

Influence of uniaxial deformation on structure of carbon-coated polyurethane surface

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Abstract. Plasma treatment of polymers is the promising technique for improving the quality of biomedical devices, in particular deformable implants. The influence of mechanical deformation on such coating has not been sufficiently studied. The effect of the uniaxial cyclic deformation on the surface structure of carbon nanolayer deposited (by the magnetron sputtering) on soft elastic polyurethane is investigated. The obtained coating is wrinkled. The mechanical load changes the structure of the surface (wavelength, amplitude and fractal dimension of the wrinkles, surface roughness); the cracks appear on the deposited layer. As the strain increases, the number of cracks rises and the strain-induced folds appear on the coating.

1. Introduction

Plasma treatment of materials improves various characteristics of products. To achieve certain goals (increase of hardness, wear and corrosion resistance [1], adhesion, biomedical characteristics [2-4]) various types of plasma treatment (sputtering, implantation, etching), environmental conditions (working gas, sputtering material), experimental properties (duration, temperature, frequency of pulses, etc.) are applied.

The effect of plasma on hard materials (metals, ceramics, plastics) has been studied extensively. Such treatment changes the chemical structure, relief and energy of the surface. In particular, modification of polymer surface [5] improves biomedical parameters: reduction of thrombogenesis [6], biocompatibility with cells and body tissues [7]. This feature opens a promising challenge of creating deformable biomedical implants with improved properties. These benefits are related to the surface energy [8], hardness [9], presence of free radicals [10] and the relief structure: unlike hard materials, the plasma treatment of soft materials leads to the formation of a wrinkled surface [11, 12]. The texture of the relief has a certain effect on the adhesion of bacteria [13] and the wrinkles of the surface significantly reduce the adhesion of staphylococcus [14].

Under the real-life conditions, elastomeric materials undergo mechanical deformations. What happens to the plasma modified surface exposed to external loading? Qualitative studies of stretched plasma-treated polymer films show regular structure of cracks and folds [14, 15]. How this will affect the interaction with the environment? To date, these issues have been studied extremely insufficient.

In this paper, the effect of cyclic uniaxial loading on the surface structure of soft elastic polyurethane coated with a carbon nanolayer deposited by the magnetron sputtering method were investigated. The



changes in the surface structure after loading, the formation of cracks and strain-induced folds were shown.

2. Materials and methods

Preparation of samples. Polyurethane was made from the two-component system of prepolymer (urethane based polyether and toluene diisocyanate) and hardener (solution of aromatic diamine in polyol); the weight ratio was 100:46.2. Prepolymer was heated to 50 °C and mixed with the hardener. The mixture was press-molded and cured at 100 °C for 20 hours. The thickness of the plates was 2 mm. Plasma treatment of the materials was carried out by the magnetron sputtering of graphite target with high power pulses (HiPIMS – High-Power Impulse Magnetron Sputtering) in Ar medium, the pressure was 0.2 Pa. The voltage of the magnetron discharge was 800 V, the current amplitude – 80 A, the pulse duration and rate – 150 µs and 150 Hz. The temperature of the samples did not exceed 100 °C. This regime is also called mixed HiPIMS-Arc and has a number of advantages: prevention of development of large defects of the deposited coating, high sputtering speed and significant fraction of sp³-bonds.

The sample was placed on an electrically insulated holder at a distance of 10 cm from the target of the magnetron. The deposition time was chosen by the measurement of the resistance R of the coating using mega-ohmmeter (APPA 605), which allows to measure resistance up to 22 GΩ. The resistance of the carbon coating deposited for 8 min was 15 GΩ. The deposition less than 8 min resulted in $R > 22$ GΩ. Four samples were prepared with the next duration of treatment: 8 min – (labeled as PU-8m), 6 min – (PU-6m), 4 min – (PU-4m) and 2 min – (PU-2m). The thickness of the coating was 25, 19, 13 and 6 nm respectively (measured by the depth of the scratch of the same layer deposited on a glass substrate).

