Vacuum 107 (2014) 184–190

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Plasma and laser treatment of PMP for biocompatibility improvement

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ARTICLE INFO

Article history:
Received 30 September 2013
Received in revised form
21 January 2014
Accepted 22 January 2014

Keywords:
Ar plasma treatment
Excimer laser
Surface modification
Thermal treatment
Surface properties
Cytocompatibility
PMP

ABSTRACT

This paper is focused on characterization of surface properties of PMP (poly-4-methyl-1-pentene) after the modification of its upper layer. PMP is a thermoplastic polyolefine, which is used e.g. in medicine for its mechanical and thermal stability, for medical and laboratory equipment. Modification was carried out by Ar plasma, KrF excimer laser beam, thermal annealing and their combinations. The changes in physico-chemical properties of surface layer, such as wettability, ablation, morphology, roughness and chemical composition, were determined. Finally, the tests of adhesion and proliferation of cells were carried out on the selected samples. PMP seems a very resistant material, but plasma exposure can affect its surface properties, e.g. wettability or atomic concentrations of elements, which cause improvement of VSMC cells ability to adhere and proliferate. All used methods have just minor effect on morphology. Except under extreme conditions, a KrF excimer laser beam has only insignificant influence on PMP changes. Because of that, PMP could be suitable as a resistant carrier for materials for the further laser modification.

1. Introduction

Modifications of polymers have a huge technological impact, because they make it possible to prepare materials with more suitable properties [1,2]. Those materials have found new applications in various and very specific fields, such are electronics or tissue engineering. While the bulk properties remain the same, the changes in the surface properties can be achieved by physical or chemical methods and their combinations [2]. The principle of these chemical methods is that the polymer is exposed to the influence of the solution, while chemical reactions are running on the surface of the material. That leads to disruption of chemical bonds (etching) or to establishing the new material (grafting) [3]. By physical treatment, either a new layer is created on the surface of the material or the changes occur directly in the upper layer. Physical modification techniques comprise e.g. flame treatment [4], corona discharge [5], plasma treatment, UV-, RTG-, γ-radiation, laser, ion, electron beam exposure, dusting or vacuum steaming [3,6].

Plasma is a strongly ionized gas which contains ions, radicals, excited molecules and free electrons. Due to the occurrence of free electrical charge, the plasma is electrically conductive and magnetic field affects it. Results of material exposure by plasma and subsequently by atmosphere can be: purification of the surface, ablation of the upper layer, surface cross-linking or modification of the chemical structure of the surface [7]. Interaction with an ion beam causes implantation, grafting and polymerization or sputtering of the surface. Inert gases are suitable for sputtering; the most widely used gas is argon because of its high sputter effect and a low price [6]. Plasma works evenly and only on the surface and it can be used on very resistant materials. Moreover, plasma requires no removing of residual solvents; it is simple and effective [8].

Excimer lasers are gas pulse lasers in the ultraviolet wavelength area. Excimers exist only in excited electron states, in the basic state there is repulsion between their components. Because of that, the bottom laser level is occupied only weakly and it easily causes formation of the inverse occupation. An excited atom of a rare gas has similar characteristics as an atom of alkaline metal, which reacts well with halogens; thereby the reaction with halogen provides a halide of the rare gas. A Krypton fluoride (KrF) laser is an excimer laser, which produces ultraviolet radiation of wavelength 248 nm. A KrF laser absorbs energy from a source, thereby the reaction of fluorine with krypton provides a temporary complex of krypton–fluorine in an excited state [9]. The formed complex could undergo spontaneous or simulated emission, therefore it reaches the reduction of its state to metastable but highly repulsive state, from which the complex quickly dissociates to form separate atoms. The laser radiation near ultraviolet spectrum arises; its energy corresponds to the difference between the basic state and the state of the excited complex [9].

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0042-207X/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2014.01.023

The laser-generated structures are used for processing polymer semiconductors and insulators [10]; by an application of the surface nanostructures on the top of polymer it is possible to improve the parameters for electronic memories of polymers [11,12]. The laser pattern is applicable also in tissue engineering because of the impact on the biological and physical properties of the material surface. It was found that the regularities of structures have a positive effect on cell adhesion to substrate [13,14]. Cell adhesion is closely related to other surface properties of the material such as, wettability, polarity, surface energy, electrical properties, morphology and roughness, chemical composition. These properties of "suitable" substrates are often not optimum and they need to be modified [15,16].

This paper is focused on characterization of surface properties of PMP (poly-4-methyl-1-pentene) after the modification of its upper layer by Ar plasma, KrF excimer laser beam, thermal annealing, and some of their combinations. PMP is an isotactically arranged aliphatic polyolefin, which can be processed or formed into various optical and electrical components, e.g. LED moulds, because it is an excellent electrical insulator. Benefits of this material are high melting point and good temperature stability, therefore PMP can be used for autoclavable medical and laboratory equipment, microwave components, and cookware. The changes in physico-chemical properties of surface layer, such as wettability, ablation, morphology, roughness and the chemical composition of the changes were determined by goniometry, gravimetry, AFM, XPS. Biological tests were carried out on the selected samples by vascular smooth muscle cells (VSMC).

