

Application Note 6

Simplified determination of the surface free energy of polymers.

Determination of wetting properties of polymer films with the DataPhysics OCA device and a single test liquid.

Problem

An accurate knowledge of the surface free energy of polymers is essential for optimising the conditions employed during a variety of coating processes. In circumstances where time is limited, sample in short supply or simply, as a result of budget restrictions, a regime that involves the measurement of contact angle of a single test liquid is viewed as an acceptable SOP.

In many industrial sectors, polymers play an important role in the production of high-quality consumer goods. In many of these industries the coating or otherwise covering of these plastic materials is of particular importance. During these coating/covering processes problems can occur because the polymeric surfaces may have relatively poor wetting or adhesion properties. This is often the result of relatively low surface free energy or the absence of polar surface groups in many of these materials. To improve the wetting properties, the polymers are often subjected to a surface treatment regime, such as plasma or corona treatment. In this way, polar groups are introduced on the surface, and the surface free energy increased as a consequence.

In order to quantify the success and effect of surface treatment, the surface energy of the plastic material must be determined. The measurement of contact angle is a simple and quantitative method of evaluating this surface property, where usually several test liquids are used. Under certain production or laboratory conditions, where a very quick and simple

method is demanded, limitation to the use of a single test liquid may be deemed appropriate.

This application note describes the method applied to polypropylene films using the an instrument from the OCA, contact angle measuring range, along with the software module, SCA 20 with just one test liquid.

Method

Many industrial processes rely on the production or use of a single polymeric material, the surface properties of which influence the success of the process. The only difference between the individual batches of polymer are variations in their handling prior to their use, within these processes. This is particularly the case is the conditions of any deliberate pre-treatment have been optimised.

If a series of samples to be examined are from the same basic material, first the surface energy, together with the polar and dispersive parts, are determined (in the conventional, multi test liquid way) on a single batch, that is considered representative of that batch. Since, in general, any deliberate (chemical or heat induced) surface treatment is unlikely to influence the dispersive portion of the surface energy, these may be assumed to be constant for a material class. This assumption is confirmed by the measuring results.

The surface energy of more samples of the same batch of polymer material can now be determined by a contact angle measurement with only one liquid.

When a drop of liquid is formed on a surface, there is a resultant equilibrium of forces between the drop and the surface. For a particular liquid drop and surface combination the surface and interfacial tension

(between the drop and the surface) are described by the Young-Dupré equation:

$$\sigma_s = \sigma_{sl} + \sigma_l \cos \theta \quad (1)$$

Where σ_s , σ_{sl} and σ_l are the surface tensions between solid and the saturated vapor of the liquid, the interfacial tensions between the drop and the solid and the surface tension of the drop towards the saturated vapor.

According to Wu (1); the interfacial tension σ_{sl} can be calculated by from the harmonic mean of the polar and dispersive portions of the surface tensions of the solid and the liquid. Here the total surface energy of the solid and the total surface tension of the liquid are described by the addition of both their parts.

$$\sigma_{sl} = \sigma_s + \sigma_l - \frac{4 \cdot \sigma_l^d \cdot \sigma_s^d}{\sigma_l^d + \sigma_s^d} - \frac{4 \cdot \sigma_l^p \cdot \sigma_s^p}{\sigma_l^p + \sigma_s^p} \quad (2)$$

$$\sigma_s = \sigma_s^d + \sigma_s^p \quad \sigma_l = \sigma_l^d + \sigma_l^p$$

σ_s^d , σ_s^p : dispersive and polar parts of the surface energy of the solid

σ_l^d , σ_l^p : dispersive and polar portion of the surface tension of the liquid

If the equations (2) are put in equation (1) and resolved towards the unknown surface energy of the solid σ_s , one gets:

$$\sigma_s = \sigma_s^d + \frac{\sigma_l^p \cdot (\sigma_l + C + \sigma_l \cdot \cos \theta)}{4 \sigma_l^p - (\sigma_l + C + \sigma_l \cdot \cos \theta)} \quad (3)$$

$$C = -4 \frac{\sigma_l^d \cdot \sigma_s^d}{\sigma_l^d + \sigma_s^d}$$

All values on the right side of equation (3) are known; so from the measurement of contact angle with just one liquid the surface energy of the solid can be calculated. For the case of polypropylene films described here, the procedure according to Wu has proved useful, because, especially with low-energy systems like polymers, it yields better reproducible results than other methods.

