

## Chapter 22

# Chemical Modification of Wood

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### 22.1. Introduction

After millions of years of evolution, wood was designed 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 degradation. The properties of wood are, for the most part, a result of the chemistry of its cell wall components. The polysaccharides (cellulose and hemicelluloses) are mainly responsible for (i) moisture uptake and release in changing environments that result in changes in wood volume (dimensional instability), (ii) recognition mechanism for biological degradation (attack by fungi, termites, etc.), (iii) thermal instability (pyrolysis and burning), (iv) chemical degradation (by acids and bases), and, to some degree, (v) degradation due to ultraviolet radiation (weathering, lignin degradation).

#### 22.1.1. Chemical modification of wood

If the chemistry of the wood cell wall polymers is changed, the polymer properties change as does the performance of the modified wood. The chemical modification of wood can be defined as a chemical reaction between some reactive part of wood and a simple single chemical reagent, with or without catalyst, to form a covalent bond between the two. This excludes chemical impregnations (monomer impregnations that polymerize in situ, but do not bond with the cell wall), polymer inclusions, coatings, and heat treatments.

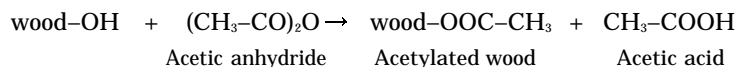
Chemical modification of wood has been used (i) to isolate various cell wall polymers, (ii) to study differences in properties as a result of changing the chemistry, and (iii) to improve the performance properties of wood.

Many chemical reaction systems have been published for the modification of wood and the systems have been reviewed in the literature [1-7]. The chemicals include anhydrides (such as acetic, butyric, phthalic, succinic, maleic, propionic, and butyric anhydride), acid chlorides, ketene carboxylic acids, isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, phthalaldehydic acid, dimethyl sulfate, alkyl chlorides, 3-propiolactone, acrylonitrile, and epoxides (such as ethylene, propylene, and butylene oxides, and difunctional epoxides).

Of all the studies of the chemical modification of wood and other lignocellulosic resources, none has gone past the research stage. During the past few years, many laboratories around the world have concentrated their efforts in this field on acetylation, using liquid acetic anhydride.

#### 22.1.2. Acetylation of 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 [8]. This by-product must be removed, as the human nose is quite sensitive to its odor. While this is easily done in the case of wood particles and fibers, 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 blocked hydroxyl groups. This is not true for a reaction where polymer chains are formed (e.g., epoxides and isocyanates). In these cases, the weight gain cannot be converted into units of blocked hydroxyl groups.

Acetylation has also been done using ketene gas [9-13]. In this case, the wall hydroxyl groups are esterified, but no by-product acetic acid is formed. While this is an interesting chemistry and eliminates a by-product, it has been shown that the reaction rate is determined by the rate of diffusion of the vapor into the wood [1]. Since the rate of diffusion into a porous solid varies inversely with the square of its thickness, the reaction of wood with ketene has been restricted to a maximum wood thickness of about 3 mm if it is to be carried out within a reasonable time length.

### 22.2. History and process of acetylation

The acetylation of wood was first performed in Germany in 1928 by Fuchs, using acetic anhydride and sulfuric acid as a catalyst [14]. Fuchs found an acetyl weight gain of over 40%, which meant that he decrystallized the cellulose in the process. He used the reaction to isolate lignin from pinewood. In the same year, Horn [15] and Suida and Titsch [16] acetylated beech wood to remove

hemicelluloses in a similar lignin isolation procedure. A year later, Suida and Titsch [17] acetylated powdered beech and pine using pyridine or dimethylaniline as a catalyst to yield an acetyl weight gain of 30% to 35% after 15 to 35 days at 100°C. In 1945, Tarkow first demonstrated that acetylated balsa was resistant to decay [10]. In 1946, Tarkow, Stamm and Erickson [18,19] 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 the acetylation of many different types of wood and agricultural resources.

Through the years, many catalysts have been tried for acetylation, both with liquid and vapor systems. These include zinc chloride [20], urea-ammonium sulfate [21], dimethylformamide [21–23], sodium acetate [18], magnesium persulfate [24–26], trifluoroacetic acid [24], boron trifluoride [22], and  $\gamma$ -rays [27].

The newest acetylation technology, developed at the Forest Products Laboratory and Chalmers University of Technology in Sweden in the early 1980s, uses a controlled and limited amount of acetic anhydride, without a catalyst or co-solvent, and a small amount of acetic acid at a reaction temperature of between 120 and 130°C for solid wood and 120 to 165°C for fibers and particles. For solid wood, vacuum is applied before the anhydride is introduced, the mixture is heated by microwaves, and the 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, the chemical recovery being done using steam. These processes are described in detail later.

