

FROM HYDROPHILICITY TO HYDROPHOBICITY: A CRITICAL REVIEW: PART I. WETTABILITY AND SURFACE BEHAVIOR

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Abstract. Surface properties of wood are important for both wettability and hydrophobic modification. Glueability of wood is related to wettability, while durability and decay resistance are affected by physical and chemical components. This review (Part I) discusses hydrophilic characteristics of surfaces. Surface theories, calculation methods for surface tension, topography, contamination, and aging are reviewed. It was found that surface tension data were often disparate; a standardized procedure for contact angle measurement would permit reproducible measurements and comparable data for surface characterization. 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 absolute values of surface tension. Few controversies exist in the literature regarding effects of surface topographic characteristics on surface tension. However, there are disputes regarding mechanisms of surface contamination and aging. Further research on surface tension of wood is warranted. Hydrophobic modifications and superhydrophobic wood are discussed in Part II.

Keywords: Hydrophobicity, hydrophilicity, wettability, surface tension, surface topography, contact angle, surface ageing, surface contamination.

INTRODUCTION

Unlike surfaces of metals and some polymer substrates, wood surfaces are soft, uneven, spotted with pits, and containing debris caused by surfacing. Most radial and tangential surfaces of a wood sample consist of concave lumen surfaces with common cell walls (Fig 1). Depending on the cutting location, lumen surfaces of wood cells are commonly intact and are major components

of radial and tangential surfaces. However, cell walls between lumens are cut longitudinally, leaving cross-sections exposed. The alternate lumen and cell-wall surfaces produce primary surface roughness.

The width of open lumens and thickness of cell walls are substantially different in earlywood compared with those in latewood. Cells of latewood have relatively smaller radial diameters, thicker walls, and smaller lumens. The range of tracheid radius (softwood) is 17-60 μm , and the ranges of radii of fiber and vessel (hardwood) are

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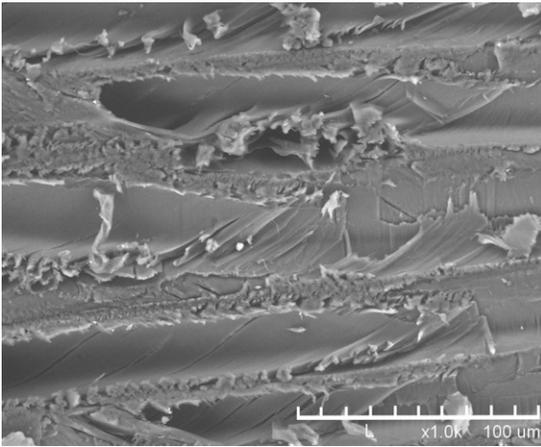


Figure 1. The microsurface of the cell walls of southern pine.

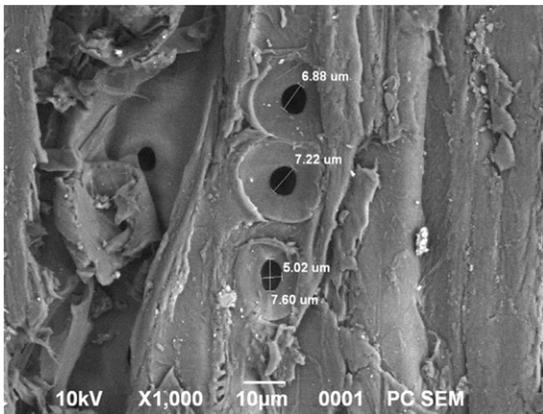


Figure 2. Pits openings on the surface of southern pine.

10–30 μm and 20–350 μm , respectively (Bodig and Jayne 1993). Therefore, a 1-mm-dia water droplet (about 4 μL) could cross 17–58 tracheids in softwoods and 33–100 fibers or 3–50 vessels in hardwoods.

Additional roughness results from pit cavities on radial surfaces of tracheids and ray lumens and cavities (radial and tangential). Figure 2 shows that the diameter of pit-pore openings of a southern pine sample is 5–7.5 μm . It was reported that pit-pore openings of Douglas-fir are 25 μm for heartwood and up to 170 μm for sapwood (Wang and DeGroot 1996). Rays are broad and readily visible in some hardwoods such as oak

and are very narrow and difficult to see, even under magnification, in softwoods and some hardwoods. Rays are essentially perpendicular to tracheids and vessels, contributing additional roughness to the surface.

Wood is composed of cellulose, hemicelluloses, lignin, and extractives and can be viewed as a heterogeneous composite (Gardner et al 1991). All contain hydroxyls, a molecular group that is responsible for cohesion between architectural materials of the three major components of the wood cell wall and for sorption of moisture. However, compared with cellulose and hemicelluloses, lignin is less hydrophilic. According to the model of building blocks of the cell wall (Bodig and Jayne 1993), the major components are organized into laminae, which, in turn, comprise cell wall layers, including a primary and secondary wall (with S_1 , S_2 , and S_3 sublayers toward the lumen). The middle lamella is a bonding medium and is not an integral part of cell wall structure. The three components of wood are not distributed uniformly between the layers of each individual cell. Lignin content is highest in the middle lamella and decreases toward the lumen, while hemicellulose content increases from middle lamella toward the lumen.

Extractives are a class of soluble organic compounds, about 3–9% of oven-wood (Koch 1972), roughly divided into hydrophobic (lipophilic) and hydrophilic constituents (Holmbom 1998). The hydrophobic constituents consist of resin acids (in softwoods), fats, fatty acids, steroids, and steryl esters (in softwoods and hardwoods), while the hydrophilic constituents consist of some phenolic and polar volatile organic compounds (VOC) (Arshadi and Gref 2005). Extractives often form coatings on the cell wall (Hillis 1971) affecting hydrophobicity or hydrophilicity.

Hydrophilicity permits wood to adsorb moisture vapor from the air, and both hydrophilicity and porosity permit wood to absorb liquid water. It is well known that moisture exists in wood as free water, bound water, or vapor. Free water is the liquid water present in lumens and other cavities,

while bound water is within the cell wall, adsorbed from attraction to hydroxyls in cellulose, hemicelluloses, and to a lesser extent lignin. Each hydroxyl attracts one (monomolecular adsorption) or more (polymolecular adsorption) water molecule. Interactions between wood and water vapor and liquid water have profound impacts on physical properties, mechanical properties, utility, and service life of wood and wood-based products. Monomolecular sorption is stronger than polymolecular sorption; thus, the first water molecule has the strongest bond with hydroxyls and takes more effort to remove (Hyvönen et al 2005). Water vapor is in the gas phase and is found in cell lumens and other cavities (Banks 1973). Vapor can be adsorbed onto the cell wall becoming bound water or condensed to free water when the surrounding lumen is at fiber saturation (Rowell and Banks 1985).

Therefore, hydrophilicity is closely related to wettability, the intimate molecular contact between a liquid and solid substrate (Wellons 1980). Because of the hydrophilicity of wood, it is wettable by aqueous- and other polar-based adhesives. For this reason, wettability has been examined extensively since the 1950s (Freeman 1959; Freeman and Wangaard 1960; Bodig 1962; Gray 1962; Herczeg 1965; Hse 1972; Wellons 1980; Gardner et al 1991). In fact, good wettability is often a predictor of high-quality adhesive bonding.

Hydrophilicity, conversely, can directly affect wood performance. It is well known that as moisture content decreases below the FSP, modulus of rupture, modulus of elasticity, impact strength, and other mechanical properties in-

crease. The strength of green wood is about 55–65% of that at 12% MC (FPL 1999). In addition, unlike materials such as metals and concrete, wood acts as a food source for many insects and fungi. When moisture content of wood is at or greater than the FSP and untreated with preservatives, service life can be significantly reduced from decay. The fact that “water is one of wood’s worst enemies” (Feist and Mraz 1978) has not changed much over time. As a result, hydrophilicity and its impact as well as hydrophobic wood have been major research topics in the field of wood science.

The present review examines hydrophilicity and hydrophobic modification of wood. Wettability, gluability, surface topography, and surface contamination of wood are considered, and wetting theories that are associated with hydrophilicity and hydrophobicity of wood are discussed. This review is built on contributions of Halligan (1969), Christiansen (1990, 1991), and De Meijer (2004). In Part II, hydrophobic modifications and superhydrophobic treatments will be considered.

