The Accurate Measurement of Contact Angle, Phase Contact Areas, Drop Volume, and Laplace Excess Pressure in Drop-on-Fiber Systems

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INTRODUCTION

Although accurate methods now exist for the measurement of contact angles in systems where the solid is available in the form of a flat plate, in many cases where the solid is not of planar form special methods have to be devised. An important instance of this type occurs when the solid is only available in fibrous form, as is always the case with natural fibers and sometimes, too, with artificial fibers. Measurement of contact angles by methods which work well with flat plates do not give very accurate or reproducible results when applied to fibers. The principal reason for this lies in the fact that when a thin cylindrical solid supports a liquid meniscus, the part of the meniscus close to the solid has principal curvatures, both of which are very high (of the order of the reciprocal of the cylinder radius) and which are of opposite sign. This high curvature of the meniscus jeopardizes those methods (the goniometer and tilted fiber methods (1, 2)) which depend for success upon accurate visual observation of the meniscus: It is not possible to draw a tangent to the meniscus at the three phase contact line with much confidence. A more viable method, based on the reflection of a point light source by the meniscus, has been described (3), but this again suffers in reliability when the fiber size becomes so low (100 μm or less) as to make the meniscus very highly curved. One method for plates which does not rely upon direct observation is the wetting balance (4, 5), but this, when applied to fibers, suffers from other disadvantages: It is difficult to ascertain the perimeter of the fiber at the three phase contact line and it is also necessary to know independently the interfacial tension of the two fluid phases.

The present paper describes a method for determining the contact angle on fibers which is analogous to the sessile drop (or drop shape) method for flat plates. It is shown that in systems where capillary rather than gravity forces mould the drop shape (i.e., where the Goucher Number Go = Fiber radius/ capillary length is small), the profile of the drop as described by three linear parameters is a sensitive function of the contact angle. It is further shown how extension of the theory allows the calculation of the drop volume, drop-fiber and drop-second phase contact areas and also of the Laplace excess pressure inside the drop.

THEORETICAL PART

Description of the Drop Profile

In the absence of significant gravitational effects, the condition for equilibrium of the drop surface is that the Laplace excess pressure ΔP across the drop surface is everywhere constant, i.e.,

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \text{constant}, \quad [1]$$

where R_1 and R_2 are the principal radii of curvature at a point in the surface and γ is the interfacial tension. At constant γ, Eq. [1] becomes

$$\frac{1}{R_1}+\frac{1}{R_2}=K_1, \qquad [2]$$

where K_1 is a constant.

Referring to Fig. 1, the parameters describing the drop-on-fiber system are x_1, the filament radius; x_2, the maximum radius of the drop in a plane normal to the filament axis; L, the drop length along the filament; and θ, the contact angle. It is seen from Fig. 1 that

$$R_1 d\phi = dx \sec\phi, \quad R_2 = x \operatorname{cosec}\phi. \qquad [3]$$

Equation [2] may now be written

$$\cos\phi\frac{d\phi}{dx}+\frac{\sin\phi}{x}=K_1, \qquad [4]$$

or

$$\frac{1}{x}\frac{d}{dx}(x\sin\phi)=K_1. \qquad [5]$$

Integration of Eq. [5] gives

$$x\sin\phi=\tfrac{1}{2}K_1x^2+K_2, \qquad [6]$$

where K_2 is the integration constant. The two constants can be evaluated from the boundary conditions

$$\begin{aligned} x&=x_1, \quad \phi=\pi/2-\theta,\\ x&=x_2, \quad \phi=\pi/2. \end{aligned} \qquad [7]$$

Equation [6] now takes the form

$$x\sin\phi=\left(\frac{x_2-x_1\cos\theta}{x_2^2-x_1^2}\right)x^2+\left(\frac{x_2\cos\theta-x_1}{x_2^2-x_1^2}\right)x_1x_2. \qquad [8]$$

