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An evaluation of poly(ethylene-glycol) films stabilized by plasma and ion beam methods

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Abstract

Poly(ethylene-glycol) (PEG) is a material allowing reliable reduction of protein adsorption. A comparison between the transformations induced by ion beam (IonB) and plasma modification (PlM) is presented in this work. Spin casted PEG films deposited onto Si(1 0 0) have been bombarded with an Ar and Ar–N_2 ion beams (500 V). Another series of samples was modified in parallel by Ar plasma in an electron cyclotron resonance reactor (1000–1400 W). Bulk and surface techniques were used to describe the changes induced on the PEG films. Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectra (XPS) outlined relevant changes in the polymer network. From the point of view of the applications, both IonB and PlM induced an increase in the water contact angle with respect to untreated PEG films, which is interpreted as an increase of their stability. Time of flight-secondary ion mass spectroscopy results of the processed PEG films confirmed the overall fragmentation of the polymer. The correlation with those results obtained by FTIR and XPS support that crosslinking and condensation are the main transformations induced in the films.
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1. Introduction

The operation of biomolecular devices such as bio-arrays used for DNA sequencing, rely on monitoring an electronic or optic signal dependent on processes of local specific binding. In order to achieve these objectives, immobilization of biomolecules in selective areas. The area selectivity consists of patterning the surface with a material that induces specific binding surrounded by another material which rejects both specific and unspecific binding of the target biomolecule. Patterning methods for protein and cell control have been extensively reviewed [1,2]. In this work, we have concentrated on the part of the surface coated with a PEG-like material, which should minimise coverage by any biomolecule. The surfaces used for these purposes are generally categorized as *anti-fouling*. Since pure polycrystalline PEG is easily dissolved in aqueous media [3], physicochemical processes have to be determined in order to stabilize it. The applications of this material, deposited as a film over both polymer and inorganic surfaces, range from the

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fabrication of antimicrobial catheters to the design of biosensor devices, preparation of protein patternings [1] and cellular guides for tissue engineering [4]. In fact, the applications at cellular level depend on the performance of PEG at protein level since the extracellular matrix proteins play a determinant role in the cell behavior [5].

The anti fouling properties of PEG are intrinsically related to its self repulsion in water, which makes of it at the same time a very soluble polymer. Grafting PEG silanes after strong acid treatments of silicon or SiO_2 substrates [4,6], self assembling oligo(ethylene-glycol) associated thiols on gold [7] and indirect chemical linking by forming complexes with $OSiCl_3$ groups [8] or amine enriched polystyrene [9] have been used as methods towards surface stabilization of PEG. Studies concerning the long term stability of grafted films have been performed recently pointing out that the films are not effective for longer than one month in cell culturing media [10].

In this work, we aim to describe the modification of the surfaces of partially crystallized PEG films deposited by spin casting. The modification has been studied in two fronts by using ion-beam treatments (IonB) and plasma processes (PlM). Special attention is paid to those modifications leading to a stable film for anti fouling applications.

2. Experimental

PEG films were prepared by spin casting (2000 rpm during 45 s) on double side polished Si(1 0 0) from a solution composed of 10 mg of PEG (Sigma–Aldrich, mean $M_w = 6000$) in 20 ml trichloroethylene. Modification of the PEG coatings in the ion beam was carried out in an IPT system powered with 150 W (Dressler Cesar 273 D, 27.120 MHz rf) and extraction and suppression voltages fixed at 500 and 100 V, respectively. (chamber pressure: 6.0×10^{-2} Pa, total gas flow: 10 sccm. Gas composition: 100% Ar or 60% Ar–40% N_2). The plasma treatments were carried out in a distributed electron cyclotron resonance (DECR) reactor with a mw power ranging between 600 and 1400 W (2.45 GHz), background pressure of 1.33×10^{-5} Pa and operation pressure of 0.133 Pa. Principal variable treatment parameters were gas composition (Ar, N_2 mixtures, total flow: 10 sccm), rf bias

voltage (13.54 MHz, 0–200 V) and exposure time (0–60 s).