The treated samples (20x5x2 mm strips) were subjected to cyclic uniaxial loading (dynamic modulus analyzer DMA / SDTA861e, METTLER TOLEDO): 1000 cycles, strain amplitude – 10%, frequency – 1 Hz. Due to the small thickness of the coating, no differences in mechanical properties were found. Microstructure of the surfaces before and after the mechanical loading was investigated by the atomic force microscope (AFM Dimension Icon). The stiff probes (RTESP) with tip radius of 10 nm were used. For the sake of statistics, from each sample several images 10x10 µm (resolution in xy-plane 1024x1024 dots) were obtained. The microstructure of strained samples was also studied in situ. In this case the sample was fixed and stretched in the small stretching device placed under the AFM scanner.

3. Results and discussion

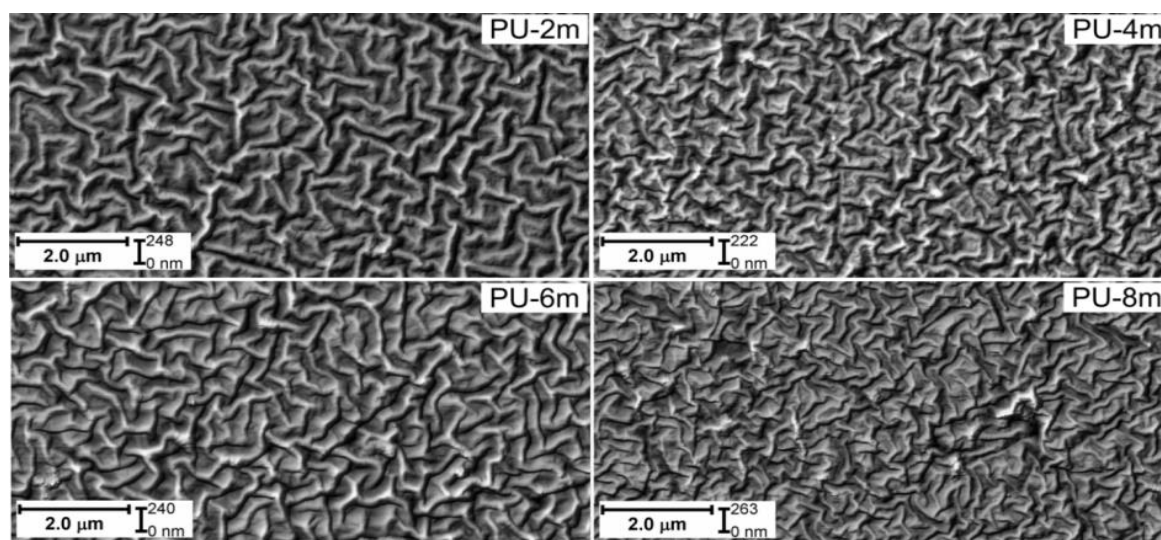


Figure 1. AFM images of magnetron-treated polyurethane.

The surface of the untreated polyurethane (not shown here) has a smooth relief without pronounced features. The surface with the deposited carbon layer has a wrinkled structure (figure 1, hereafter the AFM images are cut vertically for the sake of space). The nature of wrinkling is complex and involves both the temperature mechanism [16] accompanied with the heterogeneous structure of polyurethane at the nanoscale: rigid domains in a soft matrix.

The structural properties of the surface depend on the treatment. For quantitative analysis, wrinkles were identified by the watershed method: the regions above the mean value of height of the image were analyzed.

The surfaces after the mechanic tests are given in figure 2. Qualitative inspection of these images showed that the relief of PU-2m did not visually change; the materials PU-2m-6m has randomly oriented tiny cracks. Pronounced long cracks are visible on the material PU-8m.

The area A and the perimeter P of the contours of the wrinkles in double logarithmic coordinates ($\lg(A)$; $\lg(P)$) form a straight line (coefficient of determination of the linear approximation is $R^2 > 0.95$). Therefore, A and P of the wrinkles has the fractal dependence: $P \sim A^{D/2}$, where D is the fractal dimension.

