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Surface Science 560 (2004) 121-129



www.elsevier.com/locate/susc

Surface topographic and structural characterization of plasma treated PMAA–PMMA copolymer films

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Received 14 January 2004; accepted for publication 19 April 2004 Available online 11 May 2004

Abstract

The plasma induced surface modification of Poly(methacrylic acid)–Poly(methylmethacrylate) copolymer (PMAA– co–PMMA) thin films has been characterized in this work by using a conventional Atomic Force Microscope (AFM). The polymer films, spin casted from methanol solutions, were exposed to different plasma discharges characterized by identical power supply and exposure but with different gas composition (Ar–N₂ mixtures). The effect of the treatments on the topographic and structural properties of the surfaces has been studied with the AFM acquiring the amplitude and the phase of the oscillating cantilever. The application of statistical tools to topographic images led to the determination of organization patterns in the copolymer films. These are of special interest in the case of Ar plasma treated samples since organized motives present dimensions below 50 nm. Regarding the materials properties, a phase contrast between the two polymers constituting the film, PMAA and PMMA, was detected. Both, the evolution of compositional intermixing and the dimensions of organized motives could be ascribed to plasma energetic and chemical factors as determined from plasma diagnostic techniques. These results confirm that plasma processes are key tools towards the controlled surface modification of copolymer films.

Keywords: Atomic force microscopy; Plasma processing; Surface structure, morphology, roughness, and topography

1. Introduction

During the last decade material scientists have exploited the development of new techniques for the modification and the characterization of surfaces. Nowadays, the role of the surfaces in materials engineering has become crucial in particular in the field of biomaterials where the surfaces are the main element of the material which interacts with the biological environment [1]. This new aspect strongly involves polymers which are widely used for biomedical applications due to their mouldable chemical and physical properties [2]. The strong development of thin film polymer engineering has been enhanced by the parallel growth of the cold plasma techniques as a powerful tool for surface treatments of soft and low-melting point materials [3–5]. Atomic force microscopy [6] (AFM) techniques play a crucial role in the understanding of the mechanisms involved during the plasma treatment due to their

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imaging capability onto non-conductive surfaces [7]. They are especially useful for a non-destructive exploration of soft materials by using modulation techniques of the probe–sample interaction [8–10]. Moreover, modulation techniques can be exploited to obtain structural information of the surfaces at the nanoscale length [11]. Several researchers [12–16] have demonstrated the high sensibility of the phase signal to detect changes in the visco-elastic properties of the surfaces.

Within this frame of AFM analysis of modified polymer surfaces, a series of statistical algorithms have been applied. These statistical tools help in the extraction of conclusions regarding the organization of thin organic films at particular length scales. The combination of AFM for 3D non-destructive image construction and the statistical tools allows a quantitative measurement of the ordering behaviour of the surfaces. The quantitative analysis has been performed by using the Power Spectral Density (PSD) function of the topographical profiles of plasma treated Poly(methacrylic acid)-Poly(methylmethacrylate) (PMAA-co-PMMA). This statistical function is related to the self-affine structure of a granular film through the inverse length (frequency) [17,18]. The information extracted from PSD can indicate characteristic behaviours quantifying the shortlength range ordering degree of the analysed structures through a parameter named correlation length (L_0) .

2. Materials and methods

PMAA-co-PMMA (Fluka, $MW = 500\ 000$) was dissolved in 2% methanol solution and then spin casted onto polished silicon substrates (Siltronix [100] Boron doped). Spin coating was performed at 2000 rpm for 30 s.

Plasma treatments were performed in a previously described Distributed Electron Cyclotron Resonance (DECR) reactor [19]. A microwave power of 600 W was supplied (2.54 GHz, 2000 W) to the plasma through 16 antennas coupled to a matching circuit in order to avoid power reflection. The chamber background and working pressures were $\sim 10^{-7}$ and 10^{-3} Torr, respectively. Ar and N₂

were mixed in different proportions (Ar/N₂ 10/0, 6/4, 4/6, 0/10) keeping the total gas flow constant ($\Phi_{\rm T} = 10$ sccm). All the samples were treated during only 30 s. Plasma parameters were monitored by a Langmuir probe (Scientific Systems, Dublin, EIRE) and a quadrupole mass spectrometer (QMS) (Hiden, Manchester, UK). The QMS system was configured with a mass pass filter to obtain energy spectra. All measurements were carried out at a plasma MW power of 600 W. Mean ion energy and ion current curves were obtained combining the ionic energy spectra obtained from the mass spectrometer and the ionic current densities obtained from the Langmuir probe following a previously described method [20].

