

WOOD WAS DESIGNED after millions of years of evolution, to perform in a wet environment, and nature is programmed to recycle it, in a timely way, back to the basic building blocks of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations. We learned to use wood, accepting that it changes dimensions with changing moisture content (MC), decomposes by a wide variety of macro- and micro-organisms, burns, and is degraded by acids, bases and ultraviolet energy. The chemistry of wood has been gradually revealed based on observations over thousands of years.



# Acetylation

BY ROGER M. ROWELL

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

The ancient Egyptians pounded dry wooden wedges into indentations chiseled in granite and water was poured (into the wood to split the giant obelisks from the side of a quarry long before we studied and understood the tremendously large swelling pressure that is exerted when wood swells. The Bible records a message to Noah to build an ark using a wood known to resist decay long before we understood how microorganisms recognized wood as a food source. Finally, the Vikings burned the outside of their ships to make them water resistant and flame retardant without knowing anything about hydrophobicity or the insulating properties of char.

Long before we had formal wood science, we had a long history of observations on the properties and performance of wood. It was well known that wood swelled and shrunk with changing MC, that wood decayed, that

wood burned, and that wood was degraded by the sun. People took advantage of the positive properties and also learned to design around wood's weaknesses. It was also well known that wood was widely available, renewable, and sustainable long before we invented these words to describe these phenomena.

As we started to understand the properties and performance of wood, we discovered that the properties of wood are, for the most part, a result of the chemistry of its cell wall components. The polysaccharides (cellulose and hemicelluloses), lignin extractives, inorganics, and the matrix they are in are mainly responsible for the properties and performance of wood. Connecting studies on the chemistry of wood with observations on performance, it became clear that it was mostly the cell wall chemistry and properties that were responsible for the observed performance.

Combining all of the art and science of wood recorded from ancient times to the present, we have discovered that if you change the chemistry of wood, you change its properties and, therefore, you change its performance. From this foundation, the science of chemical modification of wood was born. We first learn by observation, progress by experimentation, and finally advance through understanding.

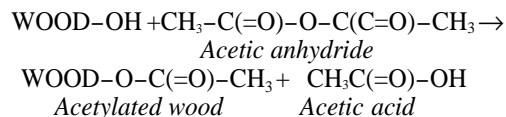
Chemical modification of wood can be defined as a process of bonding a reactive simple chemical to a reactive part of a cell wall polymer, with or without catalyst, to form a covalent bond between the two. This excludes chemical impregnations (dipping or soaking non-bonding chemicals in carrier solvents), polymer inclusions, coatings, and heat treatments.

Chemical modification of wood has historically been used to 1) isolate various cell wall components; 2) study differences in properties as a result of changing the chemistry; and 3) improve the performance properties of wood.

Many chemical reaction systems have been published for the modification of wood and the systems have been reviewed in the literature. The chemicals include anhydrides (such as acetic, butyric, phthalic, succinic, malic, propionic, and butyric anhydride), acid chlorides, ketene carboxylic acids, isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, phthalaldehydic acid, dimethyl sulfate, alkyl chlorides,  $\beta$ -propiolactone, acrylonitrile, and epoxides (such as ethylene, propylene, and butylene oxides, and difunctional epoxides).

None of the studies of the chemical modification of wood and other lignocellulosic resources have gone past the research stage, except acetylation. During the past

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 from the product as the human nose is quite sensitive to the odor 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-addition reaction, which means that one acetyl group is on one hydroxyl group with no polymerization:



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.

Acetylation has also been done using ketene gas, in this case, wall hydroxyl groups are esterified but no by-

# of Wood

## JOURNEY FROM ANALYTICAL TECHNIQUE TO COMMERCIAL REALITY

few years, many laboratories around the world have concentrated their efforts in the acetylation of biomass using liquid acetic anhydride. The successful journey of acetylation from the research stage to the commercial stage is the subject of this article.

