WETTABILITY OF WOOD PULP FIBERS
Applicability of Methodology[1]

Raymond A. Young

Assistant Professor of Fiber Science, Department of Forestry,
University of Wisconsin, Madison, WI 53706

ABSTRACT

The applicability of a newly devised technique, based on the Wilhelmy principle, for measuring wetting properties of textile fibers has been demonstrated for a series of wood pulp fibers. The wettability of unbleached kraft, neutral sulfite semichemical (NSSC), and thermomechanical pulp fibers was determined and differences are discussed in terms of variations in chemical composition and surface morphology. It was found that grafting of the kraft and NSSC pulps with styrene considerably decreased wettability due to presence of the hydrophobic styrene polymer at the surface of the pulp fiber.

Keywords: Fiber wetting, contact angle, wettability, surface properties, fiber modification, wetting theory, surface morphology, fiber grafting, kraft fibers, thermomechanical fibers, NSSC fibers, pulp fibers, *Pseudotsuga menziesii, Populus tremuloides, Abies balsamea.*

INTRODUCTION

Although textile scientists have expended considerable effort to develop techniques for measuring the wettability of single fibers (cf. Miller and Young 1975), relatively little work has been published by wood scientists on wetting of pulp fibers. Foote (1939) estimated contact angles on single pulp fibers by measuring the height of rise of liquid at the fiber surface; however, this technique does not give quantitative results. The importance of obtaining reliable wetting data on fibrous material cannot be overemphasized since wetting influences such factors as adhesion, interfiber bonding, and wicking properties of the final sheet. Current interest in the wettability of fibers and paper products stems from efforts to develop separation methods for different grades of paper based on variations in the wetting properties of these materials in the presence of surfactants (Liskowitz et al. 1976).

In the past, emphasis has been placed on the use of optical techniques for obtaining contact angles at the fiber surface as a criterion of wettability (Grindstaff 1969; Jones and Porter 1967). Such techniques have not proven totally reliable for textile fibers and present even further difficulties when working with the much smaller caliber pulp fibers. Further limitations inherent in the use of directly measured contact angles have been discussed by Miller and Young (1975).

Because of these physical difficulties combined with the chemical and morphological complexity of pulp fibers, some investigators have resorted to characterizing surfaces of cast films of isolated wood polymers (Luner and Sandell 1969; Lee and Luner 1972; Borgin 1959). Here again several limitations are notable; compared with synthetic polymers which can be formed directly into films, rather harsh treatments are usually necessary for isolation of wood polymers and this can result in considerable modification of the surface properties of these materials from the native state. In addition, the casting of films presents an altered morphological character unlike the physical state of the wood polymers naturally comprising pulp fibers. In this respect Lee and Luner (1972) have suggested that differences in wetting between various woods and fibers may be af-

TABLE 1. *Literature reported wetting characteristics of isolated wood polymers*[a]

Wood Polymer	Water Contact Angle, °	Critical Surface Tension dynes/cm	Reference
Cellulose	34°	35.5	Luner and Sandell (1969)
	33°	--	Borgin (1959)
	27.8°[b]	--	Borgin (1959)
Hemicellulose	--		Luner and Sandell (1969)
Arabinogalactan		33	
Galactoglucomannan		36.5	
Hardwood xylan		33-36.5	
Softwood xylan		35	
Lignin			Lee and Luner (1972)
Hardwood kraft	60°	36	
Softwood kraft	58°	37	

[a] Relative humidity 32%

[b] Relative humidity 66%

fected more by variations in surface topology and minor chemical constituents than by the properties of lignin, cellulose, and hemicellulose.

Nevertheless, the use of films of isolated polymers is necessary for estimating the individual wetting characteristics of the various wood components even though certain limitations are apparent. Table 1 summarizes available wetting data on isolated wood polymers obtained from contact angle measurements on cast films.

A nearer ideal situation would then be a technique which offers wettability information on the native pulp fiber, but which does not involve the direct measurement of contact angle by optical methods. Such an alternate approach, based on the Wilhelmy principle, was presented in an earlier study on wetting of single textile filaments (Miller and Young 1975). The applicability of this method for use with wood pulp fibers is shown in this investigation.