Scanning probe experiments were performed with a commercial Atomic Probe Microscope (SMENA head, Solver electronics, NT-MDT Zelenograd, Moscow, Russia). A standard silicon cantilever (NT-MDT) has been used in resonating mode ($v_{res} = 150$ KHz). The same values of Free Oscillation Amplitude (FOA) and Set Point (SP) were used in order to have comparable height images of the samples, which were measured in air. The Damping Ratio (DR) defined by DR = SP/FOA was fixed to ~ 0.5 in order to increase the visco-elastic contribution in the phase shift response of the cantilever. During the surface scanning two signals were acquired in addition to the height profile: the phase (ϕ) and the amplitude (MAG) of the cantilever harmonic motion. The control software allows to calculate the 2D resolved phase shift $(\Delta \phi)$ and the amplitude error images (AEI) by using these formulas:

$$\Delta \phi = \phi_{\rm free} - \phi_{\rm appr} \tag{1}$$

and

$$AEI = SP - MAG \tag{2}$$

where ϕ_{free} is the phase calculated with respect to a reference fixed far from the surface and ϕ_{appr} is the phase calculated with respect to the same reference after the approaching. The image lateral resolution was limited by the curvature radius of the tip $(R_{\text{tip}} \sim 20 \text{ nm})$. AFM data were treated with the Solver-NT-MDT controller program. In particular, the analysis of the scaling behaviour was car-

ried out calculating the power spectral density (PSD) function of the topographical profiles,

$$\operatorname{PSD}(f) = \frac{1}{L} \left| \int_0^L \mathrm{d}x h(x) \mathrm{e}^{i2\pi f x} \right|^2 \tag{3}$$

where h(x) is the raw height profile acquired in a 256×256 pixels image. In order to eliminate tilted plane effects the best-fit plane was calculated during each fast scan line (positive x direction) and subtracted from the image. Then PSD was performed by the Fast Fourier Transform (FFT) analysis of each scan line and then mediated over all lines. Quantitative measurements were also done in the direct space, calculating root mean square roughness ($R_{\rm rms}$) values with the statistical tools provided by the control software.

XPS measurements were carried out with an Ultra Axis spectrometer (Kratos Analytical Ltd., Manchester, UK) equipped with a monochromatic AlK α source operated at 150 W with a spot of 100 μ m in diameter. The base pressure was better than 3×10^{-9} mbar and the analysis pressure better than

 10^{-8} mbar. Survey spectra (0–1150 eV BE range) were collected at 90° take off angle (respect to the sample surface) and pass energy of 160 eV. High-resolution spectra (C1s, O1s and N1s regions) were recorded at the same conditions but with pass energy of 20 eV. A low energy flood gun was used to neutralize surface charging. Data were processed using the Vision 2 software (Kratos Analytical). Elemental composition was calculated taking the peak area after a linear background subtraction and using tabulated relative sensitivity factors. AFM and XPS measurements have been performed just after the plasma treatments of the sample in order to minimize the contamination effects after atmospheric exposure.

3. Results and discussion

AFM morphological characterization of plasma treated surfaces was carried out by acquiring height images using identical measurement conditions.



Fig. 1. Height images performed in the same experimental conditions. (a) Untreated sample; (b) treated with plasma Ar = 10 sccm; (c) Ar = 6 sccm, $N_2 = 4$ sccm; (d) Ar = 4 sccm; $N_2 = 6$ sccm; (e) $N_2 = 10$ sccm.

