

# FROM HYDROPHILICITY TO HYDROPHOBICITY: A CRITICAL REVIEW—PART II: HYDROPHOBIC CONVERSION

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**Abstract.** This review consists of two parts. Part I considered the hydrophilic nature and wettability of the surface of wood, including wetting theories, surface tension, surface topography, and surface contamination of wood. Part II focuses on chemical transformation of the surface of wood from hydrophilic to hydrophobic. Literature concerning acetylation, metal oxide treatment, sol-gel process, modification with chlorosilanes, grafting of polymers, microemulsion, layer-by-layer deposition, and plasma treatment are discussed. Conventional methods such as acetylation, metal oxide treatment, sol-gel process, and microemulsion can only reduce and/or delay water and moisture sorption. Recent increasing interest in nanotechnology provides new opportunities and perspectives on hydrophobic transformation of the wood surface.

**Keywords:** Hydrophilic, hydrophobic, acetylation, sol-gel process, grafting, layer-by-layer, plasma, wood.

## INTRODUCTION

In Part I of this review, hydrophilic characteristics of the surface of wood were discussed (Piao et al 2010). Wetting theories, surface tension of wood, surface topography, and surface contamination and aging were considered. It was found that surface tension data in the literature were often disparate. Surface tension of wood can be estimated using Zisman's critical surface tension, geometric-mean, harmonic-mean, and acid-base approaches. To date, however, no procedures have been developed for determining the absolute value of surface tension. Surface tension is affected by species, macrostructure (earlywood, latewood, sapwood, heartwood, grain directions, cross-sectional sur-

faces), anatomical microstructure (lumens, pit cavities, freshly cut cell wall surfaces), physical and chemical properties (density, moisture content, cellulose, hemicelluloses, lignin, extractives), machining methods (planing, sanding, microtoming), chemical treatments (preservatives, water repellents, fire retardants), probe liquids, contact angle measurement, and calculation methods. Wettability and surface behavior are predominantly influenced by accessible hydroxyls, topography, and extractive content and distribution on the surface of interest.

Affinity for water (hydrophilicity) is an intrinsic property of wood. Hydrophilicity permits wood to adsorb moisture vapor from air, and both hydrophilicity and porosity cause wood to absorb liquid water. Interactions between wood and water vapor and wood and liquid water have profound impacts on physical properties,

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mechanical properties, utility, and service life of wood and wood-based products. Control of moisture in wood is therefore important to guarantee performance and durability of wood in service.

Natural hydrophilicity of wood is because of accessible hydroxyls on the surface. A hydroxyl could belong to a cellulose chain, hemicellulose chain, or lignin. Therefore, chemical transformation of wood from hydrophilic to hydrophobic is often associated with blockage, modification, or removal of hydroxyls.

Various methods have been studied to protect wood. These methods can be divided into two basic categories, moisture control and biocides. Moisture control can be further divided into two subcategories, water repellents and dimensional stabilizers (Rowell and Banks 1985). Water repellents are primarily used to control the rate of water sorption, while dimensional stabilizers are used to control swelling from moisture sorption. Both water repellents and dimensional stabilizers are fully described in a review by Rowell and Banks (1985). Most commercial water repellents place nonchemically bonded paraffin waxes on cell walls or lumen surfaces. This controls sorption, but it is unable to control movement of water into wood. Therefore, water repellents cannot be used to control dimensional changes. Conversely, dimensionally stabilizing treatments chemically reduce the tendency of wood to sorb water and moisture.

In chemical modification, wood is treated to produce changes on the surface and within its cellular structure. The chemicals often undergo a reaction with hydroxyls within the wood structure. The result is a strong covalent bond, producing a new cell-wall surface. Therefore chemical modification of wood can lead to a reduction of hydroxyls, crosslinking, and/or undesired cleavage of chains. The decrease in number of accessible hydroxyls on the surface of wood in turn leads to a limited interaction with water and improved dimensional stability and antidecay performance.

Dimensional stabilization of wood was extensively studied in the 1950s and 1960s. Several methods have been developed for wood dimensional stability. Most methods focus on hydroxyls of wood constituents. They can be classified as blocking, modifying, eliminating, or crosslinking. Methods of blocking include a water-resistant surface and internal coating and cell-wall bulking. Salt, sugar, wax, and polyethylene glycol have been used as materials for cellulose bulking. The method of modifying is acetylation, which is discussed in detail subsequently. Methods of crosslinking include heat, resin, and formaldehyde treatment. All of these methods are used to stabilize wood by crosslinking accessible hydroxyls; only hydrogenation eliminates hydroxyls. Stamm (1964) has done a comprehensive review on these methods, therefore only acetylation is included in this review.

During recent years, nanosized materials have been extensively studied. Although there is a dispute over the size of nanostructures, nanomaterials are commonly assumed to be artificially made structures of 1 nm to 1  $\mu\text{m}$  (Hodes 2007). Nanotechnology involves controlling matter on the atomic scale, thereby developing new materials with nanoscale dimensions and properties that are unique and cannot be otherwise obtained with the same materials at a macroscale.

One potential application of nanotechnology is development of superhydrophobic surfaces on hydrophilic substrates such as glass, silicon wafer, or wood. A superhydrophobic surface, having a water contact angle of at least  $150^\circ$ , is characterized by micro- and nanoscale roughness and water repellence (Li et al 2007). Nanoparticles can be self-assembled to form a structure on a substrate that mimics surfaces of leaves of some plants or some insect wings. The bio-mimicked, hydrophobic structure renders the modified substrate surface superhydrophobic. Superhydrophobic surfaces do not associate with or react with water, therefore they keep the substrate dry even when exposed to rain. Such surfaces have been developed on glass strips, silicon wafers, polystyrene,

polyethylene, cotton fabrics, and wood (Artus et al 2006; Li et al 2008; Xue et al 2008). Both top-down and bottom-up approaches to atomic self-assembly have been used and structures such as nano pillars, pits, rods, beads, tubes, and filaments have been created.

