Chemical Structure and Characteristics of Films Deposited on Polyethylene Terephthalate Surfaces in Plasma

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Abstract – AFM, XPS and contact wetting angle measurements have been used to study features of formation of films deposited in plasma onto the polyethylene terephthalate (PET) surfaces. A series of common laws has been discovered during the formation of polymer films on PET substrates and metal surfaces in heptane plasma. PET destruction in plasma largely influences film growth kinetics, structure, and physicochemical characteristics of the films. The film deposited on PET is structured with a greater speed; also, its strength and polymerization degree are higher than those of the metal substrate deposited film. This takes place due to the modification of heptane conversion products by PET fragments. The latter are formed in the process of PET etching in plasma.

1. Introduction

Due to the surface hydrophilicity a number of polymer composites with high physicomechanical and thermophysical characteristics are known to lack environmental stability. The material can be affected by microorganisms, temperature and moist taken together. The reason for such destruction is associated with ester bonds present on the surface. Among these polymer materials are polyethylene terephthalate-based (lavsan) composites. To obtain surface hydrophobicity carbon groups can be introduced into the surface. An efficient technique for applying hydrocarbon layers onto material surface is their deposition in saturated hydrocarbon plasma.

The paper presented deals with the formation, growth, and physicochemical characteristics of films obtained on the polyethylene terephthalate surface by polymerization in low-temperature plasma of heptane.

2. Experimental

The the films were deposited onto polyethylene terephthalate (PET, $t_m = 280$ °C) plates. A bell-type reactor with a displacement of 200 cm^3 was used for plasma treatment performed in a dynamic mode with the samples being equidistant. The system has been pumped off to 4.66 Pa, then a monomer (heptane) with the vapor pressure before the discharge onset 12 Pa at a steady-state flow (p_0) was applied. Discharge power was 40 Wt, heptane vapor pressure prior to discharge was 12 Pa, plasma treatment duration τ_{pl} of samples varied between 5–300 s. To control heptane flow before and after glow-discharge plasma excitation by rf-field with the frequency of 40.68 MHz, a needle dosimeter was used. Atomic force microscopy (AFM) was used to study microrelief, roughness, strength and adhesive characteristics of the films. The investigations were performed with P4-Solver and P47-Solver apparatuses using the techniques described in [1, 2]. The chemical composition of the films was studied by means of XPS in accordance with [3]. The contact wetting angle of the films was measured goniometrical method as described in [4]. Chromel-copel thermocouple was used to perform temperature control in plasma reactor.

3. Results and Discussion

According to XPS, the relative content of C and O in the initial PET makes up 73 at.% and 27 at.%, respectively, which is close to stoichiometry (72:28). This can be seen from the C1s and O1s spectral lines that can be ascribed to C-O bonds ($E_b = 286.6$ and 533.5 eV, respectively) and C=O in a C(O)OR-fragment of the PET molecule ($E_b = 289.0$ eV and 531.9 eV, respectively) [5] (Fig. 1, a). A contact wetting angle $\theta = 73 \pm 2^o$ is close to the value characteristic of hydrophilic group-containing polymers [6], PET included [7].

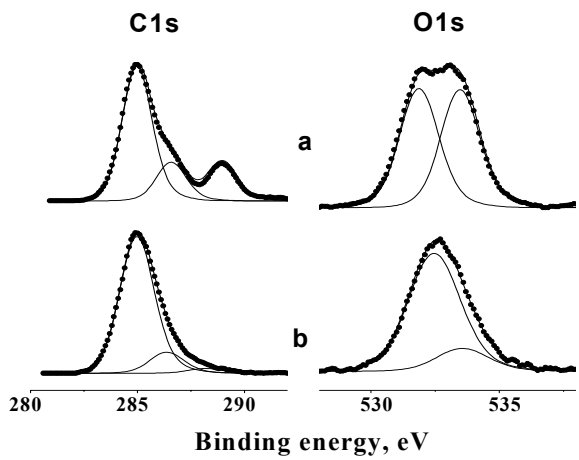

Fig. 1. XPS-spectra of polyethylene terephthalate film: a – initial, b – treated in heptane plasma ($\tau_{pl} = 5$ s)

The PET-film destructs at the loading of $S_t = 0.7$ nN. In an attempt of measuring adhesion (F_{ad}) between a silicon probe and the PET – surface "sticking" of the

probe was observed. The topography of the initial substrate is nonuniform. It includes pits and hills and has a mean square roughness $S_q = 1.5$ nm (Fig. 2, a and Fig. 3, curve 1).

