Structural-mechanical AFM study of inhomogeneous stiff nanocoating of soft polymer substrate

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Abstract. Modification of polymer with low-energy gas plasma is used to change the wettability of the surface and, as a consequence, to improve the interactions with biological objects. As a result of such treatment, a nanolayer, which is stiffer than the initial surface, is formed on a broad class of polymers. Elastic polyurethane is one of the widely used polymers. This is two-phase material consisting of soft and hard blocks. Its surface was treated by low-energy argon plasma and studied by an atomic force microscopy (AFM): the structure becomes rough and mechanically inhomogeneous depending on the part of the surface treated (hard or soft blocks of the material). The average value of elastic modulus increases with the treatment time, but the average thickness of the coating does not change, having a wide dispersion. All these features are related with the heterogeneous surface peculiarities of the initial polymer.

1. Introduction

Plasma treatment significantly changes the physicochemical, mechanical, and structural properties of the surface [1]. This is a promising way to modify the polymer surfaces. Polyurethanes, due to a wide range of thermomechanical properties from stiff plastics to soft elastomers, are used in many areas. Coatings formed by plasma modification of soft elastic polyurethanes have many potential applications, in particular in the development of biomedical products with improved properties. However, such substrates are easily deformed under the action of external loads, which often damages the coating [2] and the positive effect of the treatment falls [3]. Therefore, the low energy plasma modification of the polymer surface is of interest. Studies on the treatment of polyurethanes with oxygen [4], nitrogen [5], argon [6], or ammonia [7] low energy plasma have shown changes in surface hydrophobicity, which led to improved cell and protein adhesion.

Argon, being a noble gas, does not react with polymer atoms, but destroys C-C and C-H bonds of macromolecules; thus, free radicals are emerged and the surface activity increases [6]. At the same time, new C-C bonds are formed, and carbonization of the surface occurs [8]. The plasma-induced changes of the structural and mechanical properties of the surface should be taken into account, especially when creating coatings on soft polymers that are easily deformed. Note, that the polyurethane (PU) is a two-phase system consisting of soft and hard blocks of neat-like [9] or globular structure [10]. The influence of plasma on such an inhomogeneous material should lead to the formation of an inhomogeneous coating.

In this paper, the AFM methods are applied in study of structural-mechanical properties of the PU surface modified by the low energy argon plasma. The obtained results can be used to create deformable materials with improved biomedical properties.

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2. Materials and methods

PU was made of pre-polymer (urethane based on simple polyester and toluene diisocyanate) and hardener (MOKA). The components were heated to 70°C, vacuumed for 5 min, mixed, then vacuumed again, and cured at 100°C for 20 h. The thickness of the obtained plates was 2 mm. An initial modulus of elasticity was 30 MPa and elongation at rupture ~ 800% (measured by uniaxial mechanical tests).

The samples (20x20 mm²) were placed in a plasma unit in an electrically insulated holder cooled with water. The chamber was vacuumed to a pressure of 5*10⁻⁵ Torr. The pressure of argon was set to 2*10⁻³ Torr and a glow discharge with a current of 1 A was ignited in the source of low energy electron beam; the accelerating voltage of the electron source was 100 V. Injection of electrons into the plasma chamber provided generation of Ar plasma, which particles interacted with the surface of the samples. Treatment time τ was set to 6 or 8 minutes: preliminary study has shown that at these durations, the energy of the treated surface has a maximum and exceeds the value for raw material, i.e. the hydrophilicity increases.

Structural-mechanical study of surface properties was carried out by an AFM Ntegra Prima (by NT-MDT BV) in semi-contact regime, force modulation, as well as by nanoindentation. In all the cases, the scanning was performed by a sample. The geometry of the probe tip was evaluated by blind reconstruction method based on TipCheck samples: probe tip radii ranged from 6 to 15 nm, and the stiffness of k cantilevers was estimated by the Sader method. For quantitative comparison of the force measurements, the sensitivity of the probes was calibrated using a silicon substrate.

In semi-contact regime, the probe oscillates near the sample surface and slightly taps it, causing changes in amplitude (determines the height) and phase (shows qualitatively the heterogeneity of the surface composition) of oscillations. In this mode, stiff probes (k ~ 30 N/m) with high resonance frequency were used.

In force modulation, the probe scans the sample in the contact mode: it is pressed against the surface with certain constant force. Additionally, the scanner with the sample performs harmonic modulation (the frequency was set to 3 kHz and the amplitude ~ to 0.05 V), so the probe begins vibrating. The amplitude of these vibrations is proportional to stiffness of the surface. Soft probes (k ~ 0.5 N/m) were used in this mode.

Nanoindentation was carried out to determine a thickness of the coatings, as well as to estimate mechanical properties of the surfaces. In all cases, several areas (3x3, 5x5 µm²) of the sample were studied for statistical purposes. The indentation onset was considered to be the first point after the probe jumps to the surface; depth of indentation: u = z - d, where z is the movement of the probe base; d is the cantilever deflection. Typical curve of indentation of PU and corresponding dependence of applied load F = kd vs. the depth of indentation are shown in Figure 1a. In this case, soft probes (k = 0.5 nN/nm) were used. The modulus of elasticity was estimated using the approximation of the F(u) curves by the Hertz model.