The rate-controlling step in the chemical modification of solid wood is the penetration of the reagent into the cell wall [8]. 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  $S_2$  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 [8].

Questions have been raised about the long-term stability of the acetate group in wood. Table 22.1 shows the stability of acetyl groups in pine and aspen flakes to cyclic exposure to 30 and 90% relative humidity (RH) (3 months at 30% RH, followed by 3 months at 90% RH) [28,29]. Within the experimental error, no loss of acetyl occurred over 41 cycles. This experiment has been

**Table 22.1.** Stability of acetyl groups in pine and aspen flakes after cyclic exposure to 90 and 30% RH

| Cycles | Acetyl content (%) by 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 |

ongoing for more than 20 years; the results continue to show no loss of acetyl from humidity cycling.

The mass balance in the acetylation reaction shows that all the acetic anhydride consumed in 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 [30]. The consumption of acetic anhydride can be calculated stoichiometrically, based on the degree of acetylation and the moisture content of the wood. This is true for all wood acetylated to date.

The weight gain caused by acetylation and the acetyl content found by chemical analysis are shown in Table 22.2. At lower WPG levels, the acetyl content is higher, compared to the WPG values. This may be caused by the removal of extractives and some cell wall polymers into the acetic anhydride solution, resulting in an initial specimen weight loss. At WPG values higher than about 15, the acetyl content and the WPG values are almost the same.

**Table 22.2.** Weight percent gain (WPG) and acetyl analysis of pine and aspen

| Species | WPG (%) | Acetyl content (%) |
|---------|---------|--------------------|
| Pine    | 0       | 1.4                |
|         | 6.0     | 7.0                |
|         | 14.8    | 15.1               |
|         | 21.1    | 20.1               |
| Aspen   | 0       | 3.9                |
|         | 7.3     | 10.1               |
|         | 14.2    | 16.9               |
|         | 17.9    | 19.1               |

### 22.3. Properties of acetylated wood

#### 22.3.1. Moisture and water sorption

The replacement of some hydroxyl groups of the cell wall polymers by bonded acetyl groups reduces the hygroscopicity of wood. Table 22.3 shows the fiber saturation point for acetylated pine and aspen [4]. As the level of acetylation increases, the fiber saturation point decreases, in both softwood and hardwood. Table 22.4 shows the equilibrium moisture content (EMC) of control and acetylated pine and aspen at several levels of acetylation and three levels of relative humidity. In all cases, as the level of chemical weight gain increases, EMC is reduced in the reacted wood [31].

Sorption-desorption isotherms for acetylated spruce fibers are shown in Figure 22.1 [32]. The 10-min acetylation curve represents a WPG of 13.2 and

**Table 22.3.** Fiber saturation point for acetylated pine and aspen

| WPG (%) | Pine (%) | Aspen (%) |
|---------|----------|-----------|
| 0       | 45       | 46        |
| 6       | 24       | —         |
| 8.7     | —        | 29        |
| 10.4    | 16       | —         |
| 13.0    | —        | 20        |
| 17.6    | —        | 15        |
| 18.4    | 14       | —         |
| 21.1    | 10       | —         |

**Table 22.4.** Equilibrium moisture content of acetylated pine and aspen

| Species | WPG (%) | Equilibrium moisture content at 27°C |        |        |
|---------|---------|--------------------------------------|--------|--------|
|         |         | 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                                  | 7.3    | 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    |

the 4-h curve a WPG of 19.2. Untreated spruce reached an adsorption-desorption maximum at about 35% moisture content, while acetylated spruce at 19.2 WPG reached a maximum of about 10%. Moisture is presumed to be sorbed either as primary or secondary water. Primary water is the water sorbed to primary sites with high binding energy, such as the hydroxyl groups. Secondary water is the water sorbed to sites with less binding energy, i.e., the 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.

