POLYURETHANE MODIFIED BY PLASMA ION IMPLANTATION

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Abstract

Polyurethane was treated by nitrogen ions with energy of 20 keV and fluence of 10^{14} - 10^{16} ions/cm^2. Modified polyurethane was investigated by the IR FTIR, Raman and EPR spectroscopy, AFM microscopy. The contact angle and the surface energy of modified polyurethane are measured. Polyurethane after treatment has a carbonized layer of 70 nm thickness and partly depolymerized layer below the carbonized layer. Polyurethane after treatment have wave-like surface relief and cracks. Carbonized layer of the modified polyurethane contains highly active free radicals. It provides high hydrophilicity of modified polyurethane surface. High activity free radicals and hydrophilicity of modified polyurethane surface provides a saving of biological activity of the covalently attached proteins. As results, it provides to attachment and growing of endothelial cells on the polyurethane surface. The modified polyurethane can be applied for soft tissue medical implants.

Keywords: Carbonized layer, polyurethane, plasma ion implantation, implant, biocompatibility

1. INTRODUCTION

Inserting of synthetic medical implants induces an immune system complex of local cellular and responses of humoral immunity to a foreign body and inflammation [1,2]. The result of these reactions is the formation of a connective tissue capsule that isolates the implant, inflammatory complications, etc. The implants are rejected, become non-functional, and repeated surgical interventions are required. The risk of operations for patients in old age, patients with diabetes mellitus and other diseases is very significant. Patients receiving immunosuppressants create additional risks and are not always applicable due to side effects. For these reasons, the creation of synthetic implants without a foreign body reaction is very desirable. The recent studies on the creation of a continuous active protein layer on the implant surface show the possibility and prospects of such implants. The protein layer on the surface of the implant makes possible to exclude the contact of the cells of the body's immune system with the naked surface of the implant [3-5].

Earlier in our works, we show that the polyurethane modified by plasma-ion treatment on a device with a planar geometry of the electrode contains a surface carbonized layer about 50-70 thick and has activity, which is provided by the presence of free radicals. The high activity and hydrophilicity of the modified surface polymer layer ensures stable adsorption of the protein on the surface of the polyurethane with the formation of a covalent bond and with the preservation of the biological activity of the adsorbed protein [6,7].

2. MATERIALS AND METHODS

We synthesized polyurethane from a prepolymer based on 2,4-toluylene diisocyanate and polyether with a hardener methylene bis-orthochloroaniline. Components of polyurethane were mixed for 1 min. We get film of polyurethane in Petri dishes and anneal it in vacuum oven at a temperature of 100°C for 24 hours. The thickness of the final films was 0.5 mm. Films of polyurethane were washed in heptane and deionized water and dried in a dust-free environment.

Polyurethane was treated by nitrogen ions with energy of 20 keV at a different time of treatment, which correspond fluence of 10^{14} - 10^{16} ions/cm^2.

Modified polyurethane was investigated by the IR FTIR, Raman and EPR spectroscopy, AFM microscopy. Raman spectra were recorded on a Ramanshaw spectrometer with a microscope, a lens of x50. EPR spectra were recorded on electron paramagnetic resonance spectrometer Spinscan X. The topography of the polyurethane surface modified by plasma ion implantation was analyzed using the Park System atomic force microscope.

3. RESULTS

Raman spectra of polyurethane contain lines related to the vibrations of the polyurethane macromolecule (**Figure 1**). The most intense peaks are observed in the region of 1619 cm^{-1} (vibrations of the aromatic ring), 1453 and 1320 cm^{-1} (vibrations of the ether part of the macromolecule), as well as the less intense peaks of 1712 cm^{-1} and 1540 cm^{-1} oscillations of Amide I and II urethane groups, 1080, 1125 and 1267 cm^{-1}, the skeletal vibrations of the polyester chain. The Raman spectrum of polyurethane treated with a fluence of 10^{16} ions / cm^2 also showed polyurethane lines (1128, 1250, 1450, 1524 and 1690 cm^{-1}), but the intensity of these lines is much less than in the spectrum of untreated polyurethane. Two new intense lines, 1348 and 1595 cm^{-1}, related to the vibrations of carbon structures are also observed. The peak at 1595 cm^{-1} refers to the vibrations of E_{2g} graphite. The type of this oscillation is active in the Raman spectrum. The peak at 1348 cm^{-1} refers to the vibrations of A_{1g} graphite. This peak is not active in the Raman spectra. The appearance of this peak is associated with the presence of graphite structure defects and breaking of the selection rules for the Raman spectrum. The intensity and position of the peaks show that these lines refer to the resonance effect of Raman spectra when the absorption line of electronic levels of graphite structures coincides or is close to the laser excitation line (514 nm) in Raman spectra. According to the model of the Ferrari and Robertson carbon structures [8, 9], the position of the lines and the intensity ratio correspond to the a-C structure of amorphous carbon with graphite clusters, a characteristic size of about 2 nm. Thus, a graphite-like layer was created on the polyurethane surface as a result of plasma ion treatment.

