22nd International Symposium on Plasma Chemistry
July 5-10, 2015; Antwerp, Belgium

Copolymerization and water stability of atmospheric pressure plasma polymerized films from allylamine and styrene

R. Jijie[1,2], T. Teslaru[1], M. Dobromir[1], V. Pohoata[1], I. Topala[1], R. Boukherroub[2] and N. Dumitrascu[1]

[1] *Iasi Plasma Advanced Research Center (IPARC), Faculty of Physics, Alexandru Ioan Cuza University of Iasi,*
Bd. Carol I No. 11, RO-700506 Iasi, Romania
[2] *Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN, UMR 8520), Université Lille 1,*
Cité Scientifique, Avenue Poincaré, P.O. Box 60069, FR-59652 Villeneuve d'Ascq, France

Abstract: Atmospheric pressure plasma (co)polymerization technique has been used to deposit plasma allylamine (pPAA), styrene (pPS) and styrene/allylamine (S-co-AA) (co)polymer films. The synthesis and characterization of AA/S copolymer is studied in comparison to plasma deposited pPAA and pPS homopolymers. Special attention was focused on the stability of plasma (co)polymer in aqueous media.

Keywords: plasma (co)polymerization, water stability, self-assembly

1. Introduction

Plasma deposition is an alternative technique for thin functionalized films deposition in dry conditions with predefined surface characteristics for a variety of applications. The density of reactive functional groups (e.g., -COOH, -OH, $-NH_2$) can be tuned by optimizing the plasma processing parameters, such as plasma power, precursor flow rate, deposition time, substrate position in plasma reactor, etc. Amino functionalized plasma polymerized surfaces are of great interest in biomedical applications because these can be used as a support for the covalent bonding of different bio-molecules (like trypsin, heparin) or cell adhesion [1, 2]. Many organic monomers were employed to integrate amine functionalities by plasma polymerization, including ethylenediamine, diaminopropane, butylamine, heptylamine, aniline, diaminocyclohexane, acetonitrile and allylamine. However, allylamine is the most commonly used organic precursor in order to obtain coatings with a high retention of primary amine functionalities. The plasma polymerized allylamine coatings (pPAA) bio-applications are limited by their low stability in aqueous media. Copolymerization reactions provide an alternative way to control the coatings solubility, polarity or hydrophilic/hydrophobic balance by introducing simultaneously two compatible gaseous vapours from a monomer solution. Consequently, plasma copolymerization is an attractive technique to obtain new surfaces with controlled properties.

The purpose of this research is to determine the physico-chemical properties of homopolymers and copolymers of allylamine (AA) and styrene (S) deposited using a dielectric barrier discharge which operates in helium at atmospheric pressure. Moreover, a special attention is devoted to thin films stability during water exposure. In order to study the stability and behaviour of plasma polymerized films in water, the coatings were analyzed after 72 h of immersion in distilled water, at ambient temperature. Only few studies are focused on the stability of plasma polymerized polymers in aqueous media. The (co)polymers surface properties were evaluated by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), water contact angle measurements, and the bulk properties by Fourier transform infrared spectroscopy (FTIR) and UV-Vis absorption spectroscopy.

2. Experimental

2.1. Plasma deposition

The homopolymers and copolymer of styrene (S, C_8H_8, Fluka, 99 % purity) and allylamine (AA, C_3H_7N, Fluka, > 98%) were deposited using a *d*ielectric *b*arrier *d*ischarge (DBD), which operates in helium at atmospheric pressure as shown in Fig. 1**.** The plasma reactor consists of a stainless steel chamber containing two parallel copper electrodes, deposited as thin films on glass dielectric. The upper electrode was connected to a HV source while the lower electrode was grounded. The substrate was placed on the bottom electrode and the gap between the two electrodes was kept constant at 5 mm. Positive high voltage pulses with 6 kV amplitude, 2 kHz frequency and 250 µs width were applied on the high voltage electrode.

