14 Chemical Modification of Wood

Roger M. Rowell
USDA, Forest Service, Forest Products Laboratory,
and Department of Biological Systems Engineering,
University of Wisconsin, Madison, WI

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For the most part, humans have made the most of wood while putting up with the "natural defects" that accompany it, such as dimensional instability and degradation due to weathering, fire, and decay. Wood is a hygroscopic resource 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 the wood are modified, the performance of the modified wood would be changed. This is the basis of our chemical modification of wood—to change its properties and improve its performance. This idea is applied to both solid wood and wood composites.

In order to produce wood-based materials with a long service life, it is necessary to interfere with the natural degradation processes for as long as possible (Figure 14.1). This can be done in several ways. For example, traditional methods for decay resistance and fire retardancy treat the product with toxic or corrosive chemicals, which although are effective in providing decay and fire resistance can result in environmental concerns. In order to make property changes, you must first understand the chemistry of the components and the contributions each play in the properties of the resource. Following this understanding, you must then devise a way to modify what needs to be changed to get the desired change in property.

Properties of wood, such as dimensional instability, flammability, biodegradability, and degradation caused by acids, bases, and ultraviolet radiation, are all a result of chemical degradation reactions which can be prevented or, at least, slowed down if the cell wall chemistry is altered (Rowell 1975a, Rowell and Youngs 1981, Rowell 1983, Rowell and Konkol 1987, Rowell et al. 1988a, Hon 1992, Rowell 1992, Kumar 1994, Banks and Lawther 1994).

Biological Degradation	- Fungi, Bacteria, Insects, Termites
Enzymatic Reactions	- Oxidation, Hydrolysis, Reduction
Chemical Reactions	- Oxidation, Hydrolysis, Reduction
Mechanical	- Chewing
Fire Degradation	- Lightning, Sun
Pyrolysis Reactions	- Dehydration, Hydrolysis, Oxidation
Water Degradation	-Rain, Sea, Ice, Acid Rain, Dew
Water Interactions	- Swelling, Shrinking, Freezing, Cracking
Weather Degradation	- Ultraviolet radiation, Water, Heat, Wind
Chemical Reactions	- Oxidation, Hydrolysis
Mechanical	- Erosion
Chemical Degradation	- Acids, Bases, Salts
Chemical Reactions	- Oxidation, Reduction, Dehydration, Hydrolysis
Mechanical Degradation	- Dust, Wind, Hail, Snow, Sand
Mechanical	- Stress, Cracks, Fracture, Abrasion

FIGURE 14.1 Degradation reactions which occur when wood is exposed to nature.

BIOLOGICAL DEGRADATION
Hemicelluloses >>>> Accessible Cellulose >> Non-CrystallineCellulose >>>>>>> Crystalline Cellulose >>>>>>>>>>>>>> Lignin
MOISTURE SORPTION
Hemicelluloses >>> Accessible Cellulose >>>> Non-Crystalline Cellulose >> Lignin >>> Crystalline Cellulose
ULTRAVIOLET DEGRADATION
Lignin >>>>>>>>>>>>>>> Hemicelluloses >>> Accessible Cellulose >> Non-Crystalline Cellulose >>>>>>>> Crystalline Cellulose
THERMAL DEGRADATION
Hemicelluloses > Cellulose >>>>>>>>>>>>>>> Lignin
STRENGTH
Crystalline Cellulose >>> Matrix [Non-Crystalline Cellulose + Hemicelluloses + Lignin] >> Lignin

FIGURE 14.2 Cell wall polymers responsible for the properties of wood.

14.1 DEGRADATION OF WOOD

Figure 14.2 shows the cell wall polymers involved in each property as we understand it today (Rowell 1990). 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 (Stamm 1964, Rowell and Banks 1985) (see Chapter 4). The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, non-crystalline cellulose, lignin, and surface of crystalline cellulose also play major roles. Moisture swells the cell wall, and the fiber expands until the cell wall is saturated with water (*fiber saturation point*, or FSP). Beyond this saturation point, moisture exists as free water in the void structure and does not contribute to further expansion. This process is reversible, and the fiber shrinks as it loses moisture below the FSP.

Wood is degraded biologically because organisms recognize the carbohydrate polymers (mainly the hemicelluloses) in the cell wall and have very specific enzyme systems capable of hydrolyzing these polymers into digestible units (see Chapter 5). Biodegradation of the cell wall matrix and the high molecular weight cellulose weakens the fiber cell (Rowell et al. 1988b). Strength is lost as the cell wall polymers and its matrix undergoes degradation through oxidation, hydrolysis, and dehydration reactions.

Wood exposed outdoors undergoes photochemical degradation caused by ultraviolet radiation (see Chapter 7). This degradation takes place primarily in the lignin component, which is responsible for the characteristic color changes (Rowell 1984). The lignin acts as an adhesive in the cell walls, holding the cellulose fibers together. The surface becomes richer in cellulose content as the lignin degrades. In comparison to lignin, cellulose is much less susceptible to ultraviolet light degradation. After the lignin has been degraded, the poorly bonded carbohydrate-rich fibers erode easily from the surface, which exposes new lignin to further degradative reactions. In time, this "weathering" process causes the surface of the composite to become rough and can account for a significant loss in surface fibers.

Wood burns because the cell wall polymers undergo pyrolysis reactions with increasing temperature to give off volatile, flammable gases (see Chapter 6). The gases are ignited by some external source and combust. The hemicelluloses and cellulose polymers are degraded by heat much before the lignin (Rowell 1984). The lignin component contributes to char formation, and the charred layer helps insulate the composite from further thermal degradation.

14.2 CHEMICAL REACTION SYSTEMS

Different authors have used the term "chemical modification" to mean different things over the years. For this chapter, chemical modification will 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 all simple chemical impregnation treatments, which do not form covalent bonds, monomer impregnations that polymerize *in situ* but do not bond with the cell wall, polymer inclusions, coatings, heat treatments, etc.

There are several approaches to chemically modifying the wood cell wall polymers. The most abundant single site for reactivity in these polymers is the hydroxyl group; most reaction schemes have been based on the reaction of hydroxyl groups. Sites of unsaturation in the lignin structure can also be used as a point of reactivity, as well as free radical additions and grafting. However, the most studied class of chemical reactions are those involving hydroxyl substitutions.

In modifying wood for property improvement, one must consider several basic principles when selecting a reagent and a reaction system. Of the thousands of chemicals available, either commercially or by synthetic means, most can be eliminated because they fail to meet the requirements or properties listed below.

If hydroxyl reactivity is selected as the preferred modification site, the chemical must contain functional groups, which will react with the hydroxyl groups of the wood components. This may seem obvious, but there are several failed reaction systems in the literature using a chemical that could not react with a hydroxyl group.

The overall toxicity of the chemicals must be carefully considered. The chemicals must not be toxic or carcinogenic to humans in the finished product, and should be as nontoxic as possible in the treating stage. The chemical should be as non-corrosive as possible to eliminate the need for special stainless steel or glass-lined treating equipment.

In considering the ease with which excess reagents can be removed after treatment, a liquid treating chemical with a low boiling point is advantageous. Likewise, if the boiling point of a liquid reagent is too high, it will be very difficult to remove the chemical after treatment. It is generally true that the lowest member of a homologous series is the most reactive and will have the lowest boiling point. The boiling point range for liquids to be considered is 90–150˚C. In some cases, the lowest member of a homologous series is a gas. It is possible to treat wood with a gas system; however, there may be processing challenges in handling a pressurized gas in a continuous reactor. Gases do not penetrate deeply or quickly into the wood cell wall, so penetration of the reaction system may be limited.

Accessibility of the reagent to the reactive chemical sites is a major consideration. In some cases, this may be the rate-limiting step in a reaction system. To increase accessibility to the reaction site, the chemical should be able to swell the wood structure. If the reagents do not swell the structure, then another chemical or co-solvent can be added to aid the penetration of chemicals. Accessibility to the reactive site is a major consideration in a gas system unless there is a condensation step in the procedure.

If the chemical reaction system requires a catalyst, a strong acid or base catalyst cannot be used as they cause extensive degradation. The most favorable catalyst from the standpoint of wood degradation is a weakly alkaline one. The alkaline medium is also favored because in many cases these chemicals swell the cell wall matrix structure and give better penetration. The properties of the catalyst parallel those of reagents—low boiling point liquid, nontoxic, effective at low temperatures, etc. In most cases, the organic tertiary amines or weak organic acids are best suited.

The experimental reaction condition that must be met in order for a given reaction to go is another important consideration. If the reaction time is long, the temperature required for complete reaction must be low enough so there is little or no fiber degradation. The reaction must also have a relatively fast rate of reaction with the cell wall components. It is important to get as fast a reaction as possible at the lowest temperature without wood degradation. High temperature reactions are possible (up to 170˚C) if the reaction time is very short and no strong acid or base catalysts are used. Wood degrades rather quickly at temperatures above 175˚C (Stamm 1964) (see Chapter 6).

The moisture present in the wood is another consideration in the reaction conditions. It is costly to dry wood to less than one percent moisture, but it must be remembered that the -OH group in water is more reactive than the -OH group available in the wood components; that is, hydrolysis is faster than substitution. The most favorable condition is a reaction which requires a trace of moisture and the rate of hydrolysis is relatively slow.

Another consideration in this area is to keep the reaction system as simple as possible. Multicomponent systems will require complex separation after reaction for chemical recovery. The optimum choice would be a reactive chemical that swells the wood structure that also acts as both the solvent and catalyst.

If possible, avoid by-products during the reaction that have to be removed. If there is not a 100 percent reagent skeleton add-on, then the chemical cost is higher and will require recovery of the by-product for economic and environmental reasons.

The chemical bond formed between the reagent and the wood components is of major importance. For permanence, this bond should have great stability to withstand nature's recycling system if the product is used outdoors. In order of stability, the types of covalent chemical bonds that may be formed are ethers > acetals > esters. The ether bond is the most desirable covalent carbon-oxygen bond that can be formed. These bonds are more stable than the glycosidic bonds between sugar units in the wood polysaccharides, so the polymers would degrade before the grafted ether. It may be desired, however, to have the bonded chemical released by hydrolysis or enzyme action in the final product so that an unstable bond may be required from the modification.

The hydrophobic nature of the reagent needs to be considered. The chemical added to the wood should not increase the hydrophilic nature of the wood components unless that is a desired property. If the hydrophilicity is increased, the susceptibility to microorganism attack increases. The more hydrophobic the component can be made, the better the moisture exclusion properties of the substituted wood will be.

Single-site substitution versus polymer formation is another consideration. For the most part, a single reagent molecule that reacts with a single hydroxyl group is the most desirable. Crosslinking can occur when the reagent contains more than one reactive group or results in a group which can further react with a hydroxyl group. Crosslinking can cause the wood to become more brittle. Polymer formation within the cell wall after the initial reaction with the hydroxyl groups of the wood components gives, through bulking action, dimensional stabilization. The disadvantage of polymer formation is that a higher level of chemical add-on is required for biological resistance than in the single site reactions.

