Wettability Characterization of Printing Substrates: Facts and Interpretations

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Abstract

Methods for characterizing the wettability of printing substrates are discussed. These include characterization of porous substrates (e.g. paper) as well as non-porous substrates. Emphasis is put on explaining the theory behind each method, in order to enable distinction between established facts and less established interpretations. In some situations the theory itself is incomplete, therefore the characterization methods in these cases may and should be used on a comparative basis.

Introduction

Wettability of printing substrates is directly related to print quality. For inkjet printing, for example, when wettability is too high, large drops with feathered edges form; too low wettability leads to too small drops, low coverage, and slow drying. An important question to be asked is: why do we need wettability characterization methods? Seemingly, all one needs to do is print on the substrate and check the print quality. This, however, is not the case in many situations. Sometimes, it is costly and inconvenient to use the printer itself as a testing machine, e.g. when using large format printers. In other cases, the supplier of a printer may want to a priori specify a range of intrinsic substrate properties that would be suitable for the printer. Moreover, print quality depends on a variety of parameters, in addition to wettability. Thus, for the sake of separation of variables that is essential for problem solving, it is advantageous to measure or characterize intrinsic properties, such as wettability, rather than rely only on an integral measure, such as print quality.

Wettability of a substrate is characterized by its surface energy. However, surface energy cannot be directly measured. For a non-absorbing substrate, it can be assessed through measurement of the contact angle. This is a relatively simple measurement, however its interpretation is complex. For an absorbing (porous) substrate, the situation is more difficult, since it is impossible to directly measure the contact angle of a liquid with the solid surface inside the porous medium. Thus, methods based on the kinetics of penetration have been developed. Again, their interpretation is not a simple matter.

The goal of this paper is to review the characterization methods that are available for non-absorbing and for absorbing substrates, which have a theoretical basis. Many other methods exist that are based on empirical comparison between substrates. While such methods are extremely useful, it is not always clear what they really measure. Therefore, emphasis in the present paper is on the theoretical understanding behind the characterization methods, on their strong points, and on their limitations.

Non-Absorbing Printing Substrates

As mentioned in the introduction, wettability characterization of non-absorbing substrates is mainly based on contact angle measurements. Fig. 1 defines the contact angle, θ, on an ideal surface, which is assumed to be rigid, perfectly smooth, chemically homogeneous, and chemically inert to the liquid. It is the angle between the surface of the solid and the tangent to the liquid-air interface.

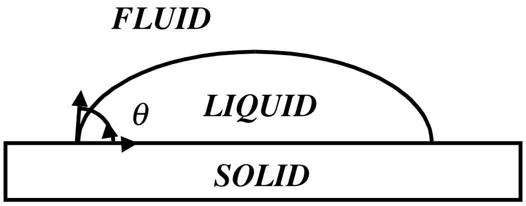

Figure 1. The contact angle on an ideal surface

The contact angle on an ideal surface (the "ideal" contact angle) is related to the three interfacial energies that are involved by the Young equation[1]:

$$\cos\theta = (\sigma_s - \sigma_{sl})/\sigma_l \qquad (1)$$

where σ_s stands for the surface energy of the solid, σ_{sl} is the solid-liquid interfacial tension, and σ_l is the surface tension of the liquid. This equation ignores, for simplicity, the effect of adsorbed vapor. Since only two of the four parameters in Eq. (1) may be measurable (the contact angle and the liquid surface tension), two unknown remain to be solved.

Applying to Eq. (1) an equation that relates σ_{sl} to σ_s and σ_l, such as the Girifalco-Good equation,[2] for example, one gets the following approximate equation for the contact angle:

$$\cos\theta \cong -1 + 2(\sigma_s/\sigma_l)^{1/2} \tag{2}$$

This is an equation in one unknown only – the surface energy of the solid. Thus, if the ideal contact angle is known, it is possible to approximately calculate the surface energy of the solid.

The main problem is that printing substrates are far from being ideal surfaces. They may be rough and they may be chemically heterogeneous. When such real surfaces are considered, there is a need to better define which contact angle is being considered.[3] Fig. 2 defines the actual contact angle that is the angle between the local tangent to the solid surface and the tangent to the liquid-air interface. It turns out that the actual contact angle equals the one given by the Young equation if the local radius of curvature of the three-phase contact line is not too small.[4]

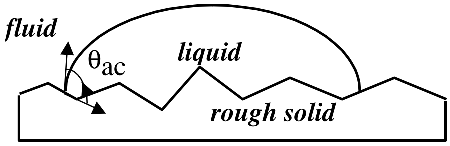

Figure 2. The actual contact angle on a rough surface

Figure 3 defines the apparent contact angle that is the angle between the tangent to the liquid-air interface and the seemingly smooth surface as seen using relatively low magnification. The apparent contact angle is the one usually measured, therefore it is essential to relate its value to the ideal contact angle given by the Young equation.

