DYNAMIC WETTABILITY PROPERTIES OF SINGLE WOOD PULP FIBERS AND THEIR RELATIONSHIP TO ABSORBENCY

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ABSTRACT

The Wilhelmy technique is used to measure dynamic wetting properties of single wood pulp fibers. Several different fiber types are examined, differing both in species and processing conditions. It is found that there are significant differences in water wettability of these fibers because of varying fiber surface chemistry. The compilation of a "dynamic wettability profile" for complex materials such as pulp fibers is advocated in order to characterize more fully the behavior of these materials in wetting situations. The bulk absorbency performance of three-dimensionally random pads of these fibers is found to be directly related to the initial advancing contact angles of single fibers. The measurement of single fiber wetting properties allows the separation of structural factors from surface chemical factors in considering the absorbency of a random network.

Keywords: Wetting, contact angle, dynamic wettability, Wilhelmy technique, absorbency, pulp fibers, Washburn theory, self-sizing, fluff pulp, penetration absorption, wicking flow, imbibition.

INTRODUCTION

The market for absorbent products made from fluff pulp has expanded sharply in recent years, and increasing efforts are being made to improve product performance. It is well known that different types of pulp and different processing sequences lead to products of widely varying absorbency, and improvements have been achieved through modification of both fiber morphology and surface chemistry.

Liquid absorbency in fiber assemblies is controlled by two factors: the individual fiber-liquid interaction and the geometrical structure of the fiber network. To understand the differences in absorbency between different fiber furnishes and, in particular, in designing strategies for its improvement, it is important to be able to separate these factors. For example, if an adsorbing surfactant is applied to the fibrous material to act as a rewetting agent, it would be useful to know if its efficacy is attributable to the improved wetting of the individual fibers (increasing the driving force for capillary imbibition) or to a debonding of the network (allowing for more rapid swelling). What is needed is an independent determination of the physical interaction between liquids and *individual* fibers and the influence upon it of changes in both the fiber and the liquid properties. Such results can then be compared to bulk absorbency data for networks (i.e., paper strips, fluff pads, etc.) composed of such fibers.

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The quantitative measure of the physical interaction between liquids and solids is generally taken to be the contact angle, θ. Through Young's equation, viz.,

$$\cos \theta = (\sigma_{SG} - \sigma_{SL})/\sigma, \quad (1)$$

it is related to the surface tension of the liquid, σ, and the surface free energies of the solid-gas and solid-liquid interfaces, σ_{SG} and σ_{SL}, respectively. While Eq. (1) appears to assign a unique value of θ to a given solid-liquid-gas combination, in real systems it is found to depend also upon whether the liquid is advancing or receding over the solid surface and the rate of the interline movement. Furthermore, as the liquid is moved with respect to the solid in either direction, the interline itself is seen to move in a succession of jumps, suggesting a variation in effective contact angle. Both the hysteresis between advancing and receding contact angles and the irregular nature of the interline movement are attributable to the heterogeneity (morphological and chemical) of real solid surfaces (Johnson and Dettre 1964). A full characterization of the solid-liquid interaction thus cannot be given in terms of a single contact angle value, and any experimental technique used for such characterization must provide information reflecting the solid surface heterogeneity.

Direct optical measurements of contact angles of liquids against fibers, such as those attempted by Foote (1939), Jones and Porter (1967), and Grindstaff (1969), are not satisfactory for characterizing the fiber-liquid interaction because (1) they yield only a single θ-value, which may be highly unrepresentative of the average properties of the heterogeneous fiber; (2) they provide no measure of contact angle hysteresis or fluctuation; and (3) opposing curvatures between the fiber surface and the observed meniscus lead to ambiguities in inferring the contact angle from the meniscus profile shape (Foote 1939). A more satisfactory approach to the determination of fiber-liquid contact angles employs the Wilhelmy principle (Adamson 1960), in which the downward force upon a fiber suspended vertically through the liquid surface is measured. Such a technique is usually used for measuring the surface tensions of liquids using a rectangular slide of known wetted perimeter and for which the contact angle is known to be 0°. When the surface tension and the wetted perimeter of the fiber are known, the contact angle may be computed from the measured force. The Wilhelmy technique for determining fiber wettability has been developed and used by Collins (1947), Miller and Young (1975), Young (1976), Okagawa and Mason (1977), Klungness (1981) and others and has recently been reviewed by Miller (1985). Among these, only Young (1976) and Klungness (1981) examined single wood pulp fibers. Static advanced angles were reported for several different fiber types. In unpublished work, Daugherty (1981) obtained dynamic advancing and receding angles for fibers of a variety of wood pulp species and processing conditions against both water and several surfactant solutions. Large differences in fiber wettability were observed.