The treated wood must still possess the desirable properties of wood—its strength should not be reduced, there should be no change in color, its good electrical insulation properties are retained, the final product not dangerous to handle, there are no lingering chemical smells, and it is still gluable and finishable—unless one or more of these properties are the object of change in the product.

A final consideration is, of course, the cost of chemicals and processing. In laboratory-scale experimental reactions, the high cost of chemicals is not a major factor. For the commercialization of a process, however, the chemical and processing costs are very important factors. Laboratory-scale research is generally done using small batch processing. But rapid, continuous processes should always be studied for scale-up. An economy of scale can make an expensive laboratory process economical.

In summary, the chemicals to be laboratory tested must be capable of reacting with wood hydroxyls under neutral, mildly alkaline, or acidic 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.

14.3 CHEMICAL REACTIONS WITH WOOD

As stated before, because the properties of wood result from the chemistry of the cell wall components, the basic properties of wood can be changed by modifying the basic chemistry of the cell wall polymers. There are several approaches to cell wall modification, depending on what property is to be modified. For example, if the objective is water repellency, then the approach

might be to reduce the hydrophilic nature of the cell wall by bonding on hydrophobic groups. If dimensional stability is to be improved, the cell wall can be bulked with bonded chemicals, or cell wall polymer components crosslinked together to restrict cell wall expansion, or groups can be bonded that reduce hydrogen bonding or increase hydrophobicity. If fire retardancy is desired, chemical groups can be bonded onto cell wall polymers that contain retardants or flame suppressants. If resistance to ultraviolet radiation is desired, UV blockers or absorbers could be bonded to lignin. The chemical modification system selected must perform the desired chemical change to achieve the desired change in performance.

Many chemical reaction systems have been published for the modification of wood, and these systems have been reviewed in the literature several times in the past (Rowell 1975a, 1983, 1991, Kumar 1994, Hon 1996, Rowell 1999). 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; phthaldehydic acid; dimethyl sulfate; alkyl chlorides; β-propiolactone, acrylonitrile; epoxides, such as ethylene, propylene, and butylene oxide; and difunctional epoxides.

14.3.1 Acetylation

Acetylation of wood using acetic anhydride has been done mainly as a liquid phase reaction. The early work was done using acetic anhydride catalyzed with either zinc chloride (Ridgway and Wallington 1946) or pyridine (Stamm and Tarkow 1947). Through the years, many other catalysts have been tried using both liquid and vapor systems. Some of the catalysts used include urea-ammonium sulphate (Clermont and Bender 1957), dimethylformamide (Clermont and Bender 1957; Risi and Arseneau 1957a; Baird 1969), sodium acetate (Tarkow 1959), magnesium persulfate (Arni et al. 1961; Ozolina and Svalbe 1972; Truksne and Svalbe 1977), trifluoroacetic acid (Arni et al. 1961a,b), boron trifluoride (Risi and Arseneau 1957a), and γ-rays (Svalbe and Ozolina 1970). The reaction has also been done without a catalyst (Rowell et al. 1986b), and by using an organic cosolvent (Goldstein et al. 1961). Gas-phase reactions have also been reported using acetic anhydride; however, the diffusion rate is so very slow that this technology has only been applied to thin veneers (Tarkow et al. 1950, Tarkow 1959, Baird 1969, Avora et al. 1979, Rowell et al. 1986a).

The reaction with acetic anhydride results in esterification of the accessible hydroxyl groups in the cell wall with the formation of by-product acetic acid (Rowell et al. 1994).

$$\mathbf{Wood\text{–}OH} + \mathbf{CH_3\text{–}C(=O)\text{–}O\text{–}C(C=O)\text{–}CH_3} \rightarrow \mathbf{Wood\text{–}O\text{–}C(=O)\text{–}CH_3} + \mathbf{CH_3\text{–}C(=O)\text{–}OH}$$

Acetic Anhydride — Acetylated Wood — Acetic Acid

Acetylation is a single-site reaction, which means that one acetyl group is on one hydroxyl group with no polymerization. All of 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 can not be converted into units of blocked hydroxyl groups.

Acetylation has also been done using ketene gas (Tarkow 1945; Karlson and Svalbe 1972, 1977, Rowell et al. 1986c). In this case, esterification of the cell wall hydroxyl groups takes place, but there is no formation of by-product acetic acid:

$$\mathbf{Wood\text{–}OH} + \mathbf{CH_2{=}C{=}O} \rightarrow \mathbf{Wood\text{–}O\text{–}C(=O)\text{–}CH_3}$$

Ketene — Acetylated Wood

While this is interesting chemistry that eliminates a by-product, it has been shown that reactions with ketene gas result in poor penetration of reactive chemicals, and the properties of the reacted wood are less desirable than those of wood reacted with acetic anhydride (Rowell et al. 1986c).

The preferred method of acetylating wood today is to use a limited amount of liquid acetic anhydride without a catalyst or cosolvent. The rest of this chapter will describe properties of wood that have been acetylated using this technology, unless otherwise noted (Rowell et al. 1986b, Rowell et al. 1986d, Rowell et al. 1991a). 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.

Many different types of wood have been acetylated using a variety of procedures, including several types of wood (Narayanamurti and Handa 1953, Rowell 1983, Rowell et al. 1986b, Rowell and Plackett 1988, Imamura et al. 1989, Plackett et al. 1990, Beckers and Militz 1994, Chow et al. 1996) as well as other lignocellulosic resources such as bamboo (Rowell and Norimoto 1987, 1988), bagasse (Rowell and Keany 1991), jute (Callow 1951, Andersson and Tillman 1989, Rowell et al. 1991a), kenaf (Rowell 1993, Rowell and Harrison 1993), wheat straw (Gomez-Bueso et al. 1999, 2000), pennywort, and water hyacinth (Rowell and Rowell 1989).

14.3.2 Acid Chlorides

Acid chlorides can also be used to esterify wood (Suida 1930). The product is the ester of the related acid chloride, with hydrochloric acid as a by-product. Using lead acetate as a catalyst with acetyl chloride,

$$\textbf{Wood–OH} + \textbf{R–C(=O)–Cl} \rightarrow \textbf{Wood–O–C(=O)–R} + \textbf{HCl}$$

Singh et al. (1981) found a lower acetyl content than with acetic anhydride. Using a 20% lead acetate solution in the reaction reduced the amount of free hydrochloric acid released in the reaction. The very strong acid released as a by-product in this reaction causes extensive degradation of the wood; as such, very little work has been done in this area.

14.3.3 Other Anhydrides

Other anhydrides have been used to react with wood. Risi and Arseneau (1958) reacted wood with phthalic anhydride, resulting in high dimensional stability. Popper and Bariska (1972), however, found that chemical weight gain was lost after soaking in water—showing that the phthaly group was lost to hydrolysis. Phthaly groups have a greater affinity for water than hydroxyl groups in wood, so phthalylated wood is more hydroscopic than untreated wood (Popper and Bariska 1972, 1973). While dimensional stability resulting from acetylation is due to bulking of the cell wall, dimensional stability from phthalylation seems to be due to mechanical bulking of the submicroscopic pores in the wood cell wall (Popper and Bariska 1975). Very high weight gains are achieved by phthalylation (40–130%), which may be a result of polymerization (Risi and Arseneau 1958, Popper 1973).

Goldstein et al. (1961) reacted ponderosa pine with propionic and butyric anhydrides in xylene without a catalyst. After 10 hours at 125°C, the reaction weight gain was 4% for propionylation and 0% for butyrylation. After 30 hours reaction time, propionylation only resulted in a weight gain of 10%. Papadopoulas and Hill (2002) reacted Corsican pine with acetic, propionic, butric, valeric, and hexanoic anhydrides. Butylation has also been done using microwave heating to improve dimensional stability and lightfastness (Chang and Chang 2003).

Succinic and malaic anhydrides have also been reacted with wood fiber (Clemons et al. 1992, Rowell and Clemons 1992). Reaction of these two anhydrides with wood made the wood thermoplastic, and it was possible to thermoform the wood fiber into a high-density composite under pressure.

14.3.4 Carboxylic Acids

Carboxylic acids have been esterified to wood catalyzed with trifluoroacetic anhydride (Arni et al. 1961a, 1961b, Nakagami et al. 1974).

$$\text{Wood–OH} + (CH_3)_2\text{–C=CH–COOH} \rightarrow \text{Wood–O–C(=O)–CH–C}(CH_3)_2$$

Several unsaturated carboxylic acids were found to react with wood by the "impelling" method to increase the oven dry volume without a change in color or a decrease in either crystallinity or moisture content (Nakagami and Yokota 1975). Reaction with α-methylcrotonic acid gave a degree of substitution high enough to make the reacted wood soluble in acetone and chloroform to the extent of 30% (Nakagami et al. 1976). Further esterification increased the solubility but was accompanied by considerable degradation of wood components. Solubilization seems to be hindered by both lignin and hemicelluloses (Nakagami 1978, Nakagami and Yokota 1978).

14.3.5 Isocyanates

The wood reacts with hydroxyls with isocyanates, forming a nitrogen-containing ester. Clermont and Bender (1957) exposed wood veneer swollen in dimethylformamide to vapors of phenyl isocyanate at 100–125°C. The resulting wood was very dimensionally stable and showed increased mechanical strength with little change in color. Baird (1969) reacted dimethylformamide-soaked cross sections of white pine and Englemann spruce with ethyl, allyl, butyl, *t*-butyl, and phenyl isocyanate.

$$\text{Wood–OH} + \text{R–N=C=O} \rightarrow \text{Wood–O–C(=O)–NH–R}$$

Isocyanate

Vapor phase reactions of butyl isocyanate in dimethylformamide gave the best results.

White cedar was reacted with 2,4-tolylene diisocyanate with and without a pyridine catalyst to a maximum nitrogen content of 3.5 and 1.2, respectively (Wakita et al. 1977). Compressive strength and bending modulus increased with increasing nitrogen content. Beech wood was reacted with a diisocyanate that gave the resulting wood very high decay resistance (Lutomski 1975).

Methyl isocyanate reacts very quickly with wood without a catalyst to give high add-on weight gains (Rowell and Ellis 1979). Ethyl, *n*-propyl, and phenyl isocyanates react with wood without the need for a catalyst, but *p*-tolyl-1,6-diisocyanate and tolylene-2,4-diisocyanate require either dimethylformamide or triethylamine as a catalyst (Rowell and Ellis 1981).