Use of the relationship

$$\frac{dz}{dx}=-\tan\phi=\frac{\sin\phi}{(1-\sin^2\phi)^{\frac{1}{2}}} \qquad [9]$$

together with Eq. [8] allows the gradient of the drop profile, dz/dx, to be expressed as a function of x. (It will be shown in the next section that the derivation of dz/dx as a function of x forms the basis for the calculation of the drop length, volume, and the two contact areas.) Substitution for $\sin\phi$ in Eq. [9] followed by expansion gives a numerator of 36 terms which after simplification leads to an expression replacing Eq. [9]:

$$-\frac{dz}{dx}=\frac{x^2(x_2-x_1\cos\theta)+x_1x_2(x_2\cos\theta-x_1)}{[x^2(x_2-x_1\cos\theta)^2(x_2^2-x^2)-x_1^2(x_2\cos\theta-x_1)^2(x_2^2-x^2)]^{\frac{1}{2}}}. \qquad [10]$$

Writing

$$a=\frac{x_2\cos\theta-x_1}{x_2-x_1\cos\theta}, \qquad [11]$$

Eq. [10] assumes the form

$$-\frac{dz}{dx}=\frac{x^2+ax_1x_2}{[(x_2^2-x^2)(x^2-a^2x_1^2)]^{\frac{1}{2}}}. \qquad [12]$$

When $\theta=0$, $a=1$ and this expression reduces to the form given by Princen (6).

Use of the transformation [13]

$$x^2=x_2^2(1-k^2\sin^2\varphi) \qquad [13]$$

where $\quad k^2=(x_2^2-a^2x_1^2)|x_2^2$

allows Eq. [12] to be integrated to give the following expression for the drop profile

$$z=\pm[ax_1F(\varphi,k)+x_2E(\varphi,k)], \qquad [14]$$

where $F(\varphi,k)$ and $E(\varphi,k)$ are elliptic integrals of the first and second kind, respectively.

Drop Length, Contact Areas, Volume and Excess Pressure

It follows from Eq. [14] that the length $L=2|z(x=x_1)|$ is given by

$$L=2[ax_1F(\varphi,k)+x_2E(\varphi,k)], \qquad [15]$$

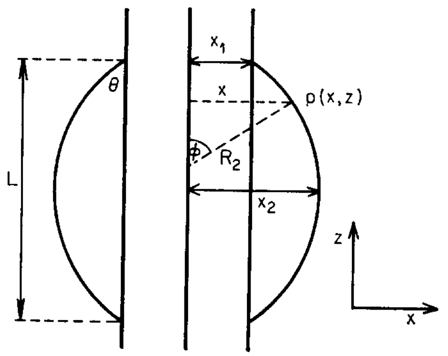

FIG. 1. Definition of symbols for drop-on-fiber system.

in which φ and k are defined by Eq. [13] with $x = x_1$.

This expression can be recast in the dimensionless form

$$\bar{L} = 2[aF(\varphi, k) + nE(\varphi, k)], \quad [16]$$

in which $\bar{L} = L/x$, and $n = x_2/x_1$.

The drop/solid contact area $S = 2\pi x_1 L$ and follows at once from Eq. [15]. In reduced form this becomes

$$\bar{S} = S/x_1^2 = 2\pi\bar{L}. \quad [17]$$

The drop/2nd fluid contact area A is calculated from

$$A(z) = 2\pi\int_{-z}^{z} x\,ds = 4\pi\int_{0}^{z} x\,ds, \quad [18]$$

where ds is an element of arc. Using the relationships

$$ds = dx\sec\phi = dx\Big/\left(1 + \left(\frac{dz}{dx}\right)^2\right)^{\frac{1}{2}}, \quad [19]$$

