

## Technical Note

### Models for Surface Free Energy Calculation

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Method:



Force Tensiometer – K100



Drop Shape Analyzer – DSA100



Keywords: Surface Free Energy, Zisman Theory, OWRK Theory, Fowkes Theory, van Oss Acid-Base Theory

## So You Want to Measure Surface Energy?

A tutorial designed to provide basic understanding of the concept of solid surface energy, and its many complications

### Background

Measuring the surface energy of a liquid is simple and straightforward. The surface energy of a liquid is identical to its surface tension, and a variety of techniques exist to measure liquid surface tension. However, determining the surface energy of a solid is not nearly as simple. The surface energy of a solid cannot be directly measured. Surface energy values are calculated from a set of liquid/solid contact angles, developed by bringing various liquids in contact with the solid. One must have prior knowledge of the surface tension values for the liquids that are used. To make matters more complicated, it is not possible to choose a universal set of liquids for use in testing solid surfaces. Specific surface interactions, surface reactivities, and surface solubilities need to be considered.

Even when an acceptable set of test liquids has been chosen, and contact angle values have been determined for those liquids on a solid, the surface energy of the solid is still not fixed. Why? Because there is no universally agreed upon definition of "surface energy" in the scientific literature. Rather, there are several widely used theories for converting contact angle data into solid surface energy values. None of these theories is universal, because none of them model reality perfectly.

The goal of solid surface energy analysis is therefore to find a proper combination of test liquids whose contact angle data on a solid fit a particular surface energy theory well enough to provide a reasonable surface energy value. There are two independent variables: the liquids that are used, and the theory that is chosen. One must also define the term "reasonable". Luckily, inherent in most (but not all)

surface energy theories is some type of error analysis. This often comes in the form of the quality of a linear fit which correlates the surface tensions of the liquids used to some variable that is based on contact angle. The exact form of this mathematics is largely theory dependent, as you will see.

By now I should be giving you the impression that the surface energy of a solid is not an exact value. Rather, it is a value that depends on which liquids are chosen for contact angle testing, and which surface energy theory is chosen for data analysis. This is the most important thing to understand about solid surface energy analysis. It is improper, and perhaps even useless, to compare any two surface energy values (for the same sample or for two different samples) that were not determined in the same

manner. Without knowledge of methodology, a solid surface energy value is meaningless.

Therefore, when you submit samples to our laboratory for surface energy measurement, also you are also asking us to establish a methodology for you. The methodology consists of a defined set of test liquids and a recommended surface energy theory which yields reasonable results. The development of a methodology for surface energy testing is based on equal parts experience and persistence. The purpose of this tutorial is to share some of our experience with those of you who want to measure surface energy yourselves.

For non-polar surfaces we tend to choose test liquids that are non-polar and surface energy theories which do not emphasize specific molecular interactions. For polar surfaces we tend to choose liquids that are polar, and surface energy theories which emphasize molecular interactions by modeling the solid as having either two or three components to its surface energy. We have also found that alcohol/water solutions are quite useful as surface energy probe liquids, because their polarity can be modified in a systematic manner by incrementing the alcohol/water ratio. However, using mixtures as probe liquids must be done with great care, because preferential wetting by one of the components of the mixture may occur.

Below I describe the four most common surface energies theories that our laboratory uses for testing solid surfaces, and highlight the most common types of surfaces to which each theory is found to apply. If you submit samples to us, we may make use of any (or all) of these theories as we search for the most appropriate and consistent one for the samples. In some cases our efforts lead to the conclusion that either of two theories might reasonably be used to calculate surface energy values for your samples (i.e. two methodologies are established with no clear superior). In such cases, our laboratory report will include two sets of surface energy values. You can then make the judgement as to which methodology you prefer for comparison of your surface energy values between samples.