Superhydrophobic surfaces have been developed on wood and cotton fiber substrates (Artus et al 2006; Xue et al 2008; Yang 2008). This review is necessary 1) to trace research on wood hydrophobic modification and demonstrate potential maps for hydrophobic research; and 2) to summarize the research frontier for better understanding current developments of hydrophobic wood. The specific objective is to focus on chemical conversion of wood surfaces from hydrophilic to hydrophobic. The review builds on research of Feist (1979), Rowell and Banks (1985), Mai and Militz (2004), and Rowell (2006).

#### CHEMICAL MODIFICATION OF WOOD

Chemical transformation of wood from hydrophilic to hydrophobic always targets hydroxyls, which serve as sorption sites for water from the environment. Many chemicals have been used to remove hydroxyls of wood substance with two major reactions, additional polymerization and single-site addition. In polymerizing addition, chemicals react with hydroxyls and become polymerized. Examples of the polymerizing addition reaction include the sol-gel process, microemulsion, and plasma treatment. In single-site addition, chemicals react with a single hydroxyl, and the modification is typically by chlorosilanes, grafting, and acetylation. Chemical conversions of wood from hydrophilic to hydrophobic can also be roughly divided into surface modification and bulk treatments. In surface modification, conversion is conducted on the surface, including layer-by-layer deposition and plasma treatment. In bulk treatments, however, hydrophobic conversions involve internal hydroxyls. Typical bulk treatment methods include acetylation, the sol-gel process, metal oxides, microemulsion, alkylchlorosilanes, and

grafting of silicone polymers, although some treatments do not deeply penetrate wood.

#### Acetylation

Many studies have been published on hydrophobic modifications of wood. According to Rowell (2006), chemicals that have been studied include anhydrides, acid chlorides, ketene carboxylic acids, isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, phthaldehydic acids, dimethyl sulfate, alkyl chlorides,  $\beta$ -propiolactone, acrylonitrile, and epoxides. All of these chemicals react with hydroxyls and impart a degree of hydrophobicity. However, none except acetylation has passed the research stage (Rowell 2006).

Acetylation is an esterification process of accessible hydroxyls using acetic anhydride. Rowell (2006) has conducted an extensive review on acetylation of wood. According to Rowell, the earliest work on wood acetylation dates to the 1920s when Fuchs and Horn acetylated pine and beech wood to isolate lignin. Tarkow (1945, 1946) was the first to discover that acetylated wood was resistant to decay and dimensionally stable in water. Subsequently, many researchers have investigated wood acetylation to improve moisture- or water-resistant properties.

Figure 1 shows the acetylation process of a hydroxyl and acetic anhydride. In the reaction, one acetyl group replaces one hydroxyl by grafting an acetate anion to a hydroxyl site, producing an acetic acid byproduct, which can be converted back into acetic anhydride and reused. However, acetic acid residue is difficult to remove from solid wood and causes a strong odor and acid hydrolysis of cellulose. After acetylation, the smaller hydroxyls in the cell wall are replaced by larger acetyl groups after which acetylated wood remains in a permanently swollen state. The effect of the treatment can be expressed as a weight percent gain (WPG) with a higher degree of acetylation producing a higher WPG. Hence, acetylated wood is often heavier and dimensionally larger than before treatment. Like untreated wood, acetylated wood consists

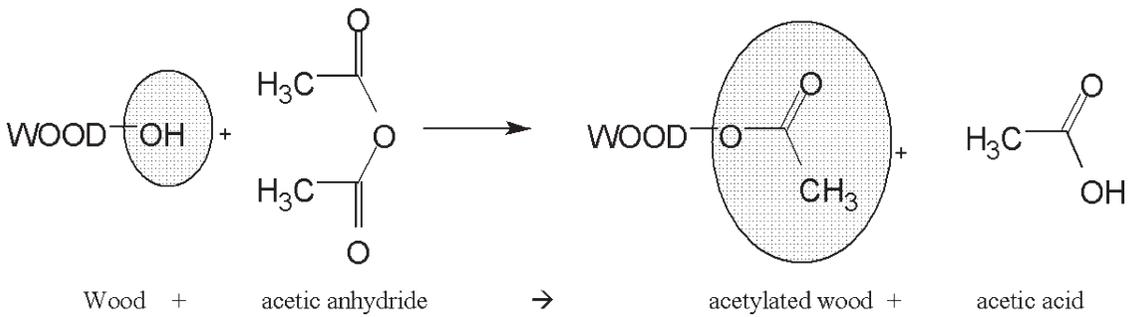


Figure 1. Acetylation: replacing OH groups by larger and heavier  $\text{CH}_3$  groups (Homan et al 2000).

only of carbon, hydrogen, and oxygen. Consequently, disposal of acetylated waste wood can be handled as untreated wood.

Acetylation can be achieved both in liquid and vapor systems with or without a catalyst. Catalysts that have been used include zinc chloride, urea-ammonium sulfate, dimethylformamide, sodium acetate, magnesium persulfate, trifluoroacetic acid, boron trifluoride, and gamma rays. In liquid acetic anhydride treatment, acetyl weight gain can be over 20% at which level bonded acetyls are distributed throughout the middle lamella and cell wall. Replacement of some hydroxyls with bonded acetyl groups reduces hygroscopicity of wood. Acetylated wood rarely exceeds 20% MC even at 90% RH, effectively reducing the FSP. Dimensional stability, decay resistance, and weathering properties of acetylated wood and wood composites are improved, while thermal and mechanical properties remain unaffected (Rowell 2006). It has been suggested that low moisture and/or blocking of specific enzymatic reactions as a result of changes in configuration and conformation of polymers in the cell wall is responsible for fungal resistance of acetylated wood. Acetylation also protects wood against UV degradation and improves acoustical and dielectric properties.

Although acetylation substantially improves moisture- and water-related properties, wood swells in contact with water. It has been reported that acetylated wood can be attacked by termites (Rowell 2006) and marine organisms (Johnson and Rowell 1988). The high cost of acetylated

treated wood and limited supply of acetic anhydride are some of the barriers that limit its use.

