OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 3, No. 8, August 2009, p. 812 - 816

Laser ablation influence on untreated and chemical-treated poly(ethylene terephthalate) films surfaces

M. AFLORI*, M. DROBOTA, M. OLARU, I. STOICA, G. HITRUC
"Petru Poni" Institute of Macromolecular Chemistry, 41A Ghica Voda Alley, 700487 Iasi, Romania

The aim of this study was the evaluation of the excimer laser ablation effect on poly(ethylene terephthalate) (PET) film surfaces by means of atomic force microscopy (AFM), Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) and contact angle measurements. Nitrogenous groups were introduced onto PET films through triethylenetetraamine (TETA) by chemical treatments. Laser ablation on both untreated and treated biaxially stretched samples provided the formation of superposed "nap" and "wall-type" structures. The size, distances between these types of surface arrangements and the root-mean-square roughness (RMS) of the ablated surfaces were found to depend on the initial chemical conditions of PET films.

(Received in revised form June 01, 2009; accepted July 20, 2009)

Keywords: Excimer laser ablation, Poly(ethylene terephthalate), Atomic force microscopy, FTIR-ATR

1. Introduction

The research activities in the field of excimer laser ablation, firstly described in 1982 [1, 2], were rapidly grow in the following years due to the possibility to produce high quality structures of micrometric dimensions in all kinds of materials. Today, a lot of fundamental and practical knowledge is available on laser ablation, being widely used in the prototyping of micro-devices [3]. Within this context, of particular interest are the methods which allow the control of surface properties, e.g., for micro channels, thus enabling the optimization of the final device [4, 5]. Laser ablation as a means of polymer surface treatment allows modification of the morphology, chemistry, and texture of the material surface. The type and extent of modification depends upon several factors including the laser wavelength and fluence, the absorption index of the polymer at the laser wavelength, and the atmosphere in which the treatment occurs [6].

Poly(ethylene terephthalate) (PET) exists both as an amorphous (transparent) and as a semi-crystalline (opaque) thermoplastic material. The semi-crystalline PET has good strength, ductility, stiffness and hardness, while the amorphous one has better ductility but less stiffness and hardness. Amorphous PET film and sheet can be used in the field of food trays, lids, cups, domes, clamshells, partition-trays and also clear-cartons, blister-packs, stationary goods, carrier tape for IC chip, vacuum forming, folding boxes, offset printing, screen printing, a.s.o. [7]. Recent applications [7] have been focused on the development of diverse techniques and treatments in order to obtain textiles with superior hydrophobic properties. Through semi-crystalline PET laser ablation, several surface effects have been identified including amorphization of the surface material, surface chemical changes, as well as surface texturing and changes in hydrophilicity depending on laser pulse number [8-10].

Surface texture effects of laser irradiation are of interest in any materials application. Four types of PET ablated surface structures were reported in literature: LIPSS (Laser Induced Periodic Surface Structures), dendrites, cones and "nap-type" or "wall-type" structures [11]. Among the various different types of noncoherent structures are wall- and nap-type ones that develop on stretched polymer foils and fibers during laser ablation [12]. Their formation has been attributed to the different optical and thermal properties of amorphous and crystalline regions within these polymers entailing differences in ablation rate [13], to hydrodynamic instabilities [14, 15] and to non-uniform laser-induced defect formation within the polymer surface [16]. However, detailed investigations have clearly demonstrated that the formation of such structures is closely related to internal stresses within the foils or fibers [17]. Uniaxial stretching prior to laser-light irradiation results in wall-type structures with one-dimensional periodicity, while biaxial stretching gives rise to nap-type structures (two-dimensional periodicity).

Previous study [18] demonstrated that nitrogenous groups can be introduced onto the surface of PET films through amines with different chain lengths. The effectiveness of the treatment was improved with the increase of the reaction time [19], although an advent of the degradation process has been registered in case of longer time exposure (higher than 30 minutes).