Eq. [12] and the transformation [13], followed by integration gives

$$A = A(z(x = x_1)) = 4\pi(ax_1 + x_2)x_2E(\varphi, k). \quad [20]$$

Equation [20] can be reduced to the dimensionless form

$$\bar{A} = A/x_1^2 = 4\pi n(a + n)E(\varphi, k). \quad [21]$$

The drop volume is calculated from the following expression for the total volume of drop and fiber lying between the planes $\pm z$:

$$V(z) = \pi\int_{-z}^{z} x^2dz = 2\pi\int_{0}^{z} x^2dz. \quad [22]$$

Use of Eqs. [12] and [13] leads to an expression which when integrated gives

$$V(z) = \frac{2\pi x_2}{3}\Big[(2a^2x_1^2 + 3ax_1x_2 + 2x_2^2)E(\varphi, k) - a^2x_1^2F(\varphi, k) + \frac{x}{x_2}(x_2^2 - x^2)^{\frac{1}{2}}(x^2 - x_1^2)^{\frac{1}{2}}\Big]. \quad [23]$$

For $\theta = 0$, Eq. [23] reduces to an expression

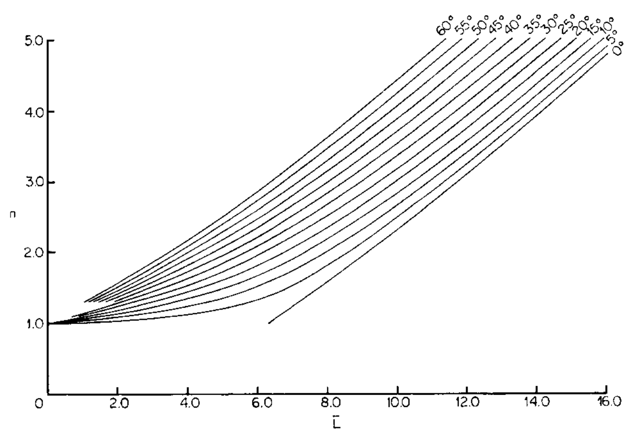

FIG. 2. Reduced drop length $\bar{L}$(abscissa) as a function of n(ordinate) for values of θ up to 60°.

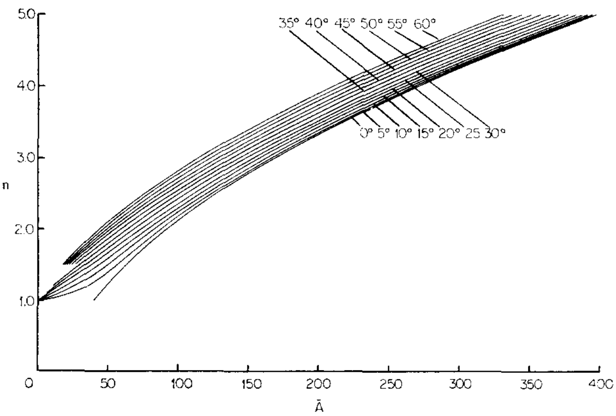

FIG. 3. Reduced drop surface area $\bar{A}$ (abscissa) as a function of n (ordinate) for values of θ up to 60°.

previously derived by Roe for zero contact angle (7).

The net (liquid) volume V of the drop is easily calculated by subtraction of the fiber volume and in reduced form is

$$\bar{V} = \frac{V}{x_1^3} = \frac{2\pi n}{3}[(2a^2 + 3an + 2n^2)E(\varphi, k) - a^2F(\varphi, k) + (n^2 - 1)^{\frac{1}{2}}(1 - a^2)^{\frac{1}{2}}] - \pi\bar{L}. \quad [24]$$

The excess pressure $\Delta P = K_1\gamma$ (Eqs. [1], [2]) and is calculated from Eqs. [6] and [8]. The expression obtained, in reduced form, is

$$\bar{P} = \frac{x_1}{\gamma}\Delta P = \frac{2(n - \cos\theta)}{n^2 - 1}. \quad [25]$$

Calculations

A Fortran IV program has been written to calculate the quantities $\bar{L}$, $\bar{S}$, $\bar{A}$, $\bar{V}$, and $\bar{P}$ as a function of n and θ. The complete results are available on microfilm in the form of tables covering the range of values n: 0(0.01)10.00 and θ: 0°(1°)20°; 20°(5°)90°.[1] This covers the range of situations likely to be met with practically (cf. final section). Representative results are shown graphically in Figs. 2–5.

