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Abstract. An integrated study of poly-*L*-lactide (PL) synthesis and the physicochemical properties of film surfaces, both modified by silver and carbon ion implantation and also unmodified PL surfaces, has been carried out. Surface modification was done using aMevva-5.Ru metal ion source with ion implantation doses of $1 \cdot 10^{14}$, $1 \cdot 10^{15}$ and $1 \cdot 10^{16}$ ion/cm^2. Material characterization was done using NMR, IRS, XPS and AFM. The molecular weight (MW), micro-hardness, surface resistivity, and limiting wetting angle of both un-implanted and implanted samples were measured. The results reveal that degradation of PL macromolecules occurs during ion implantation, followed by CO or CO_2 removal and MW decrease. With increasing implantation dose, the glycerol wettability of the PL surface increases but the water affinity decreases (hydrophobic behavior). After silver and carbon ion implantation into the PL samples, the surface resistivity is reduced by several orders of magnitude and a tendency to micro-hardness reductionis induced.

INTRODUCTION

Ion implantation is a basic and promising method for surface modification in which new material properties are brought about [1, 2]. Complicated physicochemical processes that can significantly modify the material structure and surface properties take place in the surface layers. Ion-plasma treatment is widely used to change the surface structure of polymers in order to transform their properties, such as wettability, micro-hardness, conductivity, etc. [3, 4]. In the work described here a complex approach was used, including both poly-*L*-lactide (PL) synthesis and its modification by **Ag** and **C** ion implantation, followed by investigation by various physicochemical means of the properties of the materials formed. Poly-*L*-lactide belongs to a class of biodegradable polymers which are widely used in modern medicine for the production of bioresorbable surgical sutures, immunotolerance implants and pins. Studies of the effects of ion implantation on the surface properties of PL are thus of special interest. The aim of this work is investigation of effects of silver and carbon ion implantation with different doses on some of the properties of PL.

MATERIALS AND METHODS

Poly-*L*-lactide was synthesized according to the scheme [5]:

Lactic acid solution → **Oligomers of lactic acid** → **Lactide** → **Polylactide**
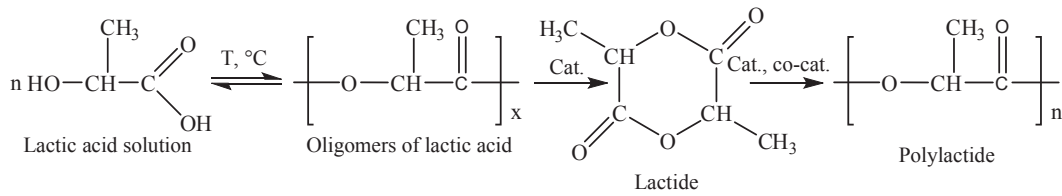
80% water solution of *L*-lactic acid (Purac, Netherlands) was used as an initial substance for production of oligomers of lactic acid (OLA). Oligomers were prepared in a Heidolph laborota 4003rotary evaporator. Initial temperature and pressure were kept at 130 °C and 500 mbar, respectively. After 80 minutes the temperature was raised step-by-step up to 145, 160 and 180 °C in 20 minute intervals. On reaching T = 180 °C the pressure was decreased to 100 mbar in 100 mbar steps each 20 minutes. The reaction was complete after 5 hours.

L-lactide was synthesized by thermal depolymerization of OLA in the presence of zinc oxide as a catalyst (0.5 mass %) at a temperature of 220 °C and pressure 13-20 mbar for 30-70 minutes. Synthesized raw lactide was purified by double recrystallization from ethyl acetate [5]. The polymerization of *L*-lactide was carried out in the same rotary evaporator at a temperature 155°C in the presence of tin octoate (catalyst) and lauryl alcohol (co-catalyst) for 6 hours. For polymerization the components ratio was as shown in Table 1.