Molecular information from the modified PEG films was obtained by Fourier transform infrared spectroscopy (FT-IR, Bruker Vector 22, resolution: 4 cm^{-1}, 4000–400 cm^{-1}, 32 scans at 10 KHz). They were further characterized by X-ray photoelectron spectroscopy using a Riber Nanoscan 50 operating in the constant analyser energy mode (Al Kα source: 12 kV, 25 mA, pressure analysis chamber: ~6 × 10^{-6} Pa). Elemental spectra were obtained at 0.7 eV resolution. Fitting was performed by using the software package from XPS International srl, (USA) using Gaussian–Lorentzian (G–L) mixtures of 0.9–0.1. A TOF-SIMS IV system equipped with a primary 25 kV Gallium liquid metal ion gun was used for time of flight secondary ion mass spectroscopy. The system was operated either in high current surface spectroscopy mode with mass resolution ($m/\Delta m$) > 8000 and lateral resolution <7 Nm. Total ion flux was maintained below 10^{13} cm^{-2} to ensure static SIMS conditions.

A topographic imaging of the samples was performed by using atomic force microscopy (AFM, NT-MDT Solver, Smena head). Si cantilevers with force constant 5 N/m and working first harmonic frequency of 158 KHz were used. Static water, alphabromonaphthalene and ehtylenglycol contact angle (CA) measurements (DGD Fast/60, GBX technologies) were obtained to trace the modification of the IonB and PlM PEG films.

3. Results and discussion

3.1. FT-IR spectroscopy

Both IonB and PlM induced notable changes in the molecular structure of the PEG film as deduced from the FTIR spectra. As an illustration, the spectrum of a PEG film exposed to an Ar plasma (600 W, −100 V) for 40 s is depicted in Fig. 1 in comparison with an untreated film. Although the characteristic bands observed in the as deposited films were detected in the treated films, certain relevant changes could be observed by comparing band transmittance ratios. It is remarkable that those bands previously attributed to parallel modes in spin casted PEG [11]
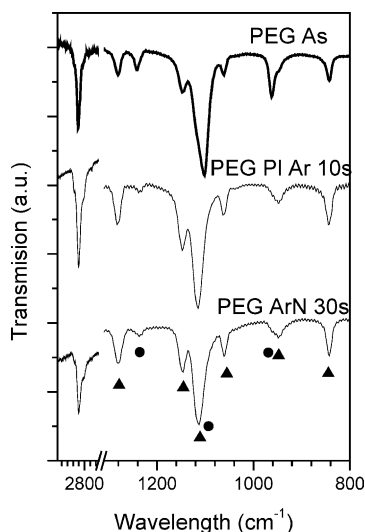
Fig. 1. FT-IR spectra from PEG films. Top: untreated. Middle: PlM in Ar atmosphere at 600 W and –100 V Bias for 40 s. Bottom: IonB in Ar–N$_2$ for 30 s. (●) Backbone parallel modes; (▲) perpendicular modes.

present a drastic decay of their relative absorbance ((●) in Fig. 1). Furthermore, the plasma modification takes place in a very fast way since no evolution with time exposure could be found for the ratio between parallel and perpendicular bands (i.e. 1234 and 1280 cm^{-1}, respectively) at shorter exposure times.

This phenomenon of parallel band absorbance decrease was also observed on IonB PEG films. In this case, a clear competition between polymer modification and sputtering process takes place. On one hand, sputtering rate was considered to be much higher than for PlM samples. On the other, the higher energy of the ions induced a similar disappearance of parallel modes at exposure times of 30 s. In this case, the relative decrease of parallel band absorbance could be monitored as a function of exposure time. At lower exposure times (for both Ar and Ar–N$_2$ IonB PEG) the molecular transformation had not reached the level reached by the Ar plasma treatment.

The most plausible interpretation for these modifications in the polymer backbone after both IonB and PlM is undoubtedly a transformation of the initially linear polymer into shorter branched structures.

Furthermore, FT-IR spectra confirm that these modifications are not only surface effective but they transform also the bulk of the PEG film.

