

TEMPERATURE DEPENDENCE OF WOOD SURFACE ENERGY

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ABSTRACT

A thorough understanding of the wood surface is required to engineer adhesive bonding in composite applications. A surface analysis technique, dynamic contact angle (DCA) analysis, was used to examine the effects of temperature on the wood surface as measured by the contact angle and surface energy. A hydrophobic surface transition was found on the wood surface at 60 C, which coincides with the glass transition of lignin as measured by differential scanning calorimetry. The change in the surface at the glass transition can be attributed to the diffusion of nonpolar molecular groups to the surface. This could be the result of the migration and deposition of extractives, reorientation of macromolecules, or a combination of the two. Similar behavior has been observed in synthetic amorphous polymers. Although the surface of wood is complex, the results indicate that it can be investigated and understood like synthetic polymer materials.

Keywords: Dynamic contact angle analysis, wood, surface energy, glass transition temperature, differential scanning calorimetry, extractives, surface reorientation.

INTRODUCTION

New wood-based composites are being developed that could benefit from a thorough and fundamental understanding of the wood surface. The large demand and need for engineered wood products have produced a number of wood composite materials such as particleboard, oriented strandboard (OSB), laminated veneer lumber (LVL), parallel strand lumber (PSL), and wood joists (Moody and Ritter 1990). Research is being conducted to combine wood with plastics, synthetic fibers, biomass, and inorganic materials (Youngquist and Rowell 1989). These products may require new adhesive systems to reach their full commercial potential. A better understanding of the wood surface and adhesive bonding is necessary because the mechanism of wood ad-

hesion is not fully understood and may change significantly with different adhesive systems (Wellons 1983).

The wood surface is a complex heterogeneous polymer composed of cellulose, hemicellulose, and lignin. The surface is influenced by polymer morphology, extractive chemicals, and processing conditions. Current knowledge of the wood surface and adhesive bonding process has been obtained largely by empirical means (Freeman 1959). Application of relatively new surface techniques, such as dynamic contact angle (DCA) analysis, can provide fundamental knowledge regarding the chemical nature of the wood surface.

Dynamic contact angle analysis has been successfully applied to synthetic fibers (Andrade 1988; Andrade and Chen 1986), wood

fibers (Young 1978), and solid wood (Casilla et al. 1981; Kalnins and Katzenberger 1987). A standard procedure for testing wood with dynamic contact angle analysis was shown to give reproducible results (Gardner et al. 1991). The standard DCA procedure uses thin end-coated wood veneers that are suspended from an electronic balance and immersed in a liquid at a controlled rate of speed. The force increase caused by the weight of the liquid in the formed meniscus between the wood veneer and liquid is related to the liquid surface tension and the contact angle. From this interaction, the wetting force (F) can be defined as

$$F = P\gamma_{LV}\cos\theta - V\rho g \quad (1)$$

where P is the sample perimeter at the interface, V is the volume of liquid in the meniscus, ρ is the liquid density, $g = 980 \text{ cm/sec}^2$ (gravity force), γ_{LV} is the liquid surface tension, and θ is the contact angle. By using a liquid of known surface tension, Eq. (1) can be used to calculate the contact angle.

An increasing body of evidence suggests that polymer surfaces are time-, temperature-, and environment-dependent (Andrade 1988). The minimization of free energy, a thermodynamic requirement, is the driving force for changes in the polymer surface. By their very nature, glassy polymers (hemicellulose and lignin) are not in thermodynamic equilibrium. Because of the low molecular mobility in the glassy phase, the response of the polymer to any perturbation occurs over time. The time-dependent response is then accelerated by temperature with the corresponding increase in molecular mobility. For a stress perturbation, this time-dependent response is exhibited in creep and stress relaxation behavior. Likewise, for a surface perturbation, molecules reorient to satisfy the thermodynamic characteristics of the surface environment.

