



Scanning-probe-microscopy of polyethylene terephthalate surface treatment by argon ion beam



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ABSTRACT

The effect of argon (Ar^+) ion beam treatment on the surface of polyethylene terephthalate (PET) samples was studied by scanning probe microscopy (SPM) and the changes in surface topography were assessed by atomic force microscopy (AFM). Kelvin probe force microscopy (KPFM) sheds light of adhesion force between treated polymer films and a Pt/Cr probe under dry conditions, obtaining the contact potential difference of material. As a result of Ar^+ ion bombardment, important surface chemical changes were detected by X-ray photoelectron spectroscopy (XPS) measurements such as chains scission and incorporation of nitrogen species. Ion beam treatment increases the surface roughness from 0.49 ± 0.1 nm to 7.2 ± 0.1 nm and modify the surface potential of PET samples, decreasing the adhesive forces from 12.041 ± 2.1 nN to 5.782 ± 0.06 nN, and producing a slight increase in the electronic work function (Φ_e) from 5.1 V (untreated) to 5.2 V (treated). Ar^+ ion beam treatment allows to potentially changing the surface properties of PET, modifying surface adhesion, improving surface chemical changes, wetting properties and surface potential of polymers.

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1. Introduction

Polyethylene terephthalate (PET) is a thermoplastic polymer produced by condensation from ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, a di-alcohol and dimethyl terephthalate $\text{CH}_3\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{CH}_3$, a di-ester. Polymeric materials such as PET are increasingly replacing the traditional engineering materials based on metals such as steel and aluminum, due to their superior properties such as better corrosion resistance, high strength to weight ratio, relatively low cost and easy recycling. According to the above, it can be possible to obtain materials with high physicochemical properties for aeronautics, automotive, civil construction and biomedical applications [1–4]. However, most polymers are innately hydrophobic and pose low surface energy, thus limiting the establishment of strong interactions between them and other materials. Polymer surface modification allows to increase the surface energy in order to make them useful for different commercial applications. The ways in which treatments affect the performance of certain surface

functions can be reflected in the potential distribution of the material surface. Several surface modification methods have been employed to modify polymer surfaces, including thermal, mechanical, electrical and plasma treatments [5–7]. Physical, chemical and photochemical effects are known to occur during plasma treatment of polymers, without affecting their bulk properties. Surface cleaning, activation, dehydrogenation, modification of polarity/wetting properties, crosslinking, chain scission, degradation and surface structural modification are some examples [8]. Plasma treatment, either at reduced or atmospheric pressure, represents an efficient tool for polymer modification. In an opposite manner to ionic bombardment, during the plasma treatment, the polymeric surface is subjected to several interactions with various reactive species, e.g., ions, radicals, excited and metastable species and photons. All of them will induce the surface modification leading to a more complex chemistry. Such modification takes place in a thin layer onto the surface compared to that one induced by the ion beam treatment, although the effect of the ion energy in the latter case is more significant compared with plasma treatment [9].

Ion beam bombardment is considered a useful tool for surface processing and chemical modification of polymers at the submicron scale [10,11]; this is mainly due to the high energy provided

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by ion irradiation within the upper layers (few μm) of polymer surfaces. Ion beam irradiation promotes interaction between an ion and polymeric film in elastic/inelastic collision, thus producing different phenomena such as chains scission, sputtering evaporation, carbonization, ionization and free radicals which can produce important surface chemical changes or surface degradation of polymer [12]. Actually, low-energy ion beam has recently received increased attention because of its feasibility in the industry of surface modification because it is a fast process at low cost, compared with other systems. The energy produced at the atomic scale in polymer surface results from both electronic ionizations (electronic energy loss) and direct collisional displacement of the target atoms (nuclear energy loss). Further, nonlinear responses of materials cause intense local excitations that produce significant changes in the surface potential of polymers [6]. In this regard, Tóth et al. [13] used low energy ion beam to modify the surface of polymer with low ion dosages, producing important chemical changes and improving the mass transport properties of gases in treated polymer membranes. Ion beam irradiation can induce important optical and rheological changes on polystyrene and polyimide surfaces; such changes strongly depend upon the chemical structure of polymer, ion doses and ion energy irradiated [14,15].

Kelvin probe force microscopy (KPFM) is an important technique that allows simultaneously obtaining the surface morphology and the electronic surface potential at the nanoscale. KPFM was introduced as an instrument to measure the local contact potential difference (CPD) between a conducting tip in the atomic force microscopy (AFM) and the sample. It allows mapping the work function or electronic surface potential of one sample with high spatial resolution [16]. KPFM helps monitor the electronic work function (Φ_e) of surfaces at atomic or molecular scales, where Φ_e is the energy necessary to remove an electron from the bulk material in vacuum and is related with the microstructural properties of a given material, including catalytic activity [17], surface reconstruction [18], doping and band-bending of semiconductors [19], charge trapping in dielectrics [20] and corrosion [21]. The map of the electronic work function produced by KPFM also gives information about the composition and electronic state of local structures on the surface of solids [22]. KPFM has been successfully employed to investigate different systems including inorganic and organic thin films [23,24] as well as proteins [25] across multiple length scales, from meso- to nano-scopic scale [26]. Recently, KPFM has also been used to study the electrical properties of biological materials [27]. The local electronic surface potential in a heterogeneous film is a direct reflection of its biomolecular structure.

Different references demonstrate the potential of KPFM in the field of hydride nanocomposites applied to organic semiconductor devices [28–30]. In this case, the work function depends on either the distribution, the shape of metallic particle or on the metallic layer process with or without pre-treatment. It could increase significantly (from 0.4 eV to 1 eV) after oxygen plasma and the surface potential could be shifted cathodically by the reductive plasma and anodically by the oxidative plasma. Besides these applications, KPFM has been also applied in polymer field, where KPFM experiments pointed out that a significant increase in the surface potential of polysilsesquioxane occurs with low-pressure O_2 plasma, in contrast to that with high-pressure O_2 plasma treatment [31].

In this work, polyethylene terephthalate (PET) samples were subjected to surface treatments with Ar^+ ion beam, in order to study the effect produced on surface topography, surface chemical changes, adherence and contact potential difference (CPD) measured by atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM).

2. Materials and methods

2.1. Samples preparation

PET samples (Melinex[®]) with dimensions of $10.0 \text{ mm} \times 10.0 \text{ mm} \times 2.0 \text{ mm}$ were treated under Ar^+ ion beam using an ion beam milling (Leica EM TIC 3X) working at low chamber pressure of 1×10^{-5} mbar and cooling with liquid nitrogen in order to limit the thermal effect of ionic bombardment. The ion energy was varied in the range of 1.0–5.0 keV, current intensity from 1.0 mA to 2.0 mA, with an average ion beam dose of 1×10^{15} ions/ cm^2 and depth of penetration about 10 nm. The ion beam treatment was done into a circular area of 2.5 mm diameter, during 3 min. The treatment conditions for the argon ion beam are listed in Table 1, where PET_1 is the untreated sample.

2.2. Samples characterization

After Ar^+ ion beam treatments, the characterization of PET samples was performed with atomic force microscope (AFM NanoScope IV-Dimension 3100, Digital Instruments, Bruker) in the conventional tapping mode. In this way the topography and the surface roughness was obtained. Force–distance curves to determine adherence force (cut-off) or adhesