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Article

Surface Property Modification of Polylactic Acid by Ion Implantation

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Abstract: We describe our investigations of the surface physicochemical and biological properties of polylactic acid modified by silver, argon and carbon ion implantation to doses of 1×10^{14}, 1×10^{15} and 1×10^{16} ion/cm^2 at energies of 20 keV (for C and Ar) and 40 keV (for Ag). X-ray analysis shows enhancement of coherent scattering regions and lattice constant increase after ion implantation. Secondary electron mass-spectrometry indicates that Ag concentration in the subsurface layer is less than 80%, but at a depth of 500 nm does not exceed 1–2%. The silver forms metal particles in the subsurface layer rather than making additional chemical bonds with polymer atoms. Atomic force microscopy reveals that the higher the irradiation dose the larger the surface roughness of the samples. Ag-irradiated samples implanted to a dose of 1×10^{16} ions/cm^2 have the highest roughness, 190 nm. Our investigation of the cytotoxicity of two individual donor macrophages shows that Ag-implanted polylactic acid has no negative impact on immune system cells and could be a promising material for biomedical application.

Keywords: polylactic acid; ion implantation; surface property modification

1. Introduction

Biodegradable materials based on polylactic acid are widely used in biomedicine and tissue engineering because of their biocompatibility and their degradation to lactic acid in biological media [1]. However, the application PLA-based materials for implants are limited by their adhesion characteristics and lack of functional groups for interaction with cellular media.

For improvement of the physicochemical characteristics, surface modification can be used. The use of ion-beam surface modification for the synthesis of new materials, modification of surface structure, formation of composite materials, and for generating predetermined surface patterns, etc., is a well-developed technology. Ion- and electron-beam irradiation of polymers are techniques widely used for polymer treatment due to their environmental friendliness and wide range of treatment conditions. The shallow ion penetration depth can modify the polymer surface functional properties while maintaining the original bulk properties of the material [2]. The chemical and physical processes leading to modification of the structural and physicochemical properties of polymer materials have been studied.

It is known that ion irradiation techniques can significantly modify the chemical and functional properties of materials. Ion irradiation leads to scission of molecular chains and emission of volatile products from the surface, and increased implantation dose leads to lower density of the implanted region [3]. Polymer chain scission accompanied by surface oxidation processes and new functional

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group formation, which contribute to the material hydrophilicity, occurs as a consequence of ion implantation [4]. Ion implantation of negative carbon ions has been found [5] to promote nerve-cell attachment and nerve line regeneration. It has been shown [6] that plasma treatment of polylactic acid surfaces causes surface roughness and an increase in contact angle, and, in turn, the increased roughness was found to improve PLA biocompatibility [7]. Electron beam treatment of PLA surfaces has been shown to cause polymer chain length transformation, with the molecular weight and degree of crystallinity decreasing proportionally to the exposure dose increase [8,9].

Plasma treatment is often used as a pre-treatment technology and for surface activation followed by distinct coating processes, e.g. chemical modification by grafting of organic functional groups [10] and deposition of plasma polymerized acrylic acid on a PLA surface [11]. It has been found that these hybrid methods of surface modification promote improved wettability, increased surface roughness, and changes in chemical composition. Bastekova and co-workers confirm [10] that their approach allows spatially distributed properties, for instance, hydrophilic and bio-adhesive on one side and hydrophobic and bio-repulsive on the other side, as is highly desirable for medical (implants) application. In contrast, Zhao et al [11], in their method of PLA modification, focus on the food packaging industry to economically and effectively protect food quality by use of an optimal combination of different gases. Morent et al have investigated the aging behavior of plasma-treated polylactic acid [12]. Contact angle decrease and XPS data reveal that the plasma discharge gas (air, nitrogen, argon or helium) has a significant influence on the ageing behavior of PLA foils. This influence can be explained by the different degree of cross-linking of the plasma-treated surfaces: helium and argon plasma-treated PLA films have a high degree of cross-linking, which limits polymer chain mobility and as a result reduces the ageing process. In contrast, the ageing behavior of air and nitrogen plasma-treated films is more pronounced due to their low degree of cross-linking. Other group have studied the aging of plasma-treated PLA, and the maximum storage time of PLA treated with atmospheric plasma for which the sample retains its good adhesion properties has been found to be lower than three days under normal atmospheric conditions [13]. The hydrophobicity and water absorption time can be enhanced by SF6 plasma treatment [14]. The authors explain this by the incorporation of fluorinated functional groups in the surface of the PLA film.

