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Argon plasma irradiation of polypropylene

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ABSTRACT

Polypropylene samples were exposed to argon plasma discharge and the changes of the PP surface properties were studied by different methods. Surface wettability was derived from contact angle measured by standard goniometry and chemical structure of the plasma modified PP was studied using X-ray photoelectron spectroscopy (XPS) and by Rutherford backscattering spectroscopy (RBS), surface morphology and roughness of samples using AFM. Zeta potential of pristine and modified PP was determined with the SurPASS. The presence of incorporated oxygen in the PP surface layer, about 60 nm thick, was observed in RBS spectra. Oxygen concentration is a decreasing function of the depth. With progressing aging time the oxygen concentration on the PP surface decreases. Plasma treatment results in a rapid decrease of the contact angle, which increases again with increasing aging time. In XPS measurement the oxygen containing structures, created by the plasma treatment, were found on the very surface of the modified PP and the zeta potential being changed too. The significant difference in zeta potential between pristine and plasma treated PP clearly indicates that the plasma treatment leads to a more hydrophilic PP surface.

1. Introduction

Polymer based materials have been applied successfully in several fields as adhesives, biomaterials, protective coatings, microelectronic components, automotive industry and in other thin-film technologies [1,2]. Owing to the consumer and technological qualities, polypropylene (PP) has very wide spectrum of application and takes the second place after polyethylene on world release – 20.5%. Polypropylene is applied for manufacture gas and water pressure head pipes, structures, sheets, film, furniture, technical products, the goods of cultural and community purpose. In general, special surface properties with regard to chemical composition, hydrophilicity, roughness, crystallinity, conductivity, lubricity and crosslinking density are required for successful applications. Surface modification techniques which can transform polymers into highly valuable finished products have became an important part of the plastic technologies [3].

Plasma treatment of polymers, including corona discharges, is now widely used industrial technique to modify surfaces of many different materials (metals, semiconductors, polymers, and ceramics). Polymers are often modified using rare gas (He, Ne, and Ar) or reactive gas (O_2 and F_2) plasma. Surface modification of polymers with low-pressure plasma has gained great scientific and industrial importance and it is often used to improve adhesion of coatings, wettability, printability, bio-compatibility and other surface related properties of polymers [4–7].

In this work, we studied surface properties of pristine and plasma treated PP with the main aim to understand surface chemistry and wettability of PP after the plasma exposure. Rutherford back scattering (RBS), X-ray photoelectron spectroscopy (XPS) were used for the characterization of the chemical structure of the modified PP and AFM for study of surface morphology and roughness of samples. The zeta potential and contact angle determination were used as methods for characterization of polymer surface.

2. Experimental

Polypropylene (PP, supplied by Visteon–Autopal, CR) in the form of 1 mm thick foils was used for the present experiments. The samples were modified in diode plasma discharge on Balzers SCD 050 device for 0–240 s using Ar^+ plasma (gas purity was 99.997%). The reaction chamber was evacuated to the pressure of 2 Pa and the working pressure during the plasma discharge was 10 Pa. The discharge powers were 3.1 and 8.3 W and the treatment was accomplished at room temperature.

Contact angle characterizing the surface wettability, was measured at six positions with distilled water at room temperature using surface energy evaluation system. The aging studies at laboratory conditions were performed on samples by measuring the

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dependence of contact angle on the time after the plasma modification [2,8].

Structural and compositional changes induced by the plasma treatment were examined about 7 days after the exposure. Meantime the plasma modified samples were stored on the air at room temperature. Oxygen concentration in the surface layer of the plasma modified PP was determined from X-ray photoelectron spectra (ARXPS), measured on Omicron Nanotechnology ESCAProbeP spectrometer. The XPS spectra were taken at different detection angles of photoelectrons which escape from the surface [9]. The spectra evaluation was carried out by CasaXPS program. Before the measurement, the samples were stored under standard laboratory conditions.

The concentration depth profile of oxygen in the modified PP surface layer was studied using RBS technique. The RBS analysis was performed in a vacuum target chamber with 2.72 MeV He^+ ions. Elemental depth profiles in the inspected polymeric samples were determined with the typical depth resolution less than 10 nm and accessible depth of a few μm. The RBS spectra were evaluated by the GISA3.99 code [10]. The typical RBS detection limit was 0.1 at.% for oxygen.

Zeta (ζ) potential of pristine and plasma treated PP was determined by SurPASS Instrument (Anton Paar). Samples were studied inside the adjustable gap cell in contact with the electrolyte (0.001 mol dm^{-3} KCl). Also the pH dependence of ζ-potential for both of PP was determined (by titration with 0.1 mol dm^{-3} HCl) in the range from 2 to 6.

