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CHEMICAL MODIFICATION OF WOOD

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ABSTRACT

Wood is, perhaps, nature's most wonderful gift to humanity, its versatile character providing unlimited scope for property manipulation and product development to suit diverse applications. Progress in the field of polymer chemistry led to the development of a new class of wood products with substantially improved physical, chemical, mechanical, and biological properties. Aesthetic superiority, uniform finish, property enhancement, and reduced maintenance made modified wood attractive for large-scale application in many industrial uses as substitutes for costly metals and alloys.

Chemical modification of the cell wall achieved significant success during the last two decades. A wide variety of wood modification reactions have been studied, of which acetylation holds great potential. Improved dimensional stability and resistance to biological degradation have made it attractive for use in high-value panels and joinery products. The high resistance to biodegradation, especially with bonded biocides, holds a bright future for its use in wood protection in view of increasing environmental controls to limit pollution of the planet Earth.

Improvement in dynamic mechanical properties of wood, resulting from bulking of the cell wall, shows promise for its utilization in the manufacture of improved musical instruments.

Keywords: Chemical modification, resin-impregnated wood, etherification, acetals, esterification, oligo-esterification, slow release biocides, dimensional stability, decay resistance, termite resistance, fire resistance.

INTRODUCTION

The fibrous nature of wood has made it one of the most appropriate and versatile raw materials for a variety of uses. The three-dimensional biopolymer complex-composite made up of cellulose, hemicellulose, and lignin is quite stable and retains its identity for long periods. Physical degradation, however, does occur at the microstructure level due to the presence of chemically reactive sites. Such degradation is accelerated by UV irradiation associated with sunlight. The most common reactive sites recognized so far are the hydroxyl groups, which are abundantly available in all the three major chemical components of wood. These hydroxyl groups adsorb water from humid environments which then enters the wood matrix. Since the adsorbed water is held by

hydrogen bonding, wood moisture changes caused by dynamic humidity conditions result in alternate swelling and shrinkage of wood and in physical degradation, sometimes leading to mechanical failure.

The cellular structure of wood is so designed by nature that it is as strong as steel on a weight for weight basis. During years of development, ways have been found to make wood more dimensionally stable, harder and stronger to meet specific needs, and even as a substitute for steel and other costly and environmentally non-friendly materials. At the same time, being of organic origin, wood components are readily degraded by microorganisms, insects, termites, and marine animals that attack wood for food, shelter, or both. Wood preservation techniques have been adopted to protect wood

against such biological degradation as well. Similarly, chemical treatments have been devised to reduce the combustibility of wood.

In recent years, a number of studies have been directed to apply chemical modification technology to solid wood to improve its behavior when used in adverse environments. Similar studies have been extended to wood chips and fibers to manufacture improved composites such as flakeboards, fiberboards, particleboards, etc. This report, however, limits itself to chemical modification of solid wood only.

TYPES OF CHEMICALLY MODIFIED WOOD

As the basic knowledge about wood increased, many attempts were made to modify wood properties by various physical, mechanical, and chemical treatments. The concept of chemical modification of wood was developed primarily to improve its dimensional stability with changes in moisture content. Improvement in physical and mechanical properties, increased durability against physical, chemical, and biological degradation came as a bonus of such treatments. These treatments range from simple application of heat to impregnation with monomers for *in situ* polymerization or alteration of chemical composition of wood by chemical reactions. Wood treated with conventional wood preservatives like creosote, pentachlorophenol, copper-chrome-arsenic, and fire retardants does not fall under the strict definition of chemically modified wood. The chemical modification treatments can be classified broadly into two different types:

- 1) Improved wood or densified wood, i.e., densification and/or resin impregnation.
- 2) Cell-wall modification with reactive chemicals.

Improved wood

Compressed wood, Impreg (resin-impregnated wood), and Compreg (resin-impregnated compressed wood) were developed during the first half of the 20th century (Stamm and Seborg 1943, 1944; Stamm et al. 1946). Be-

cause of their improved strength, high dimensional stability, high electrical resistance, increased wearing resistance, and immunity to corrosion, these materials found wide application in replacing expensive steel and other specialty metals. Densified wood laminates, which permit making the best use of lightness and directional strength of wood, found wider and more sophisticated applications. While phenol-formaldehyde is traditionally the most commonly used resin for producing densified wood/wood laminates, other resins have also been looked into. Melamine-formaldehyde-treated wood retains its original color, while dimensional stability and mechanical properties improve (Inoue et al. 1993).