Topographic 1×1 µm images from the surfaces of the processed samples are shown in Fig. 1. Pseudo-spherical granular features with homogeneous dimensions of the order of 200 nm in diameter cover the PMAA–co–PMMA film surface. The different plasma treatments generate diverse surface modifications: in particular, a gradual difference between the effects of N₂ and the Ar containing plasmas is evidenced. Fig. 1(a) shows the topography of the untreated PMAA– co–PMMA. The Ar treatment remarkably reduces the mean height of the grains (Fig. 1(b)) while surface of samples treated with a N₂ containing plasma (Fig. 1(c)–(e))) show at this scale a morphology similar to that of untreated sample.

At a first glance, the surface of the as-casted polymeric film seems to be characterized by an amorphous structure. However, at the submicrometer length scale a certain order degree can be determined.

This is illustrated in Fig. 2(a), where a cross section obtained from Fig. 1(a) is reported. A space frequency (L) and amplitude (h) of about 200 nm and 4–5 nm, respectively, can be measured. This ordering behaviour derives from the conditions during the spin casting of the polymer solution and the dynamics of the thin film formation. Basically, molecular interactions take place in an increasingly viscous medium (i.e., as a result of the gradual solvent evaporation). Similar structures of



Fig. 2. Selected cross section profiles of the untreated (a) and the Ar treated (b) samples.

the surface morphology of self-assembled copolymers have been previously described for other heterogeneous systems [21]. This molecular organization at the surface is stable in time and is unaffected by atmospheric or water contamination. Furthermore, annealing tests (100 °C for 30 min) were performed without noticeable changes of the topographic configuration confirming the high stability range of this macromolecular system. On the other hand, cross section from the Ar treated sample presented in Fig. 2(b) evidences that the periodical organization is strongly modified but not destroyed by the plasma treatment. In particular a strong reduction of the amplitude and an increase of the lateral periodicity can be noticed. Furthermore, the new profiles are decorated



Fig. 3. Power spectral density functions of the treated samples (f; inverse length (nm⁻¹)). Zoom of the PSD of the Ar treated sample. The characteristic length of the new plateau region is \approx 30 nm.

by rough motives of a considerably lower scale. In order to obtain a quantitative evaluation of the ordering phenomena in PMAA–co–PMMA films, the PSD formalism has been applied [17,18].

The log-log plot of the PSD as a function of the frequency (length frequency, f) reported in Fig. 3(a)–(c) show that two different frequency regions can be clearly identified for samples treated in N₂ containing gas mixtures (Fig. 3(a)-(c)). On one hand, a low frequency constant regime with PSD average values between 80 and 100. On the other hand, a linear decay of the PSD can be observed on the high frequency region. The periodicity on the surfaces can be monitored by the correlation length L_0 , defined as the inverse of the critical frequency, f_0 (intersection between the linear fits of the low frequency plateau and the high frequency linear decay). The values of the correlation length for the differently treated films, are reported in Table 1.

Remarkably, a different behaviour of the PSD curve can be noticed in the case of Ar treated samples at frequencies above 2.2 nm^{-1} (Fig. 3(d)). The shoulder observed in the graph allowed to estimate a second correlation length of about 36 nm.

Since L_0 increases with the Ar content (Table 1) different saturation roughness of the films should be expected. To assess this, direct measurements of roughness have been carried out in the real space by evaluating the average deviation from the mean value of the height with regard to the length scale. For statistical purposes, 20 images were acquired at different length scales and the roughness measurements were then averaged [22].

The plots of roughness versus length scale, shown in Fig. 4, evidence the different lengths at



Fig. 4. Log-log chart of the roughness versus length scale as measured in the real space for the different samples.

which the roughness reaches the saturation plateau. Since the saturation condition is fulfilled when the size of the surface features is lower than the area considered for $R_{\rm rms}$ evaluation, the direct relationship with the correlation length is evident [18]. However, the determination of this magnitude in the log–log space diagram is not as clear to obtain as it is in the frequency space. The higher accuracy of the PSD with respect to the direct method towards determination of the correlation length is thus clearly stated with this example.

Further information on the macro-molecular organization of the copolymer films were extracted by detecting the phase (ϕ) and the amplitude (MAG) of the oscillating cantilever during the acquisition of the topographic images. This allowed the formation of 2-D resolved maps of $\Delta \phi$ and AEI following Eqs. (1) and (2).