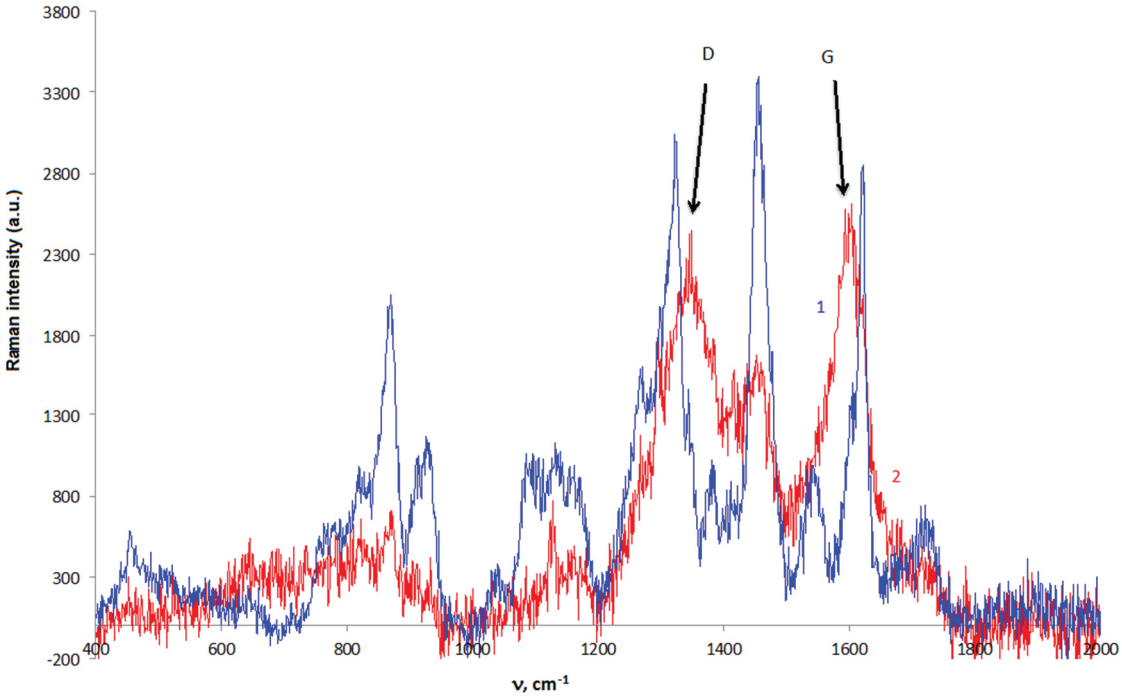

Figure 1 Raman spectra of polyurethane without the treatment (1, blue spectrum) and treated with nitrogen ions of 20 keV energy for 800 sec with a fluence of 10^{16} ions / cm^2 (2, red spectrum). Arrows show the lines D and G of carbon structures

EPR spectra show the presence of free radicals in the treated polyurethane (**Figure 2**).It supports our results of IR FTIR spectroscopy surface layer of treated polyurethane [7]. As result modified polyurethane surface is high hydrophilic. It provides to covalently attachment protein molecules on the carbonized layer of modified polyurethane and growing of endothelial cells on the polymer surface.