WETTING THEORIES

When a drop of liquid is placed on a horizontal solid substrate, three boundaries meet around the profile of the drop, ie the liquid–gas interface, gas–solid interface, and solid–liquid interface. At any planar view parallel to the substrate, the profile of the liquid drop appears to form an angle θ at the liquid–gas–solid contact line (Fig 3a) according to:

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos \theta_{Young} = 0 \quad (1)$$

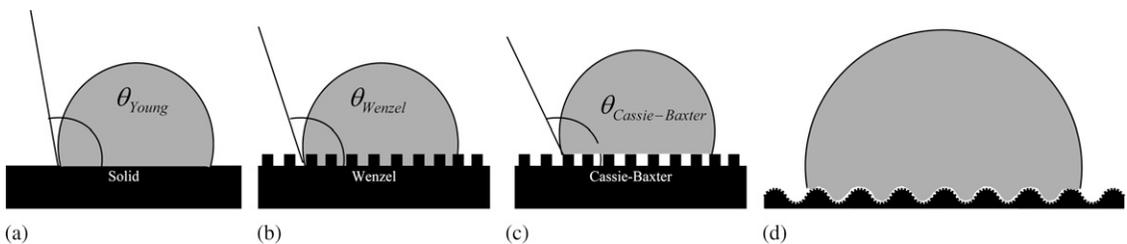


Figure 3. A small droplet in equilibrium on (a) an ideal surface; (b) a hydrophilic, rough surface; (c) a superhydrophobic, heterogeneous surface; and (d) a superhydrophobic, rough, porous surface.

where γ_{SG} is the surface tension at the solid and gas interface (N/m), γ_{SL} surface tension at the solid and liquid interface (N/m), γ_{LG} surface tension at the liquid and gas interface (N/m), and θ_{Young} contact angle at which the liquid–gas interface meets the solid–liquid interface (Fig 3a). Eq 1 is Young’s equation, which was developed by Thomas Young in 1805. Although Young’s equation is controversial (Jameson and Cerro 1976; White 1977; Liu and German 1996; Butt et al 2007), it is fundamentally important in surface science, and it is one of the most widely used equations used to describe surface wetting phenomena.

In 1869, more than 64 yr after Young developed this equation, Dupre (1869) developed an equation for calculating pull-off work (or work of adhesion), $W_{adhesion}$, associated with separating a liquid from a solid substrate (N/m):

$$W_{adhesion} = \gamma_{SG} + \gamma_{LG} - \gamma_{SL} \quad (2)$$

The combination of Eqs 1 and 2 generates the Young-Dupre equation:

$$W_{adhesion} = \gamma_{LG}(1 + \cos \theta) \quad (3)$$

The Young-Dupre equation is usually used to calculate the profile of the liquid–gas interface near the line of contact with a solid.

Young’s equation is applicable for an *ideal* surface, which is flat, perfectly smooth, rigid, topographically and chemically homogeneous, nonreactive, insoluble, and not perturbed by chemical interaction or by vapor or liquid sorption (Erbil 2006; Marmur 2009). For a rough, homogenous, nonideal surface (Fig 3b), the true wetting area is greater than its nominal (or geometric) area, and wetting properties of the surface are directly proportional to roughness of the surface (Wenzel 1936). Therefore, contact angle on a rough surface is different from the contact angle on an ideal surface, the former termed the apparent contact angle. Depending on hydrophilicity ($<90^\circ$) or hydrophobicity ($>90^\circ$), the apparent contact angle of a rough solid surface is either smaller or greater than the contact angle of the ideal regime, and it is expressed by the Wenzel equation:

$$\cos \theta_{Wenzel} = k \cos \theta_{Young} \quad (4)$$

where θ_{Wenzel} is Wenzel’s apparent contact angle of the true surface, θ_{Young} is Young’s contact angle of the nominal (or ideal) surface, and k is the roughness ratio defined as the ratio of true area of the solid surface to its nominal area. On a hydrophilic surface such as wood, more roughness often means a larger surface area for a polar liquid such as water to spread. The water contact angle of a hydrophilic, rough surface is less than 90° and $\theta_{Wenzel} < \theta_{Young} < 90^\circ$, ie increasing roughness leads to an increase of hydrophilicity of the surface. On a hydrophobic surface, however, air trapped in the micro- and/or nanoscale spaces between a wetting droplet and the rough surface reduces the wetting area. The water contact angle of a hydrophobic, rough surface is greater than 90° and $\theta_{Wenzel} > \theta_{Young} > 90^\circ$, ie increasing roughness leads to an increase of hydrophobicity of the surface (Shibuichi et al 1996; Qu  t   2002). Therefore, increasing surface roughness can enhance both hydrophilicity and hydrophobicity of a substrate (Li et al 2007).

Zisman (1963) empirically developed a linear relationship between $\cos \theta$ and γ_{LG} for a large number of low-energy solids:

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} = 1 + k(\gamma_c - \gamma_{LG}) \quad (5)$$

where γ_c is the critical surface tension for spreading and k a positive constant. The physical meaning of γ_c refers to surface tension below which a liquid will completely wet the solid ($\theta = 0$). Zisman’s critical surface tension has been determined for some wood species (Gray 1962; Marian 1962) and other polymers (Owens and Wendt 1969).

For a rough, heterogeneous surface that is composed of two surfaces with different contact angles, Cassie (1948) developed an equation:

$$E = k_1(\gamma_{S_1G} - \gamma_{S_1L}) + k_2(\gamma_{S_2G} - \gamma_{S_2L}) \quad (6)$$

where E is the energy gained when liquid spreads over a unit geometric area (N/m), γ_{S_1G} and γ_{S_1L} are the interfacial solid–gas and

solid-liquid tensions for k_1 fractional area, respectively, γ_{S_2G} and γ_{S_2L} are the interfacial tensions for k_2 fractional area, respectively, and $k_1 + k_2 = 1$. The contact angle θ'' for the composite surface can be calculated by:

$$\cos \theta'' = \frac{E}{\gamma_{LA}} = k_1 \cos \theta_1 + k_2 \cos \theta_2 \quad (7)$$

where θ_1 is the contact angle of k_1 area and θ_2 is the contact angle of k_2 area. For a porous surface such as a transverse cross-section of wood, the solid area is k_1 and gas area is k_2 . Therefore, $\gamma_{S_2G} = 0$, and the contact angle on a homogeneously porous surface can be expressed as follows:

$$\cos \theta'' = k_1 \cos \theta_1 - k_2 \quad (8)$$

For a hydrophobic, rough solid surface (Fig 3c), the Wenzel model (Eq 4) is not sufficient because the air bubbles are entrapped inside the grooves. The solid-liquid interface in such a hydrophobic, rough regime is explained by the Cassie-Baxter model illustrated subsequently (Cassie and Baxter 1944):

$$\cos \theta_{\text{Cassie-Baxter}} = k_1 \cos \theta_A - k_2 \quad (9)$$

where $\theta_{\text{Cassie-Baxter}}$ is the apparent contact angle of the Cassie-Baxter regime, k_1 is the ratio of the solid-liquid interface area to the total base area of the liquid droplet, θ_A is the advancing contact angle of the solid-liquid interface, and k_2 is the ratio of the liquid-gas interface area to the total base area of the liquid droplet ($1 - k_1$). If the liquid-gas interface area is zero, then $k_2 = 0$. In that case, the Cassie-Baxter regime becomes the Wenzel regime and Eq 9 is identical to Eq 4.

The advancing contact angle is when a droplet has the maximum volume allowable for the solid-liquid interfacial area, whereas the receding contact angle is when a droplet has the minimum volume allowable for the solid-liquid interfacial area. The θ in Eq 9 is the contact angle measured on a level surface and is a normal contact angle. Advancing and receding angles are measured when the substrate surface tilts. The difference between advancing and receding contact angles is the contact angle hys-

teresis. The magnitude of contact angle hysteresis is dependent on roughness, topography, morphology, and chemical homogeneity of the solid surface. Good (1979) suggested that the advancing contact angle represents hydrophobic areas on the surface, while the receding contact angle characterizes hydrophilic areas.

