Technical Note

Practical Contact Angle Measurement (5)

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Method:

Drop Shape Analyzer – DSA100

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Custom-made models: from contact angle to surface free energy

The determination of the surface free energy (SFE) of a solid is the ultimate in contact angle measuring techniques. The method provides the user with important information about the material surface, such as its wettability and adhesiveness. In order to plan a measurement and draw the correct conclusions from the results a good knowledge of the scientific models upon which these are based is useful.

In this final part of the Newsletter series on contact angle measurement the most important models for determining the surface free energy (SFE) are described; these are used in practice (and in KRÜSS software). In addition to the proper use of the models, it is also concerned with the practical aspects of SFE determination: selection of suitable test liquids, suitable ambient conditions and the consequences arising from the properties of the solid surface.

About models

The keyword "model" may perhaps have a sobering effect on one reader or the other: an SFE value obtained from contact angle data is not knowledge about a solid that is carved in stone, but rather an interpretation of its behavior within the framework of the model used. Strictly speaking, this applies to any scientific statement. However, many formulations from the natural laws are so familiar to us that we are now no longer aware of their model character.

Fig. 1: Copernicus' model of the solar system – since "relativized" by Einstein

The measure for the meaningfulness of a model is its consistency, the possibility of explaining observed phenomena in as simple a way as possible and of making predictions that can be confirmed empirically. This means that it is a good idea for users of the contact angle measuring technique to familiarize themselves with the theory – and limitations – of the models used.

Surface tension and surface free energy

Surface tension (ST in the following text) and SFE are equivalent physical terms; the first is conventionally used for liquids and the second for solids.

In a liquid the surface tension results from the fact that a molecule at the surface is in contact with fewer neighboring molecules that it can interact with than in the bulk of the liquid. Remaining at the surface is less attractive for molecules of a (pure) liquid. This is why liquids attempt to achieve as small as surface area as possible; work is required to increase a surface.

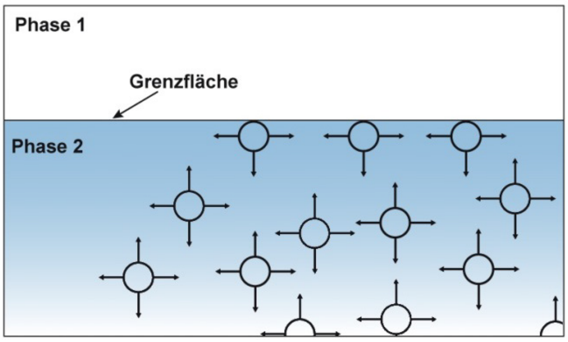

Fig. 2: Forces between molecules in the condensed phase and at the boundary

In principle the same applies to the SFE of solid phases. However, it is hardly possible to directly measure the amount of work required to increase a surface, as it is difficult to differentiate this work from the work of deformation of the bulk phase. The SFE of a solid can be measured indirectly by using its wettability by liquids. This is where the contact angle enters the picture.

Contact angle and surface free energy

As long ago as 1805 Young established a relationship between the contact angle θ and the ratio of the ST of the liquid (σ_l) and solid phase (σ_s). Young's basic equation for the contact angle was:

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \,.$$

If the contact angle is measured and if the ST of the liquid is known there are still two unknown quantities: the SFE of the solid (σ_s) and the interfacial tension between the phases (γ_{sl}). Various models were drawn up to explain the relationship between these two quantities. In them the interfacial tension (IFT) was usually derived from molecular interactions between the phases. In principle the following applies: the greater the interactions occurring at the phase boundary, the lower the IFT.

Zisman

Zisman [13] plotted the cosine of the contact angle against the surface tension of the corresponding liquid. He defined the extrapolated value for cosθ=1 (θ=0°) as the critical ST (σ_c). This quantity was supposed to correspond to the ST of a liquid in which complete wetting is just taking place. Zisman himself regarded the critical ST as being only a measure of the SFE of the solid, but did not give these two quantities the same value – in contrast to many subsequent users of the Zisman plot. In actual fact, σ_c and σ_s are only practically the same for non-polar solids and liquids, and the greater the distance between the extrapolated value for σ_c and the test liquid with the smallest ST, the more inaccurate the result.

