MODIFYING PHYSICO-CHEMICAL PROPERTIES OF BIOCOMPATIBLE POLYMERS BY ION IMPLANTATION METHOD

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МОДИФИКАЦИЯ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ БИОСОВМЕСТИМЫХ ПОЛИМЕРОВ МЕТОДОМ ИОННОЙ ИМПЛАНТАЦИИ

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Аннотация. *В данной работе было рассмотрено влияние ионной имплантации ионов серебра, цинка и магния с экспозиционными дозами $1{\cdot}10^{15}$ и $1{\cdot}10^{16}$ ион/см^2 на поверхностные свойства поливинилового спирта (ПВС). Для изучения изменения физико-химических свойств был применён метод инфракрасной (ИК) спектроскопии. Для определения средней шероховатости и структуры поверхности был задействован метод атомно силовой спектроскопии (АСМ). Расчет глубины внедрения ионов осуществляли с помощью симуляции пробега ионов в программном обеспечении TRIDYN.*

Introduction. Polymer materials are of great interest for their widespread use in different fields: from medicine to aerospace. Polyvinyl alcohol (PVA) belongs to a class of biodegradable polymers that are widely used in modern medicine for the production of implants and immunotolerant pins. Ion and plasma treatment techniques are widely used methods for alteration of polymer surface properties, for example, for modification of wettability, microhardness, conductivity, etc. [1]. The purpose of this paper is to investigate the effect of metal ion implantation on surface physicochemical properties of PVA films.

Materials and methods. PVA samples were prepared by dissolving of polyvinyl alcohol granules in water at 90 ˚C to form a 10% solution. Then the solvent was removed by drying at room temperature in a Petri dish to form material at thickness of ≈1 mm. Ion implantation was realized by MevvaV.Ru vacuum arc ion source [2]. Metallic ions under analysis were zinc (Zn^{1+}), magnesium ($Mg^{1,5+}$), and silver (Ag^{2+}). Because the accelerating voltage was always 20 kV, the ion beam energies were 20 keV, 30 keV, and 40 keV, respectively. Implantation is carried out to exposure doses of $1{\cdot}10^{15}$ and $1{\cdot}10^{16}$ ions/cm^2. The structural characteristics of implanted PVA were investigated by infrared spectroscopy using a single attenuation total reflection attachment to IR-spectrometer Nikolet 5700. Simulation of ion depth into the PVA was made in TRIDYN software. Surface morphology was studied by atomic force microscopy (AFM) using a microscope NanoScope IIIA (Bruker) in tapping mode. Gwyddion software was used for the results evaluation.

Results and discussion. Infrared spectroscopy was carried out on unimplanted and implanted samples, and the results are shown in Fig. 1. The unimplanted sample showed the basic chemical PVA bonds. There were changes for implanted samples, which showed lines in the 1700−1800 cm^{-1} region, distinctive for carbonyl (-C=O) stretching vibrations and related to surface oxidation [3]. This may be due both to local heating by ion irradiation and to the presence of excess electrons from polymer chain scission. We observed a consistent decrease in the intensity of the lines due to the valence vibrations of hydroxyl (O−H) (3100−3600 cm^{-1}), C−H (2800−3000 cm^{-1}), and hydroxyl (–C-O-H) (1560 cm^{-1})**.** It can be explained by the fact of polymer degradation and oxidation. Alteration of deformation vibrations of (−CH_2−) groups were not detected. (Characteristic lines for (−CH_2−) groups are 1465 cm^{-1}, 770-850 cm^{-1}, 1150−1350 cm^{-1}). Most of the changes occurred in the outer layer of PVA.

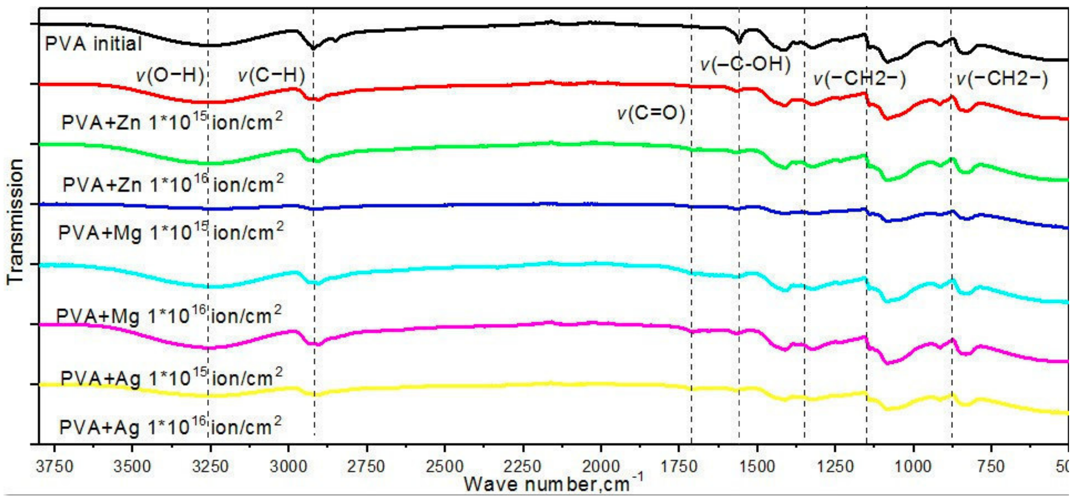
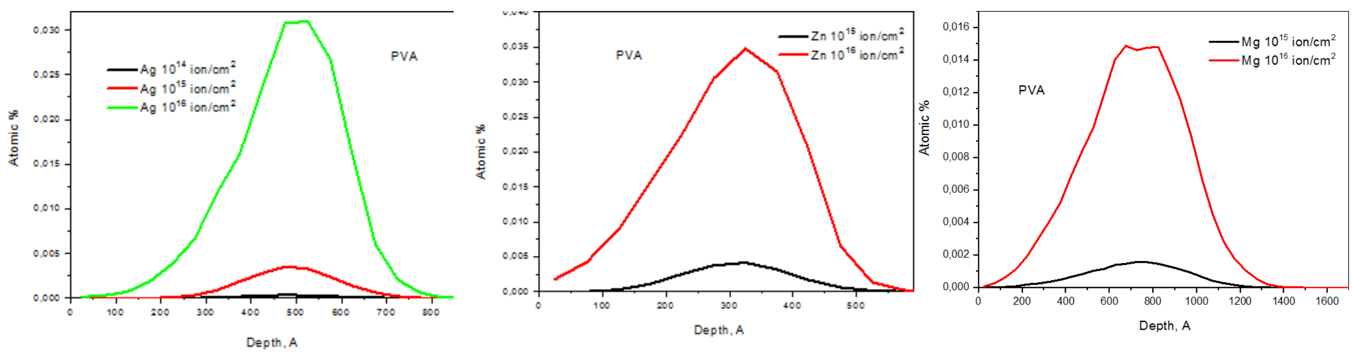