Surface relaxations are time-dependent changes in polymer surfaces. Hydrophobic polymers, which are oxidized, lose their surface oxygen functionality upon exposure to air without changing the overall chemical com-

position of the bulk polymer (Yasuda and Sharma 1981; Gagnon and McCarthy 1984; Owen et al. 1988; Tingey et al. 1988). Likewise, hydrophilic polymers, such as hydrogels, can develop hydrophobic surfaces upon exposure to air (Yasuda and Sharma 1981; Ratner and Yoon 1988; Ko et al. 1981; Tingey et al. 1988). These hydrogels can recover their surface polarity upon exposure to an aqueous environment (Lavielle and Schultz 1985; Lavielle 1988; Andrade et al. 1979; Ruckstein and Gourisankar 1985). The mechanism for these surface changes is the structural rearrangement of surface molecules, either side chain or backbone, to minimize surface free energy. This structural rearrangement has been described as a self-diffusion of the polymer molecules (Gagnon and McCarthy 1984). This self-diffusion is the same mechanism that controls viscoelastic response with stress and strain.

Surface transitions are temperature-dependent changes such as a glass or melt transition in the polymer. Polymer surface transitions have been observed by measuring contact angles over a range of temperatures in both homogenous and heterogeneous polymers (Funke et al. 1969; Neumann and Tanner 1970; Neumann 1974; Baszkin et al. 1976, 1977). On polymer surfaces, glass transitions are characterized by a peak in the contact angle and a decrease in the surface energy at the glass transition temperature. Wood has two glass transition temperatures, which correspond with the two amorphous polymer components hemicellulose and lignin. Hemicellulose has a glass transition of between -23 C and 200 C , depending upon the moisture content (Kelley et al. 1987). Lignin has a glass transition in the range of $60\text{--}200 \text{ C}$, depending upon the moisture content and measuring technique (Salmén 1984, 1990; Kelley et al. 1987).

With the detection of polymer surface transitions in mind, the objective of this paper is to examine the effect of temperature on the wood surface as measured by the contact angle and surface energy. The range of temperatures to be investigated includes the glass transition temperature of hemicellulose and lignin.

METHODS

Tests were performed with the Cahn DCA 322 Dynamic Contact Angle Analyzer (DCA). The DCA was calibrated at the start of each test session. Glassware was cleaned with a sulfuric/chromic acid solution and rinsed with distilled water. High performance liquid chromatography grade, ultra pure distilled water was used for all tests and changed for each sample. The surface tension of each test liquid was tested with a flame-cleaned glass slide.

During the DCA scan, the sample was immersed at a controlled rate of 194 microns/second to a depth of 15 millimeters and then removed from the liquid at the same rate. The data were analyzed via the least squares regression package in the DCA system to determine the contact angle. Water absorption data were obtained directly from the DCA computer display as the difference between the sample weight before and after scanning. Surface energy was calculated based on the interaction parameter equation (Kalnins and Katzenberger 1987);

$$\gamma_{sv} = \gamma_{lv}(1 + \cos \theta)/4\phi^2 \quad (2)$$

where:

γ_{sv} = solid surface free energy

ϕ = interaction parameter.

Based on Kalnins and Katzenberger's work (1987), the interaction parameter for wood and water was estimated to be 1.0.

Elevated temperatures were achieved using a jacketed beaker mounted to the DCA platform. A temperature-controlled circulating bath was connected to the beaker mount. Two small air pumps removed air from the balance chamber and the test chamber to prevent moisture build-up in the DCA components and minimize convective air currents, which cause noise in the force data. All fittings were secured to prevent vibrations. The beakers of distilled water were sealed and preheated in an oven prior to placement in the jacketed beaker assembly. Temperatures were monitored with a

digital thermometer. The test was started once the temperature of the probe liquid was stable.

Commercially cut, half-round sliced veneer was obtained from a local manufacturer. Two native species, yellow-poplar (*Liriodendron tulipifera*), a diffuse-porous hardwood, and red oak (*Quercus rubra*), a ring-porous hardwood, were utilized. The veneers were frozen prior to testing to maintain their green moisture content. Test samples were randomly selected from straight-grained, defect-free material. To minimize variation, yellow-poplar samples were selected from white-colored sapwood only. Red oak samples were selected from light pink-colored heartwood with open vessels on less than one quarter of the surface. Specimens were cut and end-sealed according to the procedure of Gardner et al. (1991). The specimens were conditioned for two weeks in darkness at 60% relative humidity and 23 C prior to testing. Wood specimens were tested parallel to the grain direction. At least five wood specimens were tested at each temperature.