In the present work, the influence of surface chemical treatments on structural changes induced by laser ablation was evidenced. As a precursor for laser ablation was used a PET film treated (short reaction time) with triethylenetetraamine (TETA).

2. Experimental results and discussion

A biaxially drawn PET film (commercial), with a thickness of 30 μm was used after ultrasonic cleaning with toluene, acetone and tri-distilled water. Then the samples were dried at 40o C and stored in a closed vessel.

AFM measurements were performed in air at room temperature, in the tapping mode using a Scanning Probe Microscope (Solver PRO-M, NT-MDT, Russia) with commercially available NSG10/Au Silicon cantilevers. The manufacturer's values for the probe tip radius were 10 nm, and the typical force constant was 11.5 N/m. In the tapping mode, the cantilever is oscillated at a frequency of 254.249 kHz, over a 5 x 5 μm^2 scan area, 256 x 256 scan point size images being thus obtained for each sample. The root-mean-square roughness (RMS) was calculated as the average value for the set of AFM frames of certain scales.

The modifications of PET surface structure were examined by FTIR-ATR spectroscopy in the wavenumber range 600-1800 cm^{-1}. The spectra were recorded on a BRUKER VERTEX 70 spectrometer at a resolution of 2 cm^{-1} and an incidence angle of 45^o. The signal-to-noise ratio was improved by co-adding 128 scans per spectrum. Peak height measurements were performed with the spectral analysis software (Opus 5).

Contact angle measurements were performed with a CAM 101 Contact Angle Goniometric System, KSV Instruments LTD, Finland.

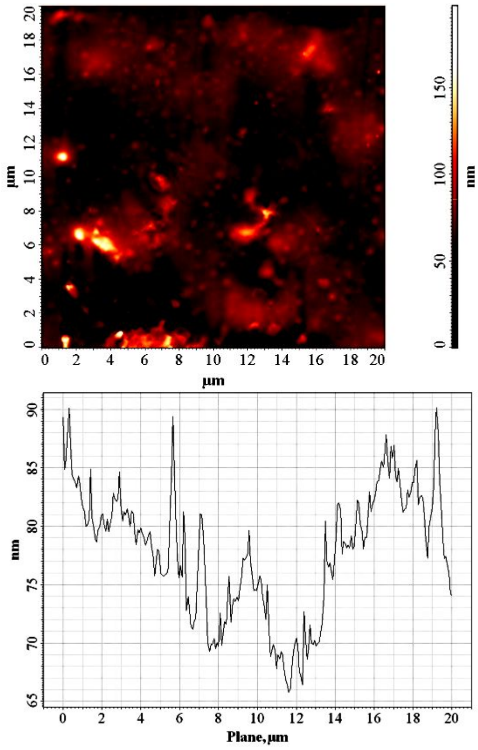

Fig. 1. Untreated PET: (a) AFM image, b) Surface profile

The PET film samples (25 x 25 mm) were submitted to triethylenetetraamine action (TETA), product used as aminolysis reagent in dark, at 90^o C for 10 min, in an oven. The sandwich model was used: two PET films samples were separated through the medium of amine. After exposure, the treated samples were rinsed with methanol and tri-distilled water with ultrasonically cleaning to remove excess of reagent. It was previously established [20] that, under the proposed conditions, the reaction with TETA occurs exclusively in the thin surface layer of the film via a macromolecular scission mechanism.

The PET static ablation (i.e., the sample is not moving during the irradiation) was realized by using a COMPexPRO (Coherent) excimer laser operating at 248 nm (KrF), which has an energetic stability of laser beam of min. 1% and allows an homogeneous profile of laser beam.

