Application Report

Wetting of fibers

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Industry section: Polymer, textile, cosmetics
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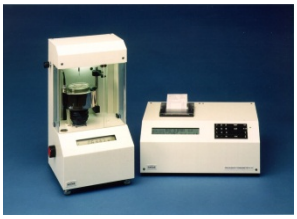
Single Fiber Force Tensiometer – K14



Force Tensiometer – K12

Method:

Keywords: glass fiber, nylon fiber, hair, composite, wetting, straw method, packed cell method, single fiber method, fiber coating

Contact Angle Determinations by the "Straw" Method and Packed Cell Method:

Good Alternatives to Arduous Single Fiber Contact Angle Experiments

Background

Contact angle is the quantitative measure of wettability for a solid surface being wetted with a liquid, which ranges from 0^{o} (perfect wetting) to 180^{o} (complete non-wetting). It is, therefore, often important to measure the contact angle of liquids against all types of solid surfaces. Small diameter fibers are no exception. Examples include glass, carbon, polymeric, and natural fibers including hair. Such fibers are maybe finish-treated, dyed, and/or used as reinforcing materials in composites, amongst other applications. Their wettability needs to be accessed to determine how well they are likely to perform in their intended application.

For example, a carbon fiber that does not wet well with the matrix material (usually a monomeric liquid to be polymerized) which it is teamed with to form a composite will cause weak bonding at the fiber/matrix interface. This, in turn, leads to a weak composite. A textile fiber that does not wet well with a certain dye may end up becoming irregularly colored.

We measure contact angle on all types of fibers in our laboratory – for any of a variety of applications. Some of the fibers have circumferences of more than 100 microns (0.1 mm). Some are much smaller – circumferences of less than 10 microns.

Single Fiber Contact Angle Measurement

The "traditional" method of measuring contact angle on such fibers is the Wilhelmy technique, using a single fiber. The Wilhelmy technique involves dipping a single fiber into a non-penetrating liquid while measuring the force on the fiber due to wetting. An advancing (wetting) contact angle for the liquid on the fiber is determined from force data obtained during submersion of the fiber into the liquid. A receding (dewetting) contact angle is likewise determined from force data pertaining to the removal of the fiber from the liquid. See Figure 1 below.

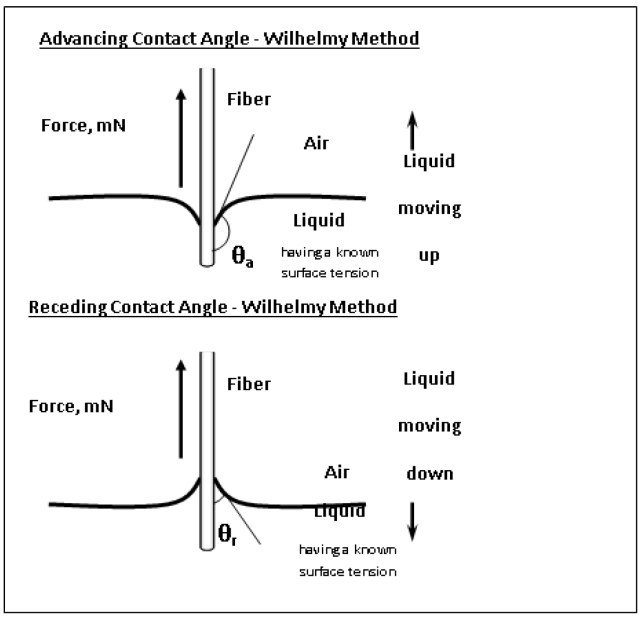


Figure 1

Contact angles are calculated from force data using the Wilhelmy equation.

$$cos\theta = \frac{F - F_b}{l\sigma}$$

wherein θ = the contact angle, l = the fiber's wetted length (circumference), σ = the surface tension of the liquid, F = the total force felt by the fiber at any submersion position, and F_b = the buoyant component of the force on the fiber at any submersion position. F_b is due to the fiber displacing liquid as it is submerged and removed. It is, in general, a distraction to Wilhelmy contact angle experimentation, since the contact angle depends on the Wilhelmy force (F_w) only, which is the wetting force, or the total force felt by the solid (F) less the buoyant force (F_b). Hence, $F_w=F-F_b$ as used in the Wilhelmy equation above.