Today test inks still work according to the critical surface tension concept: the liquid selected from a series of liquids with defined surface tensions is that liquid which just wets the solid completely.

Fowkes and Owens-Wendt-Rabel-Kaelble (OWRK)

Fowkes [2] assumed that various types of interaction are responsible for the ST of a phase – disperse and non-disperse (polar) interactions. On this basis Fowkes first determined only the disperse fractions of the ST. Owens and Wendt [9] as well as Rabel [10] and Kaelble [5] used Fowkes as a basis and determined the disperse and polar fractions of the ST of liquids and the SFE of solids.

In the two-component model according to Fowkes and OWRK the IFT γ_{ls} is obtained as the sum of the STs of the individual phases, reduced by the disperse (D) and polar (P) interactions between the phases. These interactions are calculated as geometric mean values:

$$\gamma_{ls} = \sigma_l + \sigma_s - 2\left(\sqrt{\sigma_l^D \cdot \sigma_s^D} + \sqrt{\sigma_l^P \cdot \sigma_s^P}\right)$$

In the DSA software this equation forms the basis for both the Fowkes and the OWRK method; the methods differ only in the calculation path. With OWRK the polar and disperse fractions are obtained from a graphical evaluation.

In the two-component model the IFT depends on whether the polar and disperse fractions can enter into interactions with the corresponding fractions in the bordering phase. For example, the IFT becomes smaller against the polar liquid water when the solid is also polar. In contrast, if the polar fraction of the solid is low then the square root term $\sqrt{\sigma_l^P \cdot \sigma_s^P}$ assumes a smaller value. The polar interactions then only make a small contribution to lowering the IFT; this corresponds to poor wetting – a large contact angle. In the following illustration the various types of interaction are symbolized by hands – only similar hands can grasp each other.

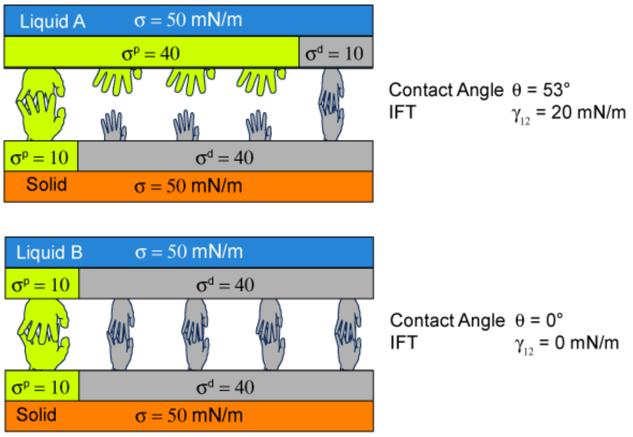

Fig. 3: Schematic diagram of phase contact in the two component model

Rabel used the model for studies on polyethylene surface treatments – it has actually proved to be workable, particularly for the activation and coating of plastics. Even when working with only two test liquids the empirical findings for wettability and adhesion often correlate well with the ST values calculated according to OWRK and the polar and disperse fractions – although Good has produced theoretical objections to the method used for calculating the polar fraction (see below).

The two-component model has far-reaching consequences for the interpretation of wettability. An IFT of 0 mN/m leads to a contact angle of 0°; conversely the IFT can be larger than zero for a contact angle of 0°. For practical coating applications, for example, this means that even for an optimally wetting liquid the adhesion can be destabilized by a residual IFT.

Fowkes (extended)

In a more recent paper [1] a three-component model has been developed in which the polar fraction has been further split up into a hydrogen bridge bonding fraction (σ^H) and a fraction for dipole-dipole interactions (σ^P).