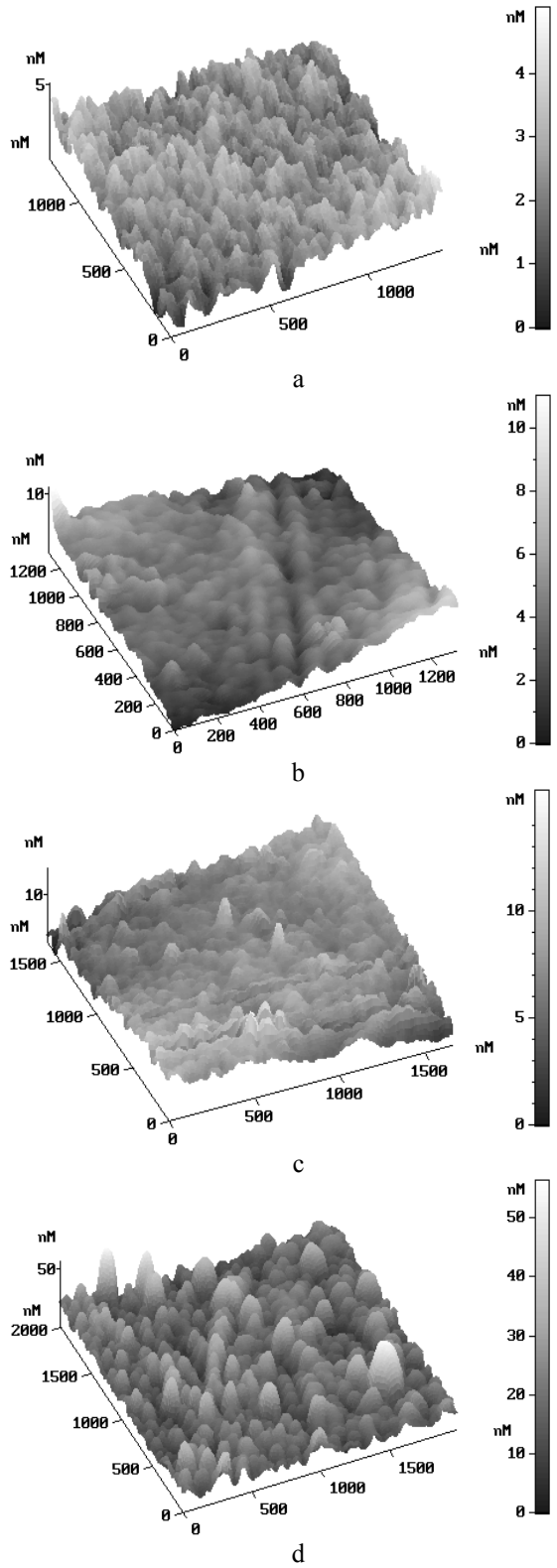

Fig. 2. Surface topography of initial PET-film (a) and films deposited on PET. τ_{pl}: b – 5 s, c – 60 s, d – 300 s

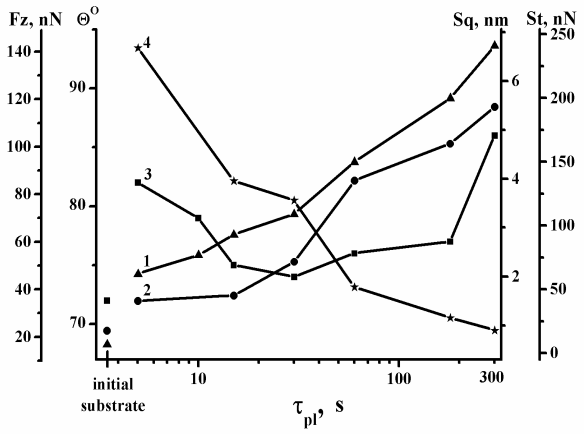

Fig. 3. Characteristics of films deposited on PET substrate: 1 – strength (S_t), 2 – roughness (S_q), 3 – contact wetting angle (θ); 4 – adhesive force between probe and sample surface (F_{ad})

