

CHARACTERIZATION OF SUPER HYDROPHILIC FILMS PRODUCED IN DBD PLASMA AT ATMOSPHERIC PRESSURE

B. G. RUSU^{a,b*}, V. POHOATA^a, C. IONITA^c, R. SCHRITTWIESER^c

^a*Iasi Plasma Advanced Research Center (IPARC), Faculty of Physics, Alexandru Ioan Cuza University of Iasi, Blvd. Carol I No. 11, Iasi 700506, Romania*

^b*Department of Pedotechnics, Faculty of Agriculture, University of Agricultural Sciences and Veterinary Medicine "Ion Ionescu de la Brad" of Iasi, 3 Sadoveanu Alley, Iasi 700490, Romania*

^c*Institute for Ion Physics and Applied Physics, University of Innsbruck, Technikerstr. 25, 6020 Innsbruck, Austria*

This study focuses on the production of polyethylene glycol-like films (ppEG) under plasma conditions, using plasma discharge polymerization at atmospheric pressure. The plasma source consists of a dielectric barrier discharge (DBD) which operates in helium gas flow with a glass-like dielectric. The films were characterized by Atomic Force Microscopy (AFM) operating in tapping mode, contact angle measurements, Fourier transform infrared spectroscopy, UV-VIS spectroscopy and X-ray photoelectron spectroscopy. XPS analysis of ppEG films revealed peaks corresponding to the chemical C-C bonds, C-O bonds and C-O-C bonds, which are in good agreement with the chemical formula. The wettability of the ppEG films showed a super-hydrophilic character (the contact angles are smaller than 10°). The topography of polymer films shows a granular structure with diameter less than 1 μm. The value of the root mean square roughness (R_{rms}) is 6.9 nm immediately after the polymerization and increases to 15.5 nm after one week. This kind of surfaces obtained under plasma condition is excellently suited for medical applications like biosensor, biochip, drug delivery etc.

(Received June 18, 2015; Accepted August 12, 2015)

Keywords: Plasma polymerization, Atmospheric pressure, Polyethylene glycol (PEG), Thin films

1. Introduction

Polyethylene glycol (PEG) films are used for protein-repelling and reducing bio-films attachment, which are important features in many applications such as food processing facilities, cardiovascular implants, biosensors and in-vitro tests [1-4]. The role of these thin films is to reduce and control the adsorption of proteins and the adhesion of cells. They are usually synthesized in low pressure plasma, UV induced graft polymerization or chemical synthesizing and numerous studies were reported in literature [5-7].

We have investigated the production of polyethylene glycol (ppEG)-like films under plasma conditions at atmospheric pressure (APP). Atmospheric pressure plasma polymerization represents a good technological solution to cover various substrates with functional layers [8-11]. Plasma polymerization has unique practical advantages which include (i) confirmative ultrathin film deposition, (ii) good adhesion to the substrate and (iii) formation of chemically and physically durable surfaces [12].

The characterization of the polymer thin films was carried out by Atomic Force Microscopy (AFM) technique operating in tapping mode, contact angle measurements, Fourier Transform Infrared Spectroscopy (FTIR), UV-VIS spectroscopy and X-ray photoelectron spectroscopy (XPS).

*Corresponding author: bogdan.rusu@uaic.ro

2. Experimental

2. a. Materials and Methods

The DBD plasma chemical reactor consists of a discharge at atmospheric pressure, working in a plane-parallel geometry. The dielectric barrier was glass with 1.1 mm thickness (Figure 1.). The electrodes are circular with 30 mm diameter. Experiments were made in helium with flow rate of 3 l/min for plasma gas (Flowmeter 1) and 0.5 l/min for monomer vaporization (Flowmeter 2). The helium spectral purity was 99.999%, and the monomer used was ethylene glycol (>99.0 % purity) from Merck-Chemical.