The above equation has been extended by a further square root term:

$$\gamma_{ls} = \sigma_l + \sigma_s - 2(\sqrt{\sigma_l^D \cdot \sigma_s^D} + \sqrt{\sigma_l^P \cdot \sigma_s^P} + \sqrt{\sigma_l^H \cdot \sigma_s^H}).$$

Accordingly this means that at least three test liquids are required for determining the SFE. This method, which is included in the DSA software as “Extended Fowkes”, is rarely used for material testing. However, it is valuable for estimating the adhesion between two phases, as hydrogen bridge bonds have greater bonding energies when compared with disperse and dipole-dipole interactions. The wettability of a solid by water depends to a great extent on the ability of the solid to form hydrogen bridge bonds.

Wu

Wu [11;12] stated that for a low SFE the harmonic mean between the particular fractions (disperse and polar) often provided more reliable values than the geometric mean. The use of the harmonic mean corresponds to the following equation:

$$\gamma_{ls} = \sigma_l + \sigma_s - 4(\frac{\sigma_l^D \cdot \sigma_s^D}{\sigma_l^D + \sigma_s^D} + \frac{\sigma_l^P \cdot \sigma_s^P}{\sigma_l^P + \sigma_s^P})$$

The empirical basis for this is provided by interfacial tension measurements between polymer melts, i.e. materials with a predominantly low surface tension for the individual phases. Accordingly the Wu method is mostly used for SFE calculations for polymers with low surface free energies (up to 30-40 mJ/m^2).

Acid-base model as per Oss and Good

The authors Oss and Good [3; 4; 8] adopted the definition of the disperse fraction from Fowkes, but split the polar fraction into an electron acceptor (acid, σ^+) and an electron donor fraction (base, σ^-). The objection to Fowkes, OWRK and Wu is that not all the polar interactions can be set in relationship to one another – a Lewis base, for example, can only enter into interactions with the acidic components of a bordering phase and not with the basic components. Accordingly the opposing components for the polar interactions are gathered together in the square root terms in the equation:

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^+ \cdot \sigma_l^-} + \sqrt{\sigma_s^- \cdot \sigma_l^+})$$

Despite the compelling theoretical nature of this approach it is currently little used in practice. This could be because the choice of test liquids with known basic and acidic fractions is relatively limited. In addition, other models such as OWRK or Wu have proven themselves many times in practice and require less measuring data than the acid-base method. Negative IFT values, which are possible in the acid-base model, are not easy to interpret.

Equation of State

The methods mentioned up to now have been linked historically and systematically to one another: after the influence of non-disperse interactions became known, its components were described by using various models.

The work Neumann et al [6;7] was carried out in a different field; their theory entered the SFE determination as an "Equation of State". According to the thermodynamic approach of Neumann, breaking down the ST into interactive components does not hit the target. The not undisputed [see 4,32] theory does not need any differentiation of interactive components and requires only one liquid with a known ST – the advantage lies in the rapid access to an SFE value. As Neumann has mainly derived his equation from results for non-polar solids with low surface free energies, his approach can primarily be used in this field. For such solids the results tend to agree with those obtained by evaluations according to Zisman or OWRK.

Selecting the liquids

Some standard test liquids were mentioned in part 1 of this Series and their use for measuring contact angles was described. The liquids that are suitable depend on the requirements of the particular model for the evaluation.

Number of test liquids

The fact that the reliability of the result increases with the number of test liquids used applies to all models. For Zisman, Fowkes, Extended Fowkes and OWRK this means that more data are used for the linear regression; in other methods more individual equations can be used to calculate an arithmetical mean SFE value.

Test liquid properties

In the multi-component models the values of the liquid components should be spread as widely as possible. For example, for Fowkes and OWRK liquids with both the largest and smallest polar fractions should be included in the selection. Water and diiodomethane is a frequently used pairing with only two liquids. Diiodomethane is ideal, because as a purely disperse or – for some authors – slightly polar liquid it has a relatively high ST and therefore forms easily measurable contact angles with many solids. In contrast, non-polar liquids which spread on almost any solid (e.g. n-hexane), are not suitable for the measurement.