TABLE 1. Ratio of componentsat the polymerization

Tin octoate, mass %	Lauryl alcohol, mass %	[lactide]:[lauryl alcohol]	[lactide]:[tin octoate]
0,13	0,17	600	800

PL was purified by precipitation while stirring its solution in chloroform to fivefold excess of ethanol, dried in a vacuum oven for 5 hours at a temperature of 50 °C and pressure 1 mm Hg. The purity of lactide was confirmed by NMR ^{1}H spectroscopy using a Bruker NMR Fourier-spectrometer AVANCE AV 300 MHz. Deuterated chloroform was used as a solvent.

The thermal properties of lactide and PL were investigated in aluminum bowls under an argon atmosphere by NETZSCH STA 449 F1 Jupiter connected toa gas mass spectrometer QMS 403 Aeolosover the temperature range 25-500 ºC in steps of 10 ºC per minute. Other properties of the PL samples before and after ion implantation were investigated by IR-spectroscopy (Nicolet 5700).

The main structural characteristics were studied by atomic force microscopy (AFM), NTEGRA Aura. Micro-hardness was measured using an Nanotest 600 nanoindenter with a load of 0.5 mN. Surface elemental composition was investigated by X-ray photoemission spectroscopy (XPS) using a PHI X-tool automated XPS microprobe. The molecular weight (MW) was determined with an Agilent 1200 LC Infinity chromatograph with refractometer detector (Agilent – Technologies, USA). The surface resistivity was measured using teraohmmeter E6-13A with measurement error in the range ± 30%. Limiting wetting angle was calculated by the sessile drop technique [6] according to the formula (1):

$$cos\theta = \frac{\left(\frac{d}{2}\right)^2 - h^2}{\left(\frac{d}{2}\right)^2 + h^2}$$

(1)

where *h* is the height of the drop and *d is the diameter of its base.*

Silver and carbon ion implantation was performed using a universal test bench equipped with a MevvaV.Ru vacuum arc metal ion source [7, 8]. The vacuum arc current was 200 A, with pulse duration 250 μs and pulse repetition frequency 1 Hz. The exposure doses were $1 \cdot 10^{14}$, $1 \cdot 10^{15}$ and $1 \cdot 10^{16}$ ion/cm^2 at an accelerating voltage of 20kV. Charge state distributions of the ion beams were measured by a time-of-flight mass-to-charge spectrometer [9]. The mean charge state for Ag ions is$<Q>_{Ag}= 2$ and thus the mean Ag ion energy in the beam is 40 keV. For carbon, the mean charge state is $<Q>_C= 1$ and thus the mean C ion energy is 20 keV [10, 11]. For measurement of ion beam current, a movable Faraday cup was used. The implantation dose rate and average power density were adjusted via the ion beam current and discharge pulse repetition frequency, and were $1 \cdot 10^{11}$ ion/(cm$^2 \cdot$sec) and 0.5 mW/cm^2,respectively. During ion beam processing, the samples were fixed on the surface of a water-cooled target holder. Their temperature did not exceed 20°C. A working pressure of $1 \cdot 10^{-6}$ Torr was maintained by a high-vacuum cryogenic pump.

EXPERIMENTAL RESULTS

One of the main requirements for materials subjected to ion-plasma treatment is chemical purity and homogeneity, since the structural units of the material (molecules, macromolecules, and supramolecular structures) are subjected toimpact by high energy ions. Such intense impacts inevitably produce various chemical transformations of the material structural units capable of changing the surface properties. Here, PL was synthesized from properly refined lactide, with NMR ^{1}H spectrum as shown in Fig. 1. The spectrum contains, as expected, only signals of two types of protons: doublet in the range 1.51-1.53 ppm corresponding to protons of the methyl group, and quadruplet in the range 5.0-5.1 ppm corresponding to protons of the methyl group of lactide.

The average molecular weight of the initial PL is 250 000 g/mol, and the IR-spectrum contains all expected valence and deformation absorption bands: CH$_3$, -CH, -C=O, -C-O-C-. According to thermal analysis results, the prepared samples correspond to L-isomer of lactide (T_m=96 °C) and a low crystalline form of poly-L-lactide (T_g= 55-60 °C, T_m = 168-170 °C).

