



Forest Products Abstracts

Review Article

December, 1983
Vol. 6
No. 12

† Chemical Modification of Wood

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Summary

Chemical modification of wood to impart resistance to termites, decay, and marine organisms, and increase dimensional stability depends on adequate distribution of reacted chemicals in water-accessible regions of the cell wall. It is essential that the chemicals used for wood modification be capable of swelling wood to facilitate penetration and react with cell wall polymer hydroxyl groups under neutral or mildly alkaline conditions at temperatures at or below 120°C. The chemicals should react quickly with hydroxyl groups yielding stable chemical bonds, with no byproducts, and the modified wood must still possess the desirable properties of untreated wood. Chemicals that have been used to modify wood include anhydrides, acid chlorides, carboxylic acids, isocyanates, aldehydes, alkyl chlorides, lactones, nitriles, and epoxides. Reaction of these chemicals with wood yields a modified wood with good biological resistance and greatly improved dimensional stability. The reaction takes place in the cell wall as evidenced by increases in wood volume in proportion to the volume of chemical added, leach resistance, and infrared data. Studies on the distribution of bonded chemical show good penetration into cell wall structure. The lignin component is highly substituted while lesser amounts of bonded chemical are in the carbohydrate components.

1 Introduction

Wood is a three-dimensional, polymeric composite made up primarily of cellulose, hemicellulose, and lignin. These polymers make up the cell wall and are responsible for most of the physical and chemical properties exhibited by wood. Wood is a preferred building/engineering material because it is economical, low in processing energy, renewable, strong, and aesthetically pleasing. It has, however, several disadvantageous properties such as biodegradability, flammability, changing dimensions with

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varying moisture contents, and degradability by ultraviolet (UV) light, acids, and bases. These properties of wood are all the result of chemical reactions involving degradative environmental agents. Wood, for example, is biologically degraded because organisms recognize the polysaccharide polymers in the cell wall and have very specific enzyme systems capable of hydrolysing these polymers into digestible units. Because high molecular weight cellulose is primarily responsible for strength in wood, strength is lost as this polymer undergoes biological degradation through oxidation, hydrolysis, and dehydration reactions. The same types of reactions take place in the presence of acids and bases.

Changing moisture content changes wood dimension because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding. This moisture swells the cell wall and the wood expands until the cell wall is saturated with water. Water, beyond this saturation point, is free water in the void structure and does not contribute to further expansion. This process is reversible and shrinkage occurs as moisture is lost.

Wood burns because the cell wall polymers undergo hydrolytic, oxidation, dehydration, and pyrolytic reactions with increasing temperature, giving off volatile, flammable gases. The lignin component contributes more than do other polymers to char formation, which helps insulate wood from further thermal degradation.

Wood exposed outdoors undergoes photochemical degradation primarily in the lignin component, due to UV light, which gives rise to characteristic colour changes. Because the lignin acts as an adhesive in wood, and holds cellulose fibres together, the wood surface becomes richer in cellulose content as the lignin degrades. Cellulose is much less susceptible to UV degradation and these poorly bonded fibres are washed off the surface during a rain, exposing new lignin to continue the degradative reactions. This 'weathering process' in time can account for a significant loss in surface fibres.

Because all of these degradative effects are chemical in nature, it should be possible to eliminate or decrease the rate of degradation by changing the basic chemistry of the wood cell wall polymers. By reacting chemicals with the hydroxyls on the cellulose component, for example, the highly specific biological enzymatic reactions cannot take place because the chemical configuration and molecular conformation of the substrate has been altered. Bulking the cell wall with bonding chemicals would reduce the tendency of wood to swell or shrink with changes in moisture, because the wood would already be in a partially, if not completely, swollen state.

It is possible to change the basic chemistry and, therefore, the properties of wood cell wall polymers through chemical reactions. Thus chemically modifying the cell wall polymer could result in wood products with greatly enhanced properties. Chemical modification is defined as a chemical reaction between some reactive part of a wood component and a simple single chemical reagent, with or without catalyst, to form a covalent bond between the two. By far the most abundant reactive chemical sites in wood are the hydroxyl groups on cellulose, hemicellulose, and lignin. Most of the research done in the area of chemical modification involves the reaction of these hydroxyl groups (Rowell, 1975a).

A review of the history of chemical modification shows that the bulk of the research conducted was aimed at improving either biological resistance or dimensional stability. Chemical modification of wood for biological resistance is based on the theory that the enzymes (cellulases) must directly contact the substrate (wood cellulose), and the substrate must have a specific configuration. If the cellulosic substrate is chemically changed, this highly selective reaction cannot take place. Chemical modification can also change the hydrophilic nature of wood. In some cases water, a necessity for decay organisms, is excluded from biological sites. The chemicals used for modification need not be toxic to the organism because their action renders the substrate unrecognizable as a food source to support microbial growth. In other words, the organisms starve in the presence of plenty.

By far the greatest amount of research for dimensional stability of wood has been carried out in the area of cell wall bulking treatments. Rowell & Ellis (1978) have shown that the increase in wood volume upon treatment is directly proportional to the theoretical volume of chemical added. The volume of wood increases with increasing chemical added to about 25 weight percent gain at which point the treated volume is approximately equal to green volume (Rowell *et al.*, 1976). When this bulked wood comes into contact with water, very little additional swelling can take place. This is the mechanism for the effect of bulking treatments on dimensional stability.

The degree of dimensional stability given to wood by different treatments is described by a variety of terms: antishrink efficiency (ASE), swelling percent, dimensional stabilization efficiency, antiswelling efficiency, and percent reduction in swelling. Generally they are calculated as follows:

$$S = \frac{V_2 - V_1}{V_1} \times 100$$

where S = volumetric swelling coefficient, V_2 = wood volume after humidity conditioning or wetting with water, and V_1 = wood volume of oven-dried sample before conditioning or wetting,

then

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

where ASE = reduction in swelling, or antishrink efficiency resulting from a treatment, S_2 = treated volumetric swelling coefficient, and S_1 = untreated volumetric swelling coefficient.

2 Requirements for reaction

2.1 Penetration

In whole wood, accessibility of the treating reagent to the reactive chemical sites is a major consideration. Penetration of the reagent can be achieved through swelling of the wood structure. If a reagent potentially capable of modifying wood does not swell wood substance, then perhaps a suitable catalyst would. If both reagent and catalyst were unable to swell the wood, a workable cosolvent could be applied to the reaction system.

Several researchers have studied the swelling of wood by various organic liquids (Stamm, 1936, 1964; Nayer, 1948; Kumar, 1957, 1958; Ashton, 1973, 1974). For the most part, these studies consisted of soaking oven-dried blocks of wood for prolonged periods in anhydrous organic liquids at room temperature. The degree of swelling or swelling coefficient represents an unadjusted average swelling coefficient and is usually expressed as a three-dimensional function, i.e. volumetric swelling coefficient. For comparative purposes, volumetric swelling coefficients are usually standardized to a volumetric swelling coefficient compared with water (setting water at 10). If, for example, the unadjusted average volumetric swelling coefficient for water was experimentally determined to be 11.7, this could be standardized to 10 by dividing 1.17 into 11.7. All other volumetric swelling coefficient values obtained would then be divided by 1.17 to standardize them to a water value of 10. In other words, adjustment is made by dividing experimental volumetric swelling coefficient values by one-tenth the average volumetric swelling coefficient value for the wood blocks treated with water.

Tables 1, 2 and 3 give the volumetric swelling coefficients for southern pine sapwood for various potential reagents, catalysts, and solvents (Rowell & Hart, 1981). These were determined under two sets of conditions. One set of oven-dried southern pine sapwood blocks were measured and their volume determined. From this large set, 10 specimens were submerged in a solution and either treated at 120°C, 150 lb/in², for 1 hour, or soaked at 25°C for 48 hours.

