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Full Length Article

Effects of ion- and electron-beam treatment on surface physicochemical properties of polylactic acid

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ABSTRACT

We describe our investigations of the surface physicochemical and mechanical 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} ions/cm^2 at energies of 20 keV (for C and Ar) and 40 keV (for Ag), and by electron beam treatment with pulse-width of 100–300 μs in 50 μs increments at a beam energy 8 keV. Carbonyl bonds (—C=O) related IR peak was reduced after ion and electron beam irradiation. Molecular weight of PLA decreases twice and does not depend on the nature of the bombarding particles. The microhardness of treated samples decreases by a factor of 1.3, and the surface conductivity increases by 6 orders of magnitude after ion implantation, and increases only modestly after electron beam treatment. Atomic force microscopy shows that surface roughness increases with irradiation dose. Samples irradiated with Ag to a dose of 1×10^{16} ions/cm^2 show the greatest roughness of 190 nm.

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1. Introduction

Polylactic acid (PLA) is a biocompatible and biodegradable polymer used in biomedicine [1] primarily for implant manufacture. 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. However PLA-based materials application for implants creation is limited by their adhesion characteristics and lack of functional groups for interaction with cellular media. To obtain materials with modified surface properties for specific applications including biomedical, ion/electron beam treatment [2–4,7,8], plasma processing [9], chemical grafting [10], as well as the combination of these methods [11] and excimer laser treatment [12] could be used as modification techniques.

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 is 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 property of materials. The ion irradiation caused scission of molecular chains in the samples and emission of volatile products from the surfaces. The exposure dose increasing leads to the ion average projected range enhancing and the irradiated part density decreasing [3]. Polymer chain scission accompanied by surface oxidation processes and new functional group formation, which contribute to the material hydrophilicity, occurs as a consequence of ion implantation [4]. It has been shown [5] that plasma treatment of polylactic acid surfaces causes roughness and increase in contact angle, and, in turn, increased roughness was found to improve PLA biocompatibility [6]. 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 [7,8].

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Plasma treatment is often used as pre-treatment technology and the way of surface activation followed by distinct processes of coating, e.g. chemical modification by grafting of organic functional groups [9] and deposition of plasma polymerized acrylic acid on PLA surface [10]. It was found that applying of such combined methods of surface modification promote the wettability improvement, surface roughness increment, chemical composition alteration. Authors of [9] confirm that their approach permits to create spatially distributed properties on the sample, for instance, hydrophilic and bio-adhesive from one side and hydrophobic and bio-repulsive from the other side that is highly desired for the medical (implants) application. On the contrast, Y. Zhao, et al. [10] focus on food packaging industry to protect economically and effectively the food quality by usage of optimal combination of different gases in their methods of PLA modification. Chemical modification of PLA microspheres by aminolysis and grafting-coating [11] demonstrate the possibility to create the material with ability to support the attachment and proliferation of chondrocytes. These results show that the collagen-coated PLA microspheres are promising candidate for cell microcarriers. Other way of PLA surface modification is excimer laser treatment described in [12], where the surface wettability, morphology and roughness changes as well as mass loss by ablation are investigated. It is revealed that the contact angle decreasing is mainly associated with number of laser pulses increasing. The excimer laser has a strong effect on the polymer ablation; the mass loss is strongly dependent on the laser fluence and number of pulses.

The literature 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 various ion kinds (silver, argon, carbon) at exposure doses of 1×10^{14}, 1×10^{15}, and 1×10^{16} ions/cm^2, and electron beam treatment with pulse-width of 100–300 μs in 50 μs increments and beam energy 8 keV, on the surface physicochemical, functional and biological properties of PLA.

2. Experimental

2.1. Preparation of PLA samples

PLA samples were prepared by dissolving polylactic acid ([-OCH(CH3)-CO-]n) with molecular weight of 250 000 g/mol in chloroform at room temperature in a 7% solution [13]. 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 10×10 mm^2.

2.2. Ion implantation

Ion implantation was done using a facility incorporating our MevvaV.Ru vacuum arc ion source [14,15]. This implantation facility operates in a repetitively pulsed mode with repetition rate 10 Hz and pulse duration 250 μs. Ion kinds used in the present work were Ag, Ar and C. Charge state distributions of the ion beams were measured by a time-of-flight mass-to-charge spectrometer [16]. 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 [17]. Implantations were carried out to accumulated doses of 1×10^{14}, 1×10^{15}, and 1×10^{16} ions/cm^2. The implantation dose rate and average 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 0.5 mW/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. Electron beam treatment

Electron beam processing was carried out using a repetitively-pulsed, forevacuum-pressure, plasma-cathode electron beam source based on a hollow-cathode glow discharge [18]. A working pressure of 5–10 Pa ($37.5 - 75 \times 10^{-3}$ Torr) was maintained by admitting air into the vacuum chamber. Electron beam irradiation was carried out by a series of 10 pulses with pulse duration 100 – 300 μs in increments of 50 μs at an energy of 8 keV and current density 4.5 A/cm^2.

2.4. Characterization techniques

Chemical structure of implanted PLA was investigated by infrared spectroscopy using a single-attenuation total reflection attachment to a Nikolet 5700 IR-spectrometer. The molecular weight (MW) and molecular weight distribution (MWD) were determined by gel permeation chromatography on Agilent 1200 LC Infinity chromatograph with refractometer detector (Agilent-Technologies, USA)(eluent – chloroform). Surface morphology was studied by atomic force microscopy (AFM) using an NTEGRA Aura scanning probe microscope in tapping mode. Water and glycerol contact angles were measured by a sessile drop technique using a Kruss Easy Drop instrument. Surface energy calculation was done using the Owens-Wendt equation [19]. Microhardness was measured with a Nanotest 600 hardness testing instrument at a load of 0.5 mN. Surface electrical resistivity (also called sheet resistance) was measured using an E6-13A teraohmmeter and calculated from the equation

$$\rho = Rb/l, \quad (1)$$

where R is the measured resistance, $b = 3$ mm is the distance between the contacts, and $l = 10$ mm is the electrode length. Graflex plates pressed tightly to a polymer sample were used as the contacts (electrodes). Surface resistivity is measured in units of Ohms/square (Ohm/□) [20,21].

3. Results and discussion

3.1. Physicochemical properties of PLA

IR-spectroscopic investigations reveal that the spectra of the initial and the ion- or electron-irradiated PLA samples are identical, with only absorption bands corresponding to the PLA functional group vibrations; see Fig. 1. Valence vibrations with wavenumbers 2944 cm^{-1} (symmetrical vibration) and 2996 cm^{-1} (asymmetrical vibration) correspond to the —CH$_3$, —CH functional groups. Moreover, there are valence vibrations of the carbonyl group (—C═O) with wavenumber 1759 cm^{-1} and the (—C(═O)—O) group with wavenumbers 1456, 1186, 1093, 1045 cm^{-1}. There are also (—C—O—C—) functional group bending vibrations with wave

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