attension

Application note #6:
Powder Wettability

This application note provides information which may be of use for researchers interested in studying the wetting of powders or porous solids. The suitable tensiometers for testing powder wetting are Attension Sigma Force Tensiometers and Attension Theta Optical Tensiometers. This application note outlines the techniques used to measure powder wetting and gives an introduction to the use of these tensiometers.

What is powder wettability?

Wetting studies usually involve measurement of contact angles as primary data. Contact angles indicate the degree of wetting when a solid and liquid interact. The lower the contact angle the greater the wetting. Contact angles below 90^o indicate that the liquid wets the solid spontaneously (in a thermodynamic rather than kinetic sense). Contact angles above 90^o indicate that the liquid does not wet the solid.

To characterize the wetting behavior of a particular liquid/solid pair you only need to measure the contact angle. It is also possible to characterize the wettability of a solid in a more general way. Various methods are used but the same basic principle applies for each, where the solid is tested against a series of liquids and contact angles are measured. Calculations based on these measurements produce a parameter (critical surface tension, surface free energy, etc) which quantifies a characteristic of the solid which mediates wetting.

The wetting of powders and porous solids also involves contact angle phenomena but is complicated by the presence of a porous architecture. Although various methods are employed to characterize this architecture, contact angles are still the primary parameters used to characterize wetting.

Rough estimates of wettability can be made by placing powders on any given liquid and observing if the solid wets into the liquid (the time required for wetting may also be noted). Solids with contact angles above 90^o will not wet into the liquid. A series of liquids of varying surface tensions can be tested against your solid. Liquids with lower surface tensions yield lower contact angles. For some liquids the contact angle with a given solid will be greater than 90^o and the solid will not wet while with a liquid of lower surface tension the contact angle will be less than 90^o and wetting will occur. Using this crude approach some relevant information on wetting of solids may be found.

How is powder wettability measured?

To produce a quantitative measure of wetting, a contact angle, two approaches are generally used: optical and force tensiometry.

Optical tensiometry: Theta

The optical tensiometry approach to contact angles involves placing a drop of liquid on a flat solid surface and analyzing the shape of the drop formed. With either a porous solid or powder packed to approximate a flat surface, penetration of the liquid into the pores or spaces between particles may occur. If the real contact angle between the liquid and the solid is less than 90^o 'spontaneous' penetration will occur. Spontaneous, as used in this context, refers to the thermodynamic favorability of the event. The actual rate of penetration may vary considerably. In some cases it may occur so slowly that reasonable values of contact angle may be measured. In other cases the penetration occurs quite rapidly. Researchers interested in studying the dynamics of wetting in this situation can use Theta goniometer to capture changing contact angles at high speed. Theta is capable of recording at 60 msec intervals and contains an on-screen trigger. This exclusive feature allows the researcher to begin the recording based on the occurrence of specific events, such as contact of liquid with the solid surface. Using this approach the researcher can produce data on the changes in apparent contact angle vs time to quantify the wetting behavior.

If the real contact angle of the interaction is greater than 90^o penetration should not occur and reproducible contact angles may be measured.

Force tensiometry: Sigma

The force tensiometry approach may be used to measure contact angles of, for example powders and porous solids. The Wilhelmy method for measuring contact angles has significant limitations when applied to powders. Some strategies include binding the powder to a solid substrate and proceeding to measure contact angle on the sample produced. Interactions with the binding element (eg tape) and quantification of the amount bound introduce factors which may affect results. An alternate approach is therefore recommended. This approach applies the Washburn theory of wetting of porous solids.