The thermal analyses were performed on a Mettler TA3000 differential scanning calorimeter (DSC) equipped with a liquid nitrogen cooler and TC10A processor. Medium pressure (20 bar or 2 MPa) crucibles with O-ring sealers and 120-microliter capacity were used. Water loss from an 80-milligram sample in this crucible was 30 micrograms (0.04% moisture content) between 40 and 210 C.

The wood samples were ground, and portions passing through 80 mesh and retained in 100 mesh were used. They were equilibrated to either 12% or 31% moisture content. The sample weights ranged from between 18 and 30 milligrams. The samples were run between 25 and 200 C at a heating rate of 10 C/minute.

RESULTS AND DISCUSSION

The results for the advancing water contact angles measured on yellow-poplar sapwood at varying temperatures are shown in Fig. 1. In general, the contact angle decreased linearly with increasing temperature from 23 to 55 C. This trend is followed by increases at 60 and

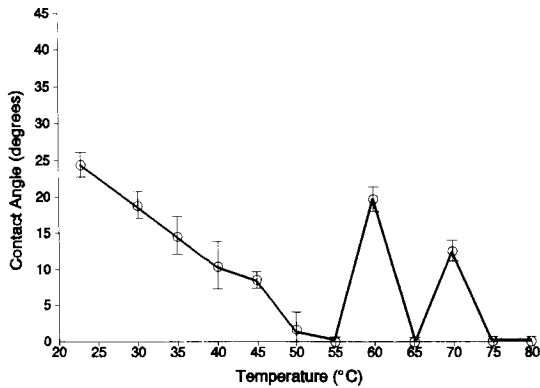


FIG. 1. Average contact angles and standard deviation for yellow-poplar sapwood at varying temperatures.

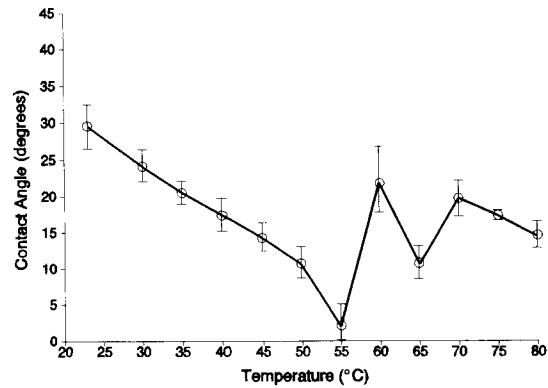


FIG. 2. Average contact angles and standard deviation for red oak heartwood at varying temperatures.

70 C. Red oak, shown in Fig. 2, followed similar trends, but with slightly larger contact angle values. The increase in the contact angle indicates a hydrophobic response between the water and the wood at 60 and 70 C. Both contact angle peaks were reproducible upon further testing.

Contact angle is a function of both the solid surface and the probe liquid. To remove the influence of decreasing liquid surface tension with increasing temperature, solid surface energy was calculated. The changes in surface energy with temperature for yellow-poplar sapwood and red oak heartwood are given in Figs. 3 and 4, respectively. The surface energy of both species increases slightly up to 55 C. At 60 C the surface energy decreases and remains fairly constant in the lower energy state. Yellow-poplar decreased from 68 dynes/cm at 55 C to 63 dynes/cm at 60 C. Red oak decreased from 67 dynes/cm at 55 C to 63 dynes/cm at 60 C. The decrease in surface energy supports the thermodynamic requirement for minimizing surface free energy in response to a transition at 60 C.

The surface of wood exhibited a change in both the contact angle and the surface energy data similar to a polymer surface undergoing a phase change or glass transition (Neumann and Tanner 1970). Differential scanning calorimetry was used to verify the glass transition

in the wood. Because of the inherent nature of the DCA test, it is difficult to know the exact moisture content of the wood surface at the advancing meniscus front. Therefore, glass transition temperatures were measured at both the equilibrium moisture content of the veneer samples and the fiber saturation point of wood, presumably corresponding to the advancing meniscus on the veneer during the DCA scan. DSC data for yellow poplar sapwood at 12% and 31% moisture content are given in Figs. 5 and 6, respectively. The first derivative of heat flow shows a glass transition occurring at 75 C for the 12% moisture content sample and at 63 for the 31% moisture content sample. DSC

