

Combined AFM and XPS investigation of plasma-polymerized films of saturated hydrocarbons deposited onto organic substrate

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The deposition of films onto metal substrates in saturated carbon plasma has already been reported [1,2]. It is now of interest to study the process of film deposition onto polymeric substrates in hydrocarbon plasma. The action of plasma is known to entail modified surface characteristics of polymers. Hence, the deposition of films onto these surfaces can result in films with completely new surface characteristics.

The present paper deals with the investigation of polymeric layers formed on a polyethylene terephthalate substrate in heptane plasma.

Polyethylene terephthalate (PET) films with the thickness of 20 μm served as the investigational objects. The samples were subjected to plasma treatment in accord with the methods described in [1,2] under the following regimes: discharge power – 40 Wt, heptane vapor pressure prior to discharge – 12 Pa, plasma treatment duration (τ_{pl}) – from 5 to 180 s. The microrelief, surface roughness and strength of films together with film surface polarity variations were studied by means of AFM according to the methods described in [1,2]. The apparatuses P4-Solver and P47-Solver by the NT – MTD company were used with this purpose. XPS was used to study the chemical composition of films following the techniques described in [1].

The initial film surface is non-uniform, with irregularities predominantly in the form of grooves and hills (Fig.1a). The shape of irregularities was determined by the film manufacturing method. Mean square surface roughness R_q is equal to 5 nm. The chemical composition of the initial film is close to stoichiometry. The atomic ratio C:O makes up 73:27. The C1s- and O1s-spectra include peaks, capable of being ascribed to C-O bonds ($E_b = 266.6$ eV and 533.5 eV) and C=O bonds ($E_b = 289.0$ eV and 531.9 eV) in a fragment of a C-O-C=O molecule of PET (Fig.2a). The film strength characteristics are so poor that as small a loading as 1 nm is required to disrupt the film. In the process of measuring the interaction forces between the tip and the sample $F(z)$ “sticking” of the tip is observed, which indicates that the polymer is not cross-linked.

Two concurrent processes take place during the film treatment in heptane plasma. These are the surface destruction of a PET film and the deposition of a film from heptane vapor. As little as 5 s of plasma-treatment is required to lower considerably the film surface roughness ($R_q = 1.7$ nm). Isolated cones now arise, and the relative content of O decreases to 7%. Peaks ascribed to the C-O-C=O fragment in the C1s- and O1s-spectra disappear, and new peaks assigned to C-O, C-O-C and C=O bonds ($E_b = 286.5$ and 533.5 eV; 286.5 and 532.5 eV; 288.0 and 532.5 eV, respectively) emerge (Fig.2b). $F(z)$ varies within the range of 0.24-0.54 mN (Fig.3a). The plasma-deposited layer, which consists of both the PET film destruction products and the products of heptane conversion in plasma, is characterized by a continuous coverage. At $\tau_{\text{pl}} = 15$ s the film surface has the lowest $R_q = 1.2$ nm. The destruction of the substrate is significant here. The film is uniform enough, with only occasional individual cones (Fig.1c). The number of O atoms increases to 10%, causing a drastic increase of the film strength. As high a loading is now required to disrupt the film as 90 nN. This increased strength in comparison with the initial film is explained by the cross-linking processes in the film due to oxygen-containing fragments of plasma gas phase. At $\tau_{\text{pl}} = 60$ s the surface roughness reaches

$R_q = 2,8$ nm. Multiple cones emerge on the film, imparting nonuniformity to it (Fig.1c). $F(z)$ at cone apexes is equal to 0.01 nN, which is actually indicative of the appearance of

