Plasma-generated nanostructure formation on polymer surfaces depending on the polymer type

P. Munzert, C. Praefke, U. Schulz, N. Kaiser
Fraunhofer Institute for Applied Optics and Precision Engineering
*peter.munzert@iof.fraunhofer.de

Introduction

To produce functional elements for optical applications, the components often have to be coated or joined together. Low adhesion is usually caused by different polarity or surface chemistry of the individual components [1]. Therefore, measures have to be taken to modify the respective interfaces to improve the adhesion. In the case of highly transparent polymers (e.g. PC, PMMA, COC, PA) this turns out to be problematic due to the demands on the optical properties. Many methods for adhesion promotion, as etching with chemicals or mechanical roughening, lead to a significant deterioration in the transparency of such components [2]. In many cases a plasma treatment alone has no sufficient effect on improving the adhesion [3]. The Fraunhofer Institute in Jena (IOF) is working several years now on the nano-structuring of polymer surfaces by plasma etching [4-6]. Except for antireflection purposes, such a structure can also be used to promote adhesion. However, large structure depths and high aspect ratios are necessary therefore. In the experiments carried out here the self-organizing formation of such nanostructures on various polymer types was studied.

Experimental procedure

For the experiments, test samples with a diameter of 55 mm and a thickness of 1 mm were used. These samples were injection-molded by Jenoptik Polymer Systems GmbH from the materials shown in Table 1.

Polymer	Trade name	Supplier
Polycarbonat PC	Makrolon Al2647	Bayer Material Science
Cycloolefinpolymer COP	Zeonex E48R	Zeon Nippon
Polyamid PA	Trogamid CX7323	Evonik Industries AG
Polyethylenterephthalat PET	Melinex ST504	Du Pont

Tab.1: Polymer materials used for the experiments

Plasma etching was performed in a vacuum evaporation system (APS 904 from Leybold Optics). For the etching experiments the plasma ion source (Advanced Plasma Source, APS) of the coating plant was used. The operating mode of this plasma source has been described elsewhere [7]. The plasma gases were argon and oxygen in a 1:2 ratio, resulting in a total pressure of 5×10^{-4} mbar. Argon and oxygen ions are accelerated by a self-bias voltage to impinge on the substrates with an energy distribution maximum at about 120 eV. Etching times were fixed at 300 s, 600 s and 1000 s. The topography of the patterned surfaces was investigated by scanning electron microscopy with a Zeiss Sigma FE-SEM. Due to the temperature sensitivity of some plastic samples the acceleration voltage must be reduced to values less than 3 kV. In order to visualize the material removal as well as the structures depth, the samples were partially masked before etching. Micrographs of this generated etching rim were acquired for an inclination angle of 45° using the microscopes SE detector. To avoid charging effects of the polymer surface, the samples were sputtered with a gold layer of approximately 20 nm thickness prior to the SEM examination.

Results and Discussion

Experiments for structuring the polymer materials indicated that for the various polymer types very different structural depths occur despite identical plasma etching conditions. In Fig.1, image sections from the scanning electron micrographs show the etching ledge and a region of the resulting structure. For the Zeonex sample (Fig. 1 on top) it is obvious that a homogeneous ablation of the material takes place without the formation of a deep texture. Elongated etching times only contribute to an increased erosion but the resulting structure still has a low aspect ratio. For PET the situation is completely different. As shown in Figure 1 (bottom), knob-like structures with a depth of ~200 nm are formed at already 300 s etching time. For longer etching times not only the ablation, but also the depth of the nanostructures became significantly greater.