Bulk absorbency, in the present context, refers to the rate of spontaneous penetration of a porous medium by a liquid under the influence of capillary forces. Also referred to as wicking, the process occurs when the liquid reservoir contacts an open fiber network from one side only and displaces air as it advances through the network. (We are not considering the closely related process of immersional absorption, in which penetration of the network occurs from all sides trapping air pockets in the matrix.) The wicking of a fiber network was first described by

Lucas (1918) and Washburn (1921), who modelled the porous solid as a bundle of round capillary tubes, each of radius r. By inserting the capillary pressure drop (pressure discontinuity due to the curvature of the advancing meniscus) into the equation for steady laminar flow in a round tube, they obtained for the linear rate of travel of the liquid front:

$$dh/dt = r\sigma \cos \theta/4\mu h + r^2\rho g \cos \beta/8\mu, \quad (2)$$

where h is the distance travelled by the liquid from the reservoir, r is some effective pore radius, θ is the liquid-solid-vapor contact angle, and μ, σ and ρ are the viscosity, surface tension and density of the liquid, respectively. The parameter β is the angle between the direction of flow and the gravitational acceleration g. When penetration is horizontal ($\beta = 90°$) or r is very small (≤ 10 μm) and $h \ll h_{eq}$ (equilibrium rise height), the second term in (2) drops out, leaving:

$$dh/dt = r\sigma \cos \theta/4\mu h. \quad (3)$$

Integration subject to the initial condition that $h = 0$ at $t = 0$ gives:

$$h = (r\sigma \cos \theta/2\mu)^{1/2}t^{1/2} = Kt^{1/2}, \quad (4)$$

which is commonly known as the Washburn equation. The grouping of constants in K is thus a constant for a given matrix-liquid system and is referred to as the Washburn slope.

There are a number of problems in applying Eq. (4) to a network of wood pulp fibers. The pore structure is extremely irregular and certainly not that of straight round cylinders of constant cross section. The actual distance the meniscus travels in a given pore can formally be expressed as $h\tau$, where h is the nominal distance measured as a straight line normal to the overall advancing front, and τ is an appropriate tortuosity factor. Thus r in Eq. (4) should be replaced by r_e/τ^2. The nonuniformity and irregularity of the pore cross sections, however, pose greater problems. Nonuniformity in pore size means that liquid will advance more rapidly in the large pores than in the small ones, giving rise to a diffuse liquid front in the matrix. Detailed measurements of liquid distribution during wicking do reveal small amounts of moisture well in advance of the main front (Everett et al. 1977). Irregularity, i.e., axial variation in the size and shape of the pore cross sections, together with the possibility of local variations in $\cos \theta$ due to surface chemical heterogeneities of the fibers, suggest that the liquid should advance through the matrix not in the quasi-steady fashion implied by Eq. (4) but in a sequence of small jumps. Microscopic observation of wicking in most porous media does reveal this type of motion. Despite these complications, when viewed macroscopically, wicking in fiber networks appears to occur in a quasi-steady manner with a reasonably sharp advancing liquid front as suggested by the Washburn equation. Evidently the pervasive interconnectedness of the pores in the fiber structure assures a natural averaging process. Thus, while it is certainly not possible to predict the rate of penetration for paper-like materials with Eq. (4), many experimental studies have confirmed that the *form* of the equation is obeyed quite well, i.e., the wicking distance is linear in the square root of time.

It has also been verified for pure liquids that the rate of imbibition is directly proportional to the surface tension and inversely proportional to the viscosity of the imbibing liquid, as predicted by the Washburn equation (Everett et al. 1977).

Such observations have made it possible to use appropriate Washburn slopes or ratios of Washburn slopes to compute either a "wicking-equivalent pore radius" for a given fibrous material or an "inferred contact angle" for a given fiber-liquid system.

The "wicking-equivalent radius" is obtained from the Washburn slope K using a reference liquid which is presumed to wet out ($\theta = 0°$) the fibers. Under these conditions, one may compute:

$$r_e/\tau^2 = 2(\mu/\sigma)_r K_r^2, \tag{5}$$

where subscript r refers to the wetting-out reference liquid. Determinations of this type have been reported by, for example, Simmonds (1934) and Back (1965). A basic problem with the technique was that it could only be *assumed* that the reference liquid wet out the fibers. There was no independent way of determining this. A second problem was that the swelling characteristics of the fibers (hence, pore size) toward the reference liquid could raise further uncertainties.

The "inferred contact angle" is obtained by comparing the Washburn slope for the desired liquid to that obtained in the same fibrous network for a wetting-out reference liquid. One may then compute:

$$\cos \theta_{inf} = (\mu/\mu_r)(\sigma_r/\sigma)K^2/K_r^2. \tag{6}$$

Aberson (1970) used such a procedure to compute inferred contact angles of water in three-dimensionally random pads composed of a variety of unbonded wood pulp fibers and found a linear relation between $\cos \theta_{inf}$ and the volume of water absorbed during a given time. The relationship between some true contact angle and the inferred contact angle, however, is not known. In a parallel study, Everett et al. (1977) measured wicking rates of various pure liquids of known surface tension, density, and viscosity into strips of glass-fiber filter paper. Differences in wicking rate could be wholly explained in terms of liquid properties, and the authors state: "The only property of the liquid not specifically accounted for is its contact angle against the solid."