Resin-modified wood has been found resistant to biological degradation and has evinced renewed interest (*vis-à-vis* other modification techniques as substitutes for conventional preservation methods using toxic chemicals (Ryu et al. 1991, 1993; Takahashi and Imamura 1990). Low molecular weight resins with active alcoholic groups and less alkalinity carry large potential as bioactive polymers to produce durable wood materials at low resin loadings (Ryu et al. 1993). Thermochemical modification of surface layers improves low grade, weaker, and softer species like alder, sugi, poplar, etc., to furniture grade timber like beech (Sadzhaya et al. 1987; Inoue et al. 1990, 1991; Shukla and Bhatnagar 1989). Compression set in surface layers can be permanently fixed by steaming to yield a hard surface with minimal loss in other strength characteristics (Inoue et al. 1993).

While phenol-formaldehyde-type resins polymerize by condensation reactions, vinyl monomers polymerize through a free radical mechanism. The process is superior to condensation polymerization as the catalysts employed, being neither acidic nor basic, do not affect the wood strength and there is no reaction by-product. A wide range of vinyl monomers like ethylene, propylene, vinyl chloride, vinyl acetate, vinylidene chloride, acrylonitrile, methyl methacrylate (MMA), styrene, etc., are available, which yield polymers with a wide

range of properties from soft rubber to brittle solids. Blending of different monomers is not uncommon to get appropriate properties and reduce processing costs. Even monomer-compatible dyes can be introduced to get colored products. The composites are commercially known as wood-plastic composites (WPC).

Phenol-formaldehyde resin is located mostly in the cell wall and produces dimensionally stable composites. Vinyl monomers, being nonpolar, fill the cell lumens unless impregnated by the solvent exchange process. Such composites are subject to dimensional changes with water uptake. Cell-wall loading incorporates decay resistance as well, whereas lumen filling lacks such ability. A good decay resistance is reported at about 10% polymer loading in the cell wall (Furuno et al. 1992), a level similar to loading with phenol-formaldehyde (Ryu et al. 1993; Takahashi and Imamura 1990).

Chemical modification of the cell wall

Dimensional movement, as well as biological degradation, of wood has been attributed to the presence of numerous hydroxyl groups in various wood components. Blockade of such sites by larger groups swells the wood permanently and not only eliminates the moisture adsorption sites but also prevents the highly specific enzymatic reactions. Because of the altered chemical configuration, the specific requirement of the enzymes to fit the substrate in a lock and key type arrangement is no longer met (Lehinger 1970).

A number of reagents capable of forming stable covalent bonds have been studied to substitute these reactive hydroxyl groups. The essential requirements are that the reacting chemicals should penetrate the cell wall and react with the available hydroxyl groups of the cell-wall polymer, preferably in neutral or mild alkaline conditions at temperatures below 120 C. The major types of linkages formed by reaction with wood are ether, acetal, ester, etc. Chemicals investigated to yield stable chemical bonds include alkyl or acid chlorides, anhydrides, carboxylic acids, epoxides, isocya-

nates, lactones, nitriles, etc. For commercial application of such treatments, the toxicity, corrosiveness, and costs are important factors in choosing the chemicals. Since the protection accorded is due to change in the chemical nature of the wood, neither the reacting chemical nor the treated wood needs to be toxic. Nevertheless, chemicals that react readily with wood hydroxyls can easily react with blood and tissue hydroxyls and can thus be dangerous (Rowell 1983b).

Among the many chemical modification reactions, acetylation and reactions with epoxides and isocyanates have been studied the most, as these chemicals have shown potential with minimum adverse side effects. Rowell (1975) reviewed the advantages and disadvantages of the reactions with these chemicals and gave a detailed account of the modified woods in another review (Rowell 1983b).

Ethers.—Methyl ether is the simplest ether formed with wood by reaction with dimethyl sulphate or methyl iodide (Rudkin 1950; Narayanamurthi and Handa 1953). Methylation occurs at hydroxyl as well as carboxyl groups, which reduces the tendency to photodegradation (Kalnins 1984). Methylated wood is mechanically impaired because of severe reaction conditions. Alkylated wood produced with acid chlorides contains acid residues, which adversely affect the mechanical properties. Reaction with acrylonitrile produces cyanoethylated wood, which is highly dimensionally stable and decay-resistant, but strength properties are impaired (Goldstein et al. 1959).

