Improved adhesion for thermoplastic polymers using oxyfluorination

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Abstract. Industrial applications of thermoplastic polymers are often limited by their poor adhesion properties. In this work the effect of surface oxyfluorination on the adhesion properties was investigated for polyethylene (PE), polyoxymethylene (POM), polybutylene terephthalate (PBT) and polyamide 6 (PA6). The adhesive joint strength was quantified using lap-shear tests. These results were correlated with the changes in the chemical composition of the surface, determined by X-ray photoelectron spectroscopy (XPS), in the surface free energy, measured by the contact angle method, and in the topography, using white-light confocal microscopy. The adhesive strength is strongly improved for all four polymers, but the degree of this increase depends on the polymer type. The surface free energy shows a similar trend for all four polymers. A high surface free energy exceeding 50 mN/m was observed after oxyfluorination, whereby the polar component was strongly predominant. Surface topography measurements show no significant increase of the surface roughness. So the effect of oxyfluorination results primarily in increased wettability and polarity due to changes of the chemical composition of the surface. XPS measurements confirm the integration of fluorine and oxygen groups in the polymer chain, which correlates with the increased polarity.

1. Introduction

Polymer materials nowadays find broad applications in nearly any industrial sector. However, most of the popular polymers are limited in some interesting applications by their poor surface properties, resulting from a low surface free energy and a low wettability. The scope of this limitation becomes obvious when considering the industrial importance of processes requiring good adhesion such as adhesive bonding, coating or printing. However, a treatment of the polymer surfaces prior to processing can open a way for such applications. In many cases, the surface properties can be enhanced without affecting the bulk material, which determines the mechanical properties of the final product. Different pretreatments have been developed, based on a variety of chemical or physical techniques, such as etching, flame treatment, corona or low-pressure plasma.

Fluorination belongs to these surface modification techniques [1-2]. Its principal application is the enhancement of barrier properties, but Schonhorn and Hansen [3] showed in the late 60s that fluorination can also be an effective way to improve polymer adhesion. It combines many advantages of its competitors, allowing an easy and fast treatment of 3D polymer shapes without supply of

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external energy. The strong exothermal reaction between elemental fluorine and the polymer surface must even be slowed down using lower pressure and dilution of fluorine.

In the presence of oxygen, this element can also react with the polymer chain and the treatment is then called oxyfluorination. The oxyfluorination was reported to increase the adhesion for thermoplastic polymers [4-5], but the investigations were limited to polyolefins. Therefore, the aim of this work was to find out which effects can be obtained with engineering polymers which have a great technical importance.

2. Experimental

2.1. Materials
Four different thermoplastic materials with varied chemical structure were investigated: polyethylene (PE), polyoxymethylene (POM), polybutylene terephthalate (PBT) and polyamide 6 (PA6). The materials types were chosen with respect to a minimal additive content and were obtained from Basell (LDPE Purell 1840H), Ticona (POM Hostaform C9021) and BASF (PBT Ultradur B4520 and PA6 Ultramid B3SK).

2.2. Surface treatment
The oxyfluorination was performed by PP Maincor GmbH & Co. KG, using an industrial fluorination chamber (6m³). Prior to fluorination, the chamber was evacuated down to 1 mbar, leading to some remaining oxygen in the chamber. A gas mixture of 80% N₂ and 20% F₂ was then introduced into the chamber by negative pressure, until the fluorination pressure was reached. After a defined exposure time, the chamber was pumped out and flushed with air three times to remove unreacted fluorine. For comparison, a low-pressure HF plasma treatment (Ilmvac Plasmaclean 4: 50 kHz, 250 W) was also performed, using air as reactive gas.

2.3. Adhesion properties
The adhesive strength was determined using a lap-shear test according to DIN 53455. Tensile bars were manufactured by injection-molding for all four materials. These bars were then cut in two parts, which were glued together using a 2-component epoxy adhesive (Araldite 2011) with an overlapping length of 10 mm. After curing for 48h at room temperature, the adhesive strength of the samples was measured using a tensile testing machine (Zwick) with a 50 kN load cell at a pulling rate of 50 mm/min. All lap-shear strength values displayed result from the measurement of 10 samples.