Plasma reactor has three gas lines, one for working gas (helium, 99.999 % purity) used to sustain the discharge and other two lines to transport individually or simultaneously the S and AA monomers vapours into the plasma volume. The liquid monomers placed in different containers were introduced into the discharge region by helium bubbling with a rate of 17 µl/min styrene and 67.5 µl/min allylamine (at room temperature). Gas flow rates were constantly kept by electronic flow-meters (MKS type 1179 B) and a flow controller (MKS type 247).

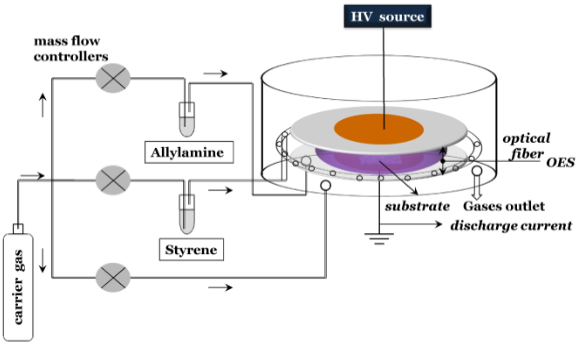


Fig. 1. Schematic representation of the experimental setup used for helium atmospheric pressure plasma polymerization.

2.2. *(Co)Polymer films characterization*

The wettability of (co)polymer coatings was evaluated by using the sessile drop technique. A horizontal optical microscope with a digital camera (OPTIKAM 4083.B5) attached was used to visualize water drops of 2 µl deposited onto the (co)polymer surface. Contact angle values were obtained from images analysis using the Image J software. All measurements were made in ambient atmosphere.

The FTIR spectra were recorded on a Bomem MB-Series 104 spectrometer. Each spectrum was collected by accumulating 5 scans at a resolution of 2 cm^{-1}, in the range of 4000 - 500 cm^{-1}. The FTIR spectra of ppAA, pPS, and S-co-AA deposited on NaCl and ZnSe substrates were acquired in the transmission mode.

The chemical composition of deposited coatings was studied using XPS. The XPS spectra were recorded with a PHI 5000 VersaProbe (Physical Elctronics) spectrometer, using a monochromatic Al Kα X-ray source (1486.7 eV), under a vacuum of about $2x10^{-6}$ Pa at a photoelectron take-off angle of 45°.

AFM technique was used to visualize and compare the topography of plasma polymer before and after immersion in distilled water for 72 h. The AFM measurements (NT-MDT Solver Pro-M type apparatus) were carried out in the tapping (non-contact mode), with commercial standard silicon-nitride tip with a radius of approximately 10 - 15 nm (NT-MDT, NSG03). The topography, magnitude and phase were recorded simultaneously for each sample on various scanned areas between 70 µm x 70 µm and 3 µm x 3 µm. Scans were repeated on different sites of the samples to check the surface uniformity, under the same condition in ambient atmosphere. The average roughness (S_a) and the root mean square roughness (S_q) were calculated for each sample using standard Nova software.

Ultraviolet-visible (UV-Vis) spectroscopy was carried out using the Thermo Scientific Evolution 300 spectrometer. Absorption spectra were measured from 190 to 500 nm with a resolution of 0.5 nm, using a 10 mm quartz cuvette and the transmission spectra from 190 to 800 nm with a resolution of 1 nm.

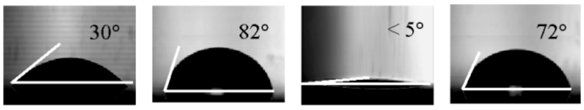
The thickness of the plasma copolymerized films was evaluated using an interferometric-based technique (Linnik MII type). For 10 min deposition time the pPS thickness is around 550 nm and for S-co-A 530 nm.

To study the water stability, each sample was immersed in 10 mL of distilled water for 72 h and then dried at 37 °C for 1 - 2 hours to evaporate the water molecules.

3. Results and discussions

3.1. *(Co)polymer films chemical composition*

The *w*ater *c*ontact *a*ngle (WCA) results show that pPAA film is highly hydrophilic due to its higher retention of amine functions and the incorporation of oxygen functional groups into the polymer surface. The water contact angle for pPS is ~82° while the value for S-co-AA is ~72°, this result suggests a retention of amino groups (hydrophylic) from allylamine in poly(styrene) matrix (Fig. 2). Thus, by alterning the S/AA ratio it is possible to controlling the hydrophilicity of the plasma polymerized coatings.



substrat pPS pPAA S-co-AA

Fig. 2. Water contact angles of the substrate and of the plasma (co)polymer films.