Wood is an anisotropic material; wood surfaces are topographically different in radial, tangential, and transverse sections. At the macroscale, the wood surface consists of earlywood and latewood; at the microscale, the wood surface consists primarily of lumen surfaces and cross-sectional walls. The water contact angle of earlywood is often different from that of latewood (Herczeg 1965; Hse 1972; Shupe et al 1998); the water contact angle in the transverse cross-section is different from the angles on radial and tangential cross-sections (Shupe et al 2001). Therefore, Cassie theory can be expanded further to a surface of more than two areas with different contact angles such as a wood surface and is represented by the following equation for tangential and radial surfaces:

$$E = k_1(\gamma_{S_1G} - \gamma_{S_1L}) + k_2(\gamma_{S_2G} - \gamma_{S_2L}) + k_3(\gamma_{S_3G} - \gamma_{S_3L}) + k_4(\gamma_{S_4G} - \gamma_{S_4L}) \quad (10)$$

and

$$\gamma_{LA} \cos \theta'' = k_1 \cos \theta_1 + k_2 \cos \theta_2 + k_3 \cos \theta_3 + k_4 \cos \theta_4 \quad (11)$$

where k_1 , θ_1 , k_2 , θ_2 , k_3 , θ_3 , and k_4 , θ_4 are fractional areas and contact angles, respectively, of lumen surfaces of earlywood, lumen surfaces of latewood, cell wall cross-sections of earlywood, and cell wall cross-sections of latewood; and $k_1 + k_2 + k_3 + k_4 = 1$ (entire radial or tangential surface). For the transverse section of wood, the following equation may be applied:

$$\cos \theta'' = k_1 \cos \theta_1 + k_2 \cos \theta_2 - k_3 \quad (12)$$

where k_1 , θ_1 and k_2 , θ_2 are area fractions and contact angles, respectively, of earlywood and latewood, and k_3 is the area fraction of air.

However, it is noted that some arbitrary terms exist regarding the definition of an ideal surface. Surface roughness, for example, can be defined

at macro, micro, nano, or even molecular scales. A visually smooth surface can often appear rough if the surface is magnified. Measurement of contact angle is, therefore, somewhat subjective (Cassie 1948). Confusion also occurs when choosing a wetting model for a practical problem. This is especially true for wood surfaces, which could be prepared by a microtome, planer, sander, sharp blade of woodworking machinery, or a dull tool (Marian et al 1958). Therefore, a criterion is necessary for predicting surface character of wood based on preparation methods and inherent properties, eg species, absorbing and adsorbing behaviors, density, and moisture content.

CALCULATION OF SURFACE TENSION OF WOOD

The γ in Eq 1 is variously termed as surface energy, surface-free energy, specific surface-free energy, and surface tension, causing tremendous confusion. Part of the confusion may result because for a one-component liquid, surface tension γ is numerically equal to the thermodynamic specific surface-free energy. However, according to Shuttleworth (1950), Gibbs pointed out that surface tension and surface-free energy for a solid are not equal. In addition, surface-free energy is always positive, but surface tension can be positive or negative. Johnson (1959) clarified the confusion surrounding the concepts. For the remainder of this review, all γ -related concepts are deemed to be surface tension.

Surface tension is a unique characteristic of a substance (solid or liquid). Surfaces of liquids and solids are often different from their bulk materials. For a liquid, surface molecules are subjected to an unbalanced force field (van der Waals forces) compared with molecules at the center of the liquid. The unbalanced force generates tension between adjacent molecules that is equal to the free energy possessed by each unit area of the surface. Herczeg (1965) believed that a solid surface does not exert mechanical tension but exerts electrical attraction. Herczeg interpreted the solid surface phenomenon as potential energy that is liberated when the surface disappears.

The thermodynamics of a liquid and solid interaction can be reflected by measurement of contact angles of liquid on the solid. Data obtained from measurements can be used to estimate the surface tension of a solid, which quantifies the characteristic of the solid surface and its wettability. Based on contact angles of surface and probe liquids, several methods have been used to calculate surface tension of wood, including Zisman's critical tension, Owens-Wendt's geometric mean, Wu's harmonic mean, and Young-Fowkes-van Oss-Good acid-base approaches.

Zisman's Critical Tension Method

Zisman (1963) empirically established a general rectilinear relationship between the cosine of the contact angle θ and surface tension γ_{LH} . This led to development of the critical surface tension of wetting, γ_c , which is defined by the intercept of the horizontal line $\cos \theta = 1$ with the extrapolated straight line plot of $\cos \theta$ vs γ_{LG} . Zisman believed that γ_c is a characteristic of only the solid. It is an empirical parameter and varies with solid surface composition, as one would expect of γ_s , surface tension of the solid.

Gray (1962) used critical surface tension γ_c to estimate surface tension γ_s of 20 species. Later, however, it was shown that critical tension of a solid is not equal to its surface tension (Herczeg 1965; Nguyen and Johns 1979). Both Wu (1979) and Gindl et al (2001) produced results that showed Zisman's critical tension gives the lowest surface tension values compared with values determined by other methods. Gardner (1996) found that critical surface tension by Zisman's approach agrees well with surface tension determined by the acid-base approach.

Owens-Wendt's Geometric-Mean Approach and Wu's Harmonic-Mean Method

For a solid-liquid interface, Girifalco and Good (1957) derived a relationship to correlate solid-liquid interface tension to the tension of each of the solid and liquid components, assuming that no other intermolecular forces are involved

except molecular dispersion force (Fowkes 1964):

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\Phi\sqrt{\gamma_S\gamma_L} \quad (13)$$

where γ_S and γ_L are surface tensions of the solid and liquid, respectively, and Φ a ratio of the free energy of adhesion to the square root of the product of the cohesion-free energies of the solid and liquid. Fowkes (1964) proposed that the total free energy at an interface is the geometric sum of contributions from different intermolecular forces involved at the interface. For an interface at which molecular dispersion is the only force involved, the Fowkes equation is:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d\gamma_L^d} \quad (14)$$

where γ_S^d and γ_L^d refer to dispersion force components of the total surface tension of the solid and liquid, respectively. By combining Eq 14 with Young's equation, Fowkes derived an equation for contact angle of a liquid on a solid in terms of dispersion force contributions of each liquid and solid:

$$1 + \cos \theta = 2\frac{\sqrt{\gamma_S^d\gamma_L^d}}{\gamma_{LG}} \quad (15)$$

Owens and Wendt (1969) expanded Fowkes equation into a polar-dispersion system. For a polar liquid such as water, polar components (hydrogen bonds) at the interface can be expressed as:

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad (16)$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (17)$$

where γ_S^p and γ_L^p refer to the polar components (hydrogen bonds) of the solid and liquid, respectively. The Young-Owens-Wendt equation can be expressed as:

$$1 + \cos \theta = 2\sqrt{\gamma_S^d}\left(\frac{\sqrt{\gamma_L^d}}{2\gamma_{LG}}\right) + 2\sqrt{\gamma_S^p}\left(\frac{\sqrt{\gamma_L^p}}{2\gamma_{LG}}\right) \quad (18)$$

Scheikl and Dunky (1998) evaluated surface tension of earlywood and latewood of spruce, pine, and beech using Zisman and Owens-Wendt harmonic approaches. Wang et al (2007) used the same approach to calculate surface tension of wood strands dried in a rotary drum, oven, microwave, and in air.

It is proposed that the harmonic mean equation developed by Wu (1971) is more accurate and, consequently, more useful for calculating surface tension than the geometric mean suggested by Eq 18 (Buckton 1995). Wu's equation is as follows (Saito and Yabe 1983):

$$\gamma_{LG}(1 + \cos \theta) = \frac{4\gamma_L^d \cdot \gamma_S^d}{\gamma_L^d + \gamma_S^d} + \frac{4\gamma_L^p \cdot \gamma_S^p}{\gamma_L^p + \gamma_S^p} \quad (19)$$

Both geometric-mean and harmonic-mean approaches (Eqs 18 and 19) require at least two probe liquids with known surface tension properties to estimate dispersive (γ_S^d) and polar components (γ_S^p) of a solid such as a wood surface.

