

# Solid surface energy analysis yesterday and today

The history of the development of solid surface energy analysis has been a source of much controversy over the years. Beginning in the 1950's with the work of Zisman and his "critical surface tension" concept, to the microscopic "geometric mean" (Good et al), "harmonic mean" (J. Wu), and "acid-base" (Fowkes et al) concepts, to the macroscopic "equation of state" concept (Neumann et al), the debate as to the real meaning of a solid surface energy rages on. The significance of the solid surface energy is, however, well recognized and remains the subject of countless publications.

In practice, the measurement of a solid surface energy is rooted in the thermodynamics of the contact angle and the Young Equation. The Young Equation is a mathematical expression that describes the stable equilibrium at a three phase boundary between a solid, liquid, and vapor system:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} * \cos\theta$$

where  $\gamma_{sv}$  is the surface tension (energy) of the solid in equilibrium with the saturated vapor of the liquid,  $\gamma_{sl}$  is the interfacial tension between the solid and liquid,  $\gamma_{lv}$  is the surface tension of the liquid in equilibrium with its saturated vapor, and theta is the equilibrium contact angle of the liquid as it sits on the surface of the solid.

Since the measurement of both  $\gamma_{sv}$  and  $\gamma_{sl}$  are precluded from a direct measurement, the Young Equation is really one equation with two unknowns. A solution for the solid surface energy,  $\gamma_{sv}$ , is thus complicated by this fact. Further complicating the picture is the existence of metastable "non-equilibrium" contact angles which can be observed experimentally to vary between a range of values intermediate between the maximum observable advancing angle and the minimum observable receding angle.

The solution to the first problem - how to calculate  $\gamma_{sv}$  is the subject of this communication. The solution to the second problem - how to minimize the experimental error associated with the measurement of contact angle is the impetus behind the development of the Thermo Scientific Dynamic Contact Angle Analysis System (Ref 1).

## Critical surface and tension and the Zisman plot

In 1950, Zisman and Fox (Ref 2) published a report documenting the existence of a quasi-linear relationship between the cosine of the advancing contact angle and the surface tension of a series of homologous liquids. By definition, the critical surface tension is the extrapolation to  $\cos e = 1$  of the best fit line through the data set which corresponds to the minimum value of the liquid surface tension required for complete spreading (see Figure 1). The critical surface tension of a solid yields, therefore, a single value that is useful in accessing the general wetting characteristics of a solid surface.

Problems with this technique can arise, however, when using polar (ie. hydrogen-bonding) liquids, such as water, that have the potential to interact with the polar component of a solid surface. When there is a potential for acid/ base interactions between a solid and liquid, the Zisman plot tends to deviate from linearity. This can lead to a significant error in the critical surface tension extrapolation, thus the Zisman plot is best used when characterizing primarily non-polar surfaces (i.e. polymers) where there is little or no potential for acid/base interactions with the polar component of a liquid.

## The geometric mean and harmonic mean concepts

In the late fifties, Good and Girifalco (Ref 3) postulated a theory to describe the interfacial tension between two phases as the geometric mean of the surface tension of each phase:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\gamma\sqrt{\gamma_1\gamma_2}$$

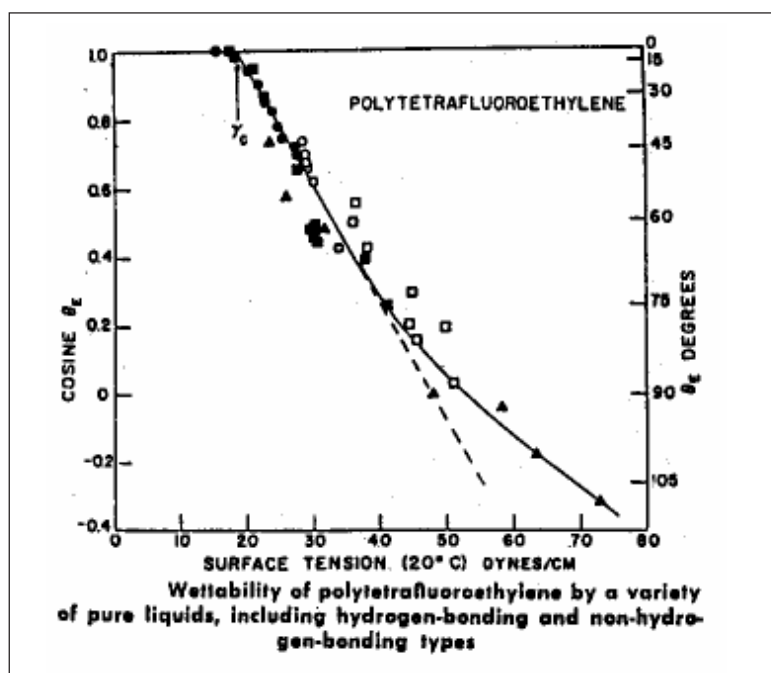


Fig. 1: Zisman plot of PTFE (polytetrafluorethylene with both polar and non -polar liquids).