METHODOLOGY

The formula of Wilhelmy (Wilhelmy 1863) shows that the pull exerted on a solid rod inserted into a mass of liquid is expressed by:

$$F = P \gamma_{LV} \cos \theta, \qquad (1)$$

where P is the perimeter of the rod along the three phase boundary line, γ_{LV} is the surface tension of the liquid, and θ is the contact angle of the system. The wettability (W) of the system is then defined as:

$$W = \frac{\text{Force per fiber}}{\text{Perimeter of fiber}} = \frac{F}{P}, \qquad (2)$$

which has been referred to in earlier literature as adhesion tension (Adamson 1960). Thus, when a fiber is suspended from a force measuring device (such as an electrobalance) and immersed in a liquid, the increase in weight can be used to calculate fiber wettability and, if desired, contact angle as well. Due to the small caliber of the pulp fibers, contributions due to buoyancy are negligible and no further corrections are necessary.

Certain additional factors must be considered, however, when using such a technique with pulp fibers. The method depends on an accurate interpretation of the perimeter of the fiber in order to obtain the wettability value W, and the contact angle θ. A modified wire measuring device (General Electric) proved suitable in earlier in-

vestigations for obtaining diameters of textile staple fibers (R. A. Young and B. Miller 1975, unpublished results). Perimeters of smaller fibers, such as from wood pulp, can be determined through observation in a light microscope equipped with a calibrated eyepiece. The range of pulp fiber dimensions can be ascertained from a tabulation published by Rydholm (1965).

A limitation of this fiber immersion method for determination of wettability, when applied to wood pulp fibers, is the swelling behavior of such cellulosic systems. On contact with water, the fiber perimeter is increased to a minor extent from the perimeter estimated in the dry state. This causes the wettability values (W) to be somewhat low. In addition, some water would be absorbed by the fiber in the swelling process resulting in a greater force (weight) reading and thus indicating a spuriously higher wettability W. However, swelling is time-dependent, and its effect on the wettability determination can be minimized by taking the initial force reading from the recorder output plot for the fiber-liquid interaction (Fig. 1). Therefore the measurements are obtained before any relaxation occurs and the initial wettability values reflect the characteristics of the unaltered surface (Luner and Sandell 1969).

A typical recorder output plot is shown for a kraft fiber in Fig. 1. The initial weight of the mounted single fiber is determined (A) and the liquid is raised until contact with the fiber is made (B). This weight (B) minus the initial weight of the assembly (A) is the fiber wetting force and is used for calculation of wettability. Increases in weight due to swelling can be noted if the fiber is left in the water as shown from (B) to (C). Depending on the length of the fiber, additional advancing wettabilities can be obtained by again raising the liquid level (D).

APPLICATION OF WETTING THEORY
TO PULP FIBERS

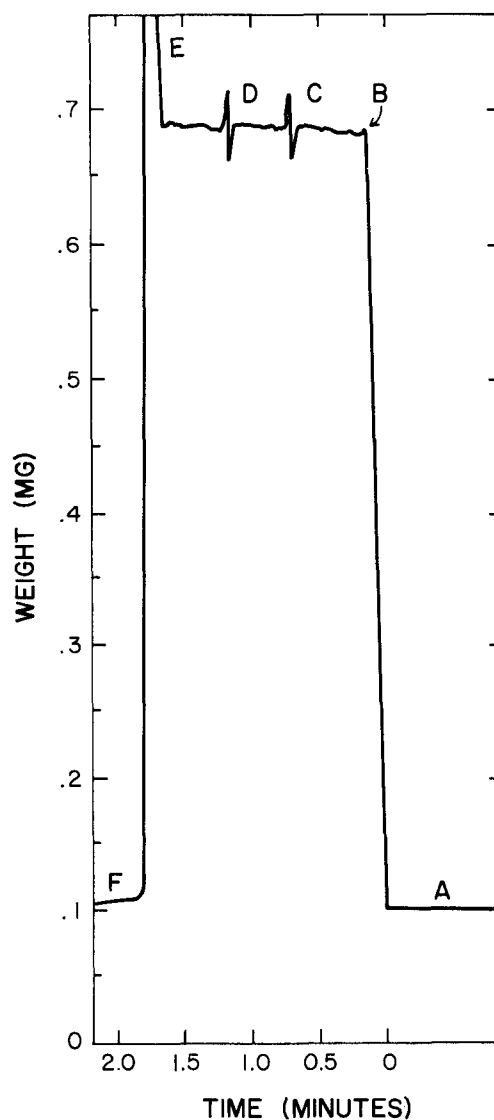For noncomposite surfaces of a single chemical constitution, the basic Young-Du