Table 1 Plasma parameters (ion current densities and average ion energy) and the variations of the correlation lengths and saturation roughness calculated from data reported in Figs. 3 and 4 (values in parentheses represent standard deviations)

Argon flow (sccm)	Total ion current (mA cm ⁻²)	$\frac{I(Ar^+)}{(mAcm^{-2})}$	$I(Ar^{++})$ (mA cm ⁻²)	$I(N_2^+)$ (mA cm ⁻²)	$I(N^+)$ (mA cm ⁻²)	$\langle E \rangle$ (eV)	L_0 (nm)	R _{sat} (nm)
0	0.13	0	0	0.12	0.01	9.66	217 (6)	1.96 (0.1)
4	0.21	0.06	0	0.15	0	10.09	243 (11)	1.70 (0.13)
6	0.27	0.13	0	0.14	0	10.16	249 (3)	1.51 (0.07)
10	0.45	0.33	0.12	0	0	10.88	266 (8)	0.46 (0.1)



Fig. 5. (a) $1 \times 1 \mu m$ AEI image of the untreated sample. (b) $500 \times 500 \text{ mm} \Delta \phi$ image of the correspondent marked square in the AEI image. (c) Cross section of the $\Delta \phi$ image performed along the red line in (b).

Fig. 5(a) presents the amplitude error image (AEI) of the as casted sample. It has been previously demonstrated [23] that the AEI images are more sensitive to the topography of the surfaces than the corresponding height images. It can be noticed that the grains constituting the surface, are surrounded by a pseudo-polygonal matrix. Fig. 5(b) shows the corresponding magnified phase image from the marked zone. It is remarkable that the phase response of the grains and of the matrix is different: the centre of the grains has a lower phase shift ($\Delta \phi$) than the matrix ($\Delta \phi_{matrix} - \Delta \phi_{erain} \sim 70^\circ$). The section profile in Fig. 5(c)

demonstrates that the phase shift is homogeneous inside the matrix and hence not an issue of the topography. This phase contrast can be explained by a block organization of the copolymer during the deposition process: PMAA and PMMA tend to form two separated phases on the surface. The resulting phase contrast is directly related to the different physico-chemical properties (elasticity, visco-elasticity, surface free energy) of the two acrylic polymers [24].

The effect of the different plasma treatments on the phase organization of the samples surface is outlined in Fig. 6.



Fig. 6. $500 \times 500 \text{ nm } \Delta\phi$ images of the samples treated with (a) $N_2 = 10 \text{ sccm}$; (b) Ar = 4 sccm, $N_2 = 6 \text{ sccm}$; (c) Ar = 6 sccm, $N_2 = 4 \text{ sccm}$; (d) Ar = 10 sccm. Vertical scale for (a)–(c): [-25; 50], for (d): [-3; 3] all the values are expressed in degrees.

The surfaces treated with plasmas containing N_2 maintain the same bi-phase surface structure of the untreated sample even if the surface distribution of the matrix and the grains is modified (Fig. 6(a)–(c)). In the case of the Ar treated sample (Fig. 6(d)), the phase contrast is completely removed.

Regarding surface composition aspects derived from XPS results (Table 2), it is important to note that all the plasma treatments induce a notable decrease of the O/C ratio, mainly due to the preferential etching of COO groups from the surface. In fact, the relative O/C content of the surface calculated by XPS is drastically reduced from 0.39 (as casted polymer) to the 0.22 (Ar treated). The decay of the O/C ratio follows a clear trend with respect to the $Ar-N_2$ content in the plasma. Table 2 evidences a lower degree of modification (O/C values nearer to those of the untreated polymer)

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Relative XPS peaks intensity for the differently treated sa	mples
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Sample treatment (Ar flow) (sccm)	O/C relative XPS intensity	N/C relative XPS intensity
Untreated	0.39	0
0	0.30	0.19
4	0.28	0.18
6	0.25	0.16
10	0.22	0.065

for increasing N₂ content, indicating a reduction of etching on the COO lateral groups from the polymer backbone. Furthermore, the presence of an amount of N (2-3%) in Ar-N₂ treated samples has also been observed while it is negligible in the Ar treated sample. This is not unexpected due to the high reactivity given by the plasma to the N_2 molecule and to the PMMA surface [25]. It is plausible that unsaturated chemical bonds on the surface are prone to react with N resulting in a parallel grafting process [26]. If we take into account the energy consumption of these chemical processes we can understand why when the plasma discharge is constituted only by N_2 the chemical modification is dominant and no relevant topographic redistribution is induced on the film surface.

