U sing the E SEM for the M easurement of Contact A ngles on Flat Samples

Marco Brugnara, Department of Materials Engineering and Industrial Technologies, University of Trento, Italy

INTRODUCTION
The contact angle (CA) $\theta$ of a liquid on a surface is widely used to predict wetting and adhesion properties of this solid by calculating its solid-vapour surface tension. Its definition is based on the horizontal equilibrium of the forces acting on the drop on an ideal surface, defined by the Young relationship:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

(1)

where $\gamma_{SV}$ is the solid-vapour interfacial tension, $\gamma_{SL}$ is the solid-liquid interfacial tension and $\gamma_{LV}$ is the liquid surface tension. Only when the surface can be considered ideal is the CA called the 'Young contact angle'.

On real surfaces however a whole range of contact angles is generally accessible experimentally causing a hysteresis of values, because contact angles are not only influenced by interfacial tensions, according to Young equation, but also by many other factors, such as surface roughness, chemical heterogeneity, sorption layers, molecular orientation, swelling, and partial solution of constituents in the material. Where the system has an absolute minimum of surface free energy, the contact angle is called the 'equilibrium contact angle', while the other possible contact angles correspond to different metastable equilibrium states, depending on the surface and on different initial conditions. The highest value of this range is commonly defined as the 'advancing contact angle', while the lowest one is defined as the 'receding contact angle'.

The equilibrium angle can be obtained by using a vibrational method (vibrationally induced equilibrium contact angle, VIECA [1]), in which donating mechanical energy to the meniscus allows the drop to relax to the equilibrium shape, independently on its initial state. An approximation to the equilibrium state of a drop displaced on a surface having a rough or chemical pattern is described by the well known equations of Wenzel and Cassie-Baxter. The drop size thus plays a fundamental role: the larger the ratio of drop-size to pattern-size, the better is this approximation [2].

However, it is sometimes necessary to measure contact angles only on very small surface regions, for instance when the sample size is small or the surface within this pattern is investigated. In these measurements the drop size needs to be very small for the static devices commonly used, while some interesting insight may be obtained by using an environmental scanning electron microscope (ESEM).

The importance of collecting angles on such a small scale comes from the consideration of the potential importance of the size effects, such as those due to roughness or to line tension; an example of the use of these kind of data is suggested by the remark that a living cell may be approximated with a little drop. But the volume of a cell is on the order of less than a picoliter ($10^{-12}$ l), which is about $10^{-6}$ of the volume of a drop used in standard CA measurements. From these considerations arises the interest in the use of a ESEM for contact angle estimation.

The wetting procedure used in the ESEM is well described in the literature [3-6]. Small droplets of water in the micrometre range can be nucleated and grown on the surface within the chamber by condensing water from the vapour phase, slowly increasing the vapour pressure towards the dew point at the appropriate temperature. To produce a drop on a particular spot of the surface is thus a very delicate step, which can take long time: if the rel-
ative pressure is too high complete condensation on the whole solid surface occurs, so very slow variation of the chamber conditions is required. An important question dealing with how the recorded image data relate to the actual geometry of the water drop has been analyzed [7]. In fact when the thickness of the water drops is very small (less than 1 µm) the effect of backscattering from the substrate can dramatically modify the intensity profile. In the present work this explicit limit was avoided by considering only drops with a thickness greater than 5 µm.

To calculate contact angles by image analysis with ESEM is normally quite problematic because the electron beam is not parallel to the surface but inclined at an angle \( \alpha \), which produces a distortion in the projection of the drop profile. While in some studies this error was just approximated and the contact angle was calculated as a raw estimate [4,5], in this article a more precise algorithm is derived and the results obtained by applying it to both real drops and to simulated spherical caps are presented.