Fig. 1. Wetting force (weight) for a softwood kraft fiber at several depths of immersion in water. Time scale indicates duration of experiment. The letters denote: (A) the initial weight of the mounted single fiber, (B) the weight of the assembly with fiber in contact with liquid, (B) to (C) increase in weight due to swelling phenomenon, (D) weight after raising liquid further along fiber surface, (E) increase in weight due to removal of liquid from fiber, (F) final weight of assembly with fiber out of liquid.

Pré equation relating the equilibrium contact angle (θ_e) to the general thermodynamic quantities is applicable (Adamson 1960),

$$\gamma_{LV} \cos \theta_e = \gamma_{SV} - \gamma_{SL}, \qquad (3)$$

where γ represents surface tension, i.e., surface free energy per unit area for the interfaces between solid (S), liquid (L) and vapor (V). Cassie (1948) modified this equation to take into account composite situations, of which a pulp fiber could be considered a typical example. Thus, this investigator suggested that if two domains of different surface free energy occupy fractions f_1 and f_2 of the surface, then it follows that,

$$\gamma_{LV} \cos \theta_c =$$
$$f_1(\gamma_{S_1V} - \gamma_{S_1L}) + f_2(\gamma_{S_2V} - \gamma_{S_2L}), \qquad (4)$$

with $f_1 + f_2 = 1$. This equation defines an additional contact angle, the so-called Cassie contact angle θ_c, which represents the composite of the individual equilibrium contact angles, θ_1 and θ_2. Equation 4 can thus be expressed more simply as,

$$\cos \theta_c = f_1 \cos \theta_1 + f_2 \cos \theta_2. \qquad (5)$$

Surface roughness is also known to influence wettability, and Wenzel (1936) argued that, if the solid surface is rough the interfacial free energies γ_{SV} and γ_{SL} should not be referred to the geometric area, but to the actual surface area. Thus if,

$$r = \frac{\text{actual surface area}}{\text{geometric surface area}}, \qquad (6)$$

then the Young-Du Pré equation (3) is modified to give the Wenzel Eq. (7),

$$r(\gamma_{SV} - \gamma_{SL}) = \gamma_{LV} \cos \theta_w, \qquad (7)$$

or,

$$\cos \theta_w = r \cos \theta_e, \qquad (8)$$

where θ_w, the Wenzel contact angle, is the equilibrium contact angle θ_e on a rough solid surface (Adamson 1960).

If a surface is sufficiently rough, the liquid may trap air, giving in effect a composite surface. This condition can be expressed through Eqs. (5) and (7) as,

$$\cos \theta = r(f_1 \cos \theta_1 - f_2 \cos \theta_2), \qquad (9)$$

and if f_2 is the fraction of open area, then γ_{S_2V} is zero and γ_{S_2L} is simply γ_{LV} and the relationship becomes (Adamson 1960)

$$\cos \theta = r f_1 \cos \theta_1 - f_2. \qquad (10)$$

It should be noted that the above treatments serve only as models, thus interpretations based solely on roughness, for example, can be contradictory. This is evident when one considers Eq. (8) which predicts that if θ is less than $90°$, it is decreased by roughness, while if θ is greater than $90°$, it is increased. Neumann (1974), however, has reported advancing contact angles below $90°$ which increased with increasing roughness demonstrating that roughness is not adequately defined by r, but is also a matter of topology; that is, the same roughness in the form of grooves gives an entirely different behavior than one in the form of pits (Adamson 1960).

These descriptions demonstrate the complex nature of interpretation of wetting of composite solid surfaces in general. Analysis of wetting of pulp fibers is even more involved since not only do these materials have a composite surface in chemical terms, but also they exhibit a morphologically diverse surface character. In the case of unbleached pulp fibers, the surface would be expected to contain some degree of lignin as well as variable carbohydrate and extractive components. The surface exposure of lignin could be particularly prevalent in the case of mechanical pulps since none of the phenylpropane polymer is removed as a result of chemical action.

