

Chemical Modification

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Introduction

Wood is a hygroscopic resource that was designed to perform, in nature, in a wet environment. Nature is programmed to recycle wood in a timely way through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations. In simple terms, nature builds wood from carbon dioxide and water and has all the tools to recycle it back to the starting chemicals. We harvest a green tree and convert it into dry products, and nature, with its arsenal of degrading reactions, starts to reclaim it at its first opportunity.

The properties of any resource are, in general, a result of the chemistry of the components of that resource. In the case of wood, the cell wall polymers (cellulose, hemicelluloses, and lignin) are the components that, if modified, would change the properties of the resource. If the properties of wood are modified, the performance of wood will be changed. This is the basis of chemical modification of wood to change properties and improve performance.

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, noncrystalline cellulose, lignin, and the 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. The swelling pressures exerted when wood swells due to the uptake of water are very large. Stamm estimated these forces to be approximately 24 000 psi (165 MPa) but could only measure a swelling force of 12 000 psi (82.7 MPa). The ancient Egyptians split their large granite stones using the swelling forces of wood. They would chip rectangular holes (approximately 7×15 cm and 10 cm deep) into the rock the desired distance from the face of the mountain. They would then drive dry wooden stakes into the holes and wet them with water. The swelling forces would then split the granite stone from the face of the mountain.

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 undergo 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 reactions with increasing temperature to give off volatile, flammable gases. The hemicellulose 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 material from further thermal degradation.

This article discusses the concept of chemically modifying wood and then briefly reviews three types of treatments, monomer–polymer treatments, surface impregnation, and heat treatment for accomplishing chemical modification. The subject of cell wall bonded chemical modification is covered in more detail because of the large amount of interest in this subject. Typical uses for each of these modification technologies are also covered.

Chemical Modification

The term ‘chemical modification’ has been used to mean different things by different authors over the years. Here chemical modification will be defined as a chemical reaction between some reactive part of a lignocellulosic cell wall polymer and a simple single chemical reagent, with or without catalyst, to form a covalent bond between the two. This excludes chemical impregnation treatments (such as simple dip or pressure treatments with wood preservatives or fire retardants, or stains or penetrating oils), which do not form covalent bonds, monomer impregnation that polymerize *in situ* but do not bond with the cell wall, polymer inclusions, coatings (such as paints, varnishes, urethanes), or heat treatments. Wood finishes, preservatives, and adhesives are covered elsewhere (see Solid Wood Processing: Adhesion and Adhesives; Finishing; Protection of Wood against Biodeterioration). Other treatments that modify wood properties without bonding in the cell wall are described briefly. Many wood-based composites can be easily chemically modified (see Solid Wood Products: Wood-based Composites and Panel Products).

Monomer–Polymer Treatments

The objective of the monomer–polymer treatments is to produce a product with greatly enhanced physical properties. A monomer, such as an acrylic derivative dissolved in a suitable solvent, is impregnated into wood using a vacuum–pressure cycle. In most systems used today, the treating solution contains both a crosslinking agent and a catalyst. After treating with this solution, the treated wood is heated to a temperature where the catalyst becomes active and polymerization, *in situ*, takes place. In most cases, the polymer is located in the cell lumen but in cases (such as phenol–formaldehyde systems) where cell wall penetration takes place by the monomer, some of

the polymer may reside in the cell wall. The final wood polymer composite (WPC) is much harder than the untreated wood and is mainly used as flooring where heavy wear is anticipated. A fire retardant can also be incorporated into the treating solution mixture to add fire retardance to the product as long as the fire retardant chemicals do not interfere with the polymerization.

Surface Impregnation

In the case of surface impregnation technology, this involves the treatment of wood with polymers that are too large to penetrate very far into the wood structure. This type of treatment is mainly done with epoxy resins that increase surface hardness and can also act as an adhesive. This technology is being used to make cold-molded boat hulls and in the preservation of degraded historical wooden objects. The object is treated with a diluted solution of the polymer (or in some cases, with an undiluted liquid polymer directly) where some surface penetration occurs.