We examined the surface morphology and roughness of pristine and plasma treated samples by AFM using VEECO CP II device working in tapping mode. Si probe RTESPA-CP with the spring constant 20–80 N/m was used. By repeated measurements of the same region (1×1 μm) we certified that the surface morphology did not change after three consecutive scans. The mean roughness value (R_a) represents the arithmetic average of the deviations from the centre plane of the sample [14].

3. Results and discussion

The dependence of contact angle of PP on the exposure time of the plasma treatment for discharge powers (8.3 and 3.1 W) is shown in Fig. 1. Rapid decrease of the contact angle was observed immediately 20 s after the modification for both plasma discharge powers. Contact angle declines to ca. 40° for PP modified at 3.1 W and to ca. 20° at 8.3 W in the first 50 s of modification. For the longer exposure times the contact angle achieves a saturated value in the range of 20–30° regardless of the plasma discharge power. The slight increase of the contact angle for higher exposure times may be related with the ablation and oxidation of the PP surface [11].

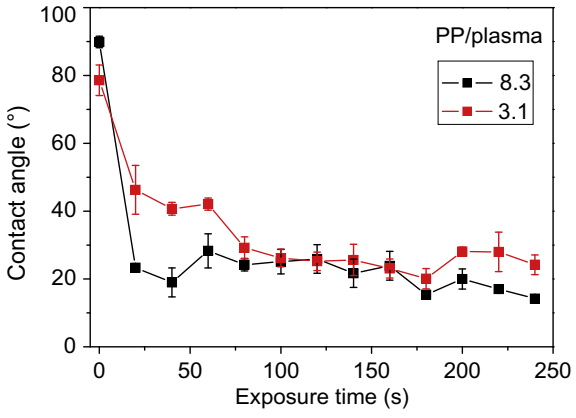

Fig. 1. The dependence of contact angle of PP on the time of the plasma treatment for discharge powers 8.3 and 3.1 W.

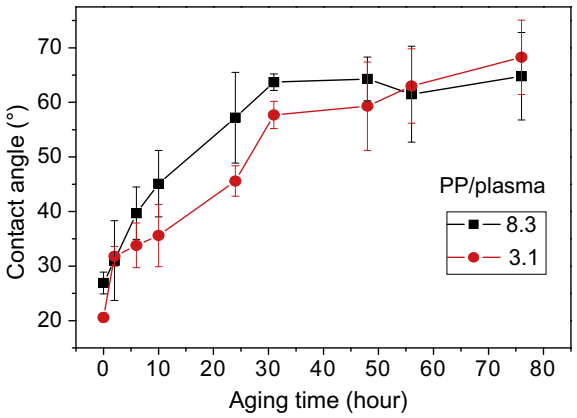

Fig. 2. The dependence of contact angle of the plasma modified PP on the time elapsed from the plasma treatment (aging time). Discharge powers were 8.3 and 3.1 W.

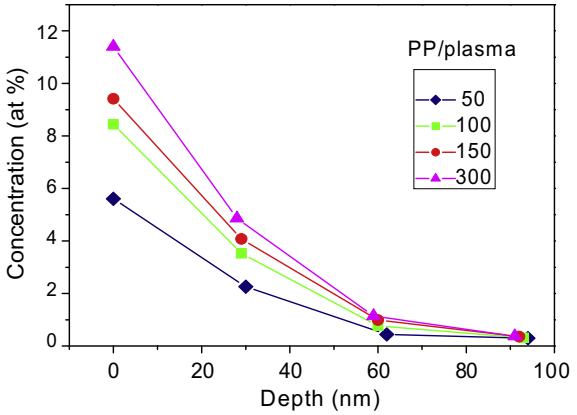

Fig. 3. Oxygen concentration depth profiles for the PP modified by the plasma discharge at 8.3 W power and exposure times (50, 100, 150 and 300 s). The profiles were obtained from RBS measurement.

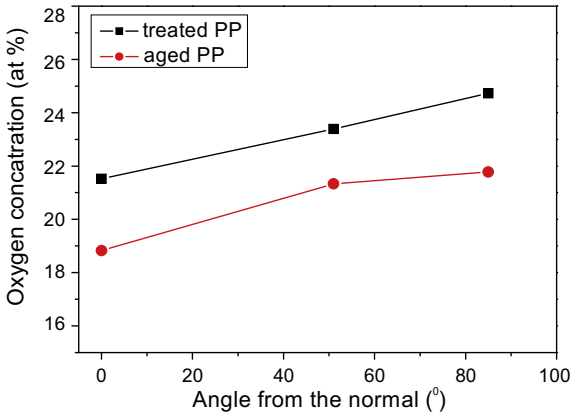

Fig. 4. Dependence of the oxygen concentration (at.%) on the ARXPS detection angles of photoelectrons which escape from the surface for plasma treated (1 h) and aged (170 h) PP.