A single pulse of 30 nsec was used on both the chemical treated and untreated samples, at a fluence of 118 mJ/cm^2 and a discharge tension of 19 kV. Treatments were carried out in a room air environment. With only 1 laser pulse, the surface topography changed dramatically from an original smooth surface (Figures 1, 2) to a surface characterized by the appearance of hills and grooves (Figures 3a, 4a). The increases of RMS values from 1.39 nm in the case of untreated PET to 3.30 nm for the chemical treated one, as well as from 3.96 nm for the ablated PET to 8.64 nm in case of the chemical precursor treatment followed by laser ablation were registered. The distance hills-to-grooves ranges from 400 nm (Figure 3b) to 1.4 μm (Figure 4b). An increase of RMS values can be associated with the increase of the newly formed structures size.

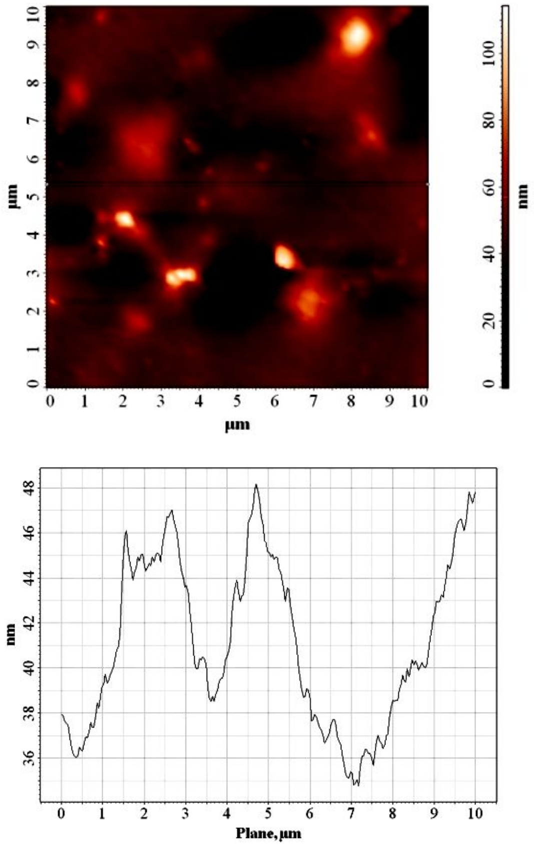

Fig. 2. Chemical-treated PET (a) AFM image, b) Surface profile

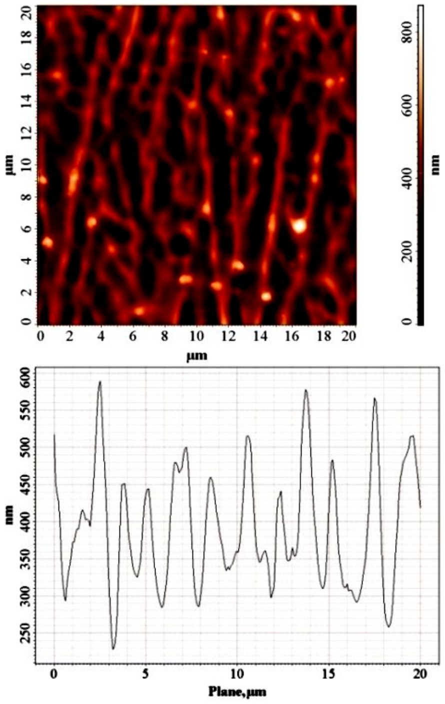

Fig.3. Untreated PET after laser ablation (a) AFM image, b) Surface profile

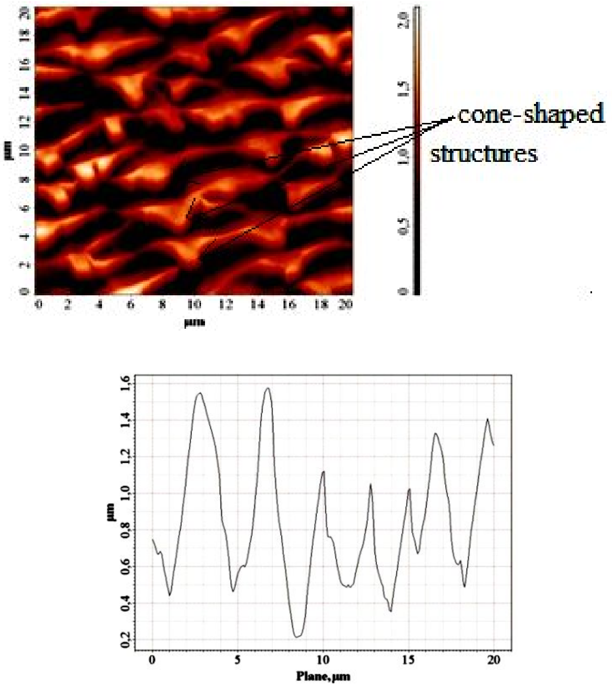

Fig. 4. Chemical-treated PET, after laser ablation (a) AFM image, b) Surface profile

With ablation, a regular, characteristic rolling texture effect is observed in the present study, with the formation of surface arrangements that can be regarded as superposed wall- and nap-type structures (static structures) with feature sizes in the nanometer (700 nm, Figure 3b) and micrometer (1.5 µm, Figure 4b) ranges that are developing upon laser irradiation at a fluence (118 mJ/cm^2) above PET ablation threshold (around 30 mJ/cm^2).

The superposition of wall and nap-type structures from PET surface can be attributed to the different extent of stretching on the two directions of the biaxially film, correlated with the different temperature values in the superheated surface material. The temperature gradients in combination with the brevity of the radiation dose result in molten portions of surface material that flow by convection around more dense portions of material. Furthermore, the borders between the static structures, which are visible through AFM measurements, are consistent with a self-organizing mechanism [15], with the formation of close-packed structures in which heat generated due to absorbed laser energy creates a thin, viscoelastic, and highly compliant layer (above the glass transition temperature) [21]. The appearance of such types of structures is similar to aligned mountain chains.