The development of the fiber balance for the independent determination of single-fiber wetting characteristics provides a powerful new tool for resolving some of the questions concerning the interpretation of wicking measurements. The objectives of the present work are thus (1) to obtain a full and independent characterization of the wetting behavior of water against a variety of single wood pulp fibers, and (2) to obtain bulk absorbency data for three-dimensional pads composed of the *same* fibers for which single-fiber data were obtained in order to permit an unambiguous assessment of the role played by single fiber wetting properties in determining the absorbency of bulk fiber networks.

METHODOLOGY

The Wilhelmy equation is the basis for the wettability experiments in this work. The force on a partially submerged object in a liquid is given as (Wilhelmy 1863):

$$F = \sigma P \cos \theta + mg - (\rho_l - \rho_v)Vg, \tag{7}$$

where F is the force on the object, P is the wetted perimeter, m is its mass, V is the submerged volume, and ρ_l, ρ_v are the liquid and vapor densities, respectively.

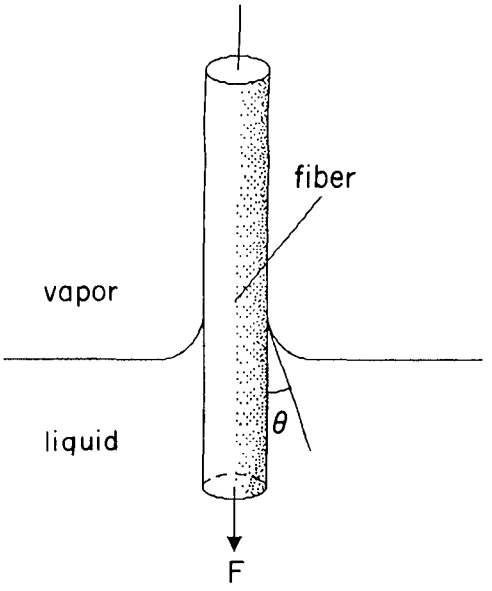

FIG. 1. Cylindrical fiber partially immersed in wetting liquid.

Figure 1 shows a partially immersed cylindrical fiber, with the associated contact angle measured through the liquid phase. The second term in Eq. (7) is simply the gravitational force, and the third term due to buoyancy. The weight of the sample can be tared out, and for small diameter (10–50 μm) filaments like wood pulp fibers, the buoyancy force is negligible. This results in the net force on the fiber being given solely by the wetting term:

$$F = \sigma P \cos \theta. \tag{8}$$

It can be seen that by measuring the force exerted on the fiber and by knowing the fiber perimeter and liquid surface tension, it is possible to calculate the contact angle directly. An accurate value of the perimeter for wood pulp fibers presents a difficult problem. First, the extremely small dimensions (10–20 μm in diameter, 2–5 mm in length) make measurement difficult, and second, the perimeter can vary significantly along the length of the fiber. It has been found that the *receding* contact angle for water and most other liquids of interest on cellulosic fibers is zero (Daugherty 1981; Klungness 1981). This fact can be exploited to eliminate the need for perimeter measurements. Assuming $\cos \theta_R = 1$, the expression for the advancing contact angle reduces to:

$$\cos \theta_A = F_A/F_R, \tag{9}$$

where F_A and F_R are the average advancing and receding forces, respectively. Thus, it is only necessary to measure the advancing and receding force over a given section of fiber to determine the advancing contact angle. This simplification is tantamount to using an average perimeter, and therefore what is obtained is an average dynamic advancing angle over the length of fiber tested.

A dynamic wettability experiment consists of advancing and receding the liquid over a given section of the fiber at a constant velocity. Typically, this cycle is

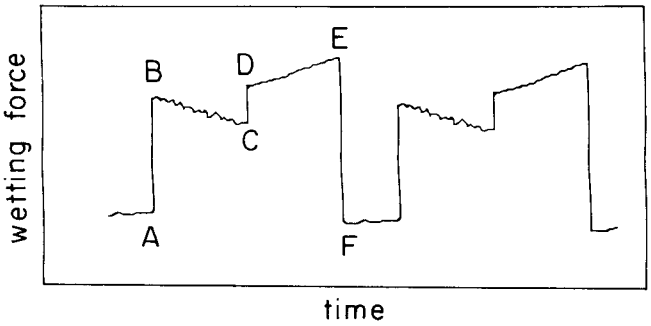

FIG. 2. Schematic of force output from single-fiber wetting experiment. Baseline force at A corresponds to the fiber in air. Force rises to B as fiber contacts liquid and varies from B to C as liquid is moved upward over the fiber. Direction of liquid movement is reversed at C and the force varies along DE as the liquid recedes. The fiber is detached at F.

carried out three times for each sample, but in certain cases it may be desirable to cycle the liquid several times. A representative trace of the force measurement for this experiment is shown in Fig. 2. The fiber sample is first tared out in air establishing a baseline (A); then the liquid contacts the fiber (B), resulting in an advancing force trace. It should be noted that a positive wetting force is observed for samples with $\theta_A < 90°$. For samples with $\theta_A > 90°$, the force output will be negative, i.e., below the baseline value. After a given section of the fiber has been scanned, the liquid direction is reversed (C) and the force output establishes its receding value (D). Eventually the fiber pulls free of the liquid (E) and the force returns to the baseline state (F). This cycle can then be repeated if desired. The average advancing and receding forces are computed and used in Eq. (9) to calculate the advancing contact angle.