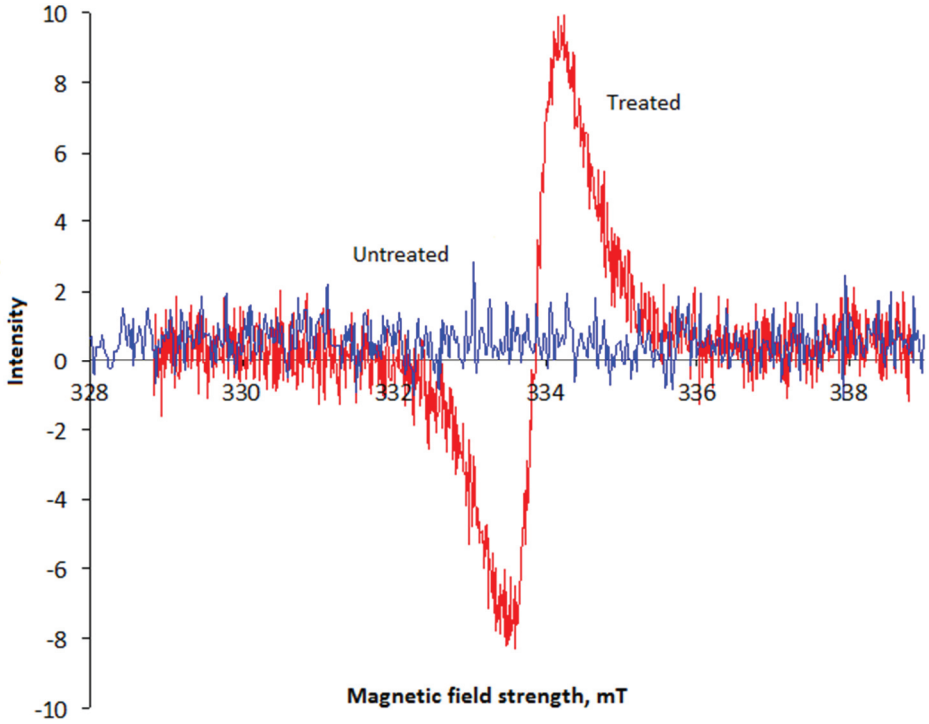

Figure 2 Electron paramagnetic resonance spectra of a polyurethane film (SCU-PFL), untreated and treated with nitrogen ions with an energy of 20 keV of 800 sec (corresponding to a fluences of 10^{16} ions / cm^2). The film was processed and stored 2.5 months in the laboratory conditions before recording the spectrum

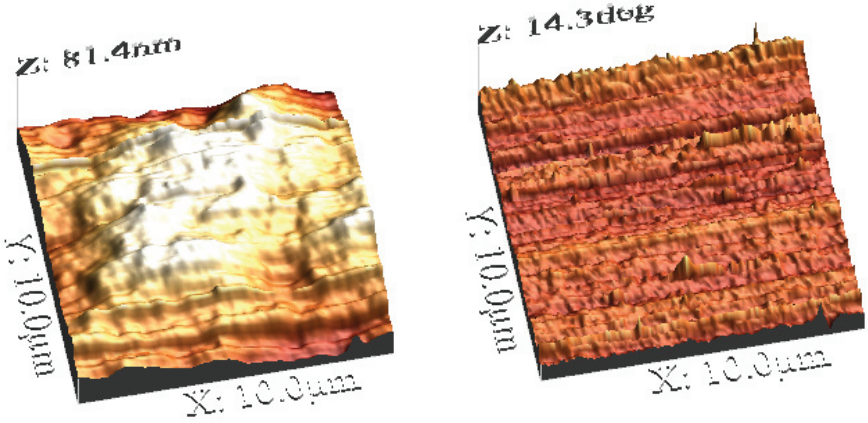

Figure 3 Topology of the surface and phase picture of interaction between cantilever and the surface for untreated polyurethane

The topology of the polyurethane film surface varies significantly after treatment (**Figures 3-4**). The surface of untreated polyurethane shows a roughness of 80 nm region for 10x10 um, but shows the homogeneity of interaction with the microscope cantilever by the phase image. The character of the surface roughness is random. The surface of the treated polyurethane is characterized by a large number of folds and cracks.

Analysis of the folds shows that the amplitude of the folds is much higher than the thickness of the modified layer (**Figure 5**). The direction of the folds is chaotic, not related to the direction of cracks or the dimensions of the sample.

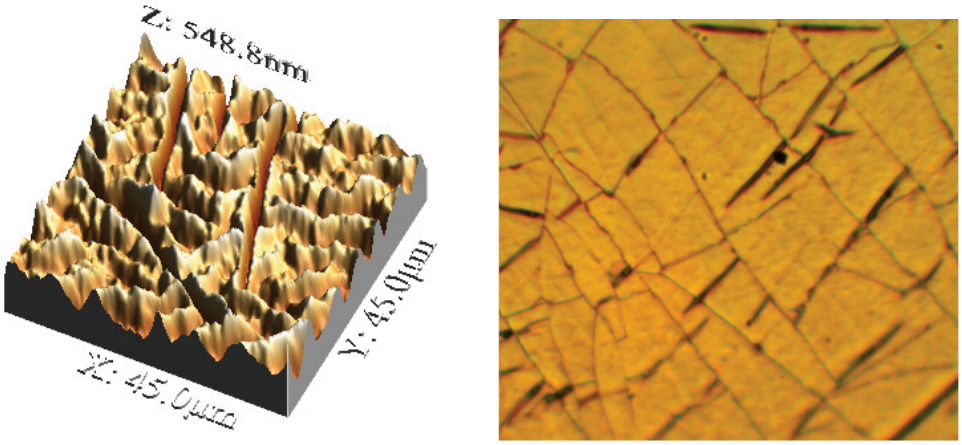

Figure 4 Topology according to the atomic force microscope and micrograph of the surface of the treated polyurethane

