

1987. *In*: Kennedy, J. F.; Phillips, G. O.; Williams, P. A., eds. Wood and cellulose: industrial utilisation, biotechnology, structure and properties. Chichester, West Sussex, England: Ellis Horwood Ltd. Chapter 45.

Wettability and water repellency of wood: A faster, more convenient method

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INTRODUCTION

Water repellency of wood is important in outdoor uses of wood and wood-based products. Use of effective water repellents on wood has been linked to improved performance of wood outdoors (Banks and Voulgaridis 1980; Voulgaridis and Banks 1981; Purslow 1982; Miniutti, et al. 1961). Conversely, good wetting is required in operations involving coatings, adhesives, and some types of protective treatments that require penetration of wood by liquids. Efficient wetting of wood by adhesives has been correlated with strength of adhesive bond (Collett 1972; Huntsberger 1978; Bodig 1962; Freeman 1959; Subramanian, et al. 1983).

Wettability is usually defined as the contact angle that a liquid makes when in contact with a solid surface. From contact angle data, surface free energy of a solid can be estimated. Good water repellency is the special case of poor wettability (large contact angle). Wood is both hygroscopic and briefly water repellent. Direct contact angle measurements (Gray 1962; Nguyen, et al. 1978), tilted plate (Freeman 1959; Bodig 1962), and capillary rise techniques (Freeman 1959) have been used to study forces acting on liquids in contact with wood surfaces, but all involve experimental complications,

and are relatively slow. A rapid, reliable procedure for measuring wettability and related properties on wood and on wood products was clearly needed, and we devised one. A modified Wilhelmy method had been used to determine the forces acting on immersed fiber samples (Young 1976; Klungness 1981). Casilla, et al. 1981; 1984 used a larger, conical wood sample to obtain a "wettability index". We used that procedure as a starting point, and combined an automatic surface tension apparatus with a microcomputer for control, data collection, and processing, for the study of wood surfaces.

EXPERIMENTAL

Wood materials

Green logs of various species were obtained immediately after harvesting and were stored at 2°C prior to sawing into edge-grain boards about 1.3 centimeters (cm) thick. The wood was kiln dried below 70°C. The boards were planed, and sawn into 3 x 0.64 cm sticks.

Automated surface tension analyzer

Surface tension measurements of liquids and determinations of forces on wood samples during immersion in liquids were done with a Fisher Model 215 Autotensiomt Surface Tension Analyzer that was interfaced with an IBM-PC-XT microcomputer using Metrabyte Corporation Dash 16 multifunction high-speed analog to digital expansion board.

The analyzer consists of a strain sensitive wire affixed at one end to the balance beam and the other to a transducer. The transducer's signal is proportional to the load. The output of the analyzer is 0 to 1 mv which is calibrated to equal 0 to 100 dynes/cm. This signal is amplified and filtered; noise above 2 HZ is attenuated before entering the Metrabyte Dash-16 Analog to Digital interface board installed in the IBM-PC-XT.

The elevator in the surface tension analyzer is controlled by the digital output port of the Dash-16.

Computer program: wood wettability study*

The BASIC program automates experimental procedures, and is divided into three major modules: Surface Tension, Run New Sample, and Analyze Data, and one major submodule, Graph.

The Surface Tension module has two main features: electronic calibration and automatic apparatus control. Surface tension of a liquid is determined, and the value is filed. Run New Sample routine calibrates and controls the apparatus. The collected data is filed under a name based on sample statistics. Analyze Sample Data module retrieves file to be analyzed and reads it into computer memory. The main module has sub-modules: Graph, Calculation of Contact Angle from Attractive Force, from Work of Adhesion, Estimate of Surface Free Energy, Calculation of Interaction Factor, and Data Summary.

GRAPH

The Graph submodule features variable axis scaling, and rescaling that enlarges sections of the graph. Figure 1 is the graph of a typical wood sample run.