The wave properties of the two-dimensional relief z were analyzed by the power spectral density: $PSD = L/n^2 \text{abs}(\text{fft}(z))^2$, where fft is the Fourier transform, n is the number of points of the AFM image of side length L . PSD shows the strength of the signal as a function of frequency f . Spatial discrete frequencies are: L^{-1} , $2L^{-1}$, ..., $0.5nL^{-1}$; the wavelength is $\lambda = 1/f$. The obtained reliefs are isotropic (the two-dimensional PSD has the radial symmetry); therefore in calculations the one-dimensional radial $PSDs$ were used.

The root mean square roughness in the frequency range $f_1 \dots f_2$ is calculated as:

$$R_{RMS} = \sqrt{\int_{f_1}^{f_2} PSD df}. \quad (1)$$

In particular, if $f_1 = f_2$ the amplitude A for the wavelength $\lambda = 1/f_1$ is estimated; if $f_2 = \max(f)$ the average roughness in a region of size $s = 1/f_1$ is calculated.

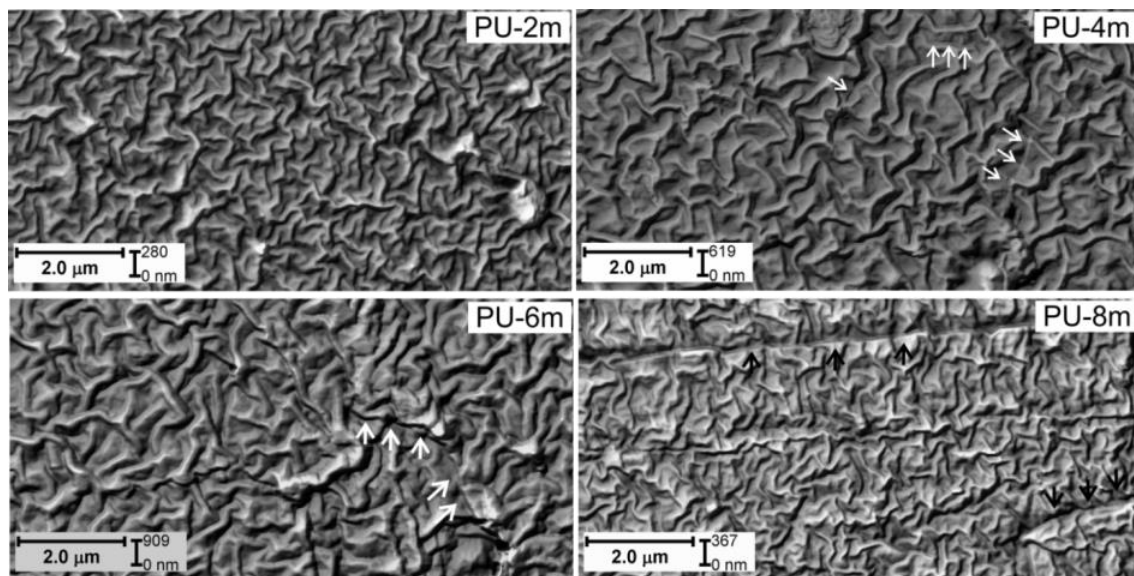


Figure 2. AFM images of the treated surfaces after cyclic uniaxial loading. Axis of deformation is vertical. Boundaries of cracks are marked by arrows.

The quantitative analysis of the surfaces before and after the mechanical load established the changes of the structural parameters of the wrinkled relief.

The roughness vs. size of the region is shown in figure 3(a) (R_{rms} of the untreated material was ~ 10 nm). As the area of observation increases, R_{rms} rises and at $s = 2...3 \mu\text{m}$ goes to the asymptote. The roughness of materials before the mechanical load changes nonlinearly: it is maximal at $t = 6$ min, and goes to minimum at $t = 8$ min. The fractal dimension of the wrinkles insignificantly decreases (figure 3b).

After the mechanical load, roughness of the materials increases. The highest changes, in comparison with the unloaded material, were achieved at $t = 4$ min; the smallest – 8 min. The fractal dimension of the wrinkles significantly falls as thickness of the coating grows, i.e. wrinkles became more tortuous after the deformation.