Washburn Method

According to this theory when a porous solid is brought into contact with a liquid the rise of the liquid into the pores of the solid will obey the following relationship:

$$T = [\eta / C \rho^2 \gamma \cos\theta] M^2$$

The terms are defined as follows:

T = time after contact

η = viscosity of liquid

C = material constant characteristic of solid sample

ρ = density of liquid

γ = surface tension of liquid

θ = contact angle

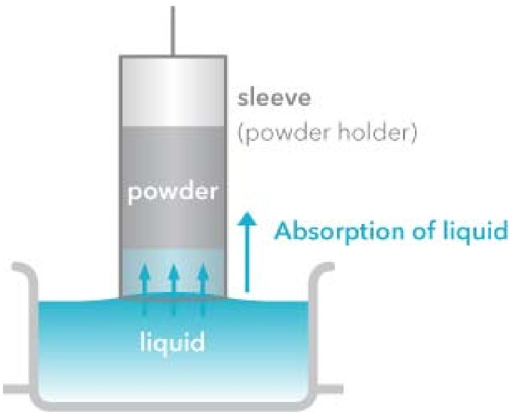
M = mass of liquid adsorbed on solid

An experiment is performed where the mass of the adsorbed liquid is measured vs time. A graph of Time vs $Mass^2$ should yield a straight line whose slope is $\eta / C \rho^2 \gamma \cos\theta$. If viscosity, density and surface tension (found using the same tensiometer) are known from separate experiments there are only two unknowns left in this term, contact angle and C the material constant for the solid. To resolve this situation an experiment is performed in which the contact angle may be assumed to be zero. This should occur when a liquid with very low surface tension is used. N-hexane would be an appropriate choice. When such an experiment is performed, the material constant for the solid may be solved for.[slope = $\eta / C \rho^2 \gamma$]. It is then possible to perform the same experiment with any test liquid and calculate the contact angle for that system. Washburn experiments thus involve testing your solid with a completely wetting liquid, assuming $\theta = 0$, and solving for C. Then, assuming C is constant, you test the same solid against various liquids to find contact angles.

Factors effecting C: The logic of this method only holds in situations where C can be assumed to remain constant for a given solid from one experiment to the next. C, the material constant, is a term which reflects the porosity of the solid and the packing of particles (in the case of powders). Because this value is *assumed* to be constant in the Washburn method any actual variation will generate error in the calculation of contact angles. It is therefore critical to attempt to insure that C actually is constant.

Porous Solids The material constant C reflects the number and orientation of the pores present in the solid sample. If you are testing porous solids that retain a definite shape (i.e. paper, fabric, etc) you need only insure that each sample has the same size, shape and orientation.

Packing For testing powders the material constant will depend on the porosity of individual particles and the packing of the particles. If all samples of your powder are from the same source the porosity may be reasonably assumed to be constant. The major variations in actual C values are usually due to variations in the packing of powders. Various methods have been attempted to try to assure consistent packing and you are welcome to try any technique. Most researcher use a technique which involves using a reproducible force to pack a known mass of powder into a sleeve with a porous bottom (either scintered glass or screen lined with filter paper). The interaction of the sleeve containing the powder and the liquid interface is diagrammed below.



In any case the container which you use to hold your powder will also contribute to the change in forces when it contacts the surface. Especially in the first few seconds the container may contribute a significant amount to the total changes of force on the balance. It is therefore useful to be able to subtract out the contribution of the container in the adsorption graphs. This can be done automatically by your Sigma software. Your containers may be tested, when empty, against a liquid of interest and you may then use that data file to subtract out the contributions of the empty container when testing solids against the same liquid.

All these procedures(including measuring surface tension) may be performed using a Sigma tensiometer. The software for these experiments includes the following features:

* real time graphics of results
* automated taring
* automated stage movement
* automatic detection of interface

* control of: - probe speed

- immersion depth
- sample interval
- force indicating interface

* data reduction including:

- calculation of material constant
- calculation of contact angle
- automatic subtraction of container effects
- automatic recalculation after parameter edit

The software for these experiments is included in the Sigma 70 package along with experiments for:

- Surface and interfacial tension by DuNouy ring or Wilhelmy plate
- Wilhelmy technique contact angles
- Automated critical micelle concentration determination

References:

D.Meyers, Surfaces,Interfaces & Colloids, VCH Pub,N.Y. (1990)

A.Marmur,in Modern Approach to Wettability,M.E.Schrader,G.Loeb, eds,Plenum Press, N.Y.(1992)

E.W.Washburn, *Phys. Review*, 17,374-382,1921

K.T.Hodgson,J.C.Berg, *J.Colloid Interface S*