PLASMA SURFACE ACTIVATION OF HIGH DENSITY POLYETHYLENE AT ATMOSPHERIC PRESSURE

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Abstract

High density polyethylene (HDPE) is often used industrial polymer because of its good mechanical properties as high flexibility and tensile strength, high chemical resistance, easy processing and low price. Low surface energy of HDPE causes its low adhesion to printings, coatings and adhesives, what limits its industrial use. The aim of this work is to improve wettability of HDPE surface while bulk properties are kept. Atmospheric Diffuse Coplanar Surface Barrier Discharge (DCSBD) operated at frequency 50 kHz in ambient air was used. The main advantages of this plasma source are possibility to operate it at atmospheric pressure, high power density and good its good applicability in-line processes. Surface properties of samples were analyzed via sessile drop contact angle measurement and calculation of surface energy and its γ^{AB} and γ^{LW} components using Owens, Wendt, Rabel and Kaelble model (OWRK). Exposure time was 1.5 - 20 s and distance between samples and electrode was 0.1, 0.2 or 0.3 mm. Obtained results show that the surface energy of treated HDPE depends not only on exposition time but also on distance between the sample and the electrode. The best results were obtained for 10 sec treatment at the lowest distance between sample and electrode. Surface energy increased up to 72 mJ/m^2 compared with 38 mJ/m^2 of untreated HDPE. Aging tests proved only weak decrease in surface energy during first 720 min after the plasma treatment.

Keywords: Atmospheric pressure plasma, Surface modification, Contact angle, HDPE, DCSBD

1. INTRODUCTION

High density polyethylene (HDPE) is widely used material for a broad range of industrial applications. The main reasons are: low cost, high chemical resistance, good mechanical properties (high flexibility, high tensile strength and ease of material processing), and high recycling potential [1]. Therefore this material has a great potential to be used in biomedicine, microelectronics, car industry, agriculture and for production of composites [2, 3].

The drawback of HDPE as a material is the extremely low surface energy of unmodified HDPE. This results in low wettability and poor adhesion of printing inks, coatings, adhesives and metals to the surface of HDPE [4]. For numerous applications, where high surface energy is necessary, the surface modification of HDPE is necessary, i.e. the surface energy of HDPE has to be increased. The increase of surface energy is usually performed by wet chemical treatment (etching or introduction of hydrophilic functional groups) [2, 5, 6]. Beside wet chemical treatment the UV-light curing, electron/ion beam irradiation, X-rays, γ-rays, lasers or plasma treatment can be used for surface modification [3, 7].

Plasma treatment is a versatile method for surface modification of polymers. It enables tailored modification of various surface properties without affecting the bulk properties of material. The plasma treatment enables increase of surface energy polymers, creation of specific functional groups on the treated surface, modification of hardness, roughness and degree of cross-linking of surface layer of polymers [8].

Low-pressure discharges (radio frequency and glow discharge) are the most common methods used for plasma modification of polymers [9, 10, 11]. Standard plasma treatment time using low-pressure methods is in the range of minutes. As the processing gases following gasses or their mixtures are used: rare gases (He, Ar), reactive gases (O_2, CO_2, N_2, NH_3). Recently there is an effort to replace the low-pressure discharge methods with the methods utilizing atmospheric pressure discharges, i.e. various jets, atmospheric pressure glow discharge (APGD) and dielectric barrier discharges (DBDs) [12, 13, 14, 15, 16]. These discharges do not require expensive vacuum systems and therefore makes the modification process cheaper and also faster because of higher concentration of active species. The typical treatment time of a few seconds and common use of air as processing gas make the atmospheric pressure discharges promising candidates for industrial ‘in-line’ applications.

The aim of this work is the optimization of conditions for plasma treatment of HDPE, in order to achieve a high surface energy of HDPE in short treatment time without use any additional chemical activation or grafting [17,18]. The so-called Diffuse Coplanar Surface Barrier Discharge (DCSBD) was used for the plasma treatment of HDPE surface. The DCSBD was operated at atmospheric pressure in air. The DCSBD plasma source and treatment conditions were chosen to ensure the applicability for ‘in-line’ industrial processes.

The influence of the distance between sample and the DCSBD electrode was studied. To determine the optimal treatment conditions three different distances between electrode and sample were tested: 0.1, 0.2 and 0.3 mm. The sessile drop method was used to measure the static contact angle of water (and diiodomethane) on untreated and plasma treated HDPE surface. Atomic force microscopy (AFM) was used to study the changes of surface morphology.

2. EXPERIMENTAL

High density polyethylene plates with the dimensions of 25×95 mm^2 and thickness of 2 mm were used as substrates in this study. Surface energy of untreated HDPE was 38 mJ/m^2. In order to model the real industrial manufacturing process the samples were not cleaned before plasma treatment. Therefore the HDPE surface was not ‘analytically clean’ during the measurement of surface properties.

