† Chemical Modification of Wood

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Contents

Summary
1 Introduction
2 Requirements for reaction
3 Reactions with wood
4 Types of wood
5 Proof of bonding
6 Distribution of bonded chemical
7 Conclusions
References

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                             | 120°C, 150 lb/in² 1 hour soaking   | 25°C soaking    |
|-------------------------------------|-------------------------------------|-----------------|-----------------|
| Methyl isocyanate                   | 52.6                                | 5.1             |
| Acetic anhydride                    | 12.3                                | 1.5             |
| Formaldehyde solution               | 12.3                                | 12.3            |
| Water                               | 10.0                                | 10.0            |
| Epichlorohydrin                     | 6.9                                 | 5.9             |

| Table 2. Volumetric swelling coefficients (S) for southern pine sapwood in various catalysts |
|-------------------------------------|-------------------------------------|-----------------|-----------------|
| Catalyst                            | 120°C, 150 lb/in² 1 hour soaking   | 25°C soaking    |
|-------------------------------------|-------------------------------------|-----------------|-----------------|
| n-Butylamine                        | 15.5                                | 15.2            |
| Piperidine                          | 13.3                                | 0.0             |
| Dimethylformamide                   | 12.8                                | 12.5            |
| Pyridine                            | 11.3                                | 13.1            |
| Acetic acid                         | 11.1                                | 8.8             |
| Aniline                             | 11.0                                | 0.5             |

| Table 3. Volumetric swelling coefficients (S) for southern pine sapwood in various solvents |
|-------------------------------------|-------------------------------------|-----------------|-----------------|
| Solvent                             | 120°C, 150 lb/in² 1 hour soaking   | 25°C soaking    |
|-------------------------------------|-------------------------------------|-----------------|-----------------|
| Dimethylsulfoxide                   | 13.3                                | 11.7            |
| Dimethylformamide                   | 12.8                                | 12.5            |
| Cellosolve                          | 10.6                                | 10.2            |
| Methyl cellosolve                   | 10.3                                | 10.0            |
| Water                               | 10.0                                | 10.0            |
| Methanol                            | 9.0                                 | 9.3             |
| 1,4-dioxane                         | 6.5                                 | 0.6             |
| Tetrahydrofuran                     | 5.4                                 | 7.2             |
| Acetone                             | 5.1                                 | 5.6             |
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. A 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; gluable; 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:

\[
\text{Wood-OH} + \text{CH}_3\text{C} (=\text{O})\text{C} (=\text{O})\text{CH}_3 \rightarrow \text{Wood-O} (=\text{O})\text{CH}_3 + \text{CH}_3\text{C} (=\text{O})\text{OH}
\]

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-amonium 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 Y-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.
Acetylation to 20-25% weight gain shows a 70% reduction in swelling or antishrink efficiency (ASE) (Tarkow et al., 1950; Koppers, 1961; Krylova, 1979). 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 acetyl 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 (Rugevitsa et al., 1977) as well as overall water resistance (Shiraishi et al., 1972; Grinberg & Okonov, 1975). Acetylation in a N₂O₄-NO-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 (Deher 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):

\[
\text{Wood-OH} + \text{CH}_2: \overset{\text{C}=\text{O}}{\longrightarrow} \text{Wood-O-C}(-\text{O})\text{-CH}_3
\]

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 (Otlesnov & 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 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:

\[
\text{Wood-OH} + R-C(=O)-Cl \rightarrow \text{Wood-O-C(=O)-R} + \text{HCl}
\]

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:

\[
\text{Wood-OH} + R-N=C=O \rightarrow \text{Wood-O-C(=O)-NHR}
\]

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-buty1 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 disocyanate (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:

\[
\text{Wood-}\text{OH} + \text{CH}_2\text{=O} \rightarrow \text{Wood-}\text{O-CH}_2\text{-OH} \rightarrow \text{Wood-}\text{O-CH}_2\text{-O-Wood}
\]