Taking into account the relationship between the optical characteristics of the laser beam and periodic surface structures with spacing and direction, the static structures are related to the number of laser shots. The literature evidences that the first pulse is causing mainly a rough surface, while subsequent pulses create periodic static structures [22].

Upon the laser pulse exposure, a rapid cooling of the surface is taking place, with the obtaining of an amorphous surface layer, with lower molecular weight and lower density than the bulk polymer. As follows, the front edge of a pulse of radiation is absorbed by a volume of surface material, leading to vaporization. The resulting plume of vaporizing gas partially blocks the remainder of the pulse, allowing only to a fraction of the remaining energy to pass through to the newly created polymer surface. The energy transmitted to the new surface is then primarily converted into heat, often reaching temperatures above the melting point of the polymer (around 265°C for PET). Due to the short span of the radiation treatment, the surface then undergoes a quench, freezing an amorphous structure into an otherwise relatively crystalline polymer [23].

Watanabe et al. tested the hydrophilicity relative to untreated PET by a dynamic wettability measurement, which indicated a hydrophilic surface for single pulse irradiation with fluencies below the ablation threshold, and a hydrophobic surface, if the fluence was above the ablation threshold [10]. In the present study, the measurements of contact angles both on unmodified and smooth ablated PET (untreated 54°, chemical treated 49°, laser ablation of the untreated 82°, laser ablation on chemical treated 79°) can be correlated with the different chains orientation of the amorphous PET layers, taking into account that such a conformational change results in a decrease of the number of OH groups at the surface and, therefore, in an increase of the surface hydrophobicity.

