

**ВЛИЯНИЕ ВЧМР ПЛАЗМЫ НА МОРФОЛОГИЮ И СТРУКТУРУ ПОВЕРХНОСТИ  
БИОРЕЗОРБИРУЕМЫХ ПОЛИМЕРНЫХ ПЛЕНОК**Н.Н. Богомолова

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**INFLUENCE OF RF MAGNETRON PLASMA ON MORPHOLOGY AND THE SURFACE  
STRUCTURE BIORESORBABLE POLYMER FILMS**N.N. Bogomolova

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***Аннотация.** Поверхность биорезорбируемого полимера (полимолочной кислоты) модифицирована методом высокочастотного магнетронного распыления твердотельной мишени из гидроксипатита. Воздействие плазмы и осаждение материала мишени на полимерную плёнку приводит к изменению морфологии её поверхности, увеличению шероховатости и кристалличности. Изменение морфологии поверхности пленок полимолочной кислоты связано с различной устойчивостью к воздействию плазмы аморфных и кристаллических фаз полимера. Рентгеноструктурным анализом подтверждено увеличение степени кристалличности полимера под действием ВЧМР плазмы.*

The most perspective bioresorbable material is polylactic acid (poly(l-lactide), PLLA) [1]. PLLA is a polymer with the degree of crystallinity dependent on the molecular weight and polymer treatment parameters. Polylactic acid is biocompatible and degrades into non-toxic components with a well-described degradation rate *in vivo*. However, the low roughness and high hydrophobicity limits the possibility of using polylactic acid. Applications of biodegradable materials such as poly(l-lactide) (C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>)<sub>n</sub> and polycaprolactone (C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>)<sub>n</sub> in an environment where attachment and proliferation of cells is important necessitate specific surface properties, namely, the surface roughness, to be within tens of nm (normally in 20–80 nm range and tailored to a specific cell line) and to be highly hydrophilic [2].

Modification of the surface by deposition of thin biocompatible calcium phosphate coatings by radio-frequency (RF) magnetron sputtering of solid targets solves this problem [3]. The method makes it possible to actively influence the surface, creating a high roughness in micro- and nano-scale and modify the structure of the polymer. Polymer films were prepared from a 4% solution of the polymeric material (Poly (l-lactide) PURASORB® PL 65, Purac) in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, Panreac Química S.L.U.). The polymer solution of 12 (±1) g was placed in a specially designed glass bath with a polished bottom and left at room temperature. After 24 h when most of the solvent had vaporized, the polymer films were removed from the bath using milli-Q water. Then the formed polymer films were placed into a vacuum chamber with initial pressure of 10<sup>-3</sup> Pa and temperature of 25 °C for 24 h to remove the residual solvent.

The PLLA films were treated on the magnetron installation designed and constructed in Hybrid biomaterials laboratory. The magnetron has an elongated electrode that is placed horizontally into the vacuum chamber and was used with a target that is made of the hydroxyapatite powder ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ). The installation has RF generator with a maximum power of 4 kW and an operating frequency of 13,56 MHz. For treatment of PLLA films argon was used as the working gas with the pressure of 0,3 Pa, specific RF power was set to 5 W/cm<sup>2</sup> and target-to-substrate distance was 50 mm. Treatment duration was 30, 60 and 150 s.

Film surface topology was studied using atomic force microscopy (AFM) (Solver-HV, NT-MDT) in air at RT under the tapping mode; Gwyddion 2,25 package was used to estimate root mean square values of surface roughness,  $R_{ms}$ . The investigation of the crystal structure of the samples was conducted by X-ray diffraction (XRD) analysis using a Shimadzu XRD 6000 diffractometer. The samples were irradiated with monochromatic Cu K $\alpha$  radiation ( $\lambda = 1,54 \text{ \AA}$ ) produced using the accelerating voltage of 40 kV and the beam current of 30 mA. The scanning angle range, scanning step size and signal collection time were 6–35°, 0,02° and 1,5 second respectively. The average size of the crystals ( $l_c$ ) of the samples was calculated using the Debye–Scherrer equation:

$$l_c = \frac{k\lambda}{\cos\theta\sqrt{\beta^2 - \beta_r^2}},$$

where  $\lambda$  is the wavelength of the incident radiation,  $\beta$  the width of the reflection at half height,  $\beta_r$  is the broadening reflex of the apparatus,  $\theta$  is the angle of diffraction and  $k = 0,9$ .