3.2. X-ray photoelectron spectroscopy

The composition of the PlM and IonB PEG films was further investigated by XPS analysis in order to monitor the differences at the surface. Remarkable changes could be again observed in the chemical environment of C atoms exposed to both PlM and IonB. The C 1s spectrum of the IonB films bombarded in an Ar–N$_2$ mixture (Fig. 2a) presents significant changes with respect to as deposited films (Fig. 2c). After this treatment two components can be identified in the C 1s transition. In contrast with the original monocomponent C − $\underline{C}$ − O contribution of untreated PEG at 286.4 eV, a new C − $\underline{C}$ − C appears in the spectrum at 285.0 eV. The intensity ratio between these contributions ($I_{285}/I_{286.4}$) was observed to be similar for IonB performed in Ar and Ar–N$_2$ mixtures. When considered together, these modifications imply a crosslinking and densification process of the polymer (branched PEG) resulting from the saturation of the ion beam broken bonds with neighbouring unsaturated atoms. The analysis of the O 1s peaks shows only a slight modification of the O environment. In fact, the O 1s spectra corresponding to Ar and Ar/N$_2$ bombarded PEG (Fig. 2d) presented mostly the same aspect as the corresponding to the as deposited polymer (BE = 532.8 eV, Fig. 2f) in spite of a slightly increased shoulder at lower BE. The following formula proposes a mechanism that explains the drastic changes in the C 1s environment while the O 1s remains almost unaffected:
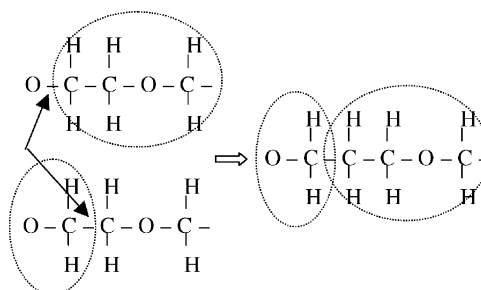
These trends were also observed in PlM PEG films (Fig. 2b and e for C1s and O 1s spectra, respectively). In fact, the relative intensity ratios of the C 1s peaks
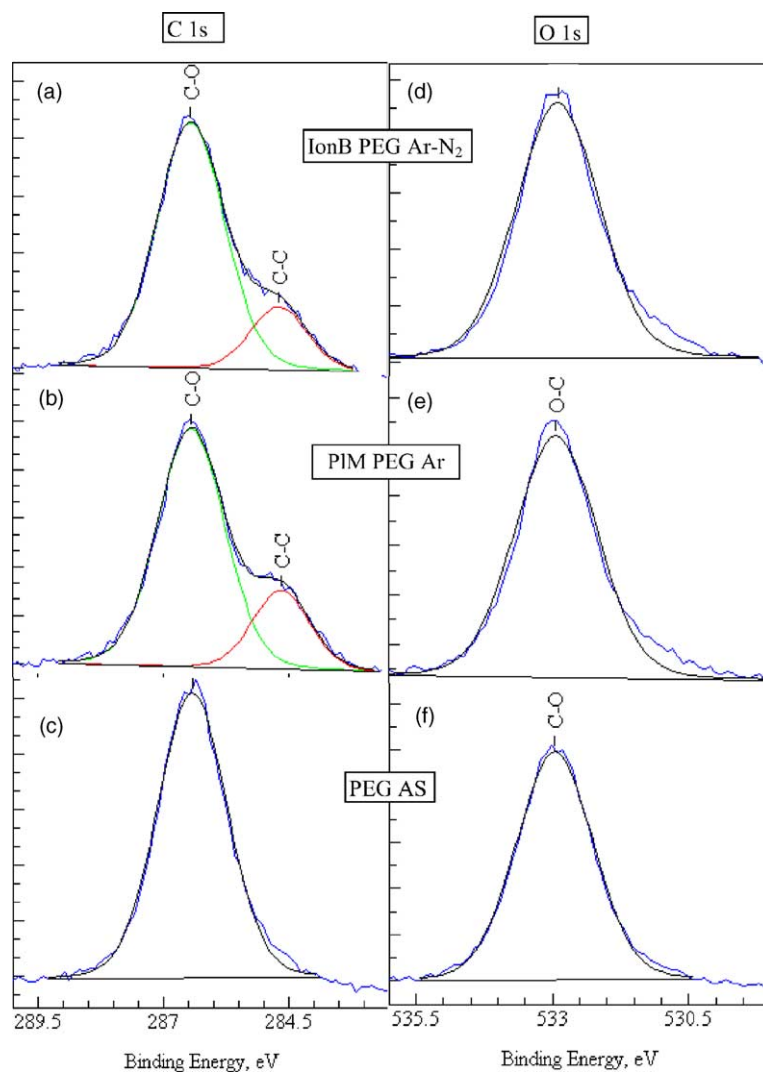
Fig. 2. XPS C 1s and O 1s transitions in the IonB PEG (treated with 60% Ar–40% N$_2$), PlM PEG (30 s) and the untreated PEG film (PEG–AS).

followed a clear trend as a function of Ar plasma exposure time. $I_{285}/I_{286.4}$) was almost 0 for as spin casted PEG and 0.21, 0.38, 0.60 for PlM PEG treated during 20, 30 and 60 s, respectively.