### Metal Oxides

While organic chemicals are beneficial in improving surface properties of wood, inorganic chemicals can also impart hydrophobicity. Compared with modification by organic chemicals, wood modified by inorganics is resistant to natural weathering and fungal damage in addition to repelling water. Inorganics that have been studied for imparting hydrophobicity include zinc stearate, Zn-Co,  $\text{Zn}(\text{OH})_2$ , ZnO,  $\text{CuSO}_4$ ,  $\text{CuCrO}_4$ ,  $\text{CuCrO}_4 \cdot 2\text{CuO}$ ,  $\text{CuCl}_2\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $\text{CrO}_3$ ,  $\text{CrCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{SnCl}_2$ , MgO, PbO,  $\text{As}_2\text{O}_3$ ,  $\text{MnO}_2$ , and  $\text{Ag}_2\text{O}$  (Smith and Williams 1973; Black and Mraz 1974; Anzai et al 1975; Feist 1977; Feist et al 1977; Kubel and Pizzi 1981). Wood treated with metal salts often has improved UV resistance and a degree of water repellency. Metal treatment also reduces dimensional change and free water absorption.

Of the inorganics, Cr and Zn oxides have been most investigated. Kubel and Pizzi (1981) found that both  $\text{CrO}_3$  and ZnO form insoluble complexes with lignin guaiacol;  $\text{CrO}_3$  forms polymeric complexes, whereas ZnO forms dimeric complexes (Fig 2). Polymeric bonds are stronger than dimeric, which in turn is stronger than a wood-water bond (Nanassy and Desai 1978). Therefore, both  $\text{CrO}_3$  and ZnO can be seeded onto cell walls and impart a degree of water repellency and UV protection. In addition, zinc

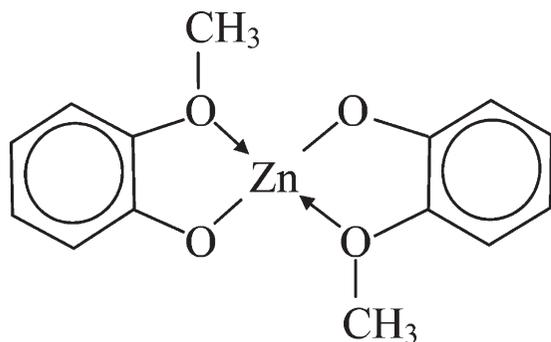


Figure 2. Dimeric bonds formed between a zinc ion and two guaiacol molecules.

stearate repels water and is the most powerful mold-resistant agent among all metallic soaps. In contrast with acetylation, some metal oxides containing Cr, Zn, Cu, and As provide protection against attack by decay fungi and termites.

### Sol-Gel Process

The sol-gel process is a chemical solution deposition technique widely used in material science. Chemicals used are often alkoxy silanes such as tetraethoxysilane (TEOS), methyl triethoxysilane (MTEOS), propyl triethoxysilane (PTEO), and methyltrimethoxysilane (MTMOS). The sol-gel process starts from a chemical solution, a sol, which acts as a precursor for a gel, an integrated network of either discrete particles or network polymers. When used to treat wood, the process often consists of three steps, solution, gelation, and drying. In the solution stage, alkoxy silanes are hydrolyzed by water bound at the cell-wall surface to form silanols. Condensation among silanols leads to formation of the sol, a mixture of alkoxy silanes, silanols, and oligomers of polysilanol. In the second step, the sol evolves gradually toward formation of a three-dimensional gel-like network containing both a liquid and solid phase. At the same time, hydrogen bonds formed between polysilanol and hydroxyls on the wood substance permit the polysilane network to be anchored. In the third step, the silane and wood composites are oven-dried to form crosslinked, highly condensed gels that are covalently bonded with the wood substance. Figure 3

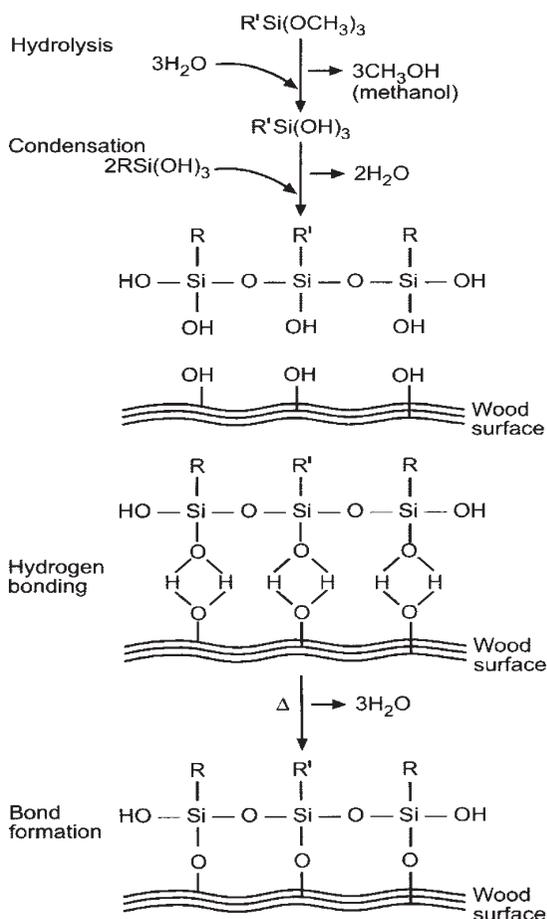


Figure 3. Scheme for sol-gel deposition of alkoxy silane on a wood surface (Tshabalala et al 2003a).

shows a typical sol-gel process that deposits polysilanes on the wood substance. Reactions in the first and second steps are conducted at ambient temperature and can be catalyzed by acids or bases. A vacuum is often applied to the reacting solution to remove gas at the wood-solution interface.

Alkoxy silanes used in the sol-gel process are bifunctional organics often consisting of one alkyl and three alkoxy groups. The covalent Si-O-C bonds that form between alkoxy silanes and wood are susceptible to hydrolysis, however the Si-C bond in the alkyl group is stable. Therefore, properties of gels are often determined by the nonhydrolyzed alkyl group (Tanno et al 1998;

Tshabalala et al 2003a; Donath et al 2004). Donath et al (2004) found that TEOS tends to condense to a brittle, transparent network; MTEOS condenses to a more elastic and less transparent silicate; and PTEO condenses to a sticky gel. The longer the alkyl groups of silanes, the better the hydrophobic properties of treated wood. Antileachability of MTMOS gel is better than that of TEOS (Saka and Ueno 1997).