Fig. 1 shows AFM images of the surface of the investigated samples for different plasma treatment times. Fig. 1(a) shows that non-modified PLLA surface has no significant cavities and protrusions. The AFM study of the surface shows the change in morphology and the increase in PLLA surface roughness with increasing the plasma treatment time (Table 1). At 150 second of the plasma treatment (Fig. 1(d)) the surface of PLLA has a brain-like appearance with a higher surface roughness. During the interaction of the PLLA surface with high-energy plasma particles, amorphous regions are less stable than crystalline. As a result, there is a destruction of predominantly amorphous regions of the polymer under the plasma influence.

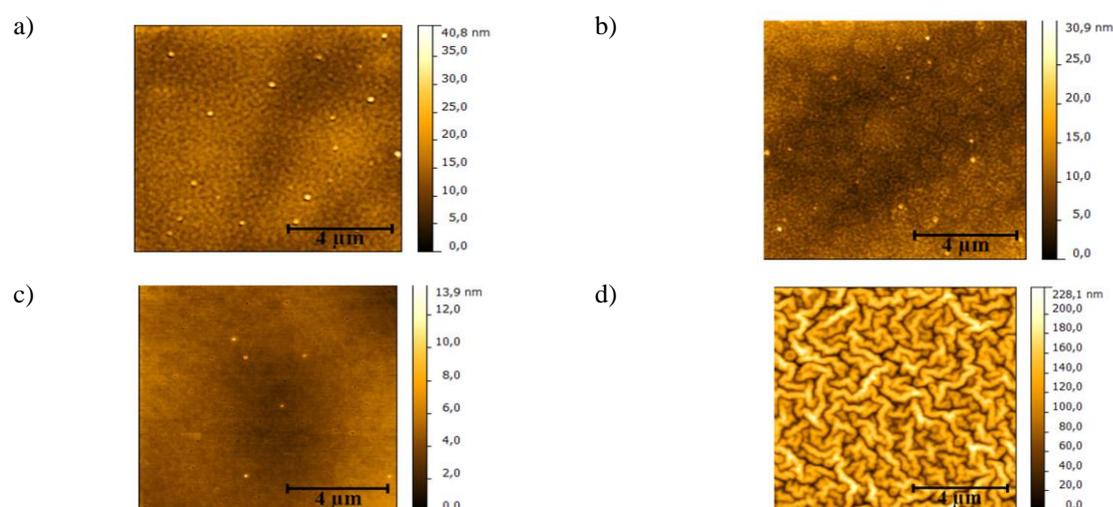


Fig. 1. AFM images of the PLLA surface at different plasma treatment times: 0 s (non-modified) (a), 30 s (b), 60 s (c) and 150 s (d)

Table 1

Surface roughness for untreated and samples treated in plasma for 30, 60 and 150 s

Plasma exposure time, $t$ (s)	0	30	60	150
Surface roughness, $R_{ms}$ (nm)	0,79	1,67	2,25	32,7

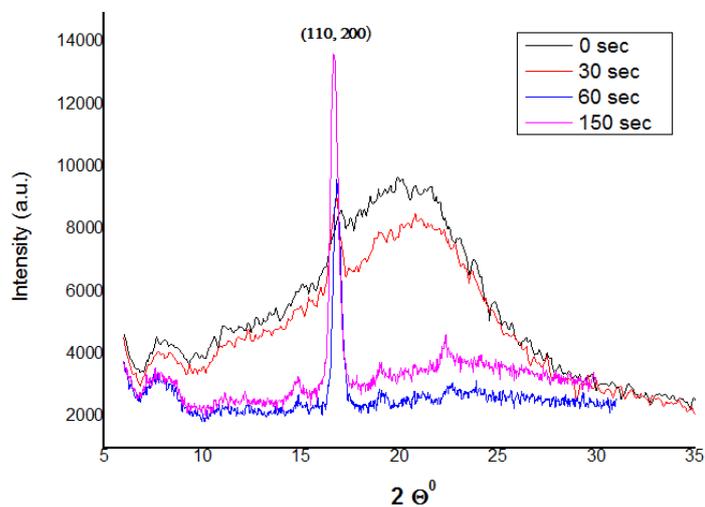


Fig. 2. XRD results of the investigated samples

X-ray diffraction intensity of the reflection is not observed before the treatment of the polymeric coating due to its amorphous structure. Fig. 2 shows changes of the reflections for treated films. Earlier in [4] it was shown that calcium phosphate coatings have an amorphous structure. There is a shift of reflex (110/200) to the region of  $16,6\text{--}16,7^\circ$  due to crystallization of the polymer film. The crystal size for 30 s treatment is less than 10 nm, for 60 and 150 s treatment times the crystal size is  $16,6 \pm 0,4$  and  $21,1 \pm 0,3$  nm, respectively.

Thus, PLLA crystallization processes in the formation of the surface relief play an important role when the time of the interaction between PLLA surface and plasma is significant.

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