FTIR-ATR spectroscopic measurements (Figure 5, a) illustrate a decrease of the intensities of the absorption bands corresponding to crystalline PET, as well an increase of the ones belonging to the amorphous PET layer after laser ablation at 248 nm, as a consequence of PET amorphization and not specifically from crystallites reorientation [24]. Moreover, a new strong absorption at about 1648 cm^{-1} assigned to the amide I band, which has a main contribution of the stretching vibration, -C=O, was evidenced in FTIR-ATR spectra. The amide II band, mainly decided by NH bending vibration (-NH) (Figure 6) appears at around 1549 cm^{-1}. From ATR-FTIR studies it was found that the normalized peak intensity for both amide I and amide II bands increased during chemical treatment of PET with TETA and laser ablation. One to be mentioned is that, during aminolysis, the carbonyl group from PET can serve as proton acceptor through hydrogen bonding interactions, thus causing a blue shift in the FTIR-ATR spectrum (3 cm^{-1}, Figure 5). Upon laser ablation, the area of the trans bands (related to the crystalline part) from 970 cm^{-1} (trans - extended) and 1340 cm^{-1} (trans), decreased as compared with the gauche bands one (connected with the amorphous structure) from 898 cm^{-1} (gauche - relaxed) [25] and 1370 cm^{-1} (gauche) conformers, respectively (Figure 5 a, b). The fraction of trans conformer (T) was calculated taking in account the areas of the two bands located at 1340 cm^{-1} (A_{1340}) and 1370 cm^{-1} (A_{1370}), respectively, assigned to trans and gauche conformers, by the following equation [24]:

$$T = \frac{A_{1340}}{A_{1340} + 6.6 \times A_{1370}} \qquad (1)$$

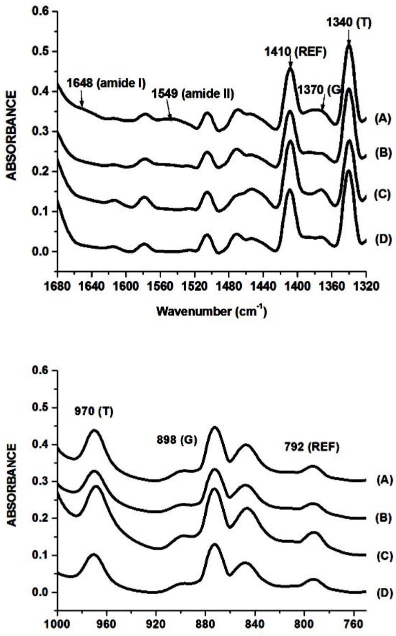

Fig.5. FTIR-ATR spectra in the following ranges: a) 1680-1320 cm-1; b) 1000-760 cm-1 of the samples: (A) laser ablation on chemical treated PET,(B) chemical treated PET, (C) laser ablation on untreated PET, (D) untreated PET

The fraction value calculated with formula (1) is decreasing in case of laser ablation on both untreated and chemical-treated PET surfaces, proving the mechanism of amorphization described herein before. The percent value of trans conformer was about 37.5 ± 2.5 %, thus evidencing a lower degree of structural order at the PET surface, as well as the decrease of the polymer film crystallinity. The percent of conformer can be estimated also taking into consideration the bands area positioned at 973 cm^{-1} and 898 cm^{-1}. In the latter case, a fraction of about 35 ± 2 % of the trans conformer fraction was found. As follows, for the trans conformer fraction, values of 27 % in case of laser ablation of the untreated PET, 20 % for PET chemical treated with TETA and 18 % for laser ablation on chemical treated PET were obtained.

3. Conclusions

Upon excimer laser irradiation, periodic surface patterns consisting of superposed wall- and nap-type structures were evidenced on both treated and untreated PET films. Upon single pulse laser ablation above ablation threshold, topographical structure changes attributed to the different geometrical orientation of the amorphous surface layers and the formation of cone-shaped type units were developed as a consequence of the different extent of stretching for the two directions of the biaxially PET films. Owing to the simplicity of this irradiation procedure, large-scale surface treatments could be done, with the improvement of the surface properties for different applications where the nano/micro roughness of the ablated surfaces is a key factor.

Further investigations will be focused toward the examination of multiple pulses influence on PET surface and the study of fundamental process underlying the formation of the nano/micrometric structure in polymers upon laser irradiation, in order to obtain an architecture that could provide adequate reactor sites to promote adhesion of endothelial cells.

