Application Report

Characterization of Porous Coatings

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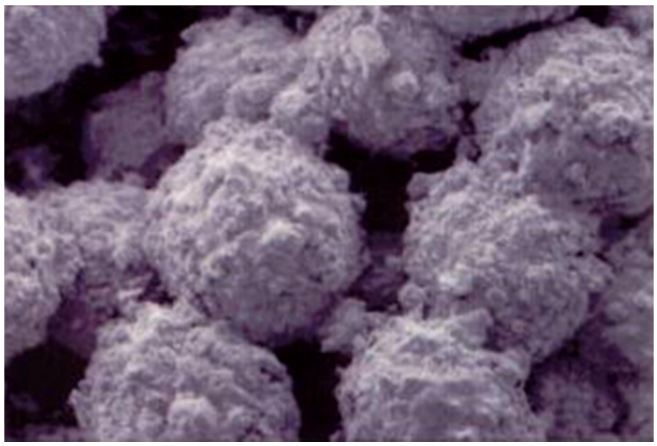
Force Tensiometer – K100

Drop Shape Analysis System DSA10

The Washburn "C" Factor for Characterization of Porous Coatings

Abstract

Porous coatings find application in a wide variety of industrial, military, and medical applications. For example, porous photo and electro catalytic coatings are used in applications ranging from chromate production to cyanide destruction – and are also being explored for use in air and water treatment. In the medical field, porous coatings are used on the surface of replacement joints to promote a stable bone-implant interface by providing support for both ingrowth and ongrowth. Porous coatings are also widely used to support various reagents for blood and plasma analysis on diagnostic strips and slides.



SEM of a Porous Bone Implant Surface

The vast majority of porous coatings are deposited on surfaces from emulsions and colloidal dispersions containing polymeric, inorganic, or even metal particles, having a typical "bead" size of anywhere from 200 µm down to 5 µm. The "bead" size and size distribution, as well the interactions between the beads during coating deposition, and post-treatment (heat or other) determine the porous properties of the coating.

Characterization of Porous Coatings

For a manufacturer of porous coatings, it obviously is of interest to be able to characterize, and, better yet, to control, a) the porous structure of the coating, and b) its wettability with liquids of interest (such as blood or other bodily fluid in the case diagnostic test materials).

Most commonly, mercury porosimetry and nitrogen adsorption techniques are used to determine pore size and pore size distribution in porous materials. And, techniques such as the Washburn wicking technique are used to determine the characteristic wetting angle of fluids imbibed into the coating. (The Washburn method is described in detail at KRÜSS application note #302, www.kruss-scientific.com).

However, we routinely employ the Washburn technique in both capacities – as a measure of wettability, and a measure of relative porosity – with successful sample differentiation which is often more reproducible than nitrogen sorption data, and is more directly related to real wetting phenomena, than is high pressure mercury porosimetry.

A case in point was some work we recently performed for a company making a porous coating from a polymeric bead dispersion (with absorbed protein), for a medical testing application. The goal was to fixate on a manufacturing process which would consistently produce a porous coating that would allow blood to spread, and more importantly imbibe, at a controlled rate.

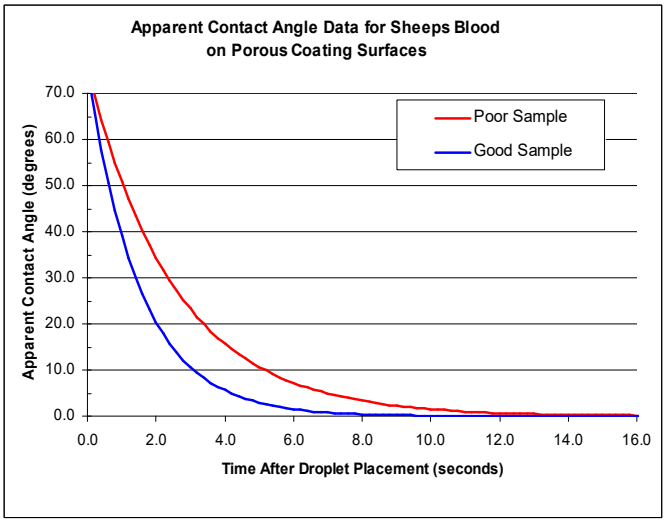
The customer initially had two coatings, of basically the same manufacture, with the exception of coating application and temperature conditions. But, they were finding more rejected samples from an automated diagnostic test device with one of the coatings versus with the other. The failures were presumably due to inefficient spreading and interior wetting rate for blood on the bad coating. The coatings were both 50.8µm thick, and cast on a polyester substrate.

