The study of island carbon coating on nitrogen-activated polyurethane surface

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Abstract. Application of stiff carbon-like coatings to improve the properties of elastic polymers is limited. Deformation of the polymer damages the coated surface. The creating of discontinuous coatings could be a good solution in this case. In this paper, the formation of carbon island coating on the surface of an elastic polyurethane is studied. The discontinuous layer is obtained on the nitrogen-activated polymer surface by the magnetron sputtering of the graphite target. Depending on the number of pulses of the sputtering (1500 or 2000), carbon islands (~70 μm wide and 25 or 46 nm thick) are formed on the surface. Some islands have a wrinkled surface and are characterized by the spectrum of amplitudes and wavelengths which reach maximum at the center of the island. Small number of pulses leads to the formation of more heterogeneous coating with pronounced wrinkles, further sputtering reduces surface heterogeneities.

1. Introduction
Surface modification by plasma methods is actively used in many applications (increase of wear and corrosion resistance, hardness, compatibility with living tissues, etc.). Depending on the purpose, the surface treatment affects the physical (surface energy [1], thermal expansion [2]), mechanical (stiffness [3], friction coefficient [4]), chemical (structural and elemental composition) and geometric (roughness and texture [1, 3]) characteristics of the surface. The effect of plasma on hard materials (metals, ceramics), as well as the treatment of polymers [5] have been studied quite extensively.

Under certain conditions, the surface of soft polymers after plasma modification becomes wrinkled. These changes depend both on the treatment parameters and on the stiffness of the polymer [Morozov18] and are associated with loss of stability of the coating [6] under internal stresses of different nature [7]. It has been established that the relief texture has a certain effect on the adhesion of bacteria [8]; in particular, the adhesion of staphylococcus on the wrinkled surface of polyurethane reduces significantly after ion-plasma implantation [9].

Application of "traditional" plasma surface modification techniques to soft polymers is limited. In real life operating conditions, soft elastic materials are always subjected to different types of deformation, which damage their coatings. Deep cracks and delamination of the plasma-modified layer of the polyurethane surface were observed after the fatigue tests [10].
The creation of discontinuous island (cluster-like) coatings could be a compromise between durability of the surface and the improvement of performance. In particular, the resistance of such surfaces to external deformations should increase. Surface texture of islands and their geometry [11] could have certain impact on interaction with biological objects like proteins, bacteria or cells.

In this work the formation of carbon island coatings by the magnetron sputtering on the nitrogen-activated surface of a soft elastic polyurethane is studied. Different island structures are investigated depending on the duration of magnetron sputtering.

2. Materials and methods
Polyurethane was prepared according to supplier's instructions from a two-component system of prepolymer (urethane based on polyether and toluene diisocyanate) and hardener (solution of aromatic diamine in polyol) in a weight ratio of 100:33.1; Shore hardness – 70, initial elastic modulus – 30 MPa.

Plasma treatment was carried out by the magnetron sputtering of a graphite target in the pulsing regime [12] with the next parameters: argon pressure – 2.7*10^{-3} Torr, the average discharge current – 30 mA, the current amplitude – 40 A, the pulse duration – 8 μs, the number of pulses in the stack – 1, the pause between pulses – 10 ms. The thickness and continuity of the coating depend on the number $N$ of such pulses.

The formation of carbon islands by simple reduction of $N$ was not achieved: continuous coating was formed at $N > 8000$ (thickness of coating 4 μm and more), at smaller $N$ the coating was absent (the structural and mechanical properties of the surface after small number of pulses were identical to the untreated material). Presumably, the discontinuous coating is exfoliated under the action of Laplace forces.

Preliminary surface activation in nitrogen plasma solved the problem. The partial pressures of argon and nitrogen were adjusted to 2*10^{-3} Torr. A glow discharge was ignited in a low-energy electron beam source (the current and the accelerating voltage were set to 2 A and 100 V respectively). The activation time $t$ was varied from 1 to 8 minutes. After the activation, the samples were treated by the magnetron sputtering of the graphite with $N = 1500$ or 2000. When the number of pulses was reduced, no coating was formed on the activated surface.

The surface energy was determined by measuring the contact angle on the DSA-4 device by the sessile drop approach. As test liquids, water and diethylene glycol were used. Determination of the surface energy was carried out by the Owens-Wendt-Rabel-Kaelble method [13].

The microstructure of the surface was studied by an optical 3D-video microscope (Hirox KH-7700) and an atomic force microscope (Nano-DST) in a semi-contact mode with a tip radius of < 10 nm.

3. Results and discussion
The energy (figure 1a) and the relief of the activated surfaces without carbon deposition change depending on the activation time $t$ (1, 2, 4 or 8 minutes). The energy of the activated surface (figure 1a) is higher than the energy of the initial polyurethane and decreases asymptotically with increasing $t$.

The roughness (figure 1b) of the surface increases sharply at 1 min (due to the nonuniform formation of the activated layer at the initial stage) and then falls. At $t \geq 4$ min, cracks appear on the surface (shown in the inset in figure 1b), causing an increase of roughness.

