Measurement with nicely deposited drops

In the second part of our practical series on contact angle measurement we are concentrating on drop deposition. What is the difference between static and dynamic contact angles? What influence does the drop volume have? How can the drops be deposited on the sample? The clarification of such questions helps to exactly match the deposition conditions to the particular problem and the functional range of the sample, and how to deal with some of the problems that occur in practice.

Contact angle instruments with computer-controlled sample tables and multi-dosing systems offer a wide range of drop deposition possibilities. The way that a drop is generated and makes contact with the sample can be matched exactly to suit the particular problem.

Dynamic or static measurement

According to Young the contact angle describes the relationship between the surface tension of the liquid and that of the solid as well as the interfacial tension between the phases. From this relationship the Young contact angle $\theta$ is used to describe the wetting processes:

$$\cos \theta = \frac{\sigma_s - \gamma_{sl}}{\sigma_l},$$

where $\sigma_s$ and $\sigma_l$ represent the surface tensions of the solid and liquid and $\gamma_{sl}$ is the interfacial tension.

The contact angle can be determined with either a constant or a varying drop volume. In the first case we are concerned with a static contact angle, in the second case with a dynamic one, with a differentiation being made between an advancing (with increasing drop volume) and a retreating (with decreasing drop volume) contact angle – the rarely measured retreating angle is not covered in this article.
On a theoretical, ideal solid surface neither chemical nor topographical inhomogeneities exist, so that the contact angle of a liquid is identical at all positions. A further requirement for the formation of an ideal Young contact angle is that no chemical reaction between the components occurs at the phase contact points. In an ideal system the static contact angle does not differ from the dynamic one; in both cases an equilibrium contact angle is formed, as is described in the Young equation. However, systems which occur in practice vary to a greater or lesser degree from the ideal state: roughness affects the wettability, the surface may be chemically inhomogeneous, or soluble components may diffuse from the solid surface into the solution – depending on the nature of the system such influences could increase or decrease the real contact angle. Differences in energy between neighboring positions could also result in the occurrence of energy barriers which cause resistance to the wetting process and therefore produce a contact angle that does not correspond to the equilibrium value of the Young equation. This does not mean that the contact angle is “wrong” – it is just this sensitivity to inhomogeneities that makes the contact angle such a useful tool for checking surface quality. However, it means that conditions under which a measurement is made must be evaluated in order to be able to interpret the contact angle and its variations in a reasonable manner. Consistency should be observed when making comparisons between different samples: static values should not be compared with dynamic ones and the same applies for the surface free energies calculated from contact angle data.

In the advancing angle the drop is “forced” to wet a neighboring position by the increase in deposition volume. When measuring the advancing angle it can frequently be observed that as the volume increases the contact angle initially increases, without any change in the contact area. When a limiting contact angle has been achieved then this angle no longer changes; instead the drop borderline moves outward with a constant contact angle – it is only in this region that we talk about an advancing angle. In an online measurement of the advancing angle this is recorded at very many closely adjacent positions so that a meaningful mean value is obtained. For this reason, and because the angle is always measured at a “fresh” contact line, the advancing angle method is frequently used. If an inhomogeneous surface is to be determined by static contact angles then a large number of single drop measurements is usually required to obtain a reliable mean value.

However, with dynamic contact angle measurements the number of evaluation methods available is reduced. Some methods, in particular the Young-Laplace method, which is the most accurate from a scientific viewpoint, include the whole of the drop shape in the analysis. In a dynamic measurement the deposition needle is still located in the upper part of the drop, so that the contour is pierced and only the contact area of the drop can be evaluated. An important criterion for deciding between static and dynamic contact angles is the technical wetting process the samples are involved in. If the process itself is dynamic, such as applying coatings to moving surfaces, then dynamic measurements provide a better model of reality. For the evaluation of quasi-static processes, e.g. bonding in semiconductor technology, static contact angles are often more meaningful.

Static measurements are also usually appropriate when inhomogeneities are not to be statistically eliminated but to be determined on the contrary. Mapping the sample – measuring the static contact angle at many sample positions – helps to provide a meaningful correlation between position and wettability.

For the choice of method the following, seemingly paradoxical, rule also applies: if the dynamics of the interface formation are to be investigated then static contact angle measurements are appropriate. For example, during absorption processes a reduction of the contact angle with time is observed after surface contact; this can be quantified by using a high-speed camera. Surface-active substances also lead to the variation of the static contact angle with time – we described an interesting application from the dental sector [hyperlink] in the last issue of this Newsletter.

