APPLICATION OF THE LIFSHITZ-VAN DER WAALS ACID-BASE APPROACH TO DETERMINE WOOD SURFACE TENSION COMPONENTS

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ABSTRACT

Improvements are being made in the fundamental descriptions of surface thermodynamics, and it is important to apply these new concepts to wood. The purpose of this paper is to determine wood surface tension components using the Lifshitz-van der Waals/acid-base approach. Zisman plot, geometric-mean, and harmonic-mean wood surface tension determinations are also made for comparative purposes. Lifshitz-van der Waal forces appear to account for the majority of wood surface tension, and the acid-base character comes primarily from the electron donating γ-sites. The contribution of γ-sites on the wood surface to fundamental wood-adhesive interactions may have considerable implications in the gluing and finishing technology of wood, and it deserves further study. The Lifshitz-van der Waals/acid-base approach provides for greater accuracy in calculating wood surface tension components than the geometric-mean and harmonic-mean equations because it is based on the contribution of contact angles from five liquids versus two liquids. In some instances, the critical surface tension of wood obtained using Zisman plots compares favorably with the total surface tension obtained by the Lifshitz-van der Waals/acid-base approach.

Keywords: Wood, surface tension, contact angle, Lifshitz-van der Waals/acid-base, pH.

INTRODUCTION

New techniques and approaches to studying fundamental aspects of surface chemistry are being applied to wood with good success (Gardner et al. 1996). In particular, instrumental analysis techniques like inverse gas chromatography (Kamdem et al. 1993), dynamic contact angle analysis (Gardner et al. 1991), atomic force microscopy (Hanley and Gray 1994), and X-ray photoelectron spectroscopy (Dorris and Gray 1978) have provided an improved understanding of the chemical and physical characteristics of the wood surface. Along with the newer instrumental techniques, improvements have been made in the fundamental descriptions of surface thermodynamics (van Oss et al. 1988; Liu et al. 1995; Wu et al. 1995). However, some recent research describing wood surface thermodynamics used approaches developed 30 to 40 years ago, including Zisman's critical surface tension determinations and Good-Girifalco surface energy calculations (Gardner et al. 1991; Liptakova and Kudela 1994). The Good-Girifalco approach of separating surface energy into polar and nonpolar (dispersive) components still remains a forefront topic in surface and colloid science (Etzler and Conners 1995), so it is not surprising to find its current application in wood science. However, it is important to apply the new fundamental descriptions of surface thermodynamics to wood.

OBJECTIVE

It is the purpose of this paper to determine wood surface tension components using the Lifshitz-van der Waals/acid-base approach (van Oss et al. 1988). Zisman plot, geometric mean, and harmonic-mean wood surface tension determinations will also be made for comparative purposes.

THEORETICAL BACKGROUND

Thomas Young, in 1805, first described the equation that determines the interaction of a liquid drop with a solid surface.

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\Theta \tag{1}$$

where γ is the surface free energy (surface tension), the subscripts S, SL, and L refer to the solid, solid-liquid, and liquid surface tensions respectively, and θ is the contact angle. Girifalco and Good (1957) derived a relationship for γ_{SL} that assumed only intermolecular force interactions were important in determining surface tension components between a liquid and a solid.

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S\gamma_L)^{\frac{1}{2}} \tag{2}$$

Furthermore, the total surface free energy γ_T is divided into polar and nonpolar (dispersive) components. Thus

$$\gamma_T = \gamma^d + \gamma^p \tag{3}$$

where γ^d surface free energy resulting from London dispersion forces. London forces result from the polarizability of electron orbitals and are common to all intermolecular interactions. The term γ^p is the surface free energy resulting from dipole-dipole, induced dipole, and hydrogen bonding interactions. Expanding the Good-Girifalco equation

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^d\gamma_L^d)^{\frac{1}{2}} - 2(\gamma_S^p\gamma_L^p)^{\frac{1}{2}} \tag{4}$$

The Good-Girifalco (geometric-mean) equation can be combined with the Young equation to calculate contact angles

$$(1 + \cos\theta)\gamma_L = 2(\gamma_S^d\gamma_L^d)^{\frac{1}{2}} + 2(\gamma_S^p\gamma_L^p)^{\frac{1}{2}} \tag{5}$$

Fowkes (1974) and more recently van Oss et al. (1988) have suggested separation of the polar components into separate Lewis acid (+) and Lewis base (−) terms. Thus

$$\gamma^p = 2(\gamma^+\gamma^-)^{\frac{1}{2}} \tag{6}$$

Van Oss et al. (1988) also offered a more rigorous derivation of nonpolar surface energy components based on Lifshitz-van der Waals

interactions γ^{LW} (where γ^d is approximately equivalent to γ^{LW}). By accounting for Lewis acid-base interactions and Lifshitz-van der Waals interactions, the Young-Good-Girifalco-Fowkes equation becomes

$$(1 + \cos\theta)\gamma_L = 2[\gamma_S^{LW}\gamma_L^{LW})^{\frac{1}{2}} + (\gamma_S^+\gamma_L^-)^{\frac{1}{2}} + (\gamma_L^-\gamma_L^+)^{\frac{1}{2}}] \tag{7}$$

By using nonpolar liquid probes (total γ^{LW}), and polar liquid probes with known electron-acceptor γ^+ (acid) and electron-donor γ^- (base) parameters, the solid surface energy components γ^{LW}, γ^+, and γ^- can be determined using contact angle measurements.

