PLASMA POLYMERS WITH CONTROLLED DEGRADATION BEHAVIOUR

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Abstract

Classical “wet“ chemistry methods can produce polymers with well-defined molecular structure, but many types of polymers are difficult to prepare with significant degree of crosslinking without residues of the crosslinking agent. On the other hand, plasma polymers usually have very high degree of crosslinking but nearly random molecular structure.

Plasma assisted vapour thermal deposition combines both methods. Classical polymers are heated in a crucible at low pressure and the released oligomeric fragments of the polymer chain are repolymerized in a glow discharge into a thin film. The number of well-preserved monomeric units between the crosslinks can be tuned e.g. from units to tens.

Poly-lactic acid (PLA) belongs to a special class of biodegradable polymeric materials. In this work, plasma assisted vapour thermal deposition was utilized to prepare PLA plasma polymers. Molar weights and chemical composition of the “precursor” polymer and of the thin films have been characterized. As the measure of degradability, behaviour of the polymers during hydrolysis has been studied using spectroscopic ellipsometry and liquid chromatography. Possibility to prepare plasma polymer films with controlled degradability was demonstrated.

Keywords: Plasma polymers, degradability, plasma assisted vapour thermal deposition, thin films

1. INTRODUCTION

Degradable and biodegradable polymers (such as polyethylene oxide or polylactic acid) have important applications in the biomedical field due to their unique biocompatibility, biodegradability and mechanical properties [1-5]. They can be also synthesized in many modifications for packaging, food industry or medicine [6-10].

Typically PLA is synthetized by polycondensation of lactic acid [11], but other synthetic methods have been also studied [7-9]. Methods based on low temperature plasma were found to be effective for fabrication of thin plasma polymer coatings [12-20].

Using classical “wet chemistry” methods, it is often difficult to prepare biodegradable polymers with high degree of crosslinking without residues of the crosslinking agents. Plasma-based methods can produce very highly crosslinked materials easily, but retention of the molecular structure of the monomer is usually low.

Plasma assisted vacuum thermal deposition is a technique that uses oligomers released during low pressure thermal decomposition of a source polymer (“precursor”) [21-25] as “monomers” for plasma polymerization. It is possible to produce plasma polymers that bridge the limits of classical polymers and plasma polymers [26, 27]. In this way various properties of the films can be controlled [28].

2. EXPERIMENTAL

2.1. Deposition of plasma polymer

The general setup of the experiment was described e.g. in [26]. The RF (13.56 MHz) electrode covered with a glass target was 4 cm below a heated crucible with solid polymer precursor (“source” polymer). The substrates (single-side polished silicon wafers, gold-coated silicon, aluminium foil, glass slides) were placed 10 cm above the crucible. During the experiment, the crucible was heated approximately linearly from 25°C to 330°C at the rate 25°C/min. As a source polymer for the process, PLA prepared by polycondensation according to [6] was used. To ignite the plasma, argon under the pressure of 4 Pa (flow rate of 8 sccm) was used. The deposition rate was monitored by quartz-crystal microbalance sensor.

2.2. Determination of film composition

Molecular weight distributions of PLA prior to and after deposition were analyzed by gel permeation chromatography (GPC) on an HT-GPC 220 system (Agilent). Samples on aluminium foil were dissolved in THF (2 mg.ml^{-1}) overnight. Separation and detection took place on a series of mixed columns (1×B, 1×D, 1×E) (300×7.8 mm, Polymer Laboratories). Analyses were carried out at 40°C in THF, 1.0 ml.min^{-1} flow rate and a loading volume of 100 µL. The infrared spectra of the films on gold-precoated substrates were obtained by FTIR-ATR (Nicolet iS5).

2.3. Characterization of hydrolysis

The physical thickness of the film during hydrolysis has been characterized in situ using spectroscopic ellipsometry (Woollam M-2000DI). The hydrolysis experiments were carried out on samples on the glass slides at 37°C in 15 ml ammonium bicarbonate buffer (0.01 mol.l^{-1}, pH 7). 0.5 ml aliquots were taken at regular intervals, centrifuged and analyzed for lactic acid by LC MS (Agilent 6530 Accurate Mass) coupled to an HPLC unit (Agilent 1260 Infinity).