The XP-spectra for both (a) the initial PL, and (b,c) samples of PL modified by Ag ion-plasma implantation with dose $1 \cdot 10^{16}$ ion/sm^2 are shown in Fig. 2. The bond energy of silver 3d-level electrons corresponds to the Ag^0-state. Obviously, Ag does not form new bonds with structural units of the matrix and is in a metallic state: IR-spectra of all modified and initial samples are identical (we don't show them here for this reason). Only absorption bands corresponding to vibrations of the functional groups of PL (-CH$_3$, -CH, -C=O, -C-O-C-) are present in the IR-spectra of samples both before and after ion implantation by Ag and carbon ions. The intensity of carbonyl group valence vibrations ν(-C=O) for initial and implanted samples is compared by the baseline method.

The calculations show that the intensity of the C=O band reduces by approximately 20% with increasing implantation dose, which may be due to decarbonylation and decarboxylation processes in macromolecular chains of PL.
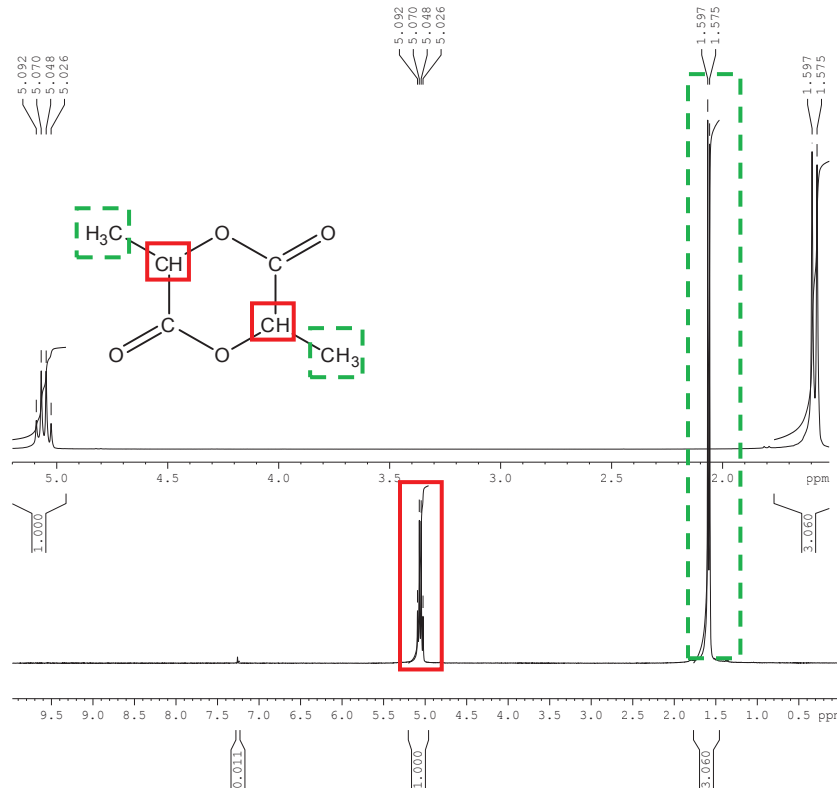

FIGURE 1. NMR ^{1}H-spectrum of refined lactide

XP-spectra provide more information about the chemical structure. Thus the XP-spectrum of oxygen 1s contains two components (Fig.2, a) related to the C–O (E_b=532.37 eV) and C=O (E_b=533.43 eV) bands, corresponding to PL.