Figure 2 shows raw force versus submersion position data from a Wilhelmy experiment on water wetting a human hair. These data were collected with Krüss Single Fiber Tensiometer K14. The "force" in the raw data presented in this plot is F, not yet corrected for the buoyant force. As a result, the plot is an out-and-back trace of the force felt by the hair as it is submerged into and removed from the water.

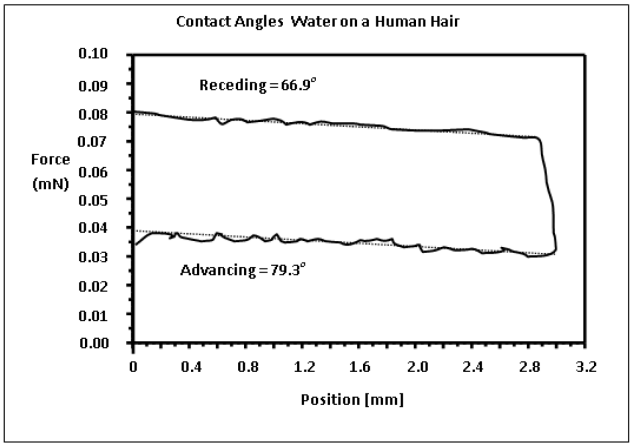


Figure 2

The lower set of forces reported on this plot at each position are forces (F) during submersion. During submersion, the buoyancy force pushes upward on the hair and F_b is negative. (Forces in the upward direction on the sample are defined as negative and forces in the downward direction are defined as positive.) The Wilhelmy force on the solid can be either positive or negative during submersion, depending on whether the advancing contact angle on the sample is less than 90° (F_w = positive) or greater than 90° (F_w = negative). As a result, during submersion of the sample, the total force ($F=F_b+F_w$) versus position data can be either positive or negative. *In the above example F_w is positive and greater than F_b at all immersion depths, therefore the force (F) is always positive*.

For a uniform sample, the force (F) linearly decreases as the sample is submerged, because the Wilhelmy force (F_w) remains constant and the buoyancy force (F_b) becomes more negative. Extrapolation of the linear portion of the force versus position data for submersion of the sample back to zero position thus provides a value of force (F) equal to the Wilhelmy force (F_w) on the fiber during submersion, because $F_b=0$ at (and only at) position zero. This value of F_w is thus used to calculate the advancing contact angle of the liquid on the fiber. The receding contact angle is likewise calculated from extrapolating the removal portion of the force versus position curve to position zero, where there is no buoyant force. For this hair/water example, the advancing contact angle is 79.3° and the receding contact angle is 66.9°.

The Difficulty with Single Fiber Contact Angle Experimentation

Human hair, however, turns out to be one of the less difficult small fibers to measure by the single fiber Wilhelmy technique. Although it does not typically have a uniform circumference along the shaft, it does typically behave quite nicely when tested by the single fiber method. Many fibers are much more difficult to test by the "traditional" single fiber technique. Common difficulties include the following:

- Curling at the Surface

  Many small fibers (particularly those with circumferences of less than about 100 microns) tend to be flexible enough to bend upon initial contact with the surface of the liquid. Even if they have contact angles of less than 90° against the test liquid, the surface tension of the test liquid is often enough force to curl the contact end of the fiber upward away from the liquid's surface. This makes measurement by the Wilhelmy method impossible without further special preparations.

- Irregular Wetted Length (Circumference)

  Since one must know the circumference of the fiber as a prerequisite for single fiber contact angle measurement, if the fiber varies in circumference along the shaft, then the Wilhelmy force will be at different as a function of depth. It is typically impossible to correct the raw force data for this, because the fiber has not been studied closely enough to know exactly where its irregularities in circumference are. This causes "noise" in the force versus immersion depth data – such as the noise that you see in hair data presented above. This noise is ignored when a best-fit extrapolation line is placed through the data to achieve a contact angle value. However, there is no guarantee that even the average circumference will be maintained if a second fiber of the same material is tested for contact angle. Therefore, reproducibility has the potential to be quite poor for single fiber contact angle experiments.