[1] Available from the author.

Referring to Fig. 2, it is seen that the drop shape as characterized by the parameters $\bar{L}$ and n is a sensitive indicator of the contact angle. Figure 2 suggests that if a low (<20°) contact angle is being measured, the greatest precision is obtained by working with small drops (n small), while for larger angles it is better to work with larger drops ($n > 2$). The accuracy of this method for measuring θ is discussed in a later section.

It is evident from Fig. 3 and 4 that the quantities $\bar{A}$ and $\bar{V}$ are less sensitive to changes in the contact angle than is $\bar{L}$. Whereas over the range (0, 90°) in θ, $\bar{L}$ typically changes by a few hundred percent, changes in $\bar{A}$ and $\bar{V}$ are generally of the order 20%. Parenthetically, it is noted from Fig. 5 that if a way could be devised of measuring the excess pressure $\bar{P}$ for small drops on fibers (low n), it would provide a very sensitive method for measuring contact angles; however, this appears to be technically very difficult.

EXPERIMENTAL PART

As a check on its validity, the new technique for contact angle measurement has been compared with a conventional optical method and, further, values for the contact angle in some well-defined systems have been obtained, using the method below.

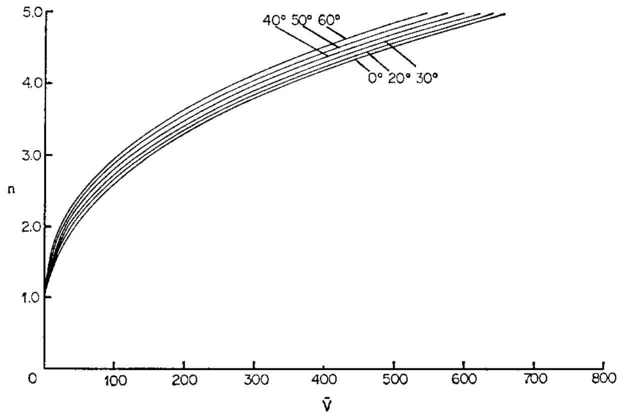

FIG. 4. Reduced drop volume $\bar{V}$ (abscissa) as a function of n (ordinate) for values of θ up to 60°.

Techniques

Apparatus previously used to study the entrainment of thin oil films by moving filaments (8) and the subsequent breakup of these films into drops (9) has been used for the present work with only minor modifications (Fig. 6). (A water-jacketed version of the glass tube has been successfully used for high melting point oils and to study temperature effects, but was not employed in this work.) The filaments to be studied were all about 200-μm diameter and consisted of short lengths of nylon 6:6, polyester, a fluoroethylene–propylene copolymer (FEP) and horse hair. These were knotted together and cleaned by prolonged immersion in "Analar" grade methanol and subsequently in "Analar" grade 60–80° petroleum spirit which had been passed through an alumina bed. The filament was driven at constant speed into the aqueous phase via the oil phase and was then stopped. About 5 min or more was allowed for the entrained oil film to break up into droplets and these were then either photographed through a low power microscope or else measurements were made directly by means of a micrometer attachment to the microscope eyepiece. When the drop was photographed, transmitted or reflected light was used depending on the opacity of the fiber. As an aid to photographic sharpness, the apparatus was used in a low-

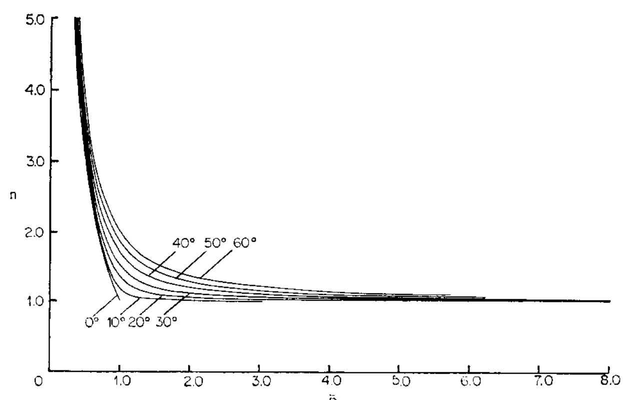

FIG. 5. Reduced excess pressure $\bar{P}$ (abscissa) as a function of n (ordinate) for values of θ up to 60°.

vibration laboratory (ambient temperature 24°C). Further details of the apparatus appear in (8, 9).

