COMPARATIVE STUDY ON THREE-DIMENSIONAL MORPHOLOGICAL CHANGES OF POLYIMIDE FILMS EXPOSED TO OXYGEN PLASMA AND PULSED UV-LASER

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The ability to pattern polyimides at different length scales has generated considerable interest in various research fields. In this context, a comparative study of the three-dimensional morphological changes induced on aromatic polyimide films, by RF O_2 plasma and pulsed UV-laser exposure is presented. The plasma treatment affects the polymer surface, generating new chemical groups and appearance of granular morphological structures. Instead, for both UV-laser exposure conditions, the surface was characterized by cone-like structures. Depending on the desired application, a convenient surface treatment can be applied to the polyimide films to meet all the requirements regarding morphology, roughness and orientation.

Keywords: polyimide, atomic force microscopy, oxygen plasma, pulse UV-laser, morphology

1. Introduction

Current investigations in physics of materials are focused on analysis of polymer properties. In industrial or medical uses, the polymers' applicability is dependent on the physical, chemical and biological interactions of molecules or

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microorganisms at their surfaces. If a polymer surface does not have the desired properties for a particular application, then undesirable surface events can lead to failure of the material and the device or system containing it. Therefore, in some cases the polymer surface properties are more important than the bulk ones. Particularly, the morphology should be carefully adapted to the pursued utilization. There are many techniques that can be used for modification of the surface properties of the polymer films. They can be divided in two main categories, namely the chemical and the physical methods. The former includes chemical treatments like surface grafting [1] and requires multiple and complicated chemical reactions. The latter category refers to plasma exposure and laser irradiation and is much easier to apply.

Plasma technology offers a unique route for surface patterning results in a smooth, ultrathin polymer films. The various excitation, ionization and dissociation reactions in the plasma generate high-energy and reactive species that interact with polymer film surface improving its wettability, biocompatibility and other related surface properties [2, 3], which are responsible for the resulting biological reactions. Depending on the nature of the working gas, this type of surface modification generates specific functional groups onto the polymer surface that can create favorable compatibility in contact with a biological medium. The interaction of laser with polymer films, which in addition absorb wavelengths similar to the incident polarized radiations, leads to surface structuring of the films. This aspect is useful not only in biomedicine, but also in microelectronics, where the alignment of macromolecular chains can induce guided cell growth and orientation of nematic molecules, respectively.

Through the studied polymer structures, polyimides (PIs) have gained a great deal of attention owing to their outstanding physical properties that are derived from their chemical structure [4]. There are particularly known for their high thermal stability, arising from the heterocyclic imide rings [5]. This property can be further improved by incorporating specific groups on the backbone and/or side groups. Moreover, the combination of rigid imide with aromatic rings leads to excellent mechanical and dielectric properties, as well as high chemical resistance – characteristics useful for microelectronics [6]. In the past years PIs were proven to be biocompatible, being used in preparation of composites highly adhesive to dentine [7], in treatment of arthritis [8] or as cell culture substrates [9].

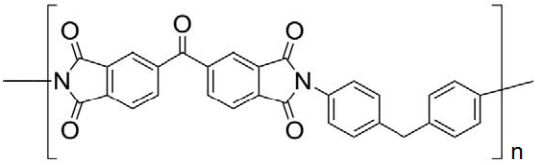
The biomedical applications of these polymers are partly limited owing to their low surface energy. Therefore, it is important to enhance the wettability of PI films by creating specific functional groups at the polymer surface. However, beside the surface chemistry it is very important to control the morphological characteristics in order to obtain a surface relief that is favorable for bio-applications.

Among the aromatic tetracarboxylic dianhydrides used as raw materials for polyimides, 3,3'-4,4'-benzophenone tetracarboxylic dianhydride (BTDA) is a unique bulky, photosensitive, and biocompatible structure, which in combination to the appropriate diamine renders new properties to the resulting imidic compound. Comparatively with other studies performed on the same PI structure modified by plasma or laser exposure [10, 11] the paper highlights new aspects by performing a comparative analysis of the surface features evolution after the treatment procedure. In addition, the morphological changes of the PI film are monitored at nano-scale also through 3D texture parameters, such as amplitude, spatial and functional parameters (*Sdr, Stdi, Vmp* , *Vmc, Vvc* , *Vvv*) that were not previously reported for these investigations. Thus, the performed measurements are opening novel perspectives in optimization of the PI surface features during specific treatments, in order to prove its usefulness in applications directly influenced by the small-scale characteristics [12].