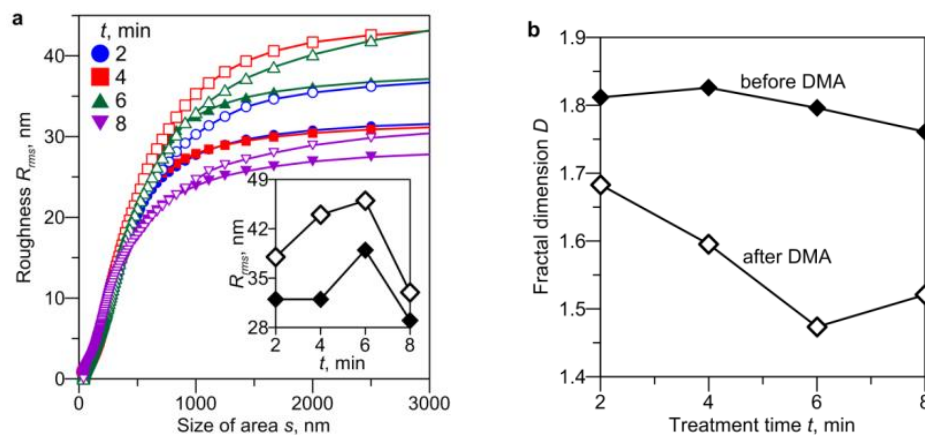
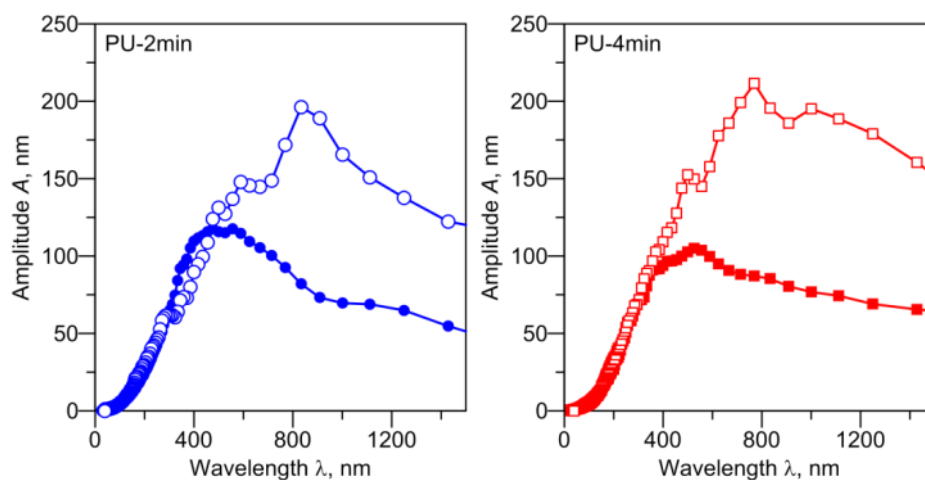


Figure 3. Surface roughness (a) and fractal dimension of the wrinkles (b) of the treated materials before (filled markers) and after (unfilled) the mechanical loading.

The wave characteristics of the surfaces are shown in figure 4. The maxima on the graphs correspond to the amplitudes and wavelengths of the wrinkles. Note, that before the load, there is no clear maximum $A(\lambda)$: the amplitude of wrinkles in the wavelength range of 400...600 nm ($t = 2...6$ min) and 600...800 nm (8 min) changes insignificantly.



