POLYESTER URETHANE (PLA/PEG) POLYMER BASED FILMS PREPARED BY PLASMA ASSISTED VAPOUR THERMAL DEPOSITION

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Abstract

Polyester urethane polymer was synthesized as linked biocompatible poly (lactide)/poly (ethylene oxide) polymers. The bulk polymer was subsequently used as precursor material for plasma assisted vapour thermal deposition of thin plasma polymer films under varying RF discharge power. The effect of plasma polymerization on the final physico-chemical characteristics was investigated. The chemical analysis of the films was performed using X-ray photoelectron spectroscopy and infrared spectroscopy. Structural analysis of plasma polymer thin film revealed the similar molecular structure as in case of precursor since PEU-characteristic bonds were preserved after the plasma polymerization. Surface properties analysed by a contact angle measurement revealed an increase of wettability in the samples prepared at higher RF power. At the same time a surface energy evaluated according to acid-base model decreased. The results indicate that plasma polymer films properties could be tuned depending on applied deposition conditions.

Keywords: Plasma polymer, plasma assisted vapour thermal deposition, poly (lactide) copolymer, poly(ethylene oxide), polyester urethane.

1. INTRODUCTION

Polyester based polymers have been extensively investigated during recent years as perspective candidates for the controlled release systems, due to their biodegradability, biocompatibility and low toxicity. The purpose of optimum drug delivery device is to release and active agent at a constant or controlled rate within predefined time, after which a polymer backbone degrade into biocompatible, nontoxic units [1] [2].

Plasma treatment and plasma-based deposition of thin films represents a perspective technique for control of the conditions of active substances release with insignificant impact on the properties of bulk material. Plasma assisted vacuum thermal deposition utilizes oligomers that are released during a source polymer thermal decomposition into the gas phase. Due to the glow discharge, these oligomer species undergo plasma polymerization leading to the preparation of thin films with tuneable properties [3-6].

Poly(lactic acid) (PLA) is known as a biodegradable thermoplastic polymer with good mechanical and processing properties [7] [8]. Its degradation rate is dependent on several factors such as time, temperature, present contaminants and catalyst. A number of studies have dealt with the preparation of PLA based copolymers for the application as resorbable medical devices of various shapes. The process of chain linking reaction based on PLA/PEG polymer using diisocyanate as a chain linker has been investigated to obtain a copolymer with higher molecular weight. PEG encompassing in the structure leads to increasing of the hydrophilicity, decreasing the glass transition temperature and thus improving the degradability characteristics of the final polymer [8-10]. The purpose of this work was to apply the method of plasma enhanced chemical vapour deposition (PE CVD) to modify the surface of PLA/PEG based polymer.

2. EXPERIMENTAL

2.1. PLA-PEG synthesis

Synthesis of PLA/PEG prepolymer

L-LA (100 ml) was inserted into a 250 ml two-neck distillation flask equipped with a stirrer that was then connected to a condenser, placed into oil bath and dehydrated for 4 h at 160 °C and pressure 20 kPa. Then PEG (7.5 %wt.) and a catalyst ($Sn(Oct)_2$) (0.5 %wt.) were added and reaction proceeded for 6 h at 10 kPa, after which the pressure was decreased to 3 kPa and the reaction followed for further 10 h. Resultant product was cooled and stored in a desiccator.

Synthesis of PEU

PLA/PEG prepolymer (30 g) was melted in a 250 ml two-neck flask equipped with a mechanical stirrer at 160 °C under N_2 atmosphere. The chain linking reaction was initiated by adding HMDI in a calculated amount, after which the reaction proceeded for 30 minutes until the mixture became viscous with amber colour. The polymer was then purified by dissolving in acetone, precipitated in cooled methanol/water (1:1) and dried in vacuum for 24 h.

2.2. Plasma deposition

A radio frequency (RF) generator 13.56 MHz was used. PEU polymer was inserted into a crucible that was placed 4 cm above an electrode covered with a glass target. Argon under the pressure of 4 Pa (flow rate of 8 sccm) was used as the working gas. 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 of 25 °C/min. The deposition rate was monitored by quartz-crystal microbalance sensor.

2.3. Thin films characterization

Chemical composition of the films

The composition of the films was characterized using X-ray photoelectron spectroscopy (XPS, Phoibos 100, Specs) and infrared spectroscopy (FTIR-ATR, Nicolet iS5, FTIR-RAS, Bruker Equinox 55).