All glass parts of the apparatus were cleaned in fresh chromic acid and were well rinsed with water prior to use. The water was twice distilled, the second time from permanganate. All the oils were passed through alumina beds prior to use and the tetrabromoethane (TBE) was also redistilled, the middle fraction being collected.

RESULTS

The systems studied and the contact angles obtained are given in Table I. The angles obtained are necessarily receding angles, as the drops are formed by the disproportionation of a cylindrical oil film. With the exception of the horsehair system, contact angles derived from different drops do not vary much in a given system. In the case of horsehair, the scatter is probably due either to surface inhomogeneity (scales) or to the variable diameter of the fiber. Two typical systems are illustrated in Fig. 7. It should be noted that no absolute scale is required to determine the contact angle; however, calculation of, for example, the drop volume requires accurate absolute measurement of the fiber radius x_1.

To determine the validity of the method the contact angle was measured directly by protractor on one photograph and the value obtained was compared with the angle obtained from the drop shape. (Direct measurement of the angle was viable because of the relatively large fiber diameter.) For the system Nujol + TBE/water/nylon, the respective methods gave $54 \pm 3°$ and $55 \pm 0.5°$, which are in excellent agreement with one another.

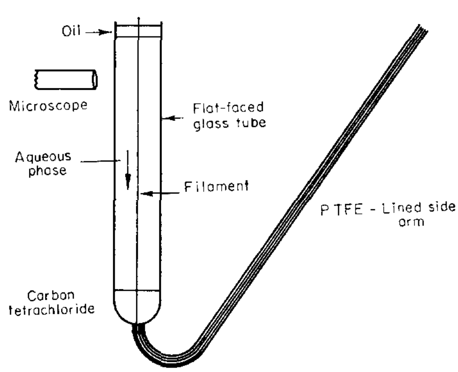

FIG. 6. Contact angle apparatus.

TABLE I

Contact Angles of Oils on Various Substrates in Water

Substrate	Oil	Contact angle/ degrees	Number of drops observed
Nylon 6.6	Nujol/TBE[a]	54	1
Polyester	Nujol/TBE	37–39	2
FEP[b]	Nujol/TBE	5–7	4
FEP	Nujol	4–5	4
Horse hair	Nujol/TBE	44–50	3

[a] Nujol is a heavy paraffin oil, density 0.88 Mg m^{-3}, b.p. circa 355°. The density of the mixture was slightly less than that of water.

[b] FEP is a fluorinated ethylene–propylene copolymer.

When photographic prints are employed for measurements, care must be taken that the inevitable distortion of the final image (by optical aberrations and by processing of the film) does not introduce a significant error into the method. A partial check on this, which did not include the effect of distortion by the microscope objective, was made. The drop dimensions were determined in some instances both from photographs and directly by use of a micrometer eyepiece on the microscope. The two angles so measured never differed by more than 1° and it is probable that they lie within the limits of reproducibility. It is estimated, from the precision with which the linear measurements can be made and from the computed tables, that the precision of this method is typically better than 1° in θ. This makes the new method better than most others by a factor 5 or more.

CONCLUDING REMARKS

Although the measurements reported here were made on large diameter fibers (200 μm diameter), the method has the great advantage that it is applicable to drops on fibers of any