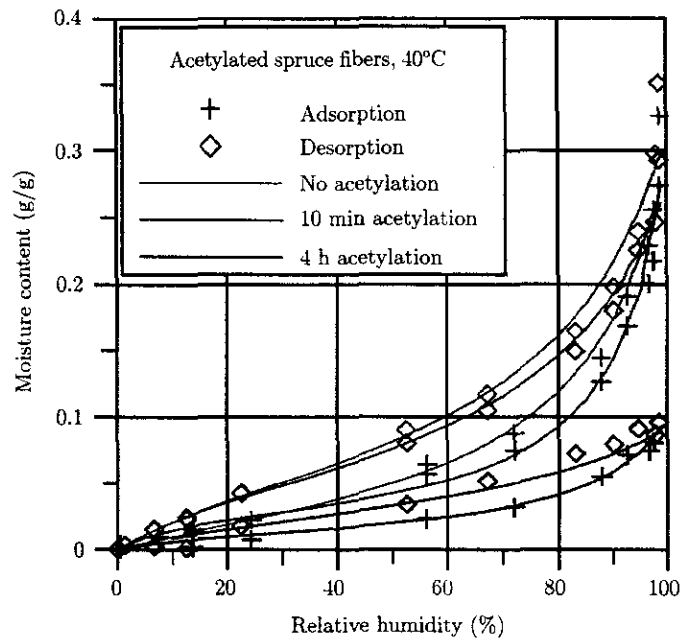


Figure 22.1. Sorption-desorption isotherms for acetylated spruce fibers [32].

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 71% 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% whereas boards made from acetylated fiber swelled less than 4%, giving an ASE of 93%. After drying at the end of the test, control boards exhibited a greater degree of irreversible swelling, compared to boards made from acetylated fiber [33].

The dimensional stability resulting from acetylation is caused by the 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.

### 22.3.2. 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 [34–40].

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 22.5 shows the resistance of pine acetylated to several levels of chemical modification to attack by brown- and white-rot fungi [35,41]. As the level of acetylation rises, the resistance to fungal attack increases.

**Table 22.5.** Resistance of acetylated pine against brown- and white-rot fungi

| 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        |

The 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, the 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 [42]. A dynamic bending creep test has been developed to determine the strength loss when wood composites are exposed to a brown- or white-rot fungus [43–45].

In a 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 *Traetes versicolor* [41,46]. At failure, the 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 [41]. 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 the mycelial development was significantly slower in control flakeboards bonded with phenol-formaldehyde. Both isocyanate- and phenol-formaldehyde-bonded acetylated flakeboards showed surface mycelium

colonization during the test. but since the fungus did not attack the acetylated flakes, little strength was lost.

In similar bending creep tests, both control and acetylated pine particle-boards made using a melamine-urea-formaldehyde adhesive failed because *T. palustris* attacked the adhesive in the glue line [46]. Mycelium invaded the inner part of all boards, colonizing in both the wood and glue line in control boards, but only in the glue line in acetylated boards. These results show that the glue line is also important in protecting composites from biological attack.

After 16-week exposure to *T. palustris*, the internal bond strength (IBS) of control aspen flakeboards made using a phenol-formaldehyde resin was reduced by more than 90%; the IBS of flakeboards made using an isocyanate resin was reduced by 85% [34]. After a 6-month exposure in moist non-sterile 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 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, it has been suggested that the reduced moisture content of acetylated wood prevents the fungus from initiating the breakdown of hemicelluloses as an energy source [47-49]. 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 1 year [41,50] (Table 22.6). These data show that no attack occurs until swelling of the wood takes place [41]. This fungal cellar test was continued for some additional 12 years, with no attack at 17.9 WPG, thus providing additional evidence that the moisture content of the cell wall is critical to fungal attack [51,52].

Acetylated solid wood and flakeboards have been subjected to in-ground tests [37,53,54] throughout the world. In the United States, Sweden, and New Zealand, specimens showed little or no attack after 10 years of exposure. In Indonesia, specimens failed in less than 3 years [53], mainly as a result of termite attack. In Sweden, acetylated pine at a WPG of 21.2 has been outperforming wood treated with chromated copper arsenate at 10.3 kg/m<sup>3</sup> after 8 years of exposure [54].

**Termites.** Table 22.7 shows the results of a 2-week termite test using *Reticulitermes flavipes* (subterranean termites) on several types of chemically

**Table 22.6.** Fungal cellar tests of aspen flakeboards made from control and acetylated flakes<sup>a,b</sup>

| WPG  | Rating at intervals (months) <sup>c</sup> |     |     |     |     |     |     |     |    |     |
|------|---|-----|-----|-----|-----|-----|-----|-----|----|-----|
|      | 2   | 3   | 4   | 5   | 6   | 12  | 24  | 36  | 72 | 144 |
| 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>Non-sterile soil containing brown-, white, and soft-rot fungi and tunneling bacteria

<sup>b</sup>Flakeboards bonded with 5% phenol-formaldehyde adhesive

<sup>c</sup>Rating system: 0 = no attack; 1 = slight attack; 2 = moderate attack; 3 = heavy attack; 4 = destroyed; S = swollen

**Table 22.7.** Resistance of acetylated pine to *Reticulitermes flavipes*

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

modified pine [41]. The lack of complete resistance to attack may be attributed to the severity of the test. However, termites can live on acetic acid and decompose cellulose to mainly acetate. The termite survival was quite high at the end of the tests, which indicates that the modified wood was not toxic to these insects.

