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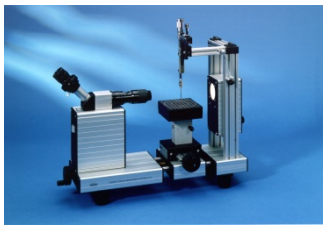
Technical Note

Comparison of Wilhelmy and Sessile Drop Technique

Technical note:	TN303e
Industry section:	Chemical, Pharma, Automotive, Paint, Energy, Polymer, Construction
Author:	CR
Date:	01/1996
Method:	
Keywords:	Contact angle measurement, Wilhelmy method, sessile drop, advancing/receding contact angle



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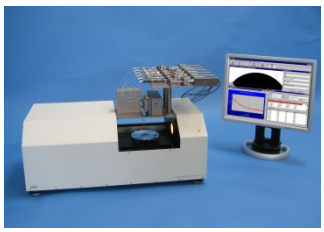

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A practical comparison of the techniques used to measure contact angles for liquids on non-porous solids

Based on a paper to be given at the 1996 Annual Meeting of the Society of Tribologists and Lubrication Engineers and submitted for publication in either *Lubrication Engineering* or *Tribology Transactions*

Background

The wetting of solid surfaces by liquids is an important process for many industrial applications. For example, how well a metal working fluid will wet and adhere to a particular metal surface is quite important to the field of tribology. How well a polymeric coating will repel solvents is important to coating manufacturers. How well biological fluids wet and disperse powder drug tablets is of importance in the pharmaceutical industry.

"Wetting", by definition, is the process of one fluid displacing another fluid at a solid surface. However, in most cases, the term is used to describe the displacement of air by a liquid. Under this definition, the most commonly used technique to quantify the susceptibility of a solid surface to being wet is contact angle measurement. For a non-porous solid surface, contact angle is the angle formed when a liquid droplet is placed on the surface. See figure 1.

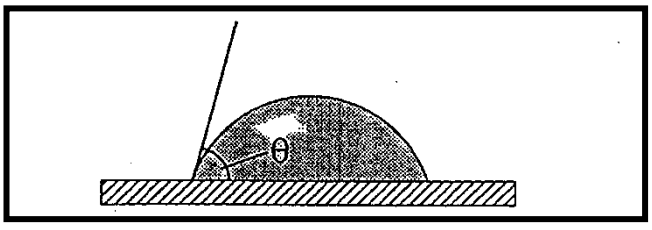

Fig. 1: contact angle on non-porous solid

If the contact angle is measured as the liquid is advancing on the surface, then the smaller the angle is the more susceptible to wetting a solid surface is. If the contact angle is measured as the solvent is receding on (or being removed from) the solid surface, then smaller angles indicate that the solid surface is less susceptible to dewetting.

There are two major methods of determining contact angles for liquids on non-porous solid surfaces. These are the goniometer method and the Wilhelmy method. Instruments are commercially available for studies by both methods. However, there are advantages and disadvantages intrinsic to each method. Understanding these advantages and disadvantages can be critical to deciding which is more useful for any given research project or quality control study.

The Goniometer Method

The goniometer method is the more straightforward of the two. Advancing contact angles can be determined using a goniometer by placing a drop of liquid on the on the surface which is viewed at a grazing angle. The drop volume is increased until the drop expands (advances on a solid surface) prior to visually, or by image analysis, measuring its contact angle. This is depicted in figure 2.

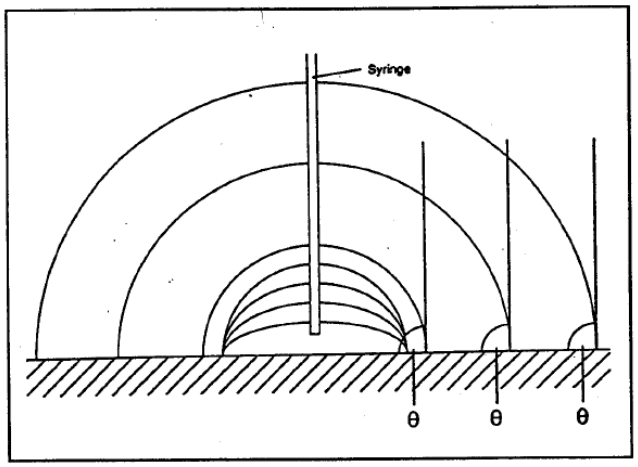

Fig. 2: advancing contact angle

Receding contact angles can be determined similarly by causing the drop to contract (recede) on the surface prior to measuring its contact angle. This is depicted in figure 3.

