

# Wetting of wood

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**Summary** Thermodynamic work of adhesion, contact angle, wettability and acid-base contributions of the wetting of four North American wood species were determined using the Wilhelmy technique. The wetting angles with water varied from 60° for Sitka spruce to 74° for Douglas-fir. The wood surfaces had a strong acidic character since the greatest interactions for all the wood species occurred with formamide (basic probe) while lesser interactions were obtained with ethylene glycol (acidic probe). In addition, dispersive and polar surface free energies of wood,  $\gamma_S^d$  and  $\gamma_S^p$  respectively, were determined using Wu's simultaneous equations. In general, 75 to 80% of the total surface free energy of wood was due to dispersion forces. Specific wettabilities of wood and advancing contact angles in thirty various organic liquids were also evaluated.

## Introduction

Some of the first notions of the relationship between surface energy and contact angle for a liquid drop on a solid surface were expressed by Young's equation (1805):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (1)$$

where:  $\gamma_{SV}$ : Interfacial surface tension between solid and vapor  
 $\gamma_{SL}$ : Interfacial surface tension between solid and liquid  
 $\gamma_{LV}$ : Interfacial surface tension between liquid and vapor  
 $\theta$ : Contact angle

Later, Dupre' (1869) developed an equation for the thermodynamic energy of interaction, which is widely known as the work of adhesion,  $W_A$ :

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (2)$$

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should be also noted by Fowkes (1991) that the acid-base work of adhesion ( $W_A^{ab}$ ) can be calculated from the molar heats of acid-base interaction between the two materials, or by measuring the surface basicity and surface acidity components of the acid-base surface tension of the phases involved (Oss 1988). The acid-base contributions to the work of adhesion are determined using a Lewis base such as formamide and a Lewis acid such as ethylene glycol with Eq. (6) and (7), and then from Eq. (5) rewritten as:

$$W_A^{ab} = W_A - W_A^d \quad (8)$$

Freeman (1959) measured wood wettability, as defined by the cosine of the advancing angle of water with wood using the inclined plate method (Adam 1938). The plate of wood used to read the angle was a representative shear-block half that had been resurfaced on a jointer shortly before the wettability determination. Relating his results to wood adhesion, he concluded that wettability, pH, and specific gravity are closely related to glue-bond quality. Specific gravity was generally more important, and pH and wettability less, with resorcinol-phenol bonds compared with urea-formaldehyde bonds (with wood).

Gray (1962) in his investigation on wood wettability measured advancing and receding contact angles of water with various different timber species. He introduced a technique for measuring solid surface tension of solids and for calculating the free energy of wetting,  $F_W$ , and the work of adhesion,  $W_A$ , of any liquid. It was also shown that surface contamination occurs rapidly on freshly cleaned surfaces.

Herczeg (1965), in his work on the wettability of Douglas-fir wood, found that the critical surface tensions,  $\gamma_C$ , were between 44 to 50 dynes/cm for summerwood and springwood, respectively. The surface-free energy of Douglas-fir,  $\gamma_S$ , was estimated to be around 60 dynes/cm, slightly higher by about 10 dynes/cm than  $\gamma_C$ . Also, the maximum work of adhesion,  $W_{A \max}$ , varied from 116.4 to 122.5 dynes/cm. Aging up to 45 hours increased contact angles,  $\theta$ , from 40.8 to 77.2 degrees, showing that wood wettability was reduced.

Chen (1970) in his work on the effect of extractives on adhesion and wettability of wood found that extractive removal improved wettability and increased the pH of the wood in all the species (tropical) tested. Wettability was obtained for each wood sample by measuring advancing contact angle,  $\theta_A$ , with distilled water (inclined plate method). Also, a positive linear correlation was found to exist between wettability and joint strength of blocks glued with urea-formaldehyde resin, however, no such correlation existed for blocks glued with resorcinol-phenol resin.

Hse (1972) measured the wettability of southern pine veneers by measuring the contact angles formed with 36 phenol-formaldehyde resins. The contact angle was found not to be correlated with the solids content of the resins. The contact angle of resins on earlywood was less than that on latewood, apparently because earlywood surfaces were rougher. Also, the contact angle was positively correlated with the glue bond quality as tested by wet shear strength, percent of wood failure, and percent of delamination. The results showed that interactions between the physico-chemical characteristics of resin and the properties of the wood substrate may strongly affect bond quality.