14.3.6 Formaldehyde

The reaction between wood hydroxyls and formaldehyde occurs in two steps. Because the bonding is with two hydroxyl groups, the reaction is called cross-linking.

$$\text{Wood–OH} + \text{H–C(=O)–H} \rightarrow \text{Wood–O–C(OH)–H}_2 + \text{Wood–OH} \rightarrow \text{Wood–O–CH}_2\text{–O–Wood}$$

Formaldehyde Hemiacetal Acetal

The two hydroxyl groups can come from (1) hydroxyls within a single sugar unit; (2) hydroxyls on different sugar residues within a single cellulose chain; (3) hydroxyls between two different cellulose chains; (4) same as 1, 2, and 3, except for reactions occurring on the hemicelluloses; (5) hydroxyl groups on different lignin residues; and (6) interaction between cellulose, hemicelluloses, and lignin hydroxyls. The possible cross-linking combinations are large and theoretically all of

them are possible. Since the reaction is a two-step mechanism, some of the added formaldehyde will be in a non–cross-linked hemiacetal form. These chemical bonds are very unstable and would not survive long after reaction.

The reaction is best catalyzed by strong acids such as hydrochloric acid (Tarkow and Stamm 1953, Burmester 1970, Ueyama et al. 1961, Minato and Mizukami 1982), nitric acid (Tarkow and Stamm 1953), sulfur dioxide (Dewispelaere et al. 1977, Stevens et al. 1979), *p*-toluene sulfonic acid, and zinc chloride (Stamm 1959, Ueyama et al. 1961). Weaker acids such as sulfurous and formic acid do not work (Tarkow and Stamm 1953). Schuerch (1968) speculated that bases such as lime water and tertiary amines can initiate the reaction.

14.3.7 Other Aldehydes

Acetaldehyde (Tarkow and Stamm 1953) and benzaldehyde (Tarkow and Stamm 1953, Weaver et al. 1960) were reacted with wood using either nitric acid or zinc chloride as the catalyst. Glyoxal, glutaraldehyde, and α-hydroxyadipaldehyde have also been catalyzed with zinc chloride, magnesium chloride, phenyldimethylammonium chloride, and pyridinium chloride (Weaver et al. 1960). Chloral (trichloroacetaldehyde) without catalyst and phthaldehydic acid in acetone catalyzed with *p*-toluenesulfonic acid have also been used as reaction systems with wood (Weaver et al. 1960, Kenaga 1957). Other aldehydes and related compounds have also been tried either alone or catalyzed with sulfuric acid, zinc chloride, magnesium chloride, ammonium chloride, or diammonium phosphate (Weaver et al. 1960). Compounds such as *N,N′*-dimethylol-ethylene urea, glycol acetate, acrolein, choroacetaldehyde, heptaldehyde, *o*- and *p*-chlorobenzaldehyde, furfural, *p*-hydroxybenzaldehyde, and *m*-nitrobenzaldehyde all bulk the cell wall, but no cross-linking seems to occur.

14.3.8 Methylation

The simplest ether that can be formed is the methyl ether. Reactions of wood with dimethyl sulfate and sodium hydroxyl (Rudkin 1950, Narayanamurti and Handa 1953) or methyl iodide and silver oxide (Narayanamurti and Handa 1953) are two systems that have been reported.

$$\textbf{Wood–OH} + \textbf{CH}_3\textbf{I} \rightarrow \textbf{Wood –O–CH}_3$$

Methylation up to 15% weight gain did not affect the adhesive properties of casein glues.

14.3.9 Alkyl Chlorides

In the reaction of alkyl chlorides with wood, hydrochloric acid is generated as a by-product. Because of this, the strength properties of the treated wood are poor. Reaction of allyl chloride in pyridine (Kenaga et al. 1950, Kenaga and Sproull 1951) or aluminum chloride resulted in good dimensional stability; but on soaking in water, dimensional stability was lost (Kenaga and Sproull 1951). In the case of allyl chloride-pyridine,

$$\textbf{Wood–OH} + \textbf{R–Cl} \rightarrow \textbf{Wood–O–R} + \textbf{HCl}$$

Alkyl Chloride

the dimensional stability was not due to the bulking of the cell wall with bonded chemicals but to the formation of allyl pyridinium chloride polymers, which are water soluble and easily leached out (Risi and Arseneau 1957d).

Other alkyl chlorides reported are crotyl chloride (Risi and Arseneau 1957b) and *n*- and *t*-butyl chlorides (Risi and Arseneau 1957c) catalyzed with pyridine.

14.3.10 β-Propiolactone

The reaction of β-propiolactone with wood is interesting in that different products are possible depending on the pH of the reaction. Under acid conditions, an ether bond is formed with the hydroxyl group on wood along with the formation of a free acid-end group.

$$\begin{array}{l} \qquad\qquad\qquad\quad \mathbf{H+} \\ \mathbf{Wood{-}OH} + \mathbf{CH_2{-}CH_2} \rightarrow \mathbf{Wood{-}O{-}CH_2{-}CH_2{-}COOH} \\ \qquad\quad | \quad | \qquad\quad \mathbf{OH-} \\ \qquad \mathbf{O{-}C{=}O} \rightarrow \mathbf{Wood\ O{-}C(=O){-}CH_2{-}CH_2{-}OH} \end{array}$$

β-Propiolactone

Under basic conditions, an ester bond is formed with the wood hydroxyl giving a primary alcohol end group.

Southern yellow pine was reacted with -propiolactone under acid conditions to give a carboxyethyl derivative (Goldstein et al. 1959, Goldstein 1959). High concentrations of β-propiolactone caused delamination and splitting of the wood due to very high swelling (Rowell unpublished data).

β-Propiolactone has now been labeled as a very active carcinogen. For this reason, this very interesting chemical reaction system will probably not be studied again.

14.3.11 Acrylonitrile

When acrylonitrile reacts with wood in the presence of an alkaline catalyst, cyanoethylation occurs.

$$\mathbf{Wood{-}OH} + \mathbf{CH_2{=}CH{-}CN} \rightarrow \mathbf{Wood{-}O{-}CH_2{-}CH_2{-}CN}$$

Acrylonitrile

With sodium hydroxide, weight gains up to 30% have been reported (Goldstein et al. 1959, Baechler 1959a,b, Fuse and Nishimoto 1961, Kenaga 1963). Ammonium hydroxide has also been used giving lower weight gains as compared to sodium hydroxide.

14.3.12 Epoxides

The reaction between epoxides and the hydroxyl groups is an acid- or base-catalyzed reaction; however, all work in the wood field has been alkali catalyzed.

$$\mathbf{Wood{-}OH} + \mathbf{R{-}CH(-O-)CH_2} \rightarrow \mathbf{Wood{-}O{-}CH_2{-}CH(OH){-}R}$$

Epoxide

The simplest epoxide (ethylene oxide) catalyzed with trimethylamine has been used as a vapor phase reaction (McMillin 1963, 1965, Aktiebolag 1965) Liu and McMillin (1965). Barnes et al. (1969) showed that an oscillating pressure was better than a constant pressure in this reaction. Sodium hydroxide has also been used as a catalyst with ethylene oxide (Zimakov and Pokrovski 1954). Other epoxides that have been studied include 1,2-epoxy-3,3,3-trichloropropane, 1,2-epoxy-4,4,4-trichlorobutane, 1-allyloxy-2,3-epoxypropane, *p*-chlorophenyl-2,3-eposypropyol ether, 1,2:3,4-diepoxybutane, 1,2:7, 8-diepoxyoctane, 1,4-butanediol diglycidal ether, and 3-epoxyethyl-7-oxabicyclo heptane (Rowell and Ellis 1984b).

Propylene and butylenes oxides have also been reacted with wood along with epichlorohydrin and mixtures of epichlorohydrin and propylene oxide (Rowell 1975a, Rowell et al. 1976, Rowell and Ellis 1984a,b). It is theoretically possible for cross-linking to occur with epichlorohydrin, resulting in the splitting out of hydrochloric acid, but this has never been observed (Rowell and Ellis 1981, Rowell and Chen 1994).

TABLE 14.1
Reaction Rates for Pine Using Different Chemicals

Chemical	Temperature (°C)	Time (min)	Weight Percent Gain
Propylene oxide–TEA	120	40	35.5
	120	120	45.5
	120	240	52.2
Butylene oxide–TEA	120	40	24.6
	120	180	36.9
	120	360	42.2
Methyl isocyanate	120	10	25.7
	120	20	40.4
	120	60	51.8
Butyl isocyanate	120	120	5.0
	120	180	16.0
	120	360	24.3
Acetic anhydride (liquid)	100	60	7.8
	100	120	11.2
	100	360	19.9
	120	60	17.2
	120	180	21.4
	140	60	17.9
	140	180	22.1
	160	60	21.4
Acetic anhydride (vapor)	120	480	7.2
	120	1440	22.1
Ketene	50–60	60	6.8
	50–60	120	21.7

In the case of the epoxy system, after the initial reaction with a cell wall hydroxyl group, a new hydroxyl group originating from the epoxide is formed. From this new hydroxyl, a polymer begins to form. Because of the ionic nature of the reaction and the availability of alkoxyl ions in the wood components, the chain length of the new polymer is probably short owing to chain transfer.

14.3.13 Reaction Rates

Table 14.1 shows the rate of reaction of southern pine reacted with propylene and butylene oxide, methyl and butyl isocyanate, and acetylated under different reaction conditions using liquid acetic anhydride, acetic anhydride vapor, and ketene gas. The propylene and butylenes oxide reactions were done using 5% triethyl amine as a catalyst. The methyl and butyl isocyanates were uncatalyzed. In the case of acetic anhydride vapor reactions, the pine veneer was suspended above a supply of acetic acid anhydride (Rowell et al. 1986a). In the case of ketene gas, the pine chips were subjected to ketene gas in batches (Rowell et al. 1986c).

In the reactions of the two epoxides and two isocyanates, the longer the reaction is run, the higher the weight percent gain (WPG). Acetylation, however, reaches a maximum WPG of about 22 no matter how it is done; further reaction time does not increase this value. The acetylation of aspen follows a similar pattern, except a maximum WPG of about 17–18 is reached. Other softwood and hardwood that have been acetylated using these procedures have followed a similar pattern.

It has been shown that the acetic anhydride reaction solution could contain up to 30% acetic acid without any detrimental effect on the reaction rate (Rowell et al. 1990). There is actually an

increase in reaction rate at 10–20% acetic acid in the impregnation solution due to the swelling effect of the acetic acid and, possibly, as an effect of the increased acidity.

Since the reaction of wood with acetic anhydride is an exothermic reaction, once the acetylation starts to take place, the temperature of the system goes up. This heating can be taken advantage of to reduce the external heat supplied to the system.

14.3.14 Effect of Moisture

Since all of the chemicals that react with wood cell wall hydroxyl groups can also react with water, the amount of water in the wood before reaction is very important (Rowell and Ellis 1984a). Hydrolysis with water is much faster than the reaction with a cell wall hydroxyl group. There is a trade off between the cost and energy to remove water below about 5% moisture content and the cost of chemical lost to hydrolysis. In the case of epoxides, reaction with water leads to the formation of nonbonded polymers in the cell wall. In the reaction with anhydrides, free acid is generated, which in the case of acetylation can be an advantage so long as the amount of acetic acid generated is not too large.