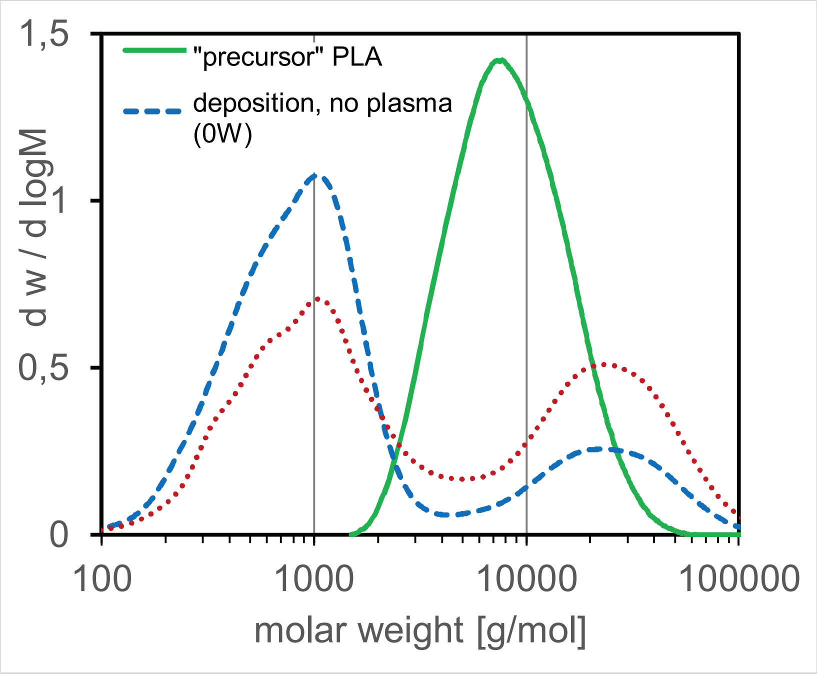

Figure 1 GPC molar weight of the precursor PLA polymer and thin films prepared without plasma and at plasma power 5 W (note: relative amount of fragments with M_r<2000 g.mol^{-1} can be overestimated)

3. RESULTS AND DISCUSSION

3.1. Preparation and composition of the films

During heating of the crucible, the deposition could be observed after attaining approximately 150°C. Most of the deposition took part at the temperature over 200°C and the deposition rate increased approximately exponentially with temperature.

The thickness of the as-deposited films was 500-3000 nm. Molar weight of the precursor polymer was M_n=6900 g.mol^{-1} (~80 monomeric units). The molar mass distribution of the plasma polymer is significantly broader (**Figure 1**). There are lower molar weight fragments (M_r=100-3000 g.mol^{-1}) present as well as the molecules with molar mass higher than the original polymer (M_r=10 000-100 000 g.mol^{-1}). This can be attributed to the fragmentation of the precursor polymer and re-polymerization of these fragments that proceeds to some extent even without the plasma. The ratio of the low molar to high molar fragments amount shifts slightly when the material is plasma-polymerized.

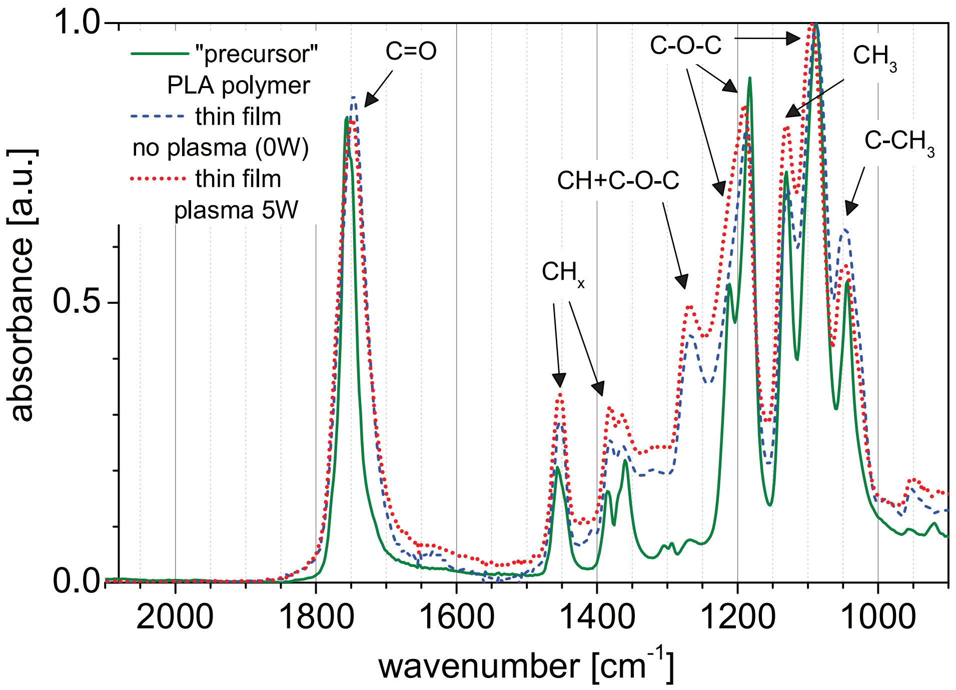

Figure 2 FTIR-ATR spectra of the precursor PLA polymer and thin films prepared without plasma and at plasma power 5 W

The FTIR ATR spectra (**Figure 2**) of the precursor and of the thin films are very similar, showing good retention of the chemical structure of polylactic acid.

However, slight broadening of the absorption peaks in the films in comparison to the precursor polymer marks some fragmentation and randomization of the structure of the thin films. That is compatible with findings of GPC. The structure of PLA is present in the peaks of C=O stretching (~1750 cm^{-1}) and C-O-C stretching (1090 cm^{-1}, 1185 cm^{-1}, 1215 cm^{-1}) vibrations. Significant increase of intensity of the peak at 1270 cm^{-1} can be attributed to coupled CH and C-O-C vibrations [29]. With the increase of intensity absorptions that can be assigned to CH_x containing groups (1045 cm^{-1}, 1130 cm^{-1}, 1380 cm^{-1}, 1450 cm^{-1}) it is another sign of fragmentation and crosslinking of the polymeric chain.