Because some hydroxyl sites on the cell-wall surface and in the cell wall are modified by silanes, wood treated by the sol-gel process often shows reduced moisture and water sorption capacity and improved dimensional stability (Miyafuji and Saka 1996; Saka and Ueno 1997; Tshabalala et al 2003a; Donath et al 2004). Both low- and high-molecular-weight alkoxy silanes are advantageous to provide hydrophobicity. Low-molecular-weight alkoxy silanes penetrate the outer surface layer and condense with hydroxyls below the surface, while high-molecular-weight alkoxy silanes condense with low-molecular-weight alkoxy silanes at the surface to form a poly-siloxane network. Therefore, the sol-gel poly-siloxane deposit not only reduces hydroxyls on the cell-wall surface, but also "stereochemically" retards the formation of hydrogen bonds with water molecules (Tshabalala et al 2003a).

In the sol-gel process, wood can be treated either from the onset of the process or after alkoxy silanes have been hydrolyzed to oligomers. Prehydrolyzed oligomeric silane often leads to higher WPG than monomeric alkoxy silane solutions. However, wood treated with monomeric alkoxy silanes shows improved cell-wall bulking, dimensional stability, moisture uptake, and durability compared with wood treated with oligomeric alkoxy silanes (Donath et al 2004). Drying of gel-wood composites also affects properties of the film. Cyclic wetting and drying of alkoxy silane-wood composites may increase hydrophobicity of wood because of the obstruction of cell-wall cavities by silicon (Donath et al 2006).

One desirable property of the sol-gel process is that it permits foreign functional molecules to be included in solutions to gain desirable surface

properties. For example, numerous studies have been conducted to develop fire-resistant inorganic wood composites using the sol-gel process (Saka et al 1992; Miyafuji and Saka 1996, 2001; Saka and Tanno 1996; Saka and Ueno 1997; Miyafuji et al 1998; Tanno et al 1998). Fire-resistant agents such as  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ , and  $\text{B}_2\text{O}_3$  have been examined for their fire-resistant performance in sol-gel coating systems (Miyafuji and Saka 1996; Saka and Tanno 1996; Miyafuji et al 1998). Introduction of a UV absorbent, trihydroxyhydroxytrimethoxy-silylpropoxy, to the sol-gel system improves photostability of treated wood (Miyafuji et al 2004).

Hydrophobicity of alkoxy silane-treated wood can be greatly improved by adding water repellent agents to the sol-gel system such as decyltrimethoxy silane, trifluoroacetic acid, and 2-hepta-decafluorooctylethyltri-methoxy silane (HFOETMOS) (Saka et al 1992; Tanno et al 1998; Tshabalala et al 2003a). HFOETMOS is a toxic, strong water repellent agent that can be incorporated into alkoxy silanes-wood composites, enhancing both their hydrophobicity and decay resistance. Miyafuji and Saka (1999) found that HFOETMOS enhanced hydrophobicity of MTMOS-wood composites, particularly at low WPG, where long, hydrophobic, HFOETMOS-derived alkyl residues substantially covered the cell-wall surface. When WPG increased,  $\text{SiO}_2$  gel started to form on lumen surfaces, interrupting the distribution of HFOETMOS on the cell walls and reducing the hydrophobicity of the wood-inorganic composites (Miyafuji and Saka 1999). Therefore, the distribution of HFOETMOS on the cell-wall surface largely determined the hydrophobicity of the composites.

Antimicrobial agents can also be integrated into the sol-gel process to improve decay resistance. An amphoteric sterilant, 3-(trimethoxysilyl) propyl (carboxymethyl) decylmethyl ammonium hydroxide inner salt (TMSAH), is antimicrobial. It has been reported that alkoxy silane-wood composites containing TMSAH show increased antimicrobial capabilities against brown-rot fungi but low capabilities against white-rot. However, introduction of HFOETMOS into this sol-gel

system substantially increased water repellency, thereby improving antimicrobial properties of treated wood against both brown- and white-rot fungi (Tanno et al 1998).

A combination of sol-gel and controlled-release processes may provide a new approach for wood preservation. Controlled release permits biocide chemicals to be slowly released from silica film for extended protection. Growth of microorganisms can be suppressed by contact with coated films containing embedded biocides (Bottcher et al 1999). The mechanism of the controlled release is shown in Fig 4. Antimicrobial chemicals such as sorbic, bensoid, and boric acids have been embedded in TEOS coating sols, which are then coated on cellulose acetate foil substrates. Release of biocidal compounds from silica film can be controlled by the mass ratio of silica to the organic compound and by adding soluble or swelling penetration agents (Bottcher et al 1999). In such a system, release of biocides is managed based on moisture content. When moisture content increases to a threshold for fungal growth, biocides are released from silica film to suppress them.

The sol-gel process has also been used to coat  $\text{TiO}_2$  onto wood and fabric surfaces (Haroshi et al 2007; Xue et al 2008). Coated films containing  $\text{TiO}_2$  have been shown to reduce water penetration into wood (Haroshi et al 2007) and form dual-sized (micro and nano) surface roughness, providing an approach for development of superhydrophobic and UV-protected cotton fabrics (Xue et al 2008).

Most recently, the sol-gel process has been used to coat a nanolayer of potassium methyl

○  $\text{SiO}_2$   
▲ Bioactive Compound (BC)

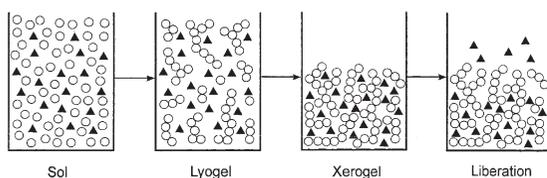


Figure 4. Incorporation and liberation of biocides within a silica sol-gel matrix (Bottcher et al 1999).

siliconate ( $\text{CH}_3\text{Si}[\text{OK}]_3$  [PMS]) particles on the surface of fabrics. PMS is a commercially available, cost-effective, water-dilutable solution that adds water repellency to a wide variety of natural stone and masonry surfaces. PMS reacts with  $\text{CO}_2$  to form an insoluble water-repellent film that reduces water sorption of the treated surface. Li et al (2008) used PMS to treat filter paper, cotton fibers, and cotton fabric. The reaction has two steps. In the first, a PMS solution is bubbled with  $\text{CO}_2$ . Silanols are formed and slowly condense to oligomeric- and polymeric-siloxanes at room temperature. When fabric is soaked in the solution, a precursor silanol film is assembled on the surface of the cellulosic material. In the second step, the fabric is washed and dried to form crosslinked, highly condensed gels, which are covalently bonded with hydroxyls. After  $\text{CO}_2$  was bubbled through the solution, the pH of the solution was quickly brought down to nearly neutral, causing little damage to fibers.