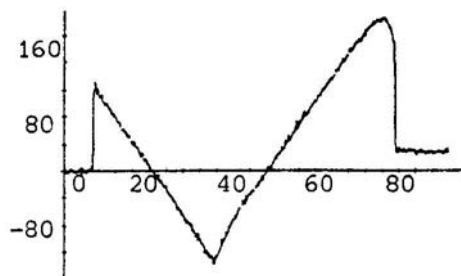


Fig. 1. Force (dynes) - vs - time (seconds).

Contact angle from attractive force

The contact angle is calculated by use of the Wilhelmy equation:

$$\text{Attractive force} = \gamma_L P \cos \theta$$

*A more detailed description of the program is available upon request.

where

γ_L = surface tension of the liquid,
 P = the perimeter of the wood sample, cm, and
 θ = the contact angle.

The point of initial contact of the wood with the immersion liquid is located, and correction for buoyancy is made. This gives the attractive force at zero immersion from which the contact angle, θ , is determined.

Contact angle from work of adhesion

The contact angle, θ , is calculated with the Young-Dupré equation:

$$\text{Work of adhesion} = \gamma_L (1 + \cos \theta)$$

The work of adhesion is obtained from the area under immersion curve (Fig. 1).

Surface free energy estimation

The well-known Zisman (1963, 1964) critical surface tension γ_C , was determined by plotting the cosine of the contact angle on a wood surface versus the surface tension of a series of liquids. The point at which $\cos \theta = 1$ (zero contact angle) line is intercepted, determines γ_C . Mixtures of water with ethylene glycol and with glycerol provided a range of surface tensions. End grain of wood samples was sealed with a small amount of beeswax to prevent rapid capillary flow of liquids into wood samples.

Interaction parameter calculation

The interaction parameter, Φ , was calculated according to the procedure used by Good (1979) and Becker (1977):

$$\cos \theta = 2 \Phi \left(\frac{\gamma_s}{\gamma_L} \right)^{1/2} - 1$$

γ_s = surface tension of solid

Aging effect

Wood samples, cut at the same time, were stored under constant 27°C, 30% relative humidity conditions for several weeks; elapsed time shown denotes

length of exposure to laboratory illumination and atmosphere. Each point represents a wood sample cut from the same board.

RESULTS AND DISCUSSION

Aging effect

The sensitivity of this experimental procedure in measuring wettability of wood samples is shown by the decreasing wettability of aspen (Fig. 2) with time of exposure to laboratory conditions. This effect has been noted before by Gray (1962), who attributed it to surface contamination and by Nguyen and Johns (1979) who suggested environmental rather than wood factors. Subtle effects of light and oxygen should also be considered.

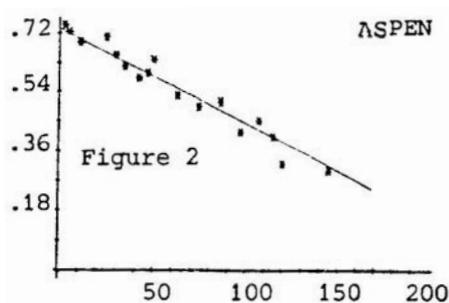


Fig. 2. Cosine of contact angle - vs - time (minutes).

Surface free energy estimates

The critical surface tension γ_e , (an approximation of the surface free energy) of birch was obtained with the Zisman plot (Fig. 3) from measured surface tension values and advancing contact angles calculated from attractive forces. The value, 49.5 dynes/cm for the birch wood surface free energy is in the range of values reported for wood previously by others (Marian 1962; Herczeg 1965; Nguyen and Johns 1979).