Surface characterization

Surface properties were analysed by contact angle measurement of prepared thin films using the method of sessile drop on Surface Energy Evaluation system (See System E, Advex Instruments s.r.o., Brno, Czech Republic). Demineralized water, diiodomethane and ethylene glycol were used as reference liquids (volume of drop was 3 µl). Contact angle was measured thrice and the mean value was used for the evaluation of surface free energy according to the Acid-base model.

3. RESULTS AND DISCUSSION

3.1. Chemical composition of the films

FTIR spectroscopy

The FTIR spectra of the original polymer and of the films are shown in the **Figure 1**. The expected structure of the original polymer is shown in **Figure 2a**. The infrared spectra [11] of the original polymer and of the thin film prepared without plasma (0W) is dominated by the ester groups of PLA part of the polymer. This corresponds to the peaks at 1750 cm^{-1} of C=O stretching vibrations, at 1090 cm^{-1} that can be attributed to alkoxy C-O stretching and the peak at 1190 cm^{-1} to acyl C-O stretching vibrations. The ether groups corresponding to PEG part of the polymer are probably present as the peaks at 1130 cm^{-1} (C-O stretching) and at 2985 cm^{-1} (C-H stretching in -O-CH_{2-3} group). Saturated CH_2/CH_3 hydrocarbon groups present in the structure of the polymer as well, corresponding to stretching vibrations at 2935 cm^{-1} and 2870 cm^{-1} and deformation vibrations at 1375 cm^{-1} and 1450 cm^{-1}. The peak at 1350 cm^{-1} can possibly show the presence of CH_3-C=O groups. The HMDI linker can be seen in the amide N-H bending (1535 cm^{-1}) and amide C=O stretching vibrations (1650 cm^{-1}). Hydroxyl end groups and amine groups of HMDI (O-H and N-H stretching) are responsible for the broad peak around 3400 cm^{-1}.

With increasing plasma power, there are several changes present. Intensity of peaks corresponding to ether part of the polymer are decreasing. The relative intensity of the saturated hydrocarbon groups and hydroxyl groups increases and the signal from C:O groups weakens. Tentatively, peaks at 940 cm^{-1} and 1420 cm^{-1} can be attributed to the O-H deformation vibrations of carboxylic acid group that can arise during polymer chain scission in plasma. The peak at 1815 cm^{-1} is a mark of the presence of C=O stretching vibrations of anhydride groups. These can arise from the abstraction of CH-CH_3 group from the PLA part of the polymer chain.

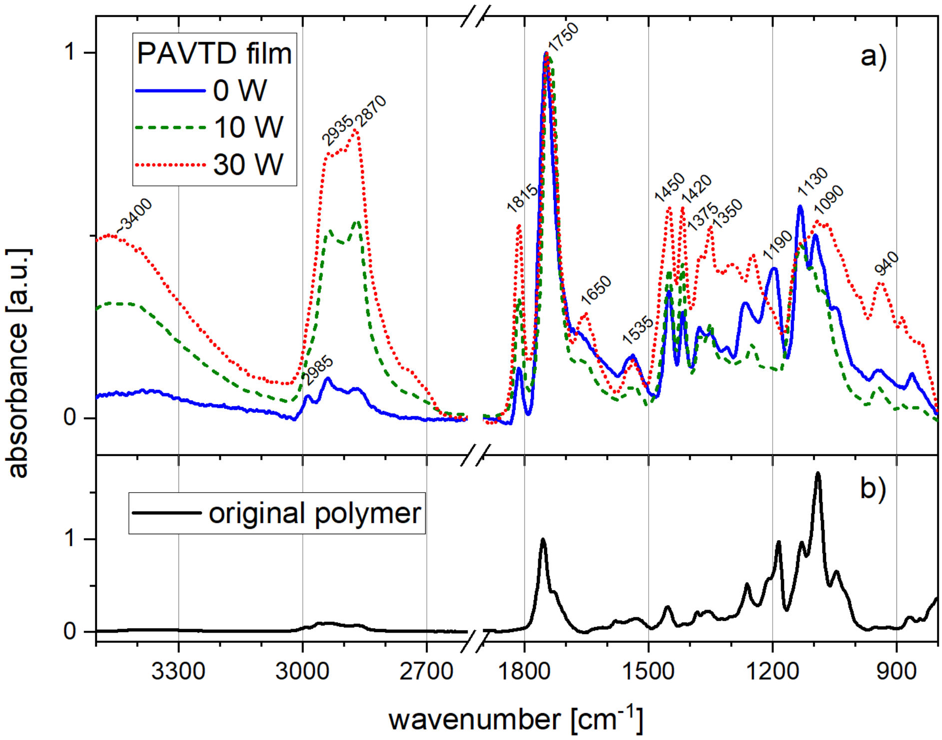

Figure 1 a) FTIR-RAS spectra of the thin films prepared without plasma and at varying plasma power (normalized on the peak 1750 cm^{-1}) b) FTIR-ATR spectra of the original PEU polymer