Nguyen and Johns (1979) used Wu's harmonic-mean approach to evaluate effects of aging and extraction on polar and dispersion components of surface tension of redwood and Douglas-fir, while Mantanis and Young (1997) used the same approach to calculate polar and dispersive components of heartwood samples of Sitka spruce, Douglas-fir, sugar maple, and quaking aspen. Wang et al (2007) examined effects of drying methods on surface tension of southern pine strands using the geometric-mean approach. Several other investigators used the geometric-mean and harmonic-mean approaches for comparisons with other methods (Wu 1979; Gardner 1996; Maldas and Kamdem 1998; Gindl et al 2001).

Young-Fowkes-van Oss-Good Acid-Base Method

Fowkes (1972) and van Oss et al (1988) suggested another approach to model polar and nonpolar interface problems. For nonpolar components, Lifshitz-van der Waals interfacial

tion is expressed according to the Young-Good-Girifalco (Girifalco and Good 1957) combining rule:

$$1 + \cos \theta = 2 \sqrt{\frac{\gamma_S^{LW}}{\gamma_L^{LW}}} \quad (20)$$

where γ_S^{LW} and γ_L^{LW} are Lifshitz-van der Waals dispersive components of the solid and liquid, respectively. For polar components, Fowkes (1972) and van Oss et al (1988) suggested further dividing γ_S^p and γ_L^p into Lewis acid and Lewis base subcomponents:

$$\gamma_S^p = 2 \sqrt{\gamma_S^+ \gamma_S^-} \quad (21)$$

$$\gamma_L^p = 2 \sqrt{\gamma_L^+ \gamma_L^-} \quad (22)$$

The complete version of the Young-Fowkes-van Oss-Good acid-base approach (hereinafter referred to as the acid-base approach) equation is:

$$(1 + \cos \theta) \gamma_{LG} = 2 \left(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+} \right) \quad (23)$$

The acid-base approach has been used by several investigators to calculate surface tension of wood (Gardner 1996; Zhang et al 1997; Maldas and Kamdem 1998; Scheikl and Dunky 1998; Shen et al 1998; Gindl et al 2001, 2004). Because there are three unknown surface tension variables in Eq 23, at least three probe liquids with known surface tension properties are required to estimate surface tension of a solid.

Between the harmonic-mean and the geometric-mean methods, it is agreed that harmonic is a better approach than geometric mean (Nguyen and Johns 1978; Wu 1979; Gardner 1996; Maldas and Kamdem 1998). Total surface tension obtained by the geometric mean is greater than total surface tension calculated by the harmonic mean in most published data. Nguyen and Johns (1978) concluded that the harmonic-mean method “more accurately reflects true surface

qualities of wood” than the geometric mean approach. Gardner (1996) also found that total surface tension of the harmonic-mean approach was closer to total surface tension of the acid-base than geometric-mean approach.

In recent and current research, several investigators have favored the acid-base approach because of its accuracy and usefulness (Gardner 1996; Maldas and Kamdem 1998; Gindl et al 2001). The acid-base approach delivers more useful information about the wood surface, ie acidic, basic, disperse, and polar components of the surface, than polar-dispersion approaches. However, results show that the predicted total surface tension of wood calculated by the acid-base method increases after wood is treated with chromated copper arsenate (CCA) (Zhang et al 1997; Maldas and Kamdem 1998), while predicted total surface tension of wood calculated by geometric- and harmonic-mean methods decreased after wood was treated with CCA (Maldas and Kamdem 1998).

These results reflect the fact that, to date, no independent methods have been developed that could be used to calculate the absolute value of surface tension of wood (Nguyen and Johns 1978, 1979; Maldas and Kamdem 1998). New theories or methods are needed to estimate the absolute surface tension of wood.

Inverse Gas Chromatography Method

Inverse gas chromatography (IGC) is a physical characterization technique used in analysis of solid surfaces. This method of determining surface tension of a solid does not rely on measurement of contact angle. It involves passing a known probe gas through Teflon columns where it interacts with an unknown packing material such as wood particles. Retention time of probe chromatograms relative to that of the reference gas is determined and net retention volume of the reference gas calculated. Finally, surface tension of wood particles is calculated using a graphic method. Wälinder and Gardner (2000) examined surface tension of Norway spruce wood particles using IGC. They found

removal of extractives from wood increases dispersive components of surface tension and surface acidity.

WETTABILITY AND SURFACE TENSION OF WOOD

According to Zisman (1963), Cooper and Nuttall established subsequent conditions for spreading of a liquid on a solid substrate:

$$S = \gamma_{SG} - (\gamma_{LG} + \gamma_{SL}) > 0 \quad (12)$$

and

$$\gamma_{SG} > \gamma_{LG} + \gamma_{SL} \quad (13)$$

where S is the spreading force (N/m); for spreading, $S > 0$; for nonspreading, $S < 0$. Eq 13 indicates that, for good wetting, surface tension of the solid must be greater than surface tension of the liquid. The higher the surface tension of the solid and/or the lower the surface tension of the liquid, the better the wetting.

Surface wetting is also affected by the probe liquid. As shown in Eq 13, the wetting liquid should have as low as possible surface tension for good wetting. A high surface tension liquid (adhesive) would increase contact angle. Air pockets in cavities would make complete wetting difficult and give rise to localized stress concentrations in the bonding area (Herczeg 1965). To obtain good bonding, pressure is required to expel air from cavities and increase contact area between adherends. According to Halligan (1969), Maxey found that contact areas between two wood samples increased from less than 10 to about 55% when pressure was increased 0.3-10.3 MPa. However, high wetting does not necessarily lead to good adhesion, because the glue line may be inadequate from excessive penetration (Hse 1972).

The wettability of a solid surface is the ease and effectiveness with which a liquid can spread over a solid surface (Gray 1962). Wettability is of importance in adhesion, surface coating, water repellency, and waterproofing. A wood surface with high wettability develops high bonding shear strength (Freeman and Wangaard 1960). Good wetting is fundamental for good

adhesion, because it provides better mechanical interlocks, molecular level interactions, and secondary force interactions (Bodig 1962; De Moura and Hernández 2005).

The contact angle of a liquid droplet can be used to determine wettability and surface tension of the surface. Wettability and contact angle are inversely related: the lower the contact angle, the greater the wettability.

Behavior of a Liquid Droplet on the Surface of Wood

Wood is a complex matrix that is hygroscopic, porous, rough, and physically and chemically heterogeneous. The behavior of a water droplet placed on a wood surface is often different from behavior on a metal or polymer surface. In addition to spreading across the surface of wood, the liquid also penetrates into wood therefore, wetting occurs at and under the wood surface. The shape and contact angle of a sessile droplet changes with time (Chen 1972) and becomes more or less stable or equilibrated after a certain period when contact angle is measured.

Changes with time of the shape and contact angle of a sessile droplet have been modeled by several investigators (Chen 1972; Liptakova and Kudela 1994; Shi and Gardner 2001; Lu and Wu 2006; Lee et al 2007). Each model was developed for a particular species and at specific wood and environmental conditions.

Sorption of a liquid into wood and evaporation of the probe liquid are continuous processes during measurement of contact angle. The wood-air-liquid equilibrium is relative and temporary. If contact angle is measured before equilibrium is reached, the measured angle would be greater than the "real" contact angle because the liquid would continue to spread and be absorbed. If contact angle is measured some time after equilibrium, the measured contact angle would be less than the "real" contact angle from evaporation of the liquid and penetration into wood.

Liptakova and Kudela (1994) divided development of a sessile droplet of water on the surface

of wood into three states based on diameter (d) of the interface between wood and water, ie increasing, constant, and decreasing d . During the first stage (increasing d), water contact angle and droplet height are decreasing, and this stage ends when d is maximized. The water contact angle and droplet height are continuously decreasing in the second stage, but the interface diameter d remains constant. Liptakoval and Kudela believed that water completely wets the surface at the end of the second stage. Also, they believed that water has also wet the wood under the interface in the second stage. In the last stage, water predominantly wets the wood under the water–wood interface, and contact angle, droplet height, and diameter d decrease.