Kajita and Skaar (1992) evaluated the wettabilities of the surfaces of some American softwoods species (using cosine  $\theta$  as the index of wettability). The

freshly shaved surfaces wet more easily than the original unshaved rotary veneer surfaces. Also, the earlywood wet more easily than did the latewood (earlywood has a greater roughness factor and a greater porosity). The wetting angles varied from 68 degrees (eastern red cedar) to 14 degrees (Alaska-cedar). The greater wettability of sapwood compared with heartwood was attributed to the extractive content of the heartwood.

Young (1976), in his work on the wettability of wood pulp fibers, demonstrated the applicability of the Wilhelmy technique for measuring wetting properties of a series of wood pulp fibers (unbleached kraft, neutral sulfite semichemical, thermomechanical). Unbleached neutral sulfite semichemical fibers exhibited much greater wettability when compared with thermomechanical pulp fibers which in turn were somewhat more wettable than unbleached kraft pulp fibers. These differences were related to variances in the nature and extent of lignin removal, the presence of hemicelluloses or other carbohydrate material, and extractives at the fiber surface. Also, morphological characteristics of the fiber surface were considered to be important. Grafting of the pulps with styrene greatly reduced the fiber wetting properties.

Hodgson and Berg (1988) also used the Wilhelmy technique to measure dynamic wetting properties of single wood pulp fibers. It was concluded that, for complex material surfaces like those of wood pulp fibers, a wettability profile is very useful in understanding fiber structure and chemistry. Highly bleached, low-lignin content fibers were more hydrophilic than high yield, high lignin content fibers, such as thermomechanical pulp fibers. The presence of residual extractives seemed to have a substantial effect on fiber wettability, especially for pulp subjected to elevated temperatures. Also, the cosine of the single-fiber advancing contact angle was found to be inversely proportional to the absorption time (wood pulp fibers).

Jacob and Berg (1993) used the technique of contact angle titration to demonstrate the change in wetting behavior of four pulp fiber furnishes with varying pH (buffer solution). The changes in wetting were indicative of dissociation or re-association of ionizable functional groups on the fiber surface and fiber-liquid interfacial free energy. The results were expressed in terms of the acid-base contribution to the work of adhesion, which simply indicates the extent of the specific chemical interactions across the fiber-buffer solution interface. Softwood bleached kraft (SWBK), hardwood bleached kraft (HWBK), and alpha-cellulose fibers had both acidic and basic functional groups, but SWBK and HWBK fibers were slightly more acidic and  $\alpha$ -cellulose fibers were slightly more basic. Chemithermomechanical (CTMP) fibers did not have as evenly balanced acid and base sites as the other three fiber types, but were instead mainly acidic. Fernandez (1993) also measured wetting of pulp fibers (sulfite, kraft, acetic acid) and concluded that the acid-base work of adhesion of different pulps were higher with the basic liquid probe (formamide) than with the acidic liquid probe (ethylene glycol), thus indicating the strong acidic character of pulp fibers.

Luner and Sandell (1969) evaluated the wetting properties of cellulose and wood hemicelluloses by Zisman's empirical parameter (1964), the critical surface tension of wetting,  $\gamma_c$ . It was found that the source of cellulose (cotton, wood and hydrolyzed cellulose), the method of film preparation (single-bath, two-bath, dry-cast, orientation), and also the physical state of the cellulose surface influenced the wettability of the samples. The critical surface tension ranged from 35.5 to 49.0 erg cm<sup>-2</sup> for cellulose and from 33.0 to 36.5 erg cm<sup>-2</sup> for hemicellulose films. The hemicellulose samples showed the smallest hysteresis effects presumably due

to the energetically more uniform surface and lower porosity. It was also concluded that the interaction of cellulose with liquids ranging from water to non-polar liquids involved, in addition to hydrogen bonding, strong dispersion forces.

Lee and Luner (1972) measured the wetting and interfacial properties of six different lignin preparations. No significant differences were found in their wetting characteristics (contact angle, critical surface tension). These similarities were considered as a result of the hydrophilic and amorphous nature of lignin. As with hemicellulose, and to some extent cellulose, monolayers of water were sufficient to equalize the surface energy of the lignins so that the surface was essentially water-like. It was additionally concluded that when a liquid interacts with lignin or cellulose, even when dry, the non-dispersion forces contribute greatly to the total energy.