METHODS AND MATERIALS

Contact angle measurements

Dynamic contact angle (DCA) measurements were made with a Cahn Instruments DCA 322 on wood veneer samples following the procedures described by Gardner et al. (1991). The sliced wood veneers were obtained from a local manufacturer. The veneers were commercially dried on a screen dryer with gas-fired jets. Feed temperature of the dryer was 79.4°C and outlet temperature was 110°C. Veneer drying time averaged eight minutes. After the veneers were received from the local producer, they were conditioned to 8% moisture content at 22°C. The species examined were heartwood of ash (*Fraxinus americana* L.), cherry (*Prunus serotina* Ehrh.), hard maple (*Acer saccharum* Marsh.), red oak (*Quercus rubra* L.), white oak (*Quercus* spp.), and walnut (*Juglans nigra* L.). Samples (25 × 25 × 0.7 mm) were sanded with 220 grit sandpaper to provide a fresh surface, and end-coated prior to DCA measurements parallel to the veneer grain. Testing speed for the DCA measurements was 194 microns/s. The contact angle probe liquids, and values of the surface tension components and parameters are found in Table 1. All contact angle probe liquids were either reagent or HPLC grade. For each species, ten contact angles were collected per probe liquid and were averaged for calculation of surface tension components. The contact angle

TABLE 1.   *Values of the surface tension components and parameters (in mJ/M²) of probe liquids used for contact angle measurements at 20°C.*[a]

Liquids	γ_L(mJ/M²)	γ^{LW}(mJ/M²)	γ^{AB}(mJ/M²)	γ^+(mJ/M²)	γ^-(mJ/M²)
α-Bromonapthalene	44.4	44.4	≈0	≈0	≈0
Ethylene glycol	48	29	19	≈1.92	≈47.0
Formamide	58	39	19	2.28	39.6
Glycerol	64	34	30	3.92	57.4
Water	72.8	21.8	51	25.5	25.5

[a] From Wu et al. (1995).

averages and standard deviations for each species and probe liquid are shown in Table 2.

Calculation of surface tension components

Determination of the solid surface energy components γ^{LW}, γ^+, and γ^- for the wood samples were calculated using Eq. 7. Because the contact angle, liquid surface tension, and liquid surface energy components are known, the solid surface energy components can be calculated using a set of simultaneous equations. In this instance, a set of five simultaneous equations representing the five probe liquids were used to calculate the three unknown wood surface energy components. The simultaneous equations were solved using a least-square routine in QuattroPro® (spreadsheet).

For comparative purposes, Eq. 5 (geometric-mean) and the harmonic-mean equation (8) were used to calculate surface tension components using the two-liquid method. Water contact angle data were used with contact angle data from the following probe liquids: α-bromonapthalene (α-brom.), ethylene glycol (E.G.), formamide (form.), and glycerol (gly.)

to calculate the geometric-mean and harmonic-mean surface tension components. The harmonic-mean equation proposed by WU (1971)

$$\gamma_{LV}(1 + \cos\Theta) = \frac{4\gamma_S^d\gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{4\gamma_S^p\gamma_L^p}{\gamma_S^p + \gamma_L^p} \quad (8)$$

is based on an empirical approach to calculating surface tension parameters and is considered to be more suitable than the geometric-mean in calculating the polar component of polymeric surfaces. Both the geometric-mean and harmonic-mean method have been used in calculating the surface tension components of wood (Nguyen and Johns 1978). Critical surface tension γ_c values were also determined by Zisman plots (Zisman 1964) using the probe liquids in Table 1. Calculations for determining the geometric-mean, harmonic-mean, and Zisman surface tension values are available in the Cahn DCA Applications Software (1991).

pH measurements

The determination of pH for the wood samples was made using the methods described by Moore and Johnson (1985). One part by weight of freshly ground (to pass 40-mesh screen) par-

TABLE 2.   *Average advancing contact angles of the probe liquids used in this study.*

