at about 35% moisture content (top), the 13.2 WPG a maximum of about 30% (middle), and the 19.2 WPG a maximum of about 10% (bottom). There is a larger difference between the adsorption and desorption (hysteresis) curves for the acetylated wood as compared to control which is not easy to explain since many of the hydroxyl groups are esterified in the acetylated samples as compared to the control.

Table 5. Equilibrium moisture content (%) of acetylated pine and aspen at 27°C.

Specimen	WPG (%)	RH (%) 30	65	90
Acetylated 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	4.4	8.4
Acetylated 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

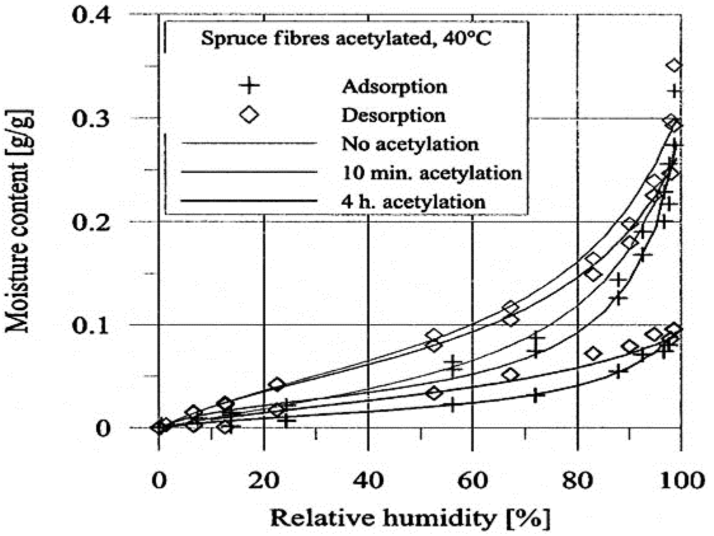

Figure 2. Sorption isotherm for control and acetylated spruce.

Moisture is presumed to be sorbed either as primary or secondary water. Primary water is water sorbed to primary sites with high binding energy, such as the hydroxyl groups (Figure 3). Secondary water is water sorbed to sites with less binding energy; water molecules are sorbed on top of the primary layer. Since some hydroxyl sites are esterified with acetyl groups, there are fewer primary sites to which water sorbs. And since the fiber is more hydrophobic as a result of *acetylation*, there may also be fewer secondary binding sites.

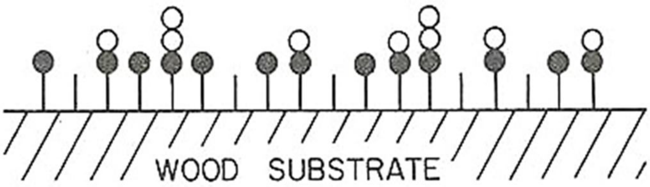

Figure 3. Primary and secondary water on cell wall hydroxyl groups.

Changes in dimensions are a great problem in wood composites as compared to solid wood. Composites undergo not only normal bulk wood swelling (reversible swelling) hut also swelling caused by the release of residual compressive stresses imparted to the board during the composite pressing process (irreversible swelling) (Youngquist et al., 1986a, 1986b). Water sorption causes both reversible and irreversible swelling; some reversible shrinkage occurs when the board dries.

The rate of swelling is much slower in acetylated wood as compared to controls. Table 6 shows the rate of swelling of fiberboards made from control and acetylated fiber. The control board has increased more than 25% in thickness after just 15 minutes and has increased over 35% after 5 days. The board made from acetylated fibers only increased less than 5% after 5 days.

Table 6. Rate and extent of thickness swelling in liquid water of pine fiberboards made from control and acetylated fiber (8% phenolic resin).