## Materials and methods

### Materials

Anhydrous organic liquids were used in this study. The test liquids and their surface tensions are shown in Tables 1 and 2. Surface tensions of the probe

Table 1. Surface tensions of organic liquids<sup>a</sup>

Liquid	Surface Tension (dynes/cm)	Probes
Water	73.00	bifunctional
Formamide	58.30	basic
Ethylene glycol	48.30	acidic
Methanol	22.61	
Ethanol	22.75	
Propanol	23.78	
Dimethylformamide	36.80	
Pyridine	38.00	
Acetone	23.70	
Methylethyl ketone	24.60	
Methylacetate	24.60	
Ethylacetate	23.90	
Propylacetate	24.30	
Nitromethane	36.80	
Furfural	43.50	
Chloroform	27.14	
Ethylene dichloride	23.40	
Carbon tetrachloride	26.95	
Benzaldehyde	40.04	
Nitrobenzene	43.90	
Toluene	28.50	
Benzyl alcohol	39.00	
Quinoline (98%) <sup>b</sup>	50.30	
Dimethylsulfoxide	43.50	
Formic acid (96%) <sup>b</sup>	47.60	
Acetic acid	27.80	
Propionic acid	26.70	
Diethylamine	16.40	
Butylamine	19.70	
Diiodomethane	50.80	neutral
Hexadecane	28.00	neutral

<sup>a</sup> Handbook of Chemistry and Physics (1993)

<sup>b</sup> Surface tensions measured experimentally

**Table 2.** Dispersion and acid-base interaction components of the surface tensions of the probe liquids

Liquid	$\gamma_L$ (dynes/cm)	$\gamma_L^{lw}$ (dynes/cm)	$\gamma_L^{ab}$ (dynes/cm)
Hexadecane	28.0	28.0	0.0
Ethylene glycol	48.3	29.3	19.0
Diiodomethane	50.8	49.5	1.3
Formamide	58.3	32.3	26.0
Water	73.0	21.6	51.4

Note:  $\gamma_L^{lw}$ : Dispersion component (Lifshitz-van der Waals)  
 $\gamma_L^{ab}$ : Acid-base interaction component

liquids were experimentally determined with a small clean glass plate. The measured values were in a good agreement with the literature values and the literature values were used in the calculations (Fernandez 1993; Handbook of Chemistry & Physics 1993). Heartwood samples of the softwoods, sitka spruce (*Picea sitchensis*) and Douglas-fir (*Pseudotsuga menziesii*), and the hardwoods, sugar maple (*Acer saccharum*) and quaking aspen (*Populus tremuloides*), were selected for this investigation. These wood species were selected as representatives of softwoods and hardwoods with different chemical compositions and specific gravities. Small square wood samples were cut from a fresh log and sawn into 3 mm thick boards. These boards were then cut into specimens 3 mm thick  $\times$  3 mm wide  $\times$  35 mm long. The specimen surface represented a flatsawn or tangential surface. Gray (1962) reported that there was no difference between radial and tangential wettability for wood surfaces; therefore, differences in grain orientation were not evaluated in this work. Wood samples were then dried in oven for 24 hours (65°C). After drying, a small quantity of epoxy was placed on the edge (wetting end) of each wood specimen so to eliminate the effect of swelling on the precision of the dynamic contact angle measurement. The average moisture content (MC) of the wood samples was approximately 6 to 7% in the oven-dry basis. Specimens for experimental use were randomly selected for a complete statistical randomization. Sitka spruce had an average specific gravity of 0.35 (g/cc). Sugar maple had a specific gravity in the range of 0.69 to 0.71; with the average of 0.70. Douglas-fir had an average specific gravity of 0.48, and quaking aspen had an average specific gravity of 0.49.

### Methods

All wetting force measurements were done with a CAHN Dynamic Contact Angle Analyzer (Fig. 1) with an IBM 3865X for data acquisition and analysis. Contact angle measurements were done by the Wilhelmy method based on the following equation:

$$F = \gamma_{LV}P \cos \theta - \delta_1 gAh \quad (9)$$

where  $F$  is the wetting force,  $\gamma_{LV}$  is the liquid surface tension,  $P$  is the sample perimeter,  $\delta_1$  is the liquid density,  $g$  is the gravitational constant,  $A$  is the cross sectional area of the wood sample, and  $h$  is the depth of immersion of the sample. Average "advancing" force values minus the buoyancy force were then used to calculate the advancing contact angle and the work of adhesion. A typical run is performed by placing a small wood sample in the electrobalance (Fig. 1) and