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, phenylmethylammonium chloride and pyridinium chloride as catalysts (Weaver et al., 1960). Glyoxal, glutaraldehyde and \( \alpha \)-hydroxyaldehydes 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 \( N,N' \)-dimethylethylene urea, glycol acetate, acrolein, chloroacetaldehyde, heptaldehyde, \( \alpha \)- and \( \beta \)-chlorobenzaldehyde, furfural, \( p \)-hydroxybenzaldehyde and \( n \)-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:

\[
\text{Wood-OH} + R-\text{Cl} \rightarrow \text{Wood-O-R} + \text{HCl}
\]

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 alkylation 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 \( \beta \)-Propiolactone

The reaction of \( \beta \)-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:

\[
\text{Wood-OH} + \text{CH}-(\text{O-CO})\text{CH}_2 \rightarrow \text{Wood-O-CH}-(\text{O-CO})\text{CH}_2 \text{-COOH}
\]

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 \( \beta \)-propiolactone reactions with this wood give a carboxyethyl derivative (Goldstein et al., 1959). High concentrations of \( \beta \)-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 \( \beta \)-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:

\[
\text{Wood-OH} + \text{CH}_2=\text{CH-CN} \rightarrow \text{Wood-O-CH}_2\text{CH}_2\text{CN}
\]

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*, *Coniophora puteana*, *Lenzites trabea* [Gloeophyllum trabeum], or *Lentinus lepideus* (Goldstein 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 10^6 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:

\[
\text{Wood-OH} + \text{R-CH(=O)-CH}_2 \rightarrow \text{Wood-O-CH}_2\text{CH(OH)R}
\]

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 & Pokrovski, 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 starvation 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 -CH2-CH- accounts for part of the heat of combustion, but
the -CH3 and -CH2CH3 added by propylene and butylene oxides, respectively, also contribute (Rowell
et al., 1983).

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.

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 oven-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.

If the chemical that caused the cell wall to swell to accommodate it is bonded to the cell wall polymers,
than 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 oxido-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.

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

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.

