Application note

Surface energy analysis for the verification of treatment effects on different polymer substrates

dataphysics
Understanding Interfaces

The effect of polymer treatments on four polymer substrates was tested by surface energy analysis using an optical contact angle measuring and contour analysis system of the OCA series from DataPhysics Instruments.

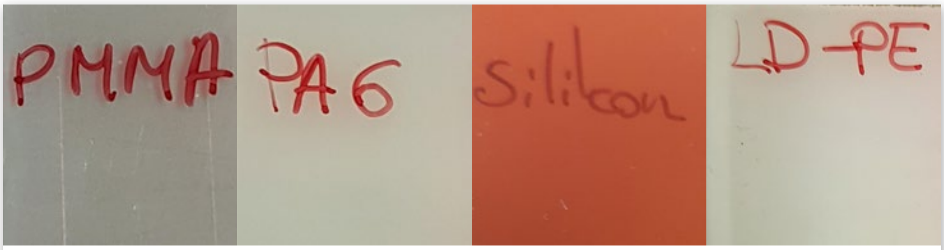

Fig. 1: Studied polymer types

Background

Being used in many diverse industries and applications, plastics have become indispensable over the last decades. Polymers vary, e.g., in composition, modification and thermal stability and can be shaped to foils as well as to complex technical elements in order to fulfil particular specifications on highest levels.

Very often untreated polymer surfaces show a weak wetting performance which is usually adverse when they have to be glued or coated. Consequently, several optimization treatments, like fluorination or flame pyrolysis, are necessary.

Such treatments can roughen the surface in a nanometre range and/or activate it introducing additional polar groups in the surface structure which can form stronger bonds than fluctuating dipoles. The effects of such treatments often persist a few days or months.

When a polymer surface treatment is required also a user-independent analysis method evaluating its effects can become necessary.

In the study presented here, the measuring task was to show different treatment effects on several polymer surfaces (Fig. 1) using a non-destructive technology. Therefore, the optical contact angle measuring and contour analysis system OCA (Fig. 2) together with its software SCA from DataPhysics Instruments was the ideal equipment.

Fig. 2: DataPhysics Instruments optical contact angle measuring and contour analysis system OCA 200

Method

Using an OCA from DataPhysics Instruments contact angles of drops on solids, adhesion and dynamic spreading processes, surface energy of solid surfaces and much more can be studied non-destructively, easily and reliably.

When surface energy has to be determined, choosing suitable test liquids is essential: On the one hand, it must be excluded in advance that the material surface is solved by the test liquids partly or even completely. On the other hand, the liquids' surface tensions must be high enough to create stable droplets on the surface which is usually the case when the liquids do not strongly interact with the non-polar or polar groups of the surface.

DataPhysics Instruments usually suggests pure chemicals, like diiodomethane, ethylene glycol and 2,2-thiodiethanol, for surface energy analysis, which differ significantly in the ratio of their polar to non-polar components (see Table 1). Water can be used as a fourth test liquid; however, it has to be considered that water, due to its hydrogen bonds, may interact with the surface. Hence, water plays a special role and is not always an appropriate test liquid.

In the presented case, the four different polymer types Polymethylmethacrylat (PMMA), Polyamide (PA), silicone rubber and soft-PE, (see Fig. 1) have been treated by fluorination and by flame pyrolysis with propane-butane gas using the coating device GVE 2 HB from Sura Instruments. Both before and after treatment a performance test on each polymer type was done using the surface energy method with the OCA in order to check the effect

For surface energy determination the three test liquids diiodomethane, ethylene glycol and 2,2-thiodiethanol have been chosen for dosing drops with a volume of 1 µL on the polymer surfaces and the respective contact angles were measured.

Table 1: Recommended test liquids and their surface tensions with the respective dispersive and polar components

Test liquid	surface tension [mN/m]		
	total	dispersive part	polar part
Diiodomethane [1]	50.8	50.8	0.0
Ethylene glycol [2]	47.7	26.4	21.3
2,2-Thiodiethanol [3]	54.0	39.2	14.8
Water [1]	72.8	21.8	51.0

In order to verify the reproducibility of the results and to check the homogeneity of the surface at least three contact angle measurements were carried out with each test liquid. On the basis of the average contact angle values the surface energy was then calculated automatically by the software SCA according to the model of Owens & Wendt [4].

Results

Differences in surface energy values could be verified not only because of different material characteristics but also with regard to the treatments done. On each substrate type treatment forced an increase of the surface energy. This was mainly the result of a significant increase of polar components.

In table 2 it can be seen that the increase of surface energy has become most significant with regard to flame pyrolysis treatment using propane-butane gas. The polar components of the polyamide surface increased by 67 % and on silicone rubber even by 90 %.

This confirms assumptions that pre-treatment is equivalent to an activation process accompanied by further changes such as mechanical properties [5]. However, the treatment results in high bonding strengths by the introduction of polar groups at the surface.

Summary

Contact angle measurement and surface energy determination with a DataPhysics OCA system have been used to examine the effects of fluorination and flame pyrolysis with propane-butane gas of four different polymer surfaces. The method proved to be an appropriate user-independent, non-destructive technology illuminating the effects of the different treatments.

In order to determine the surface energy, contact angle measurements were carried out with three well-chosen test liquids. The following calculation of the surface energy in the SCA software clearly revealed the effects of the fluorination and flame pyrolysis, namely in particular an increase of the polar component of the materials' surface energy.

References

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Table 2: Results of the surface energy analysis according to Owens & Wendt [4]

Polymer substrate	Treatment	surface energy [mN/m]		
		total	dispersive part	polar part
Polymethylmethacrylate (PMMA)	untreated	37.76	33.41	4.35
	fluorination	45.35	40.07	5.27
	flame pyrolysed	53.02	47.19	5.82
Polyamide (PA-6)	untreated	48.51	39.88	8.64
	fluorination	54.33	46.18	8.14
	flame pyrolysed	59.87	33.34	26.52
Silicone rubber	untreated	8.93	7.47	1.46
	fluorination	21.74	20.24	1.50
	flame pyrolysed	43.07	28.86	14.21
Soft-Polyethylene (LD-PE)	untreated	24.62	23.66	0.96
	fluorination	53.64	45.62	8.03
	flame pyrolysed	47.50	38.12	9.38

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