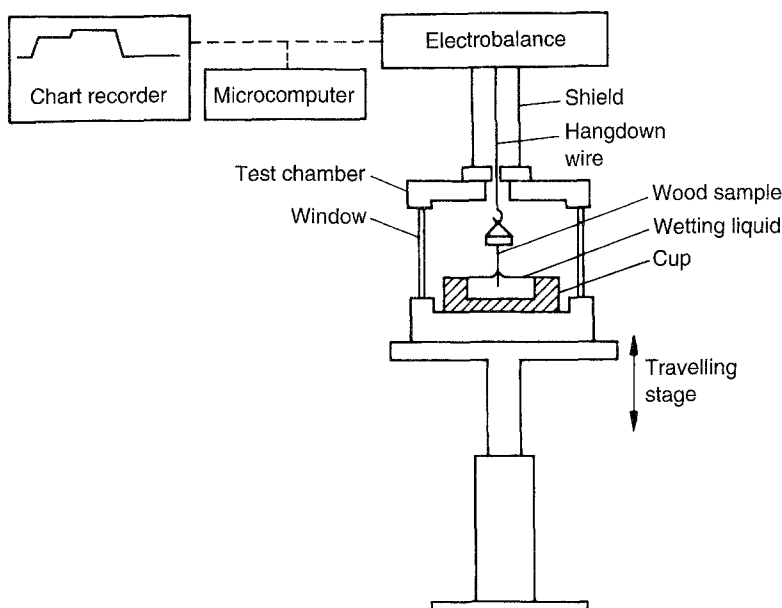


Fig. 1. Schematic diagram of CAHN dynamic contact angle analyzer

raising a beaker of wetting liquid with a small elevator until the liquid contacts the sample. The elevator speed was controlled at 150 microns per second and wetting force readings were obtained on a microcomputer. In the plot of the wetting force  $F$  versus depth of immersion  $h$ , a simple extrapolation gives the cosine of the advancing contact angle ( $\cos \theta_A$ ) since the liquid surface tension ( $\gamma_{LV}$ ) and wood sample perimeter ( $P$ ) are known as shown in Fig. 2 for sugar maple in pyridine. Formamide was used to find the acidic character of the wood surface and ethylene glycol was used to probe the basic properties.  $W_A^{ab}$  of the work of adhesion was evaluated for all wood species. Diiodomethane was used for the calculation of the Lifshitz-van der Waals forces of the wood surfaces. Hexadecane, which has a very low surface tension, was used for measuring the wood sample perimeter,  $P$ .

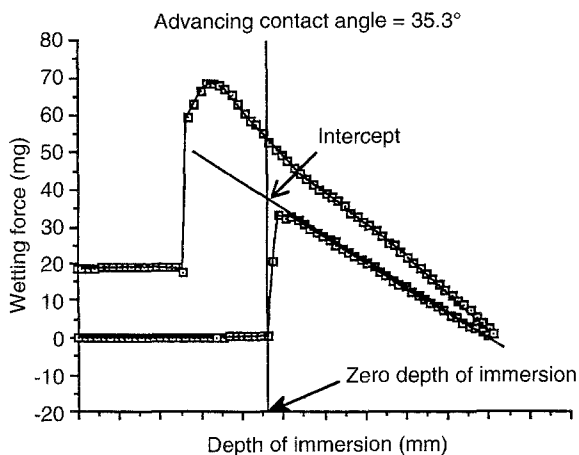


Fig. 2. Wetting force as a function of depth of immersion for sugar maple in pyridine (Wilhelmy technique)

Distilled water was used to find water wettability and water contact angles. In addition, all thirty organic liquids were used for wetting measurements with two wood species, sitka spruce (softwood) and sugar maple (hardwood), and specific wettabilities of these two wood species in the organic liquids were evaluated (using the advancing contact angle). Advancing specific wettability,  $W_s$ , is defined by the following equation:

$$W_s = \gamma \cos \theta \quad (10)$$

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where:  $\gamma$  is the liquid surface tension and  $\theta$  is the advancing contact angle.

Wu's simultaneous equations (1971) were used to calculate the  $\gamma_s^d$  and  $\gamma_s^p$  of the wood surfaces using wetting measurements with water (polar) and methylene iodide (neutral). These two liquids were used by Owens and Wendt (1969) in conjunction with an extended form of Fowkes's equation (1965). In this work, Wu's equation (Wu 1971) was rearranged to two simultaneous equations, one for water and another for methylene iodide.