X-ray photoelectron spectroscopy

The elemental composition and C1s (**Figure 2**) and O1s XPS spectra were measured. The high resolution spectra of C1s peaks were fitted by four peaks. Based on the expected structure of the polymer (**Figure 2a**), three of them are related to PLA chemical shifts, carbon-carbon bond at 285 eV, carbon single bonded to oxygen in PLA at 286.98 eV and carbon double bonded to oxygen at 289.06 eV. The last peak corresponds to PEG chemical shift at 286.45 eV. The described decomposition of C1s region for 20 W of plasma power can be seen at inset in **Figure 2**. The O1s region was similarly decomposed on peaks corresponding to PLA and PEG functional groups. Namely 532.25 eV for oxygen double bonded to carbon in PLA. 533.66 eV oxygen single bonded to carbon in PLA and 532.83 eV for oxygen - carbon bond in PEG groups.

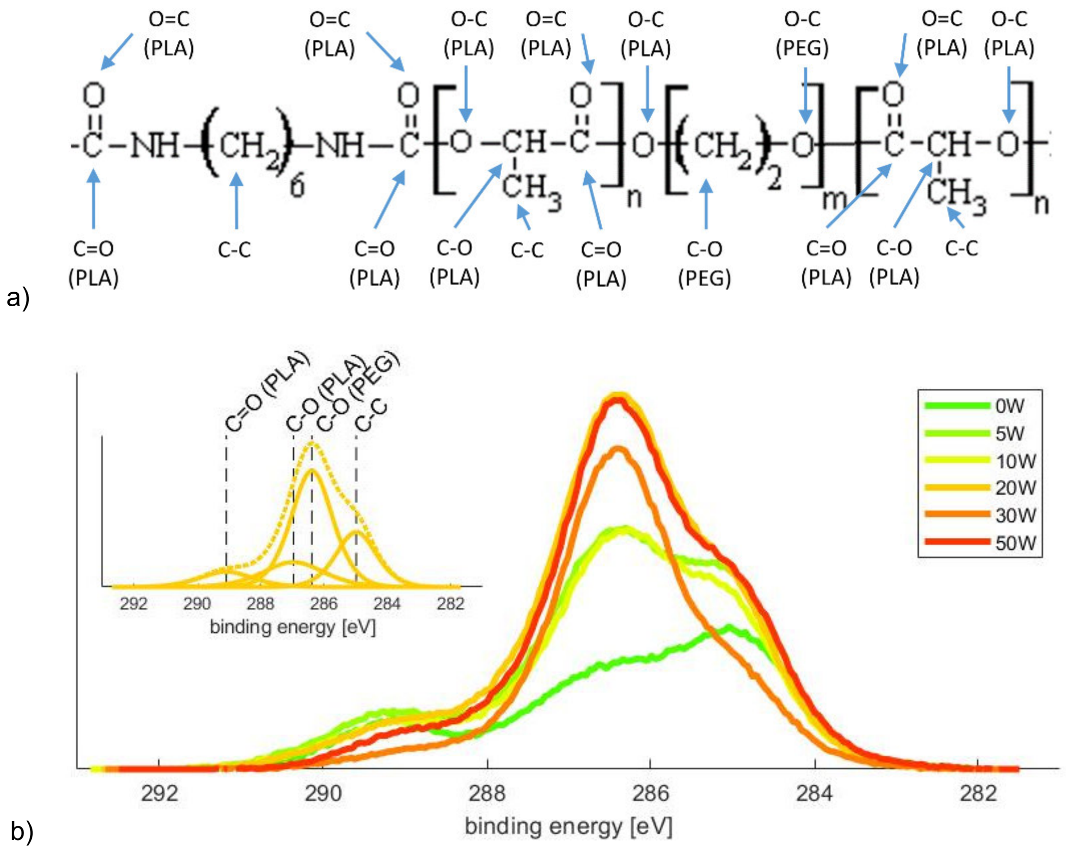

Figure 2 a) Structure of the bulk PEU polymer with the carbon and oxygen marked according to the expected XPS shift b) XPS spectra of C1s peak for varying plasma power. Inset: Decomposition of C1s peak for plasma power 20 W

The results are shown in **Figure 3**. It can be seen that the functional groups of PLA and PEG are preserved for all plasma powers. The $(CH_2)_x$ functional groups are also preserved, as the intensity of peak of aliphatic hydrocarbons cannot be described just with CH_3 group in PLA. With increasing plasma power, the C/O ratio in the films shifts into favour of carbon. The balance also shifts from the PLA-like groups to PEG-like groups.

