Gold Nanolayers on Plasma-Treated Polypropylene

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Received in final form 22 October 2009

Abstract

This work deals with characterization of polypropylene (PP) exposed to plasma discharge and gold layers deposited on the plasma modified PP. PP foils were exposed to Ar plasma and subsequently metallized with sputtered Au layer. Chemical structure of the plasma modified PP was studied using X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering (RBS). Wettability of the plasma modified PP and its changes during sample aging were determined by goniometry. Surface morphology of PP and deposited Au layers was measured with atomic force microscopy (AFM). Continuity of Au layers was characterized by measuring their sheet resistance. With increasing exposure time in the plasma discharge the water contact angle decreases and the polymer surface becomes more hydrophilic. During the aging of the plasma treated samples the contact angle increases again. Plasma treatment leads to a decrease of the PP surface roughness and to generation of oxygen-containing polar groups on PP surface. During sample aging the concentration of the oxygen-containing groups decreases.

Keywords
Polymer, plasma treatment, Au nanolayer, morphology, electrical properties

1. Introduction

Polymer based materials have been employed successfully in several fields such as adhesives, biomaterials, protective coatings, microelectronic components and in thin-film technologies. In general, specific surface properties with regard to chemi-

cal composition, hydrophilicity, roughness, crystallinity, conductivity, lubricity and cross-link density are required for their successful applications [1].

Many advances have been made in development of techniques for modification of chemical and physical properties of polymer surfaces without affecting polymer bulk properties [2–5]. Polypropylene (PP) is a material widely used in many industrial fields. PP foils exhibit many good properties such as high transparency, light weight, thermal stability, chemical resistance, simplicity of manufacture and low cost [6]. For some applications, PP surface properties have a profound importance and their appropriate modification is, therefore, an area of great scientific and commercial interest.

Plasma treatment, including corona discharges, is now a widely used industrial technique to modify surfaces of many different materials (metals, semiconductors, polymers, ceramics) [2, 3]. Polymers are often modified using rare gas (He, Ne, Ar) or reactive gas (O, F) plasmas. 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 [7–10]. Many studies have shown that substantial changes in the chemistry, electronic properties, wettability and surface energy can be achieved by the plasma treatment [11]. The recent development of non-contact mode scanning force microscopes allows to measure soft samples such as polymers [12] or biological materials [13] with very weak interaction between the tip and the surface. Several AFM studies have been done on the effects of plasma treatment on PP surface morphology [14–17]. Restructuring of the surface by the plasma treatment can occur at µm and nm scales and it can influence adhesion, optical properties and wettability of polymers. It has been shown earlier that the presence of oxygen-containing groups on the surface of the plasma treated polymers improves gold adhesion to polymer surface [18].

Another way of modifying polymer surfaces with an aim to improve metal adhesion is grafting of SH groups on modified polymer surface. The wetting of polymer and the adhesion of gold can be increased [19].

This paper focuses on plasma treatment of PP and subsequent deposition of Au layer onto plasma modified PP. The effects of plasma discharge power and exposure time on wettability and chemical composition of modified PP are studied. Atomic force microscopy (AFM) is used for determination of surface morphology. Rutherford Back Scattering (RBS) and X-ray photoelectron spectroscopy (XPS) are used for characterization of the chemical structure of the modified PP. Next step will be the study of mechanical properties of gold layers deposited onto plasma modified PP surface and its adhesion.

2. Experimental

Polypropylene (PP) (supplied by Goodfellow-UK; density: 0.9 g/cm³; upper working temperature: 90–120°C) in the form of 50 µm thick foils was used for the
present experiments (area $2 \times 2$ cm). The samples were modified in a diode plasma discharge using a Balzers SCD 050 device for 0–240 s using Ar plasma (gas purity was 99.997%, Ar flow approx. 0.3 l/s, pressure of 10 Pa, electrode distance of 50 mm and its area 48 cm$^2$, chamber volume ca 1000 cm$^3$, plasma volume 240 cm$^3$). The discharge powers were 3.1 and 8.3 W and the treatment was carried out at room temperature. Detailed description of the sputter coater and specimen chamber is given in Fig. 1.

Contact angles, which characterize the surface wettability, were measured at 6 positions with distilled water at room temperature with a Surface Energy Evaluation System (Advex Instruments, Brno, Czech Republic). The aging studies at laboratory conditions were performed on samples by monitoring dependence of contact angle on time after plasma modification [20, 21].

Structural and compositional changes induced by the plasma treatment and aging time were examined after about 7 days from the exposure. The aim was to study the morphological changes and oxygen incorporation into polymer surface onto already aged polymer surface (contact angle was constant). In the meantime the plasma modified samples were stored in air at room temperature. The surface morphology of the pristine and modified PP was examined using Atomic Force Microscopy AFM (in tapping mode), under ambient conditions with a CP II Veeco microscope.

![Figure 1. Detailed description of sputter coater (a) and specimen chamber (b).](image-url)
Etched Si probe (doped with P), RTESPA-CP, with spring constant 20–80 N/m was used. Arithmetic mean roughness \( (R_a) \) represents the arithmetic average of the deviations from the center plane of the sample.