### Results and discussions

Advancing contact angles, average cosines of  $\theta$ , and works of adhesion of wood with water, methylene iodide, formamide and ethylene glycol are presented in Table 3. Water contact angles varied from 60°–74°. Spruce and maple exhibited an average contact angle with water of 60.4 and 62.2 degrees, respectively. Douglas-fir had the largest advancing contact angle (73.5°). The low wettability of Douglas-fir is probably related to extractives and will be discussed later. Our results are in the same range as those reported by Kalnins (1993) for the wetting of western red-cedar with water (77°) and Banks and Voulgaridis (1980) (tilting plate method) for the water wetting of beech (70°) and Scots pine (80°). The work of adhesion,  $W_A$ , was also evaluated for all wood species with the probe liquids (Table 3). In general, spruce exhibited the highest work of adhesion while Douglas-fir had a lowest  $W_A$  (except in formamide). Douglas-fir had a maximum work of adhesion,  $W_A$  max, with water of about 104.5 dynes/cm, a result which is in an agreement with Marian's (1963) (118 dynes/cm) and Herczeg's work (1965) (122.5 dynes/cm).

Figure 3 shows the acid-base work of adhesion,  $W_A^{ab}$ , calculated for all wood species. It is clear that all wood surfaces have a very strong acidic character because the strongest interactions occurred with formamide (basic probe) while much weaker interactions occurred with ethylene glycol (acidic probe). Similar results were reported by Fernandez (1993) for the acid-base work of adhesion of various pulps (strong acidic character of kraft and sulfite pulp fibers). This behavior was explained by the presence of acidic type functional groups (i.e. carboxyl) on the fiber surface.

Table 4 presents the dispersive and polar surface free energies of the four wood species obtained using Wu's equations (Wu 1971) as previously described. Standard deviations are also shown in the parentheses. In general, wood shows a very high dispersive surface free energy component,  $\gamma_s^d$ . Approximately seventy five to eighty percent (on the average) of the overall wood surface energy was attributed to the dispersion forces. This is consistent with Nguyen and Johns (1979) conclusions that "the dispersion forces on the surface of wood (Douglas-fir) are predominant in surface interactions". Young et al. (1982) have also shown that wood surfaces are hydrophobic based on ESCA analyses. The total surface energy of wood varied from 48.0 dynes/cm for Douglas-fir to 61.5 dynes/cm for sitka spruce.



Table 3. Wetting parameters ( $\theta$ ,  $\cos \theta$ ,  $W_A$ ) of wood with probe liquids

Species	Water			Diiodomethane			Formamide			Ethylene glycol		
	$\theta$	$\cos \theta$	$W_A^a$	$\theta$	$\cos \theta$	$W_A$	$\theta$	$\cos \theta$	$W_A$	$\theta$	$\cos \theta$	$W_A$
Spruce	60.4	0.486	108.5	13.4	0.953	99.2	27.8	0.882	109.7	0.8	0.999	96.6
Douglas-fir	73.5	0.280	93.4	41.8	0.739	88.3	36.8	0.796	104.7	42.4	0.731	83.6
Maple	62.2	0.464	106.9	32.3	0.841	93.5	37.9	0.786	104.1	10.6	0.975	95.4
Aspen	68.2	0.369	99.9	28.1	0.877	95.4	48.9	0.653	96.4	40.0	0.763	85.2

<sup>a</sup>  $W_A$ , (dynes/cm)