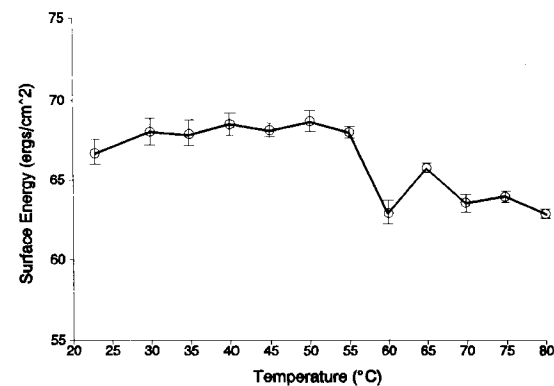


FIG. 3. Average surface energy and standard deviation for yellow-poplar sapwood at varying temperatures.

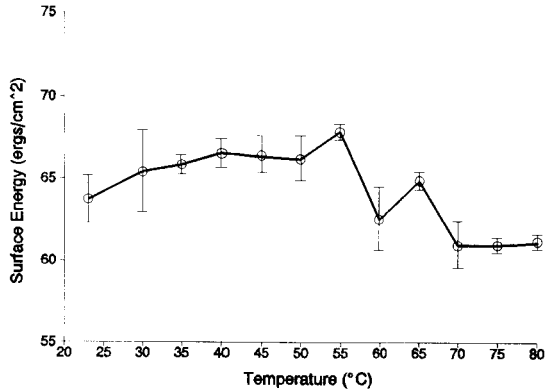


FIG. 4. Average surface energy and standard deviation for red oak heartwood at varying temperatures.

results for red oak, at the same moisture contents, are given in Figs. 7 and 8. The first derivative of heat flow shows a glass transition for red oak occurring at 68 and 66 C, respectively. The measured glass transition is in the range of literature values for lignin (Kelley et al. 1987; Salmén, 1984, 1990).

The water absorbed during the DCA scans is shown in Fig. 9 for yellow-poplar and in Fig. 10 for red oak. The water absorption for yellow-poplar increases sharply at around 40 and 70 C. This behavior can be explained by a glass transition, which causes the diffusion coefficient of the solid polymer to increase by increasing the polymer free volume (Lefebvre et al. 1989). Increased free volume translates to increased space in which diluent molecules

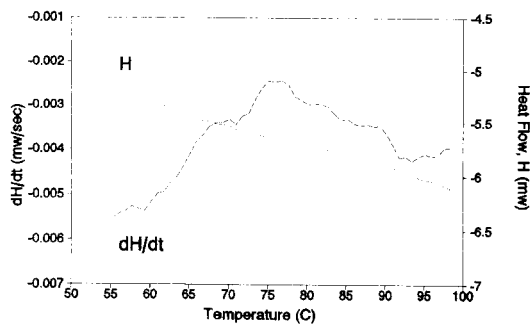


FIG. 5. Heat flow and first derivative of heat flow over a range of temperatures for yellow-poplar sapwood at 12% moisture content.

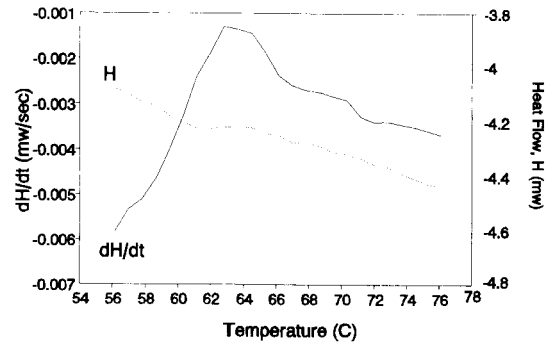


FIG. 6. Heat flow and first derivative of heat flow over a range of temperatures for yellow-poplar sapwood at 31% moisture content.

have more freedom to move, thereby increasing the diffusion coefficient and water absorption.

The red oak data are highly variable and show no apparent trends. The water absorption of wood is a combination of diffusion and capillary flow. The large open vessels on the surface of oak act as capillaries for water absorption. This mechanism will decrease the contribution of the diffusion in the solid wood polymer and may account for the variation.