## Theory #1 – Zisman Theory (a one component model for solid surface energy)

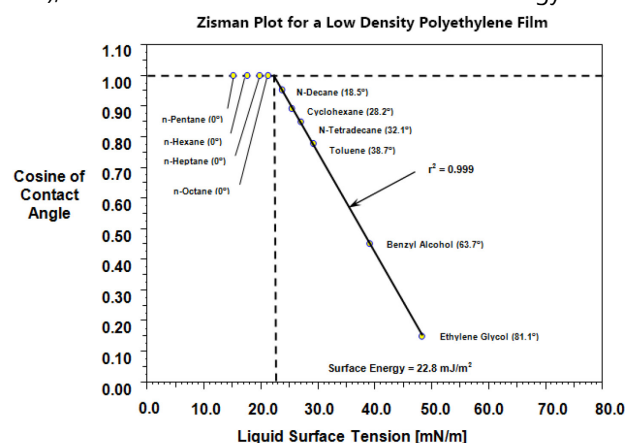
Perhaps the most widely used definition of surface energy, historically, is that of Zisman<sup>1</sup>. Zisman defines the surface energy of a solid to be equal to the surface tension of the highest surface tension liquid (real or imaginary) that will completely wet the solid, with a contact angle of 0°. This comes from the widely observed tendency of contact angle to decrease as liquid surface tension decreases on the same solid sample.

As an example of how Zisman theory is applied, consider the following contact angle data, which has been obtained for various liquids on untreated, low density poly(ethylene) film.

Test Liquid	Room Temperature Surface Tension (mN/m)	Contact Angle on Poly(ethylene) (degrees)
n-pentane	15.4	0
n-hexane	18.4	0
n-heptane	19.9	0
n-octane	21.3	0
n-decane	23.8	18.5
cyclohexane	25.5	28.2
n-tetradecane	26.4	32.1
toluene	28.4	38.7
benzyl alcohol	39.0	63.7
ethylene glycol	47.7	81.1

If this contact angle data is plotted in the form of liquid surface tension versus cosine of contact angle ( $\cos \theta$ ) and extrapolated to  $\cos \theta = 1$  ( $\theta = 0^\circ$ ), a surface tension value is obtained for the highest surface tension liquid that will completely wet poly(ethylene), with a contact angle of 0°. According to Zisman theory this value (typically reported in units of mN/m) is equal to the surface energy of poly(ethylene) in  $\text{mJ/m}^2$ . Such plots are commonly called "Zisman plots".

The Zisman plot below (based on the data given above) shows that poly(ethylene) has a surface energy of  $22.8 \text{ mJ/m}^2$ . Our confidence that this value is accurate comes in the form a line coefficient ( $r^2$ ) for the line that extrapolates the greater than 0° contact angle data to  $\cos \theta = 1$  ( $\theta = 0^\circ$ ). For our poly(ethylene) data the fit is extremely good ( $r^2 = .999$ ), so that we are confident of the surface energy result.



In general the Zisman theory works best for non-polar surfaces. Poly(ethylene) and poly(propylene) are good examples. Zisman theory does have utility for other polymeric surfaces as well. However, if a surface is even marginally polar the Zisman method becomes inadequate. A polymer surface that has been heat treated, corona treated, or plasma treated, will usually be somewhat polar (have significant heteroatom content). Also, polymers which themselves contain heteroatoms will have somewhat polar surfaces, regardless of whether they are treated or

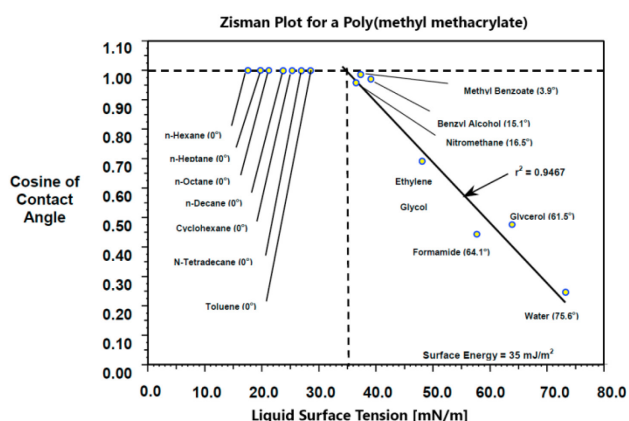
not. Examples include polyimides, polyesters, polyacrylates, polycarbonates, etc.