	Minutes			Hours			Days
	15	30	60	3	6	24	5
Control	25.7	29.8	33.5	33.8	34	34	36.2
Acetylated 21.6 WPG	0.6	0.9	1.2	1.9	2.5	3.7	4.5

The dimensional stability, as measured as anti-shrink efficiency (ASE) of acetylated solid wood varies depending on the species acetylated. Table 7 shows the ASE of two soft woods and two hardwoods. As the percent acetyl content increases, dimensional stability increases (Militz, 1991). The data indicates shows that softwoods achieve a higher weight gain in acetyl as compared to hardwoods. This may be because hardwoods contain a higher content of xylans which do not have a primary hydroxyl group in which to react. One hundred percent dimensional stability is not achieved by *acetylation* since water molecules will still interact with the wood structure even in "*completely acetylated wood,*" however, the swelling does not exceed the elastic limit of the cell wall.

Table 7. Dimensional stability of solid wood as measured as antishrink efficiency (ASE).

Wood	WPG	ASE	Wood	WPG	ASE
Ponderosa Pine	0	---	Beech	0	---
	12.0	39.4		10.6	43.8
	13.6	56.3		11.9	56.4
	17.1	64.8		15.4	66.0
	20.8	78.9		17.5	75.6
Sitka Spruce	0	---	Oak	0	---
	13.5	34.1		11.9	46.8
	14.8	46.3		13.9	65.5
	18.7	54.9		17.2	73.4
	24.1	69.5		17.8	84.9

Table 8 shows that repeated wetting and drying of acetylated pine does not decrease the dimensional stability and further indicates the stability of the acetyl group (Rowell and Ellis, 1978).

Table 8. Repeated antishrink efficiency (ASE) of acetylated solid pine.

	WPG	ASE1	ASE2	ASE3	ASE4	Weight Loss After Test
Acetic Anhydride	22.5	70.3	71.4	70.6	69.2	<0.2

Table 9 shows that a lower level of equilibrium moisture content and a higher level of dimensional stability is achieved in fiberboards made from acetylated fiber as compared to solid wood. This is due to more accessible reaction sites available at the fiber level as compared to solid wood (Rowell et al., 1991b).

Table 9. Equilibrium moisture content and antishrink efficiency.

	WPG	EMC	ASE
Fiberboard made from Acetylated pine fiber (5% phenolic resin)	0	19.6	---
	12.3	10.8	61.9
	15.8	8.9	77.1
	18.9	5.3	86.3
	20.8	3.8	94.7

4.2. *Resistance to biological attack*

4.2.1. Fungi-lab tests

Various types of solid wood, particleboards, and flakeboards made from acetylated wood have been tested for resistance to different types of organisms.

Acetylated wood has been tested with several types of decay fungi in an ASTM standard 12-week soil block test using the brown-rot fungus *Gloeophyllum trabeum* or the white-rot fungus *Trametes versicolor* (Figure 4).

Table 10 shows the resistance of pine acetylated to several levels of chemical modification to attack by brown-and white-rot fungi. As the level of *acetylation* rises, the resistance to attack increases. Weight loss resulting from fungal attack is the method most frequently used to determine the effectiveness of a preservative treatment to protect wood from decay. In some cases, especially for brown-rot fungal attack, strength loss may be a more important measure of attack since large strength losses are known to occur in solid wood at very low wood weight loss.

Table 10. Weight loss of acetylated southern pine in a soil block test.(ASTM D14113–07e1. Standard Test Method for Wood Preservatives by Laboratory Soil-Block Cultures).

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

Figure 4. ASTM standard soil block test.

Figure 5 shows the control pine sample before and after attack by the brown-rot fungus *Gloeophyllum trabeum* (Rowell et al. 1987, 1988, 2000). The wood is badly deteriorated with major damage to the cell wall structure. The figure also shows the acetylated wood after the same test. The fungal hyphae can be seen but there is no visible attack on the wood.

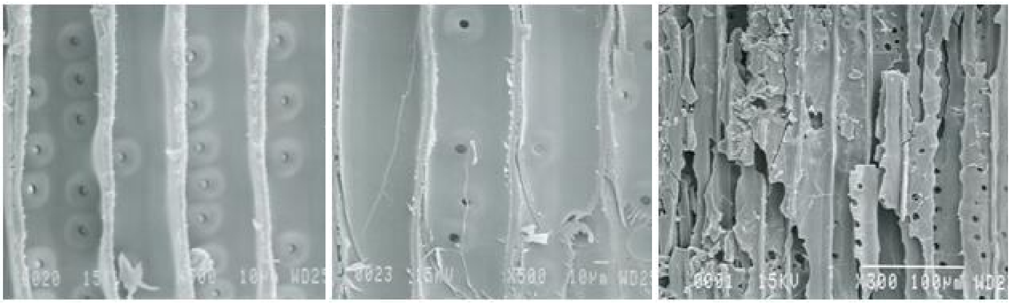

Figure 5. SEM of brown-rot fungal attack on wood. Left = control, Center= acetylated wood after 12 weeks in the ASTM soil block test, Right = after 51.1% weight loss.