<table>
<thead>
<tr>
<th>Green volume</th>
<th>Overdry volume</th>
<th>ΔV</th>
<th>Treatment</th>
<th>Overdry volume after treatment</th>
<th>Weight gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>inch³</td>
<td>inch³</td>
<td>%</td>
<td>Propylene oxide</td>
<td>inch³</td>
<td>%</td>
</tr>
<tr>
<td>3.48</td>
<td>3.24</td>
<td>6.9</td>
<td>do.</td>
<td>3.42</td>
<td>15.9</td>
</tr>
<tr>
<td>3.60</td>
<td>3.24</td>
<td>10.0</td>
<td>do.</td>
<td>3.60</td>
<td>21.1</td>
</tr>
<tr>
<td>3.66</td>
<td>3.42</td>
<td>6.6</td>
<td>do.</td>
<td>3.66</td>
<td>26.1</td>
</tr>
<tr>
<td>3.60</td>
<td>3.30</td>
<td>8.3</td>
<td>do.</td>
<td>3.66</td>
<td>34.1</td>
</tr>
<tr>
<td>3.60</td>
<td>3.36</td>
<td>6.7</td>
<td>do.</td>
<td>3.72</td>
<td>41.0</td>
</tr>
<tr>
<td>2.33</td>
<td>2.11</td>
<td>9.4</td>
<td>Acetic anhydride</td>
<td>2.30</td>
<td>13.9</td>
</tr>
<tr>
<td>2.39</td>
<td>2.15</td>
<td>10.0</td>
<td>do.</td>
<td>2.33</td>
<td>17.5</td>
</tr>
<tr>
<td>2.41</td>
<td>2.17</td>
<td>9.9</td>
<td>do.</td>
<td>2.39</td>
<td>19.5</td>
</tr>
<tr>
<td>2.37</td>
<td>2.13</td>
<td>10.1</td>
<td>do.</td>
<td>2.37</td>
<td>22.8</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Weight gain</th>
<th>Increase in wood volume with treatment</th>
<th>Calculated volume of chemical added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene oxide</td>
<td>%</td>
<td>cm³</td>
<td>cm³</td>
</tr>
<tr>
<td>26.5</td>
<td>7.1</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>28.8</td>
<td>6.4</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>34.3</td>
<td>8.4</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>36.2</td>
<td>8.9</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>Methyl isocyanate</td>
<td>12.4</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>25.7</td>
<td>0.21</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>47.7</td>
<td>0.46</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>51.2</td>
<td>0.54</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>17.5</td>
<td>3.0</td>
<td>2.9</td>
</tr>
<tr>
<td>19.5</td>
<td>3.6</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>22.8</td>
<td>3.9</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>25.7</td>
<td>0.46</td>
<td>0.77</td>
</tr>
<tr>
<td>28.7</td>
<td>0.26</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>36.0</td>
<td>0.74</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>58.0</td>
<td>0.6</td>
<td>7.6</td>
</tr>
<tr>
<td>91.4</td>
<td>0.9</td>
<td>10.1</td>
<td></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Weight loss after extracting with</th>
<th>Benzene/ethanol</th>
<th>Butylene oxide</th>
<th>Acetone</th>
<th>Acrylonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 hours Soxhlet 20 mesh</td>
<td>24 hours Soxhlet 40 mesh</td>
<td>24 hours Soxhlet 40 mesh</td>
<td>7 days soaking blocks</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Methyl isocyanate</td>
<td>10.0</td>
<td>2.9</td>
<td>...</td>
<td>...</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>23.5</td>
<td>65</td>
<td>...</td>
<td>...</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>47.2</td>
<td>9.6</td>
<td>...</td>
<td>...</td>
<td>9.7</td>
</tr>
<tr>
<td>Propylene oxide</td>
<td>29.2</td>
<td>5.2</td>
<td>...</td>
<td>...</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>38.0</td>
<td>6.8</td>
<td>10.8</td>
<td>12.5</td>
<td>...</td>
</tr>
<tr>
<td>Butylene oxide</td>
<td>27</td>
<td>3.8</td>
<td>...</td>
<td>11.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>16.3</td>
<td>2.3</td>
<td>...</td>
<td>9.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Acrylonitrile +NH₄OH</td>
<td>26.1</td>
<td>...</td>
<td>...</td>
<td>21.7</td>
<td>...</td>
</tr>
<tr>
<td>Acrylonitrile +NaOH</td>
<td>25.7</td>
<td>...</td>
<td>...</td>
<td>13.5</td>
<td>...</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>WPG 1</th>
<th>S1 2</th>
<th>ASE 1 3</th>
<th>S2 4</th>
<th>ASE 2 5</th>
<th>S3 6</th>
<th>ASE 3 7</th>
<th>S4 8</th>
<th>ASE 4 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene oxide</td>
<td>0</td>
<td>15.8</td>
<td></td>
<td>15.8</td>
<td></td>
<td>15.9</td>
<td></td>
<td>15.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>29.2</td>
<td>6.0</td>
<td>62.0</td>
<td>9.0</td>
<td>43.8</td>
<td>7.8</td>
<td>50.9</td>
<td>7.9</td>
<td>50.3</td>
</tr>
<tr>
<td>Butylene oxide</td>
<td>0</td>
<td>13.6</td>
<td></td>
<td>12.4</td>
<td></td>
<td>12.4</td>
<td></td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.0</td>
<td>3.6</td>
<td>73.5</td>
<td>5.7</td>
<td>54.0</td>
<td>5.2</td>
<td>58.1</td>
<td>5.6</td>
<td>56.6</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>0</td>
<td>13.8</td>
<td></td>
<td>13.3</td>
<td></td>
<td>13.6</td>
<td></td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.3</td>
<td>5.1</td>
<td>63.0</td>
<td>5.1</td>
<td>61.7</td>
<td>5.3</td>
<td>61.0</td>
<td>5.3</td>
<td>60.2</td>
</tr>
<tr>
<td></td>
<td>22.5</td>
<td>4.1</td>
<td>70.3</td>
<td>3.8</td>
<td>71.4</td>
<td>4.0</td>
<td>70.6</td>
<td>4.1</td>
<td>69.2</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>0</td>
<td>14.1</td>
<td></td>
<td>13.9</td>
<td></td>
<td>14.0</td>
<td></td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>+NH4OH</td>
<td>26.1</td>
<td>2.7</td>
<td>80.9</td>
<td>15.3</td>
<td>neg.</td>
<td>14.4</td>
<td>neg.</td>
<td>14.4</td>
<td>neg.</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>20.3</td>
<td></td>
<td>16.8</td>
<td></td>
<td>16.7</td>
<td></td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>+NaOH</td>
<td>25.7</td>
<td>10.5</td>
<td>48.3</td>
<td>18.8</td>
<td>neg.</td>
<td>17.5</td>
<td>neg.</td>
<td>17.5</td>
<td>neg.</td>
</tr>
<tr>
<td>Methyl isocyanate</td>
<td>0</td>
<td>14.0</td>
<td></td>
<td>13.8</td>
<td></td>
<td>13.7</td>
<td></td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.6</td>
<td>5.5</td>
<td>60.4</td>
<td>6.6</td>
<td>52.0</td>
<td>6.5</td>
<td>52.6</td>
<td>6.3</td>
<td>53.3</td>
</tr>
<tr>
<td></td>
<td>29.9</td>
<td>4.7</td>
<td>66.4</td>
<td>6.0</td>
<td>56.8</td>
<td>4.8</td>
<td>65.0</td>
<td>5.3</td>
<td>60.7</td>
</tr>
</tbody>
</table>