2. Materials and methods

2.1. Film preparation

The polyimide film for atomic force microscopy measurements was obtained by casting the poly(amic acid) (PAA) solution, prepared by the reaction of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) with stoechiometric amounts of 4,4′-diaminodiphenylmethane (DDM) in N-methyl-2-pyrrolidone (NMP) as solvent, on clean glass plates, followed by thermal imidization. The temperature treatment program was presented somewhere else [13]. The chemical structure of the obtained polyimide poly(BTDA-DDM) is presented in Fig. 1.



poly(BTDA-DDM)

Fig. 1. Chemical structure of polyimide poly(BTDA-DDM)

2.2. Plasma treatment

The polyimide film was exposed to oxygen plasma at 30 Watts for 5 and 10 minutes using an Emitech K1050X Plasma Unit with RF generator (Empdirect, Huston, Texas). The power was big enough to accelerate the plasma species

towards the PI surface and the exposure times were not very small in order to generate a roughness that still can be monitored by AFM.

2.3. UV-laser irradiation

Static ablation of polyimide sample was made on a LPX 220 excimer laser operating at 308 nm (XeCl), with pulse duration of 25 ns and an energetic stability of laser beam of minimum 1%. The samples were irradiated with incident fluence of 244 mJ/cm^2. Different number of irradiation pulses (5 and 15) was used. The laser treatment was performed above the ablation threshold with a relatively low number of pulses in order to avoid surface carbonization and also to maintain the roughness at level that allows AFM measurements.

2.4. Atomic force microscopy characterization

Atomic force microscopy (AFM) measurements were performed on Solver Pro-M (NT-MDT, Russia) scanning probe microscope, in air, at room temperature, in tapping mode, with a NSG10 (NT-MDT, Russia) rectangular silicon cantilever. The scan areas of 2x2 μm^2 were characterized by means of texture parameters. The 3D-parameters such as average roughness (*Sa*), surface area ratio (*Sdr*) and texture direction index (*Stdi*) were calculated using the height function $Z(x_i,y_j)$ defined over a rectangular area in the *XY* plane within a uniform grid of dimensions N_x and N_y and of steps Δx, Δy along the *X* and *Y* directions, respectively [14].

Sa, the most used surface roughness parameter, represent the arithmetic mean of the absolute distances of the surface points from the mean plane. Mathematically, *Sa* can be evaluated using equation (1):

$$Sa = \frac{1}{N_x N_y} \sum_{j=1}^{N_y} \sum_{i=1}^{N_x} \left| Z_{ij} \right| \tag{1}$$

with $Z(x_i,y_j)$ taken against the mean surface.

Sdr is defined as the increment of the total surface area relative to the sampling area in the *XY* plane, according to equation (2):

$$Sdr = \frac{\left(\sum_{k=1}^{N_x-1} \sum_{l=1}^{N_y-1} A_{kl} \right) - (N_x - 1)(N_y - 1)\Delta x \Delta y}{(N_x - 1)(N_y - 1)\Delta x \Delta y} \cdot 100\% \tag{2}$$

where: $(N_x - 1)(N_y - 1)\Delta x \Delta y = S2A$ is the projected area (area of the evaluation region taken in the base *XY* plane) and $\sum_{k=1}^{N_x-1}\sum_{l=1}^{N_{y-1}} A_{kl} = S3A$ is surface area (the total area of the sample surface corresponding to the sampling area in the *XY* plane) with A_{kl} defined by equation (3):

$$A_{kl} = \frac{1}{4}\Big(\sqrt{\Delta y^2 + [Z(x_k, y_l) - Z(x_k, y_{l+1})]^2} + \sqrt{\Delta y^2 + [Z(x_{k+1}, y_l) - Z(x_{k+1}, y_{l+1})]^2}\Big) \cdot \Big(\sqrt{\Delta y^2 + [Z(x_k, y_l) - Z(x_{k+1}, y_l)]^2} + \sqrt{\Delta y^2 + [Z(x_k, y_{l+1}) - Z(x_{k+1}, y_{l+1})]^2}\Big) \quad (3)$$