Owen et al. (1988) cited six possible mechanisms that could cause a hydrophobic change in a synthetic polymer surface:

1. external contamination,
2. changes in surface roughness,

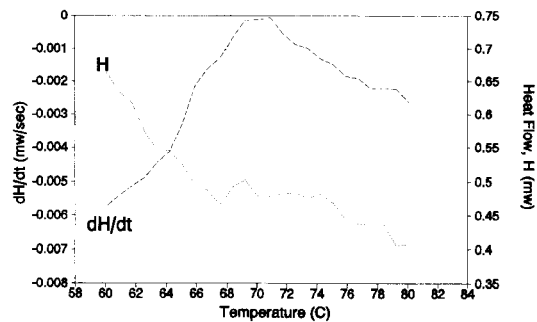


FIG. 7. Heat flow and first derivative of heat flow over a range of temperatures for red oak heartwood at 12% moisture content.

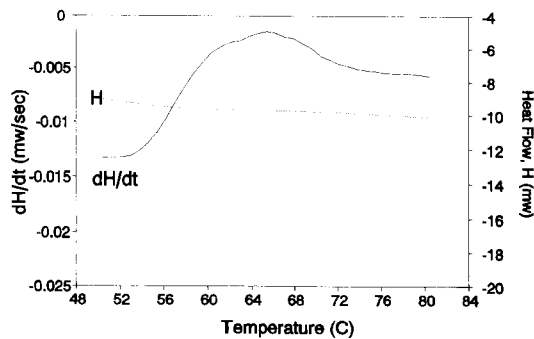


FIG. 8. Heat flow and first derivative of heat flow over a range of temperatures for red oak heartwood at 31% moisture content.

3. loss of volatile oxygen-rich species from the surface to the atmosphere,
4. reorientation of surface hydrophilic groups away from the surface,
5. migration of hydrophobic polymer chains from the bulk to the surface,
6. migration and deposition of low energy, low molecular weight molecules on the surface.

Examining the first four mechanisms reveals that they are not likely to significantly affect wood. External contamination is unlikely on low energy solids of less than 100 dynes/cm surface energy (Zisman 1963). Changes in surface roughness have been observed on compliant polymer hydrogels, but not on rigid polymers (Jhon and Yuk 1988) like lignin and hemicelluloses. The inherent roughness of wood has little effect on the measured dynamic contact angle parallel to the grain (Gardner et al. 1991). The volatile compounds in wood, i.e., extractives, are chemical compounds formed from a tree's metabolism including fats, sugars, amino acids, and myriad aromatic compounds (Rowe and Conner 1979). Loss of these extractives would be expected to cause the opposite effect of what was observed. The polymer components of wood, cellulose, hemicellulose, and lignin do not have long hydrophilic side chains that could rotate away from the surface. Elimination of these mechanisms leaves two possibilities—the structural rearrangement of bulk molecules and migration

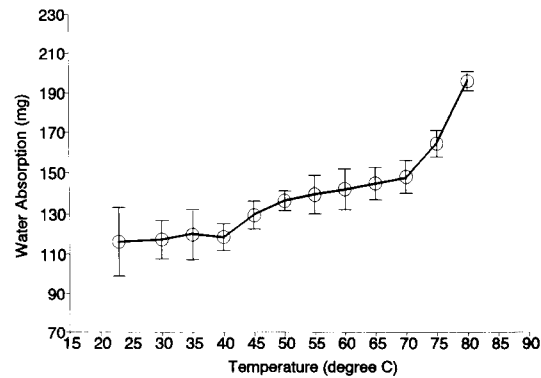


FIG. 9. Average water absorption and standard deviation for yellow-poplar sapwood during DCA tests at varying temperatures.

and deposition of extractives on the wood surface.

Surface structural rearrangements are well documented in the synthetic polymer field. Neumann (1974), Neumann and Tanner (1970), and Baszkin et al. (1976, 1977) have detected glass and melt transitions in a variety of synthetic polymers including polyethylene, polytetrafluoroethylene, and vinyl acetate-vinyl chloride copolymer with contact angle methods. However, no conclusions were given as to the specific mechanisms of these surface changes. Surface structure changes in polymers have been observed to be a diffusion-related