14.4 PROPERTIES OF CHEMICALLY MODIFIED WOOD

It is not possible to describe all of the properties of chemically modified wood in a short chapter. An entire book would be needed to describe all of the changes in properties from all of the reaction systems in the published literature. The next section will select some of the major property changes with a few examples from several of the chemical reactions systems. Since most of the historical and recent research in chemical modification of wood has been in the area of acetylation, much of the property and performance data will focus on this technology.

14.4.1 Changes in Wood Volume Resulting from Reaction

Table 14.2 shows the increase in volume of pine wood after reaction with several liquid chemicals and the calculated volume of chemical added to the cell wall after re-drying the wood. Since the

TABLE 14.2
Changes in Pine Volume and Volume of Chemical Added as a Result of Chemical Reactions

Chemical	WPG	Increase in Wood Volume[1] (cm^3)	Calculated Volume of Added Chemical[2] (cm^3)
Propylene oxide	26.5	7.1	7.5
	36.2	8.9	9.0
Butylene oxide	25.3	6.9	6.9
Methyl isocyanate	12.4	0.16	0.14
	25.7	0.21	0.27
	47.7	0.46	0.54
Acetic anhydride	17.5	3.0	2.9
	22.8	3.9	4.0
Acrylonitrile	25.7	0.46	0.77
	36.0	0.74	1.2

[1] Difference in oven-dry volume between reacted and nonreacted wood.

[2] Density used in volume calculations: Propylene and butylenes oxides:1.01, methyl isocycnate:0.967, acetic anhydride:1.049, and acrylonitrile:0.806

volume increase due to reactions with propylene and butylenes oxide, methyl and butyl isocyanates, and acetic anhydride is equal to the calculated volume of chemical added, this shows that the reaction has taken place in the cell wall and not in the void spaces of the wood (Rowell 1983). This correlation is not true for reactions of wood with, for example, acrylonitrile (Rowell 1983). In this case, the chemical is located in the voids in the wood structure.

14.4.2 Stability of Bonded Chemical to Chemical Leaching

One of the indirect ways to tell if the reaction has resulted in bonding with the cell wall is to leach the reacted wood with several solvents and determine loss of weight in the reacted sample. At least two different solvents are used. One is a solvent that the starting chemicals are soluble in, and a second is one in which any polymers that might be formed in the reaction are soluble.

Table 14.3 shows the weight loss due to leaching in benzene/ethanol, water in a soxhlet extractor for 24 hours, and water soaking for 7 days. The data shows that reactions with methyl isocyanate, butylene oxide, and acetic anhydride form chemical bonds that are stable to solvent extraction, while propylene oxide reacted wood loses some chemical in water leaching. The reaction with acrylonitrile catalyzed with either ammonium or sodium hydroxyl forms bonds that are not stable to solvent extraction.

Table 14.4 shows the stability of acetyl groups on acetylated pine and aspen to various pHs and temperatures, and Table 14.5 shows the activation energy for the deacetylation of pine and aspen (Rowell et al. 1992a, 1992b). These results show that acetylated wood is much more stable under slightly acidic conditions as opposed to slightly alkaline conditions. The data can be used to predict the stability of acetylated wood (or other wood) at any pH and temperature combinations to estimate the life expectancy of the product in its service environment. However, it must be considered that the data from this study were collected using either finely ground powder or small fiber. As a result, a very large surface area came into contact with the various pH and temperature environments. Therefore, this data represents the fastest possible degradation rates. It is well documented that in archaeological wood, acetyl groups are stable over thousands of years and little loss of acetyl has been observed.

TABLE 14.3
Oven-Dry Weight Loss of Chemically Reacted Wood Extracted with Several Solvents

Chemical	WPG	Benzene/Ethanol 4 hours Soxhlet 20 mesh (% wt loss)	Water 24 hrs Soxhlet 40 mesh (% wt loss)	Water 7 days Soxhlet 20 mesh (% wt loss)
None	0	2.3	11.2	0.6
Methyl isocyanate	23.5	6.5	11.6	1.0
Propylene oxide	29.2	5.2	10.7	4.0
Butylene oxide	27.0	3.8	11.7	1.6
Acetic anhydride	22.5	2.8	12.2	1.2
Acrylonitrile (NH_4OH)	26.1	22.3	20.4	21.7
Acrylonitrile (NaOH)	25.7	17.6	18.7	13.5

TABLE 14.4
Effects of Various pH and Temperature Conditions on the Stability of Acetyl Groups in Acetylated Pine and Aspen (Acetyl Content: Pine 20.2 WPG, Aspen 20.6 WPG)

Wood	Temperature (°C)	pH ($k \times 10^3$)	Rate Constant	Half Life (Days)
Pine	24	2	0.26	2,640
		4	0.15	4,630
		6	0.06	10,900
		8	1.40	500
Aspen	24	2	0.23	3,083
		4	0.15	4,697
		6	0.06	10,756
		8	1.11	623
Pine	50	2	2.07	340
		4	1.06	650
		6	1.71	410
		8	7.31	95
Aspen	50	2	1.18	590
		4	0.66	1,050
		6	1.29	540
		8	8.51	80
Pine	75	2	11.3	61
		4	8.41	82
		6	15.5	45
		8	32.2	22
Aspen	75	2	7.33	95
		4	4.78	145
		6	12.6	55
		8	32.5	21

Table 14.6 shows the stability of acetyl groups in pine and aspen flakes to cyclic exposure to 90% and 30% relative humidity (RH) (Rowell et al. 1992a,b). Each cycle represents exposing the flakes for three months at 30% RH and then three months at 90% RH. Within experimental error, there is no loss of acetyl over 41 cycles of humidity changes. This data was collected in 1992 and this experiment has continued. After almost 10 years of cycling these chips from 30% to 90% RH, recent acetyl analysis shows that there is still no loss of acetyl resulting from humidity cycling.

TABLE 14.5
Activation Energy for Deacetylation of Pine and Aspen over a Temperature Range of 24–75°C

Wood	pH (kJ/mole)	Activation Energy
Pine	2	58
	4	58
	6	89
	8	57
Aspen	2	63
	4	68
	6	93
	8	53

TABLE 14.6
Stability of Acetyl Groups in Pine and Aspen Flakes after Cyclic Exposure between 90% Relative Humidity (RH) and 30% RH

	Acetyl Content (%) after Cycle (Number)				
Wood	**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

14.4.3 Accessibility of Reaction Site

The rate controlling step in the chemical modification of wood is the rate of penetration of the reagent into the cell wall (Rowell et al. 1994). In the reaction of liquid acetic anhydride with wood, at an acetyl weight percent gain of about 4, there is more bonded acetyl in the S_2 layer than in the middle lamella. At a weight gain of about 10, there is an equal distribution of acetyl throughout the S_2 layer and the 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. This was found using chloroacetic anhydride and following the fate of the chlorine by energy-dispersive X-ray analysis (Rowell et al. 1994).

When larger pieces of wood are used, the time for the anhydride to penetrate increased in proportion to the size of wood used. Of course, the critical dimension is the size in the longitudinal dimension. Table 14.7 shows that if spruce chips are reacted for 30 minutes at 120°C, the WPG is 14.2 with an acetyl content of 15.6. If the chips are first reduced to fiber and then acetylated under the same reaction conditions, the WPG is 22.5 and the acetyl content is 19.2. If the acetylated chips were reduced to fiber and then reacetylated under the same conditions, the WPG is 20.4 with an acetyl content of 20.5. Since no acetyl groups were lost in the refining step, this shows that new -OH sites become available when the acetylated chips are reduced to fiber (Rowell and Rowell 1989). This also shows that some -OH groups are not accessible in a chip that becomes accessible in a fiber.

14.4.4 Acetyl Balance in Acetylated Wood

The mass balance in the acetylation reaction shows that all of 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 (Rowell et al. 1990). The consumption of acetic anhydride can be calculated stoichiometrically based

TABLE 14.7
Effects of Size of Spruce Specimen on Acetyl Content

Specimen	**WPG**	**Acetyl Content**
Chips Acetylated	14.2	15.6
Acetylated Chips to Fiber	14.2	15.4
Chips to Fiber and then Acetylated	22.5	19.2
Acetylated Chips to Fiber	22.5	19.4
Acetylated Chips to Fiber and again Acetylated	20.4	20.5

TABLE 14.8
Weight Percent Gain and Acetyl Analysis of Acetylated Pine and Aspen

Pine		Aspen	
WPG	Acetyl Content	WPG	Acetyl Content
0	1.4	0	3.9
6.0	7.0	7.3	10.1
14.8	15.1	14.2	16.9
21.1	20.1	17.9	19.1

on the degree of acetylation and the moisture content of the wood. This is true for all wood acetylated to date.

Table 14.8 shows the comparison of the weight gain due to acetylation, with the acetyl content found by chemical analysis. At the lower weight-gain levels, there is always a higher acetyl content as compared to the WPG. This may be due to the removal of extractives and some cell wall polymers into the acetic anhydride solution resulting in an initial specimen weight loss. At WPGs greater than about 15, the acetyl content and the WPG values are almost the same.

14.4.5 Distribution of Bonded Chemical

Table 14.9 shows the distribution of bonded chemicals and the degree of substitution (DS) of hydroxyl groups in methyl isocyanate reacted pine (Rowell 1980, 1982, Rowell and Ellis 1981, Rowell et al. 1994). This analysis is based on many assumptions: (1) that pine has a holocellulose content of 67% and a lignin content of 27%; (2) that the holocellulose content is 87% hexosans, 13% pentosans; (3) that the cellulose content of the holocellulose is 71.8%, 14.8% hemicellulose hexosans, and 13.4% hemicellulose pentosans; (4) that whole pine wood is 67% holocellulose, of which 48.1% is cellulose, 9.0% pentosans, and 9.9% hexosans; (5) that the calculated theoretical acetyl content of the holocellulose is 77.7% and 25.7% for the lignin; and (6) that there are 1.1 hydroxyl groups for each nine-carbon unit of lignin.

Based on this analysis, the lignin is completely substituted at a WPG of about 47 and at that point, only about 20% of the hydroxyls in the holocellulose are substituted. These calculations are also based on the added assumption that all of the theoretical hydroxyl groups are accessible during the acetylation reaction. Assuming 100% accessibility of the hemicellulose fraction but only 35% accessibility of the cellulose (based on the degree of crystallinity), the degree of substitution of the

TABLE 14.9
Distribution of Methyl Isocyanate Nitrogen and Degree of Substitution (DS) of Hydroxyl Groups in Modified Pine

	MeIsoN in Lignin		MeIsoN in Holo	
WPG	%	DS	%	DS
5.5	1.42	0.17	0.59	0.03
10.0	2.36	0.28	1.19	0.05
17.7	3.44	0.41	2.11	0.08
23.5	4.90	0.59	2.94	0.12
47.2	7.46	0.89	5.24	0.21

TABLE 14.10
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	—

accessible holocellulose would be 0.48. In experiments acetylating isolated cell wall components, lignin reacts faster than the hemicelluloses and whole wood and cellulose did not react at all (Rowell et al. 1994). It is possible that the cellulose is modified during the isolation procedure, so this result does not necessarily mean that no cellulose modification takes place during the acetylation of whole wood.