There are no new bands in the oxygen 1s spectrum after ion implantation, but the ratio of areas corresponding to C–O and C=O bands is changed. The area of the C=O band decreases fourfold (Fig. 2,*b*).
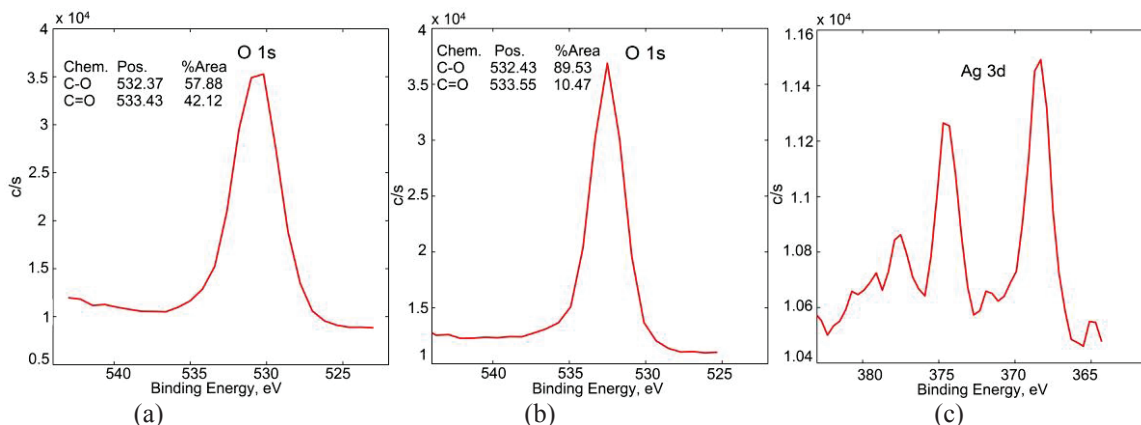

(a)   (b)   (c)

FIGURE 2. XPS-spectra of poly-*L*-lactide of: a) initial; b), c) Ag-implanted with dose of $1 \cdot 10^{16}$ ion/cm^2

The results of IR spectroscopy are fully consistent with the XP-spectra data. Probably, only processes associated with degradation of the polymer which is accompanied by the evolution of CO and/or CO_2 and reduced MW mainly occur under the conditions of ion implantation (Fig. 3). A possible mechanism for the destruction of PL during ion implantation can be represented by the scheme:
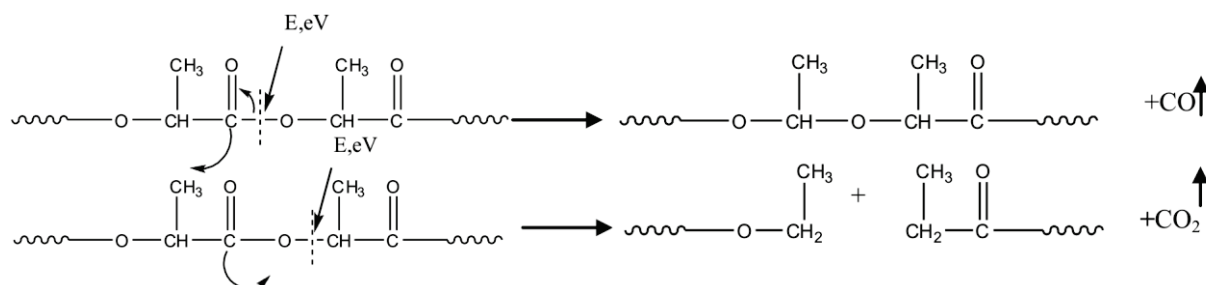
The above suggestions should inevitably lead to changes in surface properties such as wettability, which plays an important role in the biochemical processes that occur on the *ostein–liquid* border of living organisms. Limiting wetting angle measurements of the PL surface were carried out by the sessile drop technique for two liquids: polar – water and less polar – glycerol. Wetting as a phenomenon occurring at the contact of liquid with the surface of a solid body is characterized by a contact angle Θ whose vertex lies in a three phase contact point. One side belongs to the surface of "solid body – wetting liquid", the other is tangent to the surface of the wetting liquid [12]. Poly-*L*-lactide is an inherently hydrophilic material, i.e. $\Theta < 90°$. After Ag ion implantation, the limiting wetting angle is increased at the polar liquid (water) contact and hence the sample becomes less hydrophilic (Figs. 4a and b), and practically stay the same when in contact with glycerol.
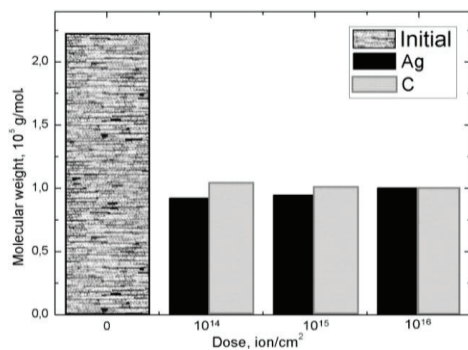
FIGURE 3. Poly-*L*-lactide molecular weight plotted versus ion implantation dose