The ratio between C-O (PLA) and C=O (PLA) should be 1:1 for PLA. However, it can be seen that mostly for higher plasma power this ratio is broken. This can be explained by formation of new groups due to polymer chain scission and restructuring, as was seen by in infrared spectra.

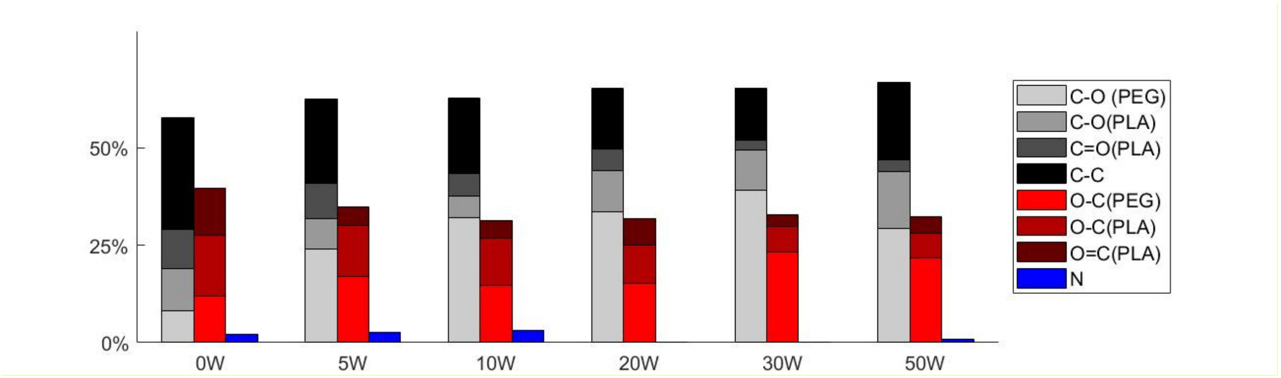

Figure 3 Elemental composition and chemical groups contributions in the films based on XPS spectra

3.2. Surface characterization

The effect of deposition conditions on the polymer surface wettability was evaluated by contact angle measurements. While hydrophobic surfaces exhibit higher contact angles and lower values of the surface energy, lower contact angles are reported for hydrophilic substrates [12]. The results of the wettability measurement are shown in **Tables 1** and **2**.

As can be seen in **Table 1**, the contact angle for water of PEU 0W sample was 29.5°, which is significantly lower than was acquired for untreated samples in some previous works. The reason could lie in the different orientation of polar group from the surface [2] [13]. The wettability of the samples even more increased with higher RF power, since the contact angle values decreased (a drop of almost 77 % was monitored in case of demineralized water when the sample prepared at 0 and 5 W is compared).

Surface energy values were analysed following the Acid-base model. Total surface energy γ^{total} is split to dispersion γ^{LW} and polar part γ^{AB}, that can be then divided to electron acceptor and electron donor component. As shown in **Table 2**, surface energy of the sample prepared at RF of 0 W was around 71 mJ/m^2. A higher RF power induced a slight reduction in the γ^{total} value (about 8 %).

Table 1 Contact angles of PEU-like thin films prepared without and with plasma

Sample	**Contact angle (°)**		
	Water	**Diiodomethane**	**Ethylene glycol**
PEU 0W	29.5±1.8	23.4±2.1	34.1±2.5
PEU 5W	6.8±0.6	17.1±0.9	8.2±0.5

Table 2 Surface energies of PEU-like thin films prepared without and with plasma

Sample	**Surface energy (mJ/m^2)**		
	γ^{total}	γ^{LW}	γ^{AB}
PEU 0W	71.1±3.4	46.7±3.1	24.4±0.8
PEU 5W	65.1±2.8	48.6±2.6	16.5±1.1

4. CONCLUSION

PEU-based thin films were prepared by plasma polymerization process to evaluate the effect of varying RF plasma power on structural and surface properties. A similar molecular structure as in case of original polymer/precursor was revealed by FTIR and XPS spectroscopy. The surface wettability was increased with higher RF power. It can be concluded that by applying the above mentioned plasma procedure, the properties of polymer films can be tuned depending on the deposition conditions.

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