14.4.6 Moisture Sorption

By replacing some of the hydroxyl groups on the cell wall polymers with bonded acetyl groups, the hygroscopicity of the wood material is reduced. Table 14.10 shows the fiber saturation point for acetylated pine and aspen (Rowell 1991). As the level of acetylation increases, the fiber saturation point decreases in both the soft and hard wood.

Table 14.11 shows the equilibrium moisture content (EMC) of control and several types of chemically-modified pine at three levels of relative humidities. In all cases, as the level of chemical weight gain increases, the EMC of the resulting wood goes down (Rowell et al. 1986b). Reaction of formaldehyde with wood is the most effective in reducing EMC as a function of chemical weight gain. Of the other chemicals, acetylation is the most effective, followed by butylene oxide reaction. Propylene-oxide–reacted wood has only a slight decrease in EMC as compared to non-reacted wood. Table 14.12 shows the EMC of acetylated pine and aspen at several levels of acetylation.

TABLE 14.11
Equilibrium Moisture Content of Control and Chemically Modified Pine

		Equilibrium Moisture Content at 27°C		
Chemical	WPG	35% RH	60% RH	85% RH
Control	0	5.0	8.5	16.4
Propylene oxide	21.9	3.9	6.1	13.1
Butylene oxide	18.7	3.5	5.7	10.7
Formaldehyde	3.9	3.0	4.2	6.2
Acetic anhydride	20.4	2.4	4.3	8.4

TABLE 14.12
Equilibrium Moisture Content of Acetylated Pine and Aspen

		Equilibrium Moisture Content at 27˚C		
Specimen	**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

In the case of acetylated wood, if the reductions in EMC at 65% RH of many different types of acetylated woods referenced to unacetylated fiber is plotted as a function of the bonded acetyl content, a straight line plot results (Rowell and Rowell 1989). Even though the points represent many different types of wood, they all fit a common curve. A maximum reduction in EMC is achieved at about 20% bonded acetyl. Extrapolation of the plot to 100% reduction in EMC would occur at about 30% bonded acetyl. This represents a value not too different from the water fiber saturation point in these fibers. Because the acetate group is larger than the water molecule, not all hygroscopic hydrogen-bonding sites are covered; thus it would be expected that the acetyl saturation point would be lower than that of water.

The fact that EMC reduction as a function of acetyl content is the same for many different types of wood indicates that reducing moisture sorption may be controlled by a common factor. The lignin, hemicellulose, and cellulose contents of all the woods are different.

Figure 14.3 shows the sorption-desorption isotherms for acetylated spruce fibers (Stromdahl 2000). The 10-minute acetylation curve represents a WPG of 13.2, and the 4-hour curve represents a WPG of 19.2. The untreated spruce reaches an adsorption/desorption maximum at about 35% moisture content, the 13.2 WPG a maximum of about 30%, and the 19.2 WPG a maximum of about 10%. There is a very large difference between the adsorption and desorption curves for both the control and the 13.2 WPG fibers, but much less difference in the 19.2 WPG fibers. The sorption of moisture is presumed to be sorbed either as primary water or secondary water. *Primary water* is the water sorbed to primary sites with high-binding energies, such as the hydroxyl groups. *Secondary water* is that water sorbed to less-binding energy sites—water molecules sorbed on top of the primary layer. Since some of the hydroxyl sites are esterified with acetyl groups, there are fewer primary sites to which water sorbs. And since the fiber is more hydrophilic due to acetylation, there may also be less secondary binding sites.

14.4.7 Dimensional Stability

Changes in dimensions in tangential and radial direction in solid wood, and in thickness and linear expansion for composites, are a great problem for wood composites (see Chapter 4). Composites not only undergo normal 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, with some of the reversible shrinkage occurring when the board dries.

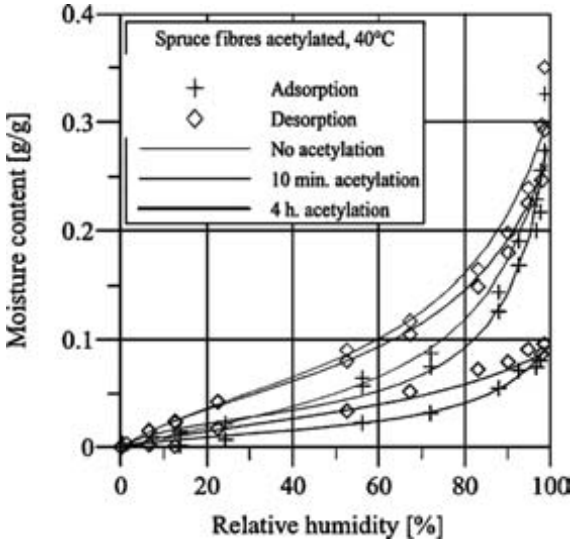

FIGURE 14.3 Sorption/desorption isotherms for control and acetylated spruce fiber.

Thickness swelling at three levels of relative humidity is greatly reduced as a result of acetylation (Table 14.13). Linear expansion is also greatly reduced as a result of acetylation (Krzysik et al. 1992, 1993). Increasing the adhesive content can reduce the thickness swelling, but not to the extent that acetylation does.

The rate and extent of thickness swelling in liquid water of fiberboards made from control and acetylated fiber is shown in Table 14.14. Both the rate and extent of swelling are 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 5%. Drying the boards at the end of the test showed that control boards exhibit a greater degree of irreversible swelling as compared to boards made from acetylated fiber (Rowell et al. 1991b).

Table 14.15 shows the thickness swelling of pine, beech, and wheat straw fiberboards after 24 hours of water swelling and the thickness of the boards after drying. In all cases, the control fiberboards swelled on water soaking and remained almost as thick after drying, while the acetylated fiberboards showed very little swelling in water and little residual swelling after drying.

TABLE 14.13
Thickness Swelling (TS) of Aspen Fiberboards Made from Control and Acetylated Fiber

		TS at 27°C		
WPG	Phenolic Resin Content (%)	30% RH (%)	65% RH (%)	90% RH (%)
0	5	0.7	3.0	12.6
	8	1.0	3.1	11.2
	12	0.8	2.5	9.7
17.9	5	0.2	1.8	3.2
	8	0.2	1.7	3.1
	12	0.1	1.7	2.9

TABLE 14.14
Rate and Extent of Thickness Swelling in Liquid Water of Pine Fiberboards Made from Control and Acetylated Fiber (8% Phenolic Resin)

	Percent Thickness Swelling at						
	Minutes			Hours			Days
Fiberboard	15	30	60	3	6	24	5
Control	25.7	29.8	33.5	33.8	34.0	34.0	36.2
Acetylated (21.6 WPG)	0.6	0.9	1.2	1.9	2.5	3.7	4.5

TABLE 14.15
Thickness Swelling of Fiberboards in Water and Thickness after Drying (10% Phenolic Resin)

Fiber	WPG	Thickness Swelling (24 hrs in Water) (%)	Residual Thickness Swelling (Oven Dry) (%)
Pine	0	21.3	19.7
	21.5	2.1	1.0
Beech	0	17.0	13.0
	19.7	2.2	0.9

Table 14.16 shows the antishrink efficiencies (ASE—see Chapter 4 for definition and calculations) of several different types of chemically modified solid pine wood. All chemically reacted pine wood shows an ASE of approximately 70 at weight gains between 22–26 WPG.

If the water-swelling test is continued through several cycles of water soaking and oven drying, the ASE may change if chemicals are lost in the leaching process. Table 14.17 shows the ASE for several types of chemically-modified solid pine. ASE_1 is calculated from the wood going from oven-dry to water-soaked (Rowell and Ellis 1978). ASE_2 is then calculated from the wood going from water-soaked back to the oven-dry state. ASE_3 and ASE_4 are the values on the second complete cycle.

TABLE 14.16
Antishrink Efficiencies of Chemically Modified Solid Pine Wood

Chemical	WPG	ASE
None	0	—
Propylene oxide	29.2	62
Butylene oxide	27.0	74.3
Acetic anhydride	22.5	70.3
Methyl isocyanate	26.0	69.7
Acrylonitrile		
NH_4OH	26.1	80.9
NaOH	25.7	48.3

TABLE 14.17
Repeated Antishrink Efficiency (ASE) of Chemically Modified Solid Pine

Chemical	WPG	ASE_1	ASE_2	ASE_3	ASE_4	Weight Loss after Test
Propylene oxide	29.2	62.0	43.8	50.9	50.3	5.7
Butylene oxide	26.7	74.3	55.6	59.7	48.1	4.6
Acetic anhydride	22.5	70.3	71.4	70.6	69.2	<.2
Methyl isocyanate	26.0	69.7	62.8	65.0	60.7	4.3
Acrylonitrile						
NH_4OH	26.1	80.9	0	0	0	22.6
NaOH	25.7	48.3	0	0	0	14.7

This data in Table 14.17 shows that the highest ASE is for acrylonitrile catalyzed with ammonium in the first wetting cycle. But redrying results in a loss of much of the chemical, so ASE_2 is zero with a final weight loss of 22.6%—almost a complete loss of reacted chemical. Propylene and butylene oxides, methyl isocyanate, and acetic-anhydride–reacted wood are more stable to swelling and shrinking cycles. Acetylation is the most stable treatment, with less than 0.2% weight loss after the two-cycle test.

14.4.8 Loss of Dimensional Stability

At very high WPG with isocyanates and epoxide-modified wood, the ASE values started to drop (Rowell and Ellis 1979, 1981, 1984a,b). Figure 14.4 shows a plot of ASE versus WPG for propylene- and butylene-oxide–reacted wood. As the WPG increases up to about 25 to 30, the ASE increases. At WPGs higher than 25–30, the ASE starts to decrease. The same effect is also observed in methyl-isocyanate–reacted wood.

Explanation of this phenomenon is observed in an electron microscopic examination of the epoxide and isocyanate reacted wood at different WPG levels. Figure 14.5 shows the electron micrographs for propylene-oxide–reacted wood. Figure 14.5a shows the unreacted wood. Figure 14.5b shows wood reacted with propylene oxide to 25 WPG. The cell wall is swollen in

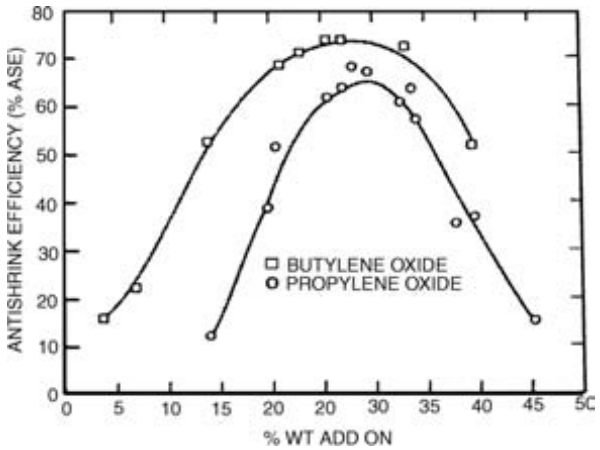

FIGURE 14.4 Loss of antishrink efficiency at high chemical weight gains.