The apparent contact angle, therefore, is measured when the surface of the wood is completely saturated by the liquid and wetting under the interface has just begun, which is at the end of the second stage. Because of the continuous nature of wetting, this specific point may be difficult to detect or not exist.

Variables That Affect Wettability and Surface Tension

The contact angles and calculated surface tension presented in various references often do not always agree for the same species (Table 1). This largely results from the different bulk and surface characteristics and use of different probe liquids and measurement conditions. Contact angle varies with measuring time, but surface tension is a unique characteristic of a particular surface and is constant. In addition to the effect of contact angle measurement, many factors potentially affect wettability and surface tension (references in each category are not exhaustive):

- (1) Probe liquids (Gardner 1996; Gindl et al 2001; Wang et al 2007)
- (2) Species (Gray 1962; Herczeg 1965; Gardner 1996; Mantanis and Young 1997; Wang et al 2007)
- (3) Macrostructure of the wood surface, including earlywood, latewood, heartwood, sap-

wood, grain directions, and cross-sectional surfaces (Herczeg 1965; Hse 1972; Scheikl and Dunky 1998; Shen et al 1998; Shupe et al 1998, 2001; Wang et al 2007)

- (4) Anatomical microstructure of the surface of wood, including lumens, pits, and other cavities (Zwieniecki and Holbrook 2000; Kohonen 2006)
- (5) Physical properties of wood (moisture content, density, growth rate, drying history) and gas and moisture contaminations (Scheikl and Dunky 1998)
- (6) Chemical properties of wood, including specific characteristics of cellulose, hemicelluloses, lignin, and extractives (Herczeg 1965; White et al 1974; Mantanis and Young 1997; Wålinder and Gardner 2000; Nzokou and Kamdem 2004; Hernández 2007)
- (7) Machining methods such as planing, sanding, sawing (Gray 1962; Wang et al 2007)
- (8) Chemicals such as preservatives and hydrophobic treatments (Zhang et al 1997; Maldas and Kamdem 1998)
- (9) Calculation methods for surface tension (Gardner 1996; Maldas and Kamdem 1998; Scheikl and Dunky 1998; Gindl et al 2001)
- (10) Contact angle measurement (Shen et al 1998)

Specific knowledge and control of these variables are absolutely essential for reproducible measurements of surface tension.

On a macroscale, the wood surface is characterized by alternating earlywood and latewood. Several investigators have investigated effects of this macro character on wettability and surface tension (Herczeg 1965; Hse 1972; Scheikl and Dunky 1998; Shupe et al 1998; Shi and Gardner 2001). It is generally agreed that earlywood has a rougher surface than latewood. Therefore, contact angle measured at the surface of earlywood is often smaller than that of latewood (Herczeg 1965; Hse 1972; Shupe et al 1998), and wettability and surface tension of earlywood is greater than that of latewood (Herczeg 1965; Scheikl and Dunky 1998). Shen

Table 1. The summary data of surface tension (mN/m) of wood in the literature.^a

Species	Method	Polar-Dispersive Components			Acid-Base Components			Reference					
		γ_{wood}^d	γ_{wood}^p	$\gamma_{wood}^d + \gamma_{wood}^p$	γ_{wood}^+	γ_{wood}^-	γ_{wood}^+						
Ash	WP	12.0	51.1	63.1	W-gly	42.6	0.0	67.4	0.6	42.2	Bromon-ethyl gly-forma-gly-w	42.9	Gardner 1996
	WP	41.8	13.2	55.0	W-Ethyl gly-forma-diiod								Mantanis and Young 1997
	SD	6.9	53.1	60.0	W-gly							50.6	Scheikl and Dunky 1998
Beech	SD	32.1	19.6	51.7									Liptakova and Kudela 1994
	WP	18.1	37.0	55.1	W-gly	47.5	0.4	28.0	6.8	54.3	Bromon-ethyl gly-forma-gly-w	48.1	Gardner 1996
Douglass-fir	SD	28.8	19.2	48.0	W-gly							52.8	Nguyen and Johns 1978
	SD	22.8	19.2	48.0	W-gly								Nguyen and Johns 1979
Extracted	SD	21.5	37.4	58.9	W-gly								Nguyen and Johns 1979
	WP	36.2	11.8	48.0	W-Ethyl gly-forma-diiod	45.5	0.5	33.2	7.9	53.3	Bromon-ethyl gly-forma-gly-w	46.8	Mantanis and Young 1997
Maple	WP	16.0	43.6	59.6	W-gly								Gardner 1996
	WP	40.2	16.4	56.6	W-Ethyl gly-forma-diiod								Mantanis and Young 1997
Poplar	SD	25.2	28.5	53.7	W-gly							53.1	Scheikl and Dunky 1998
	SD	14.9	53.8	68.7	W-ethyl-gly	45.5	0.0	57.0	2.1	47.7	W-ethyl gly-diiodometh		Maldasand Kamdem 1998
Untreated	SD	19.5	29.6	49.1	W-ethyl-gly	50.8	0.1	23.4	2.2	53.0	W-ethyl gly-diiodometh		Maldasand Kamdem 1998
	CCA-treated												
Red oak	WP	14.2	44.1	58.3		39.7	0.5	37.7	8.3	48.0	Bromon-ethyl gly-forma-gly-w	46.8	Gardner 1996
	SD	22.7	31.5	54.2	W-gly								Nguyen and Johns 1979
Extracted	SD	23.1	33.1	56.2	W-gly								Nguyen and Johns 1979
	WD	45.0	16.5	61.5	W-Ethyl gly-forma-diiod					51.0	Diiodometh-forma-gly-ethyl	42.5	Mantanis and Young 1997
Spruce	SD	2.0	71.6	55.0	W-gly							51.8	Gindl et al 2001 ^b
	SD	13.9	41.9	73.6	W-gly							53.2	Scheikl and Dunky 1998
Latewood	SD			55.8									Scheikl and Dunky 1998
	SD	37.7	6.5	44.2	W-forma-methyl-iodide	33.7	0.1	34.1	3.0	36.6	Ethyl gly-forma-methyl iodi-w		Zhang et al 1997
Southern pine	SD	25.7	16.0	41.7	W-forma-methyl-iodide	42.3	0.0	8.6	1.1	43.4	Ethyl gly-forma-methyl iodi-w		Zhang et al 1997
	SD												Wang et al 2007
Untreated	WP	35.0	7.8	42.4									Wang et al 2007
	WP	38.9	3.6	42.5									Wang et al 2007
Rotary dry	WP												Wang et al 2007
	WP												Wang et al 2007
Oven dry	WP												Wang et al 2007
	WP												Wang et al 2007
Microwave dry	WP												Wang et al 2007
	WP												Wang et al 2007
Air dry	WP												Wang et al 2007
	WP												Wang et al 2007
Scots Pine	SD	38.2	16.5	54.7	W-gly	40.7	1.7	8.4	7.6	48.3	Diiodometh-forma-w	46.3	Liptakova and Kudela 1994
	SD												Scheikl and Dunky 1998
Earlywood	SD	0.4	83.4	83.8	W-gly	38.9	0.1	17.3	1.9	40.8	Diiodometh-forma-w	50.9	Scheikl and Dunky 1998
	SD	3.0	68.1	71.1								54.3	Shen et al 1998
Latewood	SD												Shen et al 1998
	WP												Shen et al 1998
Walnut	WP	18.1	37.0	55.1	W-gly	37.9	0.1	58.9	4.6	42.6	Bromon-ethyl gly-forma-gly-w	10.8	Gardner 1996
	WP	17.6	25.8	43.4	W-gly	34.0	0.4	22.8	6.0	40.0	Bromon-ethyl gly-forma-gly-w	31.4	Gardner 1996

^a WP = Wilhelmy plate; SD = sessile drop; W-gly = water, glycerol; W-ethyl gly-forma-diiod = water, ethylene glycol, formamide, diiodomethane; W-forma-methyl-iodide = wWater, formamide, methylene iodide; Bromon-ethyl gly-forma-gly-w = bromonaphthalene, ethylene glycol, formamide, glycerol, water; W-ethyl gly-diiodometh = water, ethylene glycol, diiodomethane; Ethyl gly-forma-methyl iodi-w = ethylene glycol, formamide, methylene iodide, water; Diiodometh-forma-w = diiodomethane, formamide, water.