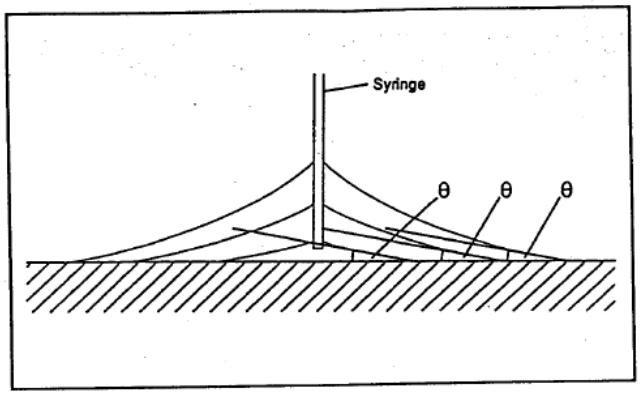

Fig. 3: receding contact angle

The biggest advantage of the goniometer method is that, under proper conditions, the contact angle between any liquid and any non-porous solid having positive curvature can be determined. If the size of the surface is substantial, the method is good for investigating surface heterogeneity, since liquid droplets can be evaluated at a number of different positions on the surface. Further, contact angle data on an individual drop can be obtained quickly and easily even under extreme temperature and pressure conditions.

However, the goniometer method suffers from some disadvantages. Using a common, commercially available goniometer, it is generally only possible to obtain two contact angle values per placed drop. One from the right side of the drop and one from the left side of the drop, can be measured as it appears from the viewing angle. Therefore, the data collected only characterize two points on the surface. Without specific surface preparation, every solid surface has some degree of surface heterogeneity. Therefore, in order to adequately characterize surfaces with the goniometer technique, several drops need to be evaluated. The reproducibility between contact angle measurements on successive drops is dependent on the level of heterogeneity of the surface. Unfortunately, reproducibility is also dependent on other factors.

Contact angle determination is dependent on the subjective placement of two lines, one characterizing the edge of the liquid drop relative to the atmosphere and one characterizing the plane of contact between the liquid drop and the solid surface. Contact angle reproducibility is influenced by the criteria used to place these lines. With commercially available computerized and automated goniometers, these criteria are based on the gray-scale analysis of a digitized drop image. Factors such as illumination intensity, focus, contrast, refractive indices of the material involved and reflectance of the solid surface all affect the measurement. A manual goniometer is influenced by the same factors. However, since the human eye is the detector, the line placement decisions are made by the user, instead of a computer. Either way, the level of reproducibility in goniometer testing is affected by subjectivity. The advantage of a video camera, digitizing board and image analysis software is that subjectivity is greatly reduced.

In practice, non-reflective surfaces pose the biggest measurement problem, because placement of the solid/liquid contact line becomes somewhat nebulous. The evaluation of low contact angles makes placement of the liquid/vapor contact angle line difficult. Having measured a wide variety of samples, it is our experience that the following levels of reproducibility are generally inherent to goniometer based contact angle measurement, even when an automated goniometer is used.

Contact Angle Range	Reproducibility
140°-25°	±0-1
25°-15°	±2-3°
15°-0°	±3-5°

The Wilhelmy Method

In contrast to the goniometer technique, the Wilhelmy method of contact angle measurement is sensitive at low contact angles. The Wilhelmy method is performed by dipping a non-porous solid sample into a liquid while measuring the force on the sample due to wetting. Commercially available instruments for this type of measurement employ a sensitive balance for the measurements of force, in conjunction with some type of clip to hold the solid sample in place. The advancing contact angle of a liquid on a solid is determined from force data obtained during submersion of the solid into the liquid. The receding contact angle is likewise determined

from force data pertaining to removal of the solid from the liquid. See figure 4.