At the same time, after carbon ion implantation the angle Θ with glycerol decreases with increasing dose (Fig. 4b), and hence the sample becomes more hydrophilic relative to the less polar liquid. C-implanted samples become more wettable with water than Ag-implanted PL samples. Possibly, the increased carbon concentration in the surface layers leads to an increase in adsorption sites. Surface energy evaluation by Owens-Wendt's equation [13] shows that surface energy values of PL C-implanted films are greater than for Ag-implanted samples.
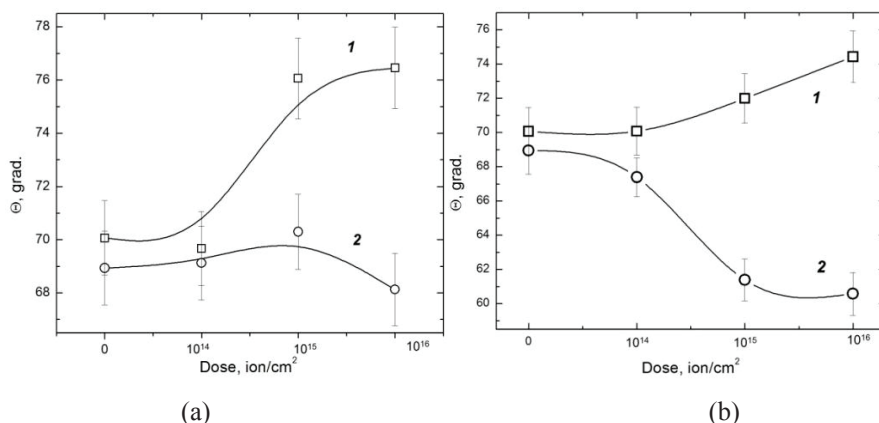

| (a) | (b) |

FIGURE 4. Ion-implanted poly-*L*-lactide limiting wetting angle in comparison to initial state:
a) Ag-implanted; b) C-implanted; 1 – water, 2 – glycerin

Biodegradable implants, being in the environment of a living organism, are actively involved in physiological processes with hundreds of reactions which have different structure, kinetics and thermodynamics. Implants may have greater or lesser wettability, ability to adsorb cells that participate in electrochemical processes, and bioresorption. There is a huge amount of easily dissociating biochemical compounds and salts in the body, and so knowledge of the surface resistivity of pure PL samples and Ag- and C- ion implanted PL samples is of great interest. Figure 5 shows the dependence of surface resistivity σ of PL Ag and C implanted samples on implantation dose. Surface resistivity of the initial, non-implanted PL is $2.1 \cdot 10^{13}$ Ohm/sq. Implantation of Ag and C ions with doses of $1 \cdot 10^{14}$ and $1 \cdot 10^{15}$ ion/cm^2 results in a slight increase of PL sample surface resistivity within one order of magnitude, which may be only measurement error. Further increase in the exposure dose to $1 \cdot 10^{16}$ ion / cm^2 leads to a decrease of 3orders of magnitude ($\sigma = 4.5 \cdot 10^{10}$ Ohm/sq.) for the C- implanted sample surface resistivity, and 5 orders of magnitude for Ag-implanted samples ($\sigma = 2.3 \cdot 10^{8}$ Ohm/sq.).