Fowkes (Ref 4) extended this concept further by breaking up the surface tension into the sum of two independent terms each representing an intermolecular force - a dispersive component and a hydrogen bonding (acid-base) component. Combining the Good-Girifalco geometric mean equation with the Fowkes theory and the Young equation, yields the infamous Young-Good-Girifalco-Fowkes equation:

$$\gamma_{lv}(1+\cos\theta) = 2\sqrt{\gamma_{lv}^d\gamma_{sv}}$$

where the superscript d signifies the dispersive (non-polar) component. This equation effectively describes the dispersive interactions at a solid-liquid interface with respect to the wettability (contact angle) at the solid/liquid interface.

In the late 1960's and early 1970's, Owens and Wendt followed this work with an extension of the geometric mean concept (Ref 5) to compute both the dispersive and polar components of the solid surface energy with the following equation:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^d\gamma_l^d} - 2\sqrt{\gamma_s^p\gamma_l^p}$$

where the superscripts d and p represent the dispersive and polar components, respectively. This concept permits a direct calculation of the unknown solid surface tension components, ( $\gamma_s^p$  and  $\gamma_s^d$ ), from contact angle measurements with two liquids with known surface tension components ( $\gamma_l^d$  and  $\gamma_l^p$ ). The solution to this equation requires the input from two or more standard high surface tension, non-associating liquids with very different polarities. Water (highly polar) and methyleneiodide (non-polar) are liquids often selected for contact angle experiments when this method is employed. A similar approach was taken concurrently by Kaelble (Ref 6).

At about the same time (1971), Wu followed with a different approach, the so-called harmonic mean or reciprocal mean equation (Ref 7):

$$\gamma_{sl} = \gamma_s + \gamma_l - 4\frac{\gamma_l^d\gamma_s^d}{\gamma_l^d + \gamma_s^d} - 4\frac{\gamma_l^p\gamma_s^p}{\gamma_l^p + \gamma_s^p}$$

which differs from the geometric mean approach only in the calculation of the dispersive and polar interaction terms. Wu demonstrated

through empirical means that his equation was perhaps more suitable than the geometric mean in calculating the polar component of a series of polymers, however both methods are extensively used today in surface energy analysis.

### Current developments and future trends

Current developments in the field of surface energy theory and analysis are focused in the direction of Lewis acid/base (electron donor/electron acceptor) interactions which are known to occur between polar groups in both liquids and solids. In essence, the "polar" component is being expanded to recognize the importance of acid/base interactions in the solid/liquid interface region. The importance of recognizing acid/base interactions, first documented by Fowkes, is being widely exploited by a number of researchers including Good, VanOss, and Chaudhury among others. This theory recognizes that an acid/base interaction can occur only when the opposite parameters are found in another molecule in contact with or part of the same material. Therefore, a basic liquid has the potential to form measurable interactions with the acidic component of a solid and viceversa.

As the number of parameters increases and the equations become more complex, the number of liquids required for contact angle analysis also increases.

### Selecting appropriate probe liquids

It is important to emphasize that the choice of liquids used in any surface energy calculation method (Zisman plot, geometric, harmonic, or acid/base method) is critical to the success of the analysis. Water, for example, is a universally used probe liquid for surface energy analysis, however, with its small molecular volume, water can more readily penetrate the pores of a solid than other probe liquids, therefore caution must be exercised when using water for any contact angle experiment (Ref 8). When selecting a pair or group of liquids for a particular analysis it is important, therefore, to consider two major factors:

(1) Liquids must be inert with respect to the solid (i.e. a liquid it

must not react, penetrate, swell, or otherwise "interact" with the solid so as to modify the surface or bulk properties of the solid).

(2) Liquid pairs or groups of liquids must be selected such that the polarities are very different from each other. If the polarities are too similar, it has been shown that even small errors in input data can cause serious errors in the final result. This is the reason why water and methylene iodide are often selected as a good pair of liquids for surface energy analysis.

For more information on surface energy analysis, contact a Thermo Fisher Scientific representative and ask for information on the Thermo Scientific Dynamic Contact Angle Analysis Systems (DCA) and the DCA Applications Software (Ref 9) which computes the surface energy of a solid by the methods discussed in this communication.

### References:

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