In the Extended Fowkes and the Acid-Base method the choice of liquids is limited, as to date only a few substances have been characterized with regard to the relevant components. Water should always be used for both methods because of its marked hydrogen bridge formation and its amphoteric character (Lewis acid and base at the same time) unless it chemically changes the solid surface.

Mixtures of liquids should not be used, because the liquids have different affinities to the solid and form a different (and unknown) mixing ratio at the interface from that in the bulk phase.

Consistency of selection

The more similar the measuring conditions, the more meaningful is the comparison between the SFE data of different samples – this also applies to the number and selection of the test liquids. As far as possible solids whose SFE values are to be compared should be measured with the same test liquids.

The databases of the KRÜSS software products contain several entries for many liquids whose data is provided by different authors. For comparative measurements the liquid data should always be taken from the same source. For two-component models with the geometric mean of the components (Fowkes, OWRK), KRÜSS recommends using the data from Ström, which are based on the geometric mean. For many liquids data has additionally been provided by the authors Fowkes, Owens or Rabel. In the Wu evaluation the required consistency cannot be completely achieved, as no liquid data exist with which the harmonic mean values of the components have been calculated. This is why the same liquid data is usually used for Wu as for Fowkes or OWRK.

Sample preparation and ambient conditions

Many solid surfaces have much higher surface free energies than liquids. For this reason they tend toward passivation, e.g. by the formation of oxidation or gas and vapor adsorption layers. This is why the SFE of solids depends more strongly on the chemical surroundings than the ST of liquids (e.g. air or inert gas, air pressure, relative humidity).

There are special methods for the measurement on high-energy samples, e.g. contact angle measurement at the interface between two liquid phases instead of in air as in the Schultz method, or measurement under inert gas. However, the contact angle is usually measured at the three-phase point liquid/solid/air. Ideally the solid sample should be stored at the intended relative humidity and temperature for a long time before the measurement – it is important that the selected standard conditions are kept the same for all samples.

Vapors of organic liquids should be avoided at all costs, as they form stable adsorption layers on many samples. In this case the contact angle with water will then be larger and the calculated SFE value lower than on an uncontaminated surface. For the same reason spreading liquids with a high vapor pressure are not suitable – within a large area around the deposited drop the sample is spoiled for measurements with other, poorly wetting liquids.

Properties of the solid

In contrast to liquids, hardly any molecules change places in a solid; this means that the surface free energy describes a static condition of the solid and not a dynamic equilibrium between mobile particles. As a result, the SFE of a chemically inhomogeneous solid may depend on the place of measurement. In addition, the macroscopic structure of the surface influences the contact angle.

Roughness

Young's equation can describe ideal solids that are smooth, flat and chemically homogeneous. The roughness of the material should be taken into consideration in every measurement: the rougher the solid the harder it is to correlate the measured values with the chemical properties of the surface.

Nevertheless, an SFE calculation for a rough solid is not without value. For example, an evaluation according to OWRK still describes the behavior of the solid toward differently polar liquids with different surface tensions. However, the user should be clear that the framework of the model has been exploded. The calculated values are only empirical quantities. As such they are still useful; however, differences between a smooth and a rough sample should not be interpreted as differences in polar and disperse interactions.

Chemical inhomogeneity

Strictly speaking, the SFE is a property of exactly that surface position at which the measurement was made. Before the measurement a decision must be taken as to whether a global value for the surface is being sought for, or whether local differences in the SFE are to be determined. In the first case drops of each liquid should be deposited as far away from each other as possible and a mean value for the contact angle obtained for each liquid across the whole sample. In the second case one drop of each test liquid should be deposited as close to one another as possible. The SFE can then be calculated for the corresponding position by using such a group of drops of different test liquids.

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