Fig. 1. IR-spectroscopy initial and implanted samples with Zn, Mg, Ag ions of PVA

TRIDYN simulations for Ag, Mg, and Zn ions showed that changes occurred in the surface layers at 30-80 nm depth. Results are shown in Fig. 2. Maximum (peak) depth of ion range for PVA samples (nm): Ag-52, Mg-80, Zn-32.5.



(a) (b) (c)

Fig. 2. Distribution profiles of a) Ag b) Zn c) Mg ions in PVA samples according to simulations in TRIDYN software

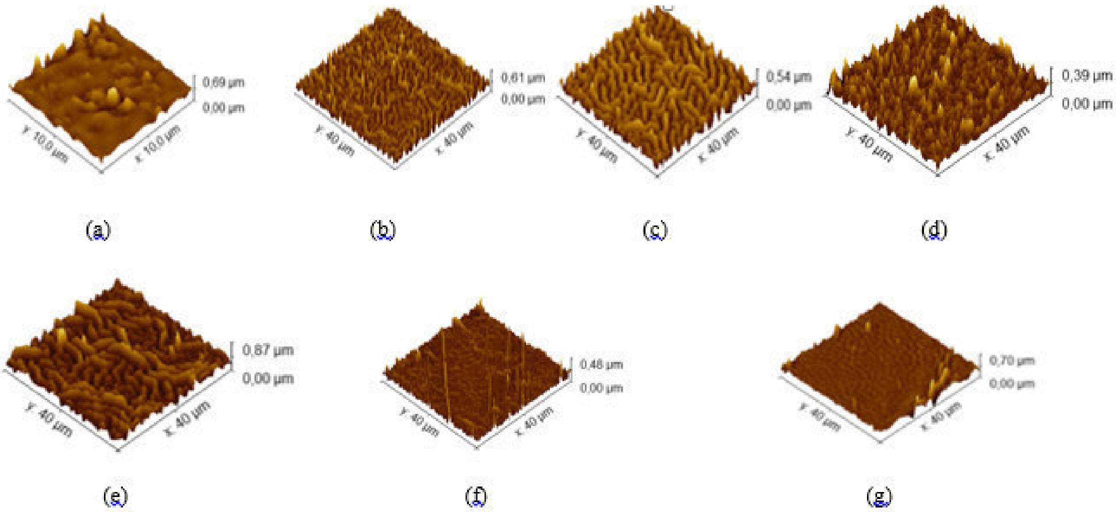


*Fig. 3. Average roughness for samples: a) PVA initial b) PVA Ag 1*10^{15} c) PVA Ag 1*10^{16} d) PVA Mg 1*10^{15} e) PVA Mg 1*10^{16} f) PVA Zn 1*10^{15} g) PVA Zn 1*10^{16}*

Results of AFM for PVA samples, before and after ion implantation, are shown in Fig. 3. Average roughness for initial PVA sample was 17.86 nm. For Ag, Mg, and Zn-implanted PVA, the average roughness increased, compared to the initial sample. For Ag-implanted PVA, samples the roughness increased with the exposure dose enhancing from 54.84nm ($1\cdot10^{15}$ ions/cm^2) to 63.24 nm ($1\cdot10^{16}$ ions/cm^2). However, the dose increasing leaded to average roughness decrease, from 84.11 nm ($1\cdot10^{15}$ ions/cm^2) to 32.23 nm ($1\cdot10^{16}$ ions/cm^2), and from 32.07 nm ($1\cdot10^{15}$ ions/cm^2) to 23.45 nm ($1\cdot10^{16}$ ions/cm^2), for Mg and Zn-implanted samples, respectively.

Conclusion. Thus, we have explored the effects of silver, zinc, and magnesium ions implantation with the exposure doses of $1\cdot10^{15}$ and $1\cdot10^{16}$ ions/cm^2 on physicochemical properties of PVA. The average roughness for all Ag, Mg, Zn-implanted PVA samples increased, compared to the initial sample. We established similarities in the chemical composition change of the PVA surface after ion implantation.

Acknowledgements. The work was carried out with the financial support of the program to improve the competitiveness of TSU No. 8.2.06.2017. Special thanks are expressed to Maria Cecilia Salvadori (Head of the Laboratory of Thin Films of the Institute of Physics of the University of São Paulo) and personally to Natalia Viktorovna Ryabova for assistance and support.

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