Marine organisms. Acetylated wood is resistant to attack by marine organisms. In Florida, control specimens were destroyed within 6 months to 1 year, mainly because of attack by *Limnoria tripunctata*, while acetylated wood showed good resistance [55] (Table 22.8). In similar tests in Sweden, acetylated wood failed after 2 years of exposure and control specimens failed in less than 1 year [54].

**Table 22.8.** Resistance of acetylated pine to marine organisms<sup>a</sup>

| WPG (%) | Exposure (years) | Mean rating of attack by various organism <sup>b</sup> |                       |
|---------|------------------|--|-----------------------|
|         |                  | Limnoriid and terebrans <sup>c</sup>                   | Shaeroma <sup>d</sup> |
| 0       | 1                | 2–4  | 3.4                   |
| 22.0    | 3                | 8  | 8.8                   |

<sup>a</sup>Teredimid borers

<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

For both control and acetylated specimens, failure was due to attacks by crustaceans and molluscs.

### 22.3.3. Thermal properties

Table 22.9 shows the results of thermogravimetric and evolved gas analysis of acetylated pine. Both unreacted and acetylated samples showed two peaks in the thermogravimetric runs. 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 [56]. 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.

**Table 22.9.** Thermal properties of acetylated pine

| WPG<br>(%) | Temperature at<br>max weight loss <sup>a</sup><br>(°C) | Heat of<br>combustion<br>(kcal/g) | Rate of O <sub>2</sub><br>combustion<br>(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> Lower temperature peak represents hemicellulose fraction and higher peak cellulose in the fiber

### 22.3.4. Weathering

The reaction of wood with acetic anhydride has also been shown to improve the ultraviolet resistance of wood [57]. After 700 h of accelerated weathering, controls eroded at a rate of about 0.12  $\mu\text{m}/\text{h}$  or about 0.2%/h (Table 22.10). Acetylation reduced the surface erosion by 50%. The depth of penetration

**Table 22.10.** Weight loss and erosion of acetylated aspen after 700 h accelerated weathering

| WPG<br>(%) | Weight loss<br>(%/h) | Erosion rate<br>( $\mu\text{m}/\text{h}$ ) | Reduction in erosion<br>(%) | Penetration depth<br>( $\mu\text{m}$ ) |
|------------|----------------------|--|-----------------------------|--|
| 0          | 0.019                | 0.121                                      | —                           | 199-210                                |
| 21.2       | 0.010                | 0.059                                      | 51                          | 85-105                                 |

caused by weathering was about 200  $\mu\text{m}$  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 [57]. The acetylated pine retained its bright color for 10 years.

#### 22.4. Mechanical properties

Wood composites made from acetylated furnish show a slight increase in strength as a result of acetylation. Acetylation increases the modulus of rupture (MOR) and the modulus of elasticity (MOE), but does not change the internal bond strength (IBS) [58,59] (Table 22.11). The MOR value is above the minimum standard as given by the American Hardboard Association [60]. Acetylation has been shown to have little effect on the strength properties of thin flakes [61]. The slight decrease in some strength properties resulting from acetylation may be attributed to the hydrophobic nature of the acetylated furnish, which may not allow the water-soluble phenolic or isocyanate resins to penetrate the flakes.

Table 22.11. Mechanical properties of fiberboards made from control and acetylated pine fiber<sup>a</sup>

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

<sup>a</sup>Fiberboards made with 10% phenolic resin. MOR, modulus of rupture; MOE, modulus of elasticity; IBS, internal bond strength

The 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  $\pm 1\%$  below FSP [54,62]. The fact that the EMC and FSP of the acetylated fiber are much lower than those 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% of its dry shear strength [63].

#### 22.5. Commercialization of acetylated wood

Despite the vast amount of research on the chemical modification of wood and, specifically, on the acetylation of wood, commercialization has not come easily. The first patent on wood acetylation was filed by Suida in Austria in 1930 [64]. Nearly two decades later, Stamm and Tarkow [65] filed a patent on the acetylation of wood and boards using pyridine as a catalyst. In 1961, the Koppers Company [66] published a technical bulletin on the acetylation of wood using no catalysis but an organic co-solvent [67,68]. Later, Otlesnov and Nikitina [69] 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 the commercial production of acetylated wood for flooring, called alpha-wood that is still in operation today.