3.3. Time of flight-secondary ion mass spectroscopy

Further information concerning the molecular transformations induced by PlM and IonB on PEG films were obtained by ToF-SIMS. For these analysis we took profit of the self induced cationisation of the

PEG chains (i.e. substitution of a chain ending H by Na) to monitor the transformation of the polymer chains. This process allows an increase in the detection yield of polymer fragments as previously reported [12]. A notable result was obtained in the case of PlM PEG. This surface analysis was sensitive enough as to detect the evolution of fragmentation as a function of plasma exposure time. Fig. 3 shows a chart with the normalised intensity corresponding to different integer multiples of a cationised PEG monomer. It is consistently observed that the intensity for a certain
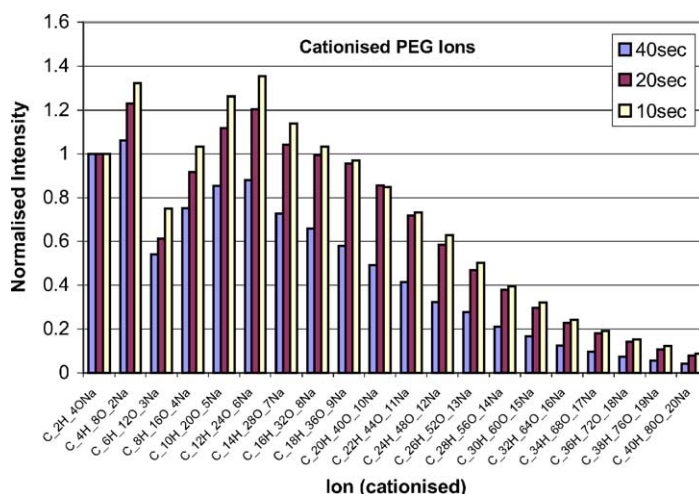
Fig. 3. ToF-SIMS normalised chart of the evolution of PlM PEG fragmentation as a function of exposure time.

polymer length is lower for samples exposed for longer times to the Ar plasma. In other words, as long as the exposure time increases the polymers are more and more fragmented. This increases at the same time the rate of condensation and crosslinking as previously supported by the C 1s peak at 285 eV.

3.4. Atomic force microscopy

Both PlM and IonB-PEG surfaces were studied by using AFM in order to reveal relevant differences in the polymer topography. Fig. 4 shows two AFM images from the treated PEG surfaces. The morphol-
ogy of the IonB PEG (Fig. 4, left) respected in general the trends observed in as deposited PEG, that is, longitudinal chains of polycrystalline spherulites concentrically organised [11]. On the other hand, PlM PEG surfaces presented a notable modification of the surface topography with deep triangular valleys. These differences are clearly related to the kinetics of the etching process induced by the two different ion characteristics of PlM and IonB and to the inhomogeneous degree of crystallization of the PEG film. In this context, high energy IonB ions can easily homogeneously etch the surface in a layer by layer mode. On the other hand, at the lower energies used for PlM
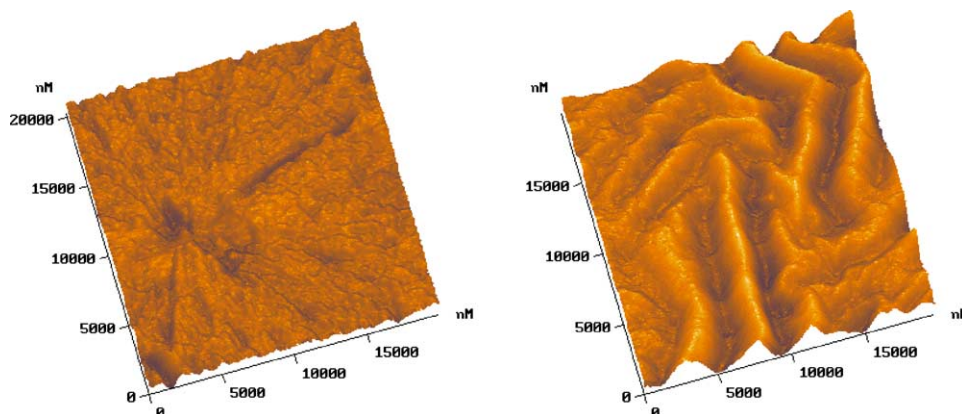