Alkylene oxides, long known to react with polysaccharides, react with wood hydroxyls to give improved wood properties. The initial reaction yields a new hydroxyl group originating from the epoxide, which results in a polymer formation. Several patents have been granted using different alkylene oxides and their mixtures (Aktiebolag 1965; Liu and McMillin 1965; Rowell and Gutzmer 1976). The various epoxides used are ethylene oxide (EO, a gas at atmospheric pressure), propylene oxide (PO), butylene oxide (BO), epichlorohydrin (ECH), and dichlorohydrin (DCH). The stability of the

treatment and the effects produced vary with the reactant and method of treatment. Reactions with epoxides generally degrade mechanical properties of wood by about 10%, and wood deteriorates in rheological properties (Norimoto et al. 1992). Hardness is the only property not affected by the treatment (Rowell and Ellis 1984). Field and laboratory tests on epoxide-treated wood showed resistance to a wide spectrum of degrading organisms at a weight percent gain (WPG) around 17 but demonstrated no protection against weathering (Feist and Rowell 1982). Epoxide-modified wood also resisted subterranean termites and marine borer attack (Rowell et al. 1979; Rowell 1982) probably due to unpalatability of the substrate, but performance was not as good as with acetylated wood (Johnson and Rowell 1988).

Acetals. — Reactions of wood hydroxyls with aldehydes yield acetals. Acetal bonds are stable to bases. Such reactions involve two hydroxyl groups and result in cross-linking. Reaction proceeds best in the presence of acid catalysts. A WPG of 2 was found adequate to ward off fungal attack (Stamm and Baechler 1960). An antishrink efficiency (ASE) of 47% at 3.1 WPG, which is far short of cross-linking all the available hydroxyl groups, leads to speculation that the cross-linking must be tying together structural units. Mechanical properties were impaired probably due to hydrolysis of cellulose units, and the wood becomes brittle after treatment with formaldehyde. Other aldehydes gave a lower ASE and impaired strength properties as in the case of formaldehyde. Dimethylol-ethylene urea with aluminum chloride and tartaric acid catalysts did not require high temperature curing and gave up to 62% ASE without adversely affecting the strength properties (Nicholas and Williams 1987). Militz (1993) reported similar results on dimensional stability with beech, but the treatment did not impart sufficient decay resistance. Videlov (1989) earlier reported a good decay resistance of dimethylol treated pinewood.

Formaldehyde cross-linking reactions improve the vibrational properties of wood

(Akitsu et al. 1991). This results from dimensional stabilization of the wood and reduction in internal friction (Akitsu et al. 1993). Formalization that affects the sound levels radiated at high frequency can be used to improve the timbre of wood used for musical instruments (Yano and Minato 1993).

Esters. — Esters are formed by reaction with acid anhydrides, carboxylic acids, and isocyanates. Ester bonds are the weakest and are liable to acid or base attack. Esterification proceeds well even in the absence of catalysts with some reactants.

(i) *Acetylation:* Acetylation of cellulose had been developed already in 1865, and cellulose acetate films dominated the market before other synthetic films became available. The first patent for acetylation of wood using acetyl chloride was granted to Suida (1930). Detailed studies on reaction parameters and properties of acetylated wood using various reagents were continued in the mid-forties. The most common reagent used for acetylation is acetic anhydride, which reacts with wood hydroxyls with or without a catalyst forming wood ester and releasing acetic acid in the wood structure. Apart from loss of almost 50 percent of the reagent, the entrapped acid is a nuisance as it emits odor and is corrosive to metal fasteners. The presence of acetic acid may also induce reversal of esterification reaction. Efforts to remove the entrapped acid did not culminate in a commercially viable technology (Koppers 1961; Otlesnov and Nikiton 1977). Efforts were therefore continued to develop methods for *in situ* destruction of the acid. Shvalbe (1988) reacted the residual acetic acid in wood with ethylene oxide or acetylene to form esters with additional modification. Acetic acid has also been neutralized with octadecylamine, resulting in improved water repellency. Carrying out acetylation in the presence of aniline neutralizes the released acetic acid forming acetanilide in wood, which has known biocidal properties and may provide additional protection (Singh et al. 1992). Acetic acid can also be reacted with wood in the presence of pyridine and a reaction promoter (PCl_3) (Dev and Ku-

mar 1989). This reaction can be used to increase the efficiency of acetylation with acetic anhydride reducing the amount of residual acetic acid.