The XPS elementary analyses reveal that all plasma polymerized coatings contain the elements present in the monomers and oxygen (Table 1). Although, the oxygen is not present in the monomer structure, is incorporate in plasma films from residual oxygen and water vapours which get into the discharge volume from the air during atmospheric pressure plasma polymerization process and/or by oxidation of unstable functional groups after exposure to room ambient atmosphere. Optical emission spectroscopy confirms the presence of atomic oxygen (777.4 nm and 845.2 nm) and hydroxyl radical (309.1 nm) in the plasma reactor during the deposition process. It is known that pPAA react with oxygen and continue to do so during storage in air atmosphere.

Table 1. The chemical composition of pPAA, pPS and S-co-AA.

Monomer/ Plasma polymer	**AA**	**pPAA**	**S**	**pPS**	**S-co-AA**
C (%)	72	72.7	100	92.3	87.7
O (%)	-	11.7	-	7.7	5.1
N (%)	28	15.6	-	-	7.2
N/C	0.38	0.21	-	-	0.08
O/C	-	0.16	-	0.08	0.06

The FTIR spectra revealed that the monomers characteristic groups are present in the plasma polymerized films structure. In addition, new functional groups are formed in the plasma such as hydroxyl, acyl or amide groups. Identification of the spectral peaks and bands was made with reference to published work [1-6]. As can be seen in Fig. 3 the monomers bands are well resolved compared to the broad spectra obtained for the plasma (co)polymers. The strong absorption band observed in the region 3500 - 3100 cm^{-1} can be attributed to the amine and OH stretching vibrations. The 2930 cm^{-1} and 2866 cm^{-1} peaks correspond to the stretching vibrations of the aliphatic C-H groups (-CH_x), while the 1452 cm^{-1} and 1430 cm^{-1} peaks are due to C-H bending in methylene (-CH_2-) and in vinyl groups (-$CH=CH_2$). The broader peak from 1734 cm^{-1} to 1500 cm^{-1} can be assigned to the deformation vibrations of N-H, the stretching vibration of C-C, imine groups or amide groups, specific of allylamine. The peaks at 3059 and 3025 cm^{-1} are due to aromatic =C-H stretching, at 1600 and 1492 cm^{-1} to aromatic C=C stretching, at 1075 and 1028 cm^{-1} to C-H in-plane deformation bending of aromatic ring, at 758 and 700 cm^{-1} to aromatic C-H bending, which are characteristic of styrene.

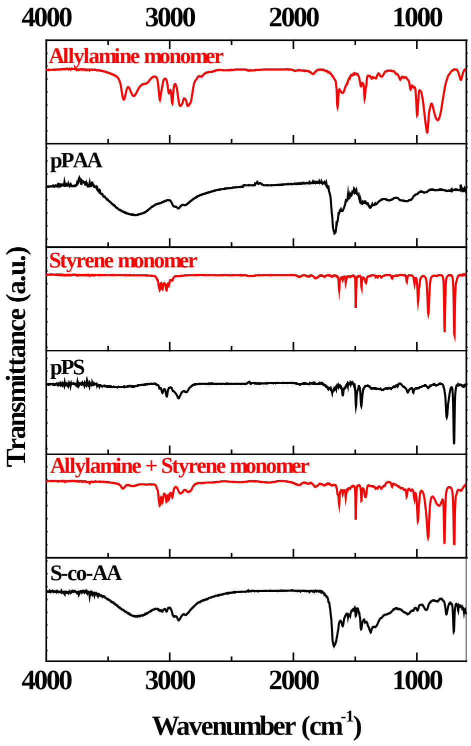


Fig. 3. FTIR spectra of monomer and of plasma polymerized allylamine (CH_2=CH-CH_2-NH_2), styrene (C_6H_5-CH=CH_2) and S-co-AA films.

3.2. Polymer behaviour in aqueous media

The efficiency of plasma polymers in bio-medical applications relies on their stability in aqueous biological solutions.