An actual wetting experiment for a wood pulp fiber produces a force output significantly more complex than that depicted in Fig. 2. The force record from a self-sized Douglas-fir fiber is shown in Fig. 3. The variations in wetting force as the liquid moves over the fiber are quite large, especially for the advancing mode. The complexity of the force trace for wood pulp fibers suggested that there might

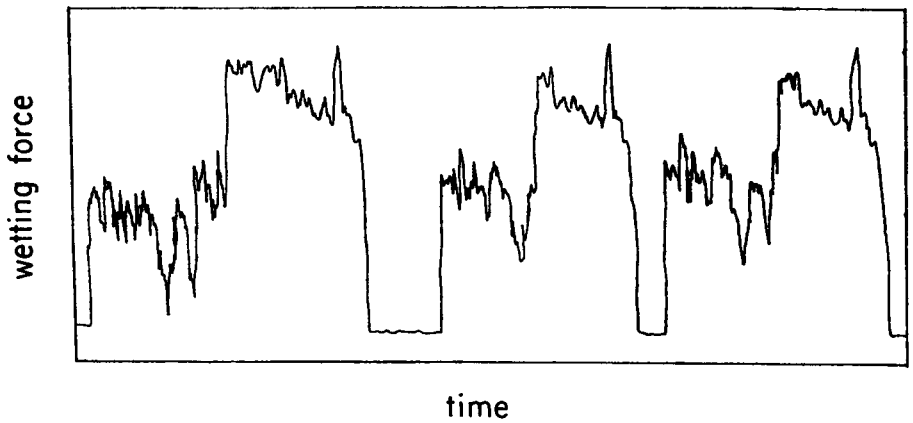

FIG. 3. Force record for wetting of self-sized Douglas-fir fiber with water. Interline velocity is 750 μm/min, and excursion distance is 1.68 mm.

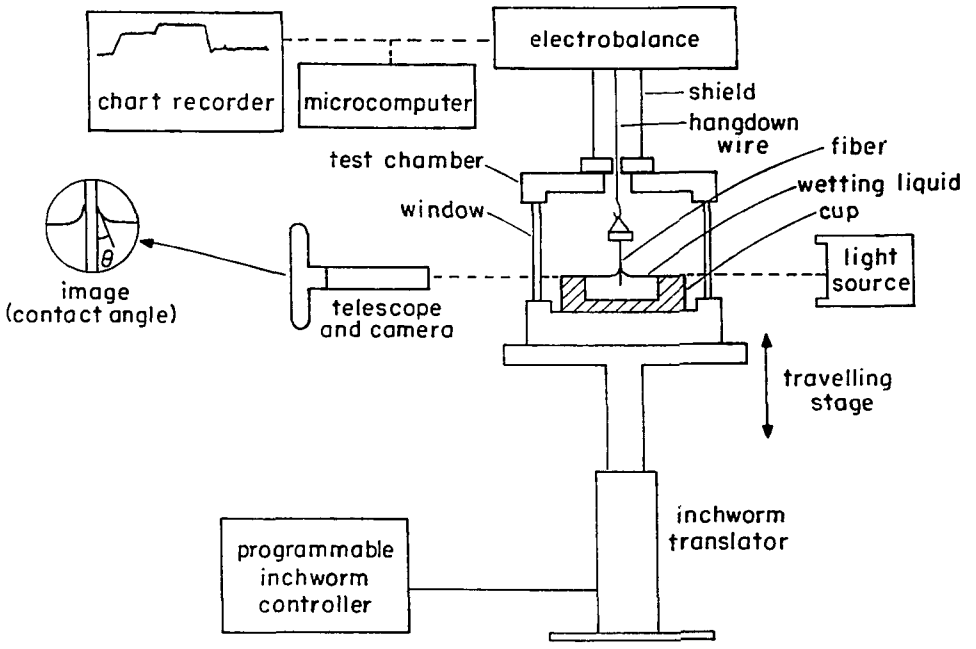

FIG. 4. Schematic diagram of fiber balance. From Berg (1986), by permission of Elsevier Science Publishers.

be more information available from a dynamic wetting experiment than simply the average advancing contact angle. The amplitude and frequency of the wetting force and the cycling behavior of a sample could potentially provide important information. Okagawa and Mason (1977) alluded to the fact that the frequency of the wetting force should be related to the size scale of the surface heterogeneities. In a similar manner, the amplitude should be an indication of the magnitude of these heterogeneities. Since the receding contact angle is zero for pulp fibers, predominantly geometrical variations should be present in the receding amplitude. The advancing amplitude, however, will reflect both surface chemical and geometrical variations.