A morphological characteristic that could alter wetting behavior is the presence of asperities at the fiber surface presumably as a result of lignin removal from the lignocellulose gel during chemical treatments in pulping. Stone and Scallan (1968) have represented surfaces of such fibers in the swollen state as a series of variably spaced lamellae resulting in wedge-shaped pores rather than circular holes. These investigators followed rather closely the structure for a cellulose microfibril outlined by Frey-Wyssling (1954) and suggested that the

TABLE 2. *Water wettability of wood pulp fibers*

Fiber	Lignin Content, %	F, mg	W,[a] dynes/cm	cos θ	θ
Kraft	8.3	0.58	44.4	0.61	52°
Thermomechanical	26.5	0.49	52.9	0.73	43°
Neutral sulfite semichemical	13.0	0.95	145.4	2.01	0°

[a] W = Advancing wettability

elementary fibrils, consisting of a core of ordered cellulose embedded in a cortex of disordered material, are associated laterally to form a lamella. Thus in a water-swollen fiber, some of the water lies within the disordered material of the lamella and water in excess of this fills the larger spaces between lamellae. Upon drying, however, the lamellae move together and the disordered material shrinks to form a more or less solid, nonporous wall (Stone and Scallan 1968). The pulp fibers utilized in this study for wetting demonstrations were in the dried state and therefore the surfaces would be expected to exhibit minimal asperities, although the general surface character would be expected to remain relatively rough and such roughness could considerably influence the resulting wettability.

RESULTS AND DISCUSSION

Wetting data obtained by the method described above are given for a series of wood pulp fibers in Table 2. The pulp fibers exhibited a greater degree of variability when compared to monofilaments. Polyester and polypropylene monofilaments have a wettability confidence interval of ±1–2 dynes/cm (Miller and Young 1975; Carlsson et al. 1976) while the pulp fibers ranged from ±4 dynes/cm for kraft to ±7 dynes/cm for thermomechanical fibers. Wettability of the NSSC fibers varied ±5 dynes/cm in the 95% confidence interval. The greater variability of the pulp fibers is expected because of the more diverse chemical and morphological characteristics

of these materials as compared to extruded monofilament.

Since the majority of wetting data in the literature is presented in terms of contact angles rather than wettability in dynes/cm, the calculated mean contact angle is also shown in Table 2 and will be referred to for comparison of results. The softwood (Douglas-fir) kraft fiber exhibits a calculated contact angle with water of 52°, which is considerably more than that observed for isolated cellulose samples (34°) but less than that observed for the isolated kraft lignin (60°). The fiber wettability reflects the composite chemical and morphological character of the fiber. The fine structure of the fiber surface could dramatically influence the wetting behavior in either direction.

Several investigators have discussed factors influencing the chemical nature of kraft pulp. Yllner and Enström (1957) postulated the presence of hemicelluloses at the surface of kraft fibers presumably readsorbed as a result of decreases in pH near the end of the cook. Luce (1964) also demonstrated by a surface esterification and peeling technique that the surface of kraft fibers contain higher proportions of xylan and glucomannan when compared to sulfite fibers. However, it is difficult to relate such results to wetting data since the wetting techniques measure only the surface monolayer of the material, whereas Luce's results necessarily reflect the whole outer cell wall. Gierer (1976) has suggested that during kraft pulping some of the lignin fragments formed in degradative

reactions may undergo subsequent condensation or polymerization, giving rise to new types of linkages in the resulting "residual lignin." This remaining lignin may also occur at the surface of kraft fibers resulting in decreased wettability.

The thermomechanical pulp (aspen) exhibits a somewhat higher wettability (W = 52.9 dynes/cm, θ = 43°) when compared to kraft. It appears that the surface character of such mechanically produced pulp fibers is significantly affected by processing temperature. Koran (1966, 1968), in a study of the mode of fiber separation in mechanical pulping of chips, has shown quite unambiguously that the fracture path proceeds through the S_l layer of the cell wall at 115 C, whereas at 170 C it proceeds through the interface between the primary wall and middle lamella. Atack (1972) recently confirmed these results and suggested that mechanical processing exists in two regimes depending on whether it is conducted above or below the lignin softening temperature in the range 120–135 C. Fibers produced above the transition temperature are heavily case-hardened with lignin and have a smooth surface, while fibers produced below this temperature exhibit a more cellulosic character but are quite rough.