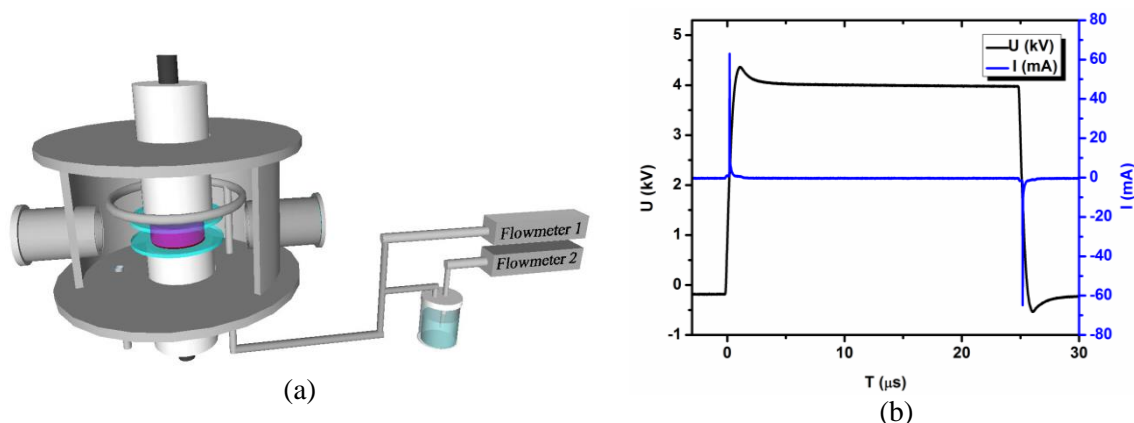


Fig. 1. Experimental set-up (a), time evolution of applied voltage and intensity plasma current (b).

High voltage monopolar pulses were delivered using a voltage amplifier (Trek Inc) connected with a waveform generator (Tabor Electronics Inc.). The electrical parameters were maintained constant at the following values: high voltage $V = 4.5$ kV, repetition rate $\nu = 2$ kHz during 10 min, which is the time of polymerization. The discharge mode is a glow discharge characterized by two current peaks during each applied voltage pulse [13, 14].

The chemical structure of the films was investigated by Fourier Transform Infrared spectroscopy and the spectra were registered with a Bomem MB-Series 104 spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$ with 4 cm^{-1} resolution.

The chemical composition of films was obtained by analysis of polymer XPS spectra. XPS analyses were performed with a 5000 VersaProbe (Physical Electronics) spectrometer, equipped with a monochromatic Al K_{α} X-ray source ($h\nu = 1486.7$ eV). During measurements, the pressure in the analysis chamber was 5.9×10^{-8} Pa and the photoelectron takeoff angle relative to the surface was 45° .

The topography of the polymer films was investigated by Atomic Force Microscopy (AFM) technique, using an NT-MDT Solver Pro-M type apparatus in tapping mode with 0.1 nm resolution in z-direction using a standard silicon nitride tip (NSC21) with a typical tip radius of 10 nm. Also the variation of the root mean square roughness (R_{rms}) and of the topography of the ppPEG films were studied, first immediately after the polymerization and then after one week for aging study.

The wettability of the films was analyzed using contact angle measurements. The volume of the water drops deposited on the polymer films was $1\ \mu\text{l}$. The contact angle values were calculated with ImageJ free software.

3. Results and Discussion

3.1. Chemical composition

FTIR spectra of the ppPEG films showed the presence of C-H in-plane deformation bending at 1073 cm^{-1} and 1029 cm^{-1} , -C-O-C- bonds at 1068 cm^{-1} , -C-C- stretching vibration at 1203 cm^{-1} and 1404 cm^{-1} , C=O vibrations bands at 1620 cm^{-1} and C-H bonds at 2961 cm^{-1} (Figure 2.). The broad band from 3200 cm^{-1} to 3600 cm^{-1} is assigned to various OH vibration modes in the film volume.