### History and Process of Acetylation

The acetylation of wood was first performed in Germany by Fuchs (1928), using acetic anhydride and sulfuric acid as a catalyst. Fuchs found an acetyl weight gain of over 40 percent, 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) acetylated beech wood to remove hemicelluloses in a similar lignin isolation procedure. Suida and Titsch (1928) 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. Tarkow (1945) first demonstrated that acetylated balsa was resistant to decay. Tarkow (1946) first described the use of wood acetylation to stabilize wood from swelling in water. Since the 1940s, many laboratories around the world have looked at acetylation of many different types of woods and agricultural resources.

product acetic acid is formed. While this is interesting chemistry and eliminates a by-product, 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.

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  $\gamma$ -rays.

The newest acetylation technology developed at the USDA Forest Products Laboratory in the United States and Chalmers University of Technology in Sweden in the early 1980s uses 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 and 120° to 165° C for fibers and particles (Rowell et al. 1986). For solid wood, a vacuum is applied to the wood before the anhydride is introduced, the mixture heated by microwaves

and chemicals are recovered in a heated vacuum step. For flakes, particles, or fiber, no vacuum or pressure is applied and the reaction is carried out in a screw reactor and chemical recovery is done using steam. These processes are described in detail later.

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 (WPG) of about 4, there is more bonded acetyl in the S<sub>2</sub> layer than in the middle lamella. At a WPG of about 10 acetyl is equally distributed throughout the S<sub>2</sub> 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.

Questions have been raised about the long-term stability of the acetate group in wood. Table 1 shows the stability of acetyl groups in pine and aspen flakes to cyclic exposure to 30 and 90 percent 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.

**Table 1. — Stability of acetyl groups in pine and aspen flakes after cyclic exposure between 90 and 30 percent RH.<sup>a</sup>**

Acetyl content by cycle number					
Species	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

<sup>a</sup> Source: Rowell et al. 1992a, 1992b.

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 MC of the wood.

### Properties of Acetylated Wood

#### MOISTURE AND WATER SORPTION

The replacement of some hydroxyl groups on the cell wall polymers with bonded acetyl groups reduces the

**Table 2. — Fiber saturation point for acetylated pine and aspen.<sup>a</sup>**

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	--

<sup>a</sup> Source: Rowell 1991.

hygroscopicity of wood. Table 2 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. Table 3 shows the equilibrium MC (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 1 shows the sorption/desorption isotherm for acetylated and control spruce fiber (Stromdahl 2000).

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. Secondary water is water sorbed to sites with less binding energy; water molecules are sorbed on top of

**Table 3. — Equilibrium MC of acetylated pine and aspen.<sup>a</sup>**

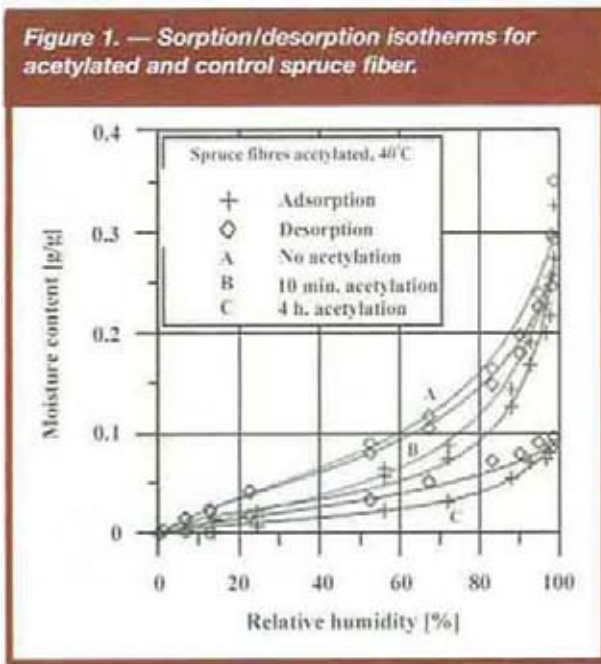
Equilibrium MC at 27°C				
Species	WPG	30% RH	65% RH	90% RH
----- (%) -----				
Pine	0	5.8	12.0	21.7
	6.0	4.1	9.2	17.5
	10.4	3.3	7.5	14.4
	14.8	2.8	6.0	11.6
	18.4	2.3	5.0	9.2
	20.4	2.4	4.3	8.4
Aspen	0	4.9	11.1	21.5
	7.3	3.2	7.8	15.0
	11.5	2.7	6.9	12.9
	14.2	2.3	5.9	11.4
	17.9	1.6	4.8	9.4

<sup>a</sup> Source: Rowell et al. 1991.