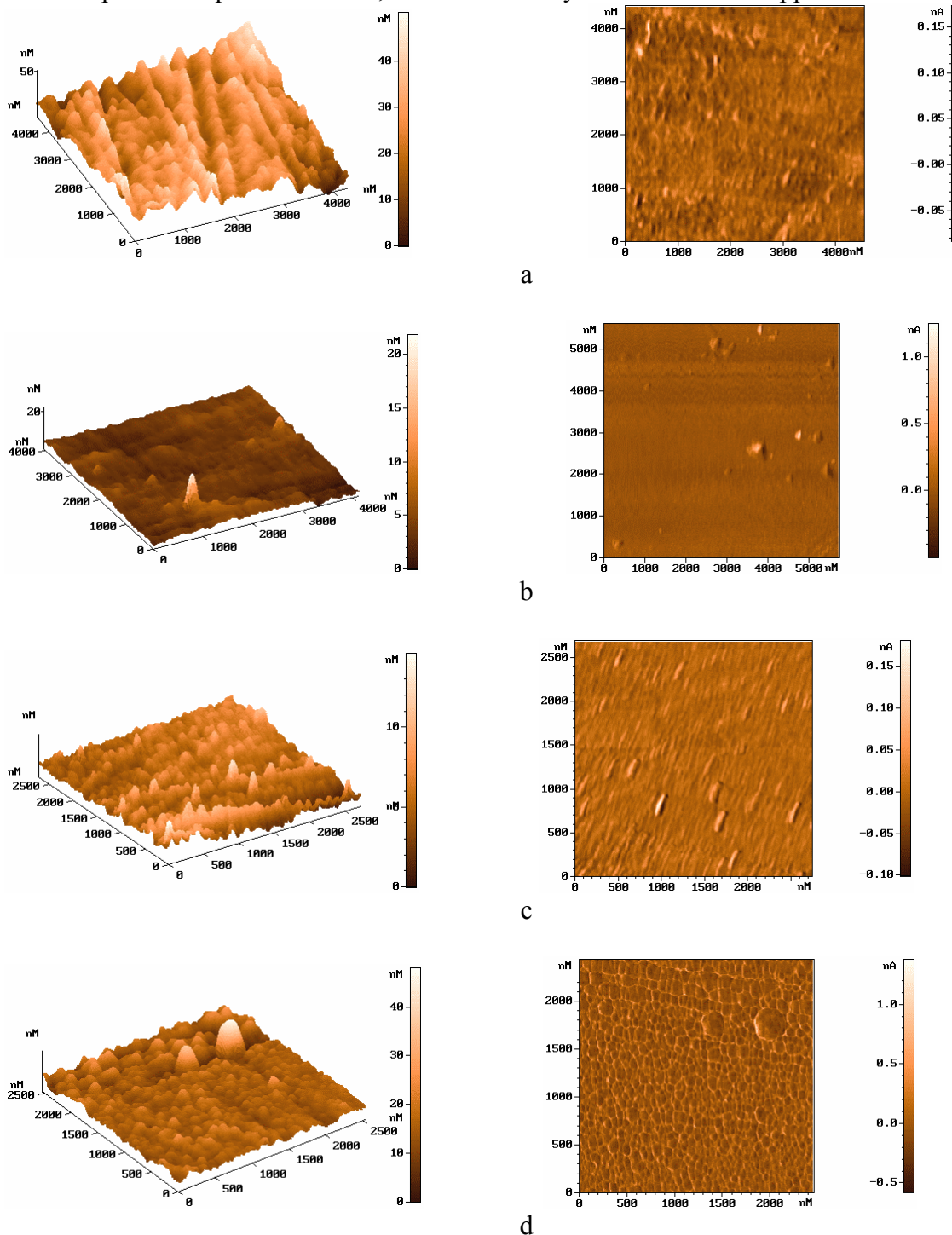


Fig.1. AFM-images (topographic and lateral forces) measured from polyethylene terephthalate film treated in heptane plasma at τ_{pl} , s: a = 0, b = 15, c = 60, d = 180.

practically hydrophobic areas, though areas where $F(z)=0.14$ nN are also present (Fig. 3c). The film strength has grown up considerably – the film now endures the maximum loading - 90 nN - applied to the probe. Even higher surface roughness is observed - $R_q = 3.9$ nm – with the further increase of τ_{pl} to 180 s. The surface is now characterized by newly formed macromolecular species 100-150 nm in size, distributed uniformly across the surface (Fig.1d). $F(z)$ varies from 0.03 to 0.07 nN, which is indicative of a higher film surface uniformity. The

film here is characterized by a high strength. All this indicates a high cross-linking degree in the film.