Coating Sample	Material Constant with Silicone Oil 2.5 cm x 2.5 cm Samples (cm^5)	Contact Angle With Sheep's Blood (deg)
Good	1.456×10^{-5}	65.1
Poor	2.562×10^{-6}	65.4

The customer was uncertain whether the problem was due to some difference in the surface energy of one of the coatings (and thus its wettability with the blood, as could be judged by contact angle) or some difference in porosity of the coating, due to changes in application conditions. They had performed mercury porosimetry, on both coatings, and found similar pore size distributions on both samples - centered around 5.0 µm. However, the coatings (normally 50.8 µm thick) had to be made much thicker to accommodate the mercury testing, and damage or compression of the pore structure was thought to have potentially occurred during the mercury porosimetry testing.

Experimental data

We first confirmed their observations about the differences in wetting rate between the two samples, using a KRÜSS Drop Shape Analysis System DSA10, and studying apparent contact angle as a function of time as a drop of blood soaked into each sample. Results from one drop of sheep's blood (several were tested – with good reproducibility) dropped onto each coating sample are shown below.



Indeed, the blood took about 13 seconds to imbibe and spread into the poor sample, as opposed to only about 8 seconds for the good sample. However, whether this is due differences in fundamental wetting properties, or simply differences in pore structure is not clear from such apparent contact angle data.

Next, we cut 2.5 cm x 2.5 cm squares of the each sample, and tested them for internal contact angle in Washburn wicking experiments on a KRÜSS K100 Tensiometer. (Following the techniques described in detail in application note #302 or #402). Samples were tested with the polyester substrate attached. A low molecular weight silicone oil was used as the perfectly wetting liquid for "c" factor determination, and the results are shown below.

Multiple tests showed good reproducibility in contact angle, and no statistically significant deviation in contact angle between the two samples. All contact angles determined were very close to the 0.5 second contact angle realized in the apparent contact data given above for both samples.

However, rather large differences were consistently seen in the "c" factor, between samples of the two types, cut to the same size. This lead to the conclusion that the difference between the samples was more in terms of pore size than in terms of wettability, as related to surface energy. In other words, the data tell us that the two samples have relatively the same fundamental chemical properties. Their pore structure is what is different.

Given that, theoretically, the material constant determined in Washburn experimentation is equal to:

$$c = \frac{1}{2} * \pi^2 * r^5 * n^2$$

wherein "c" is the material constant, r = the average pore radius, and n = the number of pores in the sample. If we were to test the same samples, but cut them to a different size (in other words change "n"), we should determine a different "c' factor, but the same contact angle.

In fact, this was the case for these samples. When they were tested by the Washburn technique as 5.0 cm x 2.5 cm samples, with the 5.0 cm edge being brought into contact with the test liquids. The following data were obtained.

Coating Sample	Material Constant with Silicone Oil 5.0 cm x 2.5 cm Samples (cm^5)	Contact Angle With Sheep's Blood (deg)
Good	5.903×10^{-5}	65.3
Poor	1.022×10^{-5}	65.5

Additionally, since both size samples became completely imbibed with fluid, and the vertical rise of liquid was held constant, so we can assume that "n" in this case is two times "n" in the case of the 2.5 cm x 2.5 cm sample testing – or that the "c" factor should be 4 times higher for a 5.0 cm x 2.5 cm piece versus a 2.5 cm x 2.5cnm piece. This was, in fact, the case (Good = 5.903×10^{-5} / 1.456×10^{-5} = 4.05, Poor = 1.022×10^{-5} / 2.562×10^{-6} = 3.99), further justifying that the difference between the two coatings was in size and possibly number of pores, and not in surface properties.

Conclusions

Using the Washburn technique for characterization of both relative pore size and contact angle has both advantages and drawbacks. On one hand, the average pore size is not absolutely determined. In the case above, we can calculate that the poor coating has a r^5n^2 value which is 5.8 times lower than the good coating. But, we have no indication of the average pore radius, or number of pores, independently from one another. However, on the other hand, the "c" factor analysis shows good differentiation between the two samples, whereas mercury porosimetry (which is a more difficult technique, particularly on thin coatings) had not.

After further testing, with different process conditions, this particular customer choose to use "c" factor analysis with silicone oil as a quality control specification, setting it at between 1.0×10^{-5} and 1.75×10^{-5}, as measured on a 2.5 cm x 2.5 cm sample, for acceptable performance. Other types of samples, may obviously have both porosity based and surface property differences, which can, of course, be judged separately by the same technique.

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