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.

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



The dimensional stability (measured as anti-shrink efficiency [ASE]) of acetylated solid pine is 78 percent at a WPG of 19.7 after a 5-day water soaking test. The rate and extent of thickness swelling in pine fiberboard (5% phenolic resin content) at the same level of acetylation is greatly reduced as a result of acetylation. At the end of 5 days of water soaking, control boards swelled 36 percent whereas boards made from acetylated fiber swelled less than 4 percent, giving an ASE of 93 percent. After drying at the end of the test, control boards exhibited a greater degree of irreversible swelling compared to boards made from acetylated fiber.

The mechanism of dimensional stability resulting from acetylation is a result of bulking of the bonded acetyl groups in the cell wall polymer hydroxyl groups. Because the volume of the cell wall is swollen to near the original green volume, little swelling can occur when water enters the wood. Acetylated wood can sorb water through capillary action and, to some extent, in the cell wall. Since the water molecule is smaller than the acetyl group, some swelling can occur in "completely acetylated wood," but swelling does not exceed the elastic limit of the cell wall.

## RESISTANCE TO BIOLOGICAL ATTACK

*Fungi* – 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*. Table 4 shows the resistance of pine acetylated to several levels

Table 4. — Resistance of acetylated pine against brown- and white-rot fungi.<sup>a</sup>

WPG	Weight loss after 12 weeks	
	Brown-rot	White-rot
	(%)	
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

<sup>a</sup> Source: Rowell et al. 1987, 1988.

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.

A dynamic bending creep test has been developed to determine strength loss when wood composites are exposed to a brown or white-rot fungus. 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* (Imamura et al. 1988, Rowell et al. 1988). At failure, weight loss averaged 7.8 percent for *T. palustris* and 31.6 percent 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 percent, 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 since the fungus did not attack the acetylated flakes, little strength was lost.

Table 5. — Fungal cellar tests of aspen flakeboards made from control and acetylated flakes.<sup>a</sup>

WPG	Rating at intervals									
	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.	12 mo.	24 mo.	36 mo.	72 mo.	144 mo.
0	S/2	S/3	S/3	S/3	S/4	--	--	--	--	--
7.3	S/0	S/1	S/1	S/2	S/3	S/4	--	--	--	--
11.5	0	0	S/0	S/1	S/2	S/3	S/4	--	--	--
13.6	0	0	0	0	S/0	S/1	S/2	S/4	--	--
16.3	0	0	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0	0	0

<sup>a</sup> Nonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria. Flakeboards bonded with 5 percent phenol-formaldehyde adhesive. Rating system: 0 = no attack; 1 = slight attack; 2 = moderate attack; 3 = heavy attack; 4 = destroyed; S = swollen. Source: Nilsson et al. 1988, Rowell et al. 1988.

In similar bending creep test, both control and acetylated pine particleboard made using melamine-urea-formaldehyde 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 glueline 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 percent; IBS of flakeboards made using an isocyanate resin was reduced 85 percent (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 percent IBS and those made using an isocyanate resin lost 64 percent 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 probably related to low moisture sorption, below that needed for biological attack. The mechanism may also be 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 MC 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.

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. Control

blocks were destroyed in less than 6 months while flakeboards made from acetylated furnish above 16 WPG showed no attack after 12 years (Table 5). These data show that no attack occurs until swelling of the wood occurs. This is additional evidence that the MC of the cell wall is critical to fungal attack.