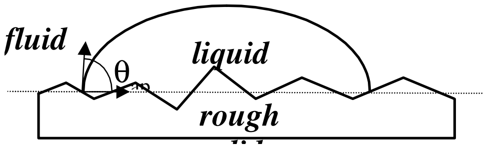

Figure 3. The apparent contact angle on a rough surface

Prior to understanding the relationship between apparent and ideal contact angles, it is essential to realize that a wide range of values can be measured for the apparent contact angle. This can be explained with the aid of Fig. 4, where the Gibbs energy of the drop on the surface is shown vs. the apparent contact angle. A fundamental feature of this curve, when calculated for a real solid surface is the existence of many minima points. This is in contrast to a system with an ideal solid surface, for which this curve has only a single minimum. The lowest minimum represents the (most) stable equilibrium state. Each of the other minima represents a metastable equilibrium state. A drop put on a surface may, in principle, land in any of these metastable states. Therefore, measurement of the apparent contact angle without identifying which metastable state is occupied by the drop is meaningless.

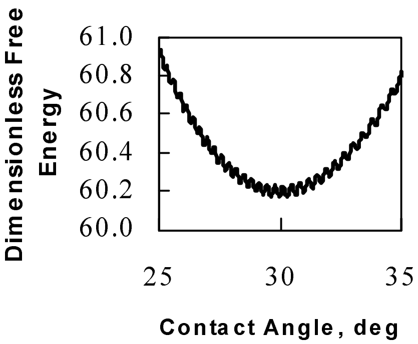

Figure 4. The Gibbs energy of a system with a real solid surface

The equilibrium state that is of main interest is the stable equilibrium state that is represented by the lowest minimum. This is so, since this is the only state for which there is a theoretical relationship between the apparent and ideal contact angles. For rough surfaces, this relationship is given by the Wenzel equation[5]:

$$\cos\theta_w = r\cos\theta \tag{3}$$

where θ_w is the apparent contact angle on a rough surface, and r is the roughness ratio. The latter is defined as the ratio of the true solid surface area to its nominal area had it been smooth. θ_w is the apparent contact angle corresponding to the most stable equilibrium condition. The Wenzel equation was developed many years ago, however its thermodynamic status has only recently been clarified[6]. It turns out that this equation is actually an approximation, which becomes better as the drop is made bigger. Thus, in principle, if θ_w and r are measured, the ideal contact angle can be calculated according to Eq. (3). Then, the surface energy of the substrate can be calculated from Eq. (2) or its equivalents.

The practical problem is how to correctly measure θ_w. There are two aspects to this problem: (1) assuring that Eq. (3) is applicable; and (2) assuring that the measured θ_w indeed corresponds to the stable equilibrium condition. The first aspect has already been covered by the theoretical understanding[6] that the drop has to be very large compared with the scale of the surface roughness. The second aspect is not yet completely solved. A possible solution is to vibrate the system in such a way that the drop descends along the energy curves by overcoming the energy barriers (local maxima in the curve). Attempts along this line are being made in our laboratory.

The situation is somewhat more complex with chemically heterogeneous substrates. Cassie[7] developed an equation similar to the Wenzel equation, which states that $\cos\theta_{apparent}$ is the weighted average of the values of $\cos\theta$ on each of the chemically different patches. The averaging is done according to the area fraction of each patch. The methodology behind applying the Cassie equation should be identical to the one used for rough surfaces: a very large drop should be used, and some form of vibrations should be applied. The difficulty lies in the quantitative characterization of the chemical heterogeneity.

Absorbing Printing Substrates

Absorbing printing substrates are more difficult in terms of wettability characterization. This is so, since they have a complex porous structure that prevents direct measurement of contact angles. The process of absorption into printing substrates usually involves finite, small amounts of liquid, in the form of small ink drops. This is a complex process that consists of a few stages. The first stage is penetration of the ink into the substrate, along with adsorption of dye or adhesion of pigment particles to the substrate. The solvent then may continue to spread in the substrate by redistribution of the liquid between small and large pores.[8] The understanding of this complex process with all its underlying stages is yet incomplete. Therefore, for characterization purposes (where separation of variables is important, as discussed above), it is more useful to refer to a continuous penetration process into the substrate.