In order to take into consideration these energetic features and their influence on the degree of modification, the ion kinetic energy and the ion current densities of the different plasmas were obtained by using a Langmuir probe and a quadrupole mass spectrometer. The results, reported in Table 1, show a dependence of the correlation length and saturation roughness on the total ion current and average energy of the plasma (i.e., the Ar content); for instance, increasing the Ar content from 40% to 100%, corresponds to an increase of I_{TOT} by a factor of 2 with a reduction of the R_{sat} of about 3. On the other hand, addition of N_2 to the plasma discharge notably reduces the ionic densities and average energies; an introduction of 40% N₂ in the discharge reduces the total ion current density by 50% and the average energy of the ions by about 1 eV. This effect is mainly due to the induction of new inelastic events such as N₂ molecule cracking, which are below the typical ionization energies for Ar and N_2 [27]. Thus, in the case of Ar/N_2 mixtures, the surface is not only considerably less exposed to Ar bombardment but also this process takes place at lower energy. This explains the lower degree of topographic modification of the PMAA-co-PMMA surfaces exposed to plasma discharges with a N₂ content. These surfaces do not present a redistribution of the morphology as reflected by the correlation length and roughness values, which are similar to those described for the as spin casted film.

With regard to the possible plasma–surface interaction mechanisms, we can infer that the plasma infringes mainly a modification of the surface by bombardment due to the high impact kinetic energies of the ions compared to the intermolecular cohesion energies. Two interrelated processes are activated by the impinging ions: (i) the new configuration of the supra-molecular organization by the intermixing of the copolymer blocks that is also reflected in a longer correlation length and a smaller saturation roughness, and (ii) a chemical modification induced by the etching process resulting in an extraction of the COO group from the polymer chain and surface saturation with N as evidenced by XPS analysis.

4. Conclusions

Atomic Force Microscopy has been used to characterize the surface topographic and structural properties of plasma treated PMAA-co-PMMA films. The surface treatments have been carried out in a DECR plasma reactor varying the gas composition, whilst XPS has been used to assess the surface chemical composition. The results were correlated with those from plasma diagnostics obtained by a Langmuir probe and a Quadropole Mass Spectrometer.

The statistical analysis of the AFM topographic images allowed the quantitative determination of molecular organization. In particular two parameters have been extracted from the AFM images: the correlation length (L_0) and the saturation roughness (R_{sat}) . These two parameters can be modulated treating the polymeric samples with plasma discharges with different gas composition. In particular, this study reveals that L_0 increases and $R_{\rm sat}$ decreases by increasing the content of Ar in the Ar/N₂ microwave discharge. On the other hand the original surface organization of the copolymer is modified by the different plasma treatment; by increasing the Ar content the copolymer structure is randomized and the block-copolymer surface organization obtained by spin casting disappears. The modulation of these surface parameters can be explained by the plasma kinetic properties. By increasing the Ar content in the discharge, the concentration of reactive species decreases but the average energies and fluxes of ions notably increase. Thus, the high energetic Ar ions induce the deepest morphological redistribution of the polymeric chains. Moreover, in a N_2 rich plasma the chemical reactivity of the molecular species becomes dominant, preventing a radical modification of the surface topography but modifying the chemical functionality of the lateral polymeric chains.

The results confirm that plasma techniques can be exploited for modulating with an accurate control the physico-chemical properties of polymeric materials that can enhance the performances of polymer-based devices.

Acknowledgements

The authors thank Dr. Pascal Colpo and Dr. Tarik Meziani for their support in the plasma diagnostics and for fruitful discussions.

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