The high wettability of the thermomechanically produced fibers used in this investigation is concordant with this scheme since the pulp was produced at 110 C, which is in the range where fiber separation occurs at the S_1 layer exposing cellulosic material at the fiber surface. The greater variability in the wettability measurement (±7 dynes/cm) for the thermomechanical pulp fibers is expected since such fibers would have a rougher and more chemically variable surface character as compared to the chemically produced pulps.

The presence of extractives at the fiber surface could also affect the wettability depending on the wood species. In this respect Rånby and Hatakeyama (1975) have found that fiber surface grafting reactions of groundwood pulp (acetic acid-hydrogen peroxide catalyst) proceeded more readily after the extractives were removed by alcohol-benzene extraction. This indicates that such phenolic extractives are present at the surface of some mechanical pulps and would be expected to lower the wettability as well as contribute to the variability of the wetting determination.

The NSSC pulp fibers show a distinctly different wetting behavior. The wettability is very high with W = 145.4 dynes/cm and the calculated contact angle θ = 0°. Some of the lignin (13% lignin content) is undoubtedly situated at the surface of these semichemical pulp fibers (Michell et al. 1965) and would be expected to result in somewhat lower wetting properties because of the more hydrophobic character of this macromolecule. Though morphological properties would certainly have an influence, the enhanced wettability of this material is most likely related to the presence of sulfonate groups which are introduced into the lignin structure during neutral sulfite pulping. In sulfite processes the middle lamella as well as the S_3 layer of the secondary fiber wall are sulfonated early in the cook (Casperson et al. 1967), and therefore it is probable that such groups are present at the surface of the fibers. The attachment of these functional groups may enhance the hydrogen bonding properties of the fibers and thus wetting characteristics with water (Hartler and Mohlin 1975).

Hartler and Mohlin (1975) determined that acid sulfite pulps exhibited approximately 15% higher bonding strength when compared to kraft and the maximum was observed at the highest lignin contents for the sulfite fibers (12–13%). These investigators suggested that the sulfonic acid groups affect the bonding characteristics of sulfite fibers. The good wetting properties of the neutral sulfite semichemical fibers analyzed in this study strengthen such arguments.

In terms of the three types of unbleached pulp fibers, some of the most obvious explanations have been offered for differences in the wetting properties. However, it is important to note a number of further

TABLE 3. *Water wettability of modified pulp fibers*

Fiber	Polymer Loading, %	Grafting Efficiency, %	F, mg	W,[a] dynes/cm	cos θ	θ
Acrylonitrile-grafted kraft	95.2	53.5	0.55	45.2	0.58	54°
Styrene-grafted kraft	32.4	16.2	0.29	22.2	0.31	72°
Styrene-grafted neutral sulfite semichemical	18.8	9.3	0.20	21.6	0.30	73°

[a] W = Advancing wettability

features, related to chemical composition and surface morphology, which are known to influence wetting of such systems. These include the degree of polymerization of surface polymers, arrangement of the molecules at the surface, the degree of surface crystallinity, and the presence of monolayers at the fiber surface (i.e., water). Further detailed studies are planned to elucidate the important parameters in the wetting of single pulp fibers.

WETTING OF MODIFIED PULP FIBERS

The wetting characteristics of modified kraft and NSSC pulp fibers are shown in Table 3. The pulps were grafted with acrylonitrile and styrene monomers by the xanthate method (Hornof et al. 1975; Young 1977) and solvent extracted to insure removal of ungrafted polymer. Fiber grafting is essentially a surface reaction and would be expected to modify the wetting properties of the pulp fibers depending on the wettability of the grafted polymer.

The acrylonitrile grafted kraft fiber exhibits only a minor decrease in water wettability compared to the ungrafted kraft pulp, from $W = 44.4$ to 42.2 dynes/cm. Apparently the wettability of the fiber-acrylonitrile copolymer with water is of similar magnitude as that of the kraft fiber-water interaction.

