Polymer functionalization by plasma treatment and plasma enhanced chemical vapor deposition for biomedical application

P. Rossini, G. Ceccone, and F. Rossi
European Commission-Joint Research Centre, Institute for Health and Consumer Protection, T.P. 203 - 21020 Ispra (VA), ITALY
Phone: +39(0)332 785497-Fax: +39(0)332 785787-E-mail: nella.rossini@jrc.it

Abstract

Polymer functionalization for biomedical devices has been carried out by means of radiofrequency inductively coupled plasma of propenoic (acrylic) acid. The RF power applied to the coil antenna of the cylindrical inductively coupled plasma reactor was varied from 20 to 150 Watt, in order to optimize precursors fragmentation and to tune selectivity of the deposited polymers. The plasma phase was investigated by Mass Spectrometry and Optical Emission Spectroscopy. The polymer films have been characterized with X-Ray Photoemission Spectroscopy (XPS) and Fourier Transformed Infrared Spectroscopy (FTIR) while growth rates were investigated with an α-step profilometer. Coating superficial properties have been studied by means of contact angle measurements. Changes in deposition rates and differences in coating structures with plasma power, substrate position (close and far post discharge), washing and aging are presented and discussed.

Introduction

A contemporary definition of Biocompatibility is “the ability of a material to perform with an appropriate host response in a specific application”[1]. When in contact with a biomedical device the body “reads” the chemical and morphological nature of the foreign material surface and responds. Therefore the fundamental key to design materials with specific biological functions and clinical applications is to modify the surface of polymeric biomaterials to optimize their interaction with biological systems.

Low-pressure plasma processes are particularly appealing for surface modification of biomedical devices, offering a very interesting alternative to wet chemistry. Only the very first layers of the surface are modified, so vascular grafts, heart valves, stents, catheters, blood bags and others can have surface covered with antifouling films (e.g. PeO), or grafted with proper “anchor” group suitable for immobilization reactions.

During these last years many studies have been led on biomolecules’ immobilization onto biomedical devices in order to improve their hemocompatibilities. Biomolecules such as Heparin or highly sulphated Hyaluronic acid are antithrombotic agents, and can be bound to – COOH groups grafted onto a polymeric biomaterial via proper spacer arm.

The carboxylic groups can be introduced in different ways, for example by O₂/H₂O RF Glow discharges, or by a thin film deposited in RFGD fed with acrylic acid vapor.

The study presented here deals with radiofrequency inductively coupled plasma of acrylic acid.
Experimental Set-Up

An Inductively Coupled Plasma source (ICP) designed by JRC was used for the deposition of the polymer films. The plasma chamber is a cylindrical quartz tube having a 230 mm diameter and a 540 mm height. The liquid precursor (Acrylic Acid of > 99% purity from Aldrich Chemical Co.) is evaporated and delivered to the chamber through a mass flow meter. An Advance Energy 13.56MHz RF power supply was connected to the 8-turn RF inductor coil surrounding the quartz chamber in order to sustain the plasma. The gases enter the chamber at the top of the quartz chamber and are pumped out in the opposite extremity of the reactor. The monomer flow rate (φ) was fixed at 5 sccm, and the coatings were deposited onto silicon wafer substrates (both side polished). The substrate holder could be moved vertically in order to investigate the substrate position effect. The samples were located at four different distances from the monomer inlet in the reactor (5, 10, 15, 20 cm), all in the plasma glow region except for the last one that was in the after glow.

Mass spectrometry and optical emission spectroscopy were carried out in the reactor in order to identify the different species present in the plasma phase. Mass Spectral analyses were realized with a Spectra Multi-Quad quadrupole interfaced to the deposition chamber. The signals were collected at the bottom of the reactor in Residual Gas Analysis mode, and the electron kinetic energy was 40 eV. Optical Emission Spectroscopy was performed with a Chromex 500IS/SM spectrometer having a 50 cm focal length for a theoretical resolution of 0.08 nm. The associate detector was a nitrogen cooled CCD camera (ST120 IRY 700S/RB Princeton Instruments). A 600 μm diameter fused silica optical fiber was used to transmit the signal to the spectrometer. The optical detection was made through a quartz window.

Surface analyses including X-Ray Photoemission Spectroscopy (XPS) and Fourier Transformed Infrared Spectroscopy (FTIR) were carried out on the deposited polymer films.

The deposition rates have been investigated with a α-step profilometer, while coating superficial properties have been studied by means of a Digidrop contact angle instrument.

The films’ stability when in contact with water was investigated by washing and aging experiments.

Acrylic acid deposition results

Pressure effect

The effect of pressure on deposition rate and monomer retention was inspected using four different total pressures in the reactor: 50, 80, 150, and 250 mtorr.