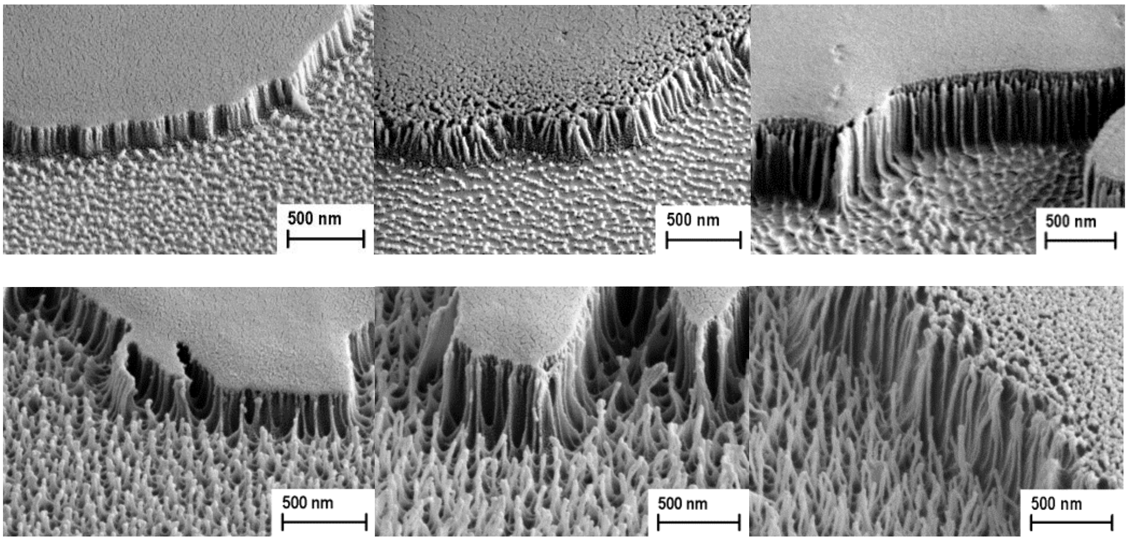

Fig.1: Scanning electron micrographs of nanostructures etched on Zeonex (top) and PET (bottom) for different plasma etching times: 300 s (left), 600 s (middle) and 1000 s (right)

If we plot the homogeneous surface ablation and the resulting structure depth in diagrams as a function of the etching time (see Figure 2) it becomes obvious that also on polymers not exhibiting a distinctive structure growth (Zeonex and Makrolon in Fig.2 right) homogeneous ablation occurs. In the case of the Zeonex material the ablation is as high as for the PET (see Figure 2 left) where deep structures can be generated. Of course the entire material erosion (and thus the etching rate) is higher for the PET because the material in between the structure features also becomes removed and must be added to the homogeneous ablation. Nevertheless the etching rate for PC and Zeonex is far from zero, so an explanation for the absence of structure formation can not be a lack of ablation.

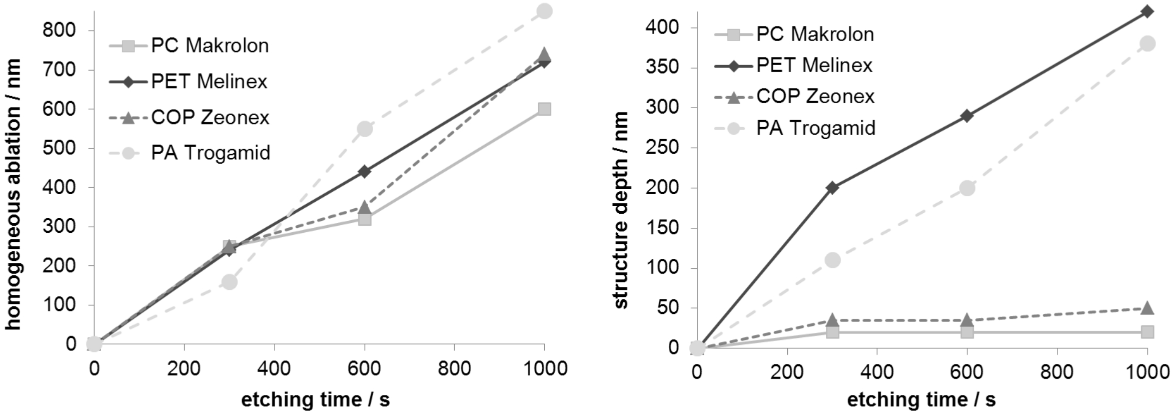

Fig.2: Homogenous ablation (left) and resulting structure depth (right) on various polymers as a function of the etching time

Summary and conclusions

Experiments were carried out to investigate the importance of the polymer type on the self-organizing formation of nanostructures on a plastic surface. This nano-texture should be generated by plasma etching and act as an effective and highly transparent adhesion promoter for subsequently applied wet-chemical laquers. It was found that a formation of up to 400 nm deep structures takes place on some polymers while on others no texture growth at all can be observed despite absolute identical etching conditions. Considering the ablation rates of the individual polymers no significant correlation to the nanostructure formation became obvious. So, the polymers chemistry and internal structure must have a crucial role in the formation of such nanostructures. This approach will be the subject of further investigations.

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