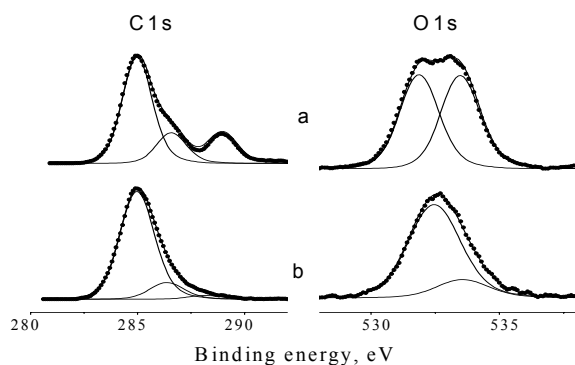


Fig.2. XPS-spectra of polyethylene terephthalate film: a – initial, b - treated in heptane plasma ($\tau_{pl} = 5$ s).

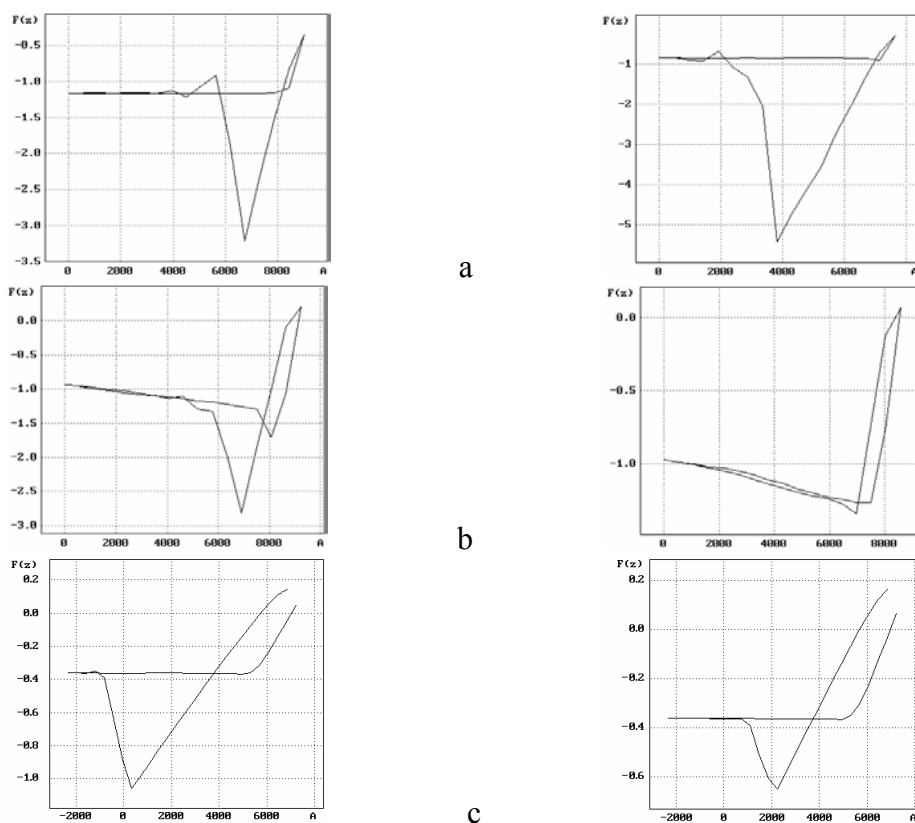


Fig.3. $F(z)$ of polyethylene terephthalate surface treated in heptane plasma at τ_{pl} , s: a=5, b=60, c=180 (Fz - (nA), with 1 nA corresponding to 150 nm).

Conclusion

1. In the process of a polymer deposition onto a polyethylene terephthalate substrate in heptane plasma, a surface layer is formed, consisting of the destruction fragments of polyethylene terephthalate and the plasma-induced conversion products of heptane.

2. The increase of the film surface layer strength is determined by the cross-linking processes in the film, with the main reason for the latter being the appearance of the O-containing fragments of polyethylene terephthalate destruction products in gas phase.

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- [1]. A.M. Lyakhovitch, A.M. Dorfman, S.G. Bystrov, V.I. Povstugar. *Low-Dim. Struct.*, 3/4, 2001, p277.
 [2]. A.M. Lyakhovitch, A.M. Dorfman, M.A. Shirobokov, *Low-Dim. Struct.*, 5/6, 2002, p137