The HDPE samples were plasma-treated using so-called Diffuse Coplanar Surface Barrier Discharge (DCSBD) [19] at atmospheric pressure conditions in ambient air. The DCSBD plasma source is made of two systems of parallel electrodes (with IDT geometry) embedded in flat dielectrics (Al_2O_3 ceramic), see **Fig. 1**. The DCSBD plasma source produces visually diffuse thin layer (0.3 mm) of plasma with power density of 4.5 W/cm^2. The active discharge area of DCSBD was 20×8 cm^2 and the discharge was generated using sine-wave high voltage with the frequency of 50 kHz. The treatment times were chosen in the range from 1.5 s up to 20 s and the distance between the sample and the electrode was set at 0.1, 0.2 and 0.3 mm.

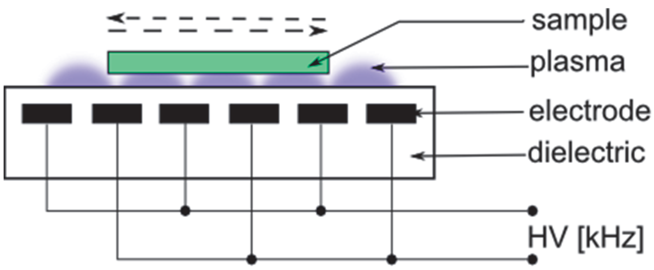

Fig. 1 Schematic picture of DCSBD electrode

Wettability and surface energy of HDPE were investigated using the static contact angle (CA) measurement utilizing the sessile drop method. The CA of two standard liquids (water and diiodomethane) was measured using the See system (Advex Instruments). Surface energy and its components were calculated using the standard Owens, Wendt, Rabel and Kaelble model (OWRK):

$$(1+\cos\theta)\gamma_l = 2\left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^{AB}\gamma_l^{AB}}\right),$$

Where *LW* represents the Lifshitz-Van der Waals component and *AB* represents the acid-base component of the total surface energy *γ* and *θ* represents the measured contact angle of liquid *l* on the solid surface *s*.

Total surface energy γ is then calculated as the sum of *LW* and *AB* components of surface energy:

$$\gamma = \gamma^{LW} + \gamma^{AB}$$

Contact angles for each sample and test liquid were measured eight times and first measurement was performed within five minutes after the plasma processing in order to reduce the effect of so-called ‘aging effect’. Surface morphology of untreated and plasma treated HDPE samples were studied using atomic force microscope (AFM) NTEGRA Prima using the semi-contact mode. The scanned area was 5×5 µm and the resolution of scanned area was 512x512 points with scan rate of 0.5 Hz.

3. RESULTS AND DISCUSSION

The wettability of HDPE was significantly improved by DCSBD plasma treatment. In **Fig. 2** the dependence of water contact angle (WCA) on plasma treatment time is given for three different distances between sample and electrode, i.e. 0.1, 0.2 and 0.3 mm. Water contact angle decreases with increasing time of activation and the most significant decrease of WCA occurred during the first 3 seconds of plasma treatment. For longer exposure times the saturation of the plasma treatment effect occur and the WCA changes only slightly. The lowest WCA were obtained in the saturated part of CA dependence. The WCA of 56°, 32° and 19° were achieved on plasma treated HDPE surface for the sample-to-electrode distance of 0.3, 0.2 resp. 0.1 mm. This shows the significant influence of the sample-to-electrode distance on the achieved minimum value of WCA. The best result, i.e. the WCA of 19° was obtained for plasma treatment using the distance of 0.1 mm and treatment time of 15 s. Surface energy of plasma modified HDPE was at this point 72 mJ/m^2.

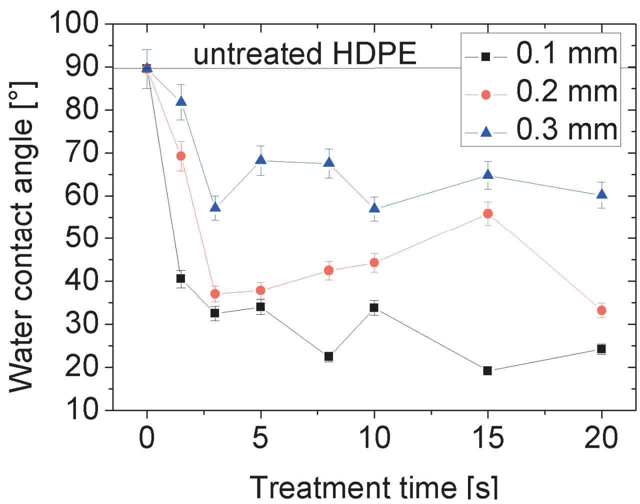

Fig. 2 Dependence of water contact angle on plasma treatment time for tree different distances between sample and electrode 0.1, 0.2 and 0.3 mm, reference WCA value on plasma untreated HDPE was 90°

Surface properties of plasma modified polymers exhibit the so-called ‘aging effect’ (ref). This means that the WCA decreases in time after the plasma treatment due to the post-plasma surface reactions with gases of ambient atmosphere and due to the molecular mobility (reorientation and diffusion of plasma-created functional groups) [20]. In **Fig. 3** the WCA is given as a function of the time after plasma treatment. The dependences of WCA on treated HDPE surface are given for the samples treated in three different sample-to-electrodes distances (0.1, 0.2 and 0.3 mm). The treatment time was 15 s in all cases. The changes of WCA were relatively small. This means that the increase of wettability of plasma treated HDPE using DSCBD was stable at least in the range of hours, which is more than enough time for the subsequent processing of treated HDPE material in the majority of industrial applications.