Acknowledgements

This research was supported in part by the National University Research Council, Romanian Ministry of Education and Research, under project nr. 83/Cp/13.09.2007, acronym LASERLAB. The authors thank to Mr. Corneliu Cotofana for laser ablation data presented on this paper.

References

[1] Y. Kawamura, K. Toyoda, S. Namba, Appl. Phys. Lett. **40**, 374 (1982).
[2] R. Srinivasan, V. Mayne-Banton, Appl. Phys. Lett. **41**, 576 (1982).
[3] M. A. Roberts, J. S. Rossier, P. Bercier, H. Girault, Anal. Chem. **69**, 2035 (1997).
[4] C. S. Effenhauser, Microsystem technology in chemistry and life science 194, Springer, Berlin, 1998.
[5] J. S. Rossier, P. Bercier, A. Schwarz, S. Loridant and H. H. Girault, Langmuir **15**, 5173 (1999).
[6] L. D. Laude, D. Martinez, C. Dicara, F. Hanus, K. Kolev, Nucl. Instrum. Methods Phys. Res. B **185**, 147 (2001).

[7] R. Morent, N. De Geyter, J. Verschuren, K. De Clerck, P. Kiekens, C. Leys, Surf. Coat. Tech. **202,** 3427 (2008).

[8] R. Srunivasan, Appl. Phys. Lett. **41**, 576 (1982).

[9] J. Anzano, M.E. Casanova, M.S. Bermúdez, R.J. Lasheras, Polym. Test. **25**, 623 (2006).

[10] H. Watanabe, T. Takata, M. Tsuge, Polym. Int. **31**, 247 (1993).

[11] R. Srinivasan, V. Mayne-Banton, Appl. Phys. Lett. **41**, 576 (1982)

[12] D. Bäuerle, Laser Processing and Chemistry, 3rd ed. Springer, Berlin, 2000.

[13] Y. Novis, J. J. Pireaux, A. Brezini, E. Petit, R. Caudano, P. Lutgen, G. Feyder, S. Lazare, J. Appl. Phys. **64**, 365 (1988).

[14] T. Bahners, E. Schollmeyer, Angew. Makromol. Chem. **151**, 39 (1987).

[15] T. Bahners, E. Schollmeyer, J. Appl. Phys. **66**, 1884 (1989).

[16] V. I. Emelyanov, K. I. Eriomin, Proc. SPIE **3343**, 1056 (1998).

[17] E. Arenholz, J. Heitz, V. Svorcik, D. Bäuerle, in Excimer Lasers, edited by L. D. Laude, NATO Adv. Stud. Instit. Series E: Appl. Sci. **265**, 237 (1994).

[18] M. Aflori, M. Drobota, D. Timpu, V. Barboiu, Optoelectron. Adv. Mater. – Rapid Comm. **2**, 291 (2008).

[19] E. Rusu, M. Drobota,V. Barboiu, J. Optoelectron. Adv. Mater. **10**, 377 (2008).

[20] B. Mangovska, C. Bogoeva-Caceva, A. Pohlers, J. Appl. Polym. Sci. **62**, 605 (1996).

[21] N. S. Murthy, R. D. Prabhu, J. J. Martin, L. Zhou, R. L. Headrick J. Appl. Phys **100**, 023538 (2006).

[22] Z. Ball, R. Sauerbrey, Laser Ablation and Desorption, **30**, Academic Press, San Diego, 1998.

[23] F. R. Wagner, PhD thesis, EPFL Lausanne, France, 2000.

[24] J. H. Walton, M. J. Liza, M. S. Conradi, T. Gullion, J. Schaefer, Macromolecules **23**, 416 (1990).

[25] A. Ajji, J. Guevremont, K. C. Cole, M. M. Dumoulin, Polymer **37**, 3707 (1996).

---

[*] Corresponding author: maflori@icmpp.ro