Weight loss resulting from fungal attack is the method most frequently used to determine the effectiveness of a preservative treatment to protect wood from decay. In some cases, especially for brown-rot fungal attack, strength loss may be a more important measure of attack since large strength losses are known to occur in solid wood at very low wood weight loss. A dynamic bending creep test (Figure 6) has been developed to determine strength loss when wood composites are exposed to a brown or white-rot fungus (Imamura and Nishimoto, 1985).

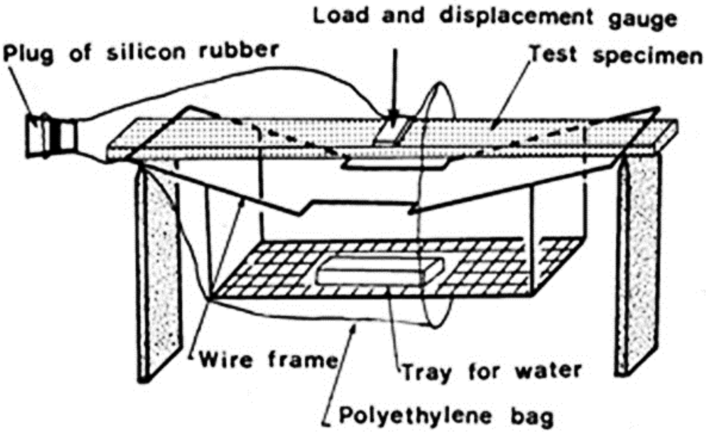

Figure 6. Test equipment for strength loss in control and acetylated wood (Imamura and Nishimoto, 1985).

In this bending creep test of aspen flakeboards, control boards made with phenol-formaldehyde adhesive failed in an average of 71 days when exposed to the brown-rot fungus *Tyromyces palustris* and in 212 days when exposed to the white-rot fungus *Trametes versicolor* (Rowell, 1988; Imamura et al., 1987, 1988). At failure, weight loss averaged 7.8% for *T. palustris* and 31.6% for *T.versicolor*. Isocyanate-bonded control flakeboards failed in an average of 20 days with *T.*

palustris and 118 days with *T. versicolor*, with an average weight loss at failure of 5.5 and 34.4 %, respectively. Very little or no weight loss occurred with both fungi in flakeboards made using either phenol-formaldehyde or isocyanate adhesive with acetylated flakes. None of these specimens failed during the 300-day test period. Mycelium fully covered the surfaces of isocyanate-bonded control flakeboards within 1 week, but mycelial development was considerably slower in control flakeboards bonded with phenol-formaldehyde. Acetylated flakeboards bonded with both isocyanate-and phenol-formaldehyde showed surface mycelium colonization during the test, but no strength loss (Figure 8).

