

A novice's guide to the DCA

A number of new DCA users who have had no prior experience with the Dynamic Contact Angle Analyzer (or the Wilhelmy technique in general) have asked me to write a simple guide in plain English which describes how to use the DCA. Before we get into the HOW, let's start with the WHY. Why should anyone in R&D be interested in using the DCA. Of course there are many WHYS, but here are five real life examples:

WHY #1 Polymer film „A“ is less prone to static electricity and can be coated more evenly than film „B“. Both films are made from the same material and they both look and feel the same. How can we distinguish film „A“ from film „B“?

WHY #2 A carbon fiber/PEEK composite made with a plasma treated carbon fiber forms an adhesive bond with the PEEK resin that is 40% stronger than an equivalent bond with the same untreated carbon fiber?

WHY #3 One manufacturer of a line of hard contact lens products is baffled by the success of a competitor who buys the raw material from the same source. A survey of contact lens wearer's reports that the competitor's product was found to be more comfortable in the eye, required less stringent cleaning, and could be worn for longer durations. What is the competitor's secret?

WHY #4 The „old“ ink formulation supplied by company X has been replaced by a „new and improved“ formulation also supplied by company X. The „new“ formulation has, according to company X, only minor differences in one surfactant and an additive that is safer toward the environment. The surface tension of both formulations is identical, so why does the new ink tend to run when applied

to the coated board material when the old formulation does not?

WHY #5 Tablet A is a generic of a popular pain reliever that is made using the same active ingredient as the original house drug. In a blind test survey of consumers, the generic was found to be slower acting and more difficult to swallow. What makes the house drug work better than the generic?

You only have to scan the surface to find the answer to all five WHY's because the answers, although slightly different in each case, are all traceable to surface wetting properties that are invisible to the naked eye. And in some cases, these differences are even invisible to sophisticated high vacuum surface analysis instruments like the ESCA or the AUGER spectrometer.

Dynamic Contact Angle Analysis is one of the simplest, yet most powerful techniques available for characterizing the top ten angstroms of a solid surface. But how does it work?

When a liquid comes in contact with the surface of a solid, the liquid will either spread out to a certain degree onto the surface and thus „wet“ or „partially wet“ the surface, or it will form a cluster or ball of liquid that „repels“ or „de-wets“ the surface. It is the nature of this interface between a solid and a liquid that is probed by the DCA and provides important insight into the chemistry or wetting thermodynamics of the surface.

A good practical example of wettability at work in everyday life is the painted surface of your automobile. When drops of rain fall onto the hood of a newly waxed car, the drops form beads that can easily roll off the hood when it is tilted at an angle. The same water drops on an unprotected car hood will form

small puddles of water that streak and do not readily roll off the surface. In the first case, the car with the waxed surface is protected by an organic hydrophobic coating (the wax) that repels water and promotes droplet formation. The unwaxed car has a surface that is more hydrophilic because the unprotected painted metal surface is more wettable than the wax covered surface. Thus, water will tend to spread out rather than form beads on an unwaxed metal surface.

Using a liquid as Probe of a Solid Surface

There are two fundamental ways to use the wettability concept when analyzing a system. The first way is to use a liquid (or several liquids) as the known standard to probe the unknown solid surface. The surface tension and polar component of the surface tension of each liquid is the „known“ in this scenario. When each liquid is brought into contact with the solid, an interface is formed that is characteristic of the attraction of the liquid for the solid. This parameter is known as the contact angle. The contact angle has a range from zero degrees (complete wetting) to 180 degrees (complete nonwetting).

A common reason for performing a series of contact angle measurements is to measure the so-called „surface energy“ or „critical surface tension“ of the unknown solid. This number can be calculated by a variety of mathematical treatments, but in all cases the contact angle with at least two different liquids is required. If the surface tension of the liquid is less than the surface energy of the solid, the liquid will try to spread out onto the surface and form a 0° wetting angle. Therefore it is important to choose liquids for a contact angle measurement that will form a positive wet-

ting angle with the solid (between 30 and 150 degrees is ideal). In addition, it is important to choose only liquids that will not interact in any way with the solid (i.e. penetrate the pores or form a chemical reaction). Finally, it is also important to choose a series or pair of liquids that have different polarities for best results. For example, water, a highly polar liquid with a high surface tension (72.6 dynes/cm) and methylene iodide, a non-polar liquid also with a relatively high surface tension (50.8 dynes/cm), are used extensively as a pair when performing a surface energy calculation.

Contact angle can also be used in a qualitative sense to probe the uniformity or homogeneity of a surface. The difference between wetting angles when the liquid is advanced over the surface as opposed to when it is receded over the surface (the contact angle hysteresis) is an important parameter that is easily measured with the DCA. In general, if the solid surface is completely smooth and uniform, there will be no hysteresis in the wetting angles. This can serve as a good parameter, for example, in a cleanliness evaluation of a solid surface.