To sum up briefly: many users prefer the dynamic contact angle because of its lower susceptibility to scattering. At the same time there are also reasons for preferring the static contact angle – arising from the problem to be solved or from practical measuring considerations.

**Drop volume**

There is no “golden rule” for choosing the drop volume. In theory the Young contact angle is not dependent on the drop volume – at least in the macroscopic range. Only with very small drops, e.g. in condensation processes, does “line tension” come into play; this is related to the excess energy of the phase-contact line compared to the surface free energies of the individual phases. This parameter is so small that it can be neglected for drop dimensions such as occur in contact angle measurements – even in micro-depositions as encountered with the DSA100M the line tension plays no part.
As described above, a dynamic measurement can result in a minimum volume above which the contact angle no longer increases; it can then be measured as the advancing angle. With ideal, completely homogeneous surfaces measurements are possible with small drops of virtually any size.

In the opposite direction the drop volume is limited by the weight of the liquid itself, this causes drop shape distortions. The surface tension $\sigma$ of the liquid and the volume-dependent drop weight $\rho \cdot g$ determine the maximum drop radius which is represented by the capillary length $\kappa^{-1}$:

$$\kappa^{-1} = \sqrt{\frac{\sigma}{\rho \cdot g}}$$

For water this results in a maximum radius of 2.7 mm; above this value a considerable influence of the weight on the drop shape is to be expected. Kranias$^1$ ... was able to show that in a volume range between 1 and 10 $\mu$l no influence of the volume on the water contact angle could be demonstrated. At higher densities or smaller surface tensions the chosen volume should not be too large; this applies in particular for the standard test liquid diiodomethane with a $\kappa^{-1}$ value of 1.2 mm.

**Deposition speed**

The deposition speed plays a role in dynamic contact angle measurements in particular. If too high a speed is selected the drop shape will also be determined by the volume flow – the correct contact angle will not be measured. With low-viscosity test liquids such as water or diiodomethane a speed of 100 $\mu$l/min should not be exceeded. The speed should be considerably reduced for high-viscosity liquids whose ultimate drop shape is only achieved after a certain time. If dynamic measurements are essential then test measurements should be made at different speeds in order to determine the speed-independent range.

**Type of surface contact**

In computer-controlled dosing systems and sample tables many possible ways are available for the liquid to contact the sample: the drop can be generated on the sample, picked up from the sample, deposited on the sample and finally dropped onto the sample. In theory the contact angle value does not depend on the type of phase contact – once again practical considerations determine the planning of the measurement.

For a dynamic measurement there is no choice regarding drop contact – as the volume is continuously altered during the measurement, drop deposition takes place on the sample and within the field of view of the camera.

In static measurements the drop frequently cannot be generated on the sample directly – when the needle is removed the drop may retreat, so that the contact angle is measured at a surface that has already been wetted. This can be counteracted by carefully picking up or depositing a sufficiently large drop suspended from the dosing needle. As the sample table movement can be set to very slow on the DSA100 from KRÜSS, picking up the drop is the most gentle phase contact method. This method is also recommended for small contact angles, for which each mechanical input of energy will lead to an unwanted stronger wetting of the sample. However, picking up has the disadvantage that the table must first be moved back to the measuring position – the first drop formation phase cannot be observed. If work has to be carried out quickly then a more rapid deposition of the drop on a sample that is already at the measuring height is suitable. In extreme cases, such as in adsorption processes, the drops can be dropped onto the sample from a low height in order to be able to record the first milliseconds of drop contact – however, a stronger mechanical influence on the drop shape must be accepted.

Extremely large contact angles, e.g. encountered with water drops on ultra-hydrophobic samples, require special treatment. It is often difficult to bring the drop onto the sample, because the cohesive forces of the liquid and the adhesion to the needle are far larger than the adhesion of the liquid to the sample. It frequently helps to first generate a small drop and then bring it into contact with the sample by moving the needle or sample table. The dosing volume can then be slowly increased until the drop is large enough to part from the needle when the distance is increased. Help is also provided by the use of special needles with a Teflon insert to which the drop adheres less strongly.

**Summary**

In this second part of our series on contact angle measurement we are concerned with drop deposition. There is no single type of drop deposition that is suitable for all cases, on the contrary a decision must be taken between static and dynamic contact angles, the drop volume and deposition speed must be selected together with the type of surface contact with the solid and liquids used – all these must be matched to the particular problem. Some criteria for the choice of deposition conditions are given in this article.

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1 Kranias, Spiridon: Effect of drop volume on static contact angles. KRÜSS Technical Note TN310e.