^b Estimated values from the figures in this article.

et al (1998) also found that surface tension parallel to grain is greater than perpendicular. Surface tension of a sanded surface is often greater than unsanded (Gray 1962). Wang et al (2007) found that polar components on radial and tangential surfaces vary with drying temperature.

Effects of surface contamination and aging on wettability and surface tension of wood have been investigated extensively since the 1950s (Gray 1962; Chen 1970; Nguyen and Johns 1979; Mantanis and Young 1997). Surface tension and wettability of a freshly cut surface decreases over time (Gray 1962; Nguyen and Johns 1979; Gardner et al 1991; Mantanis and Young 1997; Gindl et al 2004). Gindl et al (2004) found that surface tension of sanded wood surfaces decreased more rapidly in a 7-da exposure than did microtomed surfaces. Nguyen and Johns (1979) found that for Douglas-fir, both dispersive and polar components decreased with time, but the dispersive component was predominant for an unextracted surface, and the polar component is marginally dominant for the extracted. However, Mantanis and Young (1997) found that dispersive components account for 75-80% of total surface tension of four species (Douglas-fir, spruce, sugar maple, and quaking aspen). Extractives and migration in the wood are commonly believed to be causes of surface contamination. Extraction has a positive effect on surface tension, but the effect is more prominent for some species than others (Nguyen and Johns 1979; Wälinder and Gardner 2000).

Surface tension is also affected by moisture content of wood. A high moisture content or exposure to high humidity (greater than 90% RH) results in poor wettability, but the negative effect of moisture is eliminated by drying (Gray 1962). Very low moisture content can also reduce wettability of the surface. Wellons (1980) found that contact angle of Douglas-fir veneer increased 50-60° when moisture content decreased 17.9-3.4%, indicating that drying makes wood more hydrophobic. Contact angle at a moisture content of 3.4% remained above 110° for more than 4 min. Scheickl and Dunky

(1998) found that wettability decreases slowly as moisture content decreases 15-3%.

Additional literature references were examined to determine any other factors that would affect surface tension and wettability. In these studies, it was generally agreed that drying, especially high-temperature drying, inactivates the wood surface and reduces surface tension (see subsequent "surface contamination" section). Wang et al (2007) showed that polar components of oven- and rotating-drum-dried strands are greater than polar components of air- and microwave-dried strands. Maldas and Kamdem (1998) found that, after CCA treatment, wettability and surface tension of treated wood were reduced. Dispersion components of surface tension of treated wood increase and polar and base components decrease. Similar results were found by Zhang et al (1997). Most recently, Blanchard et al (2009) evaluated the potential for increasing surface energy of wood using radiofrequency induction and capacitive plasmas. Their exploratory study showed that plasma treatment results in a 30-100% increase of surface energy and adhesion for sugar maple wood.

Chemical Components on Cell-Wall Surfaces

Hydrophilicity and hydrophobicity of wood relate to chemical composition of the surface, however, these are not fully understood. For example, fractions of the three structural components on the lumen surface and cross-sectional walls are not well defined. It is known that hydroxyls at the surface of the wood attract water molecules by hydrogen bonding. X-ray photoelectron spectroscopy (XPS) provides valuable information about chemical components on the surface (Jaić et al 1996; Sinn et al 2001; Nzokou and Kamdem 2005; Inari et al 2009). However, XPS cannot be used to quantitatively determine the functional groups. It has been reported that zinc oxide forms a diametric bond with the guaiacol group of lignin, permitting wood to have a weak hydrophobicity, therefore, knowledge of lignin distribution on surfaces is important (Kubel and Pizzi 1981). Further research on physical characteristics

and chemical composition of surfaces of various wood products is important to understand and control both hydrophilic and hydrophobic performance.

Summary of Surface Tension Data in References

Table 1 presents surface tension data for 15 species of wood under different conditions of measurements or composition. For the polar-dispersive approach, when both harmonic mean and geometric mean were used, surface tension calculated using the harmonic-mean method was always selected. The calculated surface tension of wood varies with methods used to measure contact angle (Sessile drop or Wilhelmy plate), methods to calculate surface tension, probe liquids, species, and preservative treatment. The water–glycol probe system was used predominantly for polar-dispersion methods, while probes vary among investigators for the acid-base method. Critical surface tension is often less than surface tension calculated by the acid-base method, while surface tension calculated by the acid-base method is often less than that calculated by the polar-dispersion method.

The range of surface tension of hardwoods is 43.4–68.8 mN/m (average: 57.3 mN/m; standard deviation: 6.8 mN/m). For comparison, the range of surface tension of softwoods is 41.7–83.8 mN/m (average: 55.4 mN/m; standard deviation: 12.7 mN/m). It appears that dispersive values are less than polar values for both hardwoods and softwoods. The average dispersive and polar components of hardwoods are 21.7 and 35.2 mN/m, respectively, while those of softwoods are 23.9 and 31.0 mN/m, respectively. However, this comparison between dispersive and polar components of softwoods and hardwoods is a general trend and may vary with species. In most cases, dispersive components are greater than polar for softwoods. However, in several extreme cases, polar components have a higher average than dispersive components of softwoods (Table 1).

SURFACE TOPOGRAPHY

According to Wenzel (1936), apparent contact angles and wettability of the surface increase as surface roughness increases. Therefore, when the true surface area is N times greater than the apparent area, work of adhesion should be expected to be N times greater than work of adhesion for the apparent surface area (Zisman 1963).

Marian et al (1958) classified machining surfaces into three categories, first-, second-, and third-degree texture with first degree being smoothest. In first-degree texture, the surface is formed by anatomical structure only (micro-scale), consisting largely of alternating concave, lumen surfaces and cell wall cross-sections (Fig 1). This surface can only be produced by microtoming. Second-degree texture is produced by machining (planing, sanding, slicing, and sawing), where the surface has a crushed anatomical structure, cell fragments, tissues, and debris. Third-degree texture is produced by machining errors such as dull or damaged blades and machine vibration.

Glue-joint strength increased with increasing surface roughness to a point beyond which further increases in roughness diminish strength of the joint (Suchsland 1957; Marian et al 1958). It was believed that the critical roughness level at which joint strength initially changed was in the third-degree texture.

Microstructure

Kohonen (2006) found sculpturing on the lumen surface of water-conducting capillaries in trees. Species in dry habitats had a rough lumen surface covered with large prominent warts with a zero contact angle, while species in wet habitats had a smooth surface marked with small round warts and a contact angle greater than zero. Both increase wetting of the cell walls of water-conducting capillaries in trees. Zwieniecki and Holbrook (2000) evaluated contact angle and intervessel pit geometry of six species. They found contact angle in the vessel lumens ranges

42–45°, whereas the opening in the pit chambers was 144–157°.

Earlywood and Latewood

As previously discussed, surfaces of wood usually do not meet the ideal surface requirement of Young's equation; in particular, earlywood and latewood have different contact angles and wettabilities (Herczeg 1965; Hse 1972; Scheikl and Dunky 1998; Shupe et al 1998; Shi and Gardner 2001).

With respect to wettability, the major differences between earlywood and latewood are their physical structures and machining properties. At the microscale, earlywood has larger lumen diameters and thinner cell walls and is distorted more by cutting tools, leaving protruding cell fragments. Therefore, earlywood is often rougher than latewood (Marian et al 1958; Hse 1972; De Moura and Hernández 2005). Surface tension and wettability of earlywood is greater than that of latewood (Herczeg 1965; Hse 1972; Kajita and Skaar 1992; Scheikl and Dunky 1998; Shupe et al 1998). Different roughnesses of earlywood and latewood generate topographic heterogeneity on wood surfaces.

Marian et al (1958) found that roughness increased with the proportion of earlywood on the surface. Earlywood has greater roughness and thus a higher bonding strength than latewood, although earlywood is weaker. Therefore, within a failed glue joint consisting of earlywood and latewood, earlywood may have achieved its full strength but may contribute about 30% to total strength; latewood may have achieved only about 10–15% of its full strength but it may contribute 70% of total strength.