Heat Treatment

In the heat treatments, the objective is to heat the wood to increase dimensional stability and moisture resistance. The mechanisms of the increased dimensional stability and reduced hygroscopicity achieved from high temperature treatment of wood may be a combination of one or more factors. These include:

1. Degradation of the hygroscopic hemicelluloses to form soluble sugars which may undergo reversion reactions to form less hygroscopic, highly branched polysaccharides.
2. Degradation of the hemicelluloses to form free sugars which, in turn, form furan intermediates that can undergo polymerization during hot-pressing resulting in the formation of an adhesive.
3. Thermal softening of the cell wall matrix, mainly lignin, to allow reformation of a new less stressed matrix after pressing.
4. Degradation of the hygroscopic hemicelluloses to form volatile break down products that are lost during hot-pressing.
5. Crosslinking between carbohydrate polymers and/or between lignin and carbohydrate polymers.
6. Densification of the wood resulting in a reduction of pore size and void volume which restricts the flow of moisture back into the pressed wood.
7. High temperature compression to increase cellulose crystallinity.

The temperature of treatment and the presence of oxygen are critical as heating at too high a

temperature can cause great strength losses especially in the presence of oxygen. This technology is now being applied for both solid wood and wood composites. Heating wood fiber in a closed heated press, for example, at 200°C for 8 min, results in a fiberboard with an 80% reduction in dimensional instability.

Cell Wall Bonded Chemical Modification

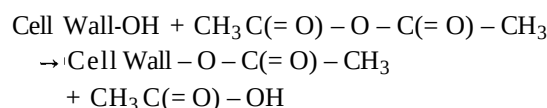
For cell wall bonded chemical modification the chemicals to be used must be capable of reacting with wood cell wall hydroxyls under neutral, mildly alkaline or acid conditions at temperatures below 170°C. The chemical system should be simple and capable of swelling the structure to facilitate penetration. The complete molecule should react quickly with wood components yielding stable chemical bonds, and the treated wood must still possess the desirable properties of untreated wood. Many chemical reaction systems have been published for the modification of various agrofibers and these systems have been reviewed in the literature several times in the past. These chemicals include anhydrides such as phthalic, succinic, malaic, propionic and butyric anhydride, acid chlorides, ketene carboxylic acids, many different types of isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, phthalaldehydic acid, dimethyl sulfate, alkyl chlorides, β -propiolactone, acrylonitrile, epoxides, such as, ethylene, propylene, and butylene oxide, and difunctional epoxides (see Table 1).

Acetylation Chemistry

While there has been much research on many different chemical reaction systems, the most research and interest, both in the past and the present,

has been in the reaction of acetic anhydride with cell wall polymer hydroxyl groups to give an acetylated wood. The acetylation process has been applied to solid wood, veneers, and many different types of wood composites. For this reason, the acetylation of wood using new acetylation technology is reviewed in detail here. Application of this technology has mainly been considered for improving both dimensional stability and decay resistance.

The reaction of acetic anhydride with cell wall polymer hydroxyl groups is shown below. The anhydride reacts to form an ester with the wood hydroxyl group and the remainder of the molecule results in byproduct acetic acid.



Properties of Acetylated Solid Wood

As the level of acetyl weight gain increases, the equilibrium moisture content (EMC) and FSP of control and acetylated pine and aspen goes down and the dimensional stability, as measured by antishrink efficiency (ASE), as calculated below, goes up.

$$S = \frac{V_2 - V_1}{V_1}$$

where S is volumetric swelling coefficient, V_1 is wood volume after wetting with liquid water, and V_2 is wood volume of oven-dried wood before wetting.