Interaction parameter calculation

If γ_c (critical surface tension) is taken for an approximation of the surface free energy of wood, γ_s , it becomes possible to calculate the interaction

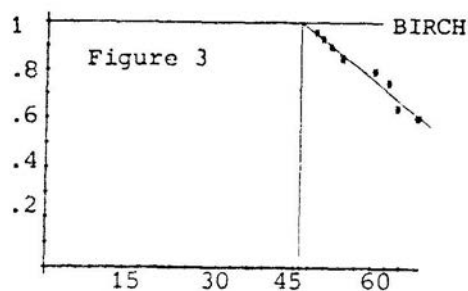


Fig. 3. Cosine of contact angle - vs - liquid surface tension

parameter Φ . Φ is a function of the properties of the solid and the liquid on a molecular level (Good 1979; Becker 1977). Its value is near unity for nonpolar liquids and solids, and generally from 0.5 to 1.0.

$$\cos \theta = 2 \Phi \left(\frac{\gamma_s}{\gamma_L} \right)^{1/2} . \quad (\text{Good 1979;}$$

Becher 1977). For birch, $\gamma_C \approx \gamma_S = 49.5$ dynes/cm, $\cos \theta = 0.608$ with H_2O , $\gamma_L = 72.4$ dynes/cm; then $\Phi = 0.97$. With ethylene glycol $\cos \theta = 0.866$, $\gamma_L = 52.3$ dynes/cm; then $\Phi = 0.96$. With glycerol $\cos \theta = 0.653$, $\gamma_L = 66.3$ dynes/cm; then $\Phi = 0.96$.

Further work is planned on the interaction parameter for wood and liquids and on the contributions of dispersion and polar forces to the free energy values. These data are presented to illustrate the information that is readily obtainable with this apparatus. The rapid determination of wettability and of liquid absorption by wood lends itself to practical applications that are related to improved solid wood products and wood-derived materials.

ACKNOWLEDGEMENTS

The authors thank Richard E. Kinney for the electronics work.

REFERENCES

- Banks, W.; Voulgaridis, E. 1980. Brit. Wood Preservers Ann. Conv. Record: 43-53.
- Becher, P. 1977. J. Colloid and Interface Sci. 59, (3) 429-432.
- Bodig, J. 1962. For. Prod. J. 12, (6) 265-275.
- Casilla, R.C., Chow, S. and Steisr, P. R. 1981. Wood Sci. Technol. 15, 31-45.
- Casilla, R.C., Chow, S., Steiner, P.R. and Warren, S.R. 1984. Wood Sci. Technol. 18, 87-96.
- Collett, B. 1972. Wood Sci. Technol. 6, 1-42.
- Freeman, A. 1959. For. Prod. J. 9, (12) 451-458.
- Gray, V. R. 1962. For Prod. J. 12, (9) 452-461.
- Good, R. J. 1979. In: Surface and Colloid Science, Good, R. J., Stromberg, R. R., eds. Vol. 11, Plenum Press, New York and London, 1979, 1.
- Herczeg, A. 1965. For. Prod. J. 15, (11) 499-505.
- Huntsberger, J. 1978. Adhes. Age. 23-27 (Dec.)
- Klungness, J. 1981. Tappi 64, (12) 65-66.
- Marian, J. R. 1952. In: Symp. on Prop. of Surf., ASTM Mater. Sci. Ser. 4: Spec. Tech. Publ. 340, Phila.:ASTM 122-149.
- Miniutti, V. P., Mraz, E.A. and Black, J.M. 1961. For. Prod. J. 11, (10) 453-462.
- Nguyen, T.; Johns, W. E. 1978. Wood Sci. Technol. 12, 63-74.
- Nguyen, T.; Johns, W. E. 1979. Wood Sci. Technol. 13, 29-40.
- Purslow, D. F. 1982. Bldg. Res. Establ., Info. Paper 20/82, Nov. 1982, 3 p. (Garston, Watford, WD2 7JR, UK).
- Subramanian, et al. 1983. Holzforschung 37, 117-120.
- Voulgaridis, E.; Banks, W. 1981. J. Inst. Wood Sci. 9, (2) 50, 72-83.
- Young, R. A. 1976. Wood and Fiber 8, (2) 120-128.
- Zisman, W. A. 1963. Ind. Eng. Chem. 55, (10) 19-38.
- Zisman, W. A. 1964. In: Contact angle, wettability, and adhesion. Adv. Chem. Ser. 43. Washington, D.C.: Am. Chem. Soc. 1.