  As an example, it is common for 30 micron glass fibers to vary in circumference by ± 1 micron along the shaft. If you measured a contact angle of 50° with water (surface tension = 72.5 mN/m), on a glass fiber using 30 microns as the known circumference, then you measured the Wilhelmy force (F_w) as 1.398×10^{-3} mN (this comes directly from the Wilhelmy equation given above). However, if you happened to have measured this Wilhelmy force on a section of the glass fiber shaft where the circumference averages only 29 microns, then the angle you should have calculated is 48.3°. This is a difference of 1.7° – and that's a good situation. Had the angle been closer to 0° the deviation would have been greater, since the cosine function gets very sensitive at low angles.

- Small Forces

  This is a bit simplistic, but well worth stating anyway. The wetting forces that are measured on small fibers are very small forces. Take the above example for instance. We had a Wilhelmy force (F_w) of 1.398×10^{-3} mN. Such forces are commonly measured with a microbalance. That's the way they are measured in the Krüss Single Fiber Tensiometer K14. However, this Wilhelmy force converted to micrograms is only 140 micrograms. A balance used to sense this type of force must be very stable. Even temperature fluctuations have a significant effect on balances in this range. So you must make the measurements in a stable environment free of vibrations.

- Penetrating Liquids

  In making a Wilhelmy contact angle measurement, it is assumed that all the force felt by the sample during submersion into a liquid is due to the Wilhelmy force (F_w) of the liquid wetting the exterior of the sample and buoyancy force (F_b). If the fiber is porous, so that it can imbibe liquid, this causes an error in the measurement. Based on the discussion of small forces given above, you might imagine that the fiber doesn't have to imbibe much liquid to cause a significant error in the calculated contact angle.

These difficulties have caused us to seek alternatives to single fiber contact angle measurement.

The "Straw" Method (for flexible fibers with lengths greater than about 3 inches)

The alternative that we use the most often is something we call the "straw" method. Fibers are prepared for "straw" method contact angle testing as depicted in the following diagram:

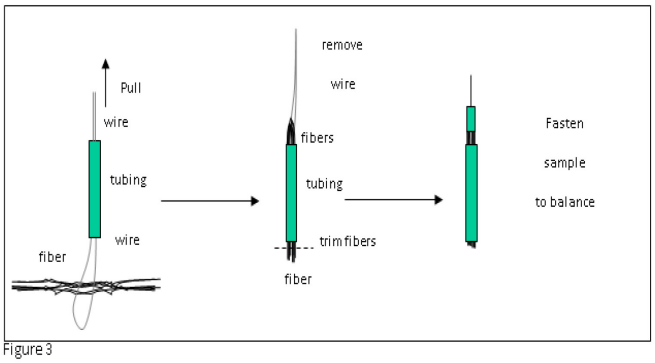


Figure 3

A more detailed description is as follows:

1. Several fibers, each having a length of about three inches are laid together as shown.
2. A thin flexible wire (copper wire works fine) is looped around the fibers.
3. Both ends of the wire are feed through a small piece of tubing (the "straw"). We typically use Teflon tubing having an inside diameter of about 1mm and a length of roughly 1 inch.
4. The wire is pulled so that the fibers are forced to double over on themselves and enter the tube. You want to use enough fibers so that the tube becomes fairly tightly packed with fiber during this step.

5. The fibers are trimmed off evenly at the bottom end of the tube, and the wire is removed from the fiber loop that is created at the top end of the tube.
6. The tube containing the fibers is attached to the balance for experimentation using a hook through the fibers, or alternative clamping technique.

What we have created is a packed bundle of fibers inside a holding device (the tube). We now treat this packed bundle of fibers as a porous solid. Irregardless of whether or not the individual fibers are porous, the bundle acts as a porous solid because capillaries are created between the individual fibers.

Porous solids can be tested for contact angle using the Washburn adsorption (wicking) technique, so long as the resulting contact angle is less than 90°. 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 equations:

$$t = A * m^2$$

wherein t = time after the solid and the liquid are brought into contact, m = mass of liquid sucked into the solid, and A = a constant which is dependent on the properties of the liquid and the solid in question.