Figure 5a shows untreated cotton fabric with a highly textured, smooth surface, while Fig 5b shows the surface of treated fibers with nano-scale spherical protuberances. Li et al (2008) believed that these protuberances were because of deposition of a polymethylsilsesquioxane network on the surface of microfibrils. The coating showed no detrimental effect on morphology of cotton fabric (Fig 5c). Figure 6e-f demonstrates that morphologies and color of both cotton fabric and filter paper remained unchanged after treatment by PMS, indicating that the coating layer was transparent. Before treatment, contact angles of cotton fabric and filter paper were nearly  $0^\circ$  because of the superhydrophilic nature of cellulose (Fig 6a); after treatment, the contact angle of the fabric was  $157^\circ$  (Figs 6b-c), which is superhydrophobic.

In summary, the sol-gel treatment is a simple and versatile process that can be used to increase water-repellent capabilities of wood or as a medium of conveying desirable chemicals to the surface. However, the sol-gel process requires a costly impregnation treatment to condense alkoxy-silanes on the surface. Impregnation takes

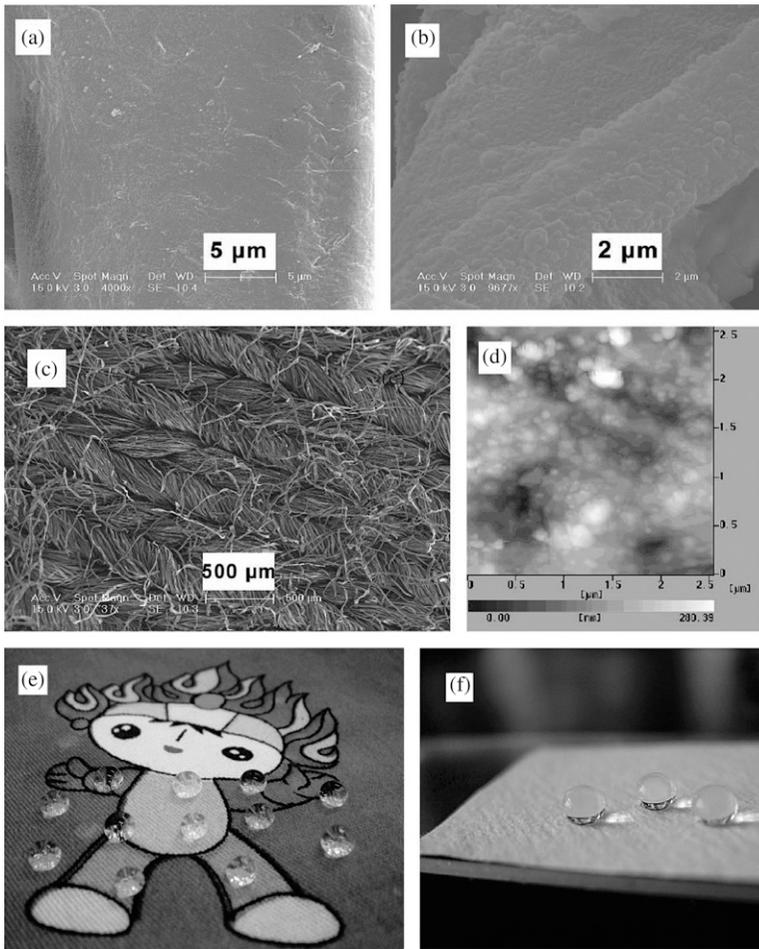


Figure 5. Field emission scanning electron microscopy images of (a) cotton fiber, (b) modified cotton fiber, and (c) modified cotton fabric; (d) three-dimensional atomic force microscopy image of modified fiber surface; (e) image of water droplets on the surface of modified cotton fabric; and (f) image of water droplets on the surface of modified filter paper (Li et al 2008).

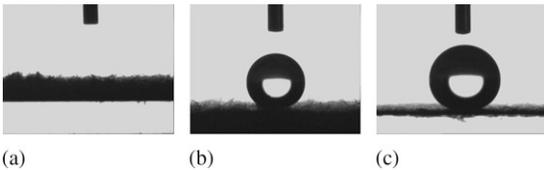


Figure 6. The contact angle of a water droplet on (a) untreated cotton fabric ( $0^\circ$ ), (b) treated cotton fabric ( $158^\circ$ ), and (c) treated filter paper ( $157^\circ$ ) (Li et al 2008).

hours or even days, often under a vacuum, in water or an organic solution (Saka et al 1992; Tanno et al 1998; Tshabalala et al 2003a, 2003b; Donath et al 2004). High-temperature curing

and drying after impregnation are usually required for a desired film quality. Furthermore, most sol-gel treatments cannot prevent wood from sorbing water when wood is directly in contact with liquid water. These properties limit the practical application of the sol-gel process in treating wood surfaces (Mai and Miltz 2004).

### Modification with Chlorosilanes

A feature common between silica (glass, quartz, vitreous silica, etc) and wood is that both contain hydroxyls and are hydrophilic. Therefore,

treatments that work for silica surfaces may be used for wood. It has been common practice to convert silica surfaces to hydrophobic by the reaction of an alkylchlorosilylating agent with hydroxyls on the surface (Trau et al 1991). The silylation reaction can be in a liquid–solid or gas–solid phase. In the liquid–solid phase, water is a key component, without which no reaction occurs between alkyltrichlorosilane and silica surfaces near or at room temperature (Tripp and Hair 1995). Conversely, in the gas–solid scheme, chlorosilanes can react directly with hydroxyls in the absence of water (Tripp and Hair 1995; Artus et al 2006).