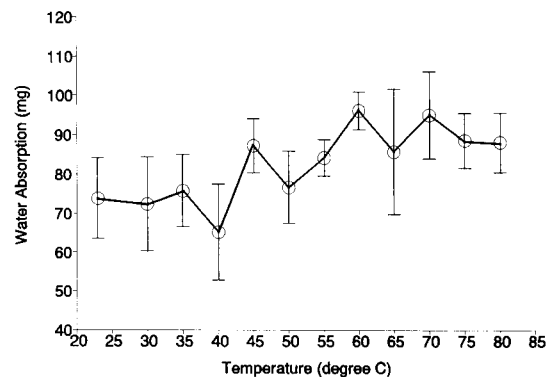


FIG. 10. Average water absorption and standard deviation for red oak heartwood during DCA tests at varying temperatures.

process where polymer viscoelasticity allowed a self-diffusion of the polymer molecules from the surface to the bulk and from the bulk back to the surface (Gagnon and McCarthy 1984). Hydrogels can exhibit either a hydrophobic or a hydrophilic surface chemistry, depending on the environmental conditions they are exposed to, i.e., aqueous (high energy) or air (low energy) (Lavielle and Schultz 1985; Lavielle 1988; Andrade et al. 1979; Ruckstein and Gourisankar (1985).

In the works of Neumann (1974), Neumann and Tanner (1970), and Baszkin et al. (1976, 1977), close agreement was found between the transitions as measured by contact angle techniques and the transition measured by DSC or differential thermal analysis (DTA). The surface energy change for wood, at 60 C, differs by approximately 10 C from the DSC and water absorption data. With a whole wood moisture content change from 12% to saturated, the glass transition of hemicellulose will change from 25 to -10 C (Kelley et al. 1987). In contrast, over the same moisture content change, the glass transition for lignin was found to change from 75 to 63 C. Therefore, the changes observed in the contact angle and surface energy data are likely to correspond with the glass transition of lignin.

The structural rearrangement of amorphous polymer molecules in wood may seem inappropriate because of the complex structure of the wood polymer matrix and the general lack of knowledge regarding the lignin-hemicellulose linkage. However, limited surface changes have been observed in other structurally rigid polymers such as polytetrafluoroethylene (Gagnon and McCarthy 1984) and polyurethanes. (Owen et al. 1988). Lavielle (1988) concluded that surface molecules have greater mobility than their bulk counterparts. Hemicellulose is a low molecular weight, branched polymer. The hemicellulose could possibly be mobile and capable of reorientation at 12% or 31% moisture content and 60 C because: 1) it should be plasticized by the moisture in the wood, 2) it is above the glass transition temperature, and 3) the short molecular chains

would allow for more freedom to move. The occurrence of a glass transition in lignin would increase the diffusion coefficient and could increase the ability of hemicellulose to move. Lignin is a three-dimensional network polymer that would not be expected to be mobile. Lignin could also be altered by the moisture in the wood. Bound water has been observed to break hydrogen bonds in lignin (Hatakeyama et al. 1983). It is also possible that only small segments of the amorphous polymers can rearrange. The small scale of the changes in surface energy may reflect this limited movement.

Extractives in yellow-poplar sapwood and red oak heartwood comprise 2.4 and 6.3% of the total wood weight, respectively (Gardner et al. 1991). In red oak, these extractives are comprised largely of polyphenolic compounds, while yellow-poplar extractives include alkaloids, fatty acids, and sugars (Rowe and Conner 1979). The increase in diffusion brought on by the glass transition of lignin could increase the ability of extractives to reach the surface. Extractives have already been shown to alter the surface chemistry of wood (Casilla et al. 1981; Christiansen 1990). The migration and deposition of extractives at the surface are thought to contribute to the "inactivation" of wood from high temperature drying (Christiansen 1990).

Low molecular weight, low surface energy compounds also occur in synthetic polymers to control processing properties. These compounds include silicone and fluorine compounds and make up from 0–2% of the polymer composition. During polymer processing, these compounds tend to migrate to and dominate the polymer-air interface (Tingey et al. 1988; Owen et al. 1988) in an analogous manner to the extractives in wood.

Fatty acids, nonpolar extractives have been shown to contribute to the low surface energy of wood (Hemingway 1969). The presence of these extractives on the wood surface would be expected to markedly decrease the surface energy to between 20 and 40 dynes/cm, although only a slight change was observed (Figs. 3 and 4). A thin monolayer of chemicals on a

surface can alter the entire surface chemistry (Zisman 1963). A monolayer assumes entire or large-scale coverage by extractives. Small coverage by a few molecules could cause the slight decreases observed. The contact angle for a heterogeneous surface should be a weighted average of the contact angles of the individual components (Cassie and Baxter 1944).