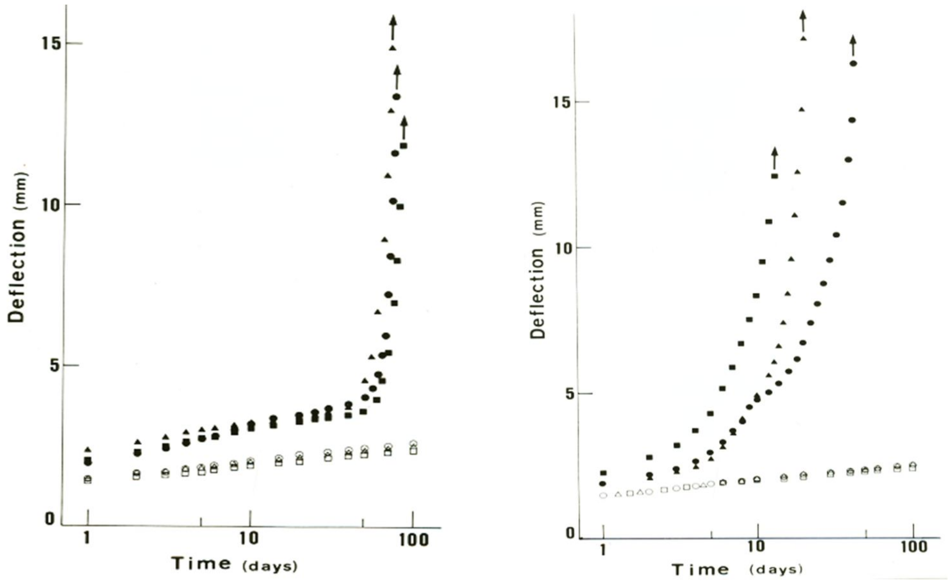

Figure 7. Deflection-time curve for control and acetylated flakeboards: phenol-formaldehyde bonded (left), isocyanate bonded (right). [Control = solid dots, acetylated = hollow dots].

In similar bending creep test, both control and acetylated pine particleboard made using melamine-ureaformaldehyde adhesive failed because *T. palustris* attacked the adhesive in the glueline. Mycelium invaded the inner part of all boards, colonizing in both the wood and glue line in control boards but only in the glueline in acetylated boards. These results show that the glueline is also important in protecting composites from biological attack. After 16 weeks of exposure to *T. palustris*, the internal bond strength (IBS) of control aspen flakeboards made using a phenol-formaldehyde resin was reduced more than 90%; IBS of flakeboards made using an isocyanate resin was reduced 85 % (Imamura et al., 1987). After 6 months of exposure in moist unsterile soil, the same control flakeboards made using a phenol-formaldehyde resin lost 65 % IBS and those made using an isocyanate resin lost 64 % IBS. Failure was due mainly to strength reduction in the wood resulting from fungal attack. Acetylated aspen flakeboards lost much less IBS during the 16-week exposure to *T. palustris* or 6-month soil exposure.

The mechanism of resistance to fungal attack by chemical modification is hypothesized to be related to low moisture sorption in the cell wall, below that needed for biological attack. Other theories suggest the mechanism may be from blocking of specific enzymatic reactions as a result of changes in configuration and conformation of the polymers in the cell wall of the modified wood. In the case of brown-rot fungal attack, researchers have suggested that the reduced moisture of acetylated wood prevents the fungus from initiating the breakdown of the hemicelluloses as an energy source. This mechanism is consistent with the data from soil block weight loss tests and strength loss tests.

Table 11 shows the sugar analysis after the 12 week soil block test with a brown-rot fungi on a control fiberboard and an acetylated fiber with a WPG of 13. The control sample lost 51.7 % in total weight and a carbohydrate loss of 86% while the acetylated sample only lost 1.4% in total weight and 13.2% carbohydrate. Almost all of the araban, rhamnan, mannan and xylan were lost in the control samples as well as most of the galactan and glucan. No glucan was lost in the acetylated sample showing that in the early stages of brown-rot decay, the cellulose is not attacked. A large portion of the araban and the rhamnan were lost in the early stages of attack on the acetylated board. There is also a significant loss of galactan, xylan and mannan during the early stages of attack. All of these sugars are in the hemicellulose polymers which is even more evidence that it is the hemicelluloses that need to be protected for fungal resistance, at least, for brown-rot fungal attack. Arabinose is the only sugar in wood that is in a strained five membered ring. It is possible that this easily hydrolyzed sugar is the recognition site for the fungal enzymes that starts the entire decay process in brown-rot fungi.

Table 11. Sugar analysis on a pine sample after the 12-week ASTM soil block test with the brown-rot fungus Gloeophyllum trabeum.