Table 1. Volumetric swelling coefficients (*S*) for southern pine sapwood in various reagents

Reagent	<i>S</i>		Reagent	<i>S</i>	
	120°C, 150lb/in ² 1 hour	25°C soaking		120°C, 150lb/in ² 1 hour	25°C soaking
Methyl isocyanate	52.6	5.1	Acrolein	6.7	7.0
Acetic anhydride	12.3	1.5	Propylene oxide	5.2	5.0
Formaldehyde solution	12.3	12.3	Acrylonitrile	4.6	4.5
Water	10.0	10.0	Methyl isothiocyanate	4.5	4.1
Epichlorohydrin	6.9	5.9	Butylene oxide	4.1	0.7

Table 2. Volumetric swelling coefficients (*S*) for southern pine sapwood in various catalysts

Catalyst	<i>S</i>		Catalyst	<i>S</i>	
	120°C, 150lb/in ² 1 hour	25°C soaking		120°C, 150lb/in ² 1 hour	25°C soaking
n-Butylamine	15.5	15.2	Water	10.0	10.0
Piperidine	13.3	0.0	Diethylamine	5.0	11.0
Dimethylformamide	12.8	12.5	N-methylaniline	2.6	0.8
Pyridine	11.3	13.1	N-methylpiperidine	2.2	1.6
Acetic acid	11.1	8.8	N,N-dimethylaniline	0.3	0.5
Aniline	11.0	0.5	Triethylamine	-0.1	2.1

Table 3. Volumetric swelling coefficients (*S*) for southern pine sapwood in various solvents

Solvent	<i>S</i>		Solvent	<i>S</i>	
	120°C, 150lb/in ² 1 hour	25°C soaking		120°C, 150lb/in ² 1 hour	25°C soaking
Dimethylsulfoxide	13.3	11.7	Dichloromethane	3.8	3.3
Dimethylformamide	12.8	12.5	Methyl ethyl ketone	3.6	5.0
Cellosolve	10.6	10.2	Ethyl acetate	2.4	4.2
Methyl cellosolve	10.3	10.0	Cyclohexanone	2.3	0.5
Water	10.0	10.0	4-methyl-		
Methanol	9.0	9.3	2-pentanone	0.4	1.5
1,4-dioxane	6.5	0.6	Xylenes	0.1	0.2
Tetrahydrofuran	5.4	7.2	Cyclohexane	0.1	0.1
Acetone	5.1	5.6	Hexanes	-0.2	0.2

The volumetric swelling coefficients for potential reagents under the two conditions are nearly the same, except for methyl isocyanate and acetic anhydride (Table 1). The amount of swelling for these two reagents is much greater at 120°C than at 25°C. The reason for this is that, at 120°C, reaction of wood has occurred with both methyl isocyanate and acetic anhydride. The large increase in volume at 120°C is due to reacted chemicals bulking the cell wall. Much less consistency between the two treating conditions is seen in Table 2, with catalysts. Piperidine and aniline have high swelling coefficients at 120°C but very low at 25°C. If the soaking at 25°C is continued, piperidine will reach an equilibrium swelling coefficient of 13.1 after 90-100 days (Stamm, 1936; Nayer, 1948) and aniline reaches a value of 10 after 90 days (Nayer, 1948). Triethylamine actually causes the wood structure to shrink slightly at 120°C. This is also observed with hexane (Table 3).

There are no striking differences between the high and low temperature soaking values for the solvents listed in Table 3. There seems to be a correlation between hydrophilic nature and degree of swelling. Stamm (1964) suggested that some solvents are actually swelling carbohydrate-type polymers in the cell wall, while others swell lignin. Nayer (1948), Kumar (1957, 1958) and Stamm (1964) have attempted to correlate observed swellabilities with certain physicochemical properties of the liquids. A few general trends were noted between degree of swelling and dielectric constant, surface tension, dipole moment, molecular size, and tendency to hydrogen-bond with methanol; but no correlation was found to be without exception.

Much research has been conducted on the swelling of wood with water. It is known that this swelling is directly related to the density of the wood (Haslam & Werthan, 1931; Erickson, 1955; Stamm, 1964). A major contributor to swelling is the summerwood of most species, which has a density more than twice that of springwood.

Many physical differences exist between summerwood and springwood. In softwoods, springwood tracheids have thin cell walls, large lumens with ends overlapping those of other tracheids, and large and numerous pit-pairs distributed along the radial face; however, pit-pairs are most abundant on the other ends where tracheids overlap each other. Summerwood tracheids have thick cell walls, narrow lumens, and fewer and smaller pit-pairs on the radial wall. In addition, the summerwood tracheids are predominantly pitted on their tangential walls (Phillips 1933; Thomas & Scheld 1964).

The thick cell walls of the summerwood, mainly owing to a thicker S₂ layer (Meier, 1964), result in less pit aspiration on drying (Griffin, 1919; Huber & Merz, 1958; Nicholas & Siau, 1973). The main flow of liquids in softwoods is through the lumens of tracheids by way of bordered pit-pairs.

A number of studies have been concerned with the penetration of liquids into summerwood and springwood (Griffin, 1919; MacLean, 1924; Erickson, 1937, 1955; Verrall, 1957; Huber & Merz, 1958; Gjovik *et al.*, 1970; Nicholas, 1972; Nicholas & Siau, 1973). Under atmospheric pressure, the penetration of nonpolar liquids into softwood summerwood may be due, in part, to capillary action in the very small lumens and passage through unspirated pit membranes; in the aspirated springwood, this would not occur. Penetration of nonpolar liquids may also be through drying checks in the thick summerwood cell walls. As the temperature and pressure of the liquid are raised, penetration of polar liquids in springwood would be expected to increase owing to softening of the pit structure and displacement of the pit membrane. Since the cell walls of springwood are thinner than summerwood, penetration into springwood walls would be quicker and facilitated by swelling. Thomas (1969) also noted that incrustation occurs in the pit membranes of southern pine summerwood; this would retard liquid penetration.

2.2 Reactants

Cellulose, the hemicelluloses and lignin are distributed throughout the wood cell wall. These three hydroxyl-containing polymers make up the solid phase of wood. The void structure or lumens in Wood can be viewed as a bulk storage reservoir for potential chemical reactants used to modify the cell wall polymers. For example, the void volume of southern pine springwood with a density of 0.33 g/cm³ is 0.77 cm³/cm³ or 2.3 cm³/g of wood. For summerwood with a density of 0.70 g/cm³, the void volume is 0.52 cm³/cm³ or 0.74 cm³/g. The cell wall can also swell and act as a chemical storage reservoir. For southern pine, the cell wall storage volume from oven-dry to water-swollen is 0.77 cm³/cm³. These data show that there is more than enough volume in the voids in wood to house sufficient chemical for reaction to take place with the cell wall polymers.

Potential reactants must contain functional groups that will react with hydroxyl groups of the wood components. This may seem obvious, but there are many literature reports of chemicals that failed to react with wood components when, in fact, they did not contain functional groups that could react.

The chemical bond desired between the reagent and the wood component is of major consideration. For permanence, this bond should have great stability to withstand environmental stresses. In such cases, the ether linkage may be the most desirable covalent carbon-oxygen bond. These are more stable than the glycosidic bonds between sugar units in the wood polysaccharide, so the carbohydrate polymers would degrade before the bonded ether did. Less stable bonds can also be formed that could be useful for the release of a bonded chemical under environmental stresses. Acetals and esters are less stable than ether bonds, and could be used to bond biological agents or fire retardants onto wood to be released under certain conditions.

It is important that 100% of the reagent skeleton bond to the wood with no byproduct generation. If a byproduct were formed during the reaction, a recovery system might have to be considered for economic reasons.

Handling problems are created by gas reactants, as high pressure equipment is required. The level of chemical substitution is usually lower than liquid systems, and penetration of gaseous reagents can be very difficult. The best success, to date, of chemical systems is with low boiling liquids that easily swell wood. If the boiling point is too high, it is difficult to remove excess reagent 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.

Some chemicals react with a single hydroxyl group and the reaction is complete. Such is the case, for example, with methylation using methyl iodide. Other chemicals, in the course of reacting, form a new hydroxyl group which reacts further. Epoxides react in this way. In other words, single-site substitution occurs in cases like methylation, while polymer formation from a single graft point occurs in cases like epoxidation. This will be discussed in detail later.

From the standpoint of industrial application of reagents for wood, toxicity, corrosiveness and cost are important factors for chemical selection. The reacted chemicals should not be toxic or carcinogenic in the finished product, and the reactant itself should be as nontoxic as possible in the treating stage. This is somewhat difficult to achieve since chemicals that react easily with wood hydroxyl groups will also react easily with blood and tissue hydroxyl-containing polymers. The reactants should be as noncorrosive as possible to eliminate the need for special treating equipment. In the laboratory experimental stage, high cost of chemicals is not a major consideration. For commercialization of a process for the chemical modification of wood, chemical cost is important.

2.3 Reaction conditions

There are certain experimental conditions that must be considered before a reaction system is selected. The temperature required for complete reaction must be low enough to cause little or no wood degradation yet enable the rate of reaction to be relatively fast. A safe upper limit is about 120°C since little degradation occurs at this temperature for a short period of time.

It is impractical to dry wood to less than 1% moisture, but the water content of the wood during reaction is, in most cases, critical. The hydroxyl in water is more reactive than the hydroxyl groups available in wood components, i.e., hydrolysis is faster than substitution. The most favourable condition is a reaction system in which the rate of reagent hydrolysis is relatively slow.

It is also important to keep the reaction system simple. Multicomponent systems that require complex separation after reaction for chemical recovery should be avoided. The optimum would be for the reacting chemical to swell the wood structure and act as the solvent as well.