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 et al. 2000); specimens showed little or no attack after 10 years of exposure. In Indonesia (Hadi et al. 1996), specimens failed in less than 3 years, mainly as a result ter-

Table 6. — Resistance of acetylated pine to *Reticulitermes flavipes*.<sup>a</sup>

WPG	Weight loss
----- (%) -----	
0	31
10.4	9
17.8	6
21.6	5

<sup>a</sup> Rowell et al. 1988.

Table 7. — Resistance of acetylated pine to marine organisms (teredinid borers).<sup>a</sup>

WPG	Exposure	Mean rating of attack by various organisms <sup>b</sup>	
		<i>Limnoriid</i> and <i>terebrans</i> <sup>c</sup>	<i>Shaeroma</i> <sup>d</sup>
(%)	(yr)		
0	1	2 to 4	3.4
22.0	3	8	8.8

<sup>a</sup> Source: Johnson and Rowell 1988.  
<sup>b</sup> Rating system: 10 = no attack; 9 = slight attack; 7 = some attack; 4 = heavy attack; 0 = destroyed.  
<sup>c</sup> Installed in Key West, FL.  
<sup>d</sup> Installed in Tarpon Springs, FL.



mite 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<sup>3</sup> after 15 years of exposure (Larsson-Brelid et al. 2000)

**Termites.** – Table 6 shows the results of a 2-week termite test using *Reticulitermes flavipes* (subterranean termites) on several types of chemically modified pine. The lack of complete resistance to attack may be attributed to the severity of the test. However, termites can live on

**Table 8. — Thermal properties of acetylated pine.<sup>a</sup>**

WPG	Temp. at maximum weight loss <sup>b</sup>	Heat of combustion	Rate of O <sub>2</sub> consumption
(%)	(°C)	(K cal/g)	(mm/g s)
0	335/375	2.9	0.06/0.13
21.1	338/375	3.1	0.08/0.14

<sup>a</sup> Source: Rowell et al. 1984.  
<sup>b</sup> Lower temperature peak represents hemicellulose fraction and higher peak cellulose in fiber.

acetic acid and decompose cellulose to mainly acetate. Termite survival was quite high at the end of the tests, which indicates that the modified wood was not toxic to these insects. The mechanism of effectiveness may again be the low MC of the acetylated wood and an increase in hardness.

**Marine organisms.** – Acetylated wood is somewhat resistant to attack by marine organisms (Table 7). 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 molluscs.

#### THERMAL PROPERTIES

Table 8 shows the results of thermogravimetric and

**Table 9. — Weight loss and erosion of acetylated aspen after 700 hours of accelerated weathering.<sup>a</sup>**

WPG	Weight loss	Erosion rate	Reduction in erosion	Depth of penetration
(%)	(%/h)	(µm/h)	(%)	(µm)
0	0.019	0.121	--	199 to 210
21.2	0.010	0.059	51	85 to 105

<sup>a</sup> Source: Feist et al. 1991.

evolved gas analysis of acetylated pine. Both unmodified and acetylated samples showed two peaks in the thermogravimetric analysis. The lower temperature peak represents the hemicellulose fraction and the higher peak the cellulose in the fiber. Acetylated pine fibers pyrolyze at about the same temperature and rate. The heat of combustion and rate of oxygen consumption are approximately the same for control and acetylated fibers, which means that the added acetyl groups have approximately the same carbon, hydrogen, and oxygen content as that of the cell wall polymers. Acetylated wood has essentially the same thermal properties as unmodified wood.

#### WEATHERING

Reaction of wood with acetic anhydride has also been shown to improve the ultraviolet resistance of wood. After 700 hours of accelerated weathering, controls eroded at a rate of about 0.12 µm/h or about 0.02%/h (Table 9). Acetylation reduced surface erosion by 50 percent. The depth of penetration caused by weathering was about 200 µm for unmodified boards and half that for acetylated boards. In outdoor tests, the color of acetylated pine flakeboards remained light yellow after 1 year while that of control boards turned from dark orange to light gray. Acetylated pine exposed behind glass retained its bright color for 10 years.