Chemical modification of PLA microspheres by aminolysis and grafting-coating [15] demonstrates the possibility to create material with the ability to support the attachment and proliferation of chondrocytes. These results show that collagen-coated PLA microspheres are a promising candidate for cell microcarriers. Another PLA surface modification technique is excimer laser treatment, described in [16], where the surface wettability, morphology and roughness changes as well as mass loss by ablation are investigated. It is revealed that decreased contact angle is associated with increased number of laser pulses. The excimer laser has a strong effect on polymer ablation; the mass loss is strongly dependent on the laser fluence and number of pulses.

Our literature review shows that ion- and electron-beam treatment of PLA leads to a reduction in molecular weight and degree of crystallinity, increased hydrophilicity, and bioresorption. However, the mechanisms occurring in PLA under ion beam irradiation have not been investigated; there are no data of PLA surface properties after Ag, C, or Ar ion implantation. Thus exploration of the effects of various kinds of ions and ion implantation conditions on PLA functional characteristics is of interest. The aim of the work described here was to study the influence of implantation of

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various ion kinds (silver, argon, carbon) at exposure doses of $1x10^{14}$, $1x10^{15}$, and 1×10^{16} ions/cm^2 on the surface physicochemical, functional and biological properties of PLA.

2. Materials and Methods

2.1. Preparation of PLA samples

PLA samples were prepared by dissolving polylactic acid ([-OCH(CH_3)-CO-]n) with molecular weight of 250 000 g/mol in chloroform at room temperature in a 7% solution [17]. The solvent was then removed by drying at room temperature in a Petri dish to form material with thickness ~1 mm, then the PLA plates were cut into samples with area 10 x 10 mm^2.

2.2. Ion implantation

Ion implantation was done using a facility incorporating our Mevva-V.Ru vacuum arc ion source [18]. This implantation facility operates in a repetitively pulsed mode with repetition rate 10 Hz and pulse duration 250μs. Ion species used in the present work were Ag, Ar and C. The charge state distributions of the ion beams were measured by a time-of-flight mass-to-charge spectrometer [19]. In this kind of ion source, gaseous ions are singly ionized and hence we used Ar^+ ions. Metal ions are in general multiply ionized; for carbon the charge state of the extracted ion beam is singly ionized C^+, while for silver the mean charge state of the extracted beam is 2+.Thus the implantation beams include Ag^{2+}, Ar^+ and C^+ ions. Since the ion source extraction voltage was always 20 kV, the ion beam energies were 40 keV, 20 keV and 20 keV, respectively. For Ar^+ ion generation we used the same ion source but somewhat modified to form a hollow cathode glow discharge mode [20]. Implantations were carried out to accumulated doses of $1x10^{14}$, $1x10^{15}$, and $1x10^{16}$ ions/cm^2. The implantation dose rate and average beam power density at the PLA target were adjusted by the ion beam current and pulse repetition rate, and were 1×10^{11}ions/(cm^2·sec) and 0.5mW/cm^2, respectively. The samples were mounted on a water-cooled target holder whose temperature did not exceed 20°C. A working pressure of 1×10^{-6}Torr was maintained by an oil-free high-vacuum cryogenic pump.

2.3. Characterization techniques

Phase composition was investigated using an XRD-7000S (Shimadzu) X-ray diffractometer with a K_αCu source. A Perkin-Elmer PHI 6300 ion microprobe secondary ion mass spectrometer was used to evaluate ion distribution profiles. Cs^+ ions with energy 7 keV and O^+ ions with energy 5 keV were used for etching the PLA samples. The sample surface was scanned by a focused primary ion bean over an area of 500 x 500 μm^2.