Wood fiber	Lost (%)							
WPG	Weight	Total Carbo	Araban	Galac-tan	Rham-nan	Glucan	Xylan	Mannan
0	51.7	85.8	87.9	71.9	90.0	83.8	90.6	92.5
13	1.4	13.2	89.0	55.2	70.0	0	38.3	42.0

4.2.2. *Fungi-fungal cellar test*

Another test to determine the fungal and bacterial resistance of acetylated composites is a fungal cellar containing brown-, white-, and soft-rot fungi and tunneling bacteria (Figure 8). Control blocks were destroyed in less than 6 months while flake-boards made from acetylated furnish above 16 WPG showed no attack after 3 years (Table 12). These data show that no attack occurs until swelling of the wood occurs. This is additional evidence that the moisture content of the cell wall is critical to fungal attack.

Figure 8. Fungal cellar test room.

Table 12. Fungal cellar tests of aspen flakeboards made from control and acetylated flakes.

WPG	Rating interval (months)							
	2	3	4	5	6	12	24	36
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/3
16.3	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0

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

4.2.3. Fungi-in ground tests

Acetylated solid wood and flakeboards have been subjected to in-ground tests in the United States and New Zealand (Rowell et al., 1997), and Sweden (Larsson-Brelid, 2000), with specimens showing little or no attack after 10 years of exposure (Figure 9). In Indonesia (Hadi, 1996) specimens failed in less than 3 years, mainly as a result 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 15 years of exposure (Larsson-Brelid, 2000).

Figure 9. Inground stake test.

4.2.4. Termites-lab tests

Table 13 shows the results of a 2-week termite test using *Reticulitermes flavipes* (subterranean termites) on control and acetylated pine (Figure 10). While protection as afforded to samples with higher levels of *acetylation*, the lack of complete resistance to attack may be attributed to the low mortality rate in termites during the test. Termites can live on acetic acid and decompose cellulose to mainly acetate.

Table 13. Wood weight loss in control and acetylated after a two-week exposure to *Reticulitermes flavipes.*

Sample	WPG	Wood Weight Loss (%)
Control	0	31
Acetylated	10.4	9
	17.8	6
	21.6	0

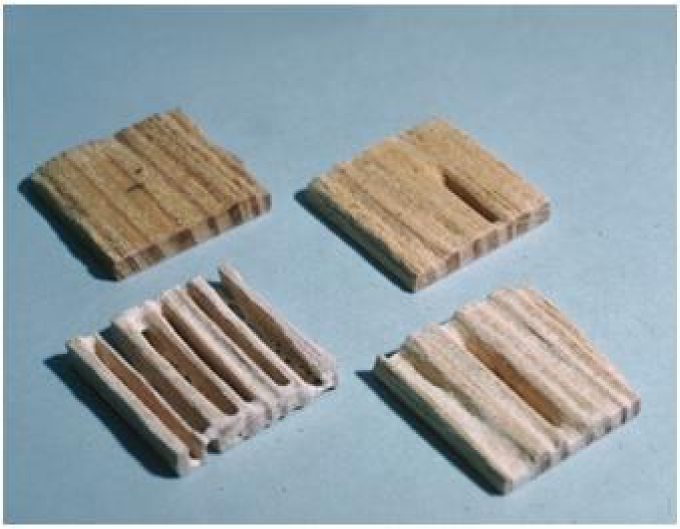

Figure 10. Termite attack on wood (upper left=acetylated to 22 WPG, upper right=acetylated to 12 WPG, lower right=acetylated to 5 WPG, lower left=control).

Figure 10 shows results of a lab termite test after 2 weeks. The termites attacked the lower density spring wood in the control samples with a 30% loss in weight. As the level of acetyl weight gain increase, the termite attack was less until at 22% gain, there was no termite attack.

Additional tests were conducted using with dry wood and subterranean termites. The two different woods were placed in test using dry wood termites (*Cryptotermes cynocephalus*). Fifty healthy and active nymphae placed in each box and the boxes were put in a dark room at an average temperature of 20 to 32°C and 81 to 89 % relative humidity (RH) for 10 weeks. At the end of the test nymphae mortality and wood weight loss were determined (Table 14).

Table 14. Acetylated pine and jabon exposed to *Cryptotermes cynocephalus*.

