Summary
This application note describes the analysis of surface energy of solid substrates using either the sessile drop technique, or a force-rebalance method. These two approaches give generally compatible values, but provide different tools for examining the surface properties of materials.

Background
The primary focus of contact angle studies is to determine the wetting characteristics of a particular liquid on the solid substrate. The contact angle is commonly used as the most direct measure of wetting. The contact angle θ is a function of the relative surface energies of the solid-liquid (SL), liquid vapor (LV), and solid vapor (SV), as shown in Figure 1.
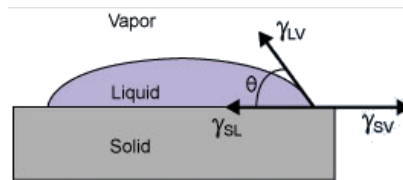

Figure 1: Contact angle as a function of the three surface energies.

Young introduced the mathematical expression of this relationship as

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} cos\theta$$

In samples where the solid substrate has a much high surface energy than the liquid, cosθ approaches 1 as the contact angle approaching zero, indicating that the liquid spreads on the surface of the substrate. When the solid has a surface energy much lower than the liquid, cosθ approaches -1 as the contact angle approaches 180º, and the liquid is almost completely non-wetting (see Figure 2).
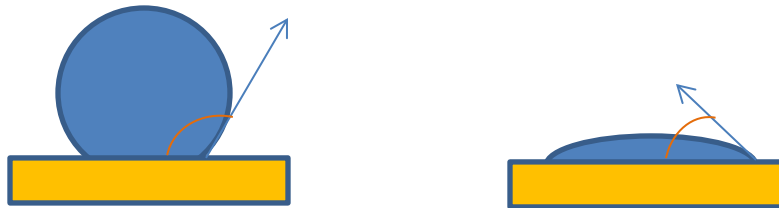

Figure 2: Contact angle of poorly wetting liquid (left) and well wetting liquid (right). Assuming the same liquid, the substrate on the left has a much lower surface energy than the substrate on the left.

Other experimental parameters may be derived directly from contact angle and surface tension results. Some examples are:

Work of Adhesion: defined as the work required to separate the liquid and solid phases, or the negative free energy associated with the adhesion of the solid and liquid phases. Used to express the strength of the interaction between the two phases. It is given by the Young-Dupre equation as:
$$W_a = \gamma(1 + cos\theta)$$

Work of Cohesion: defined as the work required to separate a liquid into two parts, it is a measure of the strength of molecular interactions within the liquid. It is given by;
$$W_c = 2\gamma$$

Work of Spreading: the negative free energy associated with spreading liquid over solid surface. Also referred to as Spreading Coefficient it is given as:

$$W_s = \gamma(cos\theta - 1)$$

Wetting Tension: a measurement of force/length defined as:

$$\tau = {F_w}/{P} = \gamma_{LV} cos\theta$$

This value, wetting force normalized for length, also represents the product of the cosine of the contact angle and the surface tension. It allows for a characterization of the strength of the wetting interaction without separate measurement of surface tension. This latter equation can be used in a separate method to determine the contact angle using the strength of interaction between the wetted meniscus and the substrate. In this configuration, a flat plate is dipped in to a liquid and the resulting meniscus generates the force *Fw*, allow extraction of the contact angle.
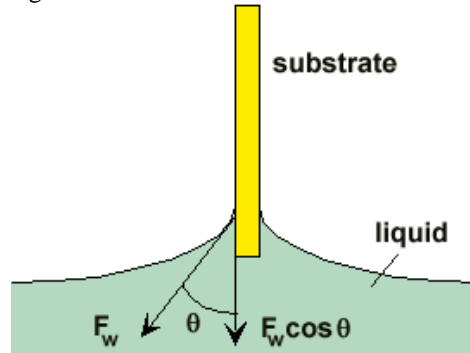

Figure 3: Schematic of forces arising from wetted interface in a flat plate configuration.

Contact Angle
The most intuitive approach for determining contact angle is directly optical measurement of the contact angle using a microscope or high resolution camera. Although the contact angle can be measured directly, it is usually calculated geometrically using the observed height and diameter of the drop on the surface. This approach removes uncertainties about the exact angle at the interface, but also results in an average contact angle and does not handle advancing and receding contact angles very well. This method is described in ASTM D 5946-01.
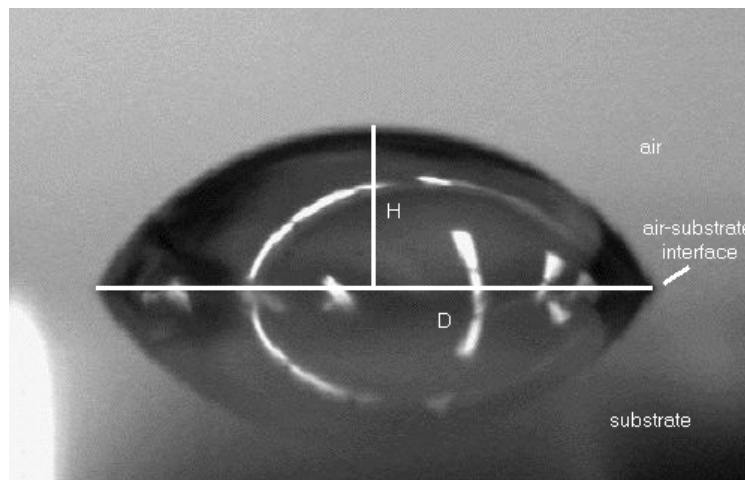