Almost all chemical reactions require a catalyst. With wood as the reacting substrate, strong acid catalysts cannot be used as they cause extensive degradation. The most favourable catalyst from the standpoint of wood degradation is a weakly alkaline one, which in many cases also swells the wood structure and gives better penetration (see Table 2). The catalyst used should be effective at low reaction temperatures, easily removed after reaction, nontoxic, and noncorrosive. In most cases, the organic tertiary amines are best suited for this purpose.

The reaction conditions must be mild enough that the reacted wood still possesses the desirable properties of wood: the strength must remain high; little or no colour change (unless a colour change is desirable); good electrical insulation; not dangerous to handle; glueable; and paintable.

3 Reactions with wood

3.1 Esters

3.1.1. Acetylation

The most studied of all the chemical modification treatments for wood has been acetylation. The early work was done with acetic anhydride catalysed with pyridine (Stamm & Tarkow, 1947) or zinc chloride (Ridgway & Wallington, 1946). In the reaction with acetic anhydride, acetylation occurs and acetic acid is split out as a by product:



The reaction is acid or base catalysed, and many catalysts have been tried including potassium and sodium acetate (Tarkow, 1959), dimethylformamide (Risi & Arseneau, 1957a; Clermont & Bender, 1957; Baird, 1969), urea-ammonium sulphate (Clermont & Bender, 1957), magnesium perchlorate (Arni *et al.*, 1961b; Ozolina & Svalbe, 1972; Truksne & Svalbe, 1977), trifluoroacetic acid (Arni *et al.*, 1961b), boron trifluoride (Risi & Arseneau, 1957a) and γ -rays (Svalbe & Ozolina, 1970). Goldstein *et al.* (1961) found the best acetylation condition to be uncatalysed acetic anhydride in xylene at 100-130°C.

Acetylation is a single-site reaction, that is, one acetyl per reacted hydroxyl group with no polymerization. This means that all the weight gain in acetyl can be directly converted into units of hydroxyl groups blocked. This is not true for a reaction in which polymer chains are formed. In this case, the weight gain cannot be converted into units of blocked hydroxyl groups.

At weight percent gains above 17, acetylated wood has been found by soil-block tests (90 days) to be resistant to attack by the fungi *Coniophora puteana* (Goldstein *et al.*, 1961), *Lentinus lepideus*

(Goldstein *et al.*, 1961), *Poria incrassata* (Goldstein *et al.*, 1961; Tarkow *et al.*, 1950). *Polyporus versicolor* [*Coriolus versicolor*] (Goldstein *et al.*, 1961; Tarkow *et al.*, 1950, Koppers, 1961), *Gloeophyllum trabeum* (Goldstein *et al.*, 1961; Koppers, 1961; Peterson & Thomas, 1978), *Poria monricola* (Goldstein *et al.*, 1961), *Poria microsporia* (Tarkow *et al.*, 1950), and *Coniophora cerebella* [*C. puteana*] (Ozolina & Svalbe, 1966; Rugevita, 1977; Svalbe *et al.*, 1978; Bekere *et al.*, 1978). Acetylated laminated veneers of yellow birch in ground contact stake tests at 19.2% weight gain had an average life of 17.5 years compared to 2.7 years for untreated controls (Gjovik & Davidson, 1973).

Acetylation to 20-25% weight gain shows a 70% reduction in swelling or antishrink efficiency (ASE) (Tarkow *et al.*, 1950; Koppers, 1961; Krylova, 1977; Sidorenko *et al.*, 1973). Southern yellow pine weathered for 12 months shows a slight decrease in acetyl content and a reduction in ASE from 78% to 64% (Koppers, 1961).

Dreher *et al.* (1964) found that acetylated wood is more dense than untreated wood and has fewer fibres of lignocellulose per unit volume. This is due to the bulking of the acetate whose density is greater than water. There is a slight wood colour change (usually darkening) upon acetylation with uncatalysed acetic anhydride with much of the natural wood brilliance lost (Goldstein & Weaver, 1963). The change in colour with catalysed acetylation varies depending on the reaction conditions and catalyst. Colour changes ranging from a slight darkening to almost black with pyridine and dimethylformamide have been found.

Acetylated wood has reduced permeability to gases compared with untreated wood (Kumar *et al.*, 1979). This is thought to be due to the bulking chemical restricting pore space. This reduction in permeability also reduces the moisture absorption by a factor of 2 to 3 (Rugevita *et al.*, 1977) as well as overall water resistance (Shiraishi *et al.*, 1972; Grinberg & Okonov, 1975). Acetylation in a N_2O_4 - N,N -dimethylformamide-pyridine system causes a permanent loss of crystallinity of the cellulose (Narayanamurti & Handa, 1953; Shiraishi *et al.*, 1976). This was found to give a uniform distribution of acetyl groups in cellulose.

The mechanical properties of acetylated wood are, in general, improved over those of untreated wood. Shear strength parallel to the grain is decreased (Dreher *et al.*, 1964), however, and there is a slight decrease in the modulus of elasticity (Narayanamurti & Handa, 1953) with 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, fibre stress at proportional limit, and work to proportional limit (Dreher *et al.*, 1964) are increased. Modulus of rupture is increased for softwoods, but decreased for hardwoods (Dreher *et al.*, 1964).

A 2-year paint study (Tarkow *et al.*, 1950) showed acetylated wood to be a better painting surface than untreated wood. Ultraviolet radiation darkens unacetylated wood, but there is no change or a slight bleached effect with acetylated wood. In general, adhesive performance is reduced (Goldstein & Weaver, 1963). Adhesive strength is reduced with urea-formaldehyde resins (Narayanamurti & Handa, 1953; Rudkin, 1950) and casein glues (Rudkin, 1950), but very little effect is observed with resorcinol-formaldehyde resins (Rudkin, 1950).

Many of the properties of acetylated wood depend on the method of acetylation. The temperature of treatment, time of reaction, and type and amount of catalysts all play a significant role in the extent of fibre degrade during treatment. The amount of moisture present in the wood is also important. Some moisture (2-5%) seems to be needed for best reaction, but above this level the water hydrolyses the acetic anhydride to acetic acid. This loss by hydrolysis accounts for a 5.7% loss of anhydride with each 1% of water in the wood (Goldstein *et al.*, 1961). The rate of acetylation decreases as moisture content increases (Tarkow *et al.*, 1950).

The anhydride method of acetylation gives an acid byproduct which results in an acidic condition in the wood and a loss of 50% of the reaction chemical. These byproducts must be removed to prevent degrade. Acetic acid, the byproduct of acetylation with acetic anhydride, is virtually impossible to remove completely from wood. This results in: (1) a product that always smells of acetic acid, (2) acid conditions present in the wood which catalyse the removal of more acetyl groups, (3) an acid hydrolysis of cellulose fibres resulting in strength losses over a long term, and (4) acid corrosion of metal fasteners used in the wood product.

Acetylation can also be done by vapour-phase treatments, but the diffusion rate varies inversely as the square of the thickness (Tarkow *et al.*, 1950; Avora *et al.*, 1979). Because of this, it has only been applied to thin veneers.

Another method for the acetylation of wood involves the reaction with ketene gas dissolved in acetone or toluene (Tarkow, 1945; Karlson & Svalbe, 1972a, 1972b; Svalbe, 1977; Karlson & Svalbe, 1977):



Reactions done at 55-60°C for 6-8 hours gave weight gains of 22% (Karlson & Svalbe, 1972b). Much of the work with ketene, however, has resulted in much lower weight gains. At the higher level of treatment, the acetylated wood showed a reduction in water absorption by 35%, tangential swelling by 77%, and radial swelling by 69% (Karlson & Svalbe, 1972a).

Singh *et al.* (1979) found that vapour phase acetylation with thioacetic acid gave a modified wood with slightly lower weight gains than acetylation with acetic anhydride. At weight gains of about 17%, the treated wood had an ASE of 48%. Thioacetic acid is less corrosive than acetic anhydride, but the treated wood continues to emit hydrogen sulphide because of the entrapment of small amounts of thioacetic acid.

In spite of the vast amount of research in the acetylation of wood, no commercial application has been realized. Two attempts, one in the United States (Koppers, 1961) and one in Russia (Otlensov & Nikitina, 1977; Nikitina, 1977). came close to commercialization but were discontinued presumably because they were not cost-effective.