Wood Species	Modification	Weight Loss (%)	Mortality (%)
Indonesian pine	Control	9.3	42
	Acetylated	1.9	99
Indonesian jabon	Control	16.5	31
	Acetylated	1.9	95

The two different woods (19 mm x 19 mm x 10 mm) were placed in test using subterranean termites *Coptotermes gestroi.* (Table 15). Each wood specimen was put in an acrylic cylindrical tube (sized 60 mm height and 80 mm diameter), and to each tube was put 150 workers and 15 soldiers of nymphae. A wet tissue was placed in each tube to maintain humidity. The tubes were put in a dark room at an average temperature of 20 to 32 °C and 81 to 89 % relative humidity (RH) for 5 weeks. At the end of the test the percentage weight loss of each specimen was determined as well as nymphae mortality. The results of this test are shown below (Alexandere, 2014).

Table 15. Acetylated pine and jabon exposed to *Coptotermes gestroi*.

Wood Species	Modification	Weight Loss (%)	Mortality (%)
Indonesian pine	Control	9.9	70
	Acetylated	1.7	100
Indonesian jabon	Control	12.5	83
	Acetylated	3.5	100

4.2.5. *Termites-in-ground tests*

Termite tests were run on acetylated wood at several test sites (Rowell, 1997). The first sites were in Indonesia: Bogor and Bandung (Table 16). Rubber wood, spruce and aspen particles were acetylated to two levels of acetyl content: low 8-12 WPG and high 20 WPG and made into particleboards. The rubber wood particle board contained 9% phenolic resin with a target density of 750 kg/m^3, the spruce fiber board contained 8% phenolic resin with a target density of 750 kg/m^3 and the aspen fiber board contained 8% phenolic resin with a target density of 800 kg/m^3 (Alexandere, 2014).

From the data collected to date, the mechanism of resistance of acetylated wood to termites may be due to several factors, including: moisture content: EMC reduced below that needed for attack, increased hardness, modification of typical nutrients (such as hemicellulose acetate, lignin acetate, i.e. no recognition message), and since the actual digestion of the wood is done by bacteria living inside the termite and acetylated wood is stable to attack by microorganisms. The termite may graze but do not attack.

Table 16. Termite ratings for wood species in Indonesia.

Species	Time (months)	Bandung rating acetyl level control	Bandung rating acetyl level low	Bandung rating acetyl level high	Bogor rating acetyl level control	Bogor rating acetyl level low	Bogor rating acetyl level high
Rubber wood	1	7	7	10	0	4	10
	3	7	7	10	--	4	10
	12	0	0	10	--	0	9
	36	--	--	0	--	--	0
Spruce	1	7	9	10	7	9	10
	3	4	9	10	0	9	10
	12	4	7	10	--	9	9
	36	0	0	0	--	0	0
Aspen	1	7	7	10	4	0	7
	3	4	0	9	0	--	7
	12	0	--	4	--	--	7
	36	--	--	0	--	--	0

Termite rating criteria:
10: No attack or a few nibbles present
9: Small tunnels on surface less than 3% of cross section area affected at any location
7: Termite attack affects 10-25% of cross section area at any location
4: Termite attack affects more than 50% of cros sectional area at one
0: Failure

4.2.6. *Marine organisms*

Acetylated wood is somewhat resistant to attack by marine organisms (Table 17, Figure 11). In Florida, control specimens were destroyed in 6 months to 1 year, mainly because of attack by *Limnoria tripunctata*, while acetylated wood showed good resistance. In similar tests in Sweden, acetylated wood failed after 2 years of exposure and control specimens failed in less than 1 year. For both control and acetylated specimens in Sweden, failure was due to attack by crustaceans and mollusks (Johnson and Rowell, 1988).

Table 17. Ratings of acetylated southern pine exposed to a marine environment.

	WPG (%)	Exposure (yrs)	Mean rating due to attack by *Limnoriid* and *Teredinid* Borers (Key West, FL) 1975-1987	Mean rating due to attack by *Shaeroma terebrans* (Tarpon Springs, FL) 1984-1987
Control	0*	1	2-4	3.4
Acetylated	22	3	8	8.8

* Rating system: 10= no attack; 9=slight attack; 7=some attack; 4=heavy attack; 0=destroyed.