**MATERIALS AND METHODS**

Polystyrene (PS) from commercial Petri dishes, polymethylmethacrylate (PMMA, Goodfellow, research grade) and commercial wax sheets for artistic applications were used here. The samples were precooled to 2-4°C, while the temperature imposed by the Peltier cooling stage during the ESEM analysis was 5°C. The relative humidity (RH) was then adjusted by changing the pressure inside the chamber. The substrate was prewetted by increasing the pressure to 6.6 torr, above the dew point, to allow condensation and then slowly decreased to obtain a reasonably steady state when drops were visible. The observations were carried out using a Philips XL 30 ESEM with a tungsten filament and equipped with a gaseous secondary electron detector (GSED) operating in the wet mode. All images were analyzed with the software ImageJ [8] with a self-developed plug-in, available on request.

**The algorithm for a spherical cap**

The two-dimensional projection of the three-dimensional spherical cap results, in general, in a combination of the projection of the three-phase base and the projection of the lateral side of the drop. The effect of gravity on the drop shape was reasonably ignored because of the very small volume of the drops. In the case of a view line parallel to the surface (\( \alpha = 0 \)) the drop projection corresponds to a circular segment and the contact angle is commonly reckoned as:

\[
\tan (\beta/2) = h/C
\]  

(2)

where \( h \) is the drop height \( EC \) and \( r \) is one half of the chord length (Figure 1).

When \( \alpha > 0 \) this situation substantially changes. First, the projection of the contact base becomes an ellipse instead of a line, while the projection of the upper part is still a circle whose top is now the point \( V \) instead of the point \( E \). By introducing \( h_c = VC \approx VC \) as the height of the projected drop shape, a projected contact angle \( \zeta \) can be reckoned by the usual formula:

\[
\tan (\zeta/2) = h_c/r
\]  

(3)

The relation between the two angles \( \zeta \) and \( \beta \) is thus derived from considering that:

\[
h_c = R - OC = R - OC \cos \alpha
\]

\[
= R - R \cos \alpha \cos \theta
\]  

(4)

and

\[
\tan (\zeta/2) = (1 - \cos \theta \cos \alpha)/\sin \theta
\]  

(5)

where \( R \) is the radius of the sphere. The same solution is valid in the case of \( \theta > 90^\circ \). Equations 4 and 5 can be used in (3) in order to write the relationship:

\[
\tan (\zeta/2) = \left(1 - \sin \alpha \sin \theta\right)/\sin \theta
\]  

(6)

As expected, the contact angle value depends both on the inclination angle \( \alpha \) and on the projected contact angle \( \zeta \).

**Using equation 7 for contact angle estimation**

The goodness of the results obtained with equation 7 was initially tested on spherical caps drawn with SolidWorks graphics software. An example is given in Figure 2. For each spherical cap the projected contact angle \( \zeta \) was measured and the real contact angle \( \theta \) was reckoned by applying equation 7 returning every time (when the equation is valid) the known value of the contact angle.

The same procedure was then used for ESEM images of drops condensed on PMMA (Figure 3), PS (Figure 4) and wax (Figure 5). In this case it is evident that just a few drops show a spherical cap shape, while often a geometrical deformation is present, perhaps due to a local heterogeneity of the material, or more likely due to interaction processes such as coalescence with other drops. The analysis was performed only on the drops showing an almost spherical shape and the results are presented in Table 3, where they are compared with static and equilibrium (VIECA) contact angles measured on the same materials.

In order to get a correct result, it is important to lead the analysis along a specific path: 1. the upper part of the drop is best fitted by a circle; this step allows one to detect the major axis of the three-phase ellipse and the separation between the base and the upper part of the spherical cap. 2. The drop base is then best fitted by an ellipse and a measure of the major and minor axes length is obtained. The value is given as half the major axis, while the inclination angle \( \alpha \); is simply reckoned as:

\[
\alpha = \arcsin (\text{minor axis}/\text{major axis})
\]  

(8)

3. The height \( h_c \) is measured as the perpendicular distance from the ellipse centre and the circle. Finally, the projected contact angle \( \zeta \) is obtained from equation 3.

It is very important to stress that there is a limitation in the rotation angle, which

Figure 2:
Spherical caps having a contact angle equal to 30°, 75° and 100°, respectively, drawn with an inclination angle equal to 0° (top) and 15° (bottom).