Specifically,

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

wherein η = viscosity of the liquid, ρ = density of the liquid, σ = surface tension of the liquid, θ = contact angle between the solid and the liquid, and c = a material constant which is dependent on the porous architecture of the solid.

Combining these two equations, followed by rearrangement, leads to the following useful form of Washburn's 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 (θ) should be used.

An inspection of the above equation 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 that is known to have a contact angle of $\theta = 0°$ ($cos\theta = 1$) on the solid, then the solid material constant (c) is the only remaining unknown in the above equation, and can thus be determined. N-hexane is typically a good choice as the liquid for material constant determining experiments, because of its low surface tension of 18.4 mN/m at room temperature.

Once a material constant (c) has been determined for a particular solid, using a low surface tension liquid such as n-hexane, 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 for 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 Processor Tensiometer K12. The porous solid (in this case our packed bundle of fibers) is simply placed in an appropriate sample holder and suspended from the balance in the Processor Tensiometer just above the surface of a test liquid. The Processor Tensiometer performs the whole experiment automatically. The liquid is raised until it just touches the bottom of the porous sample. Mass versus time data is then collected as the liquid penetrates into the solid. The rate and interval over which this data is collected is user selectable. At the end of the experiment the data can be output in either graphical or tabular format. It is also automatically converted to $mass^2$ versus time data from which a slope is taken and used in the Washburn equation to calculate either the material constant "c" or a contact angle "θ" depending on the experiment.

The requirements for the Washburn method to be useful for the determination of the contact angle on bundles for fibers are that the contact angle must be less than 90°, and the bundles must be able to be formed in a reproducible manner since two experiments are required to produce one contact angle value. If the contact angle is greater than 90°, then the liquid will not rise (wick) into the bundle, and the Washburn method cannot be used.

The "straw" method is excellent for reproducible packing, because there is little that can change between successive packings, so long as the same number of fibers are used to form each bundle. As a result, fiber contact angle data is much more reproducible with the "straw" method versus the single fiber method. The difficulties that the single fiber presents are mostly eliminated. Let's review those problems:

- Curling at the Surface

  Fiber curling is all but impossible with the "straw" method because several fibers in the bundle contact the liquid, and they are all being held firmly by the tubing.

- Irregular Wetted Length

  The "straw" method does not require knowledge of the wetted length as a prerequisite. Instead the prerequisites are the liquid's viscosity, and density, and the fiber bundle material constant "c". Viscosity and density are easily measured, and

often known properties for most liquids. However, the idea that you must determine this material constant before you can do contact angle work may be perceived as a drawback to the "straw" method.

Therefore, let's discuss the "c" factor in a little more detail. The material constant for a porous solid is theoretically given by:

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

where r = the average capillary radius within the porous solid, and n = the number of capillaries in the sample. From Washburn data alone r and n cannot be calculated independently. However, so long as the same number of fibers are packed into each bundle, the "c" factor can be determined quite reproducibly. Of course, the "c" factor will vary if you use segments of the fibers with varying circumferences from test to test. However, since you are using several fiber segments for each test, instead of just one as with the single fiber method, random variations in fiber circumference become statistically insignificant. In fact, a "c" factor determined from the Washburn method is typically precise and repeatable to at least two significant figures. This is more precise than the circumference of most fibers is known from segment to segment.

- Small Forces

  For the "straw" method we are measuring the mass of liquid adsorbed into the bundle of fibers. This is typically at least 0.1 grams (100,000 micrograms) and often upwards of 0.5 grams (500,000 micrograms) based on the "straw" size I discussed above. Measuring such masses can be done a lot more accurately, and with a lot less special care, versus measuring masses in the microgram regime, as is necessary for single fiber experiments. In fact "straw" method experiments are typically performed on a Krüss Processor Tensiometer K12 (with a four place balance), rather than on a Krüss Processor Tensiometer K14 (with a microbalance).

- Penetrating Liquids

  Penetrating liquids are not at all a problem with the "straw" method. If the individual fibers have pores which are filled by the liquid, then those pores contribute, along with the pores between the fibers, to the "c" factor determined for the fiber bundle. Therefore, we are not concerned whether the fibers are porous or not.