Figure 11. Test specimens in marine test. H 21 is acetylated to 22 WPG.

4.3. *Thermal properties*

Figure 12 and Table 18 show the results of thermogravimetric and evolved gas analysis of control and acetylated pine. The control and acetylated samples show two peaks in the thermogravimetric runs and the lower temperature peak represents the hemicellulose fraction and the higher peak represents the cellulose. Acetylated pine pyrolyze at about the same temperature and rate as controls (Rowell, 1984). The heat of combustion and rate of oxygen consumption are approximately the same for control and acetylated wood which means that the acetyl groups added have approximately the same carbon, hydrogen and oxygen content as the cell wall polymers. Acetylated wood has essentially the same thermal properties as unmodified wood.

Table 18. Thermal properties of control and acetylated pine fiber.

	WPG (%)	Temp of maximum weight loss (°C)	Heat of combustion (Kcal/g)	Rate of oxygen consumption (mm/g sec)
Control	0	335-375	2.9	0.06-0.13
Acetylated	21.1	338-375	3.1	0.08-0.14

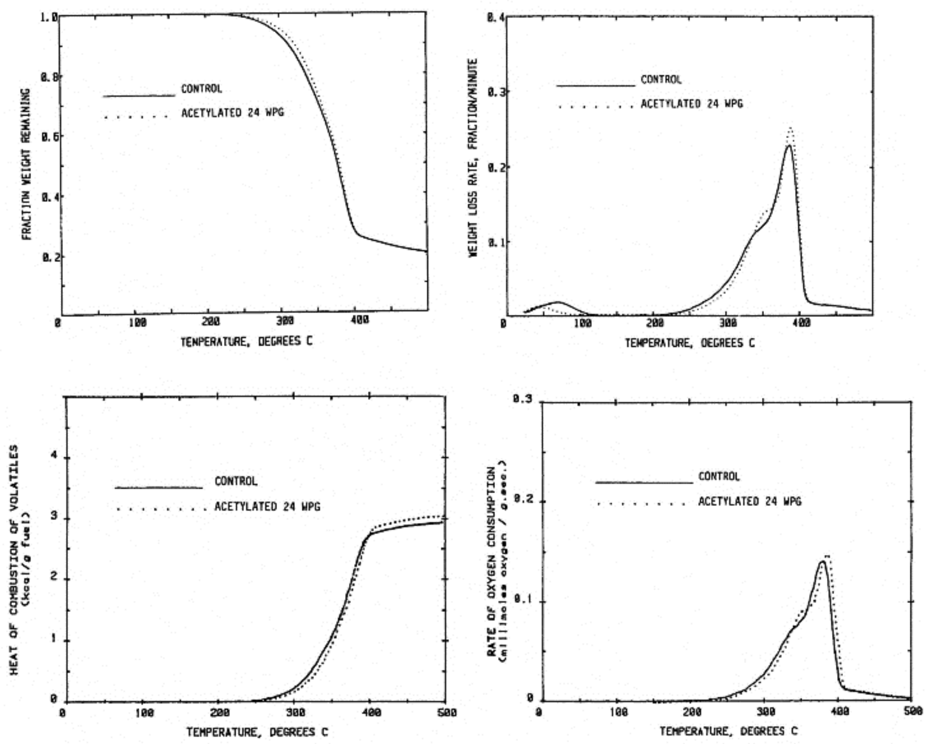

Figure 12. Thermogravimetric and evolved gas analysis of acetylated pine.

4.4. *Weathering*

Reaction of wood with acetic anhydride has also been reported to improve the ultraviolet resistance of wood (Feist, 1991). After 700 hours of accelerated weathering, controls eroded at a rate of about 0.12 µm/h or about 0.02%/h (Table 19). *Acetylation* reduced surface erosion by 50%. The depth of penetration as a result of weathering was about 200 µm for unmodified boards and half that for acetylated boards. In outdoor tests, the color of acetylated pine remained unchanged after 1 year while that of control boards turned from dark orange to light gray. After 3 years, the control wood was dark orange and parts starting to turn gray while the acetylated wood had just started turning darker. Acetylated pine exposed behind glass retained its bright color for 10 years.