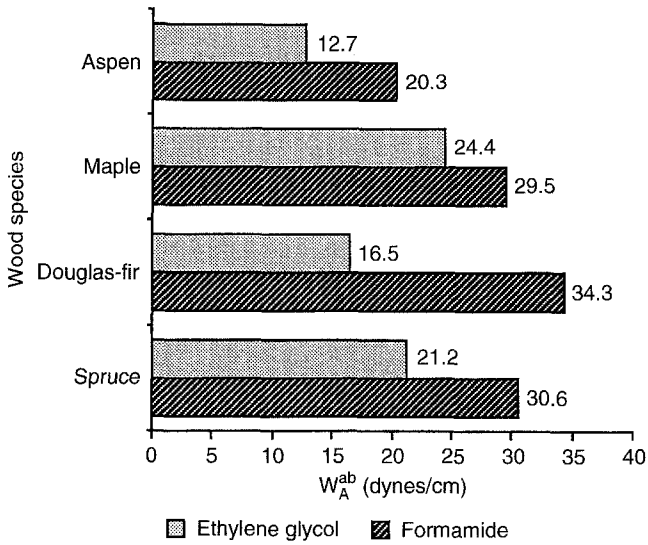


Fig. 3. Acid-base work of adhesion of wood

Marian (1963) has reported a total surface tension of wood of around 50 ergs/cm<sup>2</sup>. Similarly, Nguyen and Johns (1979) found a total surface free energy for Douglas-fir of about 48.0 dynes/cm; however, they reported a polarity ( $\gamma_s^p/\gamma_s$ ) for Douglas-fir of 40%, which is higher than our result (24%). Herczeg (1965) reported a total  $\gamma_s$  for Douglas-fir wood of about 58 dynes/cm. The  $\gamma_s$  values found in this work are also in the range of values reported for wood previously (49.5 dynes/cm for birch) (Kalnins 1987). The polarity of the wood surface was found to be in the range of 24.0 to 29.0% in this study (Table 4). Douglas-fir exhibited the lowest polarity values (24.0%) on the average. Polarity is independent of the temperature but it should be noted that the polar component of the overall surface free energy is considered to be an inadequate measure of polarity or hydrophilicity of the surface.

Table 5 shows the advancing specific wettabilities and calculated contact angles of two wood species (spruce, maple) in various wetting liquids. In general, spruce showed higher wettabilities than maple (except with nitrobenzene, benzyl alcohol, propionic acid, and DMF). Most of the liquids completely wetted both species forming zero advancing contact angles (except with water, formamide, ethylene

Table 4. Dispersive and polar components of surface free energies of wood<sup>a</sup>

Species	$\gamma_s^d$ (SD) <sup>b</sup> (dynes/cm)	$\gamma_s^p$ (SD) (dynes/cm)	$\gamma_s$ (dynes/cm)	Polarity <sup>c</sup> , $\gamma_s^p/\gamma_s$
Spruce	45.0 (2.3)	16.5 (4.5)	61.5	0.268
Douglas-fir	36.2 (3.4)	11.8 (3.5)	48.0	0.246
Maple	40.2 (5.8)	16.4 (1.7)	56.6	0.290
Aspen	41.8 (2.0)	13.2 (2.8)	55.0	0.240

<sup>a</sup> Calculated with Wu's simultaneous equations (1971)

<sup>b</sup> SD: Standard deviation

<sup>c</sup> polarity is independent of temperature

**Table 5.** Wetting parameters of spruce and maple wood in various organic liquids

Wetting liquid	Sitka spruce			Sugar maple		
	$W_S^a$ dyn/cm	$\cos \theta$	$\theta^b$ (degr)	$W_S$ dyn/cm	$\cos \theta$	$\theta^b$ (degr)
Water	35.5	0.486	60.4	33.9	0.464	62.2
Formamide	51.4	0.882	27.8	45.8	0.786	37.9
Ethylene glycol	48.2	0.999	0.8	47.1	0.975	10.6
Methanol	29.2	1.29	0	27.1	1.20	0
Ethanol	26.6	1.17	0	26.2	1.15	0
Propanol	28.1	1.18	0	26.1	1.10	0
Dimethylformamide	39.4	1.07	0	40.8	1.11	0
Pyridine	34.2	0.90	24.5	33.8	0.89	26.0
Acetone	28.0	1.18	0	27.0	1.14	0
Methylethyl ketone	32.2	1.31	0	28.5	1.16	0
Methylacetate	32.2	1.31	0	29.3	1.19	0
Ethylacetate	30.8	1.29	0	30.8	1.29	0
Propylacetate	31.1	1.28	0	29.4	1.21	0
Nitromethane	35.3	0.96	15.3	31.3	0.85	31.9
Furfural	50.4	1.16	0	46.1	1.06	0
Chloroform	35.8	1.32	0	34.5	1.27	0
Ethylene dichloride	40.2	1.72	0	37.9	1.62	0
Carbon tetrachloride	35.0	1.30	0	33.7	1.25	0
Benzaldehyde	45.6	1.14	0	45.6	1.14	0
Nitrobenzene	36.0	0.82	35.3	40.8	0.93	20.3
Toluene	34.8	1.22	0	31.1	1.09	0
Benzyl alcohol	43.3	1.11	0	44.9	1.15	0
Quinoline (98%)	50.3	1.00	1.0	49.3	0.98	11.9
Dimethylsulfoxide	53.1	1.22	0	45.7	1.05	0
Formic acid (96%)	48.1	1.01	0	47.6	1.00	0
Acetic acid	35.9	1.29	0	32.2	1.16	0
Propionic acid	32.3	1.21	0	32.8	1.23	0
Diethylamine	26.9	1.64	0	24.6	1.50	0
Butylamine	28.4	1.44	0	27.8	1.41	0
Methylene iodide	48.4	0.953	13.4	42.7	0.841	32.3