The Zisman theory is inadequate for such polymeric surfaces, as well as for surfaces like glasses, ceramics, and metals. This is because Zisman theory is a one-parameter model. By one-parameter, we mean that it attempts to characterize the surface energy of surfaces, and correspondingly the surface tension of liquids, by only one overall value. In doing so, it ignores specific liquid/solid surface interactions.

As an example, let's look at an attempt to characterize poly(methyl methacrylate) for surface energy by the Zisman method. The following contact angle data were obtained.

Test Liquid	Room Temperature Surface Tension (mN/m)	Contact Angle on Poly(ethylene) (degrees)
n-hexane	18.4	0
n-heptane	19.9	0
n-octane	21.3	0
n-decane	23.8	0
cyclohexane	25.5	0
n-tetradecane	26.4	0
toluene	28.4	0
nitromethane	36.5	16.5
methyl benzoate	37.2	3.9
benzyl alcohol	39.0	15.1
ethylene glycol	47.7	46.7
formamide	57.0	64.1
glycerol	63.4	61.5
water	72.8	75.6

A Zisman plot of this data is shown below. From it, the surface energy of poly(methyl methacrylate) is determined to be circa 35 mJ/m<sup>2</sup>. However, the fit confidence ( $r^2 = 0.9467$ ) is not very high. Also, removing any one data point, or continuing the experiment to include another liquid, could have a fairly substantial effect on the surface energy value that is obtained.



The Zisman theory does not apply as well to poly(methyl methacrylate) as it does to poly(ethylene) because of the

acrylate functionality in poly(methyl methacrylate). Dipole-dipole, and even hydrogen bonding interactions, are possible between many of our test liquids and the acrylate functionality of poly(methyl methacrylate). In surface science these interactions are referred to as "polar" interactions. Polar interactions are much stronger than the "dispersive" (van der Waals type) interactions which a completely hydrophobic surface like poly(ethylene) is capable of having with liquids. Since the poly(methyl methacrylate) surface is capable of polar type interactions with liquids, and each liquid in our set of probe liquids has a different potential for polar interactions, the Zisman method has become an inadequate characterization tool. It does not account for polar interactions, because it characterizes the potential that each probe liquid has to wet a surface by only one parameter – the overall surface tension of the liquid.

## Theory #2 – Owens/Wendt Theory (a two component model for solid surface energy)

The Owens/Wendt theory<sup>ii</sup> (also sometimes referred to as the "harmonic mean" method) was developed to account for specific (polar type) interactions between solid surfaces and liquids. Owens and Wendt envisioned the surface energy of a solid as being comprised of two components - a dispersive component and a polar component. The dispersive component theoretically accounts for van der Waals and other non-site specific interactions that a surface is capable of having with applied liquids. The polar component theoretically accounts for dipole-dipole, dipole-induced dipole, hydrogen bonding, and other site-specific interactions which a surface is capable of having with applied liquids. Based on this idea, Owens and Wendt developed a two parameter model for describing surface interactions, as opposed to the one parameter model of Zisman.

Mathematically, the theory is based on two fundamental equations which describe interactions between solid surfaces and liquids. The equations are as follows:

Good's Equation<sup>iii</sup>

$$\sigma_{SL} = \sigma_S + \sigma_L - 2(\sigma_L^D \sigma_S^D)^{1/2} - 2(\sigma_L^P \sigma_S^P)^{1/2}$$

Young's Equation

$$\sigma_S = \sigma_{SL} + \sigma_L \cos \theta$$

wherein:  $\sigma_L$  = overall surface tension of the wetting liquid,  $\sigma_L^D$  = dispersive component of the surface tension of the wetting liquid,  $\sigma_L^P$  = polar component of the surface tension of the wetting liquid,  $\sigma_S$  = overall surface energy of the solid,  $\sigma_S^D$  = dispersive component of the surface energy of the solid,  $\sigma_S^P$  = polar component of the surface energy of the solid,  $\sigma_{SL}$  = the interfacial tension between the solid and the liquid, and  $\theta$  = the contact angle between the liquid and the solid.

