

Comparative study of deep-coating and plasma processing PMMA thin films

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Plasma treatment is a unique and powerful method for modifying polymeric materials without altering their bulk properties. In this purpose we are using the plasma processing to enhance the properties of PMMA films for biomedical applications. Plasma processed PMMA thin films have been obtained in a DC glow discharge from polymer solution at different plasma powers. The results are compared with that for PMMA films obtained by deep coating method. Fourier Transform Infrared Spectroscopy (FT-IR) and atomic force microscopy (AFM) have characterized the structure and composition of the films.

(Received April 7, 2010; accepted April 26, 2010)

Keywords: Plasma polymers, Biopolymers, Thin films, PMMA, FT-IR, AFM

1. Introduction

Biomedical materials are being widely researched, and a variety of metals, metal alloys, and polymers are being used. Organic polymers (PE, PP, PMMA, PTFE, PET, etc.) are considered as significant materials in micro- and nanoengineering, mainly for biological and medical applications [1]. The polymer thin films have been used as biomaterial in the medical area from cardiovascular to plastic surgery. When a biomaterial is implanted into a living tissue generates a cascade of host reactions occurred at interface between tissue and material.

Biomaterials that have contact with the human body need an optimal combination of mechanical properties, bioactivity, biocompatibility as well as functionality [2, 3]. Proteins and blood cells from body fluids interact with the surface of the biomaterial; therefore the adsorption of different components at the surface of the biomaterial is an important issue in its design. The surface modification influences the cell-polymer interaction and is a promising way in order to satisfy the needs and to determine the choice of the suitable polymer [4, 5].

Among a wide range of polymeric materials, poly (methyl methacrylate) (PMMA) has good mechanical strength. It is biocompatible and biostable materials, and is an attractive candidate for medical applications [6, 7]. Health effects are minimal for PMMA. For biomedical grade PMMA, however, there must be no residual monomer. Unlike PMMA, MMA is allergenic, and has health implications [8].

Usually, the polymers do not possess the surface properties needed for biomedical applications, but various alternative approaches to modify the surface properties of current materials to improve their surface characteristics and biocompatibility were adopted. Different studies showed that plasma deposition processes could enhance

the compatibility with blood of vascular grafts with small diameter. Plasma processing can be used to introduce desired functional groups or chains onto the surface of materials with particular application to improve their biocompatibility [1,9].

This research focuses on the feasibility of utilizing plasma processing to enhance the surface properties of PMMA for biomedical applications as a better alternative to PMMA films obtained by deep coating method. Plasma processed PMMA thin films have been obtained in a DC glow discharge from polymer solution at different values of plasma power. The results are compared with that for PMMA films obtained by deep coating method. The PMMA films were evaluated by analysis of Atomic Force Microscopy (AFM) and Fourier Transform Infrared Spectroscopy (FT-IR).

2. Experimental

All chemical reagents were of analytical grade and used as received (Sigma-Aldrich Company). An appropriate amount of PMMA ($[\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3)]_n$, powder) was dissolved in a appropriate amount of dichloromethane (CH_2Cl_2 , $\geq 99.9\%$, $M_w=84.93$) under stirring conditions using ultrasonic processor (300 W) at room temperature.

The deposition of the PMMA thin films was carried out in DC glow discharge plasma reactor using a Rogowski electrode (anode) and a hollow cylindrical cathode with negative Rogowski shape. The distance between electrodes is variable and can be configured to adjust the plasma parameters to a specific reaction chains appropriate to chemical reaction conditions. The PMMA- CH_2Cl_2 solution was directly sprayed in plasma stream by a special designed atomizer coupled on discharge tube.

The values of plasma power during of deposition process were 7.5W, 12.5W and 17.5 W at a time of exposure of 20 min with a rate of 40 $\mu\text{l}/\text{min}$. Using the same PMMA- CH_2Cl_2 solution, the PMMA film by deep coating method was prepared.

The films were morphologically characterized by AFM, and structurally by FT-IR spectroscopy. Jasco FT/IR-6200 Spectrometer coupled with FT-IR Jasco IRT 3000 microscope was used for FT-IR spectroscopy analysis. CO_2 and water vapor were removed by background processing. The frequency contribution groups for all FT-IR spectra were evaluated with KnowItAll 7.5 software from Biorad. AFM was performed using SPM – NTegra Prima, in tapping mode.

3. Results and discussion

In Figure 1 are comparatively presented the FT-IR spectra for both the deep coating PMMA film (PMMA) and the plasma deposited PMMA film (pPMMA) at 7.5W. There are differences in the strength and breadth of the absorption peaks between the conventional and corresponding plasma processed polymer. Almost all the absorption bands attributed to PMMA are observed in the plasma processed polymer, pPMMA.

The characteristic peaks of carbonyl ($\text{C}=\text{O}$ stretching) group at 1738 cm^{-1} and C-O (ester bond) stretching vibration at 1270 cm^{-1} were observed. The $-\text{CH}_2$ and $-\text{CH}_3$ stretches at 1449 and 1387 cm^{-1} are also presented.