The styrene-grafted kraft fiber, in contrast, exhibits distinctly lower water wettability (22.2 dynes/cm) when compared with that of the ungrafted kraft fiber. This

is expected due to the hydrophobic nature of polystyrene. Ellison and Zisman (1954) have reported a polystyrene-water contact angle of 91° using optical techniques on polystyrene film. This compares with the calculated contact angle of 52° for the kraft fiber-water interaction and 72° for water on polystyrene-grafted kraft fiber. It is thus obvious that complete modification of the kraft fiber surface to a polystyrene character has not taken place by the grafting procedure. However, the resulting composite surface (see Eq. 5) has a considerably reduced wettability, and this is of significance to end-uses which require more hydrophobic materials.

The styrene-grafted NSSC pulp fibers also exhibit a much reduced wettability ($W = 21.6$ dynes/cm, $\theta = 73°$) when compared to the unmodified NSSC pulp (Table 2). It is notable that both styrene-grafted pulps (kraft and NSSC) have essentially the same wetting characteristics even though the unmodified NSSC pulp had a significantly higher initial wettability ($W = 145.4$ dynes/cm). It is probable that the sulfonate groups were modified during the grafting of the NSSC pulp, thus altering their contribution to the wetting properties of the composite styrene-grafted NSSC pulp fibers.

EXPERIMENTAL DETAILS

Pulps used in the investigation were supplied through the USDA Forest Products Laboratory, Madison, WI, and included

softwood (*Pseudotsuga menziesii*) kraft, hardwood (*Populus tremuloides*), neutral sulfite semichemical (NSSC) and softwood (*Abies balsamea*) thermomechanical. Prior to the wetting measurements, the pulp fibers were air-dried and conditioned at 21 C and 65% R.H. All advancing wetting measurements were made with distilled water on fibers mounted singly to a small wire hook with a drop of cement, as previously described by Miller and Young (1975). One to two measurements were made on five individual fibers for a total of about 14 independent observations per determination. The perimeter of each of the collapsed pulp fibers, determined prior to the wetting determinations by observation in a light microscope, was used for calculation of individual fiber wettability. At the 95% confidence level the three pulps exhibited the following variability: kraft (±4 dynes/cm), NSSC (±5 dynes/cm), thermomechanical (±7 dynes/cm). The grafted fibers showed a variability 2 dynes/cm greater than the parent fibers.

The modified pulp fibers were prepared by the xanthate method according to previously described procedures (Hornof et al. 1975; Young 1977). The grafting parameters indicated in Table 3 are defined as follows:

Polymer loading, $\% = (A - B)/B \times 100$,
Grafting efficiency, $\% = (A - B)/(D - B) \times 100$,

where A is the weight of products after copolymerization and extraction, B is the oven-dry weight of pulp, C is the weight of monomer charged, and D is the weight of products after copolymerization. The grafted fibers were thoroughly extracted (Soxhlet) to insure removal of homopolymer, N,N-dimethylformamide for acrylonitrile and acetone for styrene.

CONCLUSIONS

It has been demonstrated that the wetting technique based on the Wilhelmy principle can be applied to wood pulp fibers. Based on results obtained in this prelimi-

nary investigation, unbleached neutral sulfite semichemical fibers exhibit much greater wettability when compared with thermomechanical pulp fibers which in turn are somewhat more wettable than unbleached kraft pulp fibers. These differences are possibly 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. Morphological characteristics of the fiber surface are also considered to play an important role in the wettability. Grafting of the pulps with styrene considerably reduces the fiber wetting properties.

REFERENCES

ADAMSON, A. W. 1960. Physical chemistry of surfaces. Interscience Pub. Inc. New York. 747 pp.

ATACK, D. 1972. On the characterization of pressurized refiner mechanical pulps. Sven. Papperstidn. 75:89–94.

BORGIN, K. 1959. The properties and the nature of the surface of cellulose. II. Cellulose in contact with water. Norsk Skogind. 13:429–442.

CARLSSON, D. J., F. R. S. CLARK, AND D. M. WILES. 1976. The photo-oxidation of polypropylene monofilaments. Part I. Chemical changes and mechanical deterioration. Textile Res. J. 46:599–610.

CASPERSON, G., V. JACOBIAN, AND B. PHILLIP. 1967. Zur Veränderung der Ultrastruktur von Pappelholz im Verlaufe verschiedenartiger Aufschlussprozesse. Sven. Papperstidn. 70: 702–710.