Herczeg (1965) examined contact angles on tangential surfaces of latewood and earlywood of Douglas-fir and found that earlywood was much easier to wet. The surface tension of earlywood is greater than surface tension of latewood. Herczeg was not certain whether the difference in surface tension was from greater roughness or different chemical compositions such as extractives. The wettability of earlywood and latewood both dete-

riorated to 45 h, during which contact angle of earlywood increased 40.8–74.0° and contact angle of latewood increased 43.0–77.2°. It appears that the wettability deterioration rate of latewood (77.2–43.0° = 34.2°) is greater than that of earlywood (74.0–40.8° = 33.2°).

Hse (1972) examined wettability of southern pine veneer using 36 phenol–formaldehyde resins. The resins had various molar ratios of sodium hydroxide to phenol and formaldehyde to phenol and a range of solids. Glue bond strength, bond line wood failure, and bond line delamination improved with an increase of veneer surface wettability. The contact angle of earlywood was less than that of latewood, meaning greater wettability. Therefore, contact angle of the veneer surface was negatively correlated with glue bond quality, ie the lower the contact angle, the higher the bond quality.

Kajita and Skaar (1992) examined wettability of some US softwoods. They found that shaved and earlywood surfaces were easier to wet than original and latewood surfaces.

Shupe et al (1998) evaluated the effect of veneer side (loose; tight) and wood grain on wettability of southern pine veneer. The liquids used for contact angle evaluation were phenol–formaldehyde resin and distilled water. They found that latewood surfaces had a slightly higher contact angles than earlywood for the two liquids, and the loose side of the veneer had a lower contact angle than the tight, attributing differences to surface tension. Scheikl and Dunky (1998) also found that surface tension of earlywood is greater than that of latewood.

The extractives in southern pine latewood are greater than those in earlywood and are predominately in resin canals (Šernek 2002). Most extractives are small, nonwetttable organic molecules (<C₄₀) that reduce wettability of the surface of wood.

Sapwood and Heartwood

Heartwood often contains more nonwetttable extractives than sapwood and therefore is often

less wettable than sapwood. Kajita and Skaar (1992) found wettability of sapwood to be greater than heartwood of some US softwoods. Shi and Gardner (2001) evaluated wettability of sapwood and heartwood along and across the grain of pine and Douglas-fir. Sapwood was more wettable than heartwood for both species; the equilibrium contact angle of Douglas-fir sapwood was greater than that of southern pine sapwood, and the equilibrium contact angle of Douglas-fir heartwood was less than that of southern pine heartwood.

Cross-sectional Surfaces

Gray (1962) found that wettability of freshly sanded, green heartwood was not significantly different in radial and tangential directions. Shupe et al (2001) evaluated wettability of 22 southern hardwood species. Mean contact angles in the transverse cross section were 2.1-29.0° and 5.1-31.5° greater than contact angles in radial and tangential sections, respectively, indicating that wettability of those surfaces was greater than that of the transverse. Among three drying methods (ie oven, air, and freeze), the oven-dried surface had the greatest contact angle, while freeze-dried had the lowest.

Grain Directions

Across the grain, a wood surface consists of alternating lumen openings and cross-sectional walls, therefore, wood surfaces are often rougher across than parallel to the grain. Shen et al (1998) evaluated wettability along and across the grain for Scots pine using the sessile drop and Wilhelmy plate methods with water, formamide, and diiodomethane as probe liquids (Wilhelmy 1863). They found that contact angles along the grain were smaller than those across for both methods. Similar results were found for southern pine and Douglas-fir by Shi and Gardner (2001) and for southern pine by Lee et al (2007).

Planing, Sanding, Microtoming

Planing and sanding are two surfacing processes for lumber and both are in the second-degree

roughness classification of Marian et al (1958). Bodig (1962) compared wettability of veneers smoothed by sanding and microtome-surfacing. He found that sanded veneer showed greatest wettability followed by microtome-prepared and original veneer. Gray (1962) found that surface tension (estimated by critical surface tension) of a sanded surface (40 mN/m) was twice that of an unsanded surface (20 mN/m). Compared with an unsanded surface, sanding had a major effect on advancing contact angle and a minor effect on receding, indicating that sanding is advantageous for both wetting and gluing.

Gindl et al (2004) found that surface tension of both sanded and microtome-prepared surfaces of spruce decreases with aging. The surface tension reduction of sanded surfaces is primarily because of reduction of the disperse component, while that of planed surfaces is primarily from reduction of the polar component.

De Moura and Hernández (2005) evaluated sanding and planing effects on wettability of sugar maple. They found that planed surfaces were damage-free and consisted of more open cells, particularly vessels, while sanded surfaces had cell-wall fibrillation, scratches produced by abrasive grain, and few open vessels. The surfaces of sanded were rougher than planed wood, therefore, having higher surface energy and wettability, greater actual surface available to bonding, stronger pull-off adhesion, and better aging resistance of films. The planed surfaces permitted greater penetration but had poorer adhesion.

Preservative Treatment

Zhang et al (1997) examined CCA-treated wood for gluability, surface tension, wettability, and glue-line shear. They found that accelerated weathering decreases surface tension of both CCA-treated and untreated wood. Maldas and Kamdem (1998) evaluated surface tension and wettability of CCA-treated red maple using Zisman's critical surface tensions, geometric-mean, harmonic-mean, and acid-base approaches. Dispersive components of surface tension increased and polar components decreased after

CCA treatment, probably because some hydroxyls were blocked by CCA oxides.

SURFACE CONTAMINATION

Surface tension and wettability of a freshly cut wood surface deteriorates over time. This phenomenon, often referred to as surface contamination, surface inactivation, or aging, has been documented and investigated for decades (Adam 1949; Bodig 1962; Gray 1962; Stumbo 1964; Herczeg 1965; Halligan 1969; Nguyen and Johns 1979; Christiansen 1990, 1991; Gardner et al 1991; Ajuong and Breese 1997; Nussbaum and Sterley 2002; Gindl et al 2004). Various explanations have been proposed to explain the phenomenon, including wood extractives, dirt, dust, grease, oxidation, adsorption, hydration, and moisture content. While all seem feasible, some have been excluded, and only nonwetable extractives appear to be commonly accepted as the major cause for deterioration of the surface with time.

That a contaminated surface has reduced wettability has been verified repeatedly (Gray 1962; Marian and Stumbo 1962a, 1962b; Stumbo 1964; Herczeg 1965; Nguyen and Johns 1979). Similarly, that a contaminated surface has reduced glue bonding strength has also been verified (Marian et al 1958; Stumbo 1964). Some contrary results have been reported (Nussbaum and Sterley 2002).

Gray (1962) found that even after a few hours, a freshly machined surface in the laboratory environment had higher wettability than a similar surface exposed to the exterior environment. The effect was prominent on the advancing contact angle and less evident on the receding angle, producing large contact angle hysteresis between freshly sanded and unsanded wood surfaces. Herczeg (1965) evaluated wettability of a planed Douglas-fir surface and found that contact angle and wettability deteriorated progressively up to 45 h. During that time, contact angle of earlywood increased 40.8-74.0°, while contact angle of latewood increased 43.0-77.2°.

Stumbo (1964) examined effects of airborne contaminants and light on wettability of surfaces. Wood samples were exposed to constant 12% EMC and protected from settling of airborne contaminants and exposure to light. He found that in the absence of light, surface contamination from settling of dust and other atmospheric contaminants, or surface damage from minimized gross changes in moisture content, bond strength of redwood and Douglas-fir decreased linearly over 90 and 150 da, respectively. Thus, loss of wettability related to contamination from light and airborne particles was disproved.

In his critical reviews, Christiansen (1990, 1991) summarized physical and chemical mechanisms of surface inactivation from overdrying. The physical mechanism of inactivation includes exudation of extractives to the surface, reorientation of wood surface molecules, and irreversible closure of large micropores (ie pits) in cell walls. The chemical mechanisms of inactivation include degradation of wood surface strength, oxidation and hindrance of surface bonding sites, chemical interference with bonding and curing of resins, and elimination of surface hydroxyl bonding sites by ether formation. Based on the review, Christiansen concluded that nonwetable extractives migrate to the surface during drying, inactivating surfaces of Douglas-fir and southern pine. Later results appear to support Christiansen's conclusions. Ajuong and Breese (1997) examined effects of extractives on creep behavior of Pai wood. They found that removal of polar extractives from within cell walls accelerated creep development. The cell walls of extracted wood were also more reactive to moisture. Nzokou and Kamdem (2004) found that extracted wood adsorbed more water than unextracted wood at high RH.