For wood modification, gas–solid schemes are usually desirable because it remains dry throughout the treatment. Table 1 lists chlorosilane monomers that have been used in gas–solid coating of silica, fiber, polymer, and wood surfaces (Armistead and Hockey 1967; Owens et al 1980; Trau et al 1991; Tripp and Hair 1995; Fadeev and McCarthy 2000; Artus et al 2006). One advantage of using chlorosilanes is its strong reaction with hydroxyls, crosslinking cellulose with siloxanes.

Owens et al (1980) found that when Douglas-fir and red pine were immersed in silicon tetrachloride liquid, vigorous bubbling was observed initially, but the reaction subsided within a short period. Because of the strong reaction between chlorosilanes and wood, when chlorosilane was initially used to treat wood, it was believed that wood would be chemically dried by chlorosilane and resistant to microorganisms because all hydroxyls would be removed (Owens et al 1980). Their results showed that chlorosilane treatment significantly reduces decay caused

by both white- and brown-rot fungi, attributed to reduction of moisture sorption.

However, contrary to Owens et al, Stevens (1981) found that chlorosilane treatment did not significantly reduce decay by either fungi. In that research, all five chlorosilane monomers (Table 1) were used to treat Scots pine using both immersion and vapor deposition. No treatments gave satisfactory fungal protection. Some wood degradation by the HCl byproduct was observed for reactions with silicon tetrachloride and trimethylchlorosilane (TCMSI).

TCMSI has been used to develop superhydrophobic silicone nanofilaments on the surfaces of wood, polymers, and fibers in a gas–solid interface (Artus et al 2006). The filament is 20–50 nm in diameter and 10 nm to 1  $\mu$ m in length. The topography of the nanofilament films shows both micro- and nanoscale roughness. The surfaces are superhydrophobic, UV-reflective, and stable in most common organic solvents. Table 2 shows water contact and sliding angles of materials coated with TCMSI by the gas–solid interface. The water contact angle of coated wood surface was greater than 150°.

At the same time, Mohammed-Ziegler et al (2006) examined the surface of wood modified by dichlorodimethylsilane (DDS), dichlorodiphenylsilane (DPS), and octadecyl-trichlorosilane (OTS) in organic solutions. In contrast with TCMSI, chlorosilanes (DPS and OTS) have longer alkyl chains. As discussed previously,

Table 1. Chlorosilane monomers and their boiling points.

Chlorosilanes	Boiling point (°C)
SiCl <sub>4</sub>	56–58
CH <sub>3</sub> SiCl <sub>3</sub> (MTCS)	65–66
(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> (DMDCS)	68–70
CH <sub>3</sub> SiHCl <sub>2</sub> (MDCS)	40–45
(CH <sub>3</sub> ) <sub>3</sub> SiCl (TMCS)	54–57

Table 2. Contact and sliding angles of different substrate materials coated with polysiloxane nanofilaments (Artus et al 2006).

Substrate	Contact angle [°]	Sliding angle [°]
Glass cover slip	156	18
Frosted glass	166	<3
Cotton fabric	>150	<30
Wood	>150	>70
Polyethylene	158	8
Silicone rubber	164	19
Ceramics	160	5
Silicon	165	11
Titanium	166	4
Aluminum	168	8

hydrophobicity of silane-treated wood surface is largely determined by nonhydrolyzed alkyl chains of silanes. Longer alkyl chains in DPS and OTS produce better film properties and have greater hydrophobicity. However, the alkylchlorosilane chains are not sufficiently long to create the micro and nano roughness required for a superhydrophobicity. Contact angles of DDS-, DPS-, and OTS-modified surfaces were 108-132°. After the surfaces were further modified with a monofunctional agent, TMCSI, contact angles of surfaces were 80-141°. When comparing water contact angles between surfaces treated by TMCSI filaments and those treated with DDS, DPS, and OTS, it is evident that, although TMCSI has a short alkyl length, it evolves to crystallized filaments, which develop micro- and nanoscale roughness that is superhydrophobic. Therefore, the crystal and structure evolved from alkoxy silane are important for formation of a superhydrophobic film on a wood substrate.

The disadvantage of alkylchlorosilanes for wood surface modification is the difficulty in removal of the HCl byproduct produced during the coating reaction (Fadeev and McCarthy 2000; Li et al 2008). HCl degrades cellulose and therefore undermines protection of the hydrophobic film. Therefore, it may not be feasible to use alkylchlorosilanes to develop a hydrophobic layer on the surface of solid wood until a method is found to remove the acid byproduct.

### Grafting Silicone Polymers

Grafting is a molecular technique that chemically bonds foreign molecules to a surface. The major hurdle with successful grafting is to design a third material, often called a coupling agent, to provide stable linkage between functional groups of the wood surface and foreign molecules having desired properties. It is known that the Si-O-C bond developed by direct reaction of silanes with hydroxyls is susceptible to hydrolysis and is unstable. To form a stable bond, silicon must directly react with carbon

atoms to form stronger Si-C bonds. This can be achieved by introducing a coupling agent between hydroxyls of wood and silicon.

Sebe and Brook (2001) examined maleic anhydride and allyl glycidyl ether as coupling agents to bond silicones to the wood surface. Maleic anhydride was first used as a coupling agent to bond allyl glycidyl ether to wood through a process called oligo-esterification. Oligo-esterified wood was hydrosilylated by a series of alkoxy silanes, and silicones were attached to wood by covalent bonds. Water contact angles of the prepared surface were up to 150°, which is superhydrophobic. The study demonstrated that hydrophobic groups could be attached to the wood surface by covalent bonds that are stable and not susceptible to hydrolysis.