3.1.2 Phthalylation

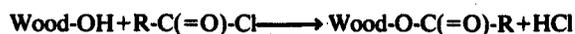
Using phthalic anhydride to modify wood gives a product that has a very high initial ASE which decreased in a repeated water-soak ASE test (Risi & Arseneau, 1958). Starting at 100% ASE on the first soak cycle, the ASE value drops to about 70% on the second cycle, 60% on the third, down to 50% on the sixth cycle. Popper & Bariska (1972) found that there is a corresponding loss of bonded chemical after each soaking, showing the susceptibility to hydrolysis of the phthalyl group. Phthalyl groups have a greater affinity for water than do the hydroxyl groups in wood, so phthalylated wood is more hygroscopic than untreated wood (Popper & Bariska, 1972, 1973). While the mechanism of ASE effectiveness by acetylation is by chemical blocking of the hydroxyl groups, phthalylation operates mainly by mechanical bulking of the submicroscopic pores in the wood cell wall (Popper & Bariska, 1975). It is interesting to note that very high weight gains are achieved with phthalylation (Risi & Arseneau, 1958; Popper, 1973). Most researchers have found acetylation weight gains from 15-21%; phthalylation weight gains from 40 to 130% have been reported (Risi & Arseneau, 1958; Popper, 1973). These high weight gains may result from a polymerization reaction.

3.1.3 Other anhydrides

Other anhydrides have been reacted with wood. Propionic and butyric anhydrides in xylene without catalyst react with wood, but at a slower rate than acetic anhydride (Goldstein *et al.*, 1961). Comparing acetic, propionic, and butyric anhydride reacted in xylene at 125°C with ponderosa pine, after 10 hours' reaction time the weight gain for acetylation was 17%, for propionylation less than 4%, and for butyrylation no weight gain. After 30 hours of reaction with propionic anhydride, a weight gain of 10% was achieved. Little or no weight gain resulted from reaction with butyric anhydride (Goldstein *et al.*, 1961).

3.1.4 Acid chlorides

Acid chlorides can also be used in esterification reactions (Suida, 1930). The product is the ester of the reacted acid chloride, with hydrochloric acid as a byproduct:



Using lead acetate as a catalyst with acetyl chloride, Singh *et al.* (1981) found a lower acetyl content than with the acetic anhydride method. Much higher ASE values, however, were obtained with acetyl chloride (60-84% for acetyl chloride versus 47% for acetic anhydride). Use of a 20% lead acetate solution reduced the amount of free hydrochloric acid released in the reaction. This very strong acid causes extensive degradation of the wood, and because of this very little work has been done in this area.

3.1.5 Carboxylic acids

Carboxylic acids have been esterified to wood catalysed with trifluoroacetic anhydride (Arni *et al.*, 1961a, 1961b; Nakagami *et al.*, 1974). Several unsaturated carboxylic acids were found to react with wood by the trifluoroacetic anhydride 'impelling' method to give an increase in oven-dry volume and antishrink efficiency, and a decrease in wood crystallinity and moisture content (Nakagami and Yokota 1975). It was found that reactions of wood with β -methylcrotonic acid gave a degree of substitution high enough to make the esterified 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 hemicellulose (Nakagami, 1978; Nakagami & Yokota, 1978).

3.1.6 Isocyanates

In the reaction of wood hydroxyls with isocyanates, a nitrogen-containing ester is formed:



Clermont & Bender (1957) exposed wood veneer swollen in dimethylformamide to vapours of phenyl isocyanate at 100-125°C. No weight gains were reported, but ASE values up to 77% were attained. The modified veneers showed increased mechanical strength with little or no change in colour. Baird (1969) reacted dimethylformamide-soaked cross sections of white pine and Engelmann spruce with ethyl, allyl, butyl, *t*-butyl and phenyl isocyanate. Vapour phase reactions of butyl isocyanate in dimethylformamide gave the best results. ASE's of 47% with a 14% weight gain and 67% at 31% weight gain were observed. Weight gains up to 50% with ASE of 75-80% were reported. The samples treated to 67% ASE had about a 25% reduction in toughness and abrasion resistance.

White cedar was reacted with 2,4-tolylene diisocyanate (Wakita *et al.*, 1977) with and without a pyridine catalyst to a maximum nitrogen content of 3.5 and 1.2, respectively. This corresponds to weight percent gains of 21.8 and 7.5. At the high weight percent gain, an ASE of 50% was achieved. Compressive strength and bending modulus increased with increasing nitrogen content. Beech wood

modified with a diisocyanate (Lutomski, 1975) up to 50% weight gain lost 4.5-8.1% weight after 6-week attack by the fungi *Coniophora cerebella* and *Polystictus versicolor*. After fungal attack, the modified wood lost almost 20% of its static bending strength as compared to modified wood before attack. At chemical add-ons over 18%, wood modified with methyl, ethyl, *n*-propyl and *n*-butyl isocyanates was found to be resistant to attack by *Gloeophyllum trabeum* (Rowell & Ellis, 1981).

Methyl isocyanate reacts very quickly without catalyst to give weight gains up to approximately 75% (Rowell & Ellis, 1979). Maximum ASE values of 60% are obtained at 25-30% weight gain. Above this level of bonded weight gain, the ASE values start to decrease. Scanning electron micrographs show that these high levels of chemical add-on to the cell wall polymers cause splitting in the tracheid wall and not in the intercellular spaces (Rowell & Ellis, 1981). In some cases the splits go through the bordered pits. Once this splitting occurs, ASE starts to drop and continues to drop as chemical weight gain increases. Splitting exposes new fibre surfaces where water can cause swelling. Swelling beyond the green volume takes place because the cell wall is ruptured and no longer acts as a restraint to swelling.

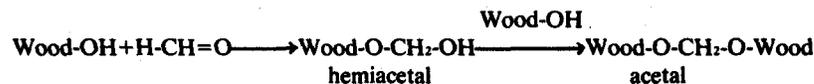
Ethyl, *n*-propyl, *n*-butyl, and phenyl isocyanates also react with wood without the need for a catalyst, but *p*-tolyl-1,6-diisocyanate and tolylene-2,4-diisocyanate require either dimethylformamide or triethylamine as a catalyst (Rowell & Ellis, 1981). High weight gains are observed with these last three isocyanates, but little or no dimensional stability results from the reaction. This indicates that polymerization is taking place in the void structure.

The isocyanates are sensitive to moisture so the reaction needs to be done on dry wood (Rowell & Ellis, 1983a). As wood moisture content increases before reaction, more nonbonded polymers are formed after reaction. Reacted moist wood shows very high ASE values on the first water-soak test, but leaching causes a significant loss in ASE. This shows the bulking chemical is not bonded to the cell wall and comes out upon water leaching.

3.2 Acetals

3.2.1 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:



The two hydroxyl groups may come from (1) hydroxyls within a single sugar residue, (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 reaction occurring on the hemicelluloses, (5) hydroxyls on different lignin residues, and (6) interaction between cellulose, hemicelluloses, and lignin hydroxyls. The possible crosslinking 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 the non-crosslinked form of hemiacetals. These bonds are very unstable and would not survive long after treatment.

The reaction is best catalysed by strong acids such as hydrochloric acid (Tarkow & Stamm, 1953; Burmester, 1970; Ueyama *et al.*, 1961; Minato & Mizukami, 1982), nitric acid (Tarkow & Stamm, 1953), sulphur dioxide (Dewispelaere *et al.*, 1977; Stevens *et al.*, 1979), *p*-toluene sulphonic acid, and zinc chloride (Stamm, 1959; Ueyama *et al.*, 1961). Weaker acids such as sulphurous and formic acid do not work (Tarkow & Stamm, 1953). Schuerch (1968) speculated that bases such as lime water or tertiary amines can initiate the reaction, but attempts with triethylamine were unsuccessful (Rowell, unpublished results).

At weight add-on levels of 2%, formaldehyde-treated wood is not attacked by fungi (Stamm & Baechler, 1960). This is far short of the quantity of crosslinking needed to prevent attack on the basis of hydroxyl blocking for enzyme inhibition. Stamm & Baechler (1960) speculated that crosslinking, which is effective at these low levels, must be tying together structural units. An ASE of 47% is achieved at a weight percent gain of 3.1, 55% at 4.1, 60% at 5.5, and 90% at 7 (Tarkow & Stamm, 1953; Stamm, 1959). Thus, a 4% weight gain results in four times the ASE as would be found by bulking treatments such as acetylation.

The mechanical properties of formaldehyde-treated wood are all reduced from those of untreated wood. Toughness and abrasion resistance are greatly reduced (Tarkow & Stamm, 1953; Stamm, 1959), crushing strength and bending strengths are reduced about 20%, and impact bending strength is reduced up to 50% (Burmester, 1967). These last two measurements were done on Y-ray-treated wood, so part of the strength reduction may be due to this. The loss in toughness is directly proportional to the ASE; i.e., a 60% ASE is equal to a 60% loss in toughness (Tarkow & Stamm, 1953).

A definite embrittlement is observed in formaldehyde-treated wood. This embrittlement may be due to the short inflexible crosslinking unit of the -O-C-O- type. If the inner carbon unit were longer, there would be more flexibility in this unit, and the embrittlement should be reduced. Most of the loss in wood strength properties is probably due to structural cellulose units being hydrolysed by the strong acid catalyst.