The thickness of the coatings was determined by stiff probes (k ~ 35 N/m). Surface relief before and after the indentation was studied in semi-contact mode. It was found that the indentation imprints remained on the surface (Fig. 1c) after the indentation with a significant load; they ranged from 80 to 400 nN, depending on the sample. A typical indentation curve of the coating on elastic PU is shown in Figure 1b: the change in slope (indicated by an arrow) corresponds to onset of piercing the coating. The surface of untreated PU is elastically recovered after the indentation to the same depth. Thus, the thickness t of the coating could be estimated by the depth of the indentation imprint. Relief irregularities in the vicinity of the imprint make it difficult to clearly determine t by the height h of the profile (Fig. 1e). Therefore, the cross-sections of the imprint depending on the depth (Fig. 1d) were analysed. The thickness of the coating was assumed to be the height of the imprint, where the ratio of the cross-section areas at the given and the previous h was minimal (Fig. 1f).
3. Results and discussion

The original untreated PU is a complex system consisting of soft and hard phases. Its surface is not perfectly smooth (Fig. 2a). The hard phase looks like a mesh of threads clearly visible on the phase contrast of the AFM-image (Fig. 2a). These threads are distributed heterogeneously and form dense agglomerates with sizes from 20 nm to 4 μm, making bumps on the surface. Roughness of the surface will be discussed further. On the distribution (statistical probability density) of elastic modulus (Fig. 2b), three areas can be distinguished: 1) indentation of soft phase (modulus ~20 MPa); 2) indentation of mixed regions; 3) indentation of hard phase, which is the main part of the material (modulus ~40 MPa).

Figure 2. (a) Surface height and corresponding phase contrast of untreated PU; (b) the distribution of elastic modulus.
The interaction of argon plasma with the PU surface causes the destruction of C-C and C-H bonds on the polymer surface, the formation of free radicals, and increase in surface hydrophilicity [6]. At the same time, carbon bonds are being rearranged and the so-called surface carbonization [8] occurs.

As a result of argon treatment, the surface changes: the neat-like structures of the hard phase at \( \tau = 6 \) min are visible on the phase contrast of AFM-images (Fig. 3a) only partially and disappear completely at \( \tau = 8 \) min (Fig. 3b). RMS roughness (Fig. 4a) of the surface depends on the size of the observation: small areas could include flat regions or rough fragments of agglomerates of the hard polymer phase: the roughness increases on the scale up to 4 \( \mu \)m, but further reaches an asymptote.

The heterogeneous relief of the surface was segmented by the watershed method into highland areas \((z > 1.1z_{avg}\text{, where } z_{avg} \text{ is the mean height of the AFM image})\) and lowland \((z < 0.9z_{avg})\) ones. As an illustration, lowland contours are shown in the top of Figure 3c; highlands – in the bottom. The size of the segmented object was defined as \(A^{0.5}\), where \(A\) is the area of contour.

The roughness increases after 6 min of plasma treatment (Fig. 4a); further treatment flattens the relief below the level of the untreated material. Such behaviour can be explained by examining lowlands and highlands areas separately, the latter being agglomerates of the hard phase of PU.
Low-energy argon plasma treatment mainly affects the structure of lowlands: the areas, where the soft phase of the initial PU prevails. Local roughness (measured separately in the areas of highlands and lowlands) increases after the treatment for 6 min, and then falls (Fig. 4b). Changes in the roughness of the highlands are insignificant, while the roughness of the lowlands has fallen by almost a half. The average size of the lowlands increased by 15 nm after the treatment, and that of the highlands – by 7 nm (Fig. 4c); it means the etching of low (soft) areas and growth of high (hard) areas. At the same time, both types of surface segments became flatter; the total roughness (Fig. 4a) at $\tau = 8$ min fell. Thus, in the terms of microstructure, the given plasma treatment primarily affects the soft phase of PU.

The stiffness of the treated surfaces is heterogeneous. For example, Figure 5a shows a map of stiffness obtained in force modulation regime for the treated PU ($\tau = 8$ min): the stiffness of the highlands is 10% higher than that of the lowlands. The statistical distributions of the stiffness (obtained by the force modulation) are given in Figure 5b; longer activation leads to the significant rise of stiffness.

Estimated values of the average elastic modulus of the treated surfaces calculated from the initial part of the indentation curves (Fig. 1b), were 60 and 300 MPa for 6 and 8 min, respectively. The deformation of the soft elastic substrate was not accounted, so the modulus of the coating itself was higher.

The coating thickness was 5±2 nm regardless the treatment time, i.e. at $\tau \leq 6$ min the limiting thickness of the surface modification in this regime is reached; further treatment changes the structure and stiffness of this layer. Wide scatter of thickness from the mean value is explained by inhomogeneous properties of the original substrate.

4. Conclusion

Low energy argon plasma treatment of soft elastic polyurethane caused structural and mechanical changes of the surface. The initial substrate is a two-phase system: thread-shaped hard blocks (elastic modulus ~40 MPa) in a softer matrix (elastic modulus ~20 MPa). Dense clusters of hard phase form agglomerates, which look like bumps on the surface. Plasma treatment caused degradation of the threads of the hard phase, significantly changing the microstructure (size and roughness) of the surface lowlands, where the concentration of the hard phase is relatively low. The structure of the highlands (agglomerates of the hard polymer phase) has changed insignificantly.

The duration of plasma treatment (6 or 8 minutes) did not affect the thickness of the modified surface layer (non-uniform thickness from 3 to 7 nm), but significantly affected the average surface stiffness, which increased compared to untreated material by 2 and 10 times, respectively. The local stiffness is heterogeneous and depends on the surface area: treated agglomerates of the hard polymer phase are 10% harder than the surrounding surface.

It is known that such treatment increases the hydrophilicity of the surface and promotes sorption of certain blood proteins, which is a promising way to improve the biomedical properties of the material.
However, a significant increase of coating stiffness in relation to the substrate can lead to undesirable consequences when deforming the treated material: under the influence of external loads the surface may be damaged. These processes require further study.

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