In high-temperature kiln drying, migration of extractives and water are expedited and "forced" by temperature and moisture gradients to move from interior to the surface. The drying temperature may exceed the boiling temperature of some VOCs such as pentanal, hexanal, and fatty acids, leading to complete evaporation. The

samples examined by Gray (1962), Stumbo (1964), and Herczeg (1965), however, were conditioned at 12% EMC before or during their experimental measurements. At that condition, moisture and temperature gradients of the wood during storage should be minimal as should be migration of solid extractives to the surface.

Extraction may not improve bond durability and strength (Dougal et al 1980; Nussbaum and Sterley 2002). Therefore, some other factors may be responsible for the time-dependent phenomenon that occurs on the surface. Marian (1967) believed that sorption of gases and moisture diminished surface tension and, hence, reactivity. Nguyen and Johns (1979) examined effects of contamination and extraction on surface tension of redwood and Douglas-fir conditioned at 12% EMC. They found that reduction of total surface tension was closely related to reductions of both polar and dispersive surface tension components, but the contribution of polar force components to total surface tension decreased with increased exposure time. They reasoned that reduction of surface tension was more related to environmental than wood factors.

For a wood surface prepared by a microtome or a planer, a change occurs to lumen surfaces and cross-sectional cell walls. The original lumen surface components are removed, and new, intact lumen surfaces become parts of the surface. The difference between new and original lumen surfaces is that the original surface has been externally exposed to possible oxidation or deposition of extraneous materials or erosion. The original lumen surface may also have airborne deposits, which, as shown by Stumbo (1964), have little effect on wettability. Therefore, original and new lumen surfaces are most likely similar in terms of free hydroxyls, surface tension, wettability, and extractives.

Next, we consider exposed cross-sectional cell-wall components of a newly planed surface. The original cross-sectional cell walls are thoroughly contaminated by gases and moisture (Marian 1967). Most hydroxyl sites on the surface of internal and cross-sectional cell walls have

adsorbed water molecules and/or VOCs. A reduced number of hydroxyl sites weakens hydrophilicity and wettability of the wood surface. The nonwetable extractives on original cross-sectional walls, if any, would have been removed. Therefore, the new surface has greater wettability than the original. In addition, cross-sectional cell walls protrude at new surfaces and are the first points of contact between two adherents. Higher bond strength would be expected for the new surface.

The wettability and glueability is, therefore, primarily dependent on free hydroxyls on new cell-wall surfaces. However, the number of free hydroxyls diminishes with an increase of exposure time, primarily because of adsorption of polar molecules. On new, open cell-wall surfaces, two kinds of polar molecules can be adsorbed to free hydroxyls, ie water and VOCs. Arshadi and Gref (2005) showed that polar VOCs in spruce and Scots pine sawdust include alkyl aldehydes (pentanal to decenal), alkanolic acids (C8 to C22), and other aromatic acids.

Most of these polar organics are liquids at room temperature. Typical low-molecular-weight aldehydes (pentanal to nonanal) have melting points lower and boiling points higher than water. For example, Pentanal (C5) melts at -60°C and boils at 102°C , while nonanal (C10) melts at -18°C and boils at 195°C . The predominant aldehyde in pine is α -pinene, which melts at 62°C and boils at about 155°C . Some alkanolic acids in pine are liquids, but most are solids at room temperature. The melting and boiling points of octanoic (C8) acid, for example, are 17 and 237°C , respectively, while melting and boiling points of octadecanoic acid are 70 and 383°C , respectively.

Some aldehyde and alkanolic acid VOCs might evaporate and be adsorbed by hydroxyls of freshly cut cell walls. However, free hydroxyls on fresh cell walls will not be completely occupied by VOC molecules, otherwise, contaminated wood surfaces would be superhydrophobic and would not contact water. At room temperature, it is almost impossible for solid polar organic

extractives to “migrate” to freshly cut surfaces. Therefore, both water and, to a lesser extent, low-molecular-weight VOCs are likely responsible for contamination or aging phenomenon of freshly cut wood.

Several investigators have found that wettability and gluability of a sanded surface is better than that of a planed surface (Marian *et al.* 1958; Bodig 1962; De Moura and Hernández 2005). For a sanded surface, both cell walls and lumen surfaces are refreshed by sanding. A sanded surface often has cell-wall fibrillation, scratches, and debris (De Moura and Hernández 2005), which produce even more free hydroxyls at new surfaces than those produced by planing. Because most protruding, cross-sectional cell walls are crushed, a sanded surface is flatter (not necessarily smoother) than planed or microtome-prepared surfaces (De Moura and Hernández 2005). Therefore, a sanded surface would have greater wettability and gluability than a planed or a microtome-prepared surface. Sanding alters distribution of nonwetable extractives on the lumen surface. A sanded surface may be contaminated by moisture in the air, polar VOCs, and some solid extractives in the lumen as well. As a result, surface tension of sanded samples may decrease more rapidly with time than surface tension of microtome-prepared or planed samples (Gindl *et al.* 2004).

When wood is dried at an elevated temperature for an extended period, nonwetable extractives are redistributed by migrating to low extractive areas, including newly opened cell walls. In a high-temperature environment, some liquid polar VOCs with low molecular weights are evaporated, while some solid polar VOCs melt and become mobile. Most adsorbed water and VOCs are removed from hydroxyls at the original surface by elevated temperature. However, nonwetable extractives might deposit on or migrate to the cell wall and lumen surfaces during cooling after drying, blocking some hydroxyls on the entire surface, reducing wettability and, subsequently, glue bond strength.

Therefore, it was believed that the wood surface (primarily freshly cut cell walls) might initially

be contaminated by moisture and, to a lesser extent, polar VOCs when a fresh, dry surface is cut. After high-temperature drying, migration and deposition of extractives could be important contributors to surface contamination (Christiansen 1990, 1991). Further research is warranted to verify and confirm this hypothesis. However, surface contamination by moisture and/or extractives would reduce hydrophilicity of the surface of wood. In this regard, the contact angle of a contaminated surface may be a better estimate of the “real” contact angle.

SUMMARY

This review discussed hydrophilic aspects of surfaces of wood, summarizing wetting theories, surface tension theories, and surface tension and wettability of surfaces. Also discussed were surface topography and contamination effects on wettability. The data reported in the references were often disparate. Wettability and surface tension of wood surfaces were largely determined by contact angle, which depends on variables such as measurement methods, surface machining techniques, measurement time, probe liquids, moisture content, and drying history. It was believed that a standardized procedure for contact angle measurement would permit reproducible measurements and comparable data for characterization of wood surfaces.

Although Young’s equation is not directly applicable to wood surfaces, they can be represented by Zisman’s linear relationship between $\cos \theta$ and γ_{LG} . Surface tension of wood can be estimated using Zisman’s critical surface tension, geometric-mean, harmonic-mean, and acid-base approaches. Critical surface tension is unique to a particular surface, having the same variables that influence contact angle. Among these approaches, it is difficult to tell which is best. To date, no procedure has been developed for determining an absolute value of surface tension. New theories or approaches such as IGC are needed to improve evaluation of surface properties of wood.

Topographic effects on surface tension and wettability have been extensively studied and reported. Few controversies exist regarding effects of surface topographical characteristics on surface tension, such as surface features (earlywood, latewood, sapwood, heartwood, cross-sectional surfaces), grain direction, machining methods (planing, sanding, microtoming), moisture content, and preservative treatment. However, there are disputes regarding mechanisms of surface contamination and aging, and additional work is needed in these areas. Most investigations have been concentrated on effect of surface tension on glueability of wood. Surface tension may affect other properties of wood such as wood acetylation, decay resistance, treatability, and mechanical performance. Therefore, further research on surface tension of wood is warranted.

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