A possible mechanism for sub-surface electrical conductivity formation may be based on direct charge transfer between conducting particles formed by embedded silver or carbon atoms when an external electric field is applied. On the other hand, the presence of "unconjugated" carbon atoms in the ion-modified sub-surface layer, which are inevitably formed due to macromolecule degradation under the action of high energy bombardment, when ions break the structural units of the experimental samples. Thus changes in the surface resistance may be the result of the cumulative effect of interstitial metal atoms and "unconjugated" carbon.
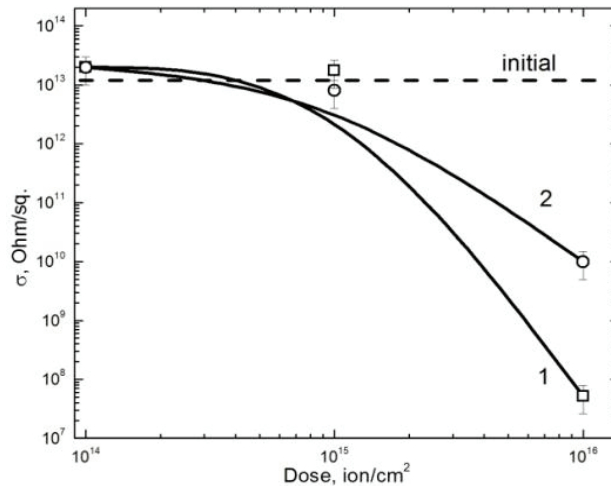
FIGURE 5. Surface resistivity of poly-*L*-lactide plotted versus implantation dose: 1 – Ag-implanted, 2 – C-implanted

Finally, mechanical parameters such as micro-hardness and surface roughness play an important role in implant quality assessment. The micro-hardness values of poly-*L*-lactide samples under a load of 0.5 mN in the initial state and after Ag and C implantation with doses of $1\cdot10^{14}$, $1\cdot10^{15}$ and $1\cdot10^{16}$ ion/cm^2 are shown in Table 2.

TABLE 2. Microhardness of initial and implanted PL samples

Samples, ion/sm^2	Micro-hardness, GPa
Initial	0.5135± 0.021
Ag $1\cdot10^{14}$	0.3858± 0.018
Ag $1\cdot10^{15}$	0.3202± 0.010
Ag $1\cdot10^{16}$	0.3792± 0.035
C $1\cdot10^{14}$	0.3861 ± 0.019
C $1\cdot10^{15}$	0.4256± 0.025
C $1\cdot10^{16}$	0.4927± 0.020

Micro-hardness of the implanted samples decreases by approximately 1.3 times in comparison with that for non-implanted PL samples. With increasing exposure dose, a tendency to micro-hardness decrease is observed in the implanted samples. This dependence could be related to the partial phase state conversion of PL, for example, transition of certain crystalline areas into an amorphous state. The largest surface roughness is for the C-implanted sample with dose of $1\cdot10^{16}$ ion/cm^2 (460-750 nm), and the least - Ag-implanted sample with dose of $1\cdot10^{16}$ ion/cm^2 (30-55 nm).

CONCLUSION

1. Biocompatible and biodegradable poly-*L*-lactide samples (molecular weight of 250 000 g/mol. and thickness of 1 mm) for subsequent Ag and C ion implantation were obtained by a three-stage synthesis of commodity lactic acid.
2. Silver and carbon ion implantation was performed using a universal test bench equipped with a MevvaV.Ru vacuum arc metal ion source.
3. Various physicochemical methods were used to investigate the properties of initial and implanted samples: atomic force microscopy, X-ray photoemission spectroscopy, infrared spectroscopy, and nuclear magnetic resonance. Molecular weight, micro-hardness, roughness, surface resistivity, limiting wetting angle and surface energy of poly-*L*-lactide were also measured.

4. The limiting wetting angle was found to increase after Ag ion implantation for water contact, and practically stay the same for contact with glycerol. However the limiting wetting angle of glycerol for C-implanted poly-*L*-lactide samples was revealed to decrease with dose increasing. C-implanted samples become more wettable with water than Ag-implanted PL samples. Possibly the carbon concentration increase in the surface layers leads to increase in adsorption sites. The surface resistivity of Ag- and C-implanted samples is reduced by 5 and 3 orders of magnitude, respectively.
5. Modified poly-*L*-lactide samples have been prepared for biomedical research, primarily for evaluation immunotolerance implants.

ACKNOWLEDGMENTS

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