Let's compare some data taken on the same fiber sample by both the single fiber method and the "straw" method. The fiber sample is a nylon fiber, which is used as a reinforcing material in rubber based composites. It has an average diameter of 15 microns (average circumference of 47.1 microns). Figure 4 shows force versus immersion depth data from three separate single fiber experiments. Only the advancing (immersion) portion of each experiment is shown.

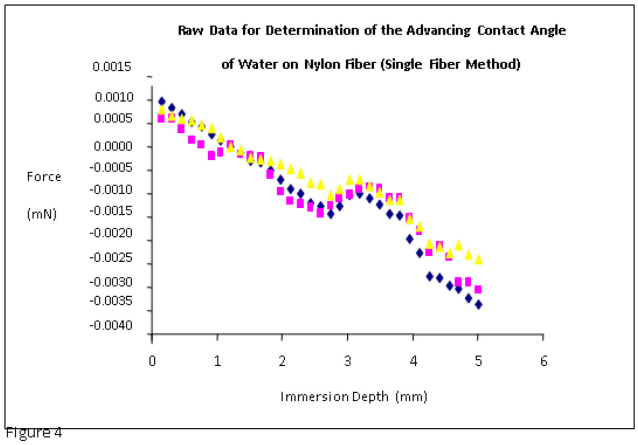


Figure 4

The advancing contact angles obtained from these three experiments were 72.0°, 79.5°, and 74.8°. So, *triplicate testing of the nylon fiber by the single fiber method yields an average contact angle of 76.6° with a standard deviation of 4.1°*. You can tell from the figure above that the high standard deviation is a result of noise in the data, which in turn is probably caused by circumference variations along the fiber.

The same nylon fiber was tested for contact angle using the "straw" method. The nylon fiber is in fact used as a "cord" made up of approximately 20 single fibers in its industrial application. We used two such cords cut to a length of about 3 inches each with a 1.8mm Teflon tube as a holder for the "straw" method testing. Figure 5 shows the raw data from three "straw" method adsorption tests with hexane for material constant ("c" factor determination).

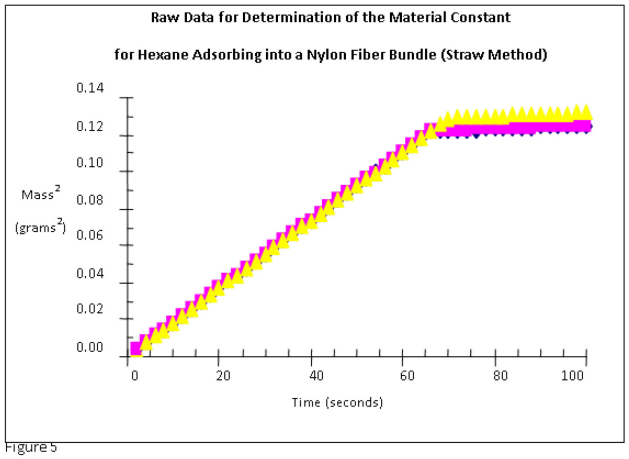


Figure 5

The "c" factors obtained from these three tests (using the initial slope of each data set, before the inevitable saturation plateau) were 7.589×10^{-7} cm^5, 7.591×10^{-7} cm^5,

and 7.5861×10^{-7} cm^5. So, triplicate testing of the nylon fiber by the straw method with hexane gave an average "c" factor 7.589×10^{-7} cm^5 with a standard deviation of 2.5×10^{-10} cm^5. This converts to a relative standard deviation of only 0.03% for the constant that will be critical for the contact angle determination. To have be as prepared for a single fiber contact angle experiment on this fiber, you would have be confident in the reported 47.1 micron average circumference to ± 0.016 microns. That's 160 angstroms! It is extremely unlikely that you would ever deal with a fiber made to those specifications. Certainly, this nylon fiber is nowhere near that uniform. So, already the "straw" method has the potential to be much more precise for this fiber versus the single fiber method, even before we have performed the actual contact angle experiment.

Figure 6 shows raw data for three contact angle experiments with water on the same nylon fiber by the "straw" method.