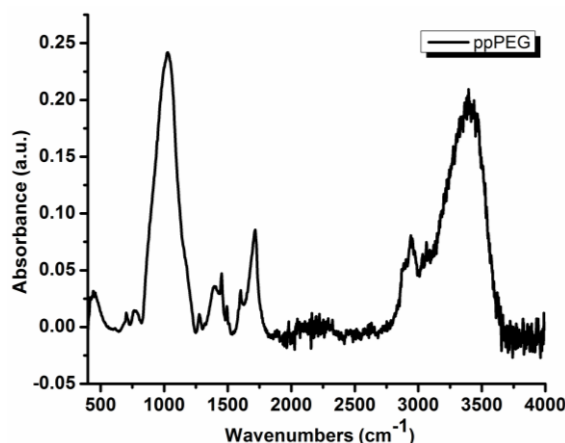


Fig. 2. Typical FTIR spectrum of ethylene glycol monomer and ppPEG obtained in APP.

The ppPEG films present low UV absorption between 50 nm and 300 nm. More information about the purity of chemical composition has been given by XPS spectra.

The XPS spectra with low resolution of ppPEG show the presence of two peaks corresponding to a C1s peak at 284 eV and an O1s peak at 534 eV. Deconvolution of C1s and O1s peaks reveal contributions of C-C bonds at 284 eV, C-O bonds at 286 eV and C-O-C bonds at 288 eV (Figure 3.).

All of these peaks identified by XPS and FTIR technique are in good correlation with the conventional PEG chemical formula: $\text{HO-CH}_2\text{-(CH}_2\text{-O-CH}_2\text{)}_n\text{-CH}_2\text{-OH}$, which means that the polymer created in the DBD plasma possesses the chemical composition of the monomer.

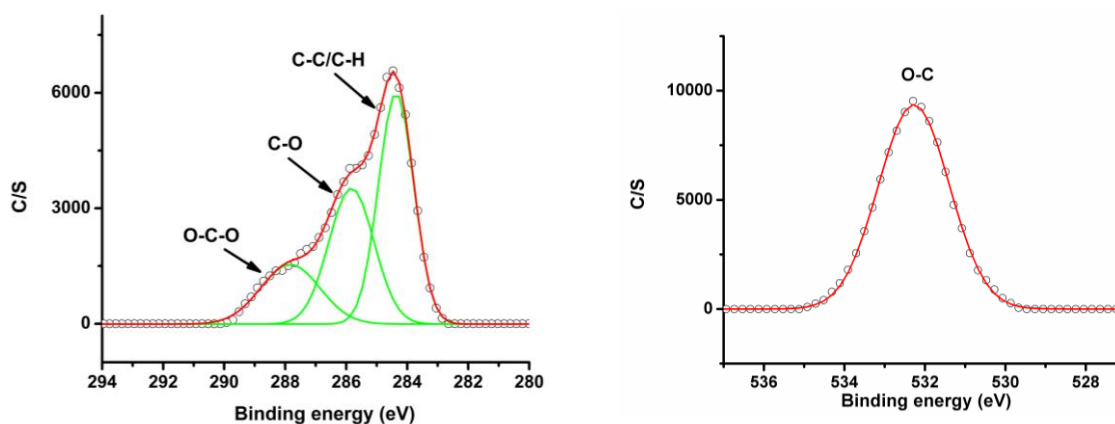


Fig. 3. Deconvolution of XPS spectrum corresponding to C1s peak of ppPEG films (a), deconvolution of XPS spectrum corresponding to O1s peak of ppPEG films (b).

The hydrophilic character was demonstrated by contact angle techniques. The contact angle average measured for the substrate (glass) is 55° and for the ppPEG thin films it is 6° . The su-

per hydrophilic character is due to hydroxyl groups presented in the chemical structure of the ppPEG thin film.

3.2. Morphology

The topography of the films shows a granular structure with diameters less than $1\ \mu\text{m}$ immediately after deposition. The morphology of the ppPEG films vary in time. After one week we observe that the structures are not clearly distinguishable because of water absorption. Also the root mean square roughness (R_{rms}) increase from $8\ \text{nm}$ to $16.2\ \text{nm}$ for the $10\times 10\ \mu\text{m}^2$ sample (Figure 4.a) and from $6.9\ \text{nm}$ to $15.5\ \text{nm}$ for the $3\times 3\ \mu\text{m}^2$ sample (Figure 4.b). This fact was demonstrated by X-ray photoelectron spectroscopy.