Stdi is defined as ratio of the average amplitude (over angle α), $A(\alpha)$, to its maximum, A_{max}, by the equation (4):

$$Stdi = (1/M)\sum_{j=0}^{M-1} A\left(\frac{\pi j}{M}\right)/A_{max} \quad (4)$$

where M is the number of the radial rays which are drawn at angles $\alpha=\alpha_j=\pi j/M$ ($j=0, 1, \ldots, M-1$) from the central point of the Fourier spectrum image.

The functional volume parameters, peak material volume (*Vmp*), core material volume (*Vmc*), core void volume (*Vvc*) and valley void volume (*Vvv*) are defined from the surface bearing area ratio curves, which is also called the Abbott curve [15].

Vmp and *Vmc* represent the volume of material comprising the texture from the highest peak to the height corresponding to a 10 % material ratio level and the texture between heights corresponding to the material ratio values of 10 % and 80 %, respectively.

Vvc and *Vvv* represent the volume of air bounded by the texture at heights corresponding to the material ratio values of 10 % and 80 % and by the texture from a plane at a height corresponding to a material ratio level of 80 % to the lowest valley.

3. Results and discussion

In order to perform the atomic force microscopy (AFM) measurements under optimal conditions, first some optimization experiments were made. To investigate the influence of the scanning area on the average roughness, multiple scans were carried out over square areas with sides starting from 0.25 μm to10 μm, on poly(BTDA-DDM) film surface. The cantilever oscillation amplitude was

kept constant by means of a current of 10.5 nA and the scan frequency was 1.56Hz. As observed in Fig. 2, where is presented the graphical representation of the evolution of *Sa* with respect to the scanning length (L_{SC}), the roughness increases when increasing scanning area until reaches a plateau starting from 2 μm, due to its uniformity. In this plateau region, the standard deviation of the Sa values was very low, STDEV=0.02 nm.

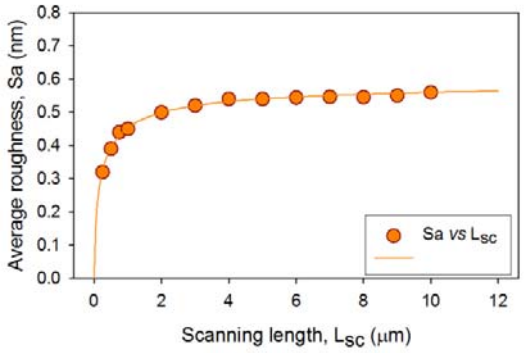


Fig. 2. Graphical representation of the average roughness (*Sa*) calculated for the pristine poly(BTDA-DDM) film surface, with respect to the scanning length (L_{SC})

Taking into consideration these results, the scan length of 2 μm was used in the following measurements, because the morphological features were easily observed. Also, proper scanning conditions were established, for which the AFM images present good contrast and resolution, avoiding undesirable image artifacts and unrealistic values for the amplitude, spatial and functional 3D texture parameters.

Fig. 3 present the bi-dimensional and three-dimensional topographical AFM images obtained for the pristine poly(BTDA-DDM) film, after the optimization process.