Several other acetylating chemicals such as ketene gas (Tarkow 1945), acetyl chloride (Singh et al. 1981), thioacetic acid (Singh et al. 1979; Kumar and Agrawal 1982) have been studied, but none has been scaled up to commercialization.

Environmental factors regulating the use of biocides for wood treatment have renewed interest in chemical modification techniques, and efforts are being made to upgrade acetylation techniques. Propionic anhydride has been proposed to replace acetic anhydride as propionic acid emits a mild odor and propionated wood is as good as acetylated wood (Rugevitsa and Embreksha 1988). Recently hepta-decenylsuccinic anhydride (a cyclic anhydride) has been investigated to modify wood (Codd et al. 1992). In the presence of dimethyl formamide (swelling agent), the cycling structure of the anhydride is reported to open up, linking it to the wood hydroxyl oxygen. Some other anhydrides have also been evaluated. Reaction with maleic anhydride (MA) and phthalic anhydride (PA) did not yield durable ester bonds. However, further reaction of the MA/PA esterified wood with epichlorohydrin (ECH) yields oligoesterified wood, resulting in a highly dimensionally stable product with durable bonds (Matsuda et al. 1988a, b). Oligoesterified wood produced with PA-ECH system was found more stable than MA-ECH system as the oligomers produced in the latter case are water-soluble and leach out in repeated wetting and drying (Matsuda et al. 1988c). Oligoesterified wood had higher bending and compressive strength, but tensile and impact strengths were adversely affected (Murakami et al. 1989).

Acetylated wood exhibits good resistance to most decay fungi (Takahashi et al. 1989; Militz 1991) but has been found ineffective in controlling the attack of lower fungi. Even a WPG of 20 conferred no protection against mold and stain fungi (Wakeling et al. 1992), and acetylated samples failed in cooling tower trials

within one year (Kumar unpublished data). Acetylation improved resistance to decay at 6–20 WPG and subterranean termites at 13–18 WPG (Kumar and Agrawal 1982; Kumar and Kohli 1986; Videlov 1986; Imamura and Nishimoto 1986, 1987). Decay hyphae limit themselves to parenchyma cells and tracheid lumens and fail to attack the acetylated cell wall (Wang et al. 1982). Acetylated wood also resisted marine borer attack, but the efficacy did not match CCA or creosote (Johnson and Rowell 1988). PA-ECH modified wood exhibited excellent resistance against weathering and biodegradation including soft rot, bacteria, termites, and marine borers (Murakami and Matsuda 1990b; Murakami et al. 1993).

Acetylation also reduced the rate of surface degradation due to UV radiation, but the protection was lost after exposure for 8 weeks due to loss of acetyl content (Plackett et al. 1992). Weathering degrade and rate and extent of swelling can be reduced by combining acetylation and lumen-filling treatment with methyl methacrylate (MMA) (Feist et al. 1991). Acetylation protects the xylans, while MMA protects the lignin. Acetylated wood exhibited color stability and reduced incidence of surface checking (Plackett et al. 1992; Dunningham et al. 1992). An antishrink efficiency of over 60% is achieved by acetylation (Tarkow et al. 1950; Kumar and Agrawal 1982; Koppers 1961). Cell-wall modification results in lowering of cell-wall moisture and the fiber saturation point (Codd et al. 1992; Kumar et al. 1991; Militz 1991). Zhao et al. (1989) reported no change in crystallinity up to 25 WPG, but a decrease in dielectric constant and equilibrium moisture content was observed.

Acetylation has been found to improve the mechanical strength of wood (Tarkow et al. 1950; Goldstein et al. 1961; Agrawal et al. 1985; Militz 1991). Creep, an important strength parameter for long-term loading of wood members, is largely reduced on acetylated wood (Norimoto et al. 1987, 1992). Extended treatment periods with thioacetic acid also caused a reversal in strength properties although values remained higher than the untreated con-

trols (Agrawal et al. 1985). Acetylation of bamboo reduced strength but increased dimensional stability (Zhou et al. 1985). Dynamic mechanical properties of acetylated wood are reported to improve, probably due to lowering of cell-wall moisture (Akitsu et al. 1993). Oligoesterification using anhydride and epoxide treatment improved vibrational properties (Murakami and Matsuda 1990a). This has direct relevance to acoustical properties. Because of increased dimensional stability, the influence of changing RH on acoustical properties is reduced (Yano et al. 1986). Resonance frequency, an important factor in instrument tones, gets stabilized in the case of acetylated wood (Sasaki et al. 1988; Yano et al. 1988).