Then:

$$\text{ASE} = \frac{S_2 - S_1}{S_1} \times 100$$

where ASE is antishrink efficiency resulting from a chemical modification, S_2 is reacted wood volumetric

Table 1 Dimensional stability and resistance to decay with a brown-rot and white-rot fungi achieved by various chemical reaction systems on pine wood

Chemical	Weight percent gain (WPG) (%)	Antishrink efficiency (ASE) (V)	Weight loss after 72 weeks fungal test	
			Brown-rot ^a	White-rot ^b
None	0	—	57.8	39.6
Methyl isocyanate	25	65	1.7	1.0
Butyl isocyanate	25	70	>3	>1
Acetic anhydride	20	75	>2	>1
Propylene oxide	28	65	32.8	4.8
Butylene oxide	25	70	2.0	1.8
Acrylonitrile	25	50	—	—
β -Propiolactone	30	60	—	—
Formaldehyde	10	a5	>3	>2

^aBrown-rot fungus: *Gloeophyllum trabeum*

^bWhite-rot fungus: *Trametes versicolor*.

swelling coefficient, and S_1 is unreacted wood volumetric swelling coefficient.

Solid acetylated wood has been tested for resistance to several different types of organisms. In a 2-week termite test using subterranean termites (*Reticulitermes flavipes*), boards acetylated at 16 to 17 weight percent gain (WPG) were very resistant to attack, but not completely so. Control and acetylated pine were exposed to a 12-week soil block test using the brown-rot fungus *Gloeophyllum trabeum* and the white-rot fungus *Trametes versicolor*. All of the acetylated boards at a WPG over about 17 show good resistance to brown- and white-rot fungi.

Acetylated Composites

Wood veneers, chips, particles, and fibers can also be acetylated using the same chemistry. These acetylated materials can be formed into plywood, chipboard, particleboard, or fiberboard. Fibers, for example, can be formed into flexible fiber mats, which can be made by physical entanglement (carding), nonwoven needling, or thermoplastic fiber melt matrix technologies. In carding, the fibers are combed, mixed, and physically entangled into a felted mat. These are usually of high density but can be made at almost any density. A needle-punched mat is produced in a machine, which passes a randomly formed machine-made web through a needle board that produces a mat in which the fibers are mechanically entangled. The density of this type of mat can be controlled by the amount of fiber going through the needle board or by overlapping needled mats to give the desired density. In the thermoplastic fiber matrix, agricultural fibers can be held in the mat using a thermally softened thermoplastic fiber such as polypropylene or polyethylene.

These acetylated mats can then be used as geotextiles, oil sorbents, or filters, or can have an adhesive added and be formed into molded products. If a thermosetting resin is used, the composites can be used for structural applications. If the acetylated fiber is mixed with a thermoplastic, then the composites can be thermomolded into a large variety of shapes for nonstructural applications. Composites made from acetylated fiber have many of the same properties of solid wood, i.e., increased dimensional stability and improved biological resistance.

Thickness swelling and linear expansion at various levels of relative humidity are greatly reduced as a result of acetylation. Increasing the adhesive content can reduce the thickness swelling but not to the extent that acetylation does.

Biological resistance has also been demonstrated with acetylated composites using brown-, white-, and soft-rot fungi and tunneling bacteria in a fungal cellar. Nonacetylated (i.e., control) flakeboards were

Table 2 Modulus of rupture (MOR), modulus of elasticity (MOE), and internal bond strength (IBS) of fiberboards made from control and acetylated pine fiber (10%, phenolic resin)

Weight percent gain	MOR (MPa)	MOE (GPa)	IBS (MPa)
0	53	3.7	2.3
19.6	61	4.1	2.3
ANSI standard	31	—	—

Data from Simonson R and Rowell RM (2000) A new process for the continuous acetylation of lignocellulosic fiber. In: Evans PD (ed.) *Proceedings of the Fifth Pacific Rim Bio-Based Composite Symposium*, pp. 190–196. Canberra, Australia.

destroyed in less than 6 months while flakeboards made from acetylated flakes above 16 WPG showed no attack after 1 year. These data show that no attack occurs until swelling of the wood occurs. This is evidence that moisture content of the cell wall is critical before attack can take place. This fungal cellar test was continued for an additional 5 years with no attack at 17.9 WPG.