3.2.2 Other aldehydes

Acetaldehyde (Tarkow & Stamm, 1953) and benzaldehyde (Tarkow & Stamm, 1953; Weaver *et al.*, 1960) have been reacted with wood using either nitric acid or zinc chloride catalysts. Good ASE is achieved with acetaldehyde modification, but an ASE of only 40% is found for benzaldehyde. Mechanical properties of these treated woods are the same as formaldehyde-treated wood.

Difunctional aldehydes (dialdehydes) have been tried with zinc chloride, magnesium chloride, phenyldimethylammonium chloride and pyridinium chloride as catalysts (Weaver *et al.*, 1960). Glyoxal, glutaraldehyde and α -hydroxyadipaldehyde all show ASE of 40% with weight percent gain of 15 and highest ASE (50%) at 20% weight gain. With these three compounds, crosslinking is possible; however, with the low ASE at high weight percent gain, it is clear that bulking is the mechanism for the ASE achieved.

Chloral (trichloroacetaldehyde) with no catalyst gives a 60% ASE at 30% weight gain (Weaver *et al.*, 1960). After 15 weeks at 70% relative humidity, however, all weight gain was lost as well as the ASE. This shows a very unstable, perhaps reversible, bond formation.

Phthaldehydic acid in acetone catalysed with *p*-toluenesulphonic acid gives ASE of 40% at weight percent gain of 34 (Weaver *et al.*, 1960). A 50-70% ASE is claimed when phthaldehydic acid or its derivatives are cured at 100°C uncatalysed for 16-24 hours (Kenaga, 1957).

Other aldehydes and related compounds have been tried either alone or catalysed with sulphuric acid, zinc chloride, magnesium chloride, ammonium chloride or diammonium phosphate (Weaver *et al.*, 1960). Compounds such as *N,N'*-dimethylolethylene urea, glycol acetate, acrolein, chloroacetaldehyde, heptaldehyde, *o*- and *p*-chlorobenzaldehyde, furfural, *p*-hydroxybenzaldehyde and *m*-nitrobenzaldehyde all achieve ASE by a bulking mechanism and not by low-level crosslinking. At weight percent gains of 15 to 25, the highest ASE reported is 40%.

3.3 Ethers

3.3.1 Methylation

The simplest ether that can be formed is the methyl ether. Reaction of wood with dimethyl sulphate and sodium hydroxide (Rudkin, 1950; Narayanamurti & Handa, 1953) or methyl iodide and silver oxide (Narayanamurti & Handa, 1953) are two systems that have been reported. Methylation up to 15% weight gain did not affect the adhesive properties of casein glues. The mechanical properties of methylated wood are greatly reduced due to the severe reaction conditions required.

3.3.2 Alkyl chlorides

In the reaction of alkyl chlorides with wood, hydrochloric acid is formed as a byproduct:

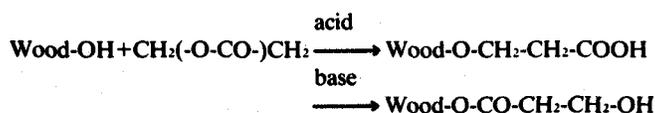


Because of this, strength properties of the treated wood are very poor. Reaction with allyl chloride in pyridine (Kenaga *et al.*, 1950; Kenaga & Sproull, 1951) or aluminium chlorides gives high initial ASE; but, on drying and resoaking, the effects of allylation are lost (Kenaga & Sproull, 1951). In the allyl chloride-pyridine case, the ASE is not due to the formation of allyl ethers in cellulose or lignin, but to the bulking due to the formation of allyl pyridinium chloride polymers which are water soluble and easily leached out (Risi & Arseneau, 1957d).

Other alkyl chlorides reported are crotyl chloride (Risi & Arseneau, 1957b), and *n*- and *t*-butyl chlorides (Risi & Arseneau, 1957c) catalysed with pyridine. Again only temporary ASE is found along with severe degradation caused by the liberated hydrochloric acid.

3.3.3 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 established with the hydroxyl group along with the formation of a free acid end group:



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

Southern yellow pine wood has a pH of approximately 5, and uncatalysed β -propiolactone reactions with this wood give a carboxyethyl derivative (Goldstein *et al.*, 1959). High concentrations of β -propiolactone caused delamination and splitting due to the very high degree of swelling (Rowell, unpublished results).

At a 25% weight gain, treated wood shows good (2% weight loss or less) rot resistance to *Lentinus lepideus*, *Lenzites trabea* [*Gloeophyllum trabeum*], *Poria monticola*, and *Coniophora puteana* in soil-block tests (Goldstein *et al.*, 1959; Goldstein, 1960). Increasing the weight percent gain to 45 did not change the rot resistance in either weathered or unweathered samples. At 30% weight gain, the treated wood has an ASE of 60%.

The major reaction problem with β -propiolactone is that it has recently been labelled a very active carcinogen. For this reason, little future research can be expected on this chemical. It would be interesting, however, to look at this chemical reaction under basic conditions where ester formation occurs.

3.3.4 Acrylonitrile

When acrylonitrile is reacted with wood in the presence of an alkaline catalyst, cyanoethylation occurs:



With sodium hydroxide, weight gain up to 30% has been achieved. At this level, the wood has an ASE of 60%. At 25% weight gain, there is no loss in weight of samples in soil-block tests with *Poria monticola*, *Contiophora puteana*, *Lenzites trabea* [*Gloeophyllum trabeum*], or *Lentinus lepideus* (Gotdstein *et al.*, 1959). With a nitrogen content of 8.5%, the treated wood is resistant to *Poria vaporaria* (Fuse & Nishimoto, 1961). With only 1% fixed nitrogen, the wood is resistant to attack by *Lentinus lepideus*, *Poria monticola*, *Lenzites trabea* [*Gloeophyllum trabeum*], and *Polyporus versicolor* [*Coriolus versicolor*] (Baechler, 1959, 1969). Cyanoethylated stakes in ground contact at 15% weight gain have an average life of 7.8 years, compared with 3.9 years for untreated stakes (Gjovik & Davidson, 1973).

To show that the decay resistance observed is due to a bulking mechanism and not the toxicity of acrylonitrile or its reaction products, Baechler (1959) extracted cyanoethylated wood with hot water and the leachate showed no toxic effects to *Lenzites trabea* [*Gloeophyllum trabeum*]. The leached blocks lost their decay resistance, which may be due to the reaction of acrylonitrile with the ammonia catalyst that was used forming water-soluble polymers in the cell wall.

Cyanoethylated wood (using sodium hydroxide as catalyst) had a lower impact strength than untreated wood (Goldstein *et al.*, 1959). Kenaga (1963), using 25% acrylonitrile in methanol followed by exposure to 10^7 rads of ionizing radiation, found an ASE of only 40% at a weight percent gain of 29. This low ASE may be due to the acrylonitrile reacting with the methanol and forming polymers in the lumen rather than in the cell wall.

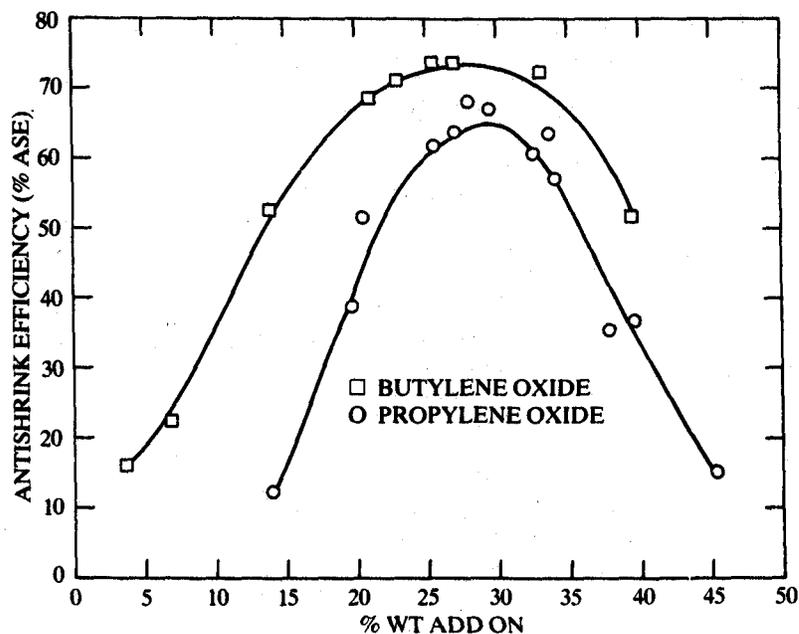
3.3.5 Epoxides

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



The simplest epoxide, ethylene oxide, catalysed with trimethylamine has been used as a vapour phase treatment. At a weight percent gain of 20, McMillin (1963) found a 60% ASE. An ASE of 82% with a weight percent gain of 10 for the same process or with propylene oxide has been claimed by Liu & McMillin (1965). Under similar conditions, a weight percent gain of 22 gives less than 1% tangential and radial shrinkage (Mo & Domsjö, 1965). Using an oscillating pressure rather than a constant pressure

Figure 1. Relation between antishrink efficiency and chemical add-on due to epoxide modification.



system with ethylene oxide and trimethylamine, an ASE of 42% is found for weight percent gain of 11 (Barnes *et al.*, 1969). More recent work (Rowell, 1975b) with propylene oxide, butylene oxide, and epichlorohydrin shows ASE of 70% at weight percent gains of 22 to 25. If sodium hydroxide is used with ethylene oxide in a vapour treatment, extensive swelling results which causes bursting of the wood structure (Zimakov & Pokrovskil, 1954).

