

RF-PLASMA DEPOSITION AND SURFACE CHARACTERIZATION OF A BIODEGRADABLE THIN FILM COATING

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INTRODUCTION: Synthetic biodegradable polymers have become very important materials for applications in biomaterials, tissue engineering and controlled drug delivery. Among these materials, poly(L-lactic acid) (PLLA) has been widely utilized either as temporary scaffolds for cell transplantation in tissue regeneration or as carriers for delivery of bioactive molecules. PLLA breaks down in the body to lactic acid, a component of the normal metabolism [1]. RF-plasma deposition has also been found to be a useful technology for biomaterials applications because of its ability to coat complex shapes with a tightly adherent thin film [2].

The surface analytical techniques X-ray photoelectron spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) have been used to study the surface chemical nature of many polymeric materials, including plasma deposited polymers [3-4] and degradation of polymers [2]. These techniques probe the chemistry of the polymer surface to a depth of between 20 and 100 Å for XPS and approximately 10 Å for ToF-SIMS. Atomic Force Microscopy (AFM) is also commonly used to probe the topography of plasma deposited polymers [5] or the evolution of polymer degradation, an example being the hydrolysis of polyester [6-7].

The aim of this study is to use plasma deposition techniques to form a thin PLLA coating using the cyclic lactide as a monomer and to study its degradation in a phosphate buffer solution (PBS, pH 7.4) at 37°C (reproducing the saline conditions of human blood) using state-of-the-art surface analysis techniques.

MATERIALS/ METHODS: The substrates used for this experiment were either glass disks (for coating optimization) or silicon wafers (for the degradation studies). The borosilicate glass disks were obtained from Carolina Biological Supply Company (NC, USA) Cat. # D8-63-3029. Their diameter was 12 mm and thickness was 0.13-0.17 mm. The Si wafers were obtained from Silicon Valley Microelectronics, Inc., (CA, USA). The precursor used to form the plasma was L-lactide or

(3 S)-cis -3,6-Dimethyl-1,4-dioxane-2,5-dione, purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA), reference 36,704-4.

The plasma chamber consists of a Pyrex tubular glass cylinder, 25.5 in. in length and 4 in. in diameter, wrapped with heating tapes to control the temperature. Two copper capacitor plates are coupled to the 13.56 MHz RF generator via a matching network to increase the power dissipation in the discharge and protect the reactor. A capacitance manometer gauge measures the pressure, using a feedback controller which moves the throttle valve to maintain the pressure as directed.

XPS (ESCA) analyses was performed at the University of Washington (NESAC/BIO) on a Surface Science S-probe or X-probe Instruments. This instrument permits analysis of the outermost 20-100 Angstroms of a sample using a square spot size that can be adjusted from 100 µm x 100 µm to 800 µm x 800 µm. For the present set of measurements the largest spot size (800 microns) was used.

ToF SIMS analysis was conducted using a Physical Electronics Model 7200 time-of-flight secondary ion mass spectrometer at NESAC/BIO. The instrument is equipped with a Cs⁺ ion source operated at 8keV, a reflectron mass analyzer, and chevron-type multichannel plate detectors. A bunched primary Cs⁺ beam (50 micron diameter, approximately 1 ns pulse width) is used and the bin width of the time-to-digital converter (TDC) is set at 1.25ns, resulting in mass resolutions (m/Δm) of >7000 at m/z=27 for electrically conducting samples. The beam is rastered over a square area that is 100 microns on a side. Charge neutralization is achieved with a pulsed electron flood gun.

RESULTS / DISCUSSION:

Plasma deposition of cyclic L-lactide has been successfully optimized to yield a poly(lactic acid)-like thin film. The XPS, ToF-SIMS and AFM characterization of such films deposited using a pulsed RF plasma showed that the chemical structure, deposition rate and degradation in phosphate buffer solution (pH 7.4, 37°C) of such

films are strongly dependent on the duty cycle of the pulses. A typical XPS spectrum is shown in Fig. 1.

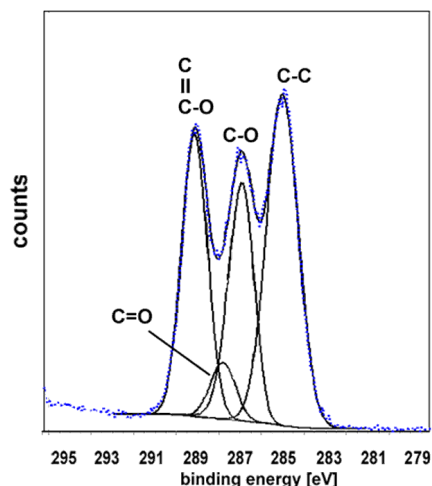


Fig. 1: Four peaks fit of C1s high resolution peak duty cycle = 2%

During the optimization process, it has been shown that the input power is the major parameter which affects the chemical structure of the deposited film. Lowering the input power increases the monomer structure retention. Since the degree of monomer retention was continuing to increase as the lower limit of continuous wave (CW) plasma stability was reached, it was necessary to use a pulsed RF plasma to reach even lower effective powers by decreasing the duty cycles. Other parameters such as sample position or deposition time were shown not to be as significant as the input power for monomer structure retention.

The characterization of the pulsed plasma deposited film showed an increase of oxygen functionalities, present as ester or alcohol groups, with decreasing duty cycle as shown in Fig. 2. The proportion of ketone groups seemed to be independent of the duty cycle. In addition, the deposition rate with a duty cycle of 33% is nearly three times the one corresponding to a duty cycle of 2%. Compared to PLLA, plasma deposited films contain more hydrocarbon species. However, the plasma-deposited PLLA films have several of the same ToF-SIMS fragments observed from a conventionally polymerized PLLA film.

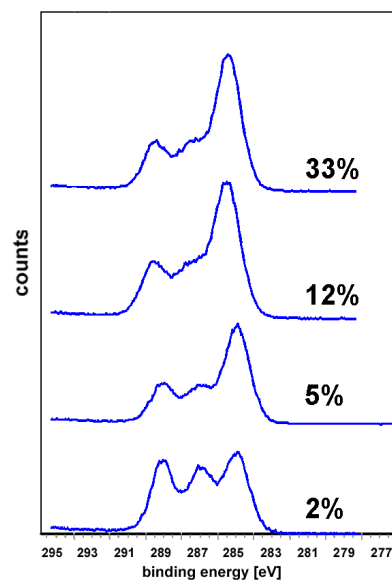


Fig. 2 C1s high-resolution peaks of pulsed plasma polymerized films for various duty cycles..

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