EXPERIMENTAL

Dynamic wettability measurements

The instrument used for dynamic wettability experiments is shown schematically in Fig. 4. This device, referred to hereafter as the fiber balance, has been described recently by Berg (1986). The wetting liquid is contained in a small diameter teflon cup which is placed inside a Rame-Hart environmental chamber. This acts as a windscreen and also allows the use of nonambient temperatures and humidities. The chamber in turn rests on the stage of a travelling elevator system, which allows the liquid to be advanced or receded over the sample at very slow, controlled rates. The elevator system must be free of vibration and any lag when the direction of travel is reversed. The Inchworm Translator, Burleigh Instruments Co., Fishers, NY, satisfies these requirements well. The fiber sample is suspended from a Cahn RG electrobalance by a hangdown wire. The

balance has a useful sensitivity of 1 μg and is interfaced to a Hewlett-Packard 87 microcomputer through an H-P 59313A A/D converter. Various data acquisition and analysis programs can be run on the computer, making data collection rapid and accurate. The electrobalance output is also sent to a chart recorder for visual monitoring, as well as a permanent record of each experiment. The optical bench and telescope from a Rame-Hart model 100 NRL contact angle goniometer are also integral parts of the fiber balance. The liquid interline can be observed and/or photographed through the 10-power telescope.

Single wood pulp fibers are mounted as follows: using extremely fine surgical forceps and a magnifying lamp, individual fibers are pulled out of a sheet or pad of the desired sample. The fiber is then placed into the crease of a prefolded strip of aluminum foil (approximately 1.7 by 0.3 cm), with 2 to 3 mm of its length protruding. The foil is then folded over onto itself three successive times, securely clamping the fiber in place. Finally, a small hole is pierced at the top of the (now) square foil mount with a hypodermic needle to allow hanging on a wire from the electrobalance. During an experiment, the servo mechanism of the Cahn balance maintains the fiber sample in a constant vertical position.

Although the elevator system is capable of a large range of velocities (0.60 μm/min to 6.0×10^4 μm/min), all wetting experiments were performed at a constant speed of 750 μm/min to avoid any viscosity effects on the dynamic contact angle. At this speed, the capillary number ($V\mu/\sigma$, where V is the interline velocity) for water is well below the threshhold value where the contact angle becomes velocity dependent (Hoffman 1975).

Bulk absorbency measurements

Absorbency performance of various fibers was quantified by measuring the rate of liquid absorption in a three-dimensionally random sample network. This network consisted of 4.0 g of defiberized pulp air laid into an unbonded cylindrical pad. The instrument used to perform these absorption tests was developed by Martinis et al. (1981) and will be described only briefly here. It has become referred to as an "FAQ Tester" (FAQ = *F*luff *A*bsorbent *Q*uality). The instrument used by Aberson (1970) is similar in many respects. Before an FAQ test can be done, a pad of fibers must be formed, which is accomplished with a pad forming device. The pad is formed in a tube with a screen on the bottom. This same tube is then removed and placed into the FAQ tester, eliminating any handling of the formed pad. A 2.5-kPa load is applied to the sample and the absorbing liquid (water) is made to contact the screen at the bottom of the tube. There are two electrical probes; one contacts the screen, the other the bottom of a weighted plunger that rests on the top of the pad. When water first contacts the screen, this is defined to be zero time and the timer is automatically started. The timer is tripped when water has penetrated through to the top of the pad and contacts the plunger. The FAQ time is then the time required in seconds for water to penetrate a given mass of fibers under constant load conditions.

Materials

The various wood pulp fibers used in this study are listed in Table 1. All of these furnishes have at one time or another been used as fluff grades, with the exception of the α-cellulose fiber. This sample is a highly pure (96% α-cellulose)

TABLE 1. *Wood pulp fiber compositions and species.*

Designation	Wood species	Pulping process
α-Cellulose	Hemlock	Mg sulfite
Southern pine	Loblolly pine	Kraft
TMP #1	50% Hemlock-50% Alder	Thermomechanical
TMP #2	100% Hemlock	Thermomechanical
Douglas-fir #1, 2; self-sized Douglas-fir	Douglas-fir	Kraft

dissolving grade pulp. The self-sized Douglas-fir pulp was produced by heating a portion of Douglas-fir #2 to 105 C for 16 hours in an oven-aging procedure. Both the dynamic wettability experiments and the bulk absorbency measurements were done at room temperature (22 C) and 50% relative humidity.