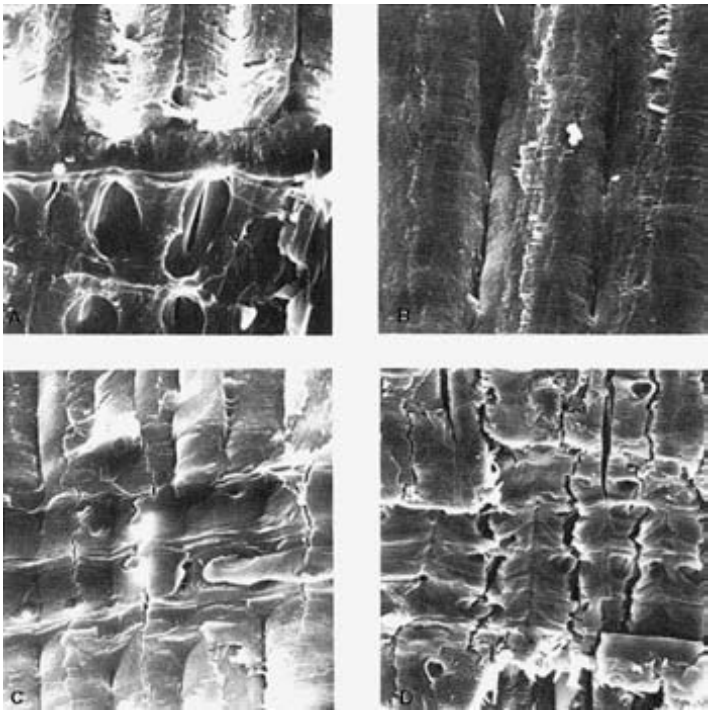

FIGURE 14.5 Scanning electron micrographs of radial-split southern pine showing swelling of wood when reacted with propylene oxide-triethylamine. A = control (1100×), B = WPG 25 (1100×), C = WPG 32.6 (600×), D = WPG 45.3 (550×).

Figure 14.5b, but no cracks are observed. Figure 14.5c shows small cracks starting to form in the tracheid walls at a WPG of 33, and major cracks are observed in Figure 14.5d at a WPG of 45. The largest cracks in Figure 14.5d are between cells. Similar results are observed in methyl-isocyanate–reacted wood.

14.4.9 Biological Resistance

Various types of woods, particleboards, and flakeboards made from chemically-modified wood have been tested for resistance to several different types of organisms (Imamura et al. 1987, Rowell et al. 1989, Chow et al. 1994, Beckers et al. 1994, Militz 1991, Wang et al. 2002).

14.4.9.1 Termite Resistance

Table 14.18 shows the results of a two-week termite test using *Reticulitermes flavipes* (subterranean termites) on several types of chemically-modified pine (Rowell et al. 1979, 1988a). Propylene and butylene oxide and acetic anhydride–modified wood becomes somewhat resistant to termite attack at about 30% for propylene oxide and about 20–25% for butylene oxide and acetic-anhydride–reacted wood. There was not a complete resistance to attack, and this may be attributed to the severity of the test. However, since termites can live on acetic acid and decompose cellulose to mainly acetate, perhaps it is not surprising that acetylated wood is not completely resistant to termite attack. Termite survival was quite high at the end of the tests, showing that the modified wood was not toxic to them.

TABLE 14.18
Wood Weight Loss in Chemically Modified Pine after a Two-Week Exposure Test to *Reticulitermes flavipes*

Chemical	WPG	Wood Weight Loss (%)
Control	0	31
Propylene oxide	9	21
	17	14
	34	6
Butylene oxide	27	4
	34	3
Acetic anhydride	10.4	9
	17.8	6
	21.6	5

14.4.9.2 Decay Resistance

Chemically-modified wood has been tested with several types of decay fungi in an ASTM standard 12-week soil-block test using either the brown rot fungus *Gloeophyllum trabeum* or the white rot fungus *Trametes versicolor* (Nilsson et al. 1988, Rowell et al. 1987, 1988a). Table 14.19 shows that all of the chemical modifications demonstrate good resistance to white-rot fungi, and all but propylene oxide shows good resistance to brown-rot fungi.

Weight loss resulting from fungal attack is the method most used to determine the effectiveness of a preservative treatment to protect wood composites from decaying. 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 (Cowling 1961). A dynamic bending-creep test has been developed to determine strength losses when wood composites are exposed to a brown- or white-rot fungus (Imamura and Nishimoto 1985, Norimoto et al. 1987, Norimoto et al. 1992).

Using this bending-creep test on aspen flakeboards, control boards made with phenol-formaldehyde adhesive failed in an average of 71 days using the brown-rot fungus *Tyromyces palustris* and 212 days using the white-rot fungus *Traetes versicolor* (Imamura et al. 1988, Rowell et al. 1988b).

TABLE 14.19
Resistance of Chemically Modified Pine against Brown- and White-Rot Fungi

		Weight Loss After 12 Weeks	
Chemical	WPG	Brown-rot Fungus (%)	White-rot Fungus (%)
Control	0	61.3	7.8
Propylene oxide	25.3	14.2	1.7
Butylene oxide	22.1	2.7	0.8
Methyl isocyanate	20.4	2.8	0.7
Acetic anhydride	17.8	1.7	1.1
Formaldehyde	5.2	2.9	0.9
β-Propiolacetone	25.7	1.7	1.5
Acrylonitrile	25.2	1.9	1.9

At failure, weight losses 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 (Rowell et al. 1988b). 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 one week, but mycelial development was significantly slower in phenol-formaldehyde-bonded control flakeboards. Both isocyanate- and phenol-formaldehyde-bonded acetylated flakeboards showed surface mycelium colonization during the test time, but little strength was lost since the fungus did not attack the acetylated flakes.

In similar bending-creep tests, both control and acetylated pine particleboards made using melamine-urea-formaldehyde adhesive failed because *T. palustris* attacked the adhesive in the glue line (Imamura et al. 1988). Mycelium invaded the inner part of all boards, colonizing in both the wood and glue lines 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 a 16-week exposure to *T. palustris*, the internal bond strength of control aspen flakeboards made with phenol-formaldehyde adhesive was reduced over 90%, and that of flakeboards made with isocyanate adhesive was reduced 85% (Imamura et al. 1987). After six months of exposure in moist unsterile soil, the same control flakeboards made with phenol-formaldehyde adhesive lost 65% of their internal bond strength, and those made with isocyanate adhesive lost 64% internal bond strength. Failure was due mainly to great strength reductions in the wood caused by fungal attack. Acetylated aspen flakeboards lost much less internal bond strength during either the 16-week exposure to *T. palustris* or a 6-month soil burial. The isocyanate adhesive was somewhat more resistant to fungal attack than the phenol-formaldehyde adhesive. In the case of acetylated composites, the loss in internal bond strength was mainly due to fungal attack in the adhesive and moisture, which caused a small amount of swelling in the boards.

The mechanism of resistance to fungal attack by chemical modification has been suggested to be due to the specific enzymatic reactions that can take place due to a change in configuration and conformation of the modified wood and/or when the reduction in equilibrium moisture content becomes too low to support fungal growth. In the specific case of brown-rot fungal attack, a mechanism has been suggested that explains the loss of strength before there is very much weight loss (Nilsson 1986, Winandy and Rowell 1984). This mechanism is consistent with the data from the soil block weight-loss tests and the strength-loss tests.

Enzymes → Hemicelluloses
(Energy source for
generation of
chemical oxidation
system) → Hemicellulose Matrix
(Strength losses)
(Energy source for generation
of β-glucosidases) → Weight Loss

Another test for fugal and bacterial resistance that has been done on acetylated composites is with brown-, white-, and soft-rot fungi and tunneling bacteria in a fungal cellar (Table 14.20). Control blocks were destroyed in less than 6 months, while flakeboards made from acetylated furnish above 16 WPG showed no attack after 1 year. (Nilsson et al. 1988, Rowell et al. 1988a). This data shows that no attack occurs until the wood begins to swell (Rowell and Ellis 1984, Rowell et al. 1988a). This fungal cellar test was continued for an additional 5 years with no attack at

TABLE 14.20
Fungal Cellar Tests of Aspen Flakeboards Made from Control and Acetylated Flakes[1,2]

	Rating at Intervals (Months)[3]							
WPG	**2**	**3**	**4**	**5**	**6**	**12**	**24**	**36**
0	S/2	S/3	S/3	S/3	S/4	—	—	—
7.3	S/0	S/1	S/1	S/2	S/3	S/4	—	—
11.5	0	0	S/0	S/1	S/2	S/3	S/4	—
13.6	0	0	0	0	S/0	S/1	S/2	S/3
16.3	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0

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

17.9 WPG. Further evidence suggests that the moisture content of the cell wall is critical before attack can take place (Ibach and Rowell 2000, Ibach et al. 2000).

In-ground tests have also been done on acetylated solid wood and flakeboards (Hadi et al. 1995, Rowell et al. 1997, Larsson Brelid et al. 2000). Specimens have been tested in the United States, Sweden, New Zealand, and Indonesia. The specimens in the United States, Sweden, and New Zealand are showing little or no attack after ten years, while the specimens in Indonesia failed in less than three years (Hadi et al. 1996). The failure in Indonesia was mainly due to termite attack.

Recent results show that acetylated pine at a WPG of 21.2 is outperforming CCA (copper-chromium-arsenic) at 10.3 kg/m^3 after 8 years in test in Sweden (Larsson Brelid et al. 2000).

14.4.9.3 Marine Organisms Resistance

Table 14.21 shows the data for chemically-modified pine in a marine environment (Johnson and Rowell 1988). As with the termite test, all types of chemical modifications of wood help resist attack by marine organisms. Control specimens were destroyed in six months to one year, mainly because of attack by *Limnoria tripunctata*, while propylene and butylene oxide, butyl isocyanate, and acetic-anhydride–reacted wood showed good resistance. Similar tests were run in Sweden on acetylated wood, and the modified wood failed in marine tests after two years (Larsson Brelid et al. 2000). The failure was due to attack by crustaceans and mollusks.