<sup>a</sup> $W_S$  = Advancing specific wettability

<sup>b</sup> Average of six replicates except for water (15 runs), formamide, ethylene glycol, and methylene iodide (12 runs)

glycol, methylene iodide, pyridine, nitromethane, nitrobenzene, and quinoline). Also, in most cases, receding contact angles were zero or near zero for all wood species. Overall, the highest specific wettabilities,  $W_S$ , for spruce were with DMSO, formamide, furfural, quinoline, methylene iodide, ethylene glycol, and formic acid (in descending order), and for maple with quinoline, formic acid, ethylene glycol, furfural, formamide, DMSO, benzaldehyde, and benzyl alcohol (in descending order). The lowest  $W_S$  were obtained with diethylamine, propanol, ethanol, methanol, and butylamine (for both wood species).

The wood wettability, in general, reflects the composite chemical and morphological character of the wood. The type of the wood species seems to affect differently the wetting behavior of wood. High water wettability can be caused by various hydrophilic components on the wood surface such as hemicelluloses. However, the presence of extractives at the wood surface can also influence the wettability depending upon the wood species (Young 1976). According to Kajita

and Skaar (1992), the extractives play a significant role affecting the water wettability of wood by two effects. One is direct on the wettability of the true surface and the other effect is the blockage by extractives of the openings between the cells, thus preventing penetration of a droplet below the surface of the wood. Also, Nguyen et al. (1979) attributed the low relatively wettability of Douglas-fir wood to nonpolar extractives. It was indeed found that the specific wettability of wood (four species) in water was inversely correlated with the percentage of extractives within the wood species (Fig. 4). The higher the extractives content, the lower the wood wettability in water. Other characteristics, as suggested by Young (1976), that can influence wettability include the degree of polymerization of some surface polymers, the degree of surface crystallinity, and the presence of monolayers at the wood surface (e.g. water).

Figures 5a and b show that an inverse linear relationship exists between the cosine of  $\theta$  and the liquid surface tension for the thirty various wetting liquids (Zisman plots), consistent with the literature. The critical surface tensions of spruce and maple were found to be 45.0 dynes/cm and 42.0 dynes/cm, respectively. Critical surface tension values for these two wood species were slightly smaller (14–16 dynes/cm) than their total surface free energies. Herczeg (1965) found that the surface free energy of Douglas-fir was 61.0 to 58.2 dynes/cm (springwood and summerwood, respectively), which were about 11.0 to 14.0 units higher than  $\gamma_c$ . Nguyen et al. (1979) reported a  $\gamma_c$  of 52.8 dynes/cm for unextracted Douglas-fir wood. Jacob and Berg (1993) found critical surface tension values of 32.0, 35.0, and 37.0 dynes/cm for softwood bleached kraft, hardwood bleached kraft, and chemithermomechanical pulp fibers, respectively. Also, Luner et al. (1969) found critical surface tensions of 36.0 to 49.0 erg/cm<sup>2</sup> for cellulose and 33.0 to 36.0 erg/cm<sup>2</sup> for hemicelluloses. As previously discussed, differences are probably due to the variable effects of the physical and chemical state of the surfaces.