Surface morphology was studied by atomic force microscopy (AFM) using an NTEGRA Aura scanning probe microscope in tapping mode. A NT-MDT Spectrum Instruments probe NSG01 with resonant frequency 150 kHz and force constant 5.1 N/m was scanned over an area of 50 x 50 μm; Gwyddion software was used for analysis. After survey, an XY autoplane correction was performed. Structural analysis was carried out by scanning electron microscopy using a Quanta 200 3D dual-beam scanning electron microscope (SEM) and focused ion beam (FIB) instrument. Magnifications from 1000 to 15000 were used at accelerating voltage of 20 kV, with spot size 2-3 nm. Before the SEM study, the samples were coated with a conducting graphite film of 2–5 nm thickness by magnetron sputtering to alleviate charge build-up on the surface.

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Cellular investigation was performed to primary evaluation of cytotoxicity. Human immune system cell (monocyte) reaction was investigated by cell-mediated immune response to monocytes CD14+. Monocytes from the blood of individual donors were separated [21], and cells were cultured in the presence of the samples for 6 days at 37°C in an atmosphere of 7.5% CO_2. Cells cultured without samples were used as controls. The viability of cells was assessed after cultivation (evaluation of metabolic activity of cells).

3. Results

3.1. Elemental and phase composition

The XPS analysis results reported in [22] reveal that silver after ion implantation does not form new chemical bonds with substrate atoms, but rather, forms metal nanoclusters in the PLA subsurface layer. A two-fold decrease of the PLA molecular weight was shown to occur after ion implantation, regardless of the ion species [23].

There are two dominant peaks, typical for *L*-lactic acid isomers, corresponding to angles $2\Theta \approx 19.1°$ and 16.9° and crystallographic plane with index [201] and [110], respectively, in XRD images of the initial and implanted PLA samples, as shown in Fig. 1. In addition, there is a low-grade peak at $2\Theta \approx 29.5°$, specific to the [020] plane, in the initial and C-implanted samples but not in other samples. A decrease of peak intensity occurs depending on the implanted ion species, associated with the PLA crystallographic parameter alteration (interplane spacing, coherent-scattering region; see Table 1) during the implantation process; the degree of intensity decrease can be arranged in the following order: Ag→Ar→C.

Table 1. Crystallographic parameters of PLA

Implanted ions	Coherent-scattering region, nm	Interplanar distance, Å
initial	11	5.252
Ag	14	5.296
Ar	12	5.277
C	10	5.271

It was found that silver ion implantation results in XRD peak narrowing and line displacement relative to the initial sample, and hence the degree of crystallinity of the material increases. Carbon ion implantation, on the contrary, leads to peak broadening, caused by an increase of crystalline phase distribution heterogeneity and crystallite size. Argon ion implantation of PLA surface does not lead to a change in the coherent-scattering region relative to the initial state.

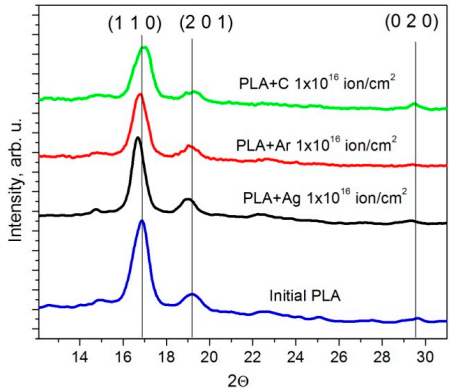

Figure 1. Diffraction patterns of initial and Ag-, Ar-, C- implanted PLA samples

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Figure 1 shows the peak with index [110], corresponding to 2Θ ≈ 16.9° in the initial sample, is shifted to 2Θ ≈ 16.7° when it is implanted with Ag ions, caused by interplanar distance alteration because of defects of the crystal lattice which are formed by silver particles localized in the surface sample (Table 1).

The atomic distribution spectrum of 1 x 10^{16} ion/cm^2 Ag-implanted PLA samples, from the surface to 600 nm depth, is shown in Figure 2. Secondary ion mass spectrometry data reveal that the maximum Ag concentration in the subsurface layers is up to 80 rel.%. At a depth of more than 500 nm, the Ag concentration does not exceed 1-2 rel.%. Moreover, there are two peak of Ag: the first is at 100 nm depth, where the maximum concentration is 80 rel.%; the second one is at 180 nm depth, where the Ag concentration is 50 rel.%. There are 40 rel.% of silver and 40 rel.% of carbon on top of the PLA surface layer. The penetration of silver ions into the polymer is carried out as follows: some ions settle on the surface and lose their charge, aggregating into metallic nanoparticles, and other ions are distributed in a more-or-less Gaussian distribution over the depth of the surface layer. The effect of ion implantation is observed to a depth of up to 600 nm.