14.4.10 Thermal Properties

Table 14.22, Figure 14.6, and Figure 14.7 shows the results of thermogravimetric and evolved gas analysis of chemically-modified pine (see Chapter 6). The unreacted, acetylated, and methyl isocyanate samples show two peaks in the thermogravimetric runs while propylene and butylene oxide only show one peak. The lower temperature peak represents the hemicellulose fraction, and the higher peak represents the cellulose in the fiber. Acetylated pine fibers pyrolyze at about the same temperature and rate (Rowell et al. 1984). The heat of combustion and rate of oxygen consumption are approximately the same for control and acetylated fibers, which means that the acetyl groups added have approximately the same carbon, hydrogen, and oxygen content as the cell wall polymers. The two peaks in control, acetylated, and methyl isocyanate samples are combined into only one large peak in the epoxide-reacted pine (Rowell et al. 1984). The hemicelluloses seem to become more thermally stable when epoxidized. The heat of combustion and rate of oxygen consumption

TABLE 14.21
Ratings of Chemically Modified Southern Pine Exposed to a Marine Environment[1]

Chemical	WPG	Years of Exposure	Mean Rating Due to Attack by *Limnoriid and Teredinid Borers*[2]	Mean Rating Due to Attack by *Shaeroma terebrans*[3]
Control	0	1	2–4	3.4
Propylene oxide	26	11.5	10	—
		3	—	3.8
Butylene oxide	28	8.5	9.9	—
		3	—	8.0
Butyl isocyanate	29	6.5	10	—
Acetic anhydride	22	3	8	8.8

[1] Rating system: 10 = no attack; 9 = slight attack; 7 = some attack; 4 = heavy attack; 0 = destroyed
[2] Installed in Key West, FL. 1975 to 1987
[3] Installed in Tarpon Springs, FL 1984 to 1987

is almost double for the epoxide-reacted samples as compared to control, acetylated, and methyl-isocyanate–modified pine.

Reactive fire retardants could be bonded to the cell wall hydroxyl groups in reactions similar to this technology. The effect would be an improvement in dimensional stability, biological resistance, and fire retardancy (Rowell et al. 1984, Ellis and Rowell 1989, Ellis et al. 1987, Lee et al. 2000).

14.4.11 Ultraviolet Radiation and Weathering Resistance

Reaction of wood with epoxides and acetic anhydride has also been shown to improve ultraviolet resistance of wood (Feist et al. 1991a, 1991b). Table 14.23 shows the weight loss, erosion rate,

TABLE 14.22
Thermal Properties of Control and Acetylated Pine Fiber

Chemical	WPG	Temperature of Maximum Weight Loss (°C)	Heat of Combustion (KCal/g)	Rate of Oxygen Consumption (MM/g sec)
Control	0	335/375	2.9	0.06/0.13
Acetic anhydride	21.1	338/375	3.1	0.08/0.14
Methyl isocyanate	24.0	315/375	2.6	0.07/0.12
Propylene oxide	32.0	380	4.3	0.23
Butylene oxide	22.0	385	4.1	0.24

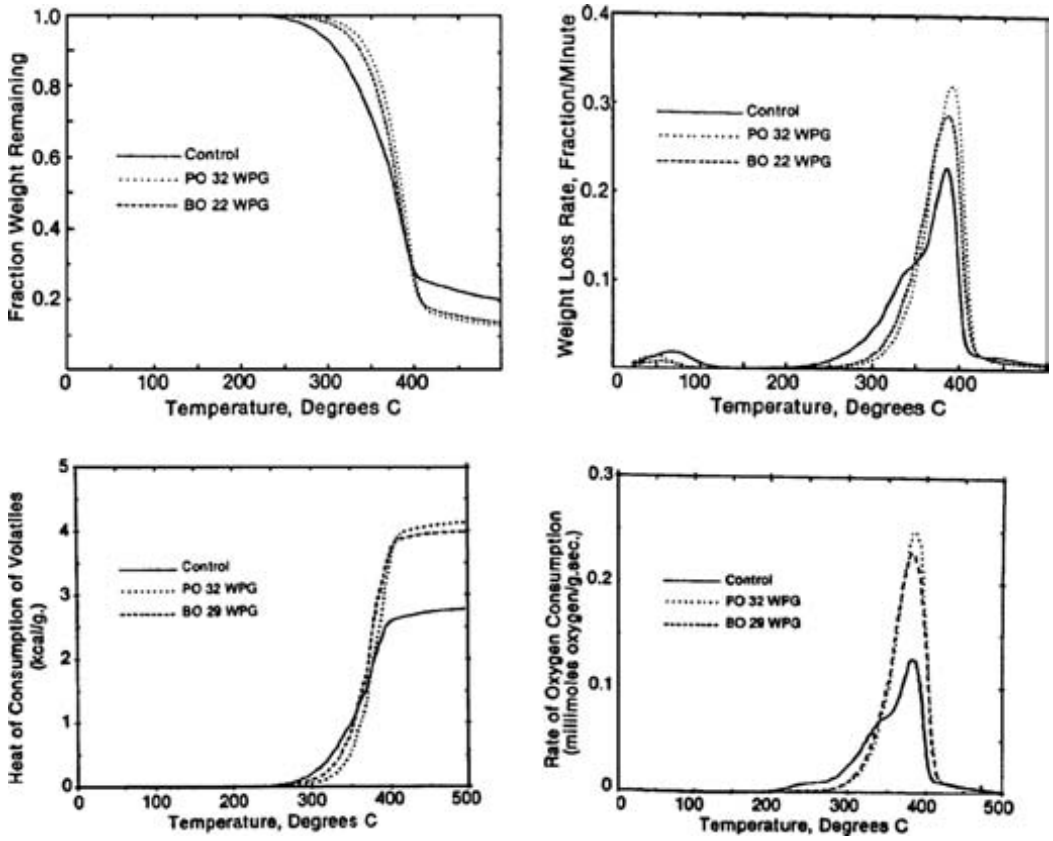

FIGURE 14.6 Thermogravimetric and evolved gas analysis of propylene and butylene oxide reacted pine.

and depth of penetration resulting from 700 hours of accelerated weathering for acetylated aspen. Control specimens erode at about 0.12 μm/hr, or about 0.02 %/hr. Acetylation reduces surface erosion by 50 percent. The depth of the effects of weathering is about 200 μm into the fiber surface for the unmodified boards and about half that of the acetylated boards.

Table 14.24 shows the acetyl and lignin content of the outer 0.5 mm surface and of the remaining specimen after the surface had been removed before and after accelerated weathering. The acetyl content is reduced in the surface after weathering, showing that the acetyl blocking group is removed during weathering (Hon 1995). UV radiation does not remove all of the blocking acetyl group, so some stabilizing effect to photochemical degradation still is in effect. The loss of acetate is confined

TABLE 14.23
Weight Loss and Erosion of Acetylated Aspen after 700 Hours of Accelerated Weathering

WPG	Weight loss in Erosion (%/hr)	Erosion Rate (μm/hr)	Reduction in Erosion (%)	Depth of Weathering (μm)
0	0.019	0.121	—	199–210
21.2	0.010	0.059	51	85–105

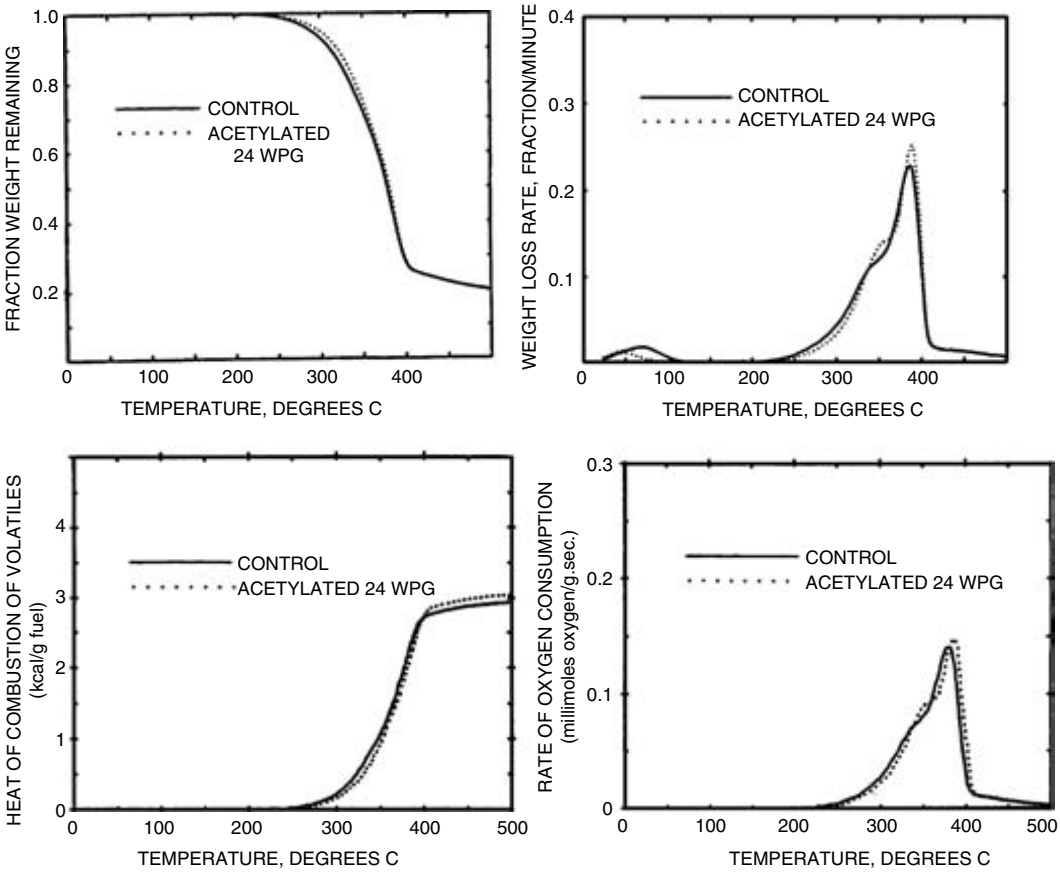

FIGURE 14.7 Thermogravimetric and evolved gas analysis of acetylated pine.

to the outer 0.5 mm since the remaining wood has the same acetyl content before and after accelerated weathering. The lignin content is also greatly reduced in the surface as a result of weathering; the main cell wall polymer has been degraded by UV radiation. Cellulose and the hemicelluloses are much more stable to photochemical degradation.

In outdoor tests, flakeboards made from acetylated pine wood maintain a light yellow color after one year while control boards turn dark orange to light gray during this time (Feist et al. 1991b). Within two years the acetylated pine had started to turn gray. Acetylated pine in indoor test settings retains its bright color after ten years, while control pine turns light orange after a few months.