Figure 3:
Environmental scanning electron micrograph of a PMMA specimen obtained at 5°C and 6.5 torr.
depends on the contact angle value. If the rotation angle $\alpha$ exceeds the contact angle $\theta$, in the final projection only the base of the drop is visible; this aspect can be easily ascertained by observing Figure 1. In this case the drop projection profile is completely fitted by an ellipse, the angle $\zeta$ cannot be measured and equation 7 cannot be used. There is then another limit, which occurs when $\alpha > 180 - \theta$, concerning instead the visibility of the drop base. If $\alpha$ is greater than the difference $180 - \theta$, the drop base is hidden by the upper part of the spherical cap and the projected image is completely fitted by a circle; also in this case equation 7 cannot provide useful information. Introducing $\beta$ as the complementary angle of $\alpha$, this angle corresponds to the inclination of the sample with respect to the horizontal and the spherical cap analysis works when the following inequality is valid:

$$\beta > |90 - \theta|$$  

(9)

This means that there exists a serious limitation in the calculation of the contact angle with this procedure: by assuming that the ESEM column is vertical, when the sample surface is horizontal it is impossible to estimate contact angles just when they are about 90°, as shown in Figure 6. By tilting the sample holder it is possible to increase the range of measurable contact angles, but for practical reasons it is very difficult to rotate the sample beyond 40°, which means a typical range of contact angles lies between 45° and 130°, which excludes the possibility of analysing very low contact angles. Apart from this important limitation and despite a large uncertainty in the results, probably due to the sum of all the potential modifications produced by the peculiar environment (X-ray, beam, chemical and heating effects), it is clear that the contact angles obtained by ESEM correlate very well with those measured with other techniques and apparently no size effect is present on these hard surfaces. It is worthy of note that the average value has a strong correspondence with the equilibrium contact angle, measured by the vibrational technique VIECA. This corresponds to the idea that on hard substrates the size effect is not very strong and that the effect of all the strains probably correlates to an energy support which makes the angles similar to those obtained through the vibrational method.

**CONCLUSIONS**

The possibility of using an ESEM for direct contact-angle measurements on topographic images was investigated. A new mathematic model has been presented in order to take into account the rotation due to an inclination of the observing point. The model provided positive results both on simulated drops, created with SolidWorks, and on real polymer surfaces. Apart from the limitations due to the secondary electron emissions and the drop size, already investigated in literature, a new important limitation on the inclination angle is also stressed. A good correlation between the contact angles on PMMA, PS and wax surfaces obtained from ESEM images and the static and equilibrium contact angles was found, despite the fact that drops condensed on the surface in the ESEM chamber often show a non-spherical shape, so careful selection is required; this factor entails that the accuracy of the results is lower than that achievable with the common techniques but this new approach is however very useful in resolving the problem of the size effect on the wettability properties of a material.

**REFERENCES**


©2007 John Wiley & Sons, Ltd

**Table 1:** A comparison of the contact angles (with standard deviations) obtained by ESEM analysis, the static contact angles (CA), and equilibrium contact angles (VIECA, as defined in the text) measured on the same materials [1]. The experimental details of the VIECA method are given in [1,9,10].

<table>
<thead>
<tr>
<th>Material</th>
<th>ESEM (degrees)</th>
<th>Static Contact Angle (degrees)</th>
<th>VIECA (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>66.4 ± 2.5</td>
<td>69.9 ± 1.6</td>
<td>65.1 ± 1.5</td>
</tr>
<tr>
<td>PS</td>
<td>85.1 ± 4.2</td>
<td>91.2 ± 1.3</td>
<td>88.2 ± 1.8</td>
</tr>
<tr>
<td>WAX</td>
<td>102.2 ± 6.3</td>
<td>108.1 ± 1.2</td>
<td>104.1 ± 1.5</td>
</tr>
</tbody>
</table>

**Figure 4:** The contact angle calculation on a polystyrene surface.

**Figure 5:** The contact angle calculation on a wax surface.

**Figure 6:** The range of $\zeta$ and $\theta$ angles which can be measurable as a function of the inclination of the surface.