### Micro- and Macroemulsion

An emulsion is a two-phase liquid colloid system, in which the functional alkylsilanes of nanosizes are dispersed in water or an organic solvent. When applied to a surface, water or organic solvents are evaporated resulting in physical deposition of alkylsilanes. Based on the dispersive size of the functional liquid, emulsion can be classified as micro- and macroemulsions. Both micro- and macroquaternary ammonium-silicone emulsions improve hydrophobicity, durability, and decay resistance of treated wood, while macroemulsions have more potential because of deposition of silicones into paths that block water flow to the interior of wood (Ghosh et al 2009).

A clear silicone microemulsion has been developed for hydrophobic treatment of mineral building materials and wood (Mayer 1987). The system is a high-performance impregnating and priming water repellent treatment consisting of basic nitrogen, glacial acetic acid, organopolysiloxane, and butyl acetate. When the mixture is heated to 90°C, a clear liquid is formed that is free of water and organic solvents. After being mixed with a large quantity of water, a transparent microemulsion is formed having silicone droplets of 10-80 nm. In comparison

with macroemulsions of an oil phase in water, which require an emulsifier, the microemulsion technology applies an additional coemulsifier that interferes with the quasicrystalline monomolecular surfactant film (Fig 7). A hydrophobic treatment using the prepared emulsion reduced water sorption of wood by more than 30% (Hager 1995).

### Layer-by-Layer Deposition

A layer-by-layer (LbL) deposition approach was first developed by Decher (1997) to deposit multilayer films of organic compounds on solid substrates.

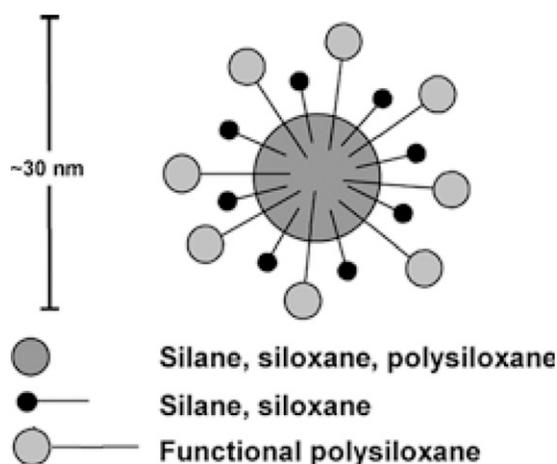


Figure 7. Composition of silicon microemulsions (Hager 1995).

LbL permits molecules of opposite electrostatic charges to be sequentially deposited in liquid solutions on a solid surface, producing nanoarchitectural films with controlled positioning of individual layers. Therefore, surface topography of the substrate becomes irrelevant. During deposition, strong electrostatic repulsion of similarly charged molecules permits self-regulation of sorption and restriction to a single layer, while electrostatic attraction of oppositely charged molecules permits sorption of a second layer on first-layer molecules. Consecutive deposition of opposite and similarly charged molecular layers leads to a tailored multilayer nanostructure on a solid substrate that could have superhydrophobic properties.

The LbL technique has been used to modify fabrics (Yang 2008). Negatively charged wood-fiber linerboards were sequentially immersed in cationic poly (diallyldimethylammonium chloride) (DADMAC) and anionic silica particle solutions. A multilayer film of DADMAC/silica particles was deposited (Fig 8). Treated linerboards had a water contact angle of  $155^\circ$ , yielding high moisture-resistant, water-resistant, and antibiological properties. Figure 9 is a scanning electron micrograph of a linerboard surface modified by DADMAC/silica particles, which shows irregularly packed multilayers of silica particles with only a few interstices.

Other research on LbL coating include conductive paper (Agarwal et al 2006; Peng et al 2008),

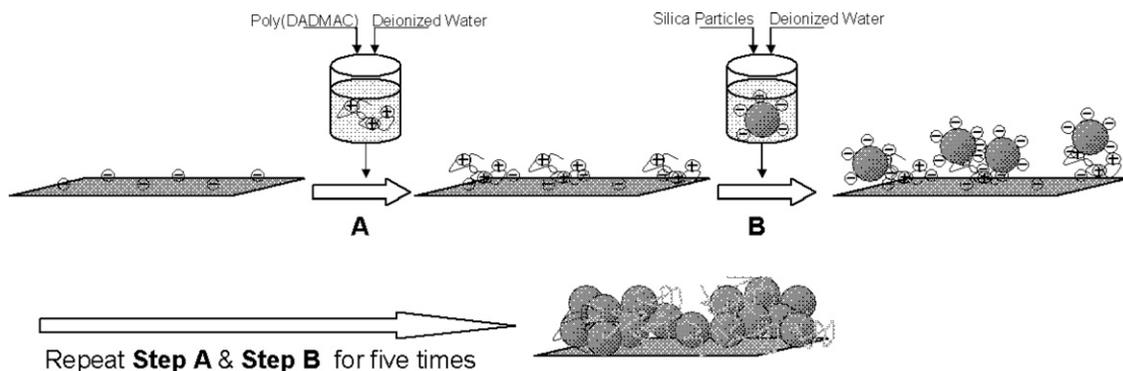


Figure 8. Schematic illustration of fabrication of multilayer film on a linerboard surface (Yang 2008).

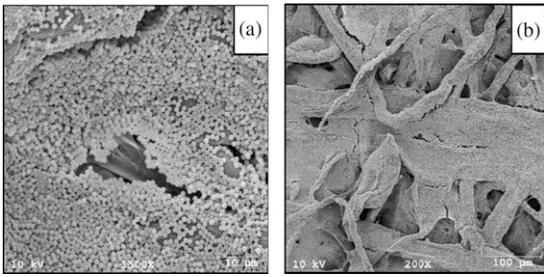


Figure 9. Scanning electron microscopic images of a linerboard surface coated with silica particles using a layer-by-layer technique followed by a fluorination. Image (b) is a magnification of (a) (Yang 2008).

cellulose composites (Cranston and Gray 2006), and modification of mechanical properties of papers (Lingstrom and Wagberg 2008). Recently, nanoscale coatings have been directly deposited on the surface of wood using the LbL approach (Rennekar and Zhou 2009). In the treatment, water-saturated wood samples were sequentially treated in solutions of polyethylenimine, polyacrylic acid, and polyallylamine hydrochloride followed by rinsing with water between each polyelectrolyte solution. In the coating process, ionic interactions play a dominant role in the sorption of polycations onto surfaces. Polyelectrolyte sorption is also facilitated by a high concentration of polymers. The coated film does not mask the microscale features of the wood surface and provides it with highly controlled surface chemistry.