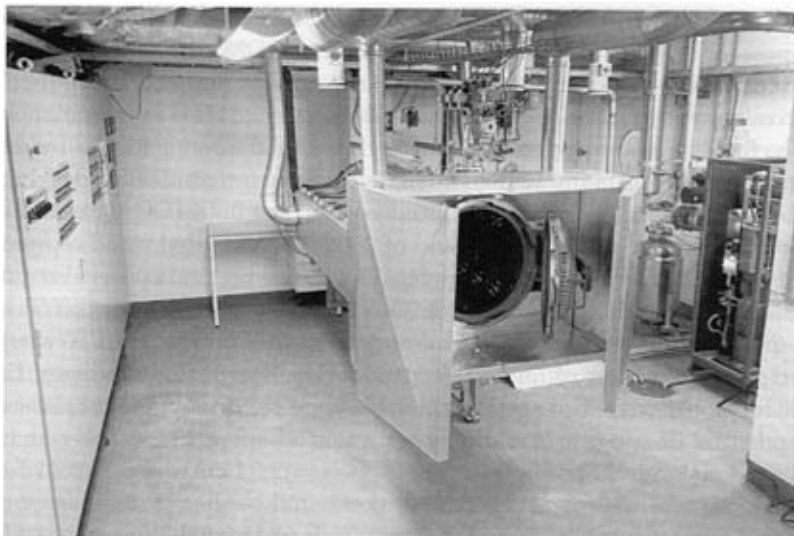
Many companies are currently involved in the commercialization of wood acetylation. Those known to the author are A-Cell in Sweden, TitanWood in Holland, and Weyerhaeuser in the United States, as well as commercial developments in North Wales, Malaysia, Sweden, Norway, Germany, The United Kingdom, and New Zealand.

Today, the preferred method of acetylating wood is to use a Limited amount of liquid acetic anhydride without a catalyst or co-solvent [70,71]. 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 under way in 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 a microwave technology. The fiber process [72-76] uses a limited amount of anhydride and utilizes a screw reactor and two stripper units to remove the anhydride and acid (Figure 22.2). The solid wood acetylation process is based on microwave heating of the anhydride



**Figure 22.2.** Fiber acetylation pilot plant in Sweden



**Figure 22.3.** Microwave reactor for solid wood in Sweden

and wood [77-79] (Figure 22.3). The absorption of the 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, then pressure is applied for a short time, and the 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 that the technology can be used to acetylate large wood members. The variation in acetyl content, both within and between samples, is less than 2%. 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 acetic acid by-product. Many past attempts have been made for the "complete removal" of the acid to eliminate its odor. A complete removal of acetic acid has not been achieved in both the fiber process and the solid wood microwave process.

#### **22.6. Applications and economics of wood acetylation**

Because of the cost of acetylation, 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 the architects, designers, and purchasing agents, as well as the general public. General applications in-

clude 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 the acceptance criteria for acetylated wood preservative systems, for the use of acetylated wood in adverse environments [80].

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% 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%. 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% market share.

For a unit size of 5/4 by 6 inches (1 inch = 2.54 cm) by 8 feet (1 foot = 30.5 cm), 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 a very early estimate for acetylated lumber is \$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 sports equipment, automotive parts, and exterior composite furniture. It has also been studied as a component in fiber-thermoplastic composites. Up to 70% 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 tons/year, the cost of fiber would be US\$0.31/lb (0.454 kg), assuming a ketene step is used in the process [81]. Under the same assumption, the DanACell company in Denmark/Sweden predicts costs of US\$0.32/lb for a 8 000 tons/year plant, US\$0.27/lb for a 20 000 tons/year plant, and US\$0.20/lb for a 100 000 tons/year plant. All of these cost projections depend on the price of acetic anhydride and the costs related to chemical recovery, equipment, and processes.

## 22.7. Conclusions

The acetylation of wood went 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 the CCA-treated wood.

Acetylation of wood reduces the hygroscopicity and increases the 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 produced in many places in the world, acetylation of wood fits into a global infrastructure of acetic anhydride production and acetate recovery.

It will be interesting to see how acetylation will be marketed around the world. Will it be sold as a preservative treatment for wood used in the decking market? Will acetylated wood 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.