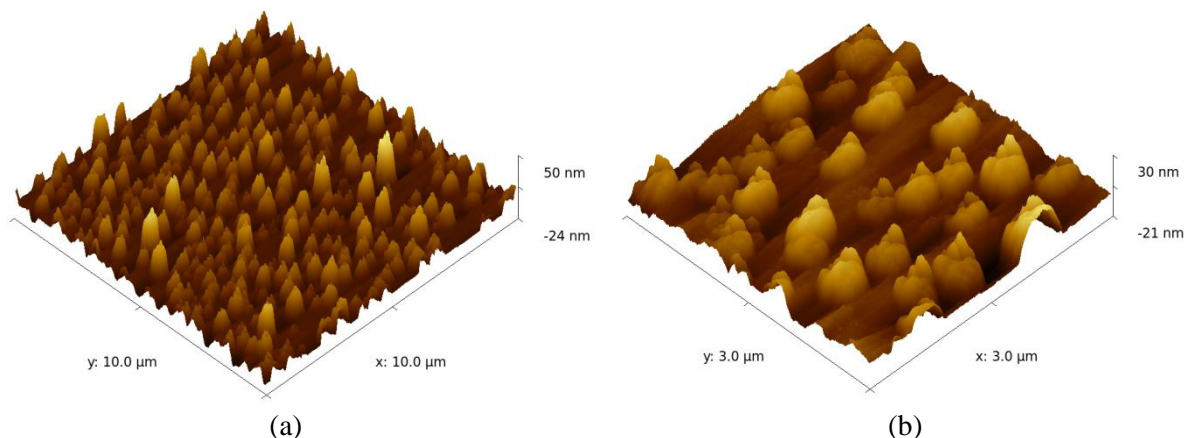


Fig. 4. AFM topography image of the ppPEG films immediately after plasma polymerization $10\times 10\ \mu\text{m}^2$ (a) and $3\times 3\ \mu\text{m}^2$ (b).

3.3. Time stability of characteristics / aging

The aging process of the same films has been studied also with X-ray photoelectron spectroscopy. After one week we observe that the concentration of C-O bonds increases from 34.71% to 42.87%. This has been correlated with the absorption of water molecules present in atmospheric conditions by the ppPEG film. This fact is due to its hydrophilic character.

Table 1.

Bounds	Concentrations of chemical groups (%)	
	Immediately	After 7 days
C-C	46.06	42.75
C-O	34.71	42.87
O-C-O	19.95	14.93

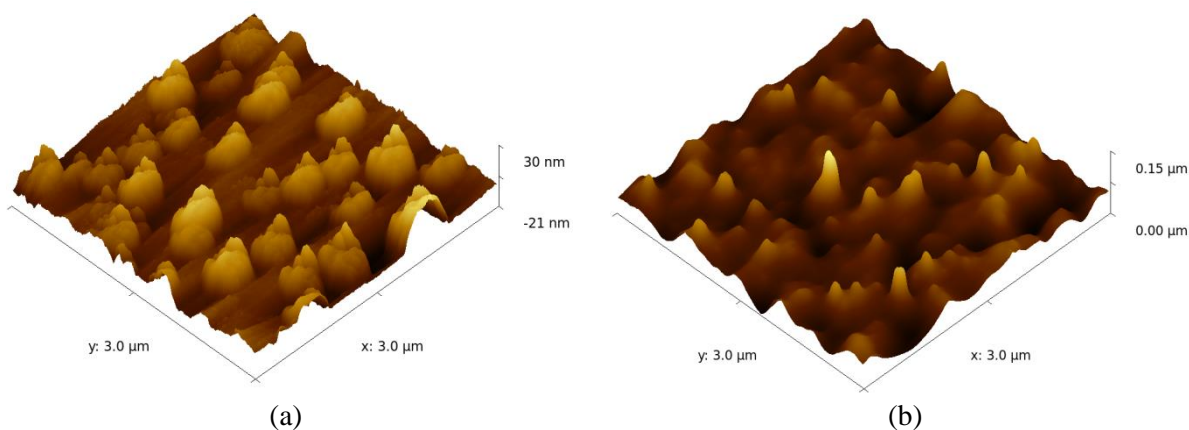


Fig.5. AFM topography image of the ppPEG films immediately after plasma polymerization (a), after one week (b).