Species	Probe liquid (average contact angle and standard deviation)				
	α-bromonapthalene	Ethylene glycol	Formamide	Glycerol	Water
Ash	9.79 (2.38)	17.47 (7.73)	0 (0)	59.82 (8.91)	23.66 (9.97)
Cherry	0 (0)	13.95 (5.21)	0 (0)	50.29 (10.73)	44.39 (5.23)
Maple	0 (0)	14.26 (4.54)	0 (0)	48.37 (2.05)	34.91 (7.06)
Red oak	0 (0)	16.23 (4.89)	28.52 (4.74)	55.96 (5.04)	40.11 (2.74)
White oak	20.38 (6.06)	55.48 (5.86)	33.13 (9.09)	58.49 (3.02)	59.56 (9.43)
Walnut	14.3 (5.72)	36.12 (5.85)	32.91 (10.53)	43.42 (10.96)	26.33 (12.88)

ticles was placed in three parts of freshly boiled and cooled distilled water. The sample and water were mixed until the particles were wet, and the pH was measured with a glass electrode pH meter after 5 min.

RESULTS

Lifshitz-van der Waals/acid-base approach

The surface tension components determined using the Lifshitz-van der Waals/acid-base approach are shown in Table 3. The total surface energy varied from 40 mJ/M² for white oak to 54.3 mJ/M² for cherry. Lifshitz-van der Waal forces appear to account for the majority of wood surface tension with values ranging from 34.02 mJ/M² for white oak to 47.46 mJ/M² for cherry. Acid-base contribution varied from 0.6 mJ/M² for ash to 8.3 mJ/M² for red oak. It is important to note that the majority of acid-base character comes from the electron donating γ^- sites on the wood surface. At first glance, this electron donating behavior goes against conventional wisdom because wood exhibits a slightly acidic pH (Table 3). However, it should be pointed out that pH measurements are made on the bulk wood, and contact angles are based on surface sensitive measurements. It is well established that extractives dominate wood surface thermodynamic behavior (Gardner et al. 1996). Many of the extractives present in the species evaluated contain aromatic compounds (Rowe and Conner 1979), and aromatic rings are considered soft bases (electron donating) (March 1977). Therefore, it is not unusual that the surface character of wood is primarily basic or monopolar in nature. In fact, many synthetic

and biopolymer materials appear to have to γ^- monopolar surfaces (van Oss et al. 1987).

Zisman plots

The critical surface tension values for the wood species are shown in Table 3. Critical surface tension values varied from 10.8 mJ/M² for walnut to 48.1 mJ/M² for cherry. The critical surface tension values for red oak and ash compared quite favorably with the surface tension values calculated using Eq. 7. However, the critical surface tension value obtained for walnut is unreasonably low. It is well known that the choice of probe liquids used to measure critical surface tensions can have an effect on the values obtained (Zisman 1977). It should be pointed out that the probes used in this study were chosen for calculating acid-base character, and they may not be the best choice for determining wood critical surface tensions. Earlier studies have shown that water-ethanol and water-acetic acid solutions are good probes for determining critical surface tensions on wood (Gardner et al. 1991; Gunnells 1992).

Geometric-mean and harmonic-mean approach

The wood surface tension components obtained by solving the geometric-mean and harmonic-mean equations are shown in Table 4. The γ_s values obtained by the geometric-mean equation were generally greater than the γ_s values obtained by the harmonic-mean equation. Nguyen and Johns (1978) favored the use of the harmonic mean-mean model for characterizing the wood surface thermodynamics. Depending on the two liquids used, γ_s calcu-

TABLE 3. *Surface tension components and parameters obtained by solving Eq. 7, and critical surface tension γ_c, values obtained by Zisman plots.*

Species	γ_c(mJ/M²)	γ_s^{TOT}(mJ/M²)	γ_s^{LW}(mJ/M²)	γ_s^{AB}(mJ/M²)	γ_s^+(mJ/M²)	γ_s^-(mJ/M²)	pH
Ash	42.9	43.23	42.63	0.6	0.001	67.35	5.9
Cherry	48.1	54.3	47.46	6.84	0.42	28.00	4.36
Maple	46.8	53.3	45.48	7.85	0.46	33.19	5.3
Red oak	46.8	47.97	39.67	8.30	0.46	37.74	4.67
White oak	31.4	40.0	34.02	5.98	0.39	22.80	4.32
Walnut	10.8	42.55	37.92	4.63	0.09	58.93	4.71

TABLE 4. *Surface tension components and parameters of wood obtained by solving the geometric-mean and harmonic-mean equations.*