The LbL approach can be used to coat a complex surface regardless of topographic characteristics. Therefore, when LbL is used to coat wood, a uniform film along the microprofile of the lumen and cell-wall surfaces can be obtained, leading to complete coverage. However, the surface of wood is chemically heterogeneous, making the electrostatic sorption mechanism different from that of pulp or cotton fibers, which is more homogeneous (Rennekar and Zhou 2009). A careful selection of solution conditions and appropriate hydrophobic functional groups is a prerequisite for development of a superhydrophobic surface on wood. However, LbL deposition can only be used to treat the outermost surface.

## Plasma Treatment

Plasma is a gas containing equal positive and negative ions, electrons, radicals, and excited and nonexcited neutral particles but without a net electrical charge. Hot and cold plasmas are the two main plasma states. Hot plasmas are composed of neutral and charged molecular and atomic species and electrons having extremely high energies and a very high degree of ionization, while cold plasmas are composed of low-energy atomic and molecular charged and neutral species of energetic electrons. Cold plasmas often operate at room temperature, therefore they are suitable for treatment of organic substrates. Surface modification with cold plasma is a dry process that alters only the outermost layer of a substrate, which is similar to the LbL approach.

For an organic substrate such as wood, hexamethyldisiloxane (HMDSO) is often used to produce plasma gas for hydrophobic modifications (Denes et al 1999; Bente et al 2004; Zanini et al 2008). The treatment leads to deposition of a hydrophobic film, which has a highly cross-linked macromolecular structure based on Si-C and Si-O-Si bonds. Most plasma treatments are conducted in a vacuum, although silane/nitrogen plasma treatments at atmospheric pressure using a dielectric barrier gas discharge have been reported (Bente et al 2004). The water contact angle of plasma-treated samples using this method is up to  $145^\circ$ , which is highly hydrophobic.

Most recently, HMDSO- and HMDSO-SF<sub>6</sub>-plasma treatments have been used to provide hydrophobicity to spruce, chestnut, and poplar wood surfaces (Zanini et al 2008). HMDSO-SF<sub>6</sub> plasma treatment was found to be more effective than HMDSO. Among the three species, poplar showed the largest contact angle of up to  $136^\circ$ , while chestnut and spruce showed essentially equal water repellency (contact angles of  $122^\circ$  and  $123^\circ$ , respectively).

Other gases such as oxygen, ethylene, acetylene, butane, and vinyl acetate have also been used to generate plasma gases for wood modification.

Oxygen plasma treatment increased surface tension and wettability of birch (Mahlberg et al 1998). Ethylene, acetylene, butane, and vinyl acetate plasma gases have been used to treat Caribbean pine (Magalhaes and de Souza 2002). The contact angle of samples treated with butane plasma gas was up to  $140^\circ$ , which was the highest among four plasma gases (butane, ethylene, acetylene, and vinyl acetate). Hydrophobicity across the grain was greater than that along the grain. However, even with these highly desirable wood–water contact angles, plasma treatment could not control moisture sorption because of uncoated capillaries.

A compact gas discharge ion source was recently used in surface modification of wood (Blantocas et al 2006, 2007; Ramos et al 2007). The ion source was a plasma but produces mixed species of  $H^+$  and  $H_2^+$  ions. In the low-energy range ( $9.6\text{--}11.2 \times 10^{-17}$  J), the irradiation of ion beams onto wood or bamboo surfaces was found to impart surface hydrophobicity, whereas in the high-energy range (greater than  $14.4 \times 10^{-17}$  J), it causes hydrophilicity (Blantocas et al 2007). It was also found that wood irradiated by low-energy hydrogen ions shows high flame resistance (Blantocas et al 2007).

#### SUMMARY

This review discusses research results in the literature on wood hydrophobic conversion. Wood is porous and hydrophilic, and transformation of the surface from hydrophilic to hydrophobic is often associated with blockage, modification, or removal of hydroxyls present in cellulose, hemicelluloses, and lignin. Acetylation, metal oxides, the sol-gel process, alkylchlorosilanes, grafting of silicone polymers, microemulsion, layer-by-layer deposition, and plasma treatment have been used to modify wood for hydrophobicity. Mechanisms of hydrophobic transformation are used to physically or chemically prevent hydroxyls from forming hydrogen bonds with water molecules. Most chemicals currently used for hydrophobic transformation are alkoxysilanes, which act as coupling agents

1) to modify hydroxyls; and 2) to chemically anchor hydrophobic alkyl groups or other functional molecules to wood. Most methods use liquid solutions, although the gas–solid interface is preferable for hydrophobic transformations. Some treatments are used to modify only the surface of wood, while others are used to treat wood at or below the surface.

Few treatments prevent wood from interaction with moisture because most cavities and micropores in the wood cell wall are still open after chemical modifications. Conventional methods such as acetylation, metal oxides, the sol-gel process, and microemulsion remove a portion of hydroxyls, therefore they can be used to reduce or delay water and moisture sorption but cannot eliminate it. Recently studied methods such as grafting polymers, layer-by-layer deposition, and plasma treatment are most commonly used to develop superhydrophobic surfaces.

Research on superhydrophobic wood has just begun and few methods have been developed for practical applications. Any successful process for superhydrophobic modification will require nearly complete coverage or transformation of all free hydroxyls that are available for water sorption in a simple, cost-effective way and without leaving any deleterious byproduct in wood.

Recent interest in nanotechnology has provided new opportunities and perspectives on conversion of wood to a hydrophobic or superhydrophobic condition. However, it is believed that nanoparticles covalently attached to a wood substance usually cannot block pit cavities in cell walls, therefore the cell-wall surface under the nanocoated layer is still accessible to free water and water vapor. The superhydrophobic layer should be sufficiently thick to withstand 1) any minor damage to the surface in service; and 2) swelling stress from inside untreated wood because of moisture and water penetration through cavities into wood under the treated layer at the surface. More research is warranted and expected on development of superhydrophobic wood.

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