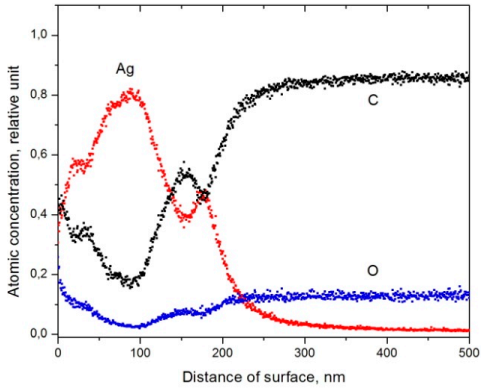
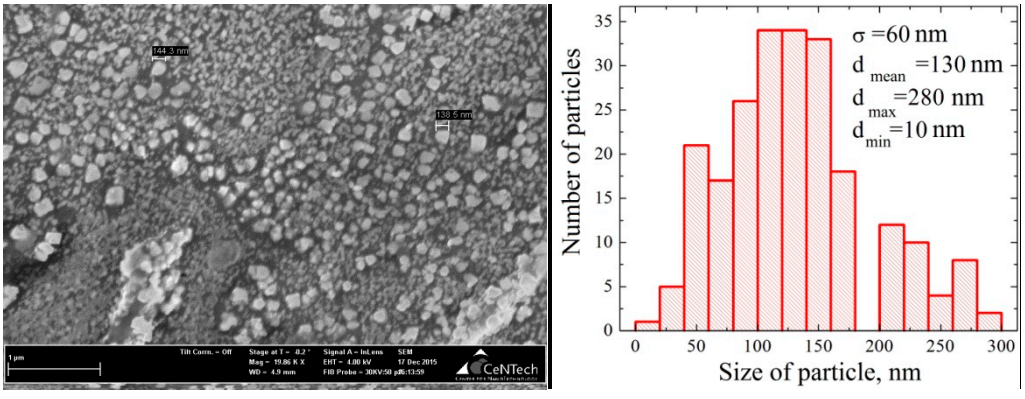


Figure 2. Atomic distribution in the subsurface layer of PLA

According to SIMS data for Ar- and C-implanted PLA, a uniform distribution of implanted ions over the depth of the implantion is observed. The calculated projected range of ions is 200-250 for the given ion energies.

3.2. Morphological characteristics

The SEM image shown in Fig. 3(a) reveals metal nanoclusters with average size 130 nm; the particle size distribution is shown in Fig. 3(b).



(a) (b)

Figure 3. (a) SEM image of 1 x 10^{16} ion/cm^2 Ag-implanted PLA; (b) Particle size distribution

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In Figure 4 the AFM results of initial and 1 x 10^{16} ion/cm^2 Ag-, Ar-, C-treated PLA samples are shown. Significant morphology modification was found to occur following ion implantation, dependent on the implanted ion species. The highest surface roughness is observed in Ag-implanted samples, and is due to formation of metal nanoparticles (Table 2). Implantation of Ar and C ions into the PLA surface causes lesser topography changes, probably due to their inertness and affinity for the substrate material, respectively. The roughness increase can promote cell adsorption improvement. When carbon ions are implanted, the formation of nanoclusters, which are located in the near-surface layer, is possible.

Table 2. Surface roughness of initial and 1 x 10^{16} ion/cm^2 Ag-, Ar-, C-implanted PLA samples

Sample	Initial	Ag-implanted	Ar-implanted	C-implanted
Roughness (R_a), nm	126	190	159	161

The TEM images shown in Figure 5 reveal that metal nanoparticles with average size of 2-3 nm are formed in the surface when PLA is implanted with Ag. On the other hand, cavitation with average pore size 10 nm is observed for the Ar- and C-implanted samples. We assume that the pores are filled with atomic argon and carbon, respectively.

