Application Note 6

Simplified determination of the surface free energy of polymers

Determination of wetting properties of polymer films with the DataPhysics OCA 20 with just one test liquid

Problem

The exact knowledge of the surface energy of polymers is essential for optimizing various coating processes. Due to restrictions of time and expenses, often a contact angle measurement with only **one** test liquid is necessary.

On many industrial sectors, plastics play an important role for the production of high-quality consumer goods. In this connection, the coating and painting of these materials is of particular importance. In these processes problems sometimes occur because the plastic surfaces have relatively bad wetting and adhesion properties. This is due to the low surface free energy of these materials and the absence of reactive free surface groups. To improve the wetting properties, the plastics are generally submitted to a surface treatment such as for instance a flame or a corona treatment. To check the success and effectivity of such a treatment, the surface energy of the plastic material must be determined. The contact angle measurement is a simple and quantitative method, where usually several test liquids are used. Under certain production or laboratory conditions, where a very quick and very simple method is demanded, the use of several test liquids may not be suitable.

With the example of polypropylene films (PP films) a method will be introduced of measur-ing the surface energy, using the contact angle measuring instrument OCA 20 and the software module SCA 20 with just one liquid.

Method

Often, in one single industrial production always the same types of plastic material are examined for their wetting properties. The only difference between the individual samples is their different previous treatment. This is especially the case if the parameters for such pre-treatments must be optimized.

If the samples to be examined are from the same basic material, first the surface energy and its polar and dispersive portions are determined in the conventional way on one of the samples with at least two liquids. Since in general the surface treatment has no influence on the dispersive portions 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 class can now be determined by a contact angle measurement with only one liquid. When a drop of liquid is formed on a surface, the resulting equilibrium of forces can be described by the interface energies of the respective interfaces. From the equilibrium of forces, it results for the respective surface and interfacial tensions (Young-Dupré equation):

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

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's [1] statement the interfacial tension σ_l can be calculated by forming the harmonic mean from the polar and dispersive portions of the surface tensions of the solid and the liquid. Here the surface energy (SE) of the solid and the surface tension (ST) of the liquid are formed by addition of both their portions.

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

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

σ_s^d, σ_s^p : dispersive and polar portion of the SE of the solid

σ_l^d, σ_l^p : dispersive and polar portion of the ST 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:

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

$$C = -4 \frac{\sigma_l^d \cdot \sigma_s^d}{\sigma_l^d + \sigma_s^d} \qquad (3)$$

All values on the right side of equation (3) are known so that from the measurement of the contact angle with just one liquid the SE of the solid can be calculated. For the case of PP 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

On the solid surface, a drop is formed with the automatic or manual dosing system of the OCA 20. With the CCD camera, 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, first the SE of three differently pre-treated PP films was determined conventionally. For this purpose the contact angles were measured with four liquids. As 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	Diiodo-methane	Ethylene glycol	Forma-mide	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

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

The evaluation according to Wu's method yielded the values shown in Table 2 for the SE for the respective type of film. As expected, the dispersive portion is scarcely changed by the treatment.

To decide which liquid is particularly suited for calculating the SE 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 (EG) , i.e. that in the case considered here, the contact angle reacts especially sensitive to the surface treatment. Therefore, EG appears particularly suited for calculating the SE from only one 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	Forma-mide	DMSO
Corona	10.6	33.9	27.4	26.2
Flame	9.9	37.4	28.1	29.9

In Diagram 1 the SE calculated according to equation (3) for different contact angles with EG as a test liquid is outlined. If this model is correct, it should be possible to predict the correct SE of the films from one contact angle with EG. For comparison, the diagram also shows the SE's that were determined according to the conventional method. The diagram shows that there are only slight deviations of the exact values from the calculated curve.

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 max. 0.9 mN/m, representing a deviation percentage of only 2%. This proves that for the considered case of PP films with different pre-treatments it is possible to predict the SE by measuring just one contact angle with an accuracy of about 2%.
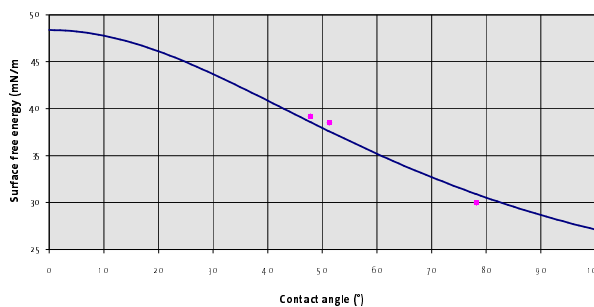
Summary

The OCA 20 offers an easy way of determining the surface energy of polymer surfaces. For the case of serial examinations on the same, only slightly modified materials as they often occur in industrial production, a method has been developed which further facilitates the determination of the surface energy. Here, the measurement of a contact angle with just one liquid is needed, thus considerably reducing the time needed. The example of PP films, which were submitted 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.

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

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