Species	Probes*	Geometric-mean γ_s(mJ/M²)	γ_s^d(mJ/M²)	γ_s^p(mJ/M²)	Harmonic-mean γ_s(mJ/M²)	γ_s^d(mJ/M²)	γ_s^p(mJ/M²)
Ash	Water-α-Brom	76.91	45.62	31.29	45.64	45.64	0
	Water-E.G.	87.84	2.68	85.16	74.02	13.87	60.15
	Water-Form.	71.52	20.63	50.89	71.45	24.31	47.14
	Water-Gly.	79.52	0.55	78.97	63.11	11.99	51.12
Cherry	Water-α-Brom	64.24	46.10	18.14	46.13	46.13	0
	Water-E.G.	54.29	16.19	38.1	55.19	20.09	35.1
	Water-Form.	62.73	42.0	20.73	63.11	35.6	27.51
	Water-Gly.	65.4	3.39	61.51	55.11	18.09	37.02
Maple	Water-α-Brom	69.12	47.06	22.06	47.12	47.12	0
	Water-E.G.	64.84	8.77	56.07	61.06	20.13	40.93
	Water-Form.	63.19	33.83	29.36	64.22	31.01	33.21
	Water-Gly.	66.2	4.67	61.53	59.59	15.98	43.61
Red oak	Water-α-Brom	67.0	46.98	20.02	47.05	47.05	0
	Water-E.G.	52.6	10.4	42.2	51.91	16.87	35.04
	Water-Form.	59.8	30.6	29.2	60.87	25.24	35.63
	Water-Gly.	66.7	2.77	63.93	58.34	14.21	44.13
White oak	Water-α-Brom	54.84	43.64	11.2	43.71	43.71	0
	Water-E.G.	46.94	5.29	41.65	46.9	8.59	38.31
	Water-Form.	50.85	35.33	15.52	50.92	29.25	21.67
	Water-Gly.	40.64	14.13	26.51	43.43	17.59	25.84
Walnut	Water-α-Brom	71.46	44.51	26.95	44.59	44.59	0
	Water-E.G.	87.42	1.28	86.14	70.35	10.07	40.93
	Water-Form.	63.19	12.03	54.52	65.35	16.95	33.21
	Water-Gly.	56.08	4.89	51.91	55.11	18.09	37.02

* Refer to text for abbreviations.

lated using the geometric-mean equation varied from 40.64 mJ/M² for white oak (water-glycerol) to 87.84 mJ/M² for ash (water-ethylene glycol). The γ_s calculated using the harmonic-mean equation varied from 43.43 mJ/M² for white oak (water glycerol) to 74.02 mJ/M² for ash (water-ethylene glycol). For a few liquid combinations, the harmonic-mean γ_s values were closer to the γ_s values obtained using the Lifshitz-van der Waals/acid-base approach (Table 3). However, there was no consistent trend among the γ_s values obtained using the three different methods of calculation.

DISCUSSION

The Lifshitz-van der Waals/acid-base approach provides for greater accuracy in calculating wood surface tension components than the geometric-mean and harmonic-mean equations because it is based on the contribution of contact angles from five liquids versus two liquids. Also, the fact that the acid-base character of the solid is obtained using Eq. 7 is a marked improvement over the geometric-mean and harmonic-mean calculations. As a *caveat*, it should be noted that there are some deficiencies in the use of acid/base measurements. There are no acid or base probe liquids with 100 percent acid or base character. Thus, different results could be obtained by use of different probe liquids. Future research should address this problem.

Any of the γ_s values obtained using the geometric-mean and harmonic-mean equations greater than 73 mJ/M² are unreasonably high. The γ_s values are larger than the surface tension of water, and are much greater than wood surface tension values reported in the literature. The thermodynamic nature of the chem-

ical components (extractives) comprising the wood surface would prohibit surface tension values greater than 73 mJ/M^2.

As mentioned earlier, the determination of critical surface tension values for wood are dependent on the choice of probe liquids. In some instances, the critical surface tension of wood obtained using Zisman plots compared favorably with the total surface tension obtained by the Lifshitz-van der Waals/acid-base approach. Therefore, the Zisman approach can still be considered a useful method for determining the total surface tension of wood. From the practical standpoint, knowing the total surface tension of wood is useful for understanding how an adhesive or finish will wet the wood. Perhaps more important, however, is understanding how the acid-base (i.e. electron donating) character of the wood surface will influence adhesive curing mechanisms. The contribution of the γ^- wood surface to fundamental wood-adhesive interactions may have considerable implications in the gluing and finishing technology of wood, and deserves further study.

CONCLUSIONS

The Lifshitz-van der Waals/acid-base approach to determine solid surface tension components was successfully applied to wood. Lifshitz-van der Waal forces appear to account for the majority of wood surface tension, and the acid-base character primarily comes from the electron donating γ^- sites. The Lifshitz-van der Waals/acid-base approach provides for greater accuracy in calculating wood surface tension components than the geometric-mean and harmonic-mean equations because it is based on the contribution of contact angles from five liquids versus two liquids. In some instances, the critical surface tension of wood obtained using Zisman plots compares favorably with the total surface tension obtained by the Lifshitz-van der Waals/acid-base approach. Therefore, the Zisman approach can still be considered a useful method for determining the total surface tension of wood.

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