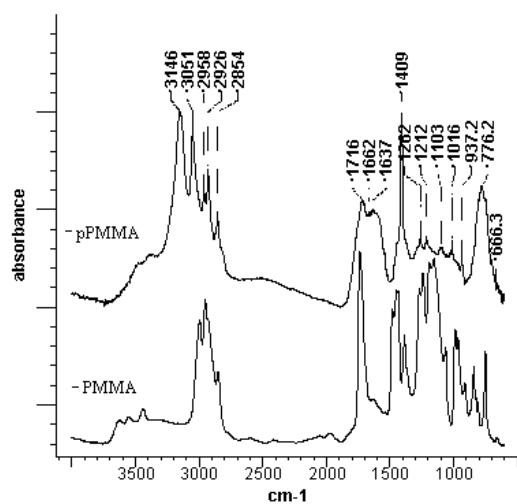


Fig. 1. FT-IR spectra of: PMMA film obtained by deep coating method, pPMMA film deposited by DC plasma processing (7.5W).

The PMMA sample exhibits C-H stretching vibration around 2950 cm^{-1} . These characteristic absorbance peaks are comparatively weak and broader (but not absent) in pPMMA, suggesting a significant amount of fragmentation and rearrangement in the plasma deposition process. The $\text{C}=\text{O}$ stretch in the pPMMA is shifted to a

lower wave number, possibly indicating the conversion of some ester moieties to the acid. The reduction in the strong band at 1262 cm^{-1} associated with the C-O (ester bond) stretching vibration also supports this change. The obtained results are in accordance with other reports [7, 10].

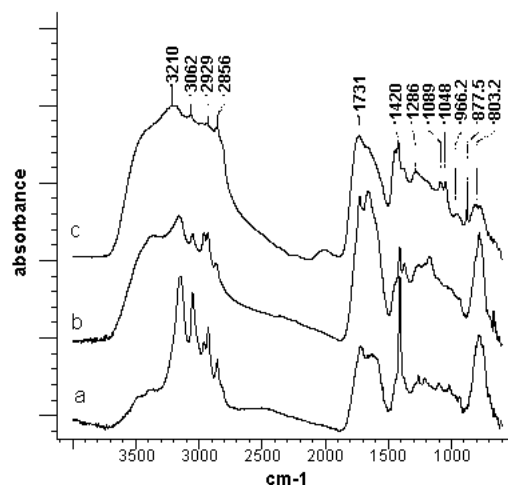


Fig. 2. FT-IR spectra of pPMMA films deposited by DC plasma processing at different plasma powers: (a) 7.5 W (b) 12.5 W, (c) 17.5 W.

The FT-IR spectra of PMMA films deposited by plasma processing at different three plasma powers are presented in the Figure 2. The development of some larger bands with lower intensities is related with the increasing of plasma power. This explains a fragmentation and rearrangement process during of plasma processing route, keeping the polymer characteristics for all three values of plasma powers.

Tapping-mode AFM images ($5 \times 5\ \mu\text{m}^2$, respectively $10 \times 10\ \mu\text{m}^2$) of PMMA, pPMMA (7.5 W), pPMMA (12.5 W) and pPMMA (17.5 W) are presented in Figure 3 (a-d) and Fig. 4 (a-d).

The surface of pPMMA (7.5 W) shows a similar morphology to those of PMMA obtained by deep coating method with a difference given by the solvent evaporation on PMMA film.

The films obtained by these two methods are continuous and adherent to substrate. Increasing the values of plasma power from 7.5 W to 12.5 W, respectively to 17.5 W might be observed a concentration of some forms on the film surface, according with root-mean-square (RMS) roughness measurements. The values of RMS (nm) from AFM images presented in Figure 4 (b-d) are: 76.164, 83.297 respectively 219.473 for pPMMA (7.5 W), pPMMA (12.5 W) and pPMMA (17.5 W). These forms could be associated with some nucleation and growing processes due of polymer breakup along with the increasing of power during of plasma processing.