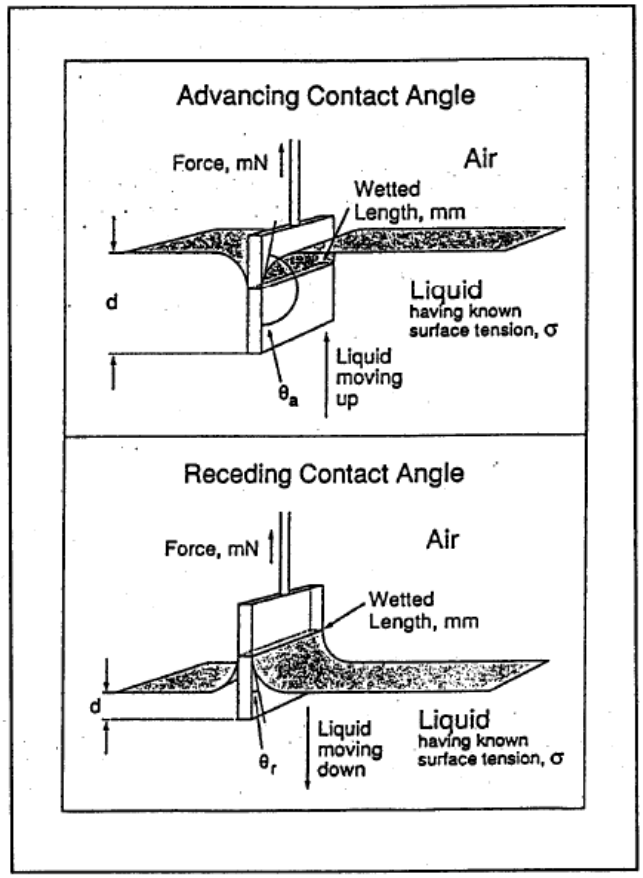

Fig. 4: advancing and receding contact angle

Contact angles are calculated from force data using the Wilhelmy equation.

$$cos\theta = \frac{F - F_b}{l\sigma}$$

wherein θ = contact angle, l = the sample's wetted length (perimeter), σ = the surface tension of the liquid, F = the total force felt by the solid at any submersion position and F_b = the buoyant component of the force on the solid at any submersion position. F_b is due to the solid displacing liquid as it is submerged and removed. It is, in general, a distraction to Wilhelmy contact angle experimentation, since the contact angle depends on the Wilhelmy force (F_W) only, which is the wetting force, or the total force felt by the solid (F) less the buoyant force (F_b). Hence, $F_W = F - F_b$ as used in the Wilhelmy equation above.

Figure 5 shows a raw force versus submerged position data from a Wilhelmy experiment on water wetting a graphite surface. The "force" in the raw data presented in this plot is F, not yet corrected for the buoyant force. As a result, the plot is an out-and-back trace of force felt by the graphite plate as it was submerged into and removed from the water.