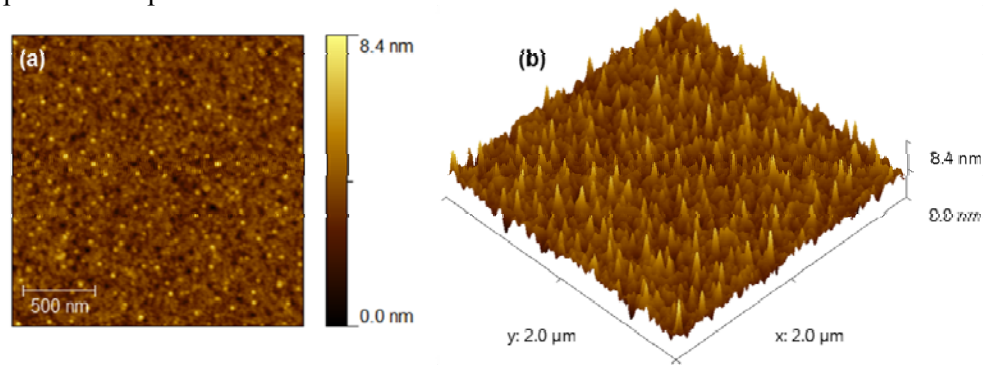


Fig. 3. Topographical AFM images of pristine polyimide film

The untreated film show uniform and flat surface morphology, derived from the manner in which the polymer chains are arranged during thermal imidization procedure [16]. The existence of a smooth surface was indicated and confirmed also by the low values of average roughness and surface area ratio presented in Table 1. Also, the high value obtained for texture direction index indicates strong isotropic morphology.

In order to improve the surface properties of the BTDA-derived polyimide for biomedical applications fields, as substrate materials in bio-micro-electromechanical-systems [17], or as microstructured substrates for contact guidance of osteoblast cell growth, the film was treated using oxygen plasma. This kind of plasma can cause the sputtering of some atoms from the surface and their substitution by oxygen atoms, producing highly polar groups (hydroxyls, carbonyls or carboxylic groups) at the surface by breaking the imide and benzene rings and forming new polar species of C–O and C–N–C [18]. These potential processes will induce the increasing of the surface polarity and wettability.

In Fig. 4 are presented the bi- and three-dimensional AFM topography images obtained after poly(BTDA-DDM) film was exposed to RF O_2 plasma (30 Watts) for 5 and 10 minutes. As we can see in Fig. 4a and b, when the treatment time was 5 minutes, the plasma treatment affects the polymer surface, generating new chemical groups and modification of the morphological structures to nanometer-scaled grains.

In this case, the calculation of the 3D-dimensional texture parameters indicate significantly higher values for *Sa* (5.2 nm) and *Sdr* (4.53 %), comparing to the values obtained for the pristine sample (*Sa*=0.5 nm and *Sdr*=0.21 %.). As the plasma exposure time was increased from 5 to 10 minutes, the AFM images presented in Fig. 4c and d have highlighted a more pronounced grainy morphology over the scanning area of 2x2 μm^2, confirmed by the values of the 3D texture parameters, namely *Sa*=9.7 nm and *Sdr*=14.97%. Moreover, according to the values obtained for *Stdi*, no preferential direction of the surface morphology was observed after plasma treatment.

The evolution of the functional volume parameters (*Vmp*, *Vmc*, *Vvc*,*Vvv*), calculated from Abbott–Firestone curves [15], with the increase of the exposure time (Table 1) indicate a well-defined nanostructured surface relief, favorable for the desired applications, such as substrates for cells culture, due also to the additional surface functionalization induced by RF O_2 plasma.