Table 2 shows data on strength properties of fiberboards made from both control and acetylated fiber. The board made from acetylated fiber has a higher modulus of rupture (MOR), modulus of elasticity (MOE), and equal internal bond strength (IBS) as compared to control boards.

Commercialization of Acetylated Wood Materials

In spite of the vast amount of research on the acetylation of both solid wood and wood composites, commercialization has been slow in coming. Two attempts, one in the USA and one in Russia, came close to commercialization but were discontinued presumably because they were not cost-effective. There are reports of a commercial acetylation plant for solid wood in Japan and a pilot plant for solid wood in the Netherlands but few details are available.

Two new processes are presently under way in Sweden to commercialize the acetylation of wood. One is a fiber process and the second a process to acetylate wood of large dimensions using microwave technology.

The Fiber Process

There is a pilot plant in Sweden with a capacity of approximately 4000 tonnes year⁻¹ of acetylated fiber. **Figure 1** shows the schematic of the new continuous fiber acetylation process. The fiber is first dried in an optional dryer section to reduce the moisture content to as low a moisture content as is economically feasible realizing that the anhydride will react with water to form acetic acid and that a certain amount of acetic acid is needed to swell the fiber wall for chemical access.

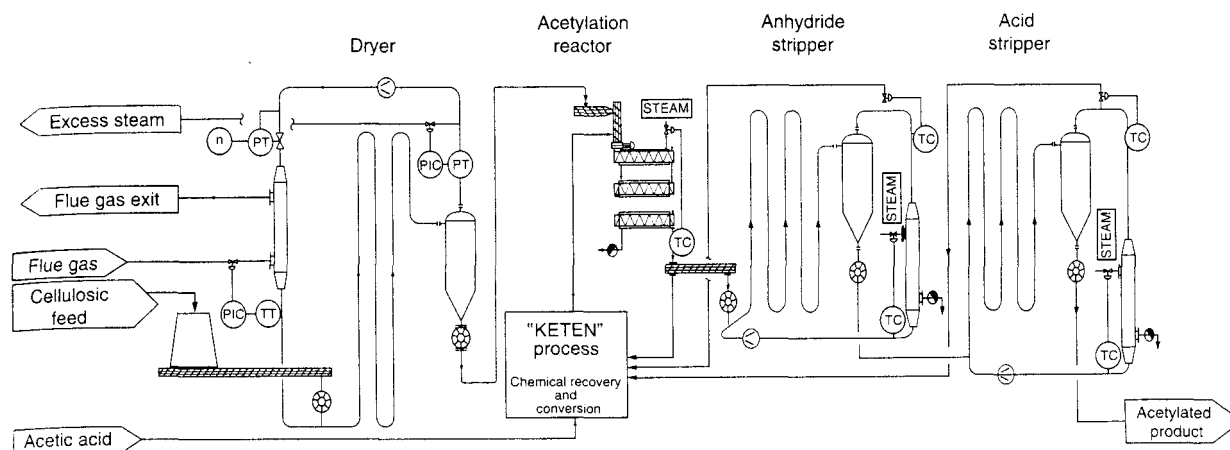


Figure 1 Schematic of the new fiber acetylation process. Reproduced with permission from Simonson R and Rowell RM (2000) A new process for the continuous acetylation of lignocellulosic fiber. In: Evans PD (ed.) *Proceedings of the Fifth Pacific Rim Bio-Based Composite Symposium*, pp. 190–196. Canberra, Australia

The dried fiber is then introduced, by a screw feeder, into the reactor section and the acetylating agent is added. The temperature in this section is within the range of 110–140°C so the acetylating agent is in the form of a vapor/liquid mixture. Back flow of the acetylating agent is prevented by a fiber plug formed in the screw feeder. A screw-conveyor or similar device is used to move the material through the reactor and to mix the fiber–reagent mixture. During the acetylation reaction, which is exothermic, the reaction temperature can be maintained substantially constant by several conventional methods. The contact time in the reactor section is 6–30 min. The bulk of the acetylation reaction takes place in this first reactor.