Water for the wettability experiments was triply distilled in an all-quartz still, and had a surface tension of 71.5 dynes/cm. Surface tension was measured before each of the wettability runs and if found to be below 71.0 dynes/cm, the water was discarded and replaced with a fresh sample. Water used in the FAQ tester was from a tap source and not multiply distilled, but typically had a measured surface tension of 70.0 dynes/cm or above at 25 C. Surface tensions were measured with a Wilhelmy slide and the Cahn RG balance.

RESULTS AND DISCUSSION

Dynamic wettability profiles for seven different wood pulp fibers are listed in Table 2. These results represent numerical averages of several measurements of each fiber type. Table 3 lists the number of fibers of each type run and also the standard error (95% confidence limits) for the initial advancing contact angle. A one-way analysis of variance test was performed on these initial angles. This

TABLE 2. *Dynamic wetting properties of wood pulp fibers. Wetting liquid: distilled water. Conditions: temp = 22 C; R.H. = 50%.*

Fiber	θ_1 (degrees)	θ_2 (degrees)	θ_3 (degrees)	Amplitude (%)	Frequency
α-Cellulose[a]	14.0	0	0	Adv. 12.8 Rec. 14.3	Low
Southern pine	23.2	14.0	0–10[b]	Adv. 11.0 Rec. 10.9	Low
Douglas-fir #1	33.0	20.9	14.5	Adv. 12.7 Rec. 16.5	Low
TMP #1	42.8	38.2	36.9	Adv. 20.3 Rec. 11.3	High
TMP #2	51.2	43.4	40.9	Adv. 20.3 Rec. 11.3	High
Douglas-fir #2	51.3	36.1	27.4	Adv. 20.3 Rec. 14.9	Moderate
Self-sized Douglas-fir #2	65.4	60.2	56.7	Adv. 38.5 Rec. 13.6	High

[a] Measurements done at 100% R.H.
[b] Contact angles between 0 and 10 degrees cannot be resolved.

TABLE 3. *Standard error of contact angles.*

Fiber	No. samples	Std. error[a,b] ± (degrees)
α-Cellulose	9	4.3
Southern pine	8	2.6
Douglas-fir #1	8	4.2
TMP #1	7	5.5
TMP #2	7	5.4
Douglas-fir #2	8	6.5
Self-sized Douglas-fir #2	7	7.6

[a] Values apply to initial contact angle, θ_1.
[b] Calculated for 95% confidence level.

procedure confirmed that the means are all significantly different; the probability that the contact angle values all emanate from a random data set is less than 1 in 10^5. In general, it can be seen in Table 2 that the advancing contact angle against distilled water always decreases upon repeated immersion. The degree to which it decreases, however, varies significantly for each fiber type. Pure α-cellulose fibers exhibit a small but finite contact angle against water. Borgin (1959) measured contact angles optically on regenerated cellulose *films* and obtained values ranging from 10 to 18 degrees, depending on the time of contact. Luner and Sandell (1969) also used regenerated films, and obtained a value of 18° at a relative humidity of 84%. Our initial value of 14.0° measured for highly pure cellulose fibers at 100% relative humidity compares favorably with these results. Subsequent immersions in water produced a zero degree contact angle. The Southern pine fiber has the lowest initial contact angle (23.2°) of any of the true fluff grades. It is also the only fluff grade fiber to achieve a near-zero-degree contact angle after only three immersions. Southern pine is known to have a low residual extractives content (Wise and John 1952), and this is no doubt partially responsible for this low contact angle. The extensive popularity of Southern pine for use as an absorbent medium in disposable products is due in large part to its high wettability. Douglas-fir is also used heavily in fluff pulp grades, having long, stiff fibers like Southern pine. Wettability behavior, however, is not quite as favorable. Douglas-fir #1 has a slightly higher initial contact angle than Southern pine (33.0° vs. 23.2°), but the second fir sample is much less wettable (θ_1 = 51.3°). Neither fiber achieves a wet out condition after repeated immersion. In fact, the third immersion contact angle of Douglas-fir #2 is still higher than the initial value for Southern pine. Although the Douglas-fir samples were pulped from the same species (*Pseudotsuga menziesii*), they were produced at different production locations, with slight differences in processing conditions. Also, Douglas-fir #2 was made predominantly from old growth chips, whereas Douglas-fir #1 came from second-growth wood. Old growth fir is known to contain a higher level of extractives than second-growth fir, which also are harder to remove (Graef 1986). These resin acids are concentrated in the ray parenchyma cells (Graef 1980). The differences in wettability of the two Douglas-fir fibers are probably due to differences in residual resins left on the surfaces of the fibers.