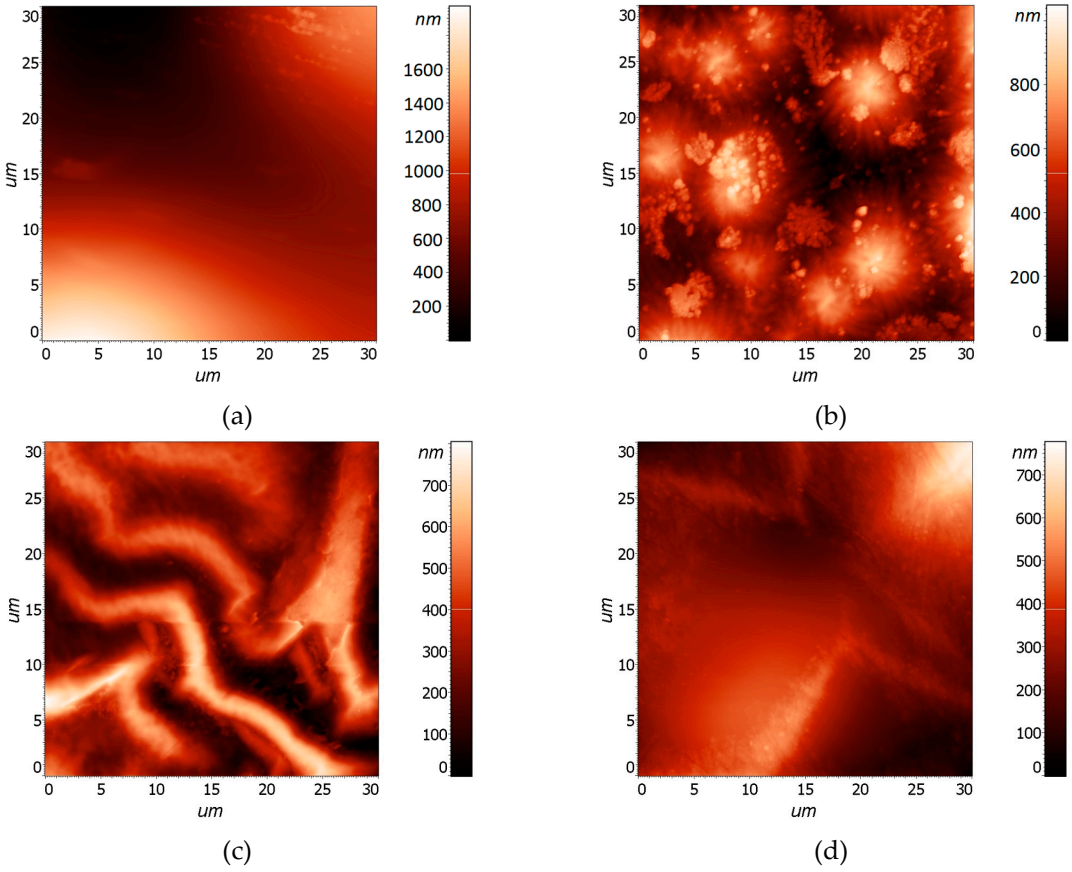

Figure 4. AFM images of PLA samples: a) initial; b) Ag-; c) Ar-; d) C-implanted with dose of 1 x 10^{16} ions/cm^2

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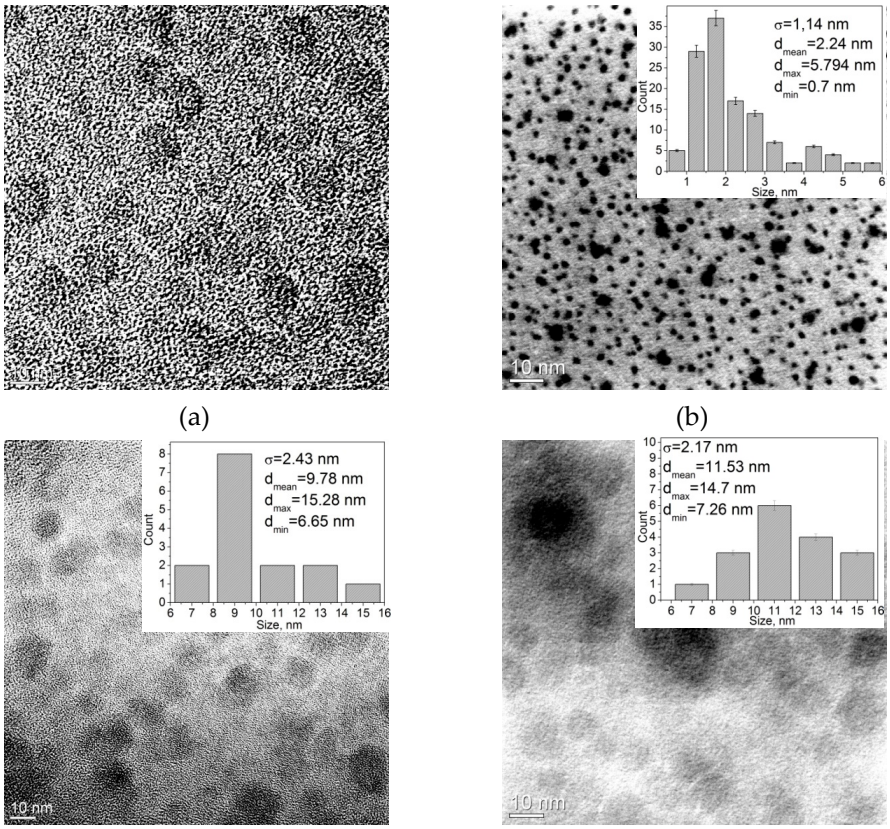