Owens and Wendt combined the equations of Good and Young to produce the following equation:

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

This equation has the linear form  $y = mx + b$ , wherein:

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

$$m = (\sigma_S^P)^{1/2}$$

$$x = \frac{(\sigma_L^P)^{1/2}}{(\sigma_L^D)^{1/2}}$$

$$b = (\sigma_S^D)^{1/2}$$

Therefore, if one has obtained contact angle data for a series of probe liquids on a solid, and knows the surface tension values (overall, polar and dispersive) for the liquids used, then he has all the information necessary to plot his contact angle data in the Owens/Wendt format (x's versus y's). Once the data is plotted in this manner, and a best fit line is applied to it, the slope of that line is used to calculate the polar component of the surface energy of the solid and the intercept is used to calculate the dispersive component of the surface energy of the solid- as per the equations given above.

It should be obvious from the mathematics that we are not quite ready to apply the Owens/Wendt theory to our poly(methyl methacrylate) contact angle data. The overall surface tension and contact angle data given on page 5 are not sufficient for application of the Owen/Wendt theory. Since the Owens/Wendt theory is a two-component model for solid surface energy, it is also a two-component model for liquid surface tension. The overall surface tension of each probe liquid must be separated into a polar and dispersive component as well. This is done using a standard reference surface.

The accepted standard reference surface for two-component liquid surface tension determination is poly(tetrafluoroethylene) (PTFE). Pure untreated PTFE is assumed to have a surface energy of 18.0 mJ/m<sup>2</sup>, and is assumed to be capable of no polar type interactions. In other words,  $\sigma_S = \sigma_S^D = 18.0 \text{ mJ/m}^2$  for PTFE, and  $\sigma_S^P = 0 \text{ mJ/m}^2$  for PTFE. Substituting these values into the primary Owens/Wendt equation (found at the bottom of page 7), followed by rearrangement yields:

$$\sigma_L^D = \frac{\sigma_L^2 (\cos \theta_{PTFE} + 1)}{72}$$

where  $\theta_{PTFE}$  = the contact angle measured between PTFE and the probe liquid.

Therefore, the dispersive surface tension component ( $\sigma_L^D$ ) can be determined for any liquid for which the overall surface tension ( $\sigma_L$ ) is known, simply by measuring the contact angle between that liquid and PTFE ( $\theta_{PTFE}$ ) and using the equation above. The polar surface energy component for the liquid is then determined by difference ( $\sigma_L^P = \sigma_L - \sigma_L^D$ ).

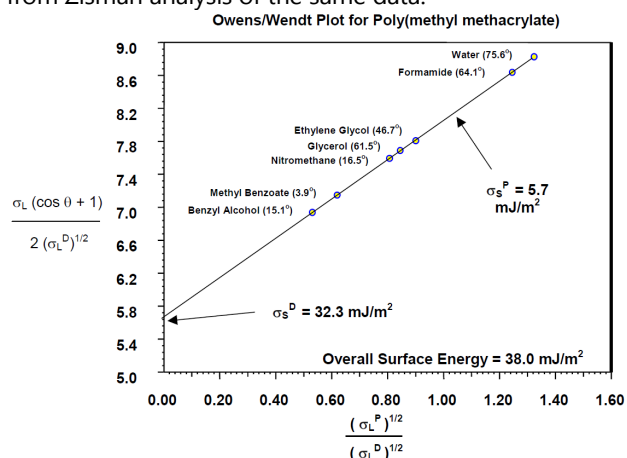
Such results are given for the probe liquids used to test poly(methyl methacrylate) below:

Liquid	Room Temperature Surface Tension (mN/m)	Contact Angle on PTFE (degrees)	Dispersive Component (mN/m)	Polar Component (mN/m)
n-hexane	18.4	12.0	18.4	0.0
n-heptane	19.9	25.6	19.9	0.0
n-octane	21.3	33.0	21.3	0.0
n-decane	23.8	42.3	23.8	0.0
cyclohexane	25.5	47.1	25.5	0.0
n-tetradecane	26.4	49.4	26.4	0.0
toluene	28.4	58.2	26.1	2.3
nitro-methane	36.5	84.8	22.0	14.5
methyl benzoate	37.2	79.3	27.0	10.2
benzyl alcohol	39.0	78.6	30.3	8.7
ethylene glycol	47.7	94.9	26.4	21.3
formamide	57.0	107.2	22.4	34.6
glycerol	63.4	100.7	37.0	26.4
water	72.8	113.7	26.4	46.4

As you study the surface tension data reported above, you will note that the surface tension of straight alkanes, and even cyclic alkanes, like cyclohexane, is purely attributable to dispersive forces. None of these liquids has any polar component to its overall surface tension. This is pleasing, since we have described dispersive forces as being non-site specific van der Waals-type forces, and we know that these are the only types of molecular interactions possible for alkanes.