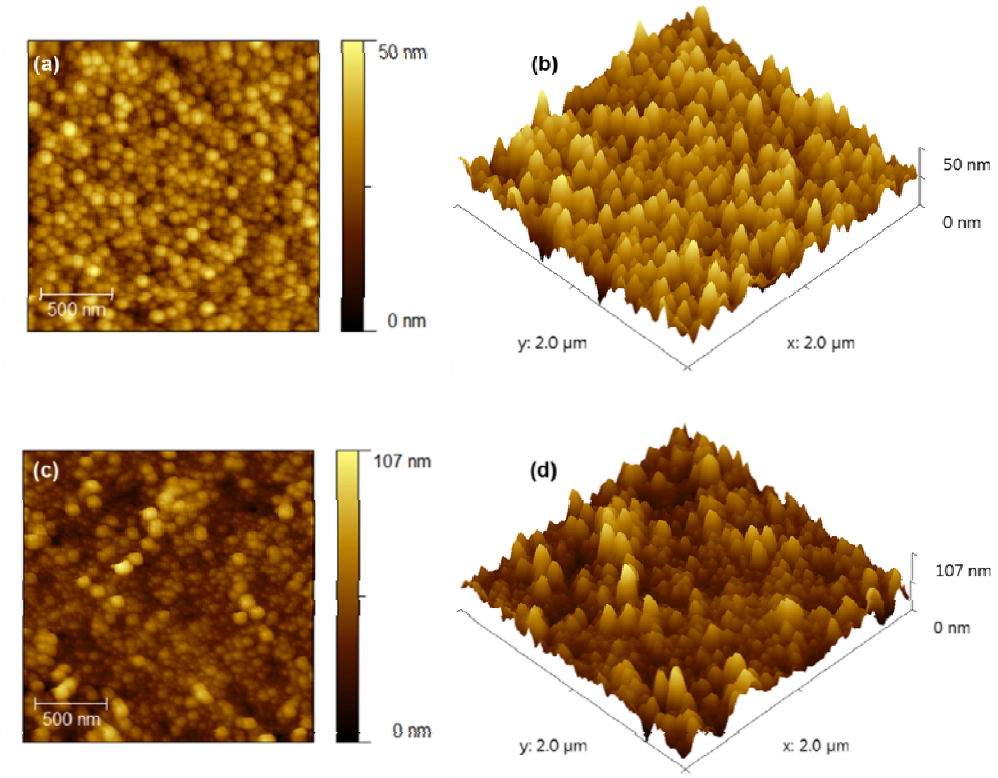


Fig. 4. Topographical AFM images of polyimide film exposed to oxygen plasma (30 Watts) for 5 minutes (a, b) and 10 minutes (c, d)

On the other hand, since for the synthesis of poly(BTDA-DDM) were used monomers containing photosensitive groups, this polyimide film is suitable to be modified, functionalized and etched by pulsed UV-laser micromachining, for tissue engineering and microelectronics purposes.

In Fig. 5 are displayed the height AFM images obtained for polyimide film after UV-laser exposure with the fluence of 244 mJ/cm^2, using 5 and 15 pulses of irradiation. The surface topography was characterized by the appearance of cone-like structures [11] uniformly distributed over the surface, with no agglomeration tendency, unlike the granular structures achieved after O_2 plasma treatment. The aspect and dimensions of these cone-shaped structural formations depend on the laser irradiation conditions. For 5 pulses of irradiation, the formations exhibit a bumpy aspect, as seen in Fig. 5a and b. Instead, the increasing of number of irradiation pulses induces formations with cliff-like shape and with heights almost doubled, as distinguished in Fig. 5c and d.