The Au layers were deposited from Au target (99.99%) using a diode sputtering technique (BAL-TEC SCD 050) onto pristine and modified PP foils. Typical sputtering parameters were room temperature, 0–500 s, 4 Pa Ar, 50 mm electrode distance and 20 mA current. The sheet resistance \( (R_s) \) of Au layers was examined by Ohm’s method with a picoampermeter KEITHLEY 487. For the measurement, two Au contacts, about 50 nm thick, were deposited on the layer surface by sputtering. The measurement was performed at a pressure of about 1 kPa to avoid contamination of the sample by water vapour from the air. The samples with lower resistances (up to 1 MΩ) were measured on the commercially available Multimeter UNI-T 83.

The thickness of the deposited Au layers was determined by atomic absorption spectroscopy (AAS) on a Varian AA 880 machine using flame-atomization technique at 242.8 nm wavelength. From the Au content on 4 cm\(^2\) area of the PP surface, the mean layer thickness was determined with a typical uncertainty of \( \pm 5\% \) [16].

Oxygen concentration in the surface layer of the plasma modified PP was determined from XPS spectra, recorded using an Omicron Nanotechnology ESCAProbeP spectrometer. The XPS spectra were taken at different detection angles of photoelectrons which escaped from the surface [4]. The results were evaluated using CasaXPS program. Oxygen concentration was determined on the basis of area under the O1s line with respect to the area under the C 1s line. Before the measurement, the samples were stored under standard laboratory conditions.

The concentration depth profile of oxygen in the modified PP surface layer was determined using the RBS technique. The RBS analysis was performed in a vacuum chamber with 2.72 MeV He\(^+\) ions. Elemental depth profiles in the inspected polymeric samples were determined with a typical depth resolution less than 10 nm and an accessible depth of a few µm. The RBS spectra were evaluated using the GISA3.99 code [22]. The typical RBS detection limit was 0.1 at.% for oxygen.

3. Results and Discussion

3.1. Surface Properties

The results of contact angle measurements on the plasma exposed PP samples are shown in Fig. 2. Rapid decrease of the contact angle was observed immediately after 20 s of modification for both plasma discharge powers. Contact angle declines to 25–35° for PP modified at 3.1 W and to 10–20° at 8.3 W. The decline in the contact angle indicates corresponding increase in the surface wettability.

The change of contact angle as a function of time from the plasma treatment (aging time) is shown in Fig. 3. With increasing aging time the contact angle increases and, thus, surface polarity decreases. A sharp increase in contact angle is observed
Figure 2. Dependence of water contact angle of modified PP on exposure time to plasma discharge for discharge powers 3.1 and 8.3 W.

Figure 3. Dependence of water contact angle of plasma modified PP on time elapsed from the plasma treatment (aging time). Discharge powers were 3.1 and 8.3 W.

in the first few hours. Then slower increase is observed for samples treated at the power of 3.1 W while for samples treated at the power of 8.3 W a maximum angle is reached already after about 20 h of aging. Regardless of the power of the plasma discharge the full surface relaxation and contact angle restoration are achieved after about 70 h of aging. Enhanced surface hydrophilicity of the plasma treated
polymers is due to the presence of oxygen-containing groups [21, 23, 26] and the subsequent relaxation is connected with their re-orientation and possibly also with rearrangement of degraded macromolecules on the polymer surface [4, 25].

Since more pronounced changes in surface polarity are observed on the samples treated at the power of 8.3 W, these samples were used in the following experiments. The presence of oxygen in the surface layer of the plasma treated PP was examined using the RBS method. The oxygen concentration depth profiles in the polymer surface layer are shown in Fig. 4. It is obvious that oxygen is present not only on the very surface of the sample, as the presence of oxygen is observed up to a depth of about 60 nm with the oxygen concentration decreasing from the surface to the bulk. From Fig. 4 it is further apparent that with increasing time of the plasma treatment the surface and total oxygen concentrations increase. Obviously, the residual oxygen contained in Ar gas flow in the plasma reaction chamber and then the oxygen from ambient atmosphere interacts with the activated PP surface and, thus, different oxidized structures are created on the PP surface. The UV radiation of the plasma and its particle bombardment produce C radical sites which react with oxygen from the air to form peroxy and hydroperoxy and their O-containing decomposition products (carboxylic acids, hydroxyls, phenols, ketones, aldehydes, ethers, etc.). Creation of carbonyl, carboxyl and ester groups on the plasma treated polyolefin has been shown earlier in similar experiments [23, 26].

The oxygen concentration (O1s) on the surface of the plasma modified PP sample was determined using the XPS technique. The oxygen concentration was measured at different detection angles of photoelectrons which escaped from the surface [4] on the plasma modified PP after 1 and 170 h of aging. The results are shown
Figure 5. Oxygen concentration in the surface layer of plasma modified PP obtained from XPS measurements accomplished 1 h (PP 1 h) and 170 h (PP 170 h) after the plasma treatment. The dependence of the concentration on the angle of the incident primary beam is shown.

in Fig. 5. The oxygen concentration decreases with increasing aging time due to rearrangement of the degraded macromolecules and oxygen-containing groups produced by the plasma treatment. These results are in agreement with the earlier results [4]. It can be also concluded that the highest concentration of oxygen is in the top surface (maximum incidence angle with respect to the surface normal), as the XPS measurement gives information from the very top surface.