### References

1. Jahn E C (1947) Chemical modified wood, *Svensk Papperst* **17**:395-401.
2. Rowell R M (1975) Chemical modification of wood: advantages and disadvantages. *Proc Am Wood Preservers' Assoc*, pp. 1-10.
3. Rowell R M (1983) Chemical modification of wood: A review, Commonwealth Forestry Bureau, Oxford, England. **6**:363-382.
4. Rowell R M (1991) Chemical modification of wood, in *Handbook on Wood and Cellulosic Materials* (Eds. Hon D N-S and Shiraishi N) Marcel Dekker, Inc., New York, Ch. 15. pp. 703-756.
5. Rowell R M (2005) Chemical modification of wood, in *Handbook of Wood Chemistry and Wood Composites* (Ed. Rowell R M) Taylor and Francis, Boca Raton, FL, Ch. 14, pp. 381-420.
6. Kumar S (1994) Chemical modification of wood. *Wood Fiber Sci* **26**:270-280.
7. Hon D N-S (1996) *Chemical Modification of Wood Materials*, Marcel Dekker, New York, 370 pp.
8. Rowell R M, Simonson R, Hess S, Plackett D V, Cronshaw D and Dunningham E (1994) Acetyl distribution in acetylated whole wood and reactivity of isolated wood cell wall components to acetic anhydride. *Wood Fiber Sci* **26**:11-18.
9. Tarkow H (1945) Acetylation of wood with ketene, USDA Forest Service, Forest Products Laboratory, Madison, WI, 2 pp.
10. Tarkow H (1945) Decay resistance of acetylated balsa, USDA Forest Service, Forest Products Laboratory, Madison, WI, 4 pp.
11. Karlson I and Svalbe K (1972) Method of acetylating wood with gaseous ketene, *Uchen Zap Latv Univ* **166**:98-104.
12. Karlson I and Svalbe K (1977) Method of acetylating wood with gaseous ketene, *Latv Lauksiamn Akad Raksti* **130**:10-21.
13. Rowell R M, Wang R H S and Hyatt J A (1986) Flakeboards made from aspen and southern pine wood flakes reacted with gaseous ketene, *J Wood Chem Tech* **6**:449-471.

14. Fuchs W (1928) Genuine lignin. I. Acetylation of pine wood, *Ber* **61B**:948-951.
15. Horn O (1928) Acetylation of beech wood, *Ber* **61B**:2542-2545.
16. Suida H and Titsch H (1928) Chemistry of beech wood Acetylation of beech wood and cleavage of the acetyl-beech wood, *Ber* **61B**:1599-1604.
17. Suida H and Titsch H (1929) Acetylated wood: The combination of the incrustation and a method of separation of the constituents of wood: *Monatsh* **53/54**:687-706.
18. Tarkow H (1946) A new approach to the acetylation of wood. USDA Forest Service. Forest Products Laboratory, Madison, WI, 9 pp.
19. Tarkow H, Stamm A J and Erickson E C O (1946) Acetylated wood. Rep. 1593, USDA Forest Service: Forest Products Laboratory, Madison, WI, 29 pp.
20. Ridgway W B and Wallington H T (1946) Esterification of wood, *Brit Patent* 579,255.
21. Clermont L P and Bender F (1957) Effect of swelling agents and catalysts on acetylation of wood, *Forest Prod J* **7**:167-170.
22. Risi J and Arseneau D F (1957) Dimensional stabilization of wood. I. Acetylation, *Forest Prod J* **7**:210-213.
23. Baird B R (1969) Dimensional stabilization of wood by vapor phase chemical treatments, *Wood and Fiber* **1**:54-63.
21. Arni P C, Gray J D and Scougall R K (1961) Chemical modification of wood. II. Use of trifluoroacetic acid as catalyst for the acetylation of wood. *J Appl Chem* **11**:163-170.
25. Ozolina I and Svalbe K (1972) Acetylation of wood by an anhydrone catalyst, *Latvijas Lauksaimniecibas Akademijas Raksti* **65**:47-50.
26. Truksne D and Svalbe K (1977) Water-repellent properties and dimensional stability of acetylated pine wood in relation to the degree and method of acetylation. *Latvijas Lauksaimniecibas Akademijas Raksti* **130**:26-31.
27. Svalbe K and Ozolina I (1970) Modification of wood by acetylation. *Plast Modif Drev* 145-146.
28. Rowell R M, Lichtenberg R S and Larsson P (1992) Stability of acetyl groups in acetylated wood to change in pH, temperature, and moisture, *Forest Res Inst Bull* (Eds. Plackett D V and Dunningham E A) Rotorua, New Zealand, **176**:33-40.
29. Rowell R M, Lichtenberg R S and Larsson P (1992) Stability of acetylated wood to environmental changes. *Wood Fiber Sci* **25**:359-364.
30. Rowell R M, Simonson R and Tillman A-M (1990) Acetyl balance for the acetylation of wood particles by a simplified procedure, *Holzforschung* **44**:263-269.
31. Rowell R M and Rowell J S (1989) Moisture sorption of various types of acetylated wood fibers. in *Cellulose and Wood* (Ed. Schuerch C) John Wiley and Sons, New York, pp. 343-356.
32. Stromdahl K (2000) Water sorption in wood and plant fibers, PhD Thesis, Department of Structural Engineering and Materials. Technical University of Denmark, Copenhagen.
33. Rowell R M, Youngquist J A, Rowell J S and Hyatt J A (1991) Dimensional stability of aspen fiberboards made from acetylated fiber, *Wood Fiber Sci* **23**:558-566.
34. Imamura Y, Nishimoto K and Rowell R M (1987) Internal bond strength of acetylated flakeboard exposed to decay hazard, *Mokuzai Gakkaishi* **33**:986-991.
35. Rowell R M, Esenther G R, Nicholas, D D and Nilsson T (1987) Biological resistance of southern pine and aspen flakeboards made from acetylated flakes. *J Wood Chem Tech* **7**:427-440.
36. Rowell R M, Imamura Y, Kawai S and Norimoto M (1989) Dimensional stability, decay resistance and mechanical properties of veneer-faced low-density particleboards made from acetylated wood. *Wood Fiber Sci* **21**:67-79.