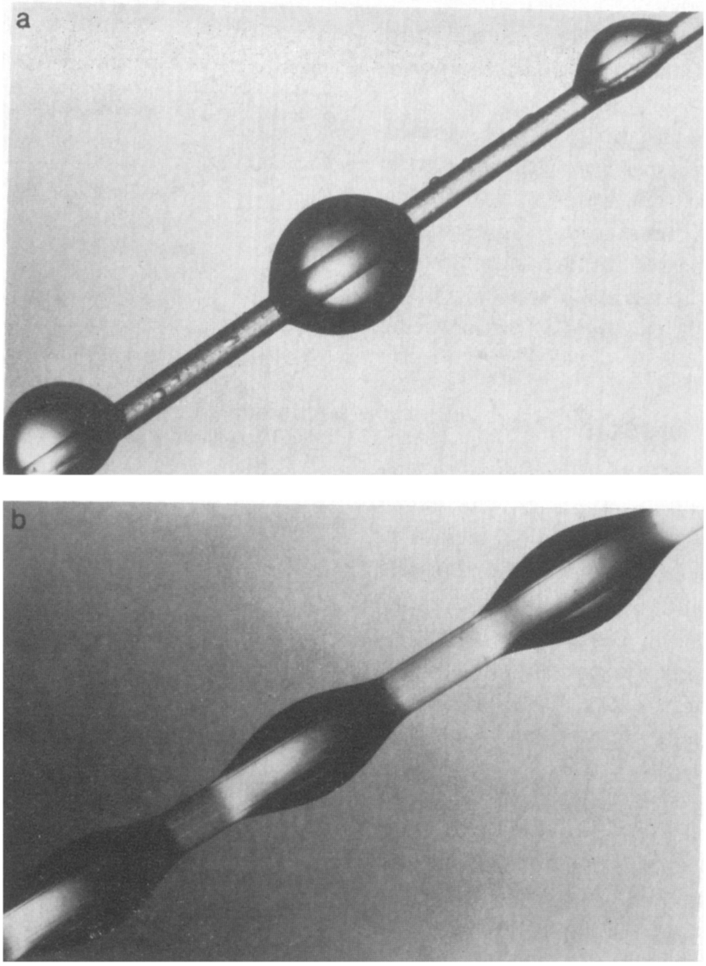

FIG. 7. Examples of drop-on-fiber systems. (a) Nujol-TBE/water/nylon 6.6. $\theta = 54°$. Note "clam-shell" drops flanking central drop. (b) Nujol/water/FEP. Faint parallel lines on fiber are of reflected light and assist in drop length measurement. $\theta = 5° \pm 0.5°$ for all drops.

size, provided only that gravity effects are negligible (i.e., $x_1 < 50$ μm in air, or larger in two-liquid systems). It is, in particular, applicable to microscopic fibers, for which no accurate method has hitherto been described. A further advantage is that measurements are possible without in any way disturbing the drop-fiber system. The computed results also allow the estimation of the volume of small drops on fibers to a higher degree of accuracy than most analytical methods could offer (a drop of oil on a typical textile fiber with $x_1 = 10$ μm would have a volume of order 0.01 μl) and this method is, besides, non-destructive.

A limitation is imposed by the fact that the calculations are confined to drops which are symmetrically disposed about the fiber axis and do not cover "clam-shell" type drops which adhere to the side of the fiber. It is found experimentally that most drops adopt the latter conformation when θ is greater than about 60°, for reasons which are not easily quantified owing to the complex geometry of the "clam-shell" system. The method is thus restricted to contact angles below about 60°, but as in principle it is possible, in two-liquid systems especially, to invert the system (water drops in oil instead of the converse), the limitation will in many cases only apply to the measurement of intermediate values of the contact angle ($60° < \theta < 120°$).

SUMMARY

Analytical expressions have been derived relating the length, surface area, volume, and Laplace excess pressure of a liquid drop adhering to a cylindrical fiber to linear drop dimensions and the contact angle. Extensive tables of dimensionless forms of these quantities have been computed. The calculations form the basis of a precise and accurate method for measuring contact angle in such systems. A description of experimental technique for contact angle measurement is given, together with results for some well-defined systems.

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Note. While this paper was being written an essentially similar method for estimating contact angles was described (10) which as far as can be ascertained gives the same results as the present work. The mathematical approach of (10) required the numerical solution of a second-order differential equation and does not extend to calculations of A, V, etc., perhaps because no expression analogous to Eq. [12] was obtained.

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