Using a Solid as Probe of a liquid Solution

The second way to use the DCA is in reverse- to completely characterize the surface tension characteristics of a liquid by first using a known solid such as glass or platinum that is completely wet by the liquid. Once the total surface tension of the liquid is known, the polar and dispersive components of the liquid surface tension can be determined by measuring the contact angle of the liquid against a non-polar solid such as Teflon or polyethylene. With this information, a calculation can be made to characterize the liquid by polarity and surface tension. This can be especially useful when formulating an ink or coating solution to match the polarity of a film or other solid surface and therefore maximize adhesion at the interface.

Using the DCA: How to approach and perform a Dynamic Contact Angle Experiment

The DCA is a research tool that when used properly can be a valuable problem solver for the R&D laboratory. Before you begin to use the DCA, it is important to understand and plan an effective strategy.

STEP #1 Plan an Effective Strategy
Avoid the temptation to combine all aspects of the system you are studying into one experiment. This is a common mistake made by the novice DCA user. For example, if you are studying the adhesion of a coating formulation onto a Teflon mandrel, the initial reaction may be to use the DCA to try to measure the contact angle of the coating formulation directly onto the Teflon mandrel.

Since the coating is naturally going to adhere to the surface of the Teflon, however, the data from a contact angle experiment of this kind will probably be difficult to interpret.

Alternatively, if standard high purity probe liquids were selected that did not adhere to the surface, the wettability of the surface could be readily determined. Using this approach, the surface energy components of both Teflon substrate and coating material could be evaluated via a simple Work of Adhesion analysis.

STEP #2 Select Good Probe Liquids
Selecting the right probe liquids is an important part of any contact angle measurement. Ideally, a liquid can be considered a viable probe liquid for a dynamic contact angle experiment if it does not swell, adhere to, or react with the solid surface. A good way to evaluate the appropriateness of a probe liquid is to use an eye dropper or syringe to deposit a drop or two of the liquid onto the surface and observe what happens to the drop. If it is immediately absorbed into the solid, or completely spreads out across the surface, eliminate this liquid and move to the next one. Any liquid that is readily absorbed into the solid will add to the force and thus obscure the contact angle calculation. The small molecular volume of a water molecule makes it a good candidate for pore penetration.

And any liquid that completely wets the solid to make a contact angle

near zero is also inappropriate since any contact angle less than 10 degrees is difficult to measure. If the goal is to determine the surface energy of a solid, select a pair or series of high surface tension liquids with a good balance between polar and non-polar characteristics. Water and Methylene Iodide are often selected as probe liquids since they both have high surface tensions and water is a very polar liquid while methylene iodide is highly non-polar. Always use the highest purity liquids available for best results and use only well cleaned beakers to preserve the quality of the data.

STEP #3 Characterize the Surface Tension of Each Probe Liquid Selected
Use high quality, clean, glass cover slides or a roughened platinum plate or wire for the surface tension measurement. To clean the glass slips, it is generally best to wash in a dilute chromic acid solution, rinse thoroughly with distilled water (use a sonicator bath to thoroughly rinse if available) and then pass through a blue oxidizing flame (i.e. propane torch). If the slides are very clean in the beginning, it may be possible to skip the chemical cleaning step and proceed with only the flame cleaning procedure. Take care not to warp the glass by moving it continuously through the flame and make sure both faces are exposed to the flame. Platinum plates are generally sand-blasted and platinum wire roughened with emery paper to increase the wettability before being brought to a red-hot glow in a propane flame.

If a surface energy measurement is the goal, select a pure sample of Teflon or polyethylene and make a contact angle measurement with each probe liquid. Use the DCA Applications Software to calculate the surface tension components (polar and dispersive) of each probe liquid.

STEP #4 Use Probe Liquids Selected in Step #3 to Run a Dynamic Contact Angle Measurement

There are several key points to remember when undertaking a dynamic contact angle experiment. The perimeter of the solid, for example, must be accurately measured. For a flat rectangular-shaped sample this can be easily done with a good precision micrometer. A digital micrometer is recommended for the

novice to save time that might otherwise be spent trying to read the scale imprinted on the micrometer. The solid must be suspended vertically from the balance to insure a perpendicular interface is made when the liquid makes contact with the solid. And when programming the experiment, always run at the slower speeds (i.e. less than 150 microns/second) to avoid speed-related errors and scan enough of the sample to provide enough data points for the linear regression analysis.

For small samples (i.e. fibers) with short scan distances, use the slowest speeds (i.e. less than 20 microns/second) to increase the number of data points available for analysis. It is also important to make sure the solid sample fits comfortably inside of the probe liquid beaker without coming in close contact with the walls of the beaker. A good rule of thumb is to keep the diameter of the sample less than 70% of the beaker diameter to avoid wall effects.

Finally, use the ionizing unit provided in the DCA accessory kit to eliminate static from the solid sample before starting the experiment. This is particularly important for polymer films and other static prone materials. When static is a problem, the force baseline will drift in one direction even before the solid comes in contact with the liquid.

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