Fig. 4. The 20 μm × 20 μm AFM topographic images from the surfaces of an IonB (left) and a PlM (right) PEG film. In both cases, treatments were carried out in 100% Ar. Identical vertical scale.

the polycrystalline regions are more resistant than the amorphous surrounding structures giving raise to a preferential sputtering from amorphous regions, thus inducing the valley structures as previously observed in several polymer surfaces [13]. However, taking into account that the T_g of PEG_{6000} is around 73 C, melting processes at the surface may be of concern as a result of ion energy dispersion. In this case, the surface would not result in homogeneous features but in rough structures due to drastic evaporation in vacuum. As an overall, AFM images demonstrate that a high topographic contrast exist between rough PlM PEG films and the homogeneous IonB PEG films (presenting root mean square roughness values not exceeding 30 nm for any gas mixture at surface scanning areas of $20 \, \mu m \times 20 \, \mu m$).

3.5. Contact angle measurements

The contact angle of water droplets onto the PEG surfaces was used to estimate the film stability. The water contact angle of as spin casted PEG was taken as the reference point for the unstabilised polymer. The self repulsion and solubilisation of the original PEG films give raise to very low CAs of $13°$ after 30 s of droplet–surface interaction. In the case of IonB PEG films the CAs for both Ar and Ar–N_2 treated surfaces were observed to increase up to 31 and $33°$ for treatments of 15 and 30 s, respectively. PlM PEG films were not found to undergo such an increase and even after exposure times of 60 s the CAs remained under $27°$. It is remarkable that the films presenting higher topographic modification express less variation in the CAs with respect to the untreated films. The lower stability of the PlM PEG films may precisely arise from this inhomogeneity of the outer surface while the topographically homogeneous IonB PEG films block the surface in a more effective way.

The higher stability of the IonB PEG allowed the determination of the surface tension components from the measurement of CAs by using three reference liquids for the dispersive (γ^D), acid (γ^+) and base (γ^-) behaviour. The CAs of α-bromonaphthalene, water and ethylene glycol onto an IonB PEG exposed during 30 s were 8, 33 and $23°$, respectively. The application of the Good–Van Oss–Chaudhury equations for the estimation of the surface tension components [14] demonstrated the dominant dispersive character of the IonB PEG films but with a notable base component clearly determining the polar behaviour (i.e. reduced but still remarkable hydrophilic character). We obtained values of 43.9, 0.2 and 20.3 mJ/m^2 for γ^D, γ^+ and γ^-, respectively, which determines a total surface tension γ^T of 47.9 mJ/m^2.

4. Conclusions

The exposure of PEG films to Ar plasmas and Ar, Ar–N_2 ion beams allows to modify the structure of the polymer chains reducing the self repulsion observed in the original PEG films. FT-IR spectra confirmed that the modification affects not only the polymer surface but also the bulk of the PEG film. Furthermore, the drastic reduction of bands related to parallel modes (with respect to the polymer backbone) suggested a transformation from an originally linear PEG to a branched structure. XPS analysis confirmed that the modified form presents a new contribution on the C 1s transition consistent with the presence of C atoms not linked to O. These carbons arise from crosslinking and condensation processes between ion induced PEG fragments. ToF-SIMS analysis revealed the fragmentation induced by the treatments and outlined surface differences in the PlM treatments with respect to exposure time which could not be detected by FT-IR. Finally, AFM images showed relevant topographic differences between PlM and IonB PEG films. The inhomogeneity of the PlM surface was suggested to be the main factor inhibiting a higher increase of the CA as compared with IonB PEG films. This was interpreted as a lower degree of stability of the PlM in comparison with IonB PEG. Further experiments are in progress to confirm not only the long term stability of the modified PEG films but also their efficacy as anti fouling layers.

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