It is very likely that a combination of surface molecular rearrangement and surface extractive migration and deposition causes the observed changes on the wood surface. The increase in diffusion above the glass transition of lignin could allow extractive migration and deposition at the wood surface, and limited movement of the amorphous components of wood, i.e., hemicellulose and lignin.

CONCLUSIONS

A wood surface energy transition was detected at approximately 60 C by DCA techniques. The data correspond to the glass transition of lignin as measured by DSC and water absorption for yellow-poplar. The occurrence of a glass transition increases the free volume, which subsequently increases diffusion in the wood. Increased diffusion could allow extractive migration and deposition or limited movement by amorphous polymer segments of wood. Either one or both of these phenomena could contribute to the hydrophobic change observed in the surface of wood. The influence of the wood surface transition in adhesive bonding could have important fundamental and processing implications for wood composite manufacture.

The observed contact angle and surface energy data for wood are similar to data obtained on synthetic polymer materials. Although the chemical and morphological structure of wood polymer matrix is complex, it can be investigated and understood like synthetic polymer materials.

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REFERENCES

- ANDRADE, J. D. 1988. Polymer surface and interface dynamics: An introduction. Pages 1-8 in J. D. Andrade, ed. *Polymer surface dynamics*. Plenum Press, New York, NY.
- , AND W. Y. CHEN. 1986. Probing polymer and interface dynamics. *Surface Interface Anal.* 8:253-256.
- , S. M. RA, R. N. KING, AND D. E. GREGONIS. 1979. Contact angles at the solid liquid interface. *J. Colloid Interface Sci.* 72(3):488-494.
- BASZKIN, A., M. NISHINO, AND L. TER-MINASSIAN-SARAGA. 1976. Solid liquid adhesion of oxidized polyethylene films. Effect of temperature. *J. Colloid Interface Sci.* 54(3):317-328.
- , ———, AND ———. 1977. Solid liquid adhesion of oxidized polyethylene films. Effect of temperature on polar forces. *J. Colloid Interface Sci.* 59(3):516-524.
- CASILLA, R. C., S. CHOW, AND P. R. STEINER. 1981. An immersion technique for studying wood wettability. *Wood Sci. Technol.* 15:31-43.
- CASSIE, A. B., AND S. BAXTER. 1944. Wettability of porous surfaces. *Trans. Faraday Soc.* 40:546-550.
- CHRISTIANSEN, A. W. 1990. How overdrying wood reduces its bonding to phenol-formaldehyde adhesives: A critical review of the literature. Part I. Physical responses. *Wood Fiber Sci.* 22(4):441-459.
- FREEMAN, H. A. 1959. Relation between physical and chemical properties of wood and adhesion. *Forest Prod. J.* 12:451-458.
- FUNKE, V. W., G. E. HELLWIG, AND A. W. NEUMANN. 1969. *Angewandte Makromolekulare Chemie.* 8:185-193.
- GAGNON, D. R., AND T. J. MCCARTHY. 1984. Polymer surface reconstruction by diffusion of organic functional groups from and to the surface. *J. Appl. Polymer Sci.* 29:4335-4340.
- GARDNER, D. J., N. C. GENERALLA, D. W. GUNNELLS, AND M. P. WOLCOTT. 1991. Dynamic wettability of wood. *Langmuir* 7(11):2498-2502.
- HATAKEYAMA, L., S. HIROSE, AND H. HATAKEYAMA. 1983. Differential scanning calorimetric studies on bound water in 1, 4-dioxane acidolysis lignin. *Makromolekulare Chemie* 184:1265-1274.
- HEMINGWAY, R. W. 1969. Thermal instability of fats relative to the surface wettability of yellow birch-wood (*Betula lutea*). *Tappi* 52(11):2149-2155.
- JHON, M. S., AND S. H. YUK. 1988. Contact angles at polymer water interfaces. Pages 25-44 in J. D. Andrade,