4. Conclusion

Using plasma discharge polymerization at atmospheric pressure in a mixture of helium and ethylene glycol monomer, we obtained super hydrophilic polymer which can be used in biomedical applications. The films demonstrate stable chemical compositions and a high hydrophilic character. The chemical analysis of the thin films with X-ray photoelectron spectroscopy prove that the new polymer formed is PEG because C-C bonds at 284 eV, C-O bonds at 286 eV and C-O-C bonds at 288 eV are present in the thin films.

After the morphological analysis of the thin films we observe the appearance of a granular structure with diameters less than 1 μm immediately after the deposition. After aging, we observe that the granular structure cannot be distinguished anymore because of adsorption of water molecules.

Acknowledgement

This work was supported by European Social Fund in Romania, under the responsibility of the Managing Authority for the Sectoral Operational Programme for Human Resources Development 2007- 2013 (grant POSDRU/159/1.5/S/ 137750). It was also supported by the Austrian Science Fund under Project No. P19901 and the CEEPUS Network AT-0063.

References

- [1] Murali Mohan Yallapu, Susan P. Foy, Tapan K. Jain, Vinod Labhasetwar, *Pharmaceutical Research*, **27**(11), 2283 (2010).
- [2] Takuro Niidome, Masato Yamagata, Yuri Okamoto, Yasuyuki Akiyama, Hironobu Takahashi, Takahito Kawano, Yoshiki Katayama, Yasuro Niidome, *Journal of Controlled Release*, **114**(3), 343 (2006).
- [3] Yuji Inada, Makoto Furukawa, Hideyuki Sasaki, Yoh Kadera, Misao Hiroto, Hiroyuki Nishimura, Ayako Matsushima *Trends in Biotechnology*, **13**(3), 86 (1995).
- [4] Keru Zhang, Xing Tang, Juan Zhang, Wei Lu, Xia Lin, Yu Zhang, Bin Tian, Hua Yang, Haibing He, *Journal of Controlled Release*, **183**, 77 (2014).
- [5] Nikolaos A. Peppas, Kelley B. Keys, Madeline Torres-Lugo, Anthony M. Lowman, *Journal of Controlled Release*, **62**(1-2), 81 (1999).
- [6] D. Sakthi Kumar, Masayori Fujioka, Kentaro Asano, Atsumu Shoji, Athipettah Jayakrishnan, Yasuhiko Yoshida, *Journal of Materials Science: Materials in Medicine* **18**, 1831 (2007).
- [7] Bryan Parrish, Rebecca B. Breitenkamp, Todd Emrick, *Journal of the American Chemical Society*, **127**(20), 7404 (2005).
- [8] A. Lazea-Stoyanova, M. Enculescu, S. Vizireanu, V. Marascu, G. Dinescu, *Digest Journal of Nanomaterials and Biostructures*, **9**(3), 1241 (2014).
- [9] C. Nastase, A. Dumitru, V. Barna, F. Nastase, *Digest Journal of Nanomaterials and Biostructures*, **8**(4), 1811 (2013).
- [10] M. Drobot, M. Aflori, V. Barboiu, *Digest Journal of Nanomaterials and Biostructures*, **5**(1), 35 (2010).
- [11] Qian Zhang, Yajun Jiang, Lan Yao, Qiuran Jiang & Yiping Qiu, *Journal of Adhesion Science and Technology*, **29** (8), 691 (2015).
- [12] Miguel Manso-Silván, A. Valsesia, D. Gilliland, G. Ceccone, F. Rossi, *Applied Surface Science*, **235**, 119 (2004).
- [13] A.S. Chiper, A.V. Nastuta, G.B. Rusu, G. Popa, *Nuclear Instruments and Methods in Physics Research B* **267**, 313 (2009).
- [14] A. S. Chiper, G. B. Rusu, C. Vitelaru, I. Mihaila, G. Popa, *Romanian Journal of Physics*, **56 S**, 126 (2011).