Two different grades of TMP pulp were examined, one containing softwood and hardwood, the other exclusively softwood. It was not possible to distinguish between the hardwood and softwood fibers of TMP #1 in sample mounting;

TABLE 4. *Mean and standard error of advancing amplitudes.*

Fiber	Mean[a] (%)	Standard error[b]
α-Cellulose	12.8	4.0
Southern pine	11.0	4.7
Douglas-fir #1	12.7	3.0
TMP #1	16.6	8.5
TMP #2	20.3	8.5
Douglas-fir #2	20.3	5.1
Self-sized Douglas-fir #2	38.5	14.6

[a] Initial advancing amplitude.
[b] Calculated for 95% confidence level.

consequently, the results represent an unknown mix of both types of fibers. Both TMP samples display fairly high contact angles against water, with TMP #2 being slightly less wettable. The more interesting result for both TMP fibers, however, is their behavior towards repeated immersion. Both fibers show only a slight lowering of the contact angle after three cycles, in contrast to the Southern pine, α-cellulose, and two Douglas-fir fibers. This is indicative of the substantially higher lignin content of TMP pulp. Only a partial amount of original lignin in the wood is removed by thermomechanical pulping and bleaching. The initial wood lignin content of 30 wt% is reduced in TMP pulping to approximately 20%. The lignin content of the non-TMP fibers in Table 2 should be well below 1%. Lee and Luner (1972) measured an advancing contact angle of 58° for water on films of isolated softwood kraft lignin. The remaining lignin in TMP pulp would appear to have a large effect on water wettability of these fibers. In processing, TMP #1 was bleached to a greater degree with hydrogen peroxide than TMP #2. This is at least part of the cause of its greater hydrophilicity, as shown in the initial advancing contact angle.

Douglas-fir is prone to undergo a process known as "self-sizing" under conditions of elevated temperature or extended storage time at room temperature (Graef 1980, 1981). Whether this self-sizing process occurs by vapor phase transport (Swanson and Cordingly 1959) or liquid phase migration (Abson 1985) is still unclear. What is certain is that a dramatic loss of absorbency will occur in fluff pulp that becomes self-sized. The self-sized sample in Table 2 had been kept at a temperature of 105 C for 16 hours in a standard oven aging test. It is clear that this fiber is much less hydrophilic than the unsized sample, especially when examining the cycling behavior. After the third immersion, the contact angle has decreased by only 13%. This behavior is typical of a furnish that has been "hard-sized," as in printing or writing grade papers.

Table 4 lists the mean and standard error of the advancing amplitude values. Analysis of variance tests revealed that the means of all fibers excluding self-sized Douglas-fir #2 were not significantly different. Comparing the mean for the self-sized fiber to that of all others showed that there *is* a statistical difference. These conclusions can be seen qualitatively from the values in Table 4. The high value of the fluctuation amplitude of the advancing angle for the self-sized fiber, compared to the much lower fluctuation amplitude of the receding value (from Table 2) indicates extensive *chemical* heterogeneity on the fiber surface.

Although the frequency data in Table 2 are only qualitative, they do appear to correlate with the amplitude values. The fibers with the higher advancing am-

TABLE 5. *Initial advancing contact angle vs. absorbency.*

Fiber	θ_i (degrees)	$(\cos \theta_i)^{-1}$	FAQ time (seconds)
α-Cellulose	14.0	1.03	3.9
Southern pine	23.2	1.09	4.4
Douglas-fir #1	33.0	1.19	5.9
TMP #1	42.8	1.36	11.3
TMP #2	51.2	1.60	15.8
Douglas-fir #2	51.3	1.60	27.6
Self-sized Douglas-fir #2	65.4	2.40	>1,000

plitudes also had high or moderate advancing force frequencies. Those with lower amplitudes had low force frequency values, indicating a more homogeneous surface. This is what would be expected on the basis of bulk chemistry of the various fiber types.

A direct comparison between bulk absorbency and independently-determined, single-fiber wetting is shown in Table 5 and Fig. 5. Table 5 lists the initial advancing contact angle for each fiber along with the FAQ time for a bulk pad composed of that fiber type. It can be seen that there is a direct relationship between single fiber wettability and bulk absorbency performance. Equation (4) suggests that the penetration time should be inversely proportional to cos θ. In Fig. 5, $1/\cos \theta_i$ is plotted against FAQ absorption time. Since the self-sized fiber FAQ time is not quantitative, it is not included in this plot. The data are seen to be well fit by a straight line, with the exception of Douglas-fir #2. This appears to be an anomalous point, and has been left out in determining the regression line. The results shown in Fig. 5 support the applicability of the Washburn theory for absorption into fluff pulp pads since the contact angle data have been measured