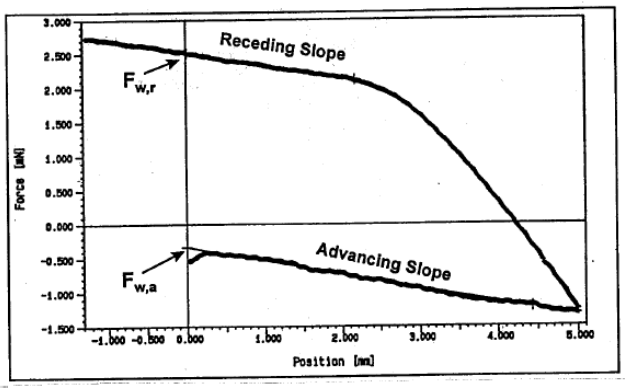

Fig. 5: Wilhelmy experiment for water wetting a graphite based solid plate

The lower set of forces reported on this plot at each position (relative to the zero position at which the sample just contacts the surface) are forces (F) during submersion. During submersion, the buoyancy force pushes upward on the solid and F_b is negative. (Forces in the upward direction on the sample are defined as negative and forces in the downward direction are defined as positive.) The Wilhelmy force on the solid can be either positive or negative during submersion, depending on whether the advancing contact angle on the sample is less than 90° (F_W = positive) or greater than 90° (F_W = negative). As a result, during submersion of the sample, the total force ($F = F_b + F_W$) versus position data can be either positive or negative. For a uniform sample, the force (F) linearly decreases as the sample is submerged, because the Wilhelmy force (F_W) remains constant and the buoyant force (F_b) becomes more negative. Extrapolation of the linear portion of the force versus position data for submersion of the sample back to zero position thus provides a value of force (F) equal to the Wilhelmy force (F_W) on the solid during submersion, because $F_b = 0$ at (and only at) position zero. This value of $F_{w,a}$ is thus used to calculate the advancing contact angle of the liquid on the sample. The receding contact angle is likewise calculated from extrapolating the removal portion of the force versus position curve to position zero, where there is no buoyant force ($F_{w,r}$). For the graphite/water example, the advancing contact angle is 94.8° and the receding contact angle is 50.9°.

It is obvious that contact angle measurement by Wilhelmy method is less straightforward than measurement by the goniometer method. However, automated instrumentation makes the method no more (and perhaps less) taxing to use. Low contact angles are much easier to measure with the Wilhelmy method since the measured parameter is force, and force actually increases with decreasing contact angle. However, the precision of the data is largely dependent on the nature of the cosine function. (Contact the author if you are interested in a more detailed discussion of this point.) The Wilhelmy method is also free of the subjectivity of the goniometer method. No contact lines need to be set and, correspondingly, reproducibility's of better than ±1° are quite common over the entire range of possible contact angles. Force measurements are subject

to far fewer influences than visual techniques. For solid/liquid combinations in which contact alters surface properties of the solid the Wilhelmy technique offers the ability to do repetitive studies. In other words, to evaluate the same area of solid surface again, after it has been wet and dewet by a liquid. This is not as simple by the goniometer method. If a sample absorbed liquid this is easy to detect by examining the final weight of the sample. It should not change from the initial value if the sample is unaffected.

One aspect of the Wilhelmy method which can be an advantage is that the contact angle values obtained represent averages over the solid's entire wetted length. Much more of the solid's surface is characterized by each test than is the case when a single drop is studied by the goniometer method. This inherent averaging procedure causes successive contact angle measurements to be more reproducible relative to goniometer contact angle data. However, it also diminishes one's ability to study a solid surface's heterogeneity. The relative smoothness of force versus position curves (such as shown in figure 5) can be evaluated to provide some indication of solid surface heterogeneity, but overall, the goniometer technique is more useful in this regard.

Strict disadvantages of the Wilhelmy method are mainly due to consideration of an experimenter's available options for solid surface preparation. In particular, a solid sample with uniform cross section in the submersion direction must be used. Also, the solid's wetted length (l) must be known with some precision, since it is directly used in the Wilhelmy equation. Wetted length is typically determined simply by measuring a sample's dimensions with calipers or a ruler. However, it can also be predetermined by running a contact angle type experiment with a perfectly wetting liquid (a liquid, such as n-hexane, which is known to have a contact angle equal to 0° on the solid), and using the results with the Wilhelmy equation to calculate "l". Nevertheless, lack of precision in determining a solid's wetted length is the most common source of errors in Wilhelmy experimentation.

The largest disadvantage of the Wilhelmy method, however, is that the solid surface must be the same on both sides of the sample. If it is not, the contact angle results will represent some average of the surface characteristics of both sides of the sample. Often solids which are only coated on one side need to be studied. This can be done by the Wilhelmy method if special sample preparation is undertaken, such as folding the sample to expose only one side to the liquid or bonding two samples together back-to-back. This special preparation, however, can be cumbersome, even in cases where it is possible. In such cases, the goniometer method can be more straightforwardly applied.

Summary

Two methods are available for those interested in contact angle measurements on non-porous solids. Each of these methods is characterized by a set of advantages and disadvantages. As a result, the method of choice is largely dependent on an experimenter's application.

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