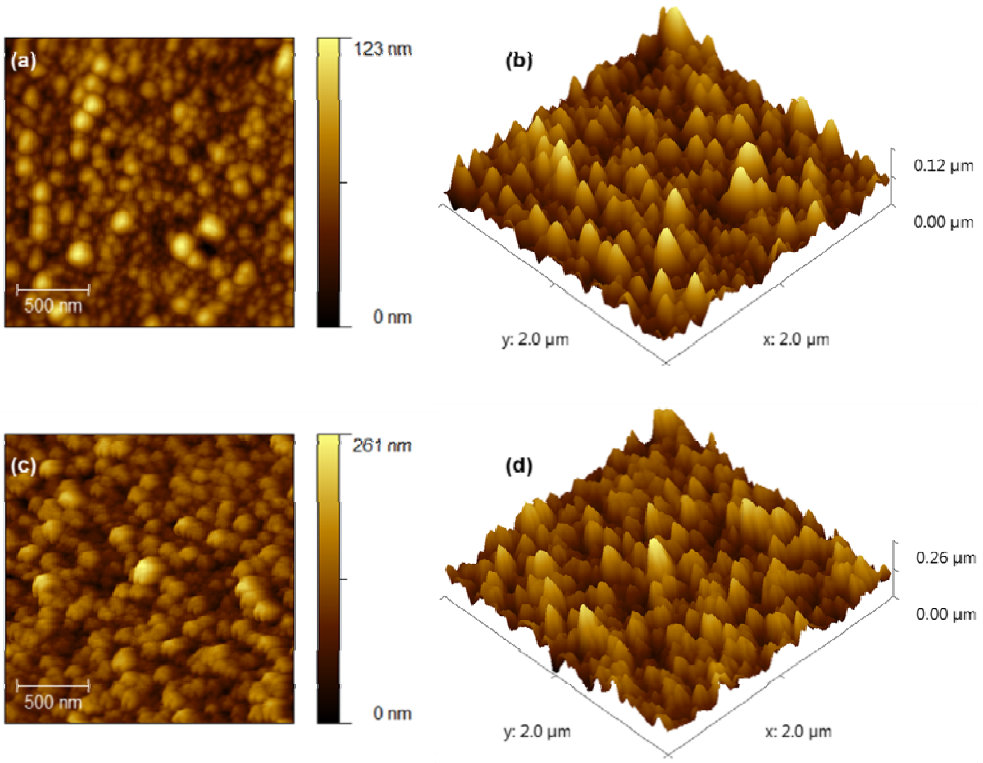


Fig. 5. Topographical AFM images of polyimide film after UV-laser irradiation with the fluence of 244 mJ/cm^2, using 5 pulses (a, b) and 15 pulses (c, d).

Table 1

3D-roughness parameters calculated from the AFM images

Parameter	Unit	poly(BTDA-DDM)				
		Pristine	O_2 plasma exposure		UV-laser exposure	
			30W, 5 min	30W, 10 min	244 mJ/cm^2, 5 pulses	244 mJ/cm^2, 15 pulses
Sa	(nm)	0.5	5.2	9.7	13.5	27.7
Sdr	(%)	0.21	4.53	14.97	17.79	97.27
Stdi	-	0.86	0.78	0.740	0.53	0.74
Vmp	(nm^3/nm^2)	0.06	0.32	0.97	1.27	2.05
Vmc	(nm^3/nm^2)	0.54	5.72	10.17	14.36	30.82
Vvc	(nm^3/nm^2)	0.73	8.51	16.80	23.12	44.29
Vvv	(nm^3/nm^2)	0.08	0.64	1.07	1.39	3.05

The surface morphology has dictated the roughness evolution, from 13.5 to 27.7 nm and the surface area ratio from 17.79 to 97.27 %. The lower value of *Stdi* obtained when 5 pulses of irradiation were used (Table 1) indicate a slight anisotropy, probably induced by a mild order of the surface formations in a certain

direction. The improved functional volume parameters noticed after pulsed UV-laser exposure make the poly(BTDA-DDM) film a good candidate for microelectronics.

4. Conclusions

A comparative study of the surface textural changes induced on films of aromatic polyimide, prepared from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 4,4'-diaminodiphenyl methane, by RF oxygen plasma and by pulsed UV-laser exposure was presented. In order to perform the atomic force microscopy (AFM) measurements under optimal conditions, first some optimization experiments were made. Thus, proper scanning conditions were established, for which the AFM images present good contrast and resolution, avoiding undesirable image artifacts and unrealistic values for 3D texture parameters. Further AFM measurements reveal uniform and flat surface morphology for the untreated film, derived from the manner in which the polymer chains are arranged during thermal imidization procedure. The plasma treatment produced surface functionalization and modification of the morphological structures to nanometer-scaled grains. The UV-laser exposure induced the modification of the surface topography from a smooth, with some irregular features, to a surface characterized by the appearance of cone-like features. It can be concluded that, depending on the required application, a convenient surface treatment can be applied to the polyimide films. The main achieving of this work is reflected in the surface analysis manner that starts from the concept of the texture amplitude, spatial and functional volume parameters. They are sensitive to nano-scale modifications of the polymer morphology exposed to physical or chemical factors. Thus, the new data reported in this paper are helpful in understanding and optimizing the topographical characteristics of treated PI films in order to make them suitable for microelectronic and bio-applications.

Acknowledgments

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