2. Materials and methods

2.1. Materials, plasma, laser and heat treatment

Linear isotactic poly-4-methyl-1-pentene (PMP, density 0.835 g cm^{-3}, $T_g = 25$ °C, $T_m = 228$ °C, crystallinity 52%, 50 m thick foils, supplied by Goodfellow, Ltd.) was used for the experiments. The samples were modified in diode plasma discharge by Balzers SCD 050 device for 0–480 s, using DC Ar plasma (gas purity was 99.997%, power 5 and 10 W). Chamber parameters were: Ar flow 0.3 l s^{-1}, Ar pressure 10 Pa, electrode area 48 cm^2, the inter-electrode electrode distance of 50 mm, chamber volume 1000 cm^3.

For irradiation of the PMP samples a KrF laser was used (Coherent Compex Pro 50, wavelength of 248 nm, pulse duration of 20–40 ns, repetition rate 10 or 30 Hz). For the irradiation the light was polarized linearly with a cube of UV grade fused silica 25 × 25 × 25 mm with active polarization layer. For homogeneous illumination of the samples, we used only the central part of the beam profile by means of an aperture (0.5 × 1.0 cm^2). The samples were mounted onto a translation stage at a perpendicular position of the sample and laser beam. The pulses were chosen from 100 to 36 000 with laser fluences in interval 6–40 mJ cm^{-2}.

Thermal treatment of the polymers was accomplished in thermostat BINDER. The samples were heated at 160 °C (Vicat softening point). The pristine and modified samples (immediately after plasma treatment) were heated for 30 min and then they were cooled down to room temperature.

2.2. Measurement techniques

2.2.1. Contact-angle

Contact-angle was determined through goniometry by a static water drop method. The measurements of water contact-angles (error ± 5%) were performed using distilled water (9 different positions) using the Surface Energy Evaluation System (SEE System, Advex Instruments, Czech Republic). By Automatic pipette the water drop of volume (8.0 ± 0.2) ml was deposited on the polymer surface and the consequent photo was evaluated. The measurement was carried out at room temperature.

2.2.2. Gravimetry

Thickness of the ablated surface layer after plasma and laser treatment was measured using a Mettler Toledo UMX2. In order to enhance the sensitivity of the measurement, the samples (diameter 2.5 cm) were exposed to the plasma from both sides. Samples modified by laser were exposed from one side only. The thickness of the ablated layer was calculated from the change in weight of 4 samples before and after the treatment using tabulated polymer density. The depolarization high-frequency gate was used to discharge the surface in order to minimize the influence of surface electrostatic charge on the measurement.

2.2.3. X-ray photoelectron spectroscopy

The presence of oxygen and carbon in the modified PMP surface layer was proved by X-ray photoelectron spectroscopy (XPS). An Omicron Nanotechnology ESCAProbeP spectrometer was used. The

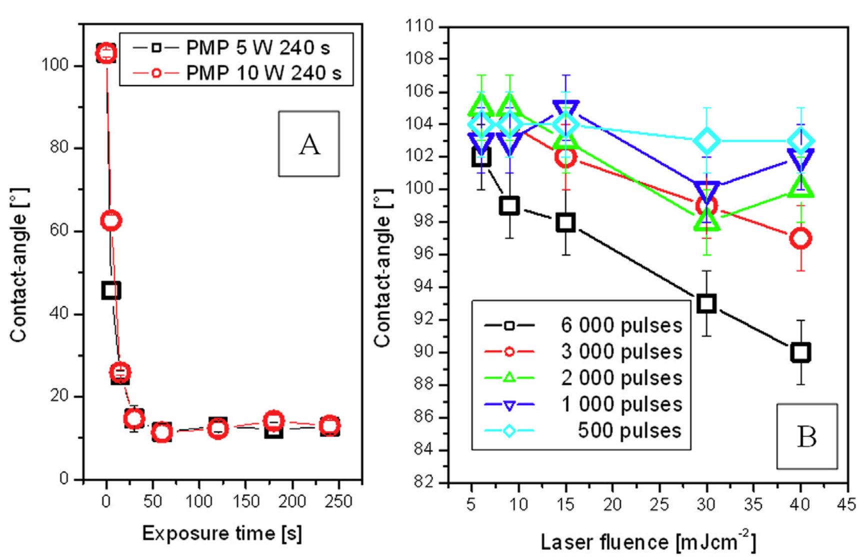

Fig. 1. Dependence of the contact-angle of (A) PMP plasma treated (with 5 and 10 W) on Ar plasma exposure time and (B) PMP modified by laser treatment (with 500 to 6000 pulses) on laser fluence.