The forces acting on a liquid drop in contact with a surface can be represented as the surface energy of the solid (γ_s), the surface tension of the liquid (γ_l), and the energy remaining at the liquid-solid interface after the liquid molecules have interacted with the solid surface (γ_{sl}). When a drop of liquid is in motionless contact with a surface, all of the forces acting upon the drop must be in equilibrium, and the forces acting in the plane of the surface must sum to zero (Figure 1). This state is described by the Young-Dupré equation:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \qquad (1)$$

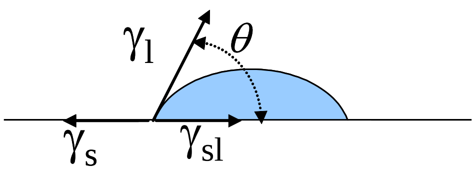

Figure 1. Relationship between the forces acting on a liquid drop in contact with a solid surface. When the drop is at rest, these forces sum to zero.

Knowledge of surface energy is important in many industrial processes because of its direct influence on practical adhesion. Surface energies of solids may be measured using several techniques [**1**] but the most common method is based on obtaining contact angle measurements of multiple fluids [**2-4**]. Although it is an indirect approach, the results have been shown to correlate very well with more fundamental methods [**5**].

However, obtaining contact angles with multiple fluids can be cumbersome, and many of the common non-water fluids used in these analyses present health and safety issues to the technician. Furthermore, because many of these non-water fluids are organic solvents they can damage common surfaces. For this reason surface energy measurements frequently qualify as destructive tests. It has been shown that simple water contact angle measurements are a robust estimator of total surface energy [**6-8**].

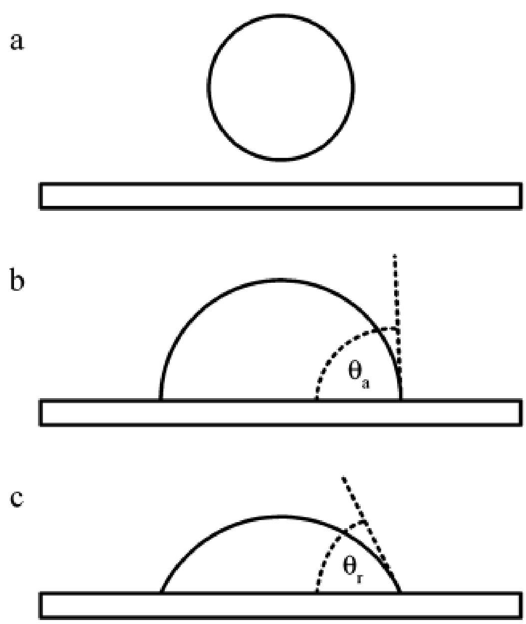

Figure 2. (a) Before deposition, the drop is spherical. (b) After deposition, if liquid is added, then the contact line advances. Each time motion ceases, the drop exhibits an advancing contact angle (θ_A). (c) If liquid is removed from the drop, the contact angle decreases to a receding value (θ_R) just as the contact line retreats. From ref [**9**].

Equation 1 shows that contact angles are a strong function of the surface energy. However, the actual angle that is established depends in part on the way that the liquid is brought into contact with the surface. The angle that is established as a liquid is slowly advanced over the surface is called the advancing angle (θ_A, Figure 2). It is the largest angle that can be obtained. The angle that is established as the liquid is retracted over the surface is called the receding angle (θ_R, Figure 2) and is the lowest angle that can be established. The difference between the advancing and receding angles is called the contact angle hysteresis and is related to the free energy of wetting [**9**].

Most contact angle measurements are made by simply depositing a liquid drop onto a surface from a syringe needle or small piece of tubing. These angles are generally in between an advancing and receding angle but are useful for comparative purposes.