37. Rowell R M, Dawson B S, Hadi Y S, Nicholas D D, Nilsson T, Plackett D V, Simonson R and Westin M (1997) Worldwide in-ground stake test of acetylated composite boards, IRGWP Section 4, Doc. no. IRG/WP 97-40088, Stockholm, Sweden, pp. 1-7.
38. Militz H (1991) Improvements of stability and durability of beechwood (*Fagus sylvatica*) by means of treatment with acetic anhydride. Proc 22<sup>nd</sup> Ann Meet IRGWP, Doc. no: WP 3645, Kyoto, Japan.
39. Beckers E P J, Militz H and Stevens M (1994) Resistance of acetylated wood to basidiomycetes, soft rot and blue stain, Proc IRGWP 25<sup>th</sup> Ann Meet, Bali, Indonesia, Doc. no: WP 94-40021.
40. Wang C-L, Lin T-S and Li M-H (2002) Decay and termite resistance of planted tree sapwood modified by acetylation, Taiwan J Forest Sci **17**:483-490.
41. Rowell R M, Youngquist J A and Imamura Y (1988) Strength tests on acetylated flakeboards exposed to a brown rot fungus, Wood Fiber Sci **20**:266-271.
42. Cowling E B (1961) Comparative biochemistry of the decay of sweetgum sapwood by white-rot and brown-rot fungus, Tech Bull 1258, USDA Forest Service, Washington, DC.
43. Imamura Y and Nishimoto K (1985) Bending creep test of wood-based materials under fungal attack, J Soc Mater Sci **34**:985-989.
44. Norimoto M, Grill J, Minato K, Okamura K, Mukudai J and Rowell R M (1987) Suppression of creep of wood under humidity change through chemical modification, Wood Industry (Japan) **42**:14-18.
45. Norimoto M, Grill J and Rowell R M (1992) Rheological properties of chemically modified wood Relationship between dimensional stability and creep stability, Wood Fiber Sci **24**:25-35.
46. Imamura Y, Rowell R M, Simonson R and Tillman A-M (1988) Bending-creep tests on acetylated pine and birch particleboards during white- and brown-rot fungal attack, Paperi ja Puu **9**:816-820.
47. Winandy J E and Rowell R M (1984) The chemistry of wood strength, in ACS Advances in Chemistry Series No. 207 (Ed. Rowell R M) Washington, DC. Ch. 4, pp. 211-255.
48. Winandy J E and Rowell R M (2005) Chemistry of wood strength, in Handbook of Wood Chemistry and Wood Composites (Ed. Rowell R M) Taylor and Francis, Boca Raton, FL, Ch. 11, pp. 303-348.
49. Nilsson T (1986) Personal communication.
50. Nilsson T, Rowell R M, Simonson R and Tillman A-M (1988) Fungal resistance of pine particle boards made from various types of acetylated chips, Holzforschung **42**:123-126.
51. Ibach R E and Rowell R M (2000) Improvements in decay resistance based on moisture exclusion, Mol Cryst Liq Cryst **353**:23-33.
52. Ibach R E, Rowell R M and Lee B-G (2000) Decay protection based on moisture exclusion resulting from chemical modification of wood. Proc 5<sup>th</sup> Pacific Rim Bio-Based Composites Symp, Canberra, Australia, pp. 197-204.
53. Hadi Y S, Rowell R M, Nilsson T, Plackett D V, Simonson R, Dawson B and Qi Z-J (1996) In-ground testing of three acetylated wood composites in Indonesia. Proc 3<sup>rd</sup> Pacific Rim Bio-Based Composites Symp, Kyoto, Japan.
54. Larsson-Brelid P, Simonson R, Bergman O and Nilsson T (2000) Resistance of acetylated wood to biological degradation. Holz als Roh- und Werkstoff **58**:331-337.
55. Johnson B R and Rowell R M (1988) Resistance of chemically-modified wood to marine borers, Mat u Organism **23**:147-156.