(ii) Isocyanates: Reactions of wood with isocyanates are generally very fast and yield stable urethane bonds. Reactions with phenyl, ethyl, butyl, allyl isocyanates in dimethyl formamide have been found to give different degrees of ASE. Methyl isocyanate reacts quite vigorously even in the absence of a catalyst, giving a WPG of 40 in twenty minutes. Although WPG as high as 75 is possible, maximum ASE of 60–70% is attained at 16–28% weight gain (Rowell and Ellis 1979). At higher WPG (~32), tracheid walls start splitting resulting in less ASE due to exposure of new surfaces (Rowell and Ellis 1981). Despite high reaction rates and high WPG obtainable with isocyanates, it is not possible to react all available hydroxyls as evidenced by IR spectra of wood treated to even very high WPG (47.2). Lignin, however, has been reported to react 10 times faster than the holocellulose (West and Banks 1986). n-Butyl isocyanate bulks the cell wall better than the phenyl isocyanate and reduces equilibrium moisture content by 70% at 37.3 WPG. The modified wood, however, continues to retain the sorption-desorption hysteresis (Martins and Banks 1991).

Although most of the chemical is bonded to the cell wall in the case of reaction of low molecular weight isocyanates with dry wood as evidenced by the increase in volume and the IR spectra of treated wood, the higher molecular weight isocyanates tend to polymerize in

cell lumens in the absence of catalysts, as evidenced by low ASE obtained even at high WPG and loss of ASE during the double soak test (Rowell and Ellis 1981; Ellis and Rowell 1984). Presence of wood moisture also leads to formation of nonbonded polymers. Compressive and bending strengths increased with treatment while toughness and abrasion resistance showed a decrease. Wood modified with most isocyanates became resistant to brown rot (Rowell and Ellis 1981). Resistance to *Gloeophyllum trabeum* has been reported at 6.8 (Phenyl) to 7.2 (Methyl) WPG (Chen 1992a).

CURRENT INDUSTRIAL STATUS AND FUTURE SCOPE

Chemical modification processes have, no doubt, opened many new facets for better utilization of the wood resource. The current exploitation is, however, limited to a few uses where the unique properties of the end product justify the added high costs. Manufacture of compressed wood products, resin-impregnated densified laminates, and wood-plastic composites is fairly well established in many countries around the world including the developing countries. National standards for their manufacture and testing have been developed by some countries (Anon. 1987; ASTM 1991; IS 1966). These products are now produced to manufacture a wide variety of machinery parts and articles such as bobbins and shuttles for textile and jute mills, silverware handles, desk legs, door handles, bearings, rollers, die mould patterns in the automobile industry, panels for electrical equipment, master shoe lasts, acid tanks, etc. Heat-stabilized compressed wood has found maximum application in textile/jute mill accessories. Compregnated wood has established itself for a large number of industrial applications. A variety of products such as bolts, rivets, gears, high and low tension circuit breakers, core rings for power transformers, turbo-generators, textile and jute mill loom shuttles, filter presses, industrial flooring, fish plates for electric rail tracks, air screws, air masts, sporting goods, chemical troughs, neu-

tron shields, chair seats, components for automatic-signalling track circuiting, H-frame supports in high voltage transmission, etc., are currently being manufactured (Anand 1981; Gurvich 1957).

Wood-plastic composites, a product of later years, have also found good market acceptance in specialized applications. Heat-catalyst polymerization is commercially being used in a number of countries like the United States, the United Kingdom, Germany, Japan, Poland, Philippines, Taiwan, India. "Acrylic Wood," the commercial name given to methyl methacrylate treated wood-polymer composites in America, although three times more expensive than the untreated red oak (normally used for flooring), has gained market popularity in high-density traffic areas, because of its long life, attractive color enhancement, and little maintenance (Witt 1980; Meyer 1982). Other uses for such modified woods are handrails, cutlery handles, bagpipes, archery bows, stair treads, golf clubs, musical instruments, gun stocks, etc.

An interesting application of this technology might be in drying problematic wood species. Increased tensile strength as a result of polymer inclusion in surface layers can be advantageously used to control check formation during drying. Surface modification with a water-soluble monomer, glycol methacrylate along with polyethylene glycol (PEG 200), was found to work well on *Eucalyptus obliqua*, a highly check-prone hardwood of Australia (Mackay 1972).