As with the methyl isocyanate system, high weight gains with propylene and butylene oxides cause the ASE to fall (Fig. 1) (Rowell *et al.*, 1976). For propylene oxide, the maximum ASE (60-70%) is attained at weight percent gains between 25 and 33. For butylene oxide, a wider range of maximum ASE is observed: 60-73% ASE at weight percent gains between 21 and 33. The difference between these two may be due to the greater hydrophobia of butylene oxide and the difference in molecular weight. Both treatments show a downward trend in ASE above about 33% weight gain.

Electron micrographs show the effects of high chemical add-on (Rowell *et al.*, 1976). At a weight percent gain of about 33, checks start to form in the tracheid walls and at 45 weight percent gain these checks become very large. The splitting is always observed in the tracheid wall, not in the intercellular spaces; in some cases the splits go through the border pits. Most of the checks occur in the summerwood portion of the treated wood. The less dense springwood may be able to accommodate more chemical before the cell wall would rupture. It is also possible that there is less chemical add-on in the springwood. If so, and since the weight percent gain is an average for the whole sample, the weight percent gain in the summerwood would be higher than 33 when cell wall rupture occurs.

Only the epoxide and isocyanate treatments have been reported to add to wood cell wall components to such a degree that they cause the wood structure itself to break apart (Rowell *et al.*, 1976; Rowell & Ellis, 1981). All other reported chemical substitution treatments of wood components add to wood up to about 35% weight gain, and no cell wall rupture has been observed. The epoxide and isocyanate system seems to swell the cell wall, react with it, and continue to swell and react to the point of cell wall rupture and beyond.

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 is probably short owing to chain transfer. The formation of a polymer located in the cell wall may be the cause of cell wall rupture at high chemical weight gains. At approximately 20% weight gain the volume of the treated wood is equal to the original untreated green volume (Kumar *et al.*, 1979). Above about 30% weight gain, the volume of the treated wood is larger than that of green wood. This is the level where the ASE starts to drop, which may mean the polymer loadings are now so high they have broken the cell wall and allowed the wood to superswell above the green volume.

The simple epoxides are sensitive to moisture levels in the wood during reaction (Rowell & Ellis, 1983a). The propylene oxide reaction system seems to be the most affected by moisture, as shown by both high weight losses by extraction of nonbonded chemical and by losses in ASE. The butylene oxide system is less sensitive to moisture, but still large amounts of nonbonded glycols are formed.

Soil burial tests with epichlorohydrin- or dichlorohydrin-treated specimens show no decay after 2 months (Pihl & Olsson, 1968). Longer field tests show that butylene oxide stakes, treated above 20% weight gain, resist attack by ground organism after 7 years in both northern and southern United States exposures (Rowell, 1982a). Laboratory soil-block tests with the brown-rot fungi *Gloeophyllum trabeum* (Rowell, 1975b, 1982a) and *Lentinus lepideus* (Rowell, 1975b) and with the white-rot fungus *Coriolus versicolor* (Rowell, 1982a) show butylene oxide-modified wood to be resistant to attack above about 17% weight gain.

Butylene oxide-modified blocks were also found to be resistant to attack by subterranean termites (*Reticulitermes flavipes*) (Rowell *et al.*, 1979). Resistance seems attributable primarily to the wood's unpalatability. While the wood treated to higher weight percent gains lost little weight under attack, termite mortality paralleled that for a starvation set. Mortality may be attributable to either an enhanced starvation effect or a slow-acting toxic effect. These two options are difficult to assess because pathogenic microbes in groups of starvationally weakened termites confound interpretation of results.

Unmodified control specimens are destroyed by marine borer attack in less than 1 year in a marine environment. Epoxide-modified specimens have been in test for over 5 years with very little marine borer attack (Rowell, 1982a). The effectiveness mechanism of modified wood in resisting attack by marine organisms is unknown. As with the laboratory termite tests, unpalatability may be the largest single factor.

Most of the mechanical properties of propylene oxide-modified wood are reduced (Rowell *et al.*, 1982). The modulus of elasticity is reduced by 14%, modulus of rupture reduced 17%, fibre stress at proportional limit reduced 9%, and maximum crushing strength reduced 10% (Rowell *et al.*, 1982). Ethylene oxide-modified wood showed no reduction in static bending tests (McMillin, 1963).

Radial, tangential, and longitudinal hardness indexes of propylene oxide-modified wood were the same as untreated controls (Rowell *et al.*, 1982). The diffusion coefficient to water vapour was increased by 29%.

The thermal stability of modified wood, as shown by both thermogravimetric analysis and evolved gas analysis decomposition temperatures, was slightly increased by epoxide bonding and by acetyl bonding and was slightly lowered by isocyanate bonding as compared with controls (Rowell *et al.*, 1983). The amount of char generated during pyrolysis was nearly the same for untreated wood and acetyl- and isocyanate-bonded wood, and less for epoxide-bonded wood. The epoxide bond seemed to stabilize the

components that degraded at 325°C (hemicelluloses), and this component apparently gasified along with the cellulose component at 385°C. The ether linkage is more chemically stable and apparently more thermally stable than the acetyl linkage bonded to the polysaccharides. Thus, the bonded epoxide may still have been bonded to the carbohydrate at the temperature at which carbohydrate pyrolysis occurred.

Acetyl- and isocyanate-bonded chemicals did not stabilize the components degrading at 325°C, but showed the same thermogravimetric and evolved gas analysis profiles as did the controls. Because ester and urethane bonds are not as stable to pyrolysis as either linkages at high temperatures, there was a partial release of bonded chemical at low temperatures (Rowell *et al.*, 1983).

Evolved gas analysis showed that the epoxide-bonded wood had a higher heat of combustion of volatiles than did the control. The heat of combustion of volatile products from acetyl and methyl isocyanate-bonded wood was almost the same as that of the control. The high heat of combustion of volatiles observed for epoxide-bonded wood is primarily due to the hydrocarbon content attached to the bonding group. The epoxide bonding group $-CH_2-CH-$ accounts for part of the heat of combustion, but the $-CH_2$ and $-CH_2CH_3$ added by propylene and butylene oxides, respectively, also contribute (Rowell *et al.*, 1983).

4 Types of wood

For the most part, chemical modification has been done with relatively few species of wood. Among the softwoods, Douglas-fir, ponderosa pine, and southern pine have commonly been used. Among the hardwoods, hard maple and birch have commonly been used. It is easy to generalize on the type of wood used and extrapolate information to an untried species with the rationale that if it worked on one it will work on the other. This is a dangerous assumption and more often than not, incorrect.

In a recent study, 13 species of wood were treated with either propylene or butylene oxide catalysed with triethylamine (Rowell & Ellis, 1983b). Weight percent gain was determined and, in most cases, so were ASE values (Table 4). It was found that species such as radiata, southern and ponderosa pines, hard maple, walnut, elm, cativo (*Prioria copatifera*) and eucalyptus all had acceptable weight gains and medium to high ASE values, but red oak and teak gave good weight gains with little or no dimensional stability. The reason for this is not clear, but the extractives in teak seem to interfere with both chemical penetration and reactivity. If additional species were used in further research, even greater variability would be expected.

5 Proof of bonding

Three criteria have been used as evidence that chemical reaction has taken place in the cell wall and that bonding has occurred with the cell wall polymers: (1) increases in wood volume as a result of reaction; (2) resistance to leaching of added chemical after reaction; and (3) infrared data.

5.1 Volume change

Oven-drying green southern pine causes a shrinkage of 610% from the original green volume (Table 5). At a weight percent gain of about 20, the wet-dry volume of the treated wood is equal to the original untreated green volume. Table 6 shows that for propylene oxide, methyl isocyanate and acetic anhydride, volume expansion in the wood is nearly equal to the volume of chemical added (Rowell & Ellis, 1978). Although this is strong evidence that the bulking chemicals have ended up in the cell wall, these results do not indicate whether or not the chemical is bonded. For acrylonitrile, there is a greater volume of chemical added than there is an increase in wood volume. This means that not all the chemical in the wood is located in the cell wall. This is very evident in the methyl methacrylate specimens, where there is a very large addition of chemical volume with very little increase in wood volume. The methacrylate polymer is mainly in the wood lumina.