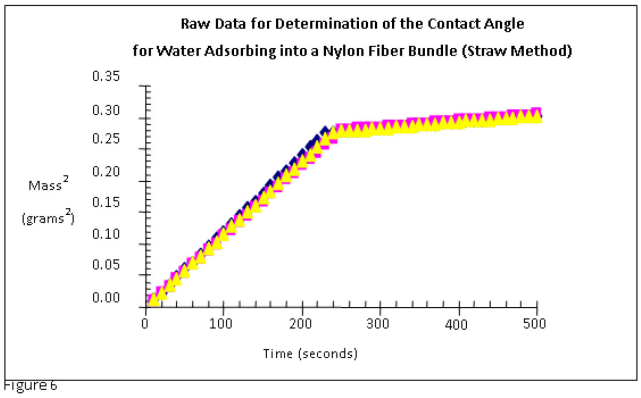


Figure 6

From the initial slopes of each data set, the contact angle values 77.4°, 78.3°, and 77.9° are obtained. So, *triplicate testing of the nylon fiber by the "straw" method yields and average contact angle of 77.9° with a standard deviation of 0.5°*. The conclusion is not only that the "straw" method provides equivalent contact angle data to the single fiber method, but also that the "straw" method is more reproducible than the single fiber method. There must be some drawbacks.

Problems with the "Straw" Method

- 90° Limitation

  The "straw" method cannot be done if the contact angle is above 90°. The liquid will not spontaneously wick into fiber bundle, so no data can be obtained.

- Advancing Contact Angles Only

  The "straw" method only provides advancing (wetting) contact angle. The fiber bundle is not dewetted, so receding contact angle is not determined, as it can be with single fiber tests.

- It's Not the "Traditional" Single Fiber Test

  It seems that no matter how much we talk to our laboratory customers about the merits of bundle as opposed to single fiber contact angle testing, some of them still want to stay with the traditional technique. I don't mean this as a criticism if you fall into this category. We are happy to work with you on single fiber measurements, if that's what you feel you need. We can do single fiber testing, and there is still a need to do so (occasionally), for purposes of obtaining receding angles and for fibers with contact angles of greater than 90°. However, given the difficulties of single fiber measurement, we prefer not to take that approach if alternatives exist. The purpose of this application note is to make you aware of those alternatives.

- Fibers are Too Short, or Too Inflexible for the "Straw" Method

  If your fibers are too short or not flexible enough for "straw" method testing, we do have yet another alternative to "bundle" them for Washburn type contact angle testing. This is discussed in the following section.

The "Packed Cell" Method

The "packed cell" method is analogous to the "straw" method in terms the procedure and mathematics used to obtain the contact angle of liquids on fibers. The only difference is in the way that the fibers are held for testing. For the "packed" cell method fibers are packed into the cylindrical cell shown below (Figure 7) for testing.

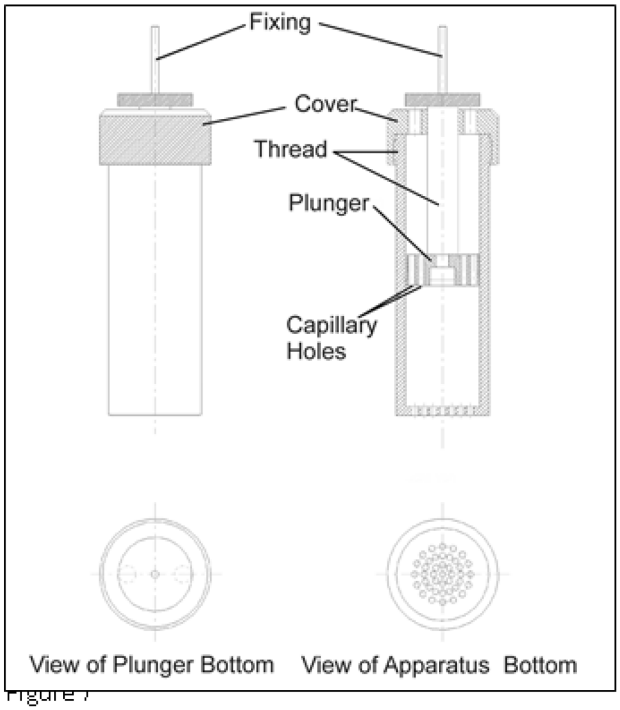


Figure 7

The cell is made of aluminum, and has approximately thirty-five 0.9 mm diameter holes in its bottom. It has an inside diameter of 12 mm. The cover for the cell is equipped with two screw threads. One to connect it with the sample chamber, and another which allows the user to guide a piston down onto the sample itself and compress it (better reproducibility in packing, and therefore "c" factor). The cell can be used to test contact angles for fibers or even for powders. The following procedure is used:

