

Application Report

Characterization of swellable nonwovens

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Wettability of Swellable Nonwovens - Determination of Contact Angle Against Swellable Nonwoven Material

Abstract

A variety of different experimental methods are available for the determination of contact angles for liquids against solid samples. Standard optical and Wilhelmy methods become difficult or impossible to solve if a sample swells when exposed to the liquid of interest. For many samples, the Washburn method becomes the experiment that can be performed with the best reproducibility. Although the Washburn results may be reproducible, the results can still be erroneous when the solvent of interest swells the sample. This is often the case with water contact angles measured against many super absorbers, natural products, and personal products. A method is shown below for extracting accurate contact angles for samples that swell in the presence of the liquid of interest.

Introduction to the Washburn Method

Washburn theory indicates that if a porous solid is brought into contact with a liquid, such that the solid is not submerged in the liquid, but rather is just touching the liquid's surface, then the rise of liquid into the pores of the solid due to capillary action will be governed by the following equation:

$$\cos \theta = \frac{m^2}{t} \frac{\eta}{\rho^2 \sigma c}$$

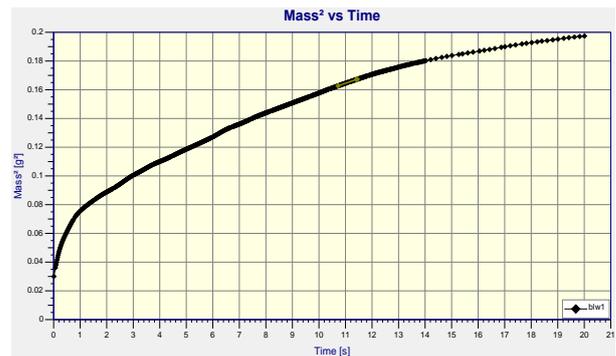
In setting up a Washburn experiment, a liquid with known density (ρ), viscosity (η), and surface tension (σ) should be used. An inspection of the equation above leads to the conclusion that if this is the case, and the mass of liquid which rises into the porous solid can be monitored as a function of time (such that m^2/t is the raw experimental data), then two unknowns remain: the contact angle of the liquid on the solid (θ) and the solid material constant (c).

However, if a Washburn experiment is performed with a liquid which is known to have a contact angle of $\theta = 0^\circ$ ($\cos \theta = 1$) on the solid, then the solid material constant (c) is the only remaining unknown in equation 3 and can thus be determined. N-hexane is typically a good choice as the liquid for determining material constants, because of its low surface tension (18.4 mN/m) at room temperature.

Once the material constant (c) has been determined for a particular solid, a second sample of the solid can be tested for wettability by another liquid. The material constant determined by the n-hexane test is simply used in the Washburn equation, in combination with m^2/t data obtained during testing with the second liquid. This allows calculation of the contact angle between the second liquid and the solid.

Washburn adsorption experiments can be easily and automatically performed on a variety of porous materials using a Krüss Force Tensiometer – K100 in combination with Krüss LabDesk software in the Adsorption mode.

This solid material constant (c -factor) contains information regarding the pore structure, pore size, and number of pores in the solid sample. This must remain constant during an experiment for the resulting contact angle measurements to be correct. For swelling solids the pore structure will change, creating a change in the c -factor. Usually the data for such an experiment becomes non-linear and can have a gentle sloping curve something like that shown below:



Since the contact angle depends on the slope of the curve in the above data, the chosen section of data for the measurement can affect the contact angle value that is calculated from this slope. If the data closer to the beginning of the experiment were analyzed the slope would be greater than that if data near the end of the experiment were used. This would provide a lower contact angle for data chosen at the beginning of the experiment than at the end of the experiment. Although data that can have comparative merit can be extracted from such curves if the same region of interest on the curves, the ideal situation would be to have no sloping curve and have a true, accurate contact angle value.

Indirect Determination of True Contact Angle

If the solvent of interest for an experiment (water in this case) cannot be measured directly, it is best to find a group of solvents for which an accurate contact angle can be determined. Then, the subsequently calculated surface energy for the sample can be used to determine the theoretical contact angle for the liquid of interest that initially caused swelling on the sample.

In the case shown here, our customer wished to determine the contact angle of water on their nonwoven pleglett material which was used to create a feminine hygiene product. Measurements with water created swelling in their sample giving unreliable results. However, with a more organic solvent such as benzyl alcohol, no swelling took place and a straight m^2/t dependence was achieved. Diiodomethane, a common solvent used in Fowkes analysis of solid surface energies, also produced overall results similar to those achieved with benzyl alcohol. No swelling occurred and a proper m^2/t curve was achieved.

| | Benzyl Alcohol | Diiodomethane |
|-----------------------------------|----------------|---------------|
| Overall Surface Tension (mN/m) | 39.0 | 50.8 |
| Polar Surface Tension (mN/m) | 8.7 | 0 |
| Dispersive Surface Tension (mN/m) | 30.3 | 50.8 |

The surface tension for diiodomethane shown above demonstrates why it is an ideal candidate for solution of surface energies by the Fowkes method. The absence of any polar component allows for the Fowkes equation below:

$$(\sigma_L^D \gamma_s^D)^{1/2} + (\sigma_L^P \gamma_s^P)^{1/2} = \frac{\sigma_L(\cos \theta + 1)}{2}$$

(where σ_L denotes liquid surface tension, γ_s solid surface energy, P the polar component, D the dispersive component, and θ the contact angle) can now be simplified to:

(where σ_L denotes liquid surface tension, γ_s solid surface energy, P the polar component, D the dispersive component, and θ the contact angle) can now be simplified to:

$$\gamma_s^D = \frac{\sigma_L(\cos\theta + 1)^2}{4}$$

After solving for the dispersive component of surface energy above, the full Fowkes equation can then be used to calculate the polar component of surface energy as well. For the pleglett samples tested here the following contact angles and surface energies were determined.

| | Data For Pleglett Material |
|------------------------------|----------------------------|
| Benzyl Alcohol Contact Angle | 6.2 degrees |
| Diiodomethane Contact Angle | 72.0 degrees |
| Polar Surface Energy | 20.0 mJ/m ² |
| Dispersive Surface Energy | 21.75 mJ/m ² |
| Overall Surface Energy | 41.75 mJ/m ² |

When the surface energy components for the solid have been calculated, the contact angle of water can then easily be solved by the following rearrangement of the Fowkes equation using the standard water surface tension values. Overall 72.8 mN/m, polar component 26.8 mN/m and dispersive component of 46 mN/m.

$$\theta = \arccos\left(\frac{((\sigma_L^D \gamma_s^D)^{1/2} + (\sigma_L^P \gamma_s^P)^{1/2}) * 2}{\sigma_L}\right) - 1$$

This finally produces a theoretical water contact angle on the swellable pleglett sample of 59.7 degrees.

Conclusions

Sometimes the contact angle of a liquid of interest cannot be determined against a sample due to swellability, solubility, or any other similar sample changing phenomenon. Do not panic! There is a method which can determine this angle. First determine a set of solvents with a variety of polar and dispersive components to their surface tension which does not create a physical problem with your sample. Then calculate the surface energy of your sample by using the Fowkes method shown earlier. Once the surface energy of the sample is known, these values along with the surface tension values of the troublesome solvent can be used in a rearrangement of the Fowkes equation to indirectly determine the contact angle of the solvent against the porous solid.