#### MECHANICAL PROPERTIES

Wood composites made from acetylated furnish show a slight increase in strength as a result of acetylation. Acetylation increases modulus of rupture (MOR) and modulus of elasticity (MOE) but does not change IBS (Table 10). The MOR value is above the minimum standard as given by the American Hardboard Association. Acetylation has been shown to have little effect on the strength properties of solid wood but a small increase in some strength properties resulting from acetylation of flakes, particles, and fibers.

The strength properties of wood are very dependent

**Table 10. — Mechanical properties of fiberboards made from control and acetylated pine fiber.<sup>a</sup>**

WPG	MOR	MOE	IBS
(%)	(MPa)	(GPa)	(MPa)
0	53	3.7	2.3
19.6	61	4.1	2.3
ANSI Standard	31	--	--

<sup>a</sup> Source: Youngquist et al. 1986a, 1986b. Fiberboards made with 10 percent phenolic resin. MOR = modulus of elasticity; MOE = modulus of elasticity; IBS = internal bond strength.

Figure 2. — Fiber acetylation pilot plant in Sweden.



Figure 3. — Wood going into a microwave reactor in Sweden.



on the MC 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 MC by only  $\pm 1$  percent below the fiber saturation point. The fact that the EMC and fiber saturation point of acetylated fiber are much lower than that of unmodified fiber alone accounts for their difference in strength properties.

Recent research has shown that bonded acetylated wood, when wet, retains more than 70 percent of its dry shear strength.

### Commercialization of Acetylated Wood

In spite of the vast amount of research on chemical modification of wood and specifically on acetylation of wood, commercialization has not come easily. The first patent on wood acetylation was filed by Suida in Austria in 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. In 1961, the Koppers Company published a technical bulletin on the acetylation of wood using no catalyst but an organic cosolvent. Later 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, which is still in operation today.

Many companies are currently involved in the commercialization of wood acetylation. For example, DanAcCell in Denmark and Sweden and Titan Wood in Holland. There are also commercial developments in the United States, North Wales, Malaysia, Sweden, Norway, Germany, The United Kingdom, and New Zealand.

Today, the preferred method of acetylating wood is to use a limited amount of liquid acetic anhydride without a catalyst or cosolvent. Variations of this procedure have been used to modify fibers, particles, flakes, chips, veneers, and wood of various sizes. The fact that only a limited quantity of acetic anhydride is used means that less chemical has to be heated during the reaction and less chemical has to be cleaned up after the reaction. A small amount of acetic acid seems to be needed in the reaction mixture to swell the cell wall.

Two new processes are presently underway in Denmark and Sweden to commercialize the acetylation of wood. One is a fiber process and the other is a process to acetylate wood of large dimensions using microwave technology. The fiber process uses a limited amount of anhydride and utilizes a continuous reactor phase and a steam stripper to remove unreacted anhydride and acid (Nelson et al. 1994, 1955a, 1995b, 1999 Simonson and Rowell 2000) (Fig. 2). The solid wood acetylation process is based on microwave heating of the anhydride and wood (Larsson-Brelid and Simonson 1997, 1999; Risman et al. 2001) (Fig. 3). The absorption of microwave energy in acetic anhydride impregnated wood is preferred to other methods of heating since it heats only specific parts of the wood, provides some self-regulation of the overall temperature rise, and promotes a more uniform heating pattern. Acetic anhydride is supplied to the reactor, under vacuum; pressure is



applied for a short time; and excess anhydride is removed by another vacuum step. Microwave energy is then applied to heat the anhydride-soaked wood. The penetration depth of the microwaves at 2450 MHz is approximately 10 cm, which means this technology can be used to acetylate large wood members. The variation in acetyl content, both within and between samples, is less than 2 percent. Microwave energy can also be used to remove the excess acetic anhydride and by-product acetic acid after acetylation.

