

Optical Contact Angle Measuring and Contour Analysis (OCA)

Why measuring with at least **three test liquids** is recommended for **Surface Energy** analysis

The surface energy (SFE) of a solid is an important parameter that can be helpful when developing new coatings or surface treatment procedures amongst others. The SFE and its polar/dispersive parts are one of the most significant parameters to verify a successful pre-treatment or cleaning process of a solid surface. Furthermore, the knowledge of the SFE facilitates an estimation of the wetting behavior and adhesive properties of the solid for further processing. Therefore, it is of great importance to measure the SFE accurately.

To determine the SFE according to the OWRK method, contact angles (CAs) of at least two different test liquids have to be measured on the sample. Water and Diiodomethane (DIM) are often used but can lead to wrong results in some cases. **Therefore at least three test liquids are still commonly recommended.** The following note gives some examples to underline the importance of choosing the correct test liquids.

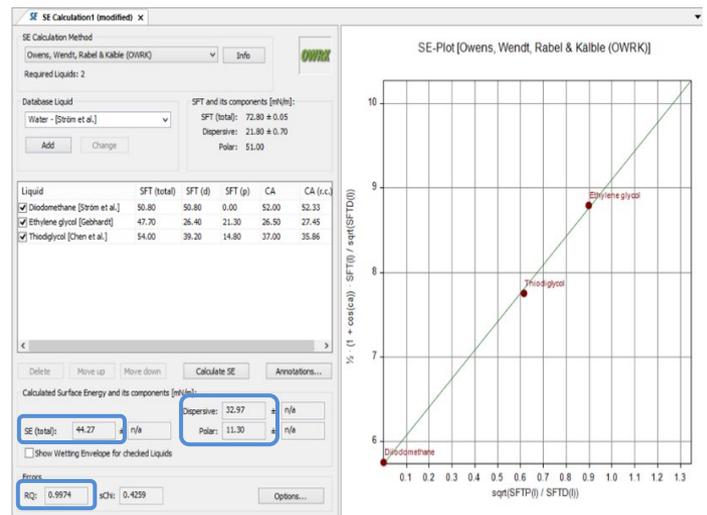


Fig. 1. Evaluation of the surface energy with the SCA software from DataPhysics Instruments.

Keywords: OCA • Surface Energy • High Accuracy • At Least Three Test Liquids

Theory

The surface energy (SFE) of a solid is evaluated by contact angle (CA) measurements with at least two different test liquids, whose surface tensions including their dispersive and polar parts are known. Very often the so-called Owens, Wendt, Rabel and Kaelble (**OWRK-model**) is used to calculate the SFE¹⁻³. It considers the geometric mean of the dispersive and polar parts of the liquid's surface tension σ_l and of the solid's SFE σ_s (equation 1):

$$\sigma_{sl} = \sigma_s + \sigma_l - \left\{ 2 \cdot \left(\sqrt{\sigma_s^d \cdot \sigma_l^d} + \sqrt{\sigma_s^p \cdot \sigma_l^p} \right) \right\} \quad (1)$$

By substituting this expression in the Young equation ($\sigma_s = \sigma_{sl} + \sigma_l \cos \theta$) a linear equation of the type $y = mx + b$ results:

$$\underbrace{\frac{\sigma_l \cdot (1 + \cos \theta)}{2 \sqrt{\sigma_l^d}}}_{y} = \underbrace{\sqrt{\sigma_s^p}}_m \cdot \underbrace{\sqrt{\frac{\sigma_l^p}{\sigma_l^d}}}_x + \underbrace{\sqrt{\sigma_s^d}}_b \quad (2)$$

In equation 2, y and x contain the known quantities (dispersive and polar parts of the test liquid's surface tension) as well as the measured CA θ . The desired dispersive σ_s^d and polar parts σ_s^p of the solid's SFE are contained in the slope **m** and in the axis interception **b** respectively. These parameters can be evaluated by a regression line (Fig. 1) when CAs of at least two test liquids are measured. However, as a regression line based on just two points contains no information on the accuracy of the result, **CA measurements with at least three test liquids** are

recommended. How well these three liquids fit into the model can be quantified by the RQ value which is ideally as close to 1 as possible. Water will often lead to too high polar parts (for an explanation see the results) of the SFE of the tested solid and thus should be substituted by other liquids.

Experiment

The SFE of a wafer, glass, protection foil, different kinds of coated titanium plates, polymers and plasma treated samples were determined by CA analysis using OWRK as calculation model.

To ensure the accuracy and reproducibility of the results, measurements were carried out three times per sample. Some of the samples were treated with a plasma handheld device piezobrush® PZ3 from Relyon Plasma (nearfield module) to compare untreated and plasma treated surfaces.

It is essential to choose suitable test liquids for determining correct SFE values. In any case, the selected test liquids need a high enough surface tensions to create drops with comfortably measurable CAs on the surface and are not allowed to chemically react with the substrate. To ensure a wide base for the regression line **x**, the test liquids should furthermore cover different dispersive and polar parts.

DataPhysics Instruments recommends using diiodomethane (DIM) (non-polar), ethylene glycol (EG), thiodiglycol (TG) and water as standard test liquids for the determination of the surface energy, which differ significantly in the ratio of their polar to non-polar components (Table 1).

Table 1. Recommended test liquids and their surface tensions with the respective dispersive and polar component.

Test liquid	σ_1 [mN/m]	σ_1^d [mN/m]	σ_1^p [mN/m]
Diiodomethane	50.8	50.8	0
Ethylene glycol	47.7	26.4	21.3
Thiodiglycol	54.0	39.2	14.8
Water	72.8	21.8	51.0
Benzyl alcohol	39.9	30.3	8.7

Besides, the SCA 21 software from DataPhysics Instruments uses RQ for the error calculation. The higher RQ the better is the linear fit and the more accurately does the OWRK model fit the surface properties (Fig. 1). Therefore, it can provide information on the accuracy of the result only when at least three test liquids are used.