5.2 Permanency

If the chemical that caused the cell wall to swell to accommodate it is bonded to the cell wall polymers, then solvent extraction would not be able to leach it out. Nonbonded chemicals would be leached out resulting in high weight loss. It can be seen in Table 7 that methyl isocyanate-, butylene oxide- and acetic anhydride-modified wood is very resistant to leaching of added chemical. The starting chemicals and nonbonded byproducts would be very soluble in benzene or water. Soxhlet extraction of 20- to 40-mesh ground modified wood is a severe environment that exposes a very large internal surface area to the extracting solvent. Propylene oxide-modified wood shows more weight loss than the three aforementioned chemical systems. Propylene oxide is more moisture-sensitive than butylene oxide, so more nonbonded polymers may be formed during reaction. Acrylonitrile modification using ammonium hydroxide as catalyst results in almost no permanently bonded chemical even in a mild water-soaking rest. If sodium hydroxide is used as catalyst for acrylonitrile, the weight loss in water is lower than in the ammonium hydroxide-catalysed system, but it is still significantly higher than in any other chemical-bonded system tried.

Another test for permanency of bonded chemical can be seen in data generated for repeated water-leaching ASE tests (Rowell & Ellis, 1978). Table 8 shows that wood modified with propylene or butylene oxide, methyl isocyanate and acetic anhydride maintains a 50-60% ASE value even after four soaking-drying cycles. This shows that the bulking chemical is staying in the cell wall. Acrylonitrile-modified wood catalysed with both ammonium and sodium hydroxides loses bulking chemical even after

Table 4. Wood species treated at 120°C, epoxide/triethylamine (95/5, v/v), 150 lb/in².

Species	Treatment ¹	Time (min)	Weight % gain	ASE ²
Red oak	PO	30	21.8	0
	PO	40	25.6	2.1
Hard maple	PO	35	27.3	41.1
	BO	60	18	52.2
	BO	180	32	61.0
Teak	PO	30	20.5	0
	PO	60	20.7	0
Walnut	PO	3	26.2	46
	BO	240	28.3	53
Elm	PO	40	28.2	46.3
Cativo	PO	40	29.7	42.2
	BO	240	22.8	64.2
Persimmon	BO	180	22	...
	BO	240	33	...
Eucalyptus obliqua	BO	240	22	46.4
Radiata pine (sapwood)	PO	40	34.2	67.3
	(heartwood) PO	40	32.1	52.3
Southern pine (sapwood)	PO	40	35.5	68.3
	(heartwood) PO	40	24.6	59.7
Ponderosa pine	PO	40	26.9	36.5
Douglas-fir	BO	300	20.7	...
	BO	360	24.6	...
Spruce	PO	40	32.6	...
	BO	360	30.4	...

¹ PO - propylene oxide; BO - butylene oxide.
² Antishrink efficiency after one water soak.

Table 5. Changes in volume of southern pine upon drying and chemical treatment.

Green volume	Ovendry volume	ΔV	Treatment	Ovendry volume after treatment	Weight gain
inch ³	inch ³	%		inch ³	%
3.48	3.24	6.9	Propylene oxide	3.42	15.9
3.60	3.24	10.0	do.	3.60	21.1
3.66	3.42	6.6	do.	3.66	26.1
3.60	3.30	8.3	do.	3.66	34.1
3.60	3.36	6.7	do.	3.72	41.0
2.33	2.11	9.4	Acetic anhydride	2.30	13.9
2.39	2.15	10.0	do.	2.33	17.5
2.41	2.17	9.9	do.	2.39	19.5
2.37	2.13	10.1	do.	2.37	22.8

Table 6. Volume changes in southern pine upon chemical treatment.

Treatment	Weight gain	Increase in wood volume with treatment ¹	Calculated volume of chemical added
	%	cm ³	cm ³
Propylene oxide	26.5	7.1	7.5
	28.8	6.4	7.2
	34.3	8.4	8.0
	36.2	8.9	9.0
Methyl isocyanate	12.4	0.16	0.14
	25.7	0.21	0.27
	47.7	0.46	0.54
	51.2	0.54	0.58
Acetic anhydride	17.5	3.0	2.9
	19.5	3.6	3.3
	22.8	3.9	4.0
Acrylonitrile	25.7	0.46	0.77
	28.7	0.26	0.39
	36.0	0.74	1.2
Methyl methacrylate	58.0	0.6	7.6
	91.4	0.9	10.1

¹ Difference in volume between treatments due to different sample size.

² Density used in volume calculations: propylene oxide, 1.01; methyl isocyanate, 0.967; acetic anhydride, 1.049; acrylonitrile, 0.806; methyl methacrylate, 0.94.

Table 7. Oven-dry weight loss of chemically modified wood leached with various solvents.

Reagent	Weight gain	Weight loss after extracting with				
		Benzene/ethanol 4 hours Soxhlet 20 mesh	Benzene 24 hours Soxhlet 40 mesh	Water 24 hours Soxhlet 40 mesh	Water 7 days soaking blocks	
	%	%	%	%	%	
Control	0	2.3	4.7	11.2	0.6	
Methyl isocyanate	10.0	2.9	1.0	
	23.5	65	1.0	
	47.2	9.6	9.7	
Propylene oxide	29.2	5.2	4.0	
	38.0	6.8	10.8	12.5	...	
Butylene oxide	27	3.8	...	11.7	1.6	
Acetic anhydride	16.3	2.3	...	9.7	1.0	
	22.5	2.8	...	12.2	1.2	
Acrylonitrile						
	+NH ₄ OH	26.1	21.7
	+NaOH	25.7	13.5

one soaking cycle. The ASE value on the second soaking cycle is negative, which means the modified wood is less dimensionally stable than the control. This may be due to hemicellulose extraction during reaction under the strong alkaline catalyst conditions.

Table 8. Volumetric swelling coefficients (S) and antishrink efficiency (ASE) as determined by the water-soaking method.

Treatment	WPG ¹	S ₁ ²	ASE ₁ ³	S ₂ ⁴	ASE ₂ ⁵	S ₃ ⁶	ASE ₃ ⁷	S ₄ ⁸	ASE ₄ ⁹
Propylene oxide	0	15.8	...	15.8	...	15.9	...	15.9	...
	29.2	6.0	62.0	9.0	43.8	7.8	50.9	7.9	50.3
Butylene oxide	0	13.6	...	12.4	...	12.4	...	12.9	...
	27.0	3.6	73.5	5.7	54.0	5.2	58.1	5.6	56.6
Acetic anhydride	0	13.8	...	13.3	...	13.6	...	13.3	...
	16.3	5.1	63.0	5.1	61.7	5.3	61.0	5.3	60.2
	22.5	4.1	70.3	3.8	71.4	4.0	70.6	4.1	69.2
Acrylonitrile +NH ₄ OH	0	14.1	...	13.9	...	14.0
	26.1	2.7	80.9	15.3	neg.	14.4	neg.
	0	20.3	...	16.8	...	16.7
+NaOH	25.7	10.5	48.3	18.8	neg.	17.5	neg.
	0	14.0	...	13.8	...	13.7	...	13.5	...
Methyl isocyanate	21.6	5.5	60.4	6.6	52.0	6.5	52.6	6.3	53.3
	29.9	4.7	66.4	6.0	56.8	4.8	65.0	5.3	60.7

¹ Weight percent gain. Samples recorded at 0 weight percent gain are controls.

² Volumetric swelling coefficient determined from initial oven-dry volume and first waterswollen volume.

³ Antishrink efficiency based on S₁.

⁴ Determined from first waterswollen volume and reovendrying.

⁵ Based on S₂.

⁶ Determined from reovendry volume and second waterswollen volume.

⁷ Based on S₃.

⁸ Determined from second waterswollen volume and second reovendrying.

⁹ Based on S₄.

5.3 Infrared evidence

Evidence that chemical reaction has taken place with wood cell wall hydroxyl groups is seen in the infrared (IR) spectra of methyl isocyanate-modified southern pine (Fig. 2). Samples were first milled to pass a 40-mesh screen and extracted with benzenethanol (2:1, v/v) followed by water in a Soxhlet extractor. Any unreacted reagent and isocyanate homopolymer formed during the reaction would be removed by this procedure. The spectrum for unreacted wood in the wave-number region of 1730 cm⁻¹ shows some carbonyl stretching vibrations (Fig. 2,A). After modification to 17.7% weight gain, the carbonyl band is stronger (Fig. 2,B), and at 47.2% weight gain (Fig. 2,C) this band becomes one of the major bands in the IR spectra. The increase in carbonyl is due to the formation of R-O-C(=O)-NH-R in the urethane bond. There is also an increase in the absorption bands as the weight percent gain increases: at 1550 cm⁻¹, due to the NH deformation frequencies of secondary amines; at 1270 cm⁻¹, which is C-N vibration of disubstituted amines; and at 770 to 780 cm⁻¹, which may be due to NH deformation of bonded secondary amines. No unreacted reagent remains in the samples as the isocyanate absorption at 2275-2240 cm⁻¹ is absent (Fig. 2,B,C).