Figure 4: Representative image of a sessile drop with construction lines shown.

$$\theta = atan\left(\frac{H}{D/2}\right)$$

In addition a different approach can be used, using techniques not defined in ASTM standards. This approach uses direct measurement of the wetting force and therefore allows simple measurement of advancing and receding contact angles and is intrinsically not at equilibrium. It is therefore frequently termed "Dynamic Contact Angle". In this method, where directly measured forces are used to determine contact angle, first the surface tension of the liquid must be determined. First a de Noüy ring is to determine surface tension. This ring is usually a thin platinum wire of perimeter p and the force required to pull it clear of the water directly relates to the surface tension through:

$$\gamma_L = \frac{F_{max}}{p}$$

Figure 5: Image of a de Noüy ring at point where meniscus is stretched to almost breaking point.

Once the surface tension is known, a separate experiment can be performed where a known geometry is dipped in to the liquid and the resulting wetting force therefore yields the contact angle from the equation above. In the case where this geometry is a flat plate it is known as a "Wilhelmy plate" (see Figure 3). This method allows determination of advancing and receding contact angles when the surface is freshly dry and already wetted and the equipment can also be used to determine wicking and other dynamic wetting phenomena.

<u>Surface Energy</u>
To characterize the wetting behavior of a particular liquid/solid pair, it is often only necessary to measure and report the contact angle. To report a surface energy, it is necessary to use a series of liquids of known surface energy. Small drops are placed on the surface of the substrate, and the contact angle is measured optically, as described in ASTM D5946.

The calculations based on these measurements produce a parameter with the units of force/unit length (or surface energy). The two common methods to determining this parameter are shown below.

Critical Surface Tension: Zisman developed a technique for estimating the surface energy of solid substrates. Using a series of homologous liquids of differing surface tensions, the contact angle θ is determined for each liquid. From these measurements, a graph of $\cos\theta$ vs γ_{LV} is drawn, where γ is the surface energy of the liquids. The line is extrapolated to $\cos\theta = 1$; the value of the surface energy where the line crosses 1 is termed the critical surface tension, and represents the maximum surface tension of a liquid that may completely wet the substrate.
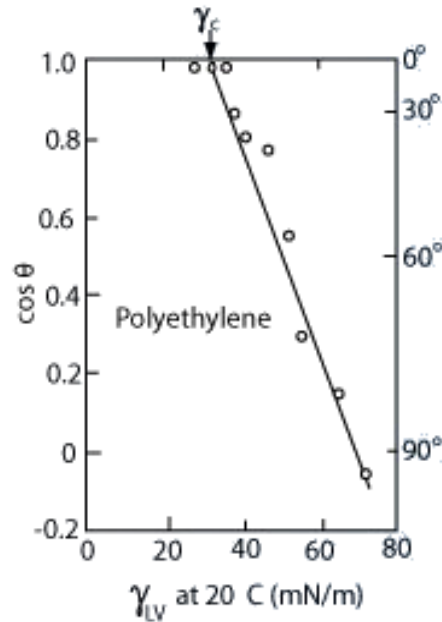
Figure 6: Critical surface energy for polyethylene determined from the Zisman plot. (from Kinloch, 1987).

Free Surface Energy: Another way to characterize a solid surface is by calculating free surface energy, also referred to as solid surface tension. This approach involves testing the solid against a series of well characterized wetting liquids. The liquids used must be characterized such that the polar and dispersive components of their surface tensions are known. The relevant equation is given by Owens and Wendt as:

$$\gamma_1 (1+ \cos \theta) / (\gamma_{ld})^{1/2} = (\gamma_{sp})^{1/2} [(\gamma_{lp})^{1/2} /(\gamma_{ld})^{1/2}] + (\gamma_{sd})^{1/2}$$

where θ is the contact angle, γ_1 is liquid surface tension and γ_s is the solid surface tension, or free energy. The addition of d and p in the subscripts refer to the dispersive and polar components of each. The form of the equation is of the type $y = mx + b$. The relationship of $(\gamma_{lp})^{1/2} /(\gamma_{ld})^{1/2}$ vs $\gamma_1 (1+ \cos \theta) / (\gamma_{ld})^{1/2}$ can then be plotted.The slope will be $(\gamma_{sp})^{1/2}$ and the y-intercept will be $(\gamma_{sd})^{1/2}$. The total free surface energy is merely the sum of its two component forces.

References:

Kinloch, A.J., Adhesion and Adhesives, Chapman and Hall, New York, 1987, p. 25.
Fox, H. W. and Zisman, W. A., J. Colloid. Science, 5 (1950), p. 514
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