14.4.12 Mechanical Properties

Strength properties are modified as a result of many of the chemical reactions performed on wood. For example, shear strength parallel to the grain is decreased in acetylated wood (Dreher et al. 1964), a slight decrease in the modulus of elasticity (Narayanamurti and Handa 1953) but no change in impact strength (Koppers 1961) or stiffness (Dreher et al. 1964). Wet and dry compressive strength (Koppers 1961, Dreher et al. 1964), hardness, fiber stress at proportional limit, and work to proportional limit are increased (Dreher et al. 1964). The modulus of rupture is increased in softwoods but decreased for hardwoods (Dreher et al. 1964, Minato et al. 2003). For isocyanate-reacted wood, compressive strength and bending modulus are increased (Wakita et al. 1977). The mechanical properties for formaldehyde-reacted wood are all reduced as compared to unreacted

TABLE 14.24
Acetyl and Lignin Analysis before and after 700 Hours of Accelerated Weathering of Aspen Fiberboards Made from Control and Acetylated Fiber

	Before Weathering		After Weathering	
WPG	Surface (%)	Remainder (%)	Surface (%)	Remainder (%)
Acetyl				
0	4.5	4.5	1.9	3.9
19.7	17.5	18.5	12.8	18.3
Lignin				
0	19.8	20.5	1.9	17.9
19.7	18.5	19.2	5.5	18.1

wood. Toughness and abrasion resistance are greatly reduced (Tarkow and Stamm 1953, Stamm 1959), crushing and bending strength are reduced 20%, and impact bending strength is reduced up to 50% (Burmester 1967). A definite embrittlement is observed in formaldehyde-reacted wood. This may be due to the short, inflexible crosslinking unit of –O-C-O- type. Some of the strength loss may also be polymer hydrolysis due to the strong acid catalyst. Strength properties of methylated wood are also reduced as a result of the strong acid used as a catalyst (Narayanamurti and Handa 1953). Cyanoethylated wood, using sodium hydroxide as a catalyst, has a lower impact strength (Goldstein et al. 1959, Kenaga 1963). Many of the mechanical properties of propylene oxide–reacted wood are reduced. Modulus of elasticity is reduced 14%, modulus of rupture is reduced 17%, fiber stress at proportional limit is reduced 9% and maximum crushing strength is reduced 10% (Rowell et al. 1982).

Wood composites made from acetylated furnish, however, do not lose mechanical properties as compared to nonreacted wood. The modulus of rupture (MOR), modulus of elasticity (MOE) in bending, and tensile strength (TS) parallel to the board surface are shown in Table 14.25 for fiberboards made from control and acetylated pine fiber. Acetylation results in an increase in MOR and MOE, but equal values in IBS (Youngquist et al. 1986a, 1986b). The MOR value is above the minimum standard as given by the American Hardboard Association (ANSI 1982). It has been shown that there is very little effect on the strength properties of thin flakes as a result of acetylation (Rowell and Banks 1987). The small decrease in some strength properties resulting from acetylation may be

TABLE 14.25
Equilibrium Moisture Content (EMC), Thickness Swelling (TS), Biological Resistance 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)

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

attributed to the hydrophobic nature of the acetylated furnish, which may not allow the water-soluble phenolic or isocyanate resins to penetrate into the flake.

It should also be pointed out that strength properties of wood are very dependent on the moisture content of the cell wall. Fiber stress at proportional limit, work to proportional limit, fiber stress at proportional limit, and maximum crushing strength are the mechanical properties most affected by changing moisture content by only +/– one percent below FSP (Rowell 1984, USDA 1999). Since the EMC and FSP are much lower for acetylated fiber than for control fiber, strength properties will be different due to this fact alone.

14.4.13 Adhesion of Chemically Modified Wood

Acetylated wood is more hydrophobic than natural wood, so studies have been done to determine which adhesives might work best to make composites (Vick and Rowell 1990, Larsson et al. 1992, Vick et al. 1993, Rowell et al. 1987, Youngquist et al. 1988, Youngquist and Rowell 1990, Gomez-Bueso et al. 1999, Rowell et al. 1996). Shear strength and wood failure was measured using acetylated yellow poplar at 0, 8, 14, and 20 WPG and adhesives including emulsion polymer isocyanate cold set, polyurethane cold set, polyurethane hot-melt, polyvinyl acetate emulsion, polyvinyl acetate cold set, polyvinyl acetate cross-link cold set, rubber-based contact-bond, neoprene contact-bond cold set, waterborne contact-bond cold set, casein, epoxy-polyamide cold set, amino resin, melamine-formaldehyde hot set, urea-formaldehyde hot set, urea-formaldehyde cold set, resorcinol-formaldehyde cold set, phenol-resorcinol-formaldehyde cold set, phenol-resorcinol-formaldehyde hot set, phenol-formaldehyde hot set, and acid-catalyzed phenol-formaldehyde. In all cases, adhesive strength was reduced by the level of acetylation—some adhesives to a minor degree and others to a severe degree.

Many adhesives were capable of strong and durable bonds at the 8 WPG level of acetylation, but not at 14 and 20 WPG levels. Most of the adhesives tested contained polar polymers, and all but four were aqueous systems, so their adhesion was diminished in proportion to the presence of the non-polar and hydrophobic acetate groups in acetylated wood (Rudkin 1950). Thermosetting adhesives produced the strongest bonds in both dry and wet conditions, but thermoplastic adhesives were capable of high shear strengths in the dry condition. With the exception of the acid-catalyzed phenol-formaldehyde adhesive, thermosetting adhesives that were hot pressed became highly mobile and tended to over-penetrate the wood because of the limited capacity of the acetylated wood to sorb water from the curing bond-line. The abundance of hydroxyl groups in the highly reactive resorcinol adhesive permitted excellent adhesion at room temperature, despite the limited availability of hydroxyl groups in the acetylated wood.

An emulsion polymer-isocyanate, a cross-linking polyvinyl acetate, a resorcinol-formaldehyde, a phenol-resorcinol-formaldehyde, and an acid-catalyzed phenolic-formaldehyde adhesive developed bonds of high shear strength and wood failure at all levels of acetylation in the dry condition. A neoprene contact-bond adhesive and a moisture-curing polyurethane hot-melt adhesive performed as well on acetylated wood as untreated wood in tests of dry strength. Only the cold-setting resorcinol-formaldehyde, the phenol-resorcinol-formaldehyde adhesive, and the hot-setting acid-catalyzed phenolic adhesive developed bonds of high strength and wood failure at all levels of acetylation when tested in a water-saturated condition.

14.4.14 Acoustical Properties

The acetylation of wood slightly reduced both sound velocity and sound absorption as compared to unreacted wood (Zhao et al. 1987, Norimoto et al. 1988, Yano et al. 1993). Acetylation greatly reduces variability in the moisture content of the cell wall polymers, thereby stabilizing the physical dimensions of wood and its acoustic properties. It was not possible to determine if acetylation effected sound quality. A violin and guitar in Japan, a violin in Sweden, and a recorder in the United States have been made from acetylated wood, and actual changes in sound quality are presently being investigated.

14.5 COMMERCIALIZATION OF CHEMICALLY MODIFIED WOOD

In spite of the vast amount of research on chemical modification of wood, only acetylation of wood has been tested for commercialization. Two attempts, one in the United States (Koppers 1961) and one in Russia (Otlesnov and Nikitina 1977, Nikitina 1977), came close to commercialization but were discontinued presumably because they were not cost-effective. There is a commercial acetylation plant for solid wood flooring in Japan and a pilot plant for solid wood in Holland.

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. One of the concerns about the acetylation of wood, 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 potential ester-hydrolysis–causing chemical. Complete removal of by-product acetic acid has now been achieved in both the fiber process and the solid wood microwave process.

14.5.1 The Fiber Process

There is a pilot plant in Sweden with a capacity of approximately 4000 tons of acetylated fiber a year. Figure 14.8 shows the schematic of the new continuous fiber acetylation process (Nelson et al. 1994, 1995a, 1995b, 1999, Simonson and Rowell 2000). The fiber is first dried in an optional dryer section to reduce the moisture content to as low a level 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.

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 devise 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 from 6 to 30 minutes. 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 formed 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

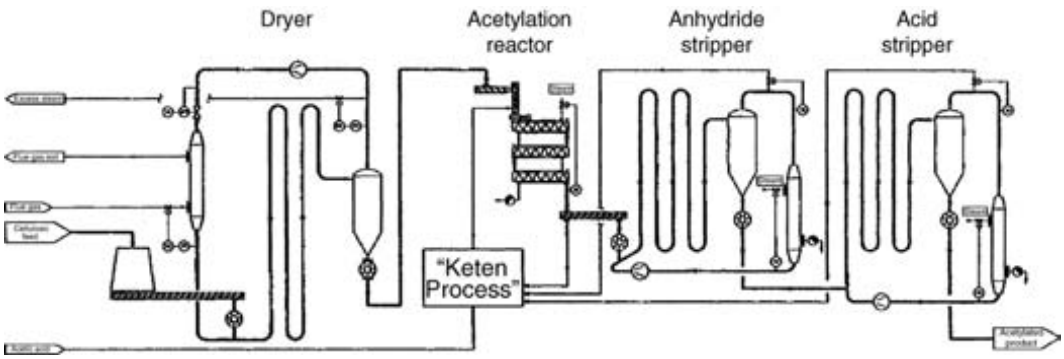

FIGURE 14.8 Schematic of the new fiber acetylation process.

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 one minute. After the second reactor (stripper), superheated vapor and fiber are separated in a cyclone. Part of the superheated vapor is recirculated after heating to the stripper fiber inlet, and the rest 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, which also acts 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 completely dry. The acetylated fiber, as a final treatment, can 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 are thus fiber and acetic acid to cover the acetyl groups introduced in the fiber. This minimizes the transportation and chemical costs and makes the process much more cost-effective.

Figure 14.9 shows the pilot plant being assembled. 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 per hour, which equals 12 tons per day or about 4000 tons per year of acetylated wood fiber. The process can be applied to any wood fiber, and fiber other than wood will be used.

14.5.2 The Solid Wood Microwave Process

Microwave energy has been shown to heat acetic anhydride and acetic anhydride–impregnated wood (Larsson-Brelid and Simonson 1997, 1999, Larsson-Brelid et al. 1999, Risman et al. 2001).

FIGURE 14.9 Acetylation pilot plant being assembled in Kvarntorp, Sweden.

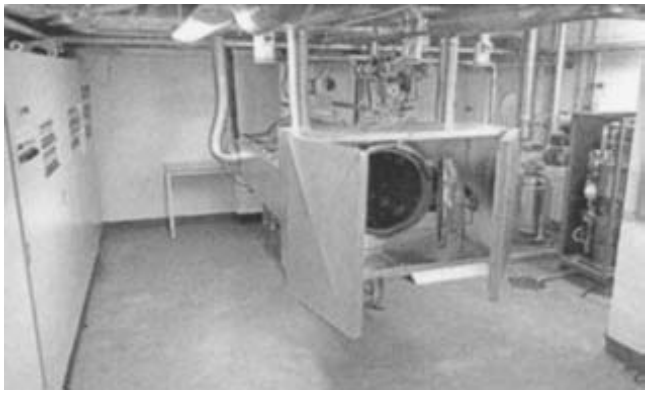

FIGURE 14.10 Microwave solid wood acetylation reactor.

Figure 14.10 shows the microwave reactor. The absorption of microwave energy in acetic anhydride–impregnated wood is preferred over 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 a vacuum, then pressure is applied for a short time, followed by another vacuum step to remove excess anhydride. 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%. Microwave energy can also be used to remove the excess acetic anhydride and byproduct acetic acid after acetylation.

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Roger M. Rowell

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