No significant structural differences in the films appeared under these conditions as a result of FTIR analysis. As a measure for the retention of the monomer structure, we define the ratio of the signal intensity for the C-H vibration at 2930 cm⁻¹ to that of OH at 3400 cm⁻¹. The I_C_H/I_O_H ratio was almost constant when pressure changes. Also the contact angle against water do not change significantly as the pressure increases, except at 250 mTorr. We tried to evaluate the acid character of the films considering the Fowkes work of adhesion (W_AB), characteristic of the acid percentage in the film surface [2]. So the acid-base interactions between NaOH (0.1N) and the different coatings were studied. From the equation (1) we can calculate W_AB on the films obtained at different pressure.

\[ W_{AB} = \gamma_L (1 + \cos \theta) - 2(\gamma_S - \gamma_L) \sqrt{\gamma_L} \]  

(1)
In this equation, $\gamma_i$ and $\gamma_i^d$ are characteristics of the reference liquid while $\gamma_s^d$ is obtained using a non-polar liquid such as $\alpha$-bromonaphthalene with no acid-basic character.

As shown in Fig. 1, a 50% variation in the work of adhesion ($W_{AB}$, going from 50 to 25 mJ/m²) was measured by the contact angle technique when pressure changes from 150 to 250 mTorr. This can be explained considering that at high pressure there is either deposition from homogeneous nucleation in the gas phase or direct vapor condensation onto the substrate surface. These effects induce a bad adhesion of the film that degrade very fast in contact with air and loose its acid properties. Further experiments were performed at 150 mTorr in order to get a high deposition rate and good film properties.

**Power effect**

During the Mass Spectrometry analysis of the plasma phase, the following key peaks characteristic of an acrylic acid discharge were observed: m/z = 72 M⁺, 27 (C₂H₅⁺), 28 (CO⁺), 44 (CO₂⁺), 45 (CO₂H⁺), 55 (CH₂CHCO⁺). As expected, the acid fragmentation in the plasma region increases with the RF power.

Films structure analysis with FTIR shows that $I_{H2}/I_{OH}$ ratio increases proportionally with the RF power.

The coatings acid behavior was studied with contact angle measurements. In Fig. 2(a) we can see the Fowkes work of adhesion, compared with the van Oss method [3].

With van Oss method we can evaluate $\gamma_{AB}$ that predicts $W_{AB}$ from the equation (2) and (3).

$$W_{AB} = 2(\gamma_1^+ \gamma_2^-)^{1/2} + 2(\gamma_2^+ \gamma_1^-)^{1/2}$$  \hspace{1cm} (2)

$$\gamma_{AB} = 2(\gamma_1^+ \gamma_1^-)^{1/2}$$  \hspace{1cm} (3)

$\gamma_1^+$ and $\gamma_1^-$ can be determined using three reference liquids, $\alpha$-bromonaphthalene, formamide and glycerol were used in our experiments. As shown in the figure, both methods are in agreement with the decrease of $W_{AB}$.

The power increase induced a loss of $\text{COOH}$ functionalities that can be correlated to the diminution of the acid content in the film structure.

The Hydrogen bond component of the surface free energy can also be measured with the Owens-Wendt 3 components method (see eq. 4) [4].
\[ \gamma_S = \gamma_{S^d} + \gamma_{S^p} + \gamma_{S^h} \]  \hspace{1cm} (4)

The dispersive, the polar and the hydrogen bond component of the different coatings can be evaluated by solving a system of three equations with three reference liquids (\(\alpha\)-bromonaphthalene, formamide and water). Fig 2(b) shows the dependence of these three components with power.

**Aging effect**

Aging effect was studied in order to understand the coatings stability with time. Figure 3 shows the aging effect on acrylic films in function of RF power. The figure shows the \(\gamma_{AB}\) of a film as measured just after deposition and on the same coatings after one-week aging in air. We can see that the polymers deposited under low power conditions (low monomer fragmentation, high functional groups retention) degrade more than those deposited under high power.

If we consider the value for the Silicon wafer surface \(\gamma_{AB} = 22,66\) mJ/m\(^2\), we can say that the films obtained at low power absorb water vapor from the air and degrade rapidly exposing the Si surface.
Conclusion

The influence of pressure, power and aging in a RF deposition of Acrylic acid has been studied in order to optimize the COOH functional groups retention. Results show that the deposition rate increases with pressure. However, above 150 mTorr, direct vapor condensations lead to an instable film which degrades rapidly in air. The power has a strong influence on acid behavior of the films. Optimum conditions for highly functionalized material are obtained at low power. However, in this case, the films deposited have insufficient crosslinking to prevent aging effect (dissolution in water vapor). Future work includes definition of optimum conditions of power and pressure for monomer groups retention and water stability.

References
