DataPhysics Instruments GmbH · Raiffeisenstraße 34 · D-70794 Filderstadt
phone ++49 (0)711 770556-0 · fax ++49 (0)711-770556-99
e-mail info@dataphysics.de · internet http://www.dataphysics.de

Application Note 4

Optimization of the determination of surface free energies on polymers

Principle example for the determination of wetting properties of polymer films with the DataPhysics OCA 20.

Problem

The exact knowledge of the surface free energy of polymers is essential for optimizing various coating processes. In the contact angle measurement process, which enables the determination of the surface free energy, the selection of appropriate test liquids is sometimes sophisticated.

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. This applies for instance to the painting of plastic bumpers and the coating of other injection-molded items. In these processes problems sometimes occur because the plastic surfaces have relatively poor wetting and adhesion properties. This is due to the relatively low surface free energy of these materials and the absence of polar surface groups. To improve the wetting properties, the plastics are generally submitted to a surface treatment such as for instance a plasma or a corona treatment. In this way, polar groups are introduced on the surface, and the surface free energy increases. The knowledge of the surface free energy of a treated plastic with its polar and dispersive portions is therefore of crucial importance when producing coatable polymers.

With the example of polypropylene films (PP films) a method will be introduced of measuring the surface free energy easily and in an optimized way, using the contact angle measuring instrument OCA 20 and the software modules SCA 20 and 21.

Method

To determine the surface free energy of a polymer with its polar and dispersive portions, the contact angle is measured with a number of test liquids and evaluated according to the method of Wu. This evaluation method is integrated in the software and is fully automatically carried out by the computer. The method requires the use of at least two test liquids with known surface tension and its polar and dispersive contributions. Each additional liquid will increase the accuracy of the estimation.

For the particular case of PP films described here, the method according to Wu has proved useful, because - as known from literature - it yields better reproducible results than other methods, especially with low-energy systems.

The accuracy of the values obtained is essentially influenced by the test liquids selected. On the one hand side, an influence on the surface by the test liquid by partial etching or disolving must be ruled out. On the other hand side, the surface tension of the test liquid must not be changed by soluble substances possibly existing on the solid surface. If one or both of the described processes take place, this manifests itself by a strong variation of the measured contact angles in spite of a visually homogeneous surface, and by a poor reproducibility of the results.

Procedure

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 picture of the drop on the surface is recorded and saved. The SCA 20 software now automatically determines the contact angle between liquid and solid.

In general water is used as a test liquid. Here, however, this cannot be considered, because when treating the plastic, very often water-soluble chemical groups form on the surface, where even before the measurement water molecules will settle down and falsify the measurement. Alternatively therefore, ethylene glycol, diiodomethane, dimethyl sulfoxide (DMSO) and formamide are used.

Results

Three types of PP films were examined, which differ by their previous treatment. One film (A) was untreated, one film was submitted to a corona treatment (B) and one to a flame treatment (C). In Table 1 the measured contact angles are summed up.

Table 1. Contact angle with different liquids in degrees

Film	Diiodo-methane	Ethylene glycol	Forma-mide	DMSO
A, untreated	61.1	78.2	85.4	57.3
B, corona	50.5	51.3	58.0	31.1
C, flame	51.2	47.8	57.3	27.4

The table shows clearly that there are drastic differences in the contact angles between the treated films and the untreated film, whereas between both treated films the differences are only small.

When evaluating according to Wu, the values as shown in Table 2 are obtained for the surface free energies of the films.

Table 2. Surface free energies and their dispersive and polar contributions in mN/m.

Film	Surface free energy	Dispersive portion	Polar portion
Untreated	29.98	29.95	0.03
Corona	38.50	30.19	8.31
Flame	39.19	30.20	8.99

From the table it becomes obvious that the surface treatment leads to an essential increase of the surface free energy. It is remarkable that the surface treatment almost exclusively influences the polar portions, which is to be expected from the creation of polar functional groups.

Summary

The OCA20 and the software modules SCA 20 and 21 offer an easy way to determine the surface energy of polymer surfaces. The polar portions of the surface energy responsible for the adhesion of coatings can be quantitatively collected by means of the contact angle measurement. In this way, wetting and adhesion properties can be predicted. Compared to the use of test inks to estimate the surface free energy, the present method has the advantage of providing a greater accuracy and let to additional information the polar and dispersive contribution of the surface free energy, which governs printability or adhesion. At the same time being independent of the experimenter, thus ruling out subjective influences.