The idea behind the wettability characterization of porous substrates is based on the "effective capillary" concept. In other words, one seeks to define a straight, cylindrical capillary, the rate of penetration into which equals the rate of absorption into the porous medium. The former is defined by its radius and by the contact angle that the liquid makes with its inner wall. Thus, the goal is to calculate the effective radius and effective contact angle of the porous substrate. This calculation is based on the Lucas-Washburn equation[9] for penetration into capillaries. For horizontal capillaries, or for capillaries that are sufficiently short for the effect of gravity to be negligible, the Lucas-Washburn equation reads:

$$x^2 = \sigma_l \,(R\cos\theta)\, t/(2\mu) \qquad (4)$$

where x is the penetration distance into the capillary, R is the capillary radius, t is the time, and μ is the viscosity of the liquid. An important feature of this equation is that R and $\cos\theta$ always appear together as a product. Therefore, measurement of the rate of penetration enables the calculation of the product $R\cos\theta$, but does not provide sufficient information to elucidate R or $\cos\theta$ separately.

This problem is seemingly solved by the two-liquids method. Using this approach, two penetration experiments are performed. In the first, a liquid that forms zero contact angle with the substrate material is used. Consequently $\cos\theta$ is assumed to be 1, and R can be calculated from the measured rate of penetration. In the second experiment, the liquid of interest is being used. Now, the value of R is assumed to be that calculated from the results of the first experiment, and $\cos\theta$ is calculated from the penetration rate.

It turns out, however, that this method is erroneous.[10] The reason can be understood with the aid of Fig. 5. This figure emphasizes the difference between two angles: the contact angle, θ, that the liquid-air interface makes with the solid surface, and the angle ϕ that this interface makes with the direction of the axis of the capillary (main direction of flow). ϕ is determined by θ and by the local geometry of the porous medium. In a straight, cylindrical capillary, these two angles are identical. In a capillary of complex shape they may be very different, as shown in Fig. 5. It is the angle ϕ that determines the driving force for capillary penetration, therefore even if $\theta = 0$, ϕ is not. Thus, assuming $\theta = 0$ for calculating the effective capillary radius in the first penetration experiment leads to an erroneous value of the effective radius.

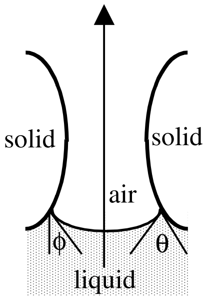

Figure 5. The difference between ϕ and θ in a non-cylindrical capillary

Detailed calculations done for a corrugated periodic capillary show that the error induced by the two-liquids method may be very large.[10] Naturally, it increases with the contact angle, and with the deviation of the capillary from the cylindrical shape. In some realistic situations the relative error may be even more than 50%. One possible way of dealing with the problem is to use such calculations as a calibration curve. For this purpose, many more calculations need to be done, and the sensitivity of the error to the specific geometry of the porous medium needs to be tested.

Another way to solve the problem is to use the vertical penetration method.[11] Using this method, it is possible to independently derive the effective radius and effective contact angle. The "price" for this additional information is the extended time period that is required for performing the experiment. The Lucas-Washburn equation for the vertical penetration into a capillary is[9]:

$$At = -Bh - \ln(1 - Bh) \qquad (5)$$

where h is the penetration height, and

$$A \equiv \frac{\rho^2 g^2 r^3}{16\sigma\mu\cos\theta} \qquad (6)$$

$$B \equiv \rho g r/(2\sigma\cos\theta) \qquad (7)$$

where ρ is the density of the liquid and g is the gravitational acceleration. From these equations it is clear that the dependencies of A and B on r and θ are different. Thus, if A and B can be determined from experimental measurement, r and θ can be independently calculated.

Measurements and calculations done for filter papers[11] showed that the effective contact angle is close to 80° for an oil that should form a zero contact angle with the paper fibers themselves. Thus, the effective contact angle may be very different from the ideal contact angle. Again, this is explained by the difference shown in Fig. 5 between θ and ϕ. The effective contact angle is sort of an average over the local values of ϕ, which, in turn, is determined by θ and the local geometry of the porous medium.

Conclusion

The measurements needed for wettability characterization of printing substrates are relatively simple from a technical point of view. However, affirmation of the correct conditions for the measurements, and accurate interpretation of the results require fundamental understanding of the theory behind the measurement.

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Biography

Prof. Abraham Marmur has been working in the field of interfacial phenomena and wetting for over twenty years. He has published many papers on the theory and practice of wetting processes, and has been consulting for major companies involved in the design and utilization of inkjet printing systems. He was also an editor of Reviews in Chemical Engineering, and was on the advisory committee of J. of Colloid and Interface Science and J. of Adhesion Science and Technology.