Water and DIM were used for a double liquid analysis. For the triple liquid analysis, we have chosen from DIM, water, EG, TG, benzylic alcohol (BA) to make sure $RQ \geq 96\%$. The purity of the test liquids was tested beforehand with the pendant drop method using the same measuring system.

Results

Fig. 2 shows that the SFE results for polymer samples 1, 3, 4 were quite similar no matter if measured with two or three test liquids. However, the SFE results of polymer 2, especially that of its polar component are obviously different between the two test liquids (water/DIM) and three test liquids (DIM/EG/TG), indicating that water is not an appropriate test liquid. The strong hydrogen bond interactions lead to too high polar parts of the SFE. Remarkably this error would not have been noticed if only water and DIM were used since only the RQ can reveal this error.

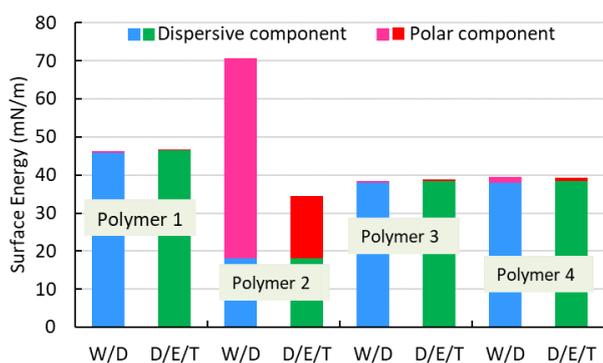


Fig. 2. Surface energy analysis of different kind polymers with two (W/D: water/DIM) and three (D/E/T: DIM/EG/TG) test liquids.

The polar components of the SFE for coated metallic samples (Fig. 3) were calculated much too high from the water/DIM system. Especially big differences were found for the plasma treated surfaces confirming again that water plays a special role, owing to its hydrogen bonding with polar surfaces. To support the point that water is the source of this error we checked the plasma treated metal 3 with combinations of

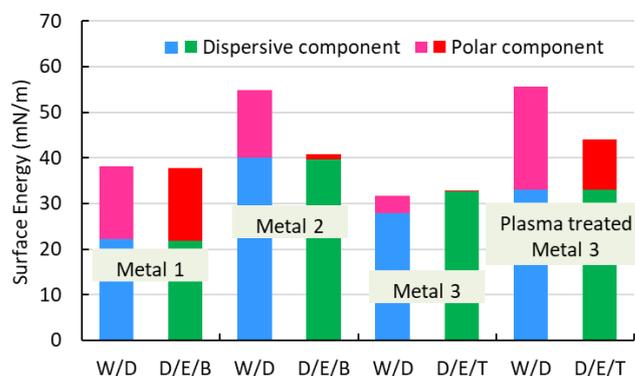


Fig. 3. Surface energy analysis of different coated metallic plates with two (W/D: water/DIM) and three (D/E/T(B): DIM/EG/TG(BA)) test liquids.

D/E/T, D/E, D/T which all lead to similar polarities while the combination W/D leads to a far too high polarity.

Further samples such as a wafer, protection foil and glass (Fig. 4) showed a similar trend underlining that water leads to an overestimation of the surface polarity.

Summary

To get **correct SFE** values we recommend to use at least **three testing liquids** in order to find out which liquids are suitable. Especially **water** can lead to wrong SFE results with far **too high polar contributions** to the SFE. For each sample type we should first find a combination of liquids that result in correct SFE values. If this was done also measurements with only two test liquids can be performed but the two test liquids should never be limited to only water and DIM. Instead, a good dosing system should allow to choose freely from DIM, TG, EG and water. This is possible with the **Double Liquid Jet (DLJ)** system from DataPhysics Instruments that can then realize a **time saving, easy to use and reliable analysis** of the SFE for **large quantities** of samples.

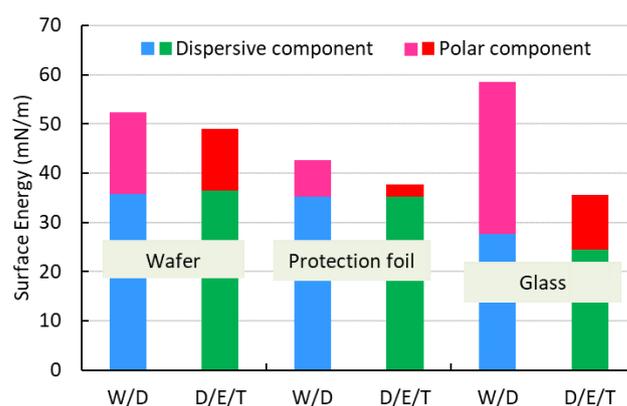


Fig. 4. Surface energy analysis of different materials with two (W/D: water/DIM) and three (D/E/T: DIM/EG/TG) test liquids.

Reference

- [1] Kaelble, H.; *J. Adhesion: Dispersion-Polar Surface Tension Properties of Organic Solids*; 1970, 2, S. 66-81.
- [2] Owens, D.; Wendt, R.; *J. Appl. Polym. Sci.; Estimation of the Surface Free Energy of Polymers*; 1969, 13, S. 1741-1747
- [3] Rabel, W.; Einige Aspekte der Benetzungstheorie und ihre Anwendung auf die Untersuchung und Veränderung der Oberflächeneigenschaften von Polymeren.; *Farbe und Lack* 77; 1971, 10;