The resultant acetylated fiber from the first reactor contains excess acetylating agent and forms acetic acid as it is fed by a star feeder into the second reactor, designed as a long tube and working as an anhydride stripper. The fiber is transported through the stripper by a stream of superheated vapor of anhydride and acetic acid. The temperature in the stripper is preferably in the range of 185–195°C. The primary function of this second step is to reduce the content of the unreacted acetylating medium remaining in the fiber emerging from the first reactor. An additional acetylation of the fiber is, however, also achieved in this step. The residence in this step is relatively short and normally less than 1 min. After the second reactor (stripper), superheated vapor and fiber are separated in a cyclone and part of the superheated vapor is recirculated after heating to the stripper fiber inlet and part is transferred to the system for chemical recovery.

The acetylated fiber from the second reactor may still contain some anhydride and acetic acid that is sorbed or occluded in the fiber. In order to remove remaining chemicals and the odor from them, the acetylated fiber is introduced into a second stripper

step also acting as a hydrolysis step. The transporting medium in this step is superheated steam, and any remaining anhydride is rapidly hydrolyzed to acetic acid, which is evaporated. The acetylated fiber emerging from the second stripper is essentially odor-free and is completely dry. The acetylated fiber can as a final treatment be resinated for fiberboard production or conditioned and baled for other uses as desired. The steam and acetic acid removed overhead from this step is processed in the chemical recovery step.

The preferred recovery of chemicals includes separation of acetic anhydride from acetic acid by distillation, and conversion of acetic acid, recovered as well as purchased, by the ketene process into anhydride. The raw materials entering the production site is thus fiber and acetic acid to cover the acetyl groups introduced in the fiber. This minimizes the transportation costs and the chemical costs and makes the process much more cost effective.

The plant was built during the spring of 2000, taken apart, and reassembled in Kvarntorp, Sweden in the summer. The designated production rate is 500 kg h⁻¹ or 12 tonnes day⁻¹ or about 4000 tonnes-year⁻¹ of acetylated wood fiber. The process can be applied to any lignocellulosic fiber and fibers other than wood will be used.

Solid Wood Microwave Process

Microwave energy has been shown to heat acetic anhydride and acetic anhydride impregnated wood. The absorption of microwave energy in acetic anhydride impregnated wood is preferred over other methods of heating since it heats less 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 a pressure is applied for a short

time, and then another vacuum step to remove excess anhydride is used. Microwave energy is then applied to heat the anhydride soaked wood.

The penetration depth of the microwaves at 2450 MHz is approximately 10cm, 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%. Microwave energy can also be used to remove the excess acetic anhydride and by-product acetic acid after acetylation.

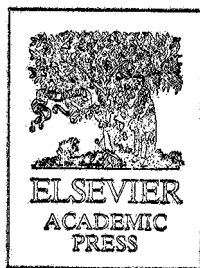
One of the concerns about the acetylation of lignocellulosics, using acetic anhydride as the reagent, has been the by-product acetic acid. Many attempts have been made for the 'complete removal' of the acid to eliminate the smell, make the process more cost effective, and to remove a chemical potentially causing ester hydrolysis. Complete removal of by-product acetic acid has now been achieved in both the fiber process and the solid wood microwave process.

See also: **Solid Wood Processing:** Adhesion and Adhesives; Finishing; Protection of Wood against Biodeterioration; Wood-based Composites and Panel Products.

Wood Formation and Properties: Chemical Properties of Wood; Formation and Structure of Wood.

Further Reading

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