An attempt to correlate wood wettability and tangential swelling of wood (Mantanis et al. 1994) in various organic solvents was unsuccessful (Fig. 6). The strong acidic character of the wood surface is a significant factor in the initial

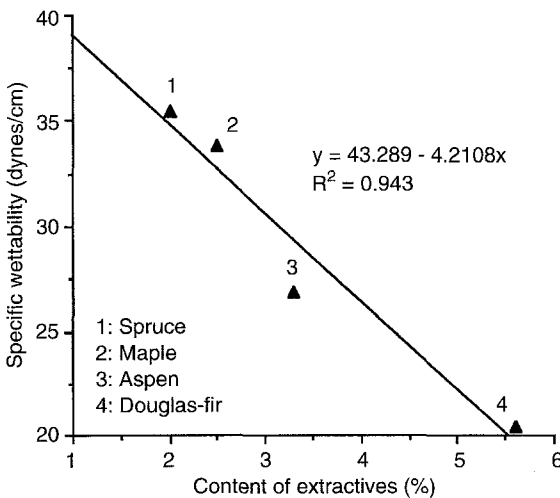


Fig. 4. Specific water wettability as a function of content of extractives for four wood species

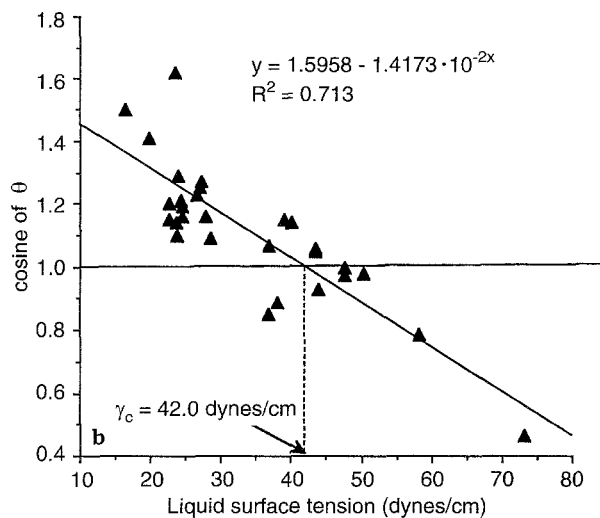
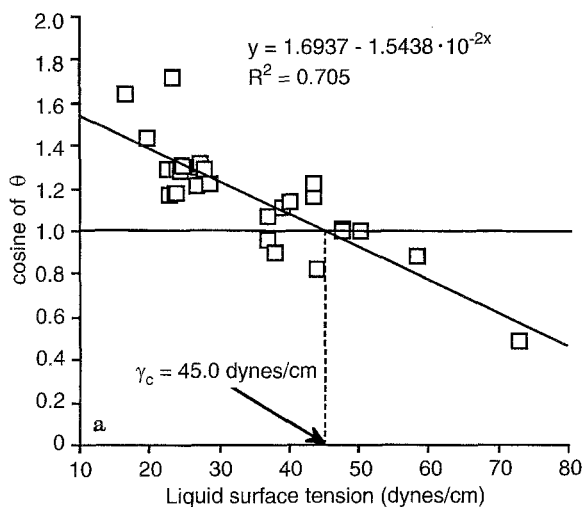


Fig. 5a,b. Determination of critical surface tension of a sitka spruce wood; b sugar maple wood

process of wetting and swelling but the ultimate swelling of wood is apparently independent of specific wettability.

### Conclusions

The wettability of wood in thirty various organic liquids was determined using the Wilhelmy technique. Wood surfaces have a strong acidic character since the greatest interactions for all four wood species occurred with the basic probe (formamide), while lower interactions occurred with the acidic probe (ethylene glycol). The total surface free energy of wood ranged from 48.0 to 61.0 dynes/cm, on the average, and 75 to 80% of this energy was attributed to the dispersion forces.

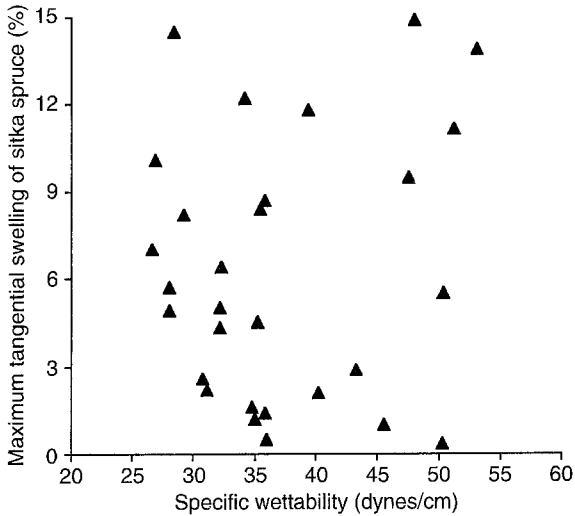


Fig. 6. Maximum tangential swelling of wood plotted against wood specific wettability (sitka spruce)

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