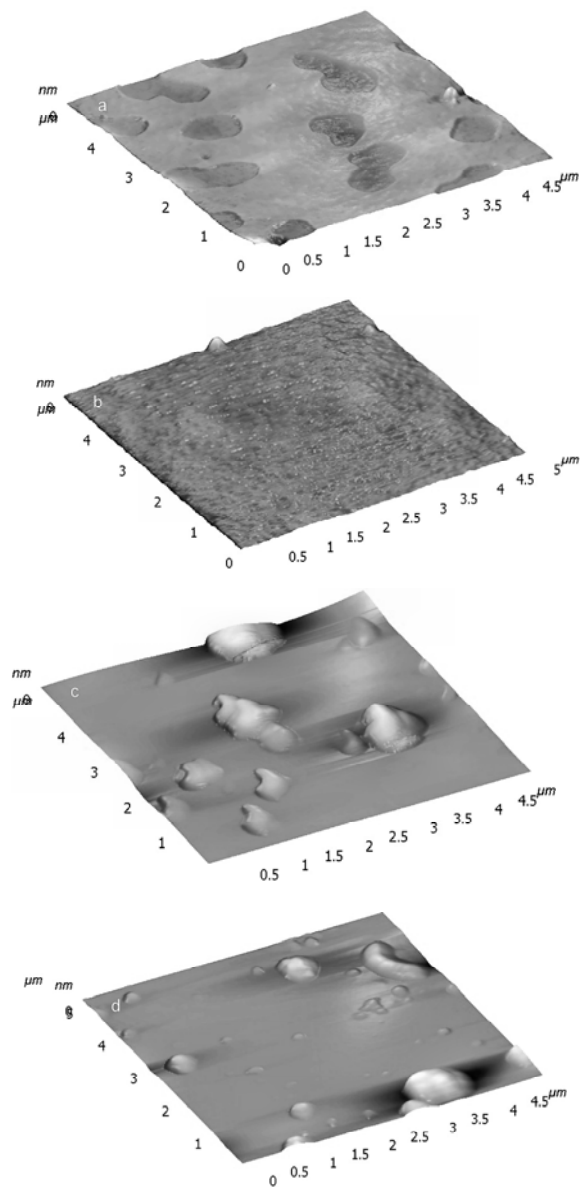


Fig. 3. Tapping-mode AFM images ($5 \times 5 \mu\text{m}^2$) of: a). PMMA, b). pPMMA (7.5 W), c). pPMMA (12.5 W), d). pPMMA (17.5 W).

The AFM results are in agreement with the information obtained by FT-IR spectroscopy and prove the modification of polymer surface with the increasing of power value.

The AFM analysis indicates that the topography of pPMMA surface was changed by modification of plasma parameters with the formation of some functional groups on the surface, in concordance with the information obtained by FT-IR spectroscopy, respectively a broad band around $3400\text{-}3500 \text{ cm}^{-1}$.

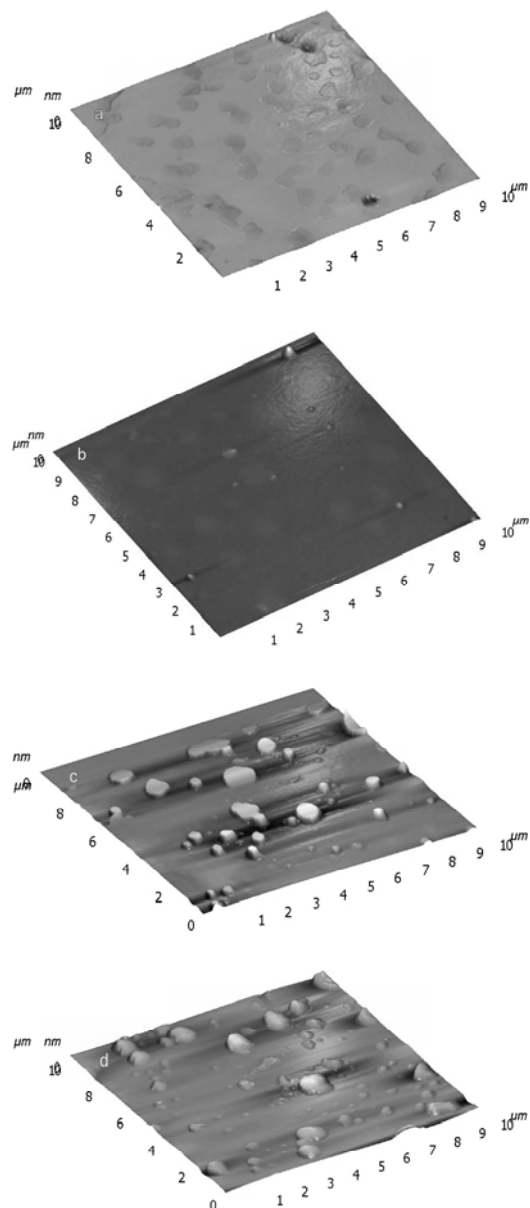


Fig. 4. Tapping-mode AFM images ($10 \times 10 \mu\text{m}^2$) of: a). PMMA, b). pPMMA (7.5 W), c). pPMMA (12.5 W), d). pPMMA (17.5 W).

4. Conclusions

Present work is related to the feasibility of using plasma processing instead of deep coating method to enhance the PMMA film properties for biomedical applications. The results show that the plasma processing is suitable alternative to PMMA films obtained by deep coating method. Moreover, the plasma processing parameters seems to play a major role in the film surface properties. It was revealed that the topography of pPMMA surface is influenced by plasma parameters (value of power). The study supports future investigations aimed to investigate the performance of PMMA films obtained by plasma processing for specific biomedical applications.

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