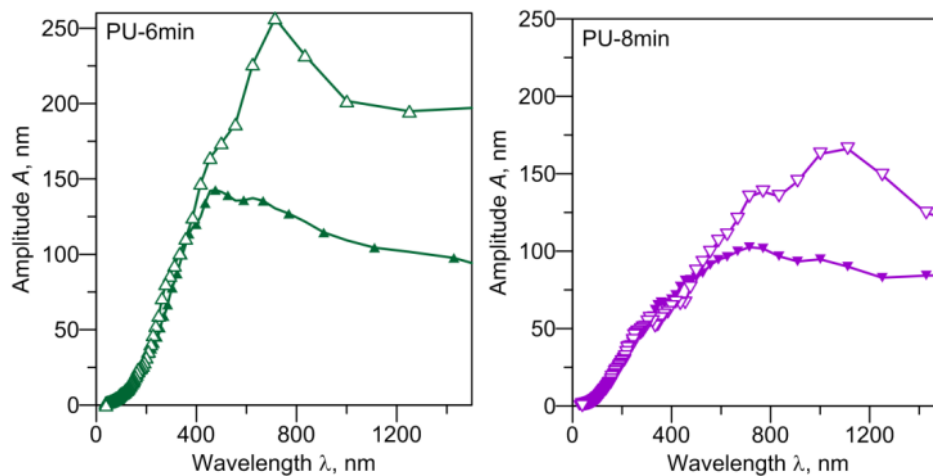


Figure 4. Amplitudes and wavelengths of wrinkles: before (filled markers) and after (unfilled) the mechanical loading.

After the deformation, the amplitude and wavelength of the wrinkles increase – the maxima on the graphs (figure 4) shift to the right, and the peaks of $A(\lambda)$ are sharper, i.e. wrinkles become more pronounced. Moreover, additional local maxima $A(\lambda)$ appear after the mechanical load.

The mechanical load considered above was only 10%. In the case of elastic polyurethane, capable of stretching by hundreds of percent, such deformation is small. Figure 5 shows the relief of PU-2m stretched to 25% and 100%.

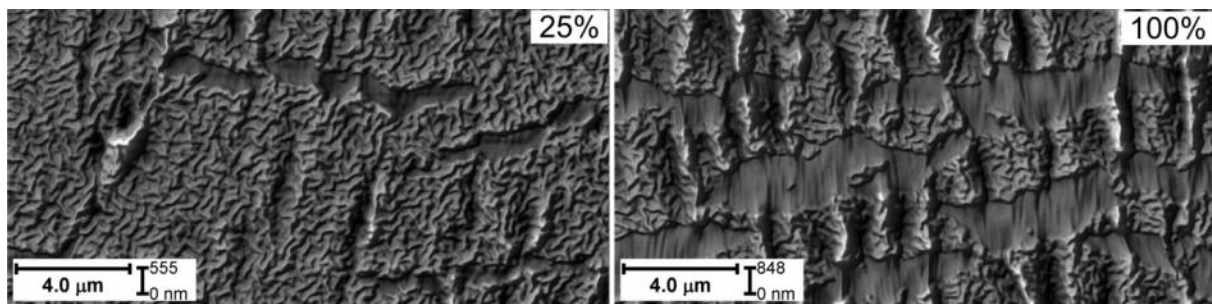


Figure 5. AFM images of PU-2m stretched up to 25% and 100%.

The open cracks are visible on the stretched surface. As the load increases, folds, parallel to the loading direction, appear (the result of material compression).

The removal of such high load doesn't restore the initial surface even qualitatively (as in the case of the low load, figure 3), the traces of cracks and longitudinal folds will exist permanently on the unloaded surface.

4. Conclusions

The effect of deformation on the structure of carbon nanolayer deposited by magnetron sputtering on the surface of soft elastic polyurethane was investigated. The thickness of the coating depends on the treatment time (2, 4, 6, 8 min) and was 6, 9, 13, 25 nm. The treated surface has a fractal wrinkled structure, the parameters of which vary nonlinearly with the duration of treatment. Each surface is characterized by a wavelength spectrum of 200 nm width and amplitude from 100 to 150 nm.

The samples were subjected to cyclic uniaxial deformation (strain amplitude 10%, frequency 1 Hz). Mechanical load changed the structure of the surface: the roughness increased, the wrinkles became more tortuous, their amplitudes and wavelengths increased. These structural changes are related to inelastic properties of the coating.

Single microcracks were observed on the coatings of 9...13 nm thickness; in the case of 25 nm extended, orthogonal to the loading axes, cracks appeared. No cracks were found on the 9 nm coating. Investigation of materials in the stretched state established the appearance of open cracks (25% of deformation). At 100% of deformation the cracks are accompanied with folds, caused by the compression of the material.

Changes in the structure of surfaces after loading, as well as damage of the coating, require further study of interaction of plasma-treated deformed polymers with the environment, in particular, with biological tissues. Another possible direction is the development of discontinuous coatings [6] which could be more resistant to the external deformations.

5. Acknowledgement

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6. References

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