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Plasma immersion ion implantation of Pebax polymer

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Abstract

Nitrogen plasma immersion ion implantation (PIII) was applied to Pebax thin films and plates using doses ranging from 5×10^{14} to 10^{17} ions/cm^2 at applied voltages of 5, 10, 20 and 30 kV. The analysis of the Pebax structure after implantation was performed using FTIR ATR, Raman, UV–vis transmission spectra, tensile and AFM contact mode data. The carbonization and depolymerisation processes were observed in the surface layer of Pebax. It was found, that graphitic- and diamond-like structures in Pebax are formed at PIII treatment of 30 kV applied voltage. AFM measurement data showed that the hardness of the Pebax surface layer increased sharply at PIII treatment with a dose higher then 10^{16} ions/cm^2. The bulk mechanical properties of the Pebax film after PIII remained unchanged.

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1. Introduction

Medical devices are interesting product applications for polymers, both temporarily devices such as catheters as well as permanent implanted devices in living organism intended for a variety of goals [1]. For these applications the unique properties of polymer materials enables optimal exploitation characteristics of the device. Surface hardness is an important mechanical characteristic of polymers [2–4]. A part made out of polymer usually operates at low mechanical load, far from breaking stresses, however even a low mechanical load can cause a defect of the microstructure, which can progress at high loads into macro cracks and final destruction of the part. Prevention of the initial defect has as such a strong influence on the exploitation life-time and thus in this case the medical device for which operation reliability is mandatory. An increase of surface layer hardness can prevent the structure defects to appear at low scratch load.

An example of a medical device in respect to the importance of surface hardness is a stent delivery system (SDS) as used for placing a stent in coronary or peripheral blood vessels [5]. A thin-walled polymer balloon is part of this SDS. The balloon is folded after which the metallic stent is crimped around the folded balloon to a very small diameter to enable the delivery of the system to very stenosed regions. Once the delivery system has been guided through the vascular system to its destination, increasing the pressure inside of the balloon up to about 20 atmospheres will expand the balloon, opening up the stenosed blood vessel as well as deploy the stent simultaneously. The balloon wall must be soft and thin to allow the medical device to be guided through tortuous vascular systems without doing any damage to the vessel wall, on the other hand; the balloon wall must be strong enough to withstand the high inflation pressure and withstand potentially very high point forces caused by a high degree of calcification in hard lesions. It is therefore essential that the metal stent as

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crimped on a folded balloon will not scratch the balloon to assure that the balloon will not fail under these potential circumstances. Following these contradicting requirements, the solution we pursued was to increase only a very thin surface layer in hardness without significant changes to the bulk properties of the balloon wall. For thin layer modification, one of the effective methods for hardness increase is ion beam modification [6,7].

Ion beam treatment of polymers is characterized by a high level of macromolecule defects in a thin surface layer which cause structure transformations by way of chemical reactions of free radicals into the formation of a carbonized layer [8–10]. The thickness of this layer corresponds to the distribution of the defects which is determined by the implantation energy, type of ion and polymer. The carbonization and oxidation processes in the surface layer have been observed for different kinds of polymers [11–13]. Conventional ion beam implanters are expensive and large machines, and only few industrial applications can be found in regards to polymer modification. Plasma immersion ion implantation (PIII) is a reliable technology, compatible with well known plasma reactors by simple equipment attachment and therefore far less expensive. The effects of PIII modification are quite similar to ion beam implantation. PIII methods are used primarily in metal and semiconductor industry.

In our studies, Pebax balloons (Boston Scientific, Maple grove, USA) have been modified for hardness improvement. Pebax is a block co-polymer of polyamide and polyether with suitable mechanical characteristics for vascular stents balloons [14–17]. The goal of the investigation was to improve the hardness of the surface layer while maintaining the mechanical properties and structure of the bulk film.

2. Experiment

Thin films (10 μm thick), plates of size $20 \times 20 \times 1$ mm and balloons (2 mm and 4 mm diameter, wall thickness 22 μm made out of Pebax 8200 polymer (Arkema Inc., USA) were used. The balloons (Boston Scientific, USA) were cleaned by alcohol and dried before treatment.

Nitrogen plasma immersion ion implantation was used for the surface modification of the polymer samples. The plasma immersion ion implanter of the Rossendorf Research Center (Germany) was used in the experiments [18]. The pressure of residual air was 10^{-3} Pa, working pressure of nitrogen at PIII was 10^{-1} Pa. Plasma of 100 W power was generated using a 13.56 MHz RF generator with an inductive antenna. High voltage pulses were applied to the sample holder. The samples were positioned on the top of the sample holder and covered by a metal mesh positioned 30 mm above the sample surface. The mesh was electrically connected with the sample holder. The high voltage pulses, 5 μS duration, 30, 20, 10 and 5 kV values peak voltage were applied. Due to the additional mesh the energy of ions on the target had distribution with maximal value of applied voltage. Pulse repetition frequency in the range of 0.2–200 Hz was used. Regulation of pulse frequency was used in order to exclude overheating of the samples during the PIII treatment. The PIII treatment of the samples was carried out with doses from 5×10^{14} to 10^{17} ions/cm^2.

Spectra of FTIR ATR were recorded on a spectrometer Nicolet 230 with a diamond ATR crystal and on a spectrometer Nicolet Magna 750 with a Ge ATR crystal. Number of scans was 100, resolution 2 cm^{-1}. Software of OMNIC Nicolet was used for spectra analysis.

UV transmission spectra were recorded on UV–vis spectrometer. Spectra were recorded with steps of 10 nm in the 200–700 nm wavelength spectral region. The optical density scale was used for quantitative analysis.

Micro-Raman spectra were recorded in a backscattering mode excited by Nd:YAG laser irradiation (2ω, $\lambda = 532.14$ nm) on a diffraction double monochromator spectrometer HR800, Jobin Yvon with LabRam System 010. Optical microscope was used for focusing of the exciting laser beam and for collection of Raman scattered light. The objectives of 5, 20 and 100 units were used. The sample surface position alignment during the Raman signal was controlled by imagine from CCD camera attached with microscope and projected on a screen. The intensity of the laser beam was controlled to avoid overheating of the samples. Spectral resolution was 4 cm^{-1}. Number of scans was selected from 100 to 4000 for sufficient signal/noise ratio. LabRam software was used for spectra analysis.

Tensile tests on Pebax strips of $30 \times 2 \times 0.03$ mm^3 size were done on a Zwick tensile machine (Germany). The strips were cut from the balloons with multi-blades knife having a fixed distance between the blades. For strong mechanical fixing in the clamps, the ends of the strips were attached to aluminum folia using epoxy. Tested area of the strips was $20 \times 2 \times 0.03$ mm^3. A load rate of 5 mm/min was applied. The mode of destruction was analyzed for each sample. Using the strain–stress diagram, modulus, elongation and stress at break were analyzed. The modulus was determined by the linear part of strain–stress curve between 0.01% and 1% of elongation.

The atomic force microscope (AFM) was used for the hardness measurements of the surface layer. The measurements were performed with an atomic forces microscope (Dimension 3100 from Digital instruments Veeco Metrology Group, Santa Barbara, CA) in contact mode. A silicone probe with a cantilever spring constant of 20 nN/nm and a resonant frequency of 300 kHz was used. Tip curvature radius measured by standard gold particles imaging was 20 nm. The frequency of the tip vibration was 0.5 Hz. Software of Digital instruments with a compensating lateral motion was used for data analysis. Silicon wafer was used as reference material for module calculation.

3. Results

The structure changes of the Pebax surface layer after PIII are observed in FTIR ATR spectra. A new line in