2.4. Surface characterization
The surface of the samples was characterized in terms of energy, chemical composition and topography. The surface free energy was determined by the Owens, Wendt & Kaeble method, using contact angle measurements (Dataphysics OCA 30) from 3 liquids (diiodomethane, formamide and thiodiglycol). This method allows to split the energy into disperse and polar components. The chemical composition of the surface was determined by X-ray photoelectron spectroscopy (XPS) (PHI 5600ci). The surface topography was investigated using white-light confocal microscopy (Nanofocus µsurf).

3. Results and discussion

3.1. Adhesive strength
The results of the lap-shear tests are given in Fig. 1. A very strong increase of the lap-shear strength can be observed after fluorination, which reflects a strong improvement of the adhesion properties. However, this increase is not the same for all the polymers. For example, the increase for PE is relatively limited in the absolute value, but due to its initial very poor adhesion, the improvement proportionally to the untreated state is the strongest for this material. It achieves indeed a strong
improvement of nearly a factor 10, whereas the improvement obtained with other polymers remained lower than a factor 5.

Fluorination is a free-radical chain reaction, which means that the exposure time of the polymer surface to fluorine gas should be an important parameter of this treatment. However, Fig. 1 shows that a strong effect is already achieved by short fluorination times. Increasing the exposure time does not significantly influence the adhesive strength. A treatment time of 5 minutes can then be considered as an optimum and used for the comparison of oxyfluorination and low-pressure HF plasma treatment, as displayed in Fig 2.

![Figure 1. Influence of the exposure time to fluorine gas on the adhesive strength of different polymers.](image1)

![Figure 2. Influence of oxyfluorination or low-pressure plasma treatment on the adhesive strength of different polymers.](image2)

Both treatments lead to an improvement of the adhesion properties for all four polymers. However, the oxyfluorination seems to have a stronger effect than the plasma treatment for the parameters chosen. This is particularly true for POM, where oxyfluorination leads to an increase of the adhesive strength twice as high as the plasma treatment.

The effects of the amount of oxygen remaining in the chamber and of the water absorption of the polymer surface are currently under investigation.

3.2. Surface free energy

The determination of the surface free energy, represented in Fig. 3, gives some information about the reason for the improvement of the adhesion properties. First of all, the total surface energy was increased for all four polymers, up to a relatively similar value exceeding 50 mN/m. This high surface energy allows a good wettability of the polymer surface by the adhesive, which is one important requirement for a good adhesion. Both treatments influence the wettability to a very similar extent. This finding can explain the similar influence of fluorination and plasma treatment on the adhesive strength.

![Figure 3. Influence of oxyfluorination or low-pressure plasma treatment on the surface free energy of different polymers.](image3)
Additionally to the improved wettability, both treatments result in a strong increase of the surface polarity. This reinforces the electrostatic interactions between the polymer surface and the adhesive molecules, and thereby contributes to the improvement of the adhesion. However, the extent and the mechanism of this increase differ strongly between the two treatments. Oxyfluorination leads in the same time to a pronounced increase of the polar component of the surface energy and to a decrease of the disperse component. This suggests a very strong modification of the chemical structure of the polymer chain. On the other hand, the plasma treatment improves the total surface energy by increasing the polar component, without influencing the disperse component.

The investigation of the surface topography showed no significant roughening of the surface, which could contribute mechanically to an increase of the adhesive strength. So the combination of increased wettability and polarity is the main reason for the improved adhesion.

### 3.3. Chemical composition

The improvement of the surface energy can be correlated to changes in the chemical composition of the surface, which are displayed in Fig. 4, in the case of PBT. Both treatments introduce polar oxygen groups in a similar amount: the O/C ratio is increased from 0.3 up to about 0.45. This contributes to the increase of the surface polarity. Despite the low volume fraction (below 1%) of oxygen in the fluorination chamber, the reaction performed can be considered as oxyfluorination. The integration of oxygen strongly influences the adhesion properties.

![Figure 4. Influence of oxyfluorination or low-pressure plasma treatment on the surface chemical composition of PBT.](image)

However, fluorination additionally integrates fluorine, another strong electro-negative element. The F/C ratio reaches about 0.6, so the important amount of fluorine reinforces the effect of oxygen. The detailed carbon peak displayed in Fig. 5 shows that oxyfluorination strongly modifies the chemical structure of the polymer chain, as suggested by the surface energy. Detailed investigations of the surface are still ongoing and will be published separately.

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