56. Rowell R M, Susott R A, De Groot W G and Shafizadeh F (1984) Bonding fire retardants to wood. Part I, *Wood Fiber Sci* **16**:214–223.
57. Feist W C, Rowell R M and Youngquist J A (1991) Weathering and finish performance of acetylated aspen fiberboard, *Wood Fiber Sci* **23**:260–272.
58. Youngquist J A, Rowell R M and Krzysik A (1986) Mechanical properties and dimensional stability of acetylated aspen flakeboards. *Holz als Roh- und Werkstoff* **44**:453–457.
59. Youngquist J A, Rowell R M and Krzysik A (1986) Dimensional stability of acetylated aspen flakeboard, *Wood Fiber Sci* **18**:90–98.
60. ANSI (1982) Basic hardboard. ANSI/AHA 135.4 (reaffirmed Jan, 1988), American Hardboard Association, Palatine, IL.
61. Rowell R M and Banks W B (1987) Tensile strength and work to failure of acetylated pine and lime flakes. *Brit Polym J* **19**:479–482.
62. FPL (1999) Wood Handbook. Agr. Handbk 72. Gen. Tech. Rpt. FPL-GTR-113, USDA Forest Service, Forest Products Laboratory, Madison, WI.
63. Frihart C R and Brandon R (2005) Personal communication.
64. Suida H (1930) Acetylating wood. Austrian Patent 122,499.
65. Stamm A J and Tarkow H (1947) Acetylation of wood and boards. US Patent 2,417,995.
66. Koppers' Acetylated Wood (1961) Dimensionally stabilized wood. New Materials Tech Info No. (RDW-400) E-106, 23 pp.
67. Goldstein I S, Jeroski E B, Lund A E, Nielson J F and Weater J M (1961) Acetylation of wood in lumber thickness, *Forest Prod J* **11**:363–370.
68. Dreher W A, Goldstein I S and Cramer G R (1964) Mechanical properties of acetylated wood, *Forest Prod J* **14**:66–68.
69. Otlesnow Y and Nikitina N (1977) Trial operation of a commercial installation for modification of wood by acetylation, *Latvijas Lauksaimniecibas Akademijas Raksti* 13050-53.
70. Rowell R M, Simonson R and Tillman A-M (1986) A simplified procedure for the acetylation of chips for dimensionally stable particle board products, *Paperi ja Puu* **68**:740-744.
71. Rowell R M, Tillman A-M and Simonson R (1986) A simplified procedure for the acetylation of hardwood and softwood flakes for flakeboard production. *J Wood Chem Tech* **6**:427-448.
72. Nelson H L, Richards D I and Simonson R (1994) Acetylation of lignocellulosic materials, Eur Patent 650,998.
73. Nelson H L, Richards D I and Simonson R (1995) Acetylation of lignocellulosic materials, Eur Patent 746,570.
74. Nelson H L, Richards D I and Simonson R (1995) Acetylation of lignocellulosic fibers, Eur Patent 799,272.
75. Nelson H L, Richards D I and Simonson R (1999) Acetylation of wood materials, Eur Patent EP 0 650 998 B1.
76. Simonson R and Rowell R M (2000) A new process for the continuous acetylation of wood fiber. Proc 5<sup>th</sup> Pacific Rim Bio-Based Composite Symp (Ed. Evans P D) Canberra, Australia, pp. 190-196.
77. Larsson-Brelid P and Simonson R (1997) Chemical modification of wood using microwave technology, Proc 4<sup>th</sup> Int Conf Frontiers of Polymers and Advanced Materials. Cairo, Egypt.
78. Larsson-Brelid P and Simonson R (1999) Acetylation of solid wood using microwave beating. Part II: Experiments in laboratory scale. *Holz als Roh- und Werkstoff* **57**:383–389.

79. Risman P O, Simonson R and Larsson-Brelid P (2001) Microwave system for heating voluminous elongated loads, Swedish Patent 521,315.
80. ICC Evaluation Service, Inc. (2005) Acceptance criteria for acetylated wood preservative systems, AC 297, 8 pp.
81. Sheen A D (1992) The preparation of acetylated wood fibre on a commercial scale. Chemical modification of lignocellulosics, FRI Bull **176**:1-8. 1<sup>st</sup> Pacific Rim Bio-Based Composite Symp, Rotorua, New Zealand.

Stoyko Fakirov  
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Handbook of

# Engineering Biopolymers

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