The comparison of the XPS (Table 2) and FTIR (Fig. 4) results before and after immersion in distilled water for 72 h at ambient temperature reveals that the composition of the pPS and S-co-AA films has not changed significantly (Table 2). For all samples was detected a decrease of carbon with 8 - 9 % and an increase of oxygen content. The overall decrease in the pPS and S-co-AA infrared spectra intensity is due to a decrease in coatings thickness.

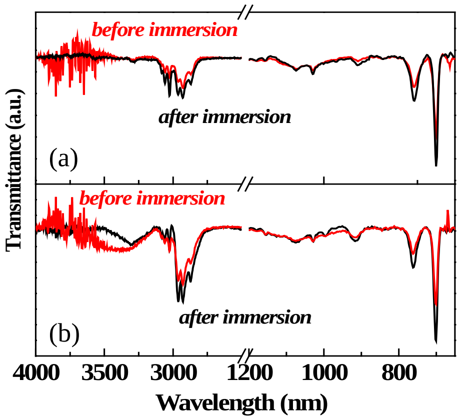


Fig. 4. Comparison of (a) pPS and (b) S-co-AA films FTIR spectra before and after 72 h immersion in distilled water.

Table 2. Atomic composition of pPS and S-co-AA before and after immersion in distilled water for 72 h.

Plasma polymer	**Condition**	**C (%)**	**N (%)**	**O (%)**	**N/C**	**O/C**
pPS	before	92.3		7.7	-	0.08
	after	84.8		15.2	-	0.17
S-co-AA	before	87.7	7.2	5.1	0.08	0.06
	after	80.2	7	12.8	0.09	0.16

Our results concerning the aging of plasma (co)polymerized films in air proved that after 14 days of exposure to room ambient conditions, there was no significant differences in the ppS and S-co-AA FTIR spectra and water contact angle measurements (Fig. 5). The wettability of the coating after 72 h immersion in distilled water is affected, the films becomes more hydrophilic indicating a possible degradation of films.

UV-Vis measurements of liquid and films were performed to have an estimation of the amount of material dissolved in water. As can be seen in Fig. 6 after few minutes of water immersion the pPAA is washed away from the substrate. Also, after immersing the ppS and S-co-AA films in distilled water for 72 h was observed a partial dissolution and swelling.

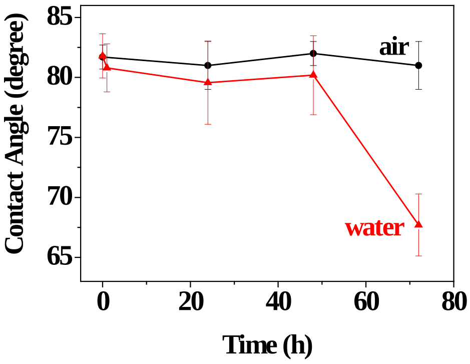


Fig. 5. Contact angles of pPS measured as function of the storage time on ambient air or immersion time in distilled water. Error bar shows ± a standard deviation.

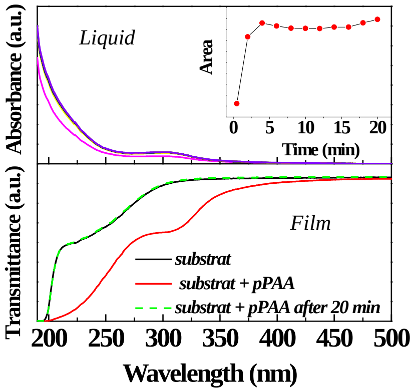


Fig. 6. Stability test of pPAA by immersion in distilled water for 20 min.

3.3. Polymer surface properties

The pPS films surfaces analyzed by AFM show a modified morphology after immersion in water (Fig. 7). Whereas the initial plasma polymerized films are smooth and uniform, without specific morphological aspects, after 72 h immersion in distilled water, the pPS coating become highly porous and onto the pPS films surface were observed structures with sizes ranging from 2 to 5 µm. It can be seen from Table 3 that with increasing the samples immersion time in distilled water the S_a and S_q values gradually increase. This increasing roughness is due the polymer surface self-organization during water exposure.