1. Place a 11.5mm (7/16 inch) diameter circle of filter paper in the bottom of the sample cell. (This is always required for powders, but may or may not be required for fiber testing, depending on the nature of the fiber.). The filter paper prevents the sample from escaping from the bottom of the cell during packing and testing.
2. Place a controlled quantity of fiber (or powder) into the cell. For fibers this could mean X number of fibers or a certain mass. This quantity should be great enough that the fibers are compressed together a fair amount during step 4 of this procedure. If this is the case, then reproducibility of your material constants and contact angles will be dependent almost solely on your ability to put the same amount of fiber in the cell for each test.
3. Place a second piece of 11.5mm (7/16 inch) diameter filter paper on top of the fibers that you have placed in the cell. This will prevent fibers from extending through the holes in the piston during the compression process and/or during the experiment.
4. Screw the cover onto the sample cell and screw the piston **completely** down. You should have placed a quantity of fiber into the cell such that there is some resistance to screwing down the piston, but not so much that it is impossible for you to screw the piston completely down with your fingers alone. Defining this happy medium, in terms of quantity of fiber to test, takes a couple of tries. However, once you have it, you have a good technique to reproducibly pack fibers for contact angle testing. For most fibers, a good amount is in the range of 1 to 2 grams of fiber.

Once the cell is packed, it is attached to a balance (usually of a Krüss Processor Tensiometer K12) and brought down to contact the surface of the liquid to be tested (the instrument does this automatically). The adsorption data is completely analogous to that described for the "straw" method, and the data is treated using the Washburn theory to determine the advancing contact angle. Again, the reason for using this technique, as opposed to the "straw" technique, is simply that you are dealing with short or inflexible fibers that cannot be done by the "straw" technique.

Let's look at some data to compare the traditional single fiber method to the "packed cell" method. This time we will use, as an example, a finished glass fiber of the type used as a reinforcement material in "fiberglass" roofing materials. This fiber has an average diameter of 16 microns (circumference = 50.3 microns).

Figure 8 shows force versus immersion depth data from three separate single fiber experiments. Only the advancing (immersion) portion of each experiment is shown.

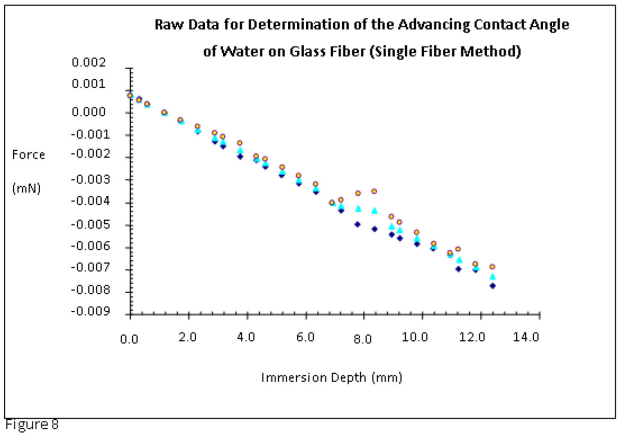


Figure 8

The advancing contact angles obtained from these three experiments were 51.2°, 48.5°, and 46.4°. So, *triplicate testing of the glass fiber by the single fiber method yields and average contact angle of 48.7° with a standard deviation of 2.4°*. This is a little better reproducibility than we had seen for the nylon fiber. However, you can still tell from the Figure above that the standard deviation is a result of noise in the data, which in turn is probably caused by circumference variations along the fiber.

The same glass fiber was tested for contact angle using the "packed cell" method. 2.0 grams of the short (approximately ¾ inch) fibers were packed into the fiber cell. Figure 9 shows the raw data from three "packed cell" method adsorption tests with hexane for material constant ("c" factor determination).