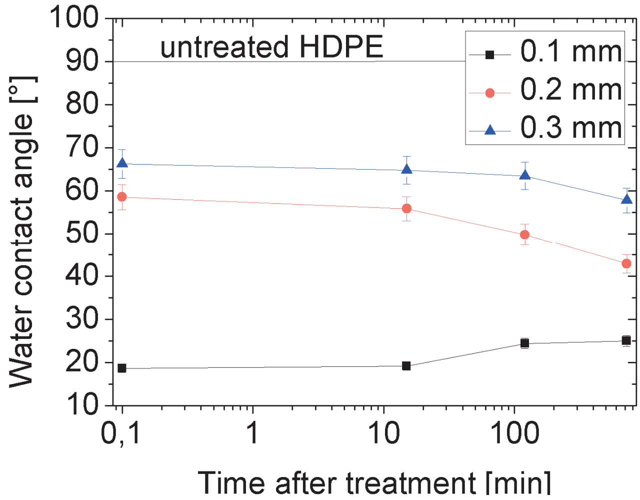

Fig. 3 Aging of HDPE treatment in ambient air during first 720 minutes after DCSBD plasma treatment, reference WCA value on plasma untreated HDPE was 90°

Plasma treatment of polymers is commonly associated with the changes of morphology and roughness of treated surfaces [21]. It was reported that the increase of wettability after plasma activation could be interpreted also as a consequence of surface roughness induced by the plasma treatment [21, 22]. In **Fig. 4** the comparison of the surface morphology is given for plasma untreated and plasma treated HDPE samples (treatment time 15 s, distance 0.1 mm from electrode).

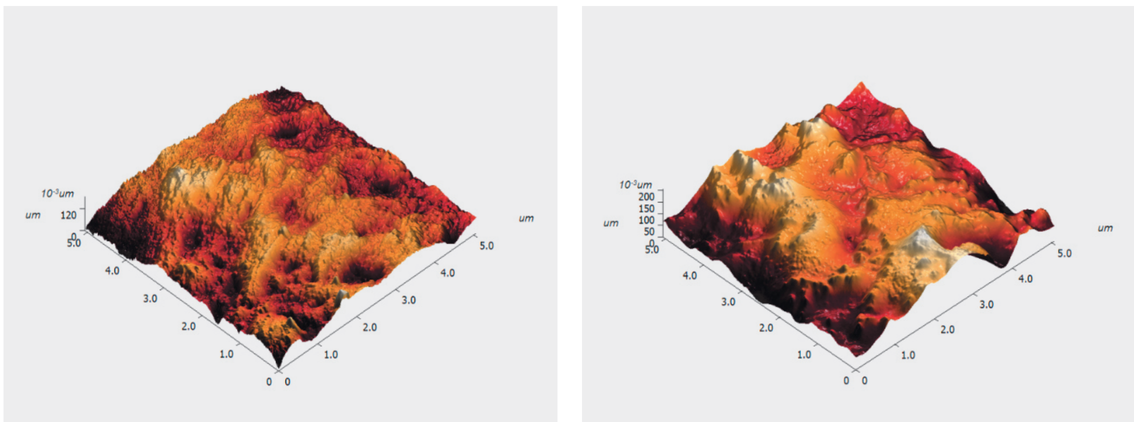

Fig. 4 Surface morphology of untreated HDPE (left) and plasma treated HDPE (treatment time 15 s, distance 0.1 mm from electrode)

The surface of plasma untreated HDPE samples exhibit high surface unhomogeneity and roughness and the plasma treatment does not affect the surface morphology significantly. Owing to that the connection between the changes of surface morphology and the increase of surface wettability after plasma treatment can not confirmed in our case, most likely due to the inherent high surface roughness of tested HDPE samples.

4. CONCLUSION

Major improvement of HDPE wettability was achieved after plasma treatment of HDPE in DCSBD at atmospheric pressure performed in ambient air. We have found a strong dependence of the plasma treatment effect on the distance between the sample and the surface of DCSBD plasma source (electrode). The minimum value of water contact angle was achieved for the smallest distance between sample and electrode. Excellent value of water contact angle 19° was achieved for distance 0.1 mm, where the typical water contact angle of plasma treated HDPE usually does not decrease bellow 30° to 35°. The AFM measurements confirmed that surface roughness after the plasma treatment was not changed.

So we can conclude that the described technology of HDPE modification based on DCSBD plasma source is applicable in industry for HDPE surface modification. This conclusion is based on the following findings: The high surface energy of HDPE was achieved at atmospheric pressure in ambient air processing conditions with processing time in order of seconds and without mechanical deterioration of treated surfaces.

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