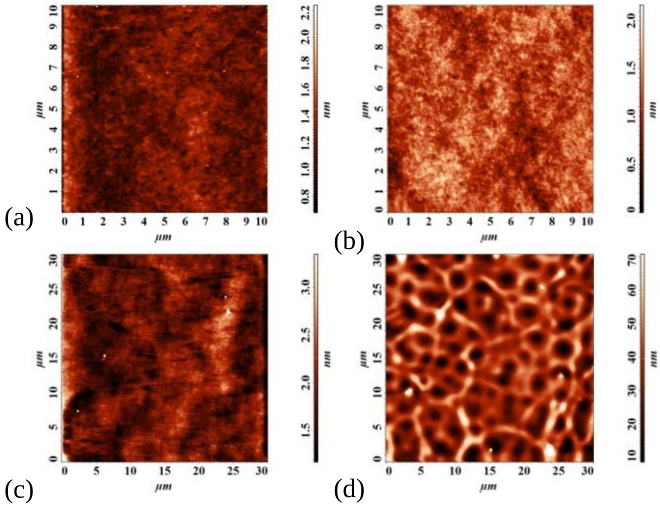


Fig. 7. AFM images 10x10 µm^2 of the (a) pPAA (S_a = 0.12 nm, S_q = 0.16 nm); (b) S-co-AA (S_a = 0.2 nm, S_q = 0.26 nm) films; and 30x30 µm^2 of pPS film (c) before and (d) after 72 h of immersion in distilled water.

Table 3. Average roughness (S_a) and the root mean square roughness (S_q) of the pPS and S-co-AA before and after immersion in distilled water for different time intervals.

pPS	**initial**		**1 h**		**24 h**		**72 h**	
	S_a (nm)	**S_q (nm)**	**S_a (nm)**	**S_q (nm)**	**S_a (nm)**	**S_q (nm)**	**S_a (nm)**	**S_q (nm)**
30x30 µm²	0.25	0.37	5.14	6.58	12.11	14.43	9.1	11.8
10x10 µm²	0.14	0.17	5.58	6.95	11.4	9.2	8	10
3x3 µm²	0.109	0.14	1.47	2.09	1.83	2.24	1.5	1.93

4. Conclusions

The atmospheric pressure plasma polymerization is a versatile technique allowing the deposition of amino functionalized plasma polymerized surfaces. The coatings stability is strongly related to the deposition parameters. Our results show that plasma condition such as the deposition time and monomer flow rate employed affect the stability of the plasma polymerized films during water exposure. The films deposited at low monomer flow rate are more stable compared to the films deposited at a high monomer vapour pressure and low deposition time.

The main causes of the material loss in aqueous media are the hydrolysis of low molecular weight material non-covalently bonded to the film matrix and the washing out of the uppermost polymer layer and is related with plasma polymer cross-linking density [1-2].

5. References

[1] A. Abbas, *et al.* “Preparation and Multi-Characterization of Plasma Polymerized Allylamine Films”. *Plasma Process. Polymers*, **6**, 593-604 (2009)

[2] M. Bashir, *et al.* “Plasma polymerization in a microcapillary using an atmospheric pressure

dielectric barrier discharge". *Surf. Coat. Technol.*, **234**, 82-91 (2013)

[3] R. Morent, *et al.* "Stability study of polyacrylic acid films plasma-polymerized on polypropylene substrates at medium pressure". *Appl. Surf. Sci.*, **257**, 372 -380 (2010)

[4] Finke, *et al.* "Structure Retention and Water Stability of Microwave Plasma polymerized Films From Allylamine and Acrylic Acid". *Plasma Process. Polymers*, **6**, S70-S74 (2009)

[5] Ardhaoui, *et al.* "Biosensor based on laccase immobilized on plasma polymerized allylamine/carbon electrode". *Mat. Sci. Engng.*, **C33**, 3197-3205 (2013)

[6] Fahmy, *et al.* "Surface and Bulk Structure of Thin Spin Coated and Plasma – Polymerized Polystyrene Films". *Plasma Chem. Plasma Process.*, **32**, 767-780 (2012)