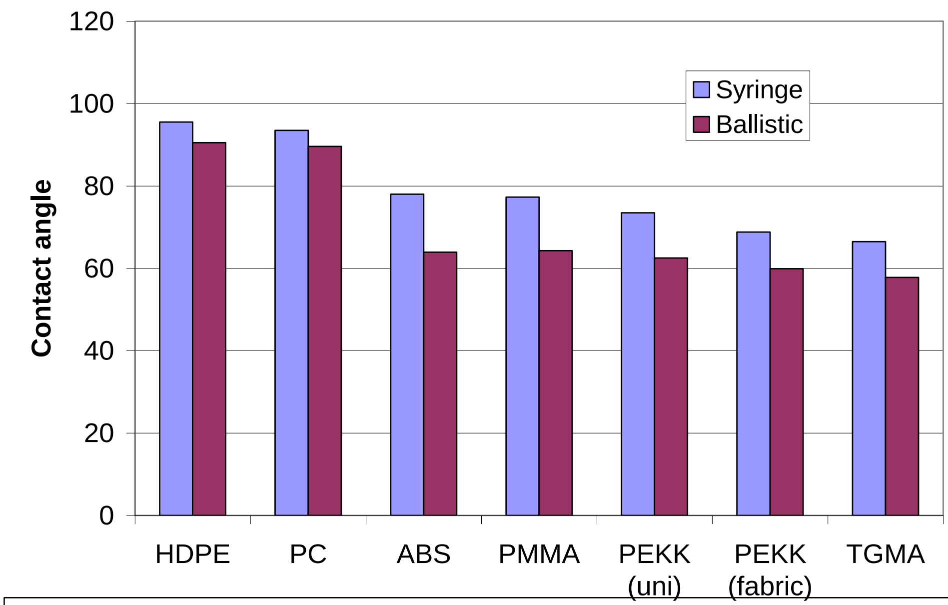

Figure 3. Water contact angles for smooth polymer surfaces: syringe deposited drops versus ballistically deposited drops.

The Surface Analyst™ doesn't deposit a fully formed liquid drop, but rather constructs a drop on the surface by the coalescence of a pulsed stream of microdrops. This process is called Ballistic Deposition™ and facilitates wetting measurements on surfaces that are non-planar, textured, and non-horizontal. In general these drops establish a contact angle that is lower than the advancing angle. The exact angle depends on the surface energy as well as the deposition

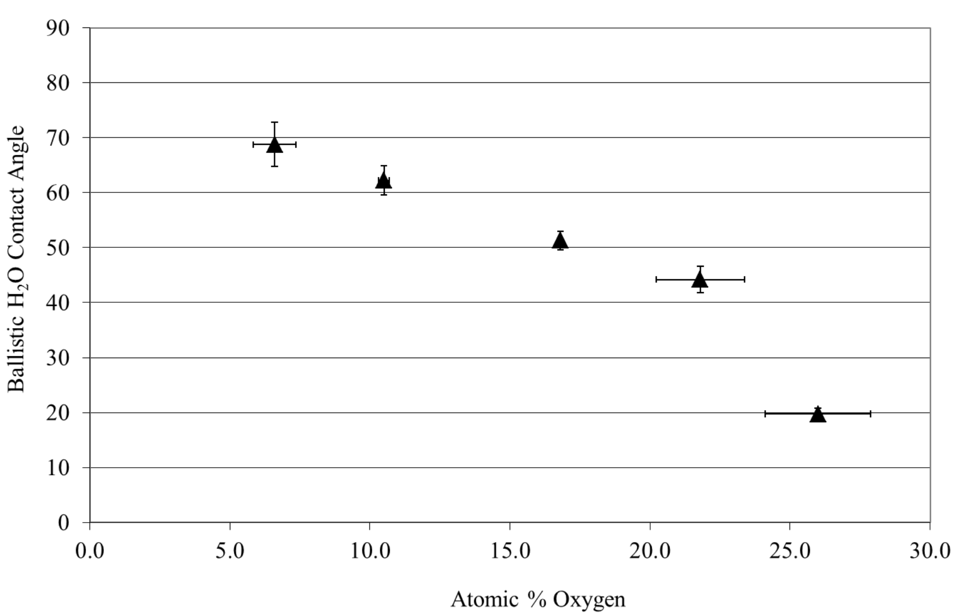

Figure 4. Ballistic water contact angles versus atomic % oxygen for plasma treated polyethylene. Atomic composition determined via X-ray photoelectron spectroscopy (XPS).

conditions (size and velocity of the microdroplets).

As an example, Figure 3 shows a comparison of contact angles obtained from syringe-deposited water droplets with those obtained via ballistic drop deposition. The ballistically deposited drops exhibited contact angles that averaged 9° lower than those obtained from the syringe deposited drops. The ranking of the polymers by contact angle was identical for both methods of drop deposition.

The Ballistic Deposition™ process can be tuned to provide the true receding angle [**10**], but because the receding angle for many high energy treated surfaces is 0°, it is generally more useful to use an angle in between the advancing and receding angle.

An example of the excellent correlation of the contact angle returned by the Surface Analyst™ with important properties such as surface chemistry is shown in Figure 4, which demonstrates the correlation of the ballistic contact angle with the amount of oxidation of polyethylene surfaces treated to different levels with an atmospheric pressure plasma process.

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