The "c" factors obtained from these three tests (using the initial slope of each data set, before the inevitable saturation plateau) were 1.601×10^{-7} cm^5, 1.546×10^{-7} cm^5, and 1.576×10^{-7} cm^5. So, triplicate testing of the glass fiber by the packed cell method with hexane gave an average "c" factor 1.574×10^{-7} cm^5 with a standard deviation of 2.7×10^{-9} cm^5. This converts to a relative standard deviation of 1.79% for the constant that will be critical for the contact angle determination. This precision is a little worse than we saw for the nylon fiber by the "straw" method. However, as you will see, it's still not overly bad. To be as prepared for a single fiber contact angle experiment on the glass fiber, you would have be confident in its reported 50.3 micron average circumference to about ± 0.9 microns. These fibers could be made to those specifications, but they are most likely are not for a bulk application like reinforcement.

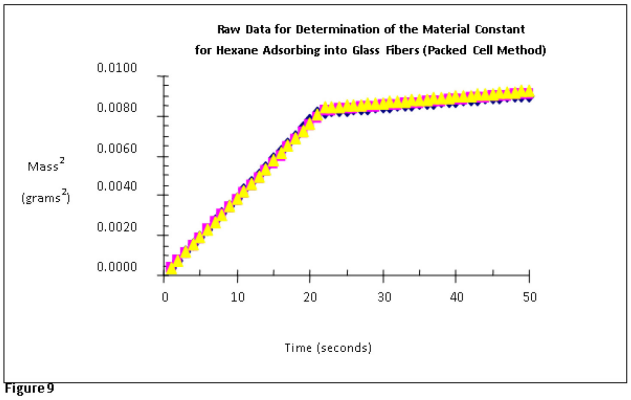


Figure 9

Figure 10 shows raw data for three contact angle experiments with water on the glass fiber by the "packed cell" method.

From the initial slopes of each data set, the contact angle values 50.3°, 49.2°, and 49.6° are obtained. So, *triplicate testing of the glass fiber by the "packed cell" method yields and average contact angle of 49.7° with a standard deviation of 0.6°*. As with the straw method, the conclusion is not only that the "packed cell" method provides equivalent contact angle data to the single fiber method, but also that the "packed cell" method is more reproducible than the single fiber method.

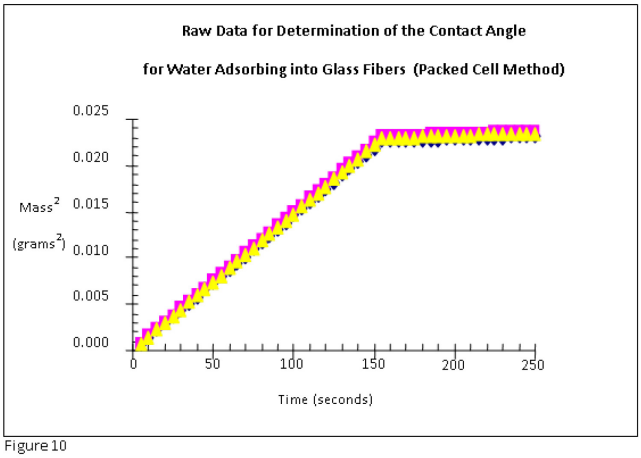


Figure 10

Summary

In this application note, I have highlighted the need for alternatives to single fiber contact angle testing, for those who need to measure the contact angle of liquids against small fibers to characterize wettability. I have then presented two alternative methods to single fiber contact angle testing – both of which produce equivalent contact angle results, without many of the difficulties involved in single fiber testing. Each of these methods has been found to be more reproducible than the single fiber method in numerous trials in our laboratory. I have presented some supporting data to that effect. Of the two methods, I recommend the "straw" method, as a first choice, when fibers can be obtained in lengths of greater than about three Inches, and they are flexible enough to fold back on themselves without breaking. For fibers that don't meet these criteria, I recommend the "packed cell" method. Performing either of these methods to determine the contact angle of liquids on small fibers is much more satisfying than trying to run single fiber contact angle experiments. If, however, receding angles need to be determined, or fibers with contact angles of greater than 90° must be tested, the single fiber method is still the only alternative.

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