The strong absorption at 3400 cm⁻¹ and 2950 cm⁻¹ in all the IR spectra is due to hydroxyl absorption. Because substitution is not high enough to eliminate all hydroxyl groups, these bands are always present.

The holocellulose (cellulose and hemicellulose) from a methyl isocyanate-modified sample at 17.7% weight gain was isolated by the sodium chlorite procedure (Green, 1963). The IR spectrum of the holocellulose (Fig. 2,D) shows that urethane bonding has taken place in the carbohydrate component of wood. The IR spectrum of lignin isolated from a methyl isocyanate-modified sample at 47.2% weight gain by the sulphuric acid procedure (Moore & Johnson, 1967) shows that urethane bonding has occurred in the lignin component of wood (Fig. 2,E). The lignin spectrum shows the characteristic aromatic skeletal vibration at 1515 cm⁻¹ (Sarkanen *et al.*, 1967). This band is missing from the modified holocellulose curve (Fig. 2,D), which shows that the chlorite procedure does remove substituted lignins.

Similar results are observed on IR spectra of acetylated wood (Rowell, 1982b). As the weight percent gain increases upon acetylation, the absorption band at 1730 cm⁻¹ increases owing to the carbonyl group in the acetyl bond.

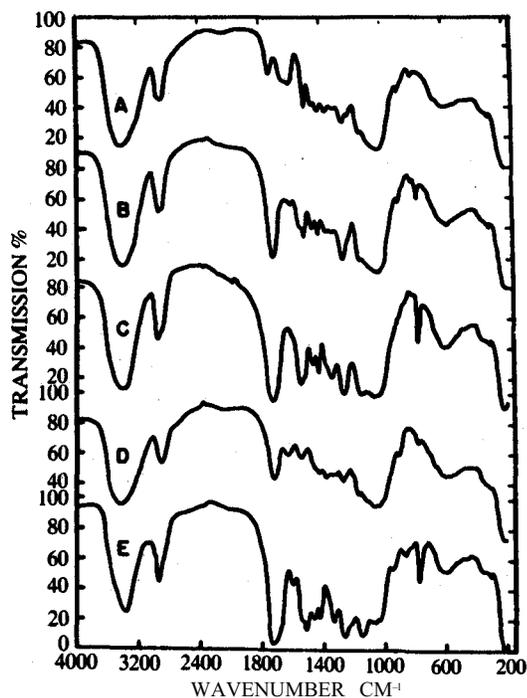


Figure 2. Infrared spectra of methyl isocyanate-modified southern pine:

- A. Southern pine control.
- B. Methyl isocyanate-modified southern pine to 17.7 weight percent gain.
- C. Methyl isocyanate-modified southern pine to 47.2 weight percent gain.
- D. Holocellulose fraction from methyl isocyanate-modified southern pine to 17.7 weight percent gain (0.07% lignin).
- E. Lignin fraction from methyl isocyanate-modified southern pine to 47.2 weight percent gain.

6 Distribution of bonded chemical

Chemical modification of wood to impart decay resistance and to provide dimensional stability depends on adequate distribution of reacted chemicals in water-accessible regions of the cell wall. It is important, therefore, to determine the distribution of bonded chemicals as this information may lead to a better understanding of how chemical modification of wood changes the chemical properties of cell wall polymers.

The distribution of bonded chemical as a function of depth of penetration was determined by tracing the fate of chlorine in epichlorohydrin-reacted wood (Rowell, 1977) and acetyl groups in acetylated wood (Rowell, 1982b). Outside, middle, and inner samples were taken from specimens $\frac{1}{2} \times \frac{1}{2}$ inch up to 2×2 inches from epichlorohydrin-modified southern pine. Up to $1\frac{1}{2} \times 1\frac{1}{2}$ inches, no significant differences were observed in chlorine content from the three sections analysed. Beyond $1\frac{1}{2}$ inches, a concentration difference occurred between the outside and the inner part of the wood treated. Similar results were obtained for acetylated wood (Rowell, 1982b).

The epichlorohydrin reaction system was also used to determine the distribution of chlorine in springwood, summerwood, sapwood and heartwood of southern pine (Rowell, 1978). The very polar epoxy system reacts more quickly, and with greater weight gains, with the springwood - as opposed to summerwood - cell wall components. Although a larger amount of the epoxides was found in heartwood, benzene extraction of the reacted wood effected a greater weight loss from the heartwood than from the sapwood. This may have been due to reaction of the epoxides with heartwood extractives which were then removed on benzene extraction.

A study of soft-rot decay patterns showed that the tangential cell wall is reacted to a higher degree than radial cell walls in ponderosa pine reacted with butylene oxide at 8% weight gain (Nilsson & Rowell, 1982). The radial wall in the summerwood is nearly twice as thick as the tangential wall, so the radial wall may not be totally penetrated by the epoxide system.

In energy-dispersive X-ray analysis for bromine in wood acetylated with tribromoacetyl bromide, Peterson & Thomas (1978) found bromine to be distributed throughout the entire secondary wall, suggesting chemical reaction with lignin. Using a similar technique, the greatest percentage of chlorine in epichlorohydrin-modified wood was found in the S_2 layer of the cell wall. This is the thickest cell wall layer and contains the most cellulose.

By taking apart the cell wall of a modified wood specimen and separating the cell wall components from one another, it is possible to determine the distribution of bonded chemicals in the cell wall polymer. It is more difficult to delignify modified wood than unmodified wood, which means that the lignin has been substituted (Callow, 1952; Rowell, 1980, 1982b). This was true for wood reacted with both acetic anhydride and methyl isocyanate. It can be seen in Table 9 that the lignin component is always more substituted than the holocellulose components (Rowell, 1980). This would indicate that either the lignin is more accessible for reaction or more reactive. Callo (1951) found that lignin was more reactive to acetylation than was cellulose.

Table 9. Degree of substitution (DS) of hydroxyl groups in methyl isocyanate-modified southern pine.

Weight percent gain	Lignin	Holocellulose	Ratio lignin DS
	DS	DS	holocellulose DS
5.5	0.17	0.025	7.4
10.0	.28	.047	6.0
17.7	.41	.084	4.9
23.5	.59	.117	5.1
47.2	.89	.209	4.3

For acetylated wood at approximately 25% chemical weight gain, all of the lignin hydroxyls were found to be substituted (Truksne, 1977; Rowell, 1982b). Truksne (1977) found more bonded acetyl on the cellulose than the hemicelluloses at low (13.5%) chemical weight gain, but this was reversed at higher (24.5%) weight gain.

It is important to note that the hydroxyl substitution calculations are based on the assumption that all hydroxyl groups are accessible and that reaction with acetic anhydride or methyl isocyanate is a single-site substitution reaction - i.e., only one reagent reacting with one hydroxyl and no polymerization. It has been shown that only 60% of the total hydroxyl groups in spruce wood are accessible to tritiated water (Sumi *et al.*, 1964). It has been further estimated that 65% of the cellulose in wood is crystalline and therefore probably not accessible for reactions involving these hydroxyl groups (Stamm, 1964). Taking these estimates into consideration, if it is assumed that only 35% of the cellulose hydroxyls are accessible for substitution, then the degree of substitution in the holocellulose component is much higher in the accessible regions than Table 9 shows.

The data on the distribution of bonded chemicals suggest that high lignin substitution does not contribute significantly to the overall protection mechanism of wood from decay or dimensional stabilization. The degree of substitution in lignin was high in samples at lower weight percent gain of bonded chemical where little or no protection from decay or dimensional stabilization was observed. If the degree of substitution in lignin does have an effect in these mechanisms, it is only observed at very high levels. The degree of substitution in the holocellulose components seems to be the most important factor in decay resistance and dimensional stability.

7 Conclusion

The future of chemical modification of wood lies in end-product property enhancement. If, for example, fire retardancy is important in a wood material, the fire retardant could be bonded permanently to the cell wall. If the level of chemical addition were high enough, dimensional stability and some degree of resistance to biological attack would also be achieved at no additional cost. The greatest single application of the research would be in reconstituted products in which standard operating procedures call for dry wood materials, spray chemical addition for maximum distribution, small sample size for good penetration, and high temperature and pressure in product formation. These are exactly the procedures required for successful chemical modification. Permanently bonded chemicals that provide fire retardancy, ultraviolet stabilization, colour changes, dimensional stability, and resistance to biological attack to wood products may be possible through chemical modification.

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