The surface morphology of the PP, plasma modified at 8.3 W power for different exposure times, was examined by AFM technique. The measured dependence of the arithmetic mean roughness ($R_a$) on exposure time is shown in Fig. 6. A decline in surface roughness with increasing exposure time is observed. Surface morphology of pristine and plasma treated PP will be discussed later.

3.2. Au Nanolayers on Modified PP

The Au layers were deposited on pristine and plasma modified PP (power 8.3W, exposure time 240 s) for sputtering times from 10 to 500 s. The samples prepared under these conditions exhibit most significant change in the contact angle (see Fig. 2) and in the surface roughness (see Fig. 6). The dependence of the layer thickness on sputtering time is shown in Fig. 7 for pristine and plasma modified PP. The dependence is nearly linear and the same for both pristine and plasma modified PP. Obviously, the plasma treatment does not affect the thickness of the sputtered layer.

The sheet resistance ($R_s$) of Au layers deposited on the plasma modified PP as a function of sputtering time is shown in Fig. 8. The resistance decreases with in-
Figure 6. Dependence of the surface roughness ($R_a$) of the plasma modified PP (discharge power 8.3 W) on the exposure time.

Figure 7. Dependence of the thickness of the Au layer on the sputtering time for pristine and plasma treated PP (exposure time 240 s, power 8.3 W).

Increasing sputtering time (and increasing layer thickness). An electrically continuous layer ($R_s$ is aprox. constant) is formed earlier for Au sputtered on PP modified at 3.1 W discharge power in comparison to that modified at 8.3 W. After about 60 s sputtering time (average layer thickness of 10 nm) the Au layer becomes electrically continuous for both discharge powers.
Figure 8. Dependence of the sheet resistance on the Au sputtering time for Au layers deposited onto PP plasma modified at the discharge powers of 3.1 and 8.3 W (exposure time 240 s).

AFM images of the surface morphology of the pristine and plasma modified PP (8.3 W, 240 s) are shown in Fig. 9(a) and (9b). Plasma treatment and aging of modified PP leads to surface roughness decrease and a granular structure becomes apparent on the PP surface. The surface morphology of the PP modified for 240 s at 3.1 and 8.3 W discharge powers and then sputtered with Au for 30 and 160 s can be seen from Fig. 9(c)–9(f). The surface morphology and the roughness of the electrically discontinuous Au layers (sputtering time 30 s) are shown in Fig. 9(c) and 9(e) for the layers deposited on the PP modified at 3.1 W power. The same is seen for the PP modified at 8.3 W power in Fig. 9(d) and 9(f). It may be concluded that the morphology of sputtered Au layer is analogous to that of the plasma modified polymer. With increasing sputtering time the deposited Au clusters become larger with a maximum size of about 15 nm and the mean roughness slightly increases.

4. Conclusion

In accord with similar previous studies it was found that the plasma treatment results in pronounced changes in the surface properties of PP. Higher discharge power leads to more significant decrease of the contact angle in comparison to pristine polymer, thus leading to the dramatic increase of the PP surface wettability. With increasing time from the plasma treatment the contact angle increases and after about 70 h the contact angle reaches a saturated value because of re-orientation of plasma modified polymer chains. RBS and XPS measurements show the presence of oxygen-containing groups on the PP surface modified by the plasma discharge. According to the RBS measurements the oxygen depth profile extends up to a depth
of about 60 nm, the oxygen concentration being a decreasing function of the depth. A decrease of the surface roughness with increasing exposure time in the plasma discharge was observed. The thickness of the Au layer sputtered onto pristine and plasma modified PP is nearly a linear function of the sputtering time and it is not affected by the plasma treatment. The sheet resistance of the deposited Au layers decreases rapidly with increasing deposition time. The decrease being more rapid on samples modified at lower plasma discharge power. The surface roughness de-

Figure 9. AFM images of the pristine PP (a) and the plasma modified PP (8.3 W, 240 s) (b). AFM images of the Au layers sputtered onto the PP plasma modified for 240 s at the discharge powers of 3.1 W (Au sputtering time 30 s (c) and 160 s (d)) and 8.1 W (Au sputtering time 30 s (e) and 160 s (f)). $R_a$ is the arithmetic mean surface roughness in nm.
creases after the plasma modification and a granular structure appears on the PP surface. The surface morphology of sputtered Au layer is analogous to the morphology of the plasma modified polymer, but with the increasing sputtering time Au clusters becomes larger and the surface roughness slightly increases.

Acknowledgements

This work was supported by the Grant Agency of the CR under projects No. 106/09/0125 and 106/09/P046, Ministry of Education of the CR under Research programs No. 6046137302 and LC 06041, and Academy of Sciences of the CR under projects KAN400480701 and KAN200100801.

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