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Application Note 4

Optimisation of the determination of surface free energies of polymers.

Description of a reliable method for the determination of the wetting properties of polymer films with the DataPhysics Optical Contact Angle series of instrumentation.

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 order to reliably carry out the routine measurement of contact angles, as the method of determining surface free energy, the selection of chosen, 'test' liquids is sometimes sophisticated.

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. A common example might be the spray or dip painting/coating of plastic bumpers or the coating of a huge variety of other injection molded items. In these 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.

A test method, therefore, that can reliably and easily evaluate the surface free energy of a raw and/or treated plastics (together with their polar and disperse parts) will be of great benefit to all companies intending to coat polymers materials, bought in or produced by their own colleagues.

The following example discusses a method for the determination of surface free energy, of a series of polypropylene films (PP films), by an evaluation of contact angles, using a contact angle measuring instrument OCA xx and the software modules SCA 20 and SCA 21.

Method

To determine the surface free energy of a polymer, along with the polar and dispersive contributions, the contact angles of a number of test liquids are measured and inserted into the evaluation method formulated by Wu. This calculation method, along with several other highly respected alternatives, is integrated into the SCA 21 software. The Wu method requires the use of at least two test liquids, with known surface tensions and the relative contributions from their polar and dispersive parts. Adding a third or fourth liquid acts to increase the accuracy of the Wu calculation.

Wu is particularly robust for the evaluation of low energy systems. The polypropylene films, evaluated in this paper, fall within this category.

Note: Test liquids must be selected with great care (bearing in mind the 'reactivity' of the liquids chosen, with the surface under investigation). Any partial etching or dissolving of the surface, by the test liquid, must be ruled out. The nature/homogeneity of the surface effected by etching and the surface tension of the test liquid effected by the inclusion of any soluble constituents of the partially dissolved surface. If one or both of these processes is induced the reliability and accuracy of the data will be greatly affected.

Procedure

A drop is formed and placed on the polymer surface by the manual dosing system (MS) or electronic dosing system (ES) of the OCA xx device. A digital picture of the drop, on the surface, is recorded, evaluated and saved by the instrument optics/CCD camera. Finally the software automatically determines and reports 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 DataPhysics Optical Contact Angle devices OCA xx and the software modules SCA 20 and '21 provide an easy and reliable way to determine the surface energy of polymer surfaces. The polar and disperse parts of this surface energy are responsible for the adhesion of coatings and can be quantitatively determined by means of a series of such contact angle measurements. Via this method the wetting and adhesion properties can be predicted.

Compared to the more traditional use of test inks, to estimate the surface free energy, the method described here is less subjective, relying, as it does, on an automated sequence of drop placement/evaluation steps. It also has the further advantage of providing greater accuracy and the additional information of the polar and dispersive parts of the total surface free energy, which govern printability and/or adhesion.