Figure 5. TEM images of PLA samples: a) initial; b) Ag-; c) Ar-; d) C-implanted with dose of 1 x 10^{16} ions/cm^2

3.3. Biocompatibility of PLA

The primary evaluation of cytotocxicity with macrophage from two individual donors reveals that both initial and 1 x 10^{16} ions/cm^2 Ag-implanted PLA samples benefit immune system cells (Fig. 6). The macrophage level after 6 days of culturing with PLA samples remains approximately the same as the control sample (pure glass). When cells are interacted with the Ag-implanted PLA sample, though, the cell survivability decreases relative to the control and initial PLA sample, but the cells remain alive. We found that the amount of living immune system cells is slightly diminished in the presence of Ag on the PLA surface; however there is no sharp rejection of implanted material by biological medium.

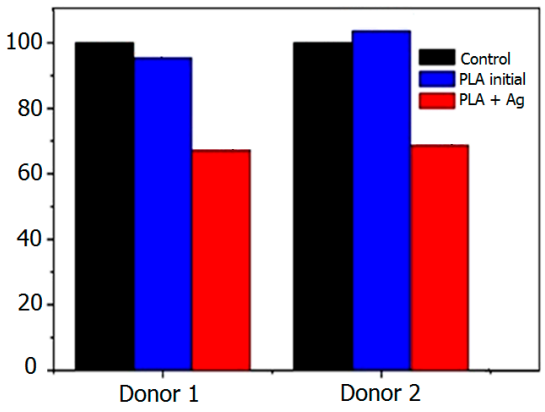

Figure 6. Cytotoxocity of PLA in vitro

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4. Conclusion

The effect of 1 x 10^{14}, 1 x 10^{15}, and 1 x 10^{16} ion/cm^2 Ag, Ar, and C ion implantation on PLA surface physicochemical and biological properties was investigated. We find that ion implantation influences the elemental compound and structural-phase composition. Thus implanted silver does not form new chemical bonds with polymer molecules but aggregates as metal nanoparticles on the PLA surface. It was established that the PLA molecular weight decreases by a factor of two after ion implantation regardless of the ion species used. The surface properties of the polymer are modified by energetic ion impact. XRD analysis revealed that the coherent-scattering region and interplanar distance of PLA are enhanced due to ion bombardment and crystallographic parameter alteration. According to SIMS, the Ag concentration in the subsurface layer is 80 rel.%, and for depth greater than 500 nm does not exceed 1-2 rel.%. It was found that the surface roughness increases with implantation dose; 1 x 10^{16} ion/cm^2 Ag-implanted samples have the greatest roughness of 190 nm. Evaluation of cytotocxicity with the macrophage of two individual donors was carried out and it was revealed that ion beam treated material does not negatively influence immune system cells and could thus be a promising material for biomedical application.

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Author Contributions: Irina Kurzina is the leader of the group; she conceived and designed the experiments. Konstantin Savkin performed the ion implantation of polylactic acid. Irina Vasenina and Olesya Laput investigated the surface property of the modified samples. Irina Vasenina, Olesya Laput and Daniil Zuza analyzed the data. Irina Vasenina wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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