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 water-swollen volume.
3 Antishrink efficiency based on S1.
4 Determined from first water-swollen volume and re-oven-drying.
5 Based on S2.
6 Determined from re-oven-drying and second water-swollen volume.
7 Based on S3.
8 Determined from second water-swollen volume and second re-oven-drying.
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 benzene-ethanol (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.
Chemical Modification of Wood

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 ½ × ½ inch up to 2 × 2 inches from epichlorohydrin-modified southern pine. Up to 1½ × 1½ inches, no significant differences were observed in chlorine content from the three sections analysed. Beyond 1½ 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 S2 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. Callol (1951) found that lignin was more reactive to acetylation than was cellulose.
For acetylated wood at approximately 25% chemical weight gain, all of the lignin hydroxyls were found to be substituted (Truskin, 1977; Rowell, 1982b). Truskin (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.

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

<table>
<thead>
<tr>
<th>Weight percent gain</th>
<th>Lignin DS</th>
<th>Holocellulose DS</th>
<th>Ratio lignin DS holocellulose DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>0.17</td>
<td>0.025</td>
<td>7.4</td>
</tr>
<tr>
<td>10.0</td>
<td>0.28</td>
<td>0.047</td>
<td>6.0</td>
</tr>
<tr>
<td>17.7</td>
<td>0.41</td>
<td>0.084</td>
<td>4.9</td>
</tr>
<tr>
<td>23.5</td>
<td>0.59</td>
<td>0.117</td>
<td>4.9</td>
</tr>
<tr>
<td>47.2</td>
<td>0.89</td>
<td>0.209</td>
<td>3.4</td>
</tr>
</tbody>
</table>

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.

References


Karlsohn, I.M.; Svalbe, K.P. (1972a) [Method of acetylation with gaseous ketene.] Uchenye Zapiski, Latvisskit Universitet No. 166, 98-104.

Karlsohn, I.M.; Svalbe, K.P. (1972b) Effect of chemical changes from the acetylation action of ketene on the hydrophobic nature of wood. Uchenye Zapiski, Latvisskit Universitet No. 166, 89-94.


Kumar, V.B. (1958) Swelling studies in wood. Norsk Skogindustri 12(9) 337.


MacLean, J.D. (1924) Relation of temperature and pressure to the absorption and penetration of zinc chloride solution into wood. Proceedings, American Wood-Preservers' Association 20, 44-73.


Chemical Modification of Wood