Judging by the XPS-data, already after 5 s of plasma treatment the substrate surface is covered with a layer of the deposited fragments (Fig. 1, b) along with the reduction of the content of O-atoms in the film surface layer to 7 at.% is an evidence of it. The content of O-atoms in the film surface layer is within the range of 9 ± 2 at.% during the total treatment time interval τ_{pl}. Also approximately similar is the composition of hydrophilic oxygen-containing fragments: C-O-C, C-OH и C=O (E_b of C1s- and O1s-spectra 286.5 and 533.5 eV, 286.5 and 532.5 eV, 288.0 and 532.5 eV, respectively [5]). A roughness increase is observed on the surface of plasma-treated PET-substrate (Fig. 3, curve 1). As a consequence, small cone-like structures with the dimensions: $d = 40$–50 nm, h as high as 3 nm, uniformly cover the whole surface (Fig. 2, b), witnessing uniformity of the film stress field. The strength of the plasma treated PET became almost an order of magnitude higher; a 10° increase of θ was stated (Fig. 3, curves 2, 3); also, the adhesive interaction between the probe and the film lessened (no sticking of the probe was observed enabling quantitative assessment of the adhesive force F_{ad} to be made) (Fig. 3, curve 4). Hence, a conclusion can be made that a film deposited on PET in the time interval 5 s is noticeably structured. It is known that the action of low-temperature plasma strength (St), on polymers results in their etching [8–10]. In our case the PET-etching can be assumed to lead to the modification of heptane conversion products by the PET-fragments formed during etching, as was the case with the series of polymers [8, 10, 11]. These fragments could then embed into the forming film [12].

At $\tau_{pl} = 15$ s isolated cones 50 nm in diameter and 5–7 nm in height appear at the surface (Fig. 2, c). Their number constantly grows with τ_{pl} (Fig. 2, d), with their distribution being statistical. Further structurization of the film on the PET surface can be evidenced by its 2.5-fold strengthening as well as a sharp

decrease of adhesive interaction between the probe and film (Fig. 3, curves 2, 4). Given hindered reorientation of hydrophilic groups around a polymer chain during polymer structuring, as was the case with the film forming on a steel substrate [4], further hydrophobicity of the film on PET should be expected. In fact, however, a 10° drop in θ is observed (Fig. 3, curve 3). Due to the accumulation of the PET etching products the decreased hydrophobicity of the film on PET can be explained in terms of constant increase of bulk and surface oxygen content. Such an increase takes place up to $\tau_{pl} = 30$ s. As τ_{pl} grows to 180 s surface hydrophobicity of the films increases. At the same time the films become stronger (Fig. 3, curve 2). This implies even larger degree of cross-linking and branching of macromolecule chains. In the range of τ_{pl} between 180 and 300 s small cones coalesce into larger ones (Fig. 2, d). At $\tau_{pl} = 300$ s $d = 150–200$ nm cones appear. In this time interval (plasma temperature 104 °C) traces of PET destruction such as color changes and film strain arise.

In [4] it was shown that when a film was deposited on a steel substrate up to $\tau_{pl} = 60$ s, a polymer layer practically reproduced surface relief of a substrate. Its roughness remained unchanged. After that isolated cones could be seen on the surface. Only a slight growth of the film hydrophobicity on a steel substrate was observed despite an approximately similar content of polar groups in the film surface layer in comparison with a PET substrate. This evidences that the reorientation of these groups is hindered insignificantly [4]. In other words, the conjecture about a weak film structuring or incomplete monomer polymerization is true. Also, attempts in measuring F_{ad} demonstrated that up to $\tau_{pl} = 60$ s areas of the probe sticking were observed on the film. A slower increase of hydrophobicity and strength is observed in case of the steel substrate deposited film. Thus, the strength of the film deposited on metal substrate at $\tau_{pl} = 180$ s makes up 80 nN, and in the case of PET-deposited film it is 200 nN.

At $\tau_{pl} = 300$ s physicochemical characteristics of the films become less dependent on a substrate. The limiting value of θ reaches 103° in case of the films deposited in heptane plasma onto steel substrates [4] and 94° for the films deposited onto PET. Both substrates exhibit cones 150–200 nm in size. The values of strength characteristics become closer (160 nN metal substrate and 240 nN in the case of PET substrate). It can be assumed that further τ_{pl} increase should have given similar film surface characteristics. Unfortunately, it was impossible to confirm because of the signs of PET destruction, such as color change and film deformation, which appeared already at $\tau_{pl} = 300$ s.

4. Conclusions

1. AFM, XPS and contact wetting angle measurements have been used to study features of formation of films deposited in plasma onto the polyethylene terephthalate (PET) surfaces

2. A series of common laws has been discovered during the formation of polymer films on PET substrates and metal surfaces in heptane plasma.

3. Ground has been given to the assumption that PET destruction in plasma largely influences film growth kinetics, structure, and physicochemical characteristics of the films. The film deposited on PET is structured more rapidly and has a higher strength and degree of structuring. This can result from the modification of heptane conversion products by PET fragments. The latter are formed in the process of PET etching in plasma.

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