Taking into account the energy and the formation of cracks, the carbon coatings were deposited to the surface activated for 2 minutes. As a result, the discontinuous island coatings (figure 2) were obtained on the polyurethane surface. The average size of an island is ~70 μm (from 40 to 200 μm and it is independent of the treatment).
Figure 1. Energy (a) and roughness (b) of the activated surface of the uncoated polyurethane. Individual markers in (a) show the energy of a surface with an island coating.

The surface energy of the carbon islands (figure 1a) is smaller than the energy of the activated surface and rises with decreasing \( N \). Thus, at the given conditions of deposition, smaller and thinner carbon islands could be obtained by increasing substrate surface energy.

Figure 2. Optical images of islands on the activated polyurethane surface treated with 1500 (a) and 2000 (b) pulses of carbon deposition.

The thickness \( h \) of the islands (height difference at the island boundary) was 25 and 46 nm for 1500 and 2000 pulses, respectively. Dark dendritic structures in the middle of large islands in figure 2 are the wrinkled regions. The surface structure outside the islands is indistinguishable from the activated uncoated samples. The surface of islands outside the wrinkles is smoother, in comparison with the activated surface. The examples of wrinkled regions are shown in figure 3.
Figure 3. Central regions of islands: 1500 (a) and 2000 (b) pulses of carbon sputtering. The arrow on (a) indicates the area where the wrinkles have small amplitudes and wide wavelength. The insert on (b) shows the interface between the island and the activated surface.

The wrinkles are characterized by the spectrum of the wavelengths $\lambda$ and the amplitudes $A$. The quantitative values of $A$ and $\lambda$ were determined by the image processing algorithm based on the empirical mode method [14]. Figure 4 shows the contour lines of amplitudes (a) and wavelengths (b) of the surface given in figure 3b. The values have maximum at the center and decrease approaching the boundary of the coating.

The treatment with 1500 pulses gave the more heterogeneous structure of wrinkles; high amplitudes alternate with regions where $A$ is small with the same wavelength. One of these areas is indicated by the arrow in figure 3a.

The wavelengths and the corresponding amplitudes are shown in figure 5. For the deposition with $N = 1500$, the values of $A$ are 10...60 nm, $\lambda = 500...1000$ nm (figure 5a); the lower values were obtained for $N = 2000$: 10...40 nm and 400...800 nm (figure 5b). Different amplitudes can have the same wavelength, especially for $N = 1500$, where the significant amplitude scattering was obtained (figure 5a).

According to the theory of the loss of stability of a plate on an elastic substrate, the wavelength of the wrinkle is proportional to the thickness and elastic modulus of the coating [15]: $\lambda = 2\pi h (E_f / 3E_s)^{1/3}$, where $E_f$, $E_s$ are the elastic moduli of the coating and substrate, respectively. Following this approach, the islands with $N = 2000$ should have wider wrinkles in comparison with $N = 1500$. However, the opposite is observed. This indicates that the wrinkles are formed at the initial stage of island formation. Further carbon deposition is accompanied by the growth of the thickness of the coating and the smoothness of the wrinkled surface.

The origin of wrinkles is the internal stresses [7] arising due to the various elastic moduli of the soft polyurethane substrate and the hard carbon coating.
The presence of a spectrum of wavelengths and amplitudes of wrinkles is explained by the heterogeneous structure of polyurethane at the nanoscale [16], as well as by the presence of local surface defects.

4. Conclusions
Activation of the polyurethane surface by nitrogen increased the surface energy and created the conditions for the growth of a discontinuous island carbon coating. The optimal activation time was established as 1 minute at the given setup; the higher values of $t$ lead to the cracking of the polymer surface. Island coating on the activated surface was formed by the pulsed magnetron sputtering of the graphite target. Depending on the number of pulses (1500 or 2000), the thickness of the carbon islands

Figure 4. The contour lines of the amplitudes (a) and wavelengths (b) of the wrinkled surface from figure 3b. All values are given in nanometers.

Figure 5. Wavelengths and the corresponding amplitudes of the islands: 1500 (a) and 2000 (b) pulses. The average and standard deviation are shown.
was 25 or 46 nm with planar sizes of 40...200 μm. The energy of the surface with discontinuous coating depends on 𝑁 and is less than the energy of the pure activated surface.

Some islands have a wrinkled structure, which is characterized by a spectrum of wavelengths and amplitudes; they are maximal in the central part and decrease when approaching the boundaries. The structure of thinner islands (with 1500 pulses) is more heterogeneous. This suggests that the wrinkles are formed at the initial stage of carbon islet growth. With a further increase in the number of sputtering pulses, the wrinkles are reduced. The nature of this phenomenon is the internal stresses arising at the interface between the soft elastic polyurethane and the hard carbon coating.

The obtained structures have good adhesion with the polymer, remaining after the samples were washed in an ultrasonic bath. Further studies are aimed to investigate these coatings under the stretching and their interaction with blood proteins.

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5. References
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