The remainder of the liquids in the list (aside from toluene) contain heteroatoms (nitrogen and/or oxygen) in the form of hydroxyl, carbonyl, amide, or nitrate functionally. This causes these liquids to be capable of polar type interactions with surfaces to which they are applied. That capability is reflected in the fact that they all have a substantial polar components to their overall surface tensions. Water has the greatest surface polarity (calculated as  $100\% \times \sigma_L^P / \sigma_L$ ) of any of the heteroatom containing liquids at 63.7%. This is due to its substantial hydrogen bonding capability. Benzyl alcohol has the least surface polarity amongst the heteroatom containing liquids at 22%. It is also interesting that toluene (structurally a benzene ring with one methyl substituent) has a surface polarity of about 8%, even without any heteroatom functionally. This is mainly attributed to the polarizability of the  $\pi$ -cloud electrons in its benzene ring. One can also assume that this  $\pi$ -cloud effect contributes to the 22% surface polarity obtained for benzyl alcohol.

Now that we have the polar and disperse component surface tensions for the probe liquids that we used to study poly(methyl methacrylate), we can combine them with the contact angle data reported earlier (page 5) and apply the Owens/Wendt model. The resultant Owens/Wendt plot is shown below with seven liquids used for the analysis (only liquids which have non-zero contact angles can be used in the Owens/Wendt model). The results are an overall surface energy for poly(methyl methacrylate) of 38.0 mJ/m<sup>2</sup>, with 5.7 mJ/m<sup>2</sup> (about 15%) of that total attributable to polar interaction capability. The fit confidence ( $r^2 = 0.998$ ) is much better than that obtained from Zisman analysis of the same data.



The Owens/Wendt theory is typically the most applicable to surfaces which have low surface charge and are moderately polar in nature. Polymeric materials containing heteroatoms, like poly(vinylchloride), polyurethanes, and the aforementioned polyimides, polyesters, polyacrylates, polycarbonates are all good examples.

### Theory #3 – Fowkes Theory (another two component model for solid surface energy)

Although the Owens/Wendt theory works very well for surfaces of moderate polarity, it is also usually a fair amount of work to use. Numerous probe liquids need to be tested for contact angle against the solid being evaluated. In addition, Owens and Wendt leave the choice of probe liquids up to the experimenter. As a result, the Owens/Wendt theory is not the most widely used two component surface energy theory in the literature.

The most widely used two component surface energy theory is Fowkes<sup>iv</sup> theory. Like Owens/Wendt theory, Fowkes theory describes the surface energy of a solid as having two components (a dispersive component and a "non-dispersive" (or polar) component). In fact, Fowkes theory is mathematically equivalent to Owens/Wendt theory. However, the philosophy behind it is somewhat different.

Fowkes theory is based on three fundamental equations which describe interactions between solid surfaces and liquids. These equations are as follows:

Young's Equation

$$\sigma_s = \sigma_{SL} + \sigma_L \cos \theta$$

wherein:  $\sigma_L$  = overall surface tension of the wetting liquid,  $\sigma_s$  = overall surface energy of the solid,  $\sigma_{SL}$  = the interfacial tension between the solid and the liquid, and  $\theta$  = the contact angle between the liquid and the solid.

Dupre's Definition of Adhesion Energy

$$I_{SL} = \sigma_s + \sigma_L - \sigma_{SL}$$

wherein:  $I_{SL}$  = energy of adhesion per unit area between a liquid and a solid surface.