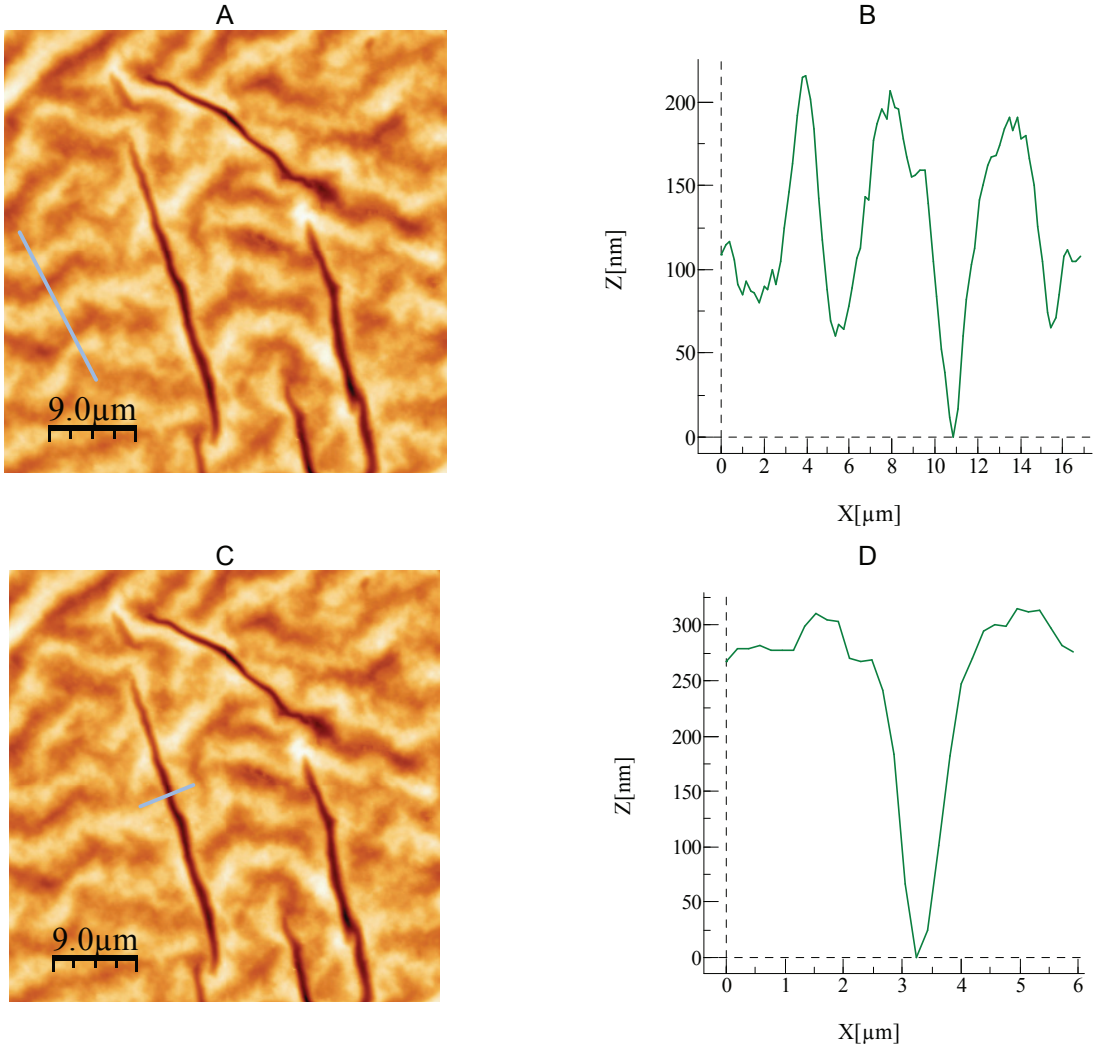

Figure 5 Surface analysis of treated polyurethane: amplitude of folds (A, B) and depth of cracks (C, D)

4. CONCLUSION

The treatment by 20 keV energy nitrogen ions creates on the surface of a polyurethane implant a carbonized layer consisting of amorphous carbon with inclusions of graphite clusters. Carbonized layer of modified polyurethane contains highly active free radicals. Treated polyurethane surface is highly hydrophilic. Polyurethane after treatment has a wave-like surface relief with cracks. High activity free radicals and hydrophilicity of the modified polyurethane surface provides a saving of biological activity of the covalently attached proteins. It provides to attachment and growing of endothelial cells on the polyurethane surface. The modified polyurethane can be applied for soft tissue medical implants.

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