One concern about the acetylation of wood, using acetic anhydride as the reagent, has been the by-product acetic acid. Many past attempts have been made for the "complete removal" of the acid to eliminate its odor. Complete removal of by-product acetic acid has now been achieved in both the fiber process and the solid wood microwave process.

### Applications and Economics of Wood Acetylation

Because of the cost of acetylating wood, acetylated wood will find applications in value-added products. Since acetylated wood has greatly improved properties as compared to unmodified wood, codes and standards will need to be developed. Consumer acceptance will require the education of architects, designers, and purchasing agents as well as the general public. General applications include transportation, sports equipment, military, and construction, where higher tolerances for stability and durability are required. In 2005, The ICC Evaluation Service drafted a document on acceptance criteria for acetylated wood preservative systems, for the use of acetylated wood in adverse environments.

The first suggested application of acetylated solid wood is for the residential decking market. For many years, the main product for residential decking was wood pressure treated with chromated copper arsenate (CCA), until it was withdrawn from the market at the end of 2003. CCA-treated wood represented 80 percent of the total market up to that point. Wood/plastic lumber has also entered the residential decking market; as of 2005, it had achieved a market share of 16 to 20 percent. Acetylated wood could compete in this market, but it would be limited by the amount of anhydride production. Projections indicate that if the entire global output of acetic anhydride were to be used to acetylate wood for residential decking, it would only represent about a 20 percent market share.

For a unit size of 5/4 by 6 inches by 8 feet, the cost of acetylated lumber compared to that of standard treated wood and plastic lumber is as follows: standard treated lumber is \$0.50 to \$0.65; plastic lumber is \$2.75 to \$5.90; and very early estimates for acetylated lumber indicate \$3.50 to \$4.50. The range of prices depends on the seller, and the price for acetylated wood is the best estimate at this time. Based on these data, acetylated wood could be cost effective for the residential decking market. In the construction sector, acetylated wood has also been considered for exterior doors and windows, for wet rooms, for use under roofs and siding composite boards, and for reusable construction plywood.

Acetylated fiber will also find applications in value-added composites and has already been used to produce experimental exterior-profiled door skins, window components, lightweight spurs equipment, automotive parts, and exterior composite furniture. It has also been studied as a component in fiber-thermoplastic composites. Up to 70 percent acetylated fiber has been used to make a conical extruded polypropylene thermoplastic composite.

The cost of acetylated fiber depends on the size of the plant: the larger the plant, the lower the fiber cost. In 1992, Sheen from British Petroleum projected that for a fiber acetylation plant that produces 10,000 tonnes/year, the cost of fiber would be US\$0.31/lb (0.454 kg), assuming a ketene step is used in the process. Under the same assumption, the DanACell company in Sweden predicts costs of US\$0.32/lb for a 8,000 tonnes/year plant, US\$0.27/lb for a 20,000 tonnes/year plant, and US\$0.20/lb for a 100,000 tonnes/year plant. All of these cost projections depend on the price of acetic anhydride, and the costs related to chemical recovery, equipment, and processes.

### Conclusions

Acetylation of wood progressed from an analytical technique to isolate cell wall polymers in the 1920s to a commercial reality in Japan in the late 1980s. It may be a commercial reality in several other countries in the near future. Its first application in North America may be acetylated solid wood for decking material, replacing CCA-treated wood.

Acetylation of wood reduces hygroscopicity and increases dimensional stability and resistance to biological attack. It has found and will continue to find value-added markets where these two properties are desired, or required. Since acetic anhydride is being produced in many places in the world, acetylation of wood fits into a global infrastructure of chemical production and recovery.

It will be interesting to see how acetylated wood will be marketed around the world. Will it be sold as a preservative treatment for wood used in the decking market? Will it be considered as a new wood species because of its higher content of naturally occurring acetyl groups? Will its increased dimensional stability and biological resistance open up new markets for wood? It will also be interesting to see how acetylated wood is accepted in the marketplace by consumers, builders, and craftsmen. Codes and standards will need to be developed as well as guarantees of service life. Acetylated wood certainly will have a high life cycle-to-benefit ratio.

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