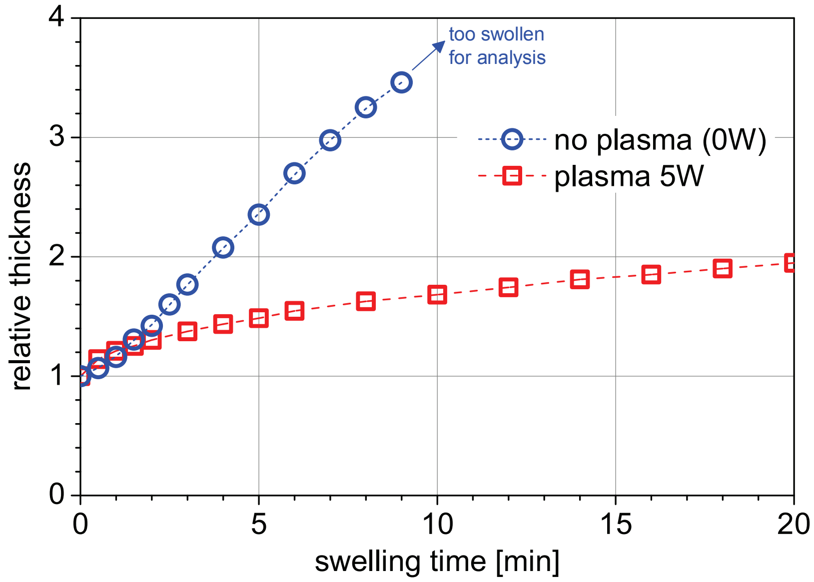

Figure 3 Swelling behaviour of the films in water observed by in-situ by spectroscopic ellipsometry for films prepared without plasma and at plasma power 5 W

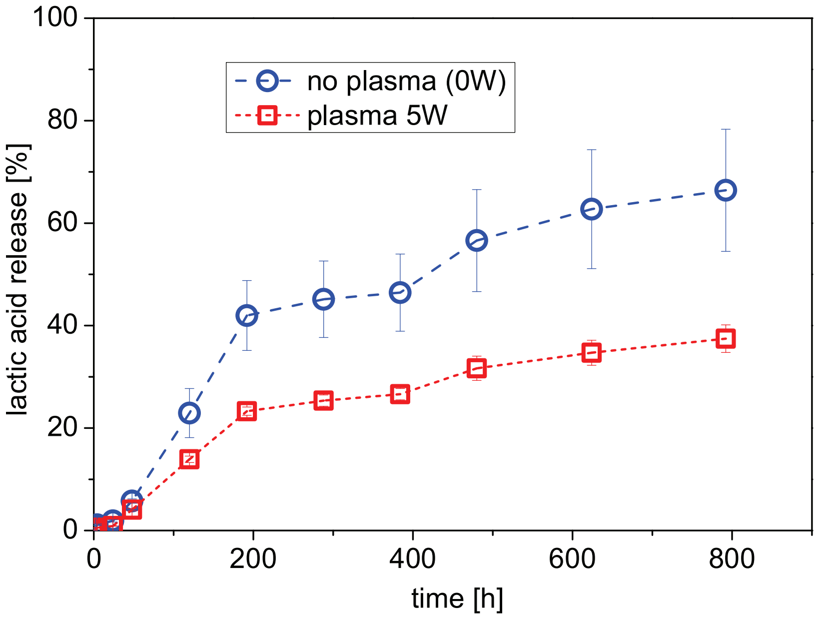

Figure 4 Lactic acid release from hydrolyzed PLA plasma polymer films determined by LC-MS for films prepared without plasma and at plasma power 5 W

3.2. Properties of the films during degradation by hydrolysis

The in-situ monitoring of thin films immersion in water using spectroscopic ellipsometry (**Figure 3**) revealed a marked difference between films prepared without plasma and with plasma power 5 W. While they differ only mildly in composition, the difference in the swelling behaviour was much more pronounced. The films prepared without plasma have swollen to more than three times of the initial thickness in less than 10 minutes without clear sign of slowing of the swelling and dissolving. Films prepared at plasma power 5 W swelled in the same time only by about 60%.

When the hydrolysis of the films was monitored (**Figure 4**), it was found that the lactic acid release was higher during the first 200 hours. The lactic acid release was faster for the films deposited without plasma discharge, showing faster degradation by hydrolysis.

4. CONCLUSION

PLA-like plasma polymer films were prepared using plasma-assisted vacuum thermal deposition. These films well correspond in structure and chemical composition to the original PLA polymer. The properties of the films in terms of (bio) degradability can be varied by the deposition conditions. Even mild plasma polymerization of the thermally released fragments of the source polymer significantly slow down the degradation of the resulting films.

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