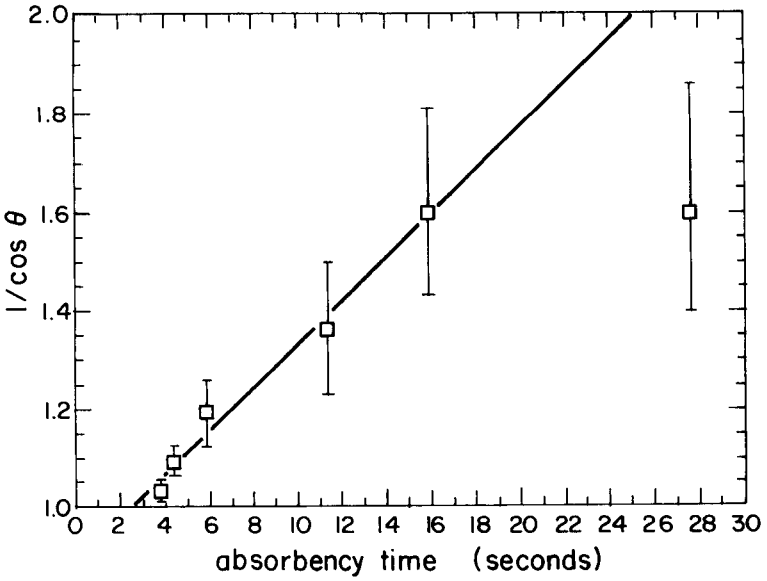

FIG. 5. Relationship between single-fiber advancing contact angle and bulk absorbency time for fluff pads.

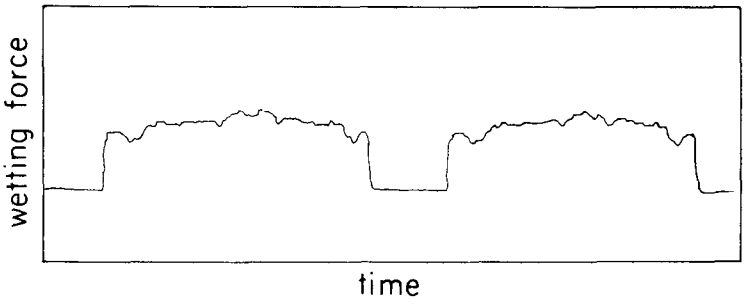

FIG. 6. Force record for wetting of self-sized Douglas-fir fiber with methanol, showing absence of hysteresis. Interline velocity is 750 μm/min, and excursion distance is 1.73 mm.

independently. The absorption of the self-sized Douglas-fir pulp exceeded the time limit of the FAQ tester, which means that for all practical purposes, water would not completely penetrate a pad of these fibers. Since the advancing contact angle is less than 90° (and thus the capillary pressure is positive), one might ask why saturation does not occur. One possible reason lies in the magnitude of the advancing force amplitude. During wetting experiments with self-sized fir fibers, it was noticed that the advancing force periodically had negative local values. The local contact angle at these points would be greater than 90° (as can be seen from Eq. (9)), even though the overall average contact angle was about 65°. It would follow that in wicking flow, water would simply stop at these points of high local contact angle. The observed result then is that the pad appears to be essentially nonwetting.

Two other experimental results are worth noting. Although earlier work had established that the receding contact angle for wood pulp fibers was always zero, this assumption would be most seriously questioned for a fiber with a high advancing contact angle. To check this, a self-sized Douglas-fir fiber with an average advancing angle of 61° against water was run with methanol as the wetting liquid. A low surface tension (σ = 22.6 dynes/cm) polar liquid such as methanol should have a zero degree receding contact angle on cellulosic fibers. This is confirmed in Fig. 6, which shows the force trace using methanol as the wetting liquid. The fact the advancing and receding forces are "mirror images" of each other proves that $\theta_A = \theta_R = 0$ for methanol, since real surfaces will always exhibit some hysteresis unless the contact angle is identically zero. The fiber perimeter was then calculated from the measured receding forces for both methanol and water, assuming the receding contact angle for water to be zero. The calculated perimeter was identical within experimental error, confirming that the zero receding angle condition using water is met. Additionally, it was thought that fiber swelling in water might have an effect on the dynamic wettability results due to a change in perimeter. An α-cellulose fiber was partially immersed in a receded condition in water and allowed to stand overnight. The wetting force from the electrobalance was monitored on a chart recorder. If the fiber became significantly swollen, the change in perimeter would cause the wetting force to increase. No significant change in the receding force was observed.

Finally, although single fiber wettability is a dominant factor in absorption performance, the structure and pore size of the network will also affect the pen-

etration rate. The different fiber types examined here possess varying physical properties, such as length, diameter, stiffness, etc. It should be expected that because of these differences, the resulting fiber networks will be slightly different with regard to pad structure, even though the intent was to make them as nearly identical as possible. The small amount of scatter in Fig. 5 is probably due to these structural effects.

CONCLUSIONS

The Wilhelmy technique has been successfully used to determine a "dynamic wettability profile" for wood pulp fibers, which includes other properties in addition to the advancing contact angle. For complex material surfaces like those of wood pulp fibers, it is seen that a wettability profile is useful in understanding fiber structure and chemistry. In general, highly bleached, low-lignin content fibers are more hydrophilic than high yield, high lignin content fibers, such as TMP. The presence of residual extractives can have a substantial effect on fiber wettability, especially for pulp subjected to elevated temperatures. The wetting properties of single wood pulp fibers have been found to be a critical factor in determining liquid absorption performance of bulk structures composed of these fibers. The cosine of the independently measured, single-fiber advancing contact angle is found to be inversely proportional to the absorption time as measured by the FAQ test, in accord with Washburn analysis.

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