CASSIE, A. B. D. 1948. Contact angles. Discussions Faraday Soc. 3:11–12.

ELLISON, A. H., AND W. A. ZISMAN. 1954. Wettability studies of nylon, polyethylene terephthalate and polystyrene. J. Phys. Chem. 58:503–506.

FOOTE, J. W. 1939. A method for the measurement of the angle of contact formed between a liquid surface and a fiber, and the application of this and swelling data to pore diameter measurements. Paper Trade J., Tappi Section. October:40–48.

FREY-WYSSLING, A. 1954. The fine structure of cellulose microfibrils. Science 119:80–82.

GIERER, J. 1976. Possible condensation and polymerization reactions of lignin fragments during alkaline pulping processes. Appl. Polym. Symp. 28. Part III, pp. 1195–1211.

GRINDSTAFF, T. H. 1969. A simple apparatus and technique for contact-angle measurements on small-denier single fibers. Textile Res. J. 39:958–962.

HARTLER, N., AND U.-B. MOHLIN. 1975. Cellulose fiber bonding. Part 2. Influence of pulping on interfibre bond strength. Sven. Papperstidn. 78:295–299.

HORNOF, V., B. V. KOKTA, AND J. L. VALADE. 1975. The xanthate method of grafting. II. Effect of operating conditions on the grafting of acrylonitrile onto wood pulp. J. Appl. Polymer Sci. 19:545–556.

JONES, W. C., AND M. C. PORTER. 1967. A method for measuring contact angles on fibers. J. Coll. Interface Sci. 24:1–3.

KORAN, Z. 1966. Electron microscopy of radial tracheid surfaces of black spruce separated by tensile failure at various temperatures. Tappi 50:60–67.

———. 1968. Electron microscopy of tangential tracheid surfaces of black spruce produced by tensile failure at various temperatures. Sven. Papperstidn. 71:567–576.

LEE, S. B., AND P. LUNER. 1972. The wetting and interfacial properties of lignin. Tappi 55:116–121.

LISKOWITZ, J. W., M. PEREZ, AND G. WELSHANS. 1976. Wettability of various paper grades. Tappi Annual Mtg. Preprints. New York. P. 265.

LUCE, J. E. 1964. Radial distribution of properties through the cell wall. Pulp Paper Mag. Can. 65:T419–T423.

LUNER, P., AND M. SANDELL. 1969. The wetting of cellulose and wood hemicelluloses. J. Polymer Sci.: Part C. 28:115–142.

MICHELL, A. J., A. J. WATSON, AND H. G. HIGGINS. 1965. An infrared spectroscopic study of Eucalyptus regnans. Tappi 48:520–532.

MILLER, B., AND R. A. YOUNG. 1975. Methodology for studying the wettability of filaments. Textile Res. J. 45:359–365.

NEUMANN, A. W. 1974. Contact angles and their temperature dependence: Thermodynamic status, measurement, interpretation and application. Adv. Colloid Interface Sci. 4:105–191.

RYDHOLM, S. A. 1965. Pulping processes. Interscience Pub., Inc. New York. P. 51.

RÅNBY, B., AND H. HATAKEYAMA. 1975. Grafting of vinyl monomers to pulps using acetic acid-hydrogen peroxide as initiator system. Cellulose Chem. Technol. 9:583–596.

STONE, J. E., AND A. M. SCALLAN. 1968. A structural model for the cell wall of waterswollen wood pulp fibers based on their accessibility to macromolecules. Cellulose Chem. Technol. 2:343–358.

WENZEL, R. N. 1936. Resistance of solid surfaces to wetting by water. Ind. Eng. Chem. 28:938–994.

WILHELMY, J. 1863. Ueber die Abhändigkeit der Capillaritats-Constanten des Alkohols von Substanz und Gestalt des benetzten festen Körpers. Ann. Physik 119:177–217.

YLLNER, S., AND B. ENSTRÖM. 1957. Studies on the adsorption of xylan on cellulose fibers during the sulphate cook. Sven. Papperstidn. 60:547–554.

YOUNG, R. A. 1977. Modification of high-yield pulp fibres by the xanthate method. J. Agric. Food Chem. 25:738–742.