Similarly, many fast-growing, low-density woods like sugi or poplar can be surface treated to give high surface strength and hardness to enable their utilization for better purposes (Inoue et al. 1993). Density can be further improved by precompression prior to or after surface modification. Pilot plant trials have been conducted to upgrade alder by thermochemical modification using urea-methenamine resin (Sadzhaya et al. 1987). Such applications can increase the raw material base by bringing into use hitherto unusable wood species.

Wood-plastic composites can be tailored to

suit specific applications and many new application areas are being explored. Possibilities of incorporating biocides/fire retardants in aqueous solutions of alkyd resins and *in situ* curing of resins to form polymers have been examined (Vasisht 1983). Introduction of bioactive monomers along with bulk monomers into the wood voids is being looked into to develop more efficient and environmentally safe wood protection methods (Rowell 1984; Subramanian 1984). Wood treated with void-filling polymers containing slow-release bioactive materials can find use in many high hazard applications such as marine structures. Such treatments can be useful for other areas as well, as a single treatment incorporates durability, improves strength and possibly dimensional stability especially in case of treatments that modify the cell wall as well. Many polymer toxicants like pentachlorophenol acrylate/methacrylate, pentabromophenol acrylate/methacrylate, and tri-n-butyltin acrylate/methacrylate have been synthesized and successfully anchored to the wood components via *in situ* polymerization in laboratory studies (Subramanian et al. 1978, 1981a, b; Rowell 1983a). Biocides bonded to cell walls protect better against biodegradation than the slow-release formulations. Several chlorophenyl isocyanates and polyhalogenated phenyl methyl carbamates have shown antifungal and antitermite activity when bonded to wood (Rowell 1984; Chen and Rowell 1987; Chen et al. 1990). Isocyanates are well-known fumigants (Corden and Morrell 1988) and form very stable bonds with wood. Modified forms capable of bonding with the cell-wall-like p-toluene sulfonyl isocyanate have been found to provide resistance to decay at low weight gains (Chen 1992b). Refinement in reaction techniques and synthesis of low cost and reactive biocides have good potential in the future of chemical modification and wood preservation.

Modification of wood with formaldehydes or related compounds has been found to improve the sound resonance properties of wood (Minato and Yano 1990; Minato et al. 1990; Yano et al. 1986, 1990). Acetylation also re-

duces the effect of changing humidity on acoustic properties due to stabilization of the cell wall (Yano et al. 1986; Sasaki et al. 1988). Sound modulation by using modified wood for components of musical instruments offers opportunities to improve the performance of string instruments like violins, guitars (Yano and Minato 1989, 1993), and pianos (Yano et al. 1988).

Cell-wall modification studies have been receiving the greatest attention during the past few years, and many reactions like acetylation, epoxide formation, etc., yielding enhanced wood properties have shown technical feasibility. Several groups in Europe are actively engaged in acetylation studies using acetic anhydride. Microwave technology has been developed for rapid reaction of acetic anhydride with wood in Sweden at Chalmers University. Technology has been developed to overcome the problem of residual acetic acid in Netherlands. As of today, the main property advantage in cell-wall modification is its resistance to biodegradation, and improved dimensional stability and acoustic properties. At the same time, we have to trade off with loss of certain mechanical properties (butylene oxide-modified wood attains higher creep and can not be used for load-bearing components). The high processing costs do not justify such treatments at the current level of development as conventional wood preservation techniques are relatively much cheaper and equally effective. Rising environmental concerns have, however, threatened to phase out some of the conventional wood preservatives, and chemical modification seems a good alternative. Immediate application of the technology appears feasible for treatment of surface veneers for high quality panels as some treatments like acetylation, while not interfering with gluing (Arora and Rajawat 1982), have been found to slow down surface deterioration due to checking and discoloration (Feist et al. 1991; Plackett et al. 1992). Joinery products using acetylated wood are expected to hit the Dutch market in 2–4 years. B.P. Chemicals (UK), manufacturers of acetic anhydride, working in

cooperation with medium density fiberboard (MDF) manufacturers, have started commercial trials.

Chemical modification also offers possibility of bonding fire-retardant chemicals like organo-phosphorus monomers by *in situ* polymerization (Raff et al. 1966) or by cell-wall reactions (Rowell et al. 1984). Conventional fire-retardant treatments are expensive, require heavy chemical loadings to be really effective, and interfere with mechanical and gluing behavior. Wood modification reactions bonding fire-retardant chemicals can become technically superior and economically viable alternatives.

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