Table 19. Weight loss and erosion of control and acetylated aspen after 700 hours of accelerated weathering.

	WPG	Weight loss in erosion (%/hr)	Erosion rate (μm/hr)	Reduction in rrosion (%)	Depth of weathering (μm)
Control	0	0.019	0.121	---	199-210
Acetylated	21.2	0.010	0.059	51	85-105

Table 20 shows the acetyl and lignin analysis before and after 700 hours of artificial weathering. It can be seen that the acetyl level before and after weathering in the surface and interior of the acetylated wood is about the same however the amount of lignin in the surface in both the control and acetylated samples is greatly reduced.

Table 20. Acetyl and lignin analysis before and after 700 hours of accelerated weathering of aspen fiberboards made from control and acetylated fiber.

		WPG	Before surface weathering (%)	Remainder (%)	After surface weathering (%)	Remainder (%)
Acetyl	Control	0	4.5	4.5	1.9	3.9
	Acetylated	19.7	17.5	18.5	12.8	18.3
Lignin	Control	0	19.8	20.5	1.9	17.9
	Acetylated	1.7	18.5	19.2	5.5	18.1

4.5. *Acoustical properties*

As a result of several years of experimentation on the effects of *acetylation* on the acoustical properties of wood, it can be concluded that *acetylation* of wood slightly increases density, and slightly (about 5%) reduces both sound velocity and sound absorption when compared to unreaceted wood (Akitsu et al., 1991, 1993; Yano et al., 1993). *Acetylation* does not change the acoustic converting efficiency. *Acetylation* reduces the amount of moisture in the cell wall decreasing the effect of moisture on the viscose properties of wood. This gives an instrument made from acetylated wood a greater range of moisture conditions it can be played in without losing tone quality or pitch. *Acetylation* also greatly stabilizes the physical dimensions of the wood. The major effect of *acetylation* of wood, therefore, is to stabilize its acoustic properties (Rowell, 2013).

4.6. *Mechanical properties*

Table 21 shows the strength and stiffness properties of control and acetylated pine. There is considerable loss of wet strength and wet stiffness in non-acetylated wood as compared to acetylated wood. There is a loss of over 60% in wet strength in non-acetylated wood while acetylated only drops 10%. There is a loss of over 35% in wet stiffness of non-acetylated wood while acetylated wood only loses less than 9% in wet stiffness. *Acetylation* has been shown to slightly increase the strength properties of fiberboards and flakeboards. Strength properties of wood are very dependent on the moisture content of the cell wall. The mechanical properties of fiber stress at proportional limit, work to proportional limit, and maximum crushing strength are most affected by changing moisture content by only ±1% below the fiber saturation point. The fact that the EMC and fiber saturation point of acetylated wood are much lower than that of unmodified wood alone accounts for their difference in strength properties.

Table 21. Dry and wet strength and stiffness of pine control and acetylated.

Sample	MOR Strength (N/mm^2)		MOE Stiffness (N/mm^2)	
	Dry	Wet	Dry	Wet
Pine	63.6	39.4	10,540	6,760
acetylated (19WPG)	64.4	58.0	10,602	9,690

5. Conclusions

The commercial deployment of acetylated wood, after several false starts, has finally begun in earnest. In addition to solid wood *acetylation*, Accsys Technologies has formed a joint venture with Ineos, a global chemicals company, to develop and commercialize its proprietary *acetylation* technology for the production and licensing of acetylated wood elements (under the brand name Tricoya®) for use within medium density fiberboard (MDF), particle board and wood plastic composites. The Tricoya process technology been licensed to Medite Europe Limited, a subsidiary of Ireland's state-owned Coillte group.

With the existing commercial and pilot production at Accsys' European plants and potential production of acetylated wood being actively considered in other locations, acetylated wood has moved from the sole preserve of scientists in laboratories into the maelstrom of the commercial world. No doubt there will be challenges ahead. But, as the world seeks more sustainable building materials, acetylated wood looks set to become a material of choice.

For further information on acetylated wood: see (http://www.accoya.com/acetylated-wood)

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