Application note #2:

Measuring contact angle by the Wilhelmy technique

Contact angles are used as a measure of the wetting interaction between a liquid and a solid. Two techniques are commonly employed: optical tensiometry and force tensiometry. This application note explains how contact angles may be measured using the Attension Sigma Force Tensiometer.

How can contact angle be measured with a force tensiometer?

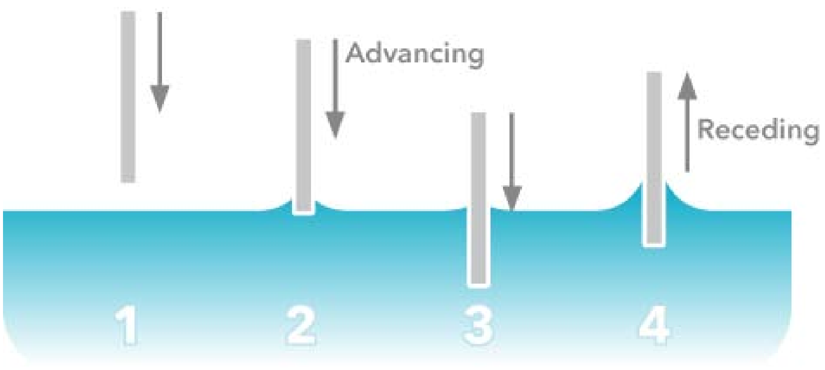
Force tensiometers measure the forces that are present when a sample of solid is brought into contact with a test liquid. If the forces of interaction, geometry of the solid and surface tension of the liquid are known then the contact angle can be calculated. The user first makes a measurement of the surface tension of the liquid using either a Wilhelmy plate or a Du Nouy ring. The sample of the solid to be tested is hung on the balance and tared. The liquid is raised to contact with the solid. When the solid contacts the liquid the change in forces is detected and this elevation is set as zero depth of immersion. As the solid is pushed into the liquid the forces on the balance are recorded. The forces on the balance are:

F(total) = wetting force + weight of probe - buoyancy

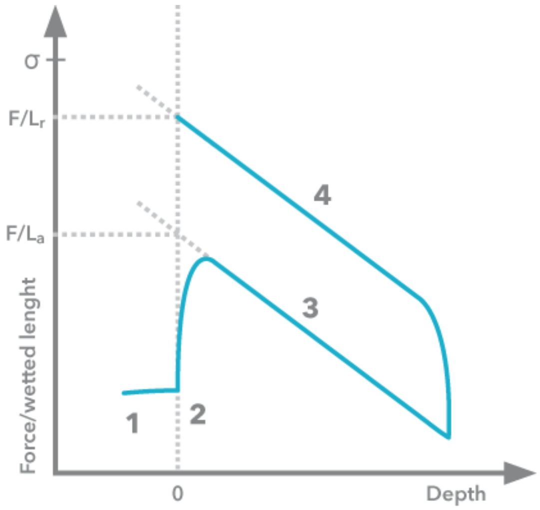
Attension Sigma uses the tare weight of the probe and removes the effects of buoyancy by extrapolating the graph back to zero depth of immersion. The remaining force component is the wetting force which is defined as:

$$\text{Wetting force} = \gamma_{lv} P \cos\theta$$

where γ_{lv} is the liquid surface tension, P is the perimeter of the probe and θ is the contact angle. With a known liquid the surface tension is known and the perimeter of the sample probe is also know. Wetting force is measured, and the contact angle can be calculated from the data obtained at any depth of immersion. This contact angle, which is obtained from data generated as the probe advances into the liquid, is the advancing contact angle. The sample is immersed to a set depth and the process is reversed. As the probe retreats from the liquid data collected is used to calculate the receding contact angle.



The graph of force/wetted length vs depth of immersion appears as follows:



1. The sample is above the liquid and the force/ length is zeroed.
2. The sample hits the surface. For the sample as shown, with a contact angle < 90°, the liquid rises up causing a positive force.
3. The sample is immersed, buoyant force increases causing a decrease in force on the balance. Forces are measured for advancing angle.
4. After having reached the desired depth the sample is pulled out of the liquid. Forces are measured for receding angle.

The contact angles measured in this way are dynamic contact angles. The difference between advanced and advancing (or receded and receding) is that in the first case motion is about to appear and in the latter case the drop is actually moving.

Why don't more researchers use this technique?

The use of force tensiometry to measure contact angles was outlined quite early in the literature of wetting measurements. However, general application of this technique was significantly delayed due to the absence of commercially available tensiometers which had the precision and versatility needed for easy measurement of contact angles. Without a sophisticated tensiometer designed for contact angle measurement the Wilhelmy plate technique is difficult. Sigma 700 and 701 are force tensiometers enabling fast and accurate contact angle measurements.

Control features of Sigma force tensiometers

The two most important considerations when considering a force tensiometer are the quality of workmanship and the quality of the software powering it. Attension produces tensiometers that are unsurpassed in quality. The finest components are integrated into a complete package which is durable, reliable and precise. The software for Sigma is a Windows-based and is simple to use yet provides the widest range of control options available.

The software controls available include;
* speed of wetting
* speed of dewetting
* detection force recognizing interface
* start depth for subsequent cycles
* maximum wetting depth
* sample interval time
* number of cycles tested
* delay between cycles
* automatic taring option

The software contains other pre-programmed experiments which include;
* surface/interfacial tension by DuNouy ring or Wilhelmy plate
* powder wettability
* absorption profiles
* critical micelle concentration

Advantages

The use of force tensiometry for measurement of contact angle has several advantages over conventional goniometry. At any point of the immersion graph, all points along the perimeter of the solid at that depth contribute to the force measurement recorded. Thus the force used to calculate θ at any given depth of immersion is already an averaged value. You may calculate an averaged value for the entire length of the sample or average any part of the immersion graph data to assay changes in contact angle along the length of the sample.

Hysteresis, the difference between advancing and receding angles, is very easy to determine using this method. Using multiple cycles you can identify variations in surface structure and notice adsorption phenomena. Analysis of fibers, very problematic for optical tensiometry, is handled easily by a force tensiometer. Fibers with diameters below 10 microns should give reliable data. It is also easy to test the contact angle of coatings. Simply coat a solid substrate, for example a microscope slide, and test the coated solid.

The references for this note include several papers comparing the efficacy of force tensiometry and optical tensiometry for measuring contact angles.

Limitations

There are two major limitations for the application of this technique. Firstly the user must have enough of the liquid being tested available so that he can immerse a portion of his solid in it. Secondly the solid in question must be available in samples which meet the following constraints. The sample must be formed or cut in a regular geometry such that it has a constant perimeter over a portion of the length. Rods, plates or fibers of known perimeter are ideal. The sample must have the same surface on all sides which contact the liquid. The sample must also be small enough so that it can be hung on the balance of the tensiometer.

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