- ed. Polymer surface dynamics. Plenum Press, New York, NY.
- KALNINS, M. A., AND C. KATZENBERGER. 1987. Wettability and water repellency of wood: A faster, more convenient method. Wood and cellulose: Industrial utilization, biotechnology, structure and properties. Ellis Horwood Ltd., West Sussex, England. Chapter 45.
- KELLEY, S. S., T. G. RIALS, AND W. G. GLASSER. 1987. Relaxation behavior of the amorphous components of wood. *J. Mater. Sci.* 22:617-624.
- KO, V. C., B. D. RATNER, AND A. S. HOFFMAN. 1981. Characterization of hydrophilic-hydrophobic polymeric surfaces by contact angle measurements. *J. Colloid Interface Sci.* 82(1):25-37.
- LAVIELLE, L. 1988. Orientation phenomenon at polymer-water interfaces. Pages 45-66 in J. D. Andrade, ed. Polymer surface dynamics. Plenum Press, New York, NY.
- , AND J. SCHULTZ. 1985. Surface properties of graft polyethylene in contact with water. *J. Colloid Interface Sci.* 106(2):438-445.
- LEFEBVRE, D. R., D. A. DILLARD, AND T. C. WARD. 1989. A model for the diffusion of moisture in adhesive joints. Part I. Equations governing diffusion. *J. Adhesion* 27: 1-18.
- MOODY, R., AND M. RITTER. 1990. Structural wood products. Pages 41-52 in Serviceability and Durability of Construction Materials: Proceedings of the 1st Materials Engineering Congress. American Society of Civil Engineers, New York, NY.
- NEUMANN, A. W. 1974. Contact angles and their temperature dependence: Thermodynamic status, measurement, interpretation and application. *J. Colloid Interface Sci.* 4:105-191.
- , AND W. TANNER. 1970. The temperature dependence of contact angles—polytetrafluoroethylene/n-decane. *J. Colloid Interface Sci.* 34(1):1-8.
- OWEN, M. J., T. M. GENTLE, T. ORBECK, AND D. E. WILLIAMS. 1988. Dynamic wettability of hydrophobic polymers. Pages 101-110 in J. D. Andrade, ed. Polymer surface dynamics. Plenum Press, New York, NY.
- RATNER, B. D., AND S. C. YOON. 1988. Polyurethane surfaces: Solvent and temperature induced structural rearrangements. Pages 137-152 in J. D. Andrade, ed. Polymer surface dynamics. Plenum Press, New York, NY.
- ROWE, J. W., AND A. H. CONNER. 1979. Extractives in eastern hardwoods—A review. USDA Forest Service General Technical Report FPL-18, USDA Forest Products Laboratory, Madison, WI.
- RUCKSTEIN, E., AND S. V. GOURISANKAR. 1985. Environmentally induced restructuring of polymer surfaces and its influence on their wetting characteristics in an aqueous environment. *J. Colloid Interface Sci.* 107(2): 488-502.
- SALMÉN, L. 1984. Viscoelastic properties of in situ lignin under water saturated conditions. *J. Mater. Sci.* 19:3090-3096.
- . 1990. Thermal expansion of water saturated wood. *Holzforschung.* 44:17-19.
- TINGEY, K. G., J. D. ANDRADE, C. W. MCGARY, AND R. J. ZDRAHALA. 1988. Surface analysis of commercial biomedical polymers. Pages 153-170 in J. D. Andrade, ed. Polymer surface dynamics. Plenum Press, New York, NY.
- WELLONS, J. D. 1983. The adherends and their preparation for bonding. Adhesive bonding of wood and other structural materials. Pennsylvania State University, University Park, PA. Chapter 3.
- YASUDA, H., AND A. K. SHARMA. 1981. Effect of orientation and mobility of polymer molecules at surface on contact angle and its hysteresis. *J. Polymer Sci. Polymer Physics Edition.* 19:1285-1291.
- YOUNG, R. A. 1978. Wettability of wood pulp fibers. *Wood Fiber Sci.* 8(2):120-128.
- YOUNGQUIST, J. A., AND R. M. ROWELL. 1989. Opportunities for combining wood with nonwood materials. Pages 141-157 in T. M. Maloney, ed. Proceedings of the 23 International Particleboard/Composite Materials Symposium. Washington State University, Pullman, WA.
- ZISMAN, W. A. 1963. Surface energetics of wetting, spreading, and adhesion. *Ind. Eng. Chem.* 55(10):19-38.