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Application Report

Ozone Treatment of Polymer Surfaces

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Authors:	CBK/FT
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Drop Shape Analyzer – DSA100

Methods:		
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How plastics lose their hydrophobia

Abstract

Wetting problems of plastics with aqueous systems are countered by selective surface pretreatment, such as ozonization; this has the effect of polarizing the surface and thus giving it a greater affinity for polar solutions and dispersions. The effectiveness of the treatment and the influence of its duration have been quantified for the two plastics POM and PBT by using surface free energy determinations obtained with the Drop Shape Analyzer – DSA100.

Method

Plastics are replacing metals as manufacturing materials to an ever-increasing extent. The polymers used frequently cause difficulties when they have to be coated or are to be used as composites. Plastics normally have lower surface free energies than metals and have either no polar fraction at all, or only a small one; this often results in poor wetting by aqueous systems. Help is provided by selective surface treatments such as plasma treatment, fluorination or ozonization which increase the surface free energy of the solid and, above all, increase its polar fraction.

The effectiveness of such measures can be quantified by using contact angle measurements. Measurements using several test liquids with known surface tension values and evaluation according to Owens/Wendt/Rabel/Kaelble allow the influence of the treatment on the polar fraction of the surface free energy of the solid to be determined and therefore the greater affinity to aqueous solutions and dispersions.

Experiment and results

Samples of the plastics polyoxymethylene (POM) and polybutyleneterephthalate (PBT) were obtained from ITT-WEDECO GmbH and subjected to an oxidative surface treatment with ozone. This method, which is already established in many technological branches, can be used in plastic processing to improve the wettability without damaging the material.
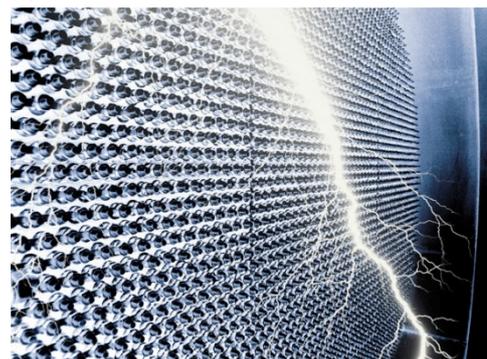

Fig. 1: Detailed view of an ozone generator. Photo: WEDECO

In order to obtain surface free energy data of the samples the KRÜSS Drop Shape Analyzer – DSA100 was used to measure the contact angles with water, 1,5-pentandiol and diiodomethane. In the sequence given above these liquids have a decreasing polar fraction of the surface tension (ST) – up to diiodomethane, which only enters into disperse interactions with the solid boundary surface (polar fraction =0 mN/m):

Test liquid	ST [mN/m]	Dispersive fraction [mN/m]	Polar fraction [mN/m]
Water	72.8	21.8	51
1,5-Pentandiol	43.4	27.6	15.7
Diiodomethane	50.8	50.8	0.0

Tab. 1: Surface tensions of test liquids with their polar and disperse fractions

By using the Owens/Wendt/Rabel/Kaelble equation

$$\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P} = \sigma_l(\cos\theta + 1)/2$$

the contact angle data of at least two test liquids can be used to calculate the surface free energy fractions σ_s^D (disperse fraction) and σ_s^P (polar fraction) of the solid. σ_l stands for the surface tension of the liquid, which is also made up from a disperse (σ_l^D) and a polar fraction (σ_l^P); the symbol θ is used for the contact angle.

As the contact time in the ozonization chamber has a considerable influence on the surface treatment, contact angles were measured on one POM sample and two PBT samples for treatment times of 30, 60, 150, 300 and 600 s. From the following plot of the polar fraction of the surface free energy against the contact time the success of the treatment can be recognized:
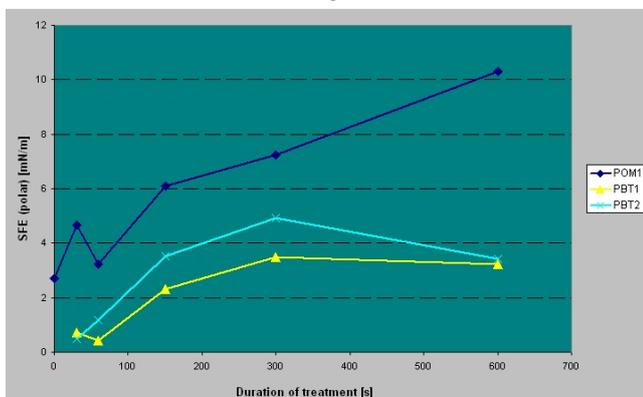

Fig. 2: Ozone treatment increases the polar fraction of the surface free energy of plastics

It can be seen that – and this is crucial for wettability by aqueous systems – the polar fraction of the surface free energy is clearly increased by the treatment. In addition, for the PBT ozonization it is evident that a contact time of longer than 300 s does not make sense.

If the surface free energy of a solid is known together with its polar and disperse fractions then it is possible to predict its wettability by any liquids, provided that their surface tension data is known. A helpful presentation is the *wetting envelope*, which can be used to show the range of optimal wettability (θ = 0°) of a solid. Such a *wetting envelope* is shown for both the untreated POM sample and one treated with ozone for 600 s:
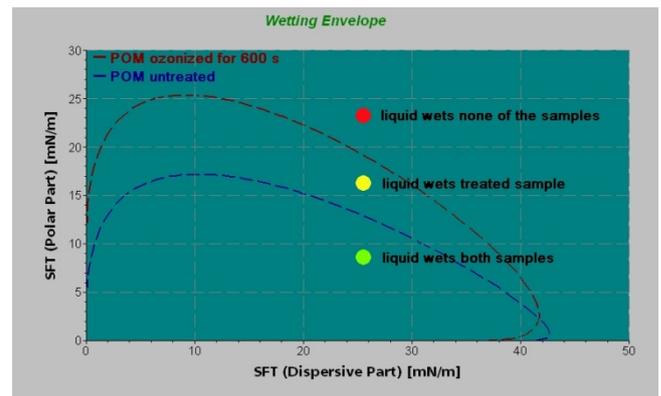

Fig. 3: Comparative wetting envelopes for an untreated POM sample and one exposed to ozone

The polar fractions of the surface tension of any liquids are plotted against their disperse fractions. The dotted lines indicate that combination of fractions which would result in a contact angle of 0°, i.e. optimal wetting. The rule is that the further the data of a liquid lies above the curve, the poorer it will wet the solid. It can be clearly seen that the acceptance of the treated sample toward liquids with a high polar fraction is considerably greater and that they are better prepared for wetting processes in which aqueous systems are involved.

Summary

Ozonization is one of the methods with which the wettability of a plastic surface by aqueous systems can be improved. By using contact angle measurements on POM and PBT samples the effect of ozonization and the influence of the treatment time were quantified. By using an exemplary presentation of a wetting envelope for treated and untreated POM samples it was possible to demonstrate that as a result of the treatment a clearly improved wetting behavior by liquids with a high polar fraction is to be expected.

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