Results

A drop is formed, on the solid surface, with the automatic or manual dosing system of the OCA system. With the optics/camera system of choice, a digital image of the drop, on the surface, is recorded and saved. The SCA 20 software now automatically determines the contact angle between liquid and solid.

To test the method introduced here, the surface energy of three differently pre-treated polypropylene films was determined in the conventional manner. (For this purpose the contact angles were measured with four liquids.) The test liquids, ethylene glycol, diiodomethane, dimethyl sulfoxide (DMSO) and formamide were used. The results are summed up in Table 1.

Table 1. Contact angles with different liquids in degrees

Film	Diiodomethane	Ethylene glycol	Formamide	DMSO
Untreated	61.1	78.2	85.4	57.3
Corona	50.5	51.3	58.0	31.1
Flame	51.2	47.8	57.3	27.4

The evaluation according to Wu's method yielded the values shown in Table 2 for the total surface energy (and the polar and dispersive contributions) for the respective type of film. As expected, the dispersive portion is scarcely changed by the treatment.

Table 2. Surface energies and their dispersive and polar portions

Film	SE (mN/m)	Dispersive portion (mN/m)	Polar portion (mN/m)
Untreated	29.98	29.95	0.03
Corona	38.50	30.19	8.31
Flame	39.19	30.20	8.99

To decide which liquid is particularly suited for calculating the surface energy, from just one contact angle, the changes of the contact angles between

the untreated film and the treated films are shown in Table 3.

The comparison clearly shows that the greatest change occurs with ethylene glycol

i.e. that in the case considered here, the contact angle of ethylene glycol on these surfaces is particularly sensitive to surface treatment. Therefore, ethylene glycol is considered particularly suited for use within a procedure that sets out to determine surface energy with only one liquid/ contact angle.

Table 3. Change of the contact angle on treated films as compared to the untreated film in degrees

Film	Diiodo-methane	Ethylene glycol	Formamide	DMSO
Corona	10.6	33.9	27.4	26.2
Flame	9.9	37.4	28.1	29.9

In Diagram 1, the surface energy, calculated according to equation (3), for different contact angles with ethylene glycol as a test liquid is outlined. If this model is correct, it should be possible to predict the correct surface energy of the films from one contact angle with ethylene glycol.

For comparison, the diagram also shows the surface energies that were determined according to the conventional (four liquid) method. The diagram shows that there are only slight deviations of the exact values from the calculated curve.

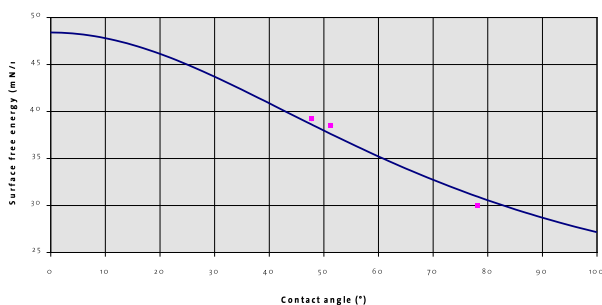


Diagram 1 Surface energies as a function of the contact angle with ethylene glycol

A more detailed comparison is given in Table 4.

Table 4. Comparison of the exact and the calculated SE in mN/m

Method	Flame 47.8 °	Corona 51.3 °	untreated 78.2 °
Exact	39.19	38.50	29.98
Model	38.58	37.58	30.90
Diff.	0.61	0.92	0.92

The summary shows that the difference between the exact value and the model value is a maximum of 0.9 mN/m, representing a deviation percentage of only 2%. This proves that for the described case of polypropylene films, with different pre-treatments, it is possible to predict the surface energy by measuring just one contact angle with an accuracy of about 2%.

Summary

The DataPhysics OCA range provides an easy way of determining the contact angle of liquid drops on the surface of polymers as a prelude to surface energy calculation. For applications that call for a series of examinations of the same or only slightly modified materials, as often occurs in industrial production environments, a method has been described here which further facilitates the determination of the surface energy with just one liquid, thus considerably reducing the time needed. The example of polypropylene films, subjected to different surface treatments, showed that the new method can predict the surface energy with an accuracy of 2%.

[1] Wu S., J. Adhesion, Vol. 5, (1973) 39-55.