And, Fowkes' theory that the adhesive energy between a solid and a liquid can be separated into interactions between the dispersive components of the two phases and interactions between the non-dispersive (polar) components of the two phases.

$$I_{SL} = 2 \left[ (\sigma_L^D)^{1/2} (\sigma_s^D)^{1/2} + (\sigma_L^P)^{1/2} (\sigma_s^P)^{1/2} \right]$$

wherein:  $\sigma_L^D$  = dispersive component of the surface tension of the wetting liquid,  $\sigma_L^P$  = polar component of the surface tension of the wetting liquid,  $\sigma_s^D$  = dispersive component of the surface energy of the solid, and  $\sigma_s^P$  = polar component of the surface energy of the solid.

These three equations are combined to yield the primary equation of the Fowkes' surface energy theory:

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

Note that a division of both sides of this equation by  $(\sigma_L^D)^{1/2}$  yields the primary Owens/Wendt equation – thus the mathematical equivalency of the two theories.

The first step in determining a solid surface energy using the Fowkes' theory is to test the solid for contact angle with a liquid which has only a dispersive component to its surface tension (i.e. a liquid for which  $\sigma_L^P = 0$ , so that  $\sigma_L^D = \sigma_L$ ). In this case, the primary equation reduces to:

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

and  $\sigma_s^D$  can be calculated directly from the contact angle data obtained.

The second step is to test the solid for contact angle with another liquid which has both a dispersive component and a non-dispersive (polar) component to its surface tension. Knowing that liquid's surface tension components, the contact angle that the liquid has on the solid, and  $\sigma_s^D$  (as calculated in step 1), one can calculate  $\sigma_s^P$  as the only unknown in the primary equation (bottom of page 12). The overall surface energy of the solid,  $\sigma_s$ , is then calculated as  $\sigma_s = \sigma_s^D + \sigma_s^P$ .

Typically, Fowkes theory is applied using contact angle data from only two liquids. The recommended liquids are diiodomethane and water. Diiodomethane is a liquid which has a relatively high overall surface tension of 50.8 mN/m. However, because of its molecular symmetry, diiodomethane has no polar component to its overall surface tension, so that  $\sigma_L = \sigma_L^D = 50.8 \text{ mN/m}$ . Diiodomethane is thus used as the probe liquid for in the first step described above. Water ( $\sigma_L^P = 46.4 \text{ mN/m}$ , and  $\sigma_L^D = 26.4 \text{ mN/m}$ ) is then used as liquid for the second step described above.



Fowkes theory can alternately be used with multiple liquids having only a dispersive component, and multiple liquids having both polar and dispersive components, by linearizing the primary equation in each case. However, in practice it is difficult to find enough liquids with only dispersive components to make this approach useful, except for surfaces with very low energies (which are usually well characterized by the Zisman theory anyway).

Being a two parameter model, the Fowkes theory generally works well for the same types of surfaces as the Owens/Wendt theory. In addition, it typically fits to somewhat higher energy surfaces than the Owens/Wendt theory does.

Being a theory that has its basis in adhesion, Fowkes theory is also often used to model adhesive and coating problems. Many of our customers find it quite useful to characterize their substrates for surface energy by the Fowkes method, and also characterize their coatings for component surface tensions as described in the Owens/Wendt section. Then, they can apply Fowkes' definition of adhesion energy ( $I_{SL}$ ), to calculate the adhesion energy between the adhesive or coating and the substrate. Fowkes' definition of adhesion energy ( $I_{SL}$ ) predicts that the greatest adhesion will occur when a substrate with a given percentage of surface polarity is wet with an adhesive or coating that has the same percentage of surface polarity. Fowkes method data therefore guides substrate treatment and adhesive and coating modification decisions for these customers.

Returning our poly(methyl methacrylate) example, the contact angle for diiodomethane on poly(methyl methacrylate) is measured to be 53.6°. Using this value the dispersive component of the surface energy for poly(methyl methacrylate) is calculated to be  $\sigma_s^D = 32.2 \text{ mJ/m}^2$ . Using this value, and the contact angle data for water on poly(methyl methacrylate) given above, 75.6°, the polar component for solid surface energy is calculated to be  $\sigma_s^P = 5.7 \text{ mJ/m}^2$ . By comparison, the results discussed earlier from the Owens/Wendt theory were  $\sigma_s^D = 32.3 \text{ mJ/m}^2$  and  $\sigma_s^P = 5.7 \text{ mJ/m}^2$ . Conclusion: The Owens/Wendt theory and the Fowkes theory agree nearly perfectly for poly(methyl methacrylate). However, Fowkes theory required much less experimental work, to get the same answer.

#### Theory #4 – van Oss Theory (a three component model for solid surface energy)

The van Oss theory<sup>v</sup> focuses on separating the surface energy of a solid into three components (a dispersive component, an acid component, and a base component). As with the two component theories discussed above, the dispersive component is intended to characterize all of the non-specific (van der Waals type) interactions that the surface is capable of making with a wetting liquid. However, the polar component from the two component theories is divided into an acid component and a base component by van Oss. The acid component, in theory, characterizes the propensity of a surface to interact by

specific interactions (dipole-dipole, induced dipole-dipole, and hydrogen bonding type) to wetting liquids which have the ability to donate electron density (act basic). The base component, in theory, characterizes the propensity of a solid surface to interact with wetting liquids which have the ability to accept electron density (act acidic).

The primary equation is as follows:

$$\sigma_L (1 + \cos \theta) = 2 [ (\sigma_s^D \sigma_L^D)^{1/2} + (\sigma_s^+ \sigma_L^-)^{1/2} + (\sigma_s^- \sigma_L^+)^{1/2} ]$$

wherein:  $\sigma_L$  = the overall surface tension of the liquid tested,  $\sigma_L^D$  = the dispersive component of the surface tension of the liquid,  $\sigma_L^+$  = the acid component of the surface tension of the liquid,  $\sigma_L^-$  = the base component of the surface tension of the liquid,  $\sigma_s^D$  = the dispersive component of the surface energy of the solid,  $\sigma_s^+$  = the acid component of the surface energy of the solid, and  $\sigma_s^-$  = the base component of the surface energy of the solid.

To determine the three components for the surface energy of a solid, three test liquids are used. First, a liquid with only a dispersive component to its surface tension is used. After a contact angle is obtained experimentally with this liquid, the primary equation, which reduces to the following form in the case of a liquid with only dispersive forces:

$$\sigma_L (1 + \cos \theta) = 2 [ (\sigma_s^D \sigma_L^D)^{1/2} ]$$

is used to calculate the dispersive component of the surface energy of the solid.

Once the dispersive component of the surface energy of a solid is known, contact angle data from two more liquids are required to determine the acid and base components of surface energy of the solid. Contact angle data from one liquid which has no acid component to its surface tension, but does have a base component, is used to calculate the acid component of the solid surface energy. The primary equation is reduced to the following in this case:

$$\sigma_L (1 + \cos \theta) = 2 [ (\sigma_s^D \sigma_L^D)^{1/2} + (\sigma_s^+ \sigma_L^-)^{1/2} ]$$

Contact angle data from one liquid which has no base component to its surface tension, but does have an acid component, is used to calculate the base component of the solid surface energy. The primary equation is reduced to the following in this case:

$$\sigma_L (1 + \cos \theta) = 2 [ (\sigma_s^D \sigma_L^D)^{1/2} + (\sigma_s^- \sigma_L^+)^{1/2} ]$$

If either finding a surface compatible test liquid which has no acid component to its surface tension, or finding a surface compatible test liquid which has no acid component to its surface tension, is problematic, one only needs to find one or the other of the two liquids. Once the dispersive component of solid surface energy and either the acid or the base component is obtained, the primary equation can be used with a liquid having both an acid and base component to determine the remaining component of solid surface energy.

Because of its orientation toward the non-dispersive (polar) portion of solid surface energy (two of the van Oss theory's three parameters deal with polar interactions), the van Oss theory works best for inorganic surfaces, organometallic surfaces, and surfaces containing ions. Examples are

pigments, pharmaceutical powders, and, most notably, paper.

The most common difficulty in applying the van Oss method has been defining a set of standard solids which can be used to characterize probe liquids for acid and base surface tension components. Amongst users of the theory, there seems to be no agreed upon standard set of solids for this purpose. However, the following liquids are generally agreed to have the properties listed below at room temperature:

Liquid	Overall Surface Tension (mN/m)	Dispersive Component (mN/m)	Acid Component (mN/m)	Base Component (mN/m)
cyclo-hexane	25.5	25.5	0.0	0.0
chloro-form	27.1	23.3	3.8	0.0
tetra-hydro-furan	27.4	12.4	0.0	15.0
diiodome thane	50.8	50.8	0.0	0.0
water	72.8	26.4	23.2	23.2

We have had success using diiodomethane, chloroform, tetrahydrofuran, and the van Oss theory to characterize paper as either acidic, basic, or neutral. In these cases contact angle values were determined by the Washburn method. *The Washburn method is a well-known technique for determining the contact angle of liquids on porous solids. Those interested in the details of the Washburn method should request a copy of Krüss application note #302.*

As an example of the application of the van Oss theory to paper, we have recently obtained the data shown on the following page for two paper products. Paper #1 was known to be fairly acidic. Paper #2 is a pH neutral grade from the same supplier.

Data	Paper #1 (acidic)	Paper #2 (pH neutral)
Contact Angle with Diiodomethane	68.7	70.0
Contact Angle with Tetrahydrofuran	20.1	38.6
Contact Angle with Chloroform	16.1	11.0
Overall Surface Energy (mJ/m <sup>2</sup> )	32.2	30.4
Dispersive Component (mJ/m <sup>2</sup> )	23.6	22.9
Acidic Component (mJ/m <sup>2</sup> )	6.0	3.8
Basic Component (mJ/m <sup>2</sup> )	2.6	3.7

The van Oss theory characterizes the acidic paper (paper #1) as having an acid component to its surface

energy (6.0 mJ/m<sup>2</sup>) that is more than twice its base component (2.6 mJ/m<sup>2</sup>). However, the pH neutral paper is found to have acid and base components to its surface energy which are essentially equal (3.8 mJ/m<sup>2</sup> and 3.7 mJ/m<sup>2</sup>) respectively. Another good example of the van Oss theory's application in the paper industry is the work of Lyne and Huang, who characterized the sorption of liquids into alkaline paper.<sup>vi</sup>

## Summary

I hope this tutorial has been instructive for you. My intent in writing it was not to try to cover all of the surface energy theories that are available in the literature. That would require a much larger manuscript. Rather, this tutorial is intended to help clear up some of the mystery and confusion that seems to surround the term "surface energy".

Surface energy is an important value for the characterization of solid surfaces, but the term itself has become something of a buzz-word. Surface energy values are often reported, even in the literature, without reference to how they were obtained. Therefore, I wanted make it clear that surface energy characterization cannot be properly done by a few simple contact angle tests, without any regard for methodology. The surface energy of a solid is not an absolute value. It is always dependent on the methodology used to obtain it. Surface energy values are relatively (if not absolutely) meaningless if they are viewed separately from the methodology used to obtain them.

Having impressed the methodology issue on you, I next wanted to introduce you to some of your standard options in terms of choosing a methodology. That is, I wanted to introduce you to some of the most popular surface energy theories – the ones that we, as a contract surface science laboratory, use most often for characterizing solid surface energy. I believe I have adequately and accurately described the theories of Zisman, Owens and Wendt, Fowkes, and van Oss, and their utilities. However, I encourage you to go back to the original literature if you desire more detail.

As far as our lab services are concerned, the four theories that I have described here form our basis for surface energy analysis. They are the theories which apply to the widest variety of our customer's samples. However, we do use other theories in special situations. One notable example is Schultz theory<sup>7</sup>. Schultz theory is used to characterize high energy surfaces (like bare metals), and requires contact angle measurements between a liquid and a solid submerged in a second liquid. The mathematical complexity of the Schultz theory, as much as its infrequent use, kept me from discussing it in detail in this tutorial. However, it is probably our fifth most commonly used theory. I encourage you to go back to the original literature if you desire more detail on the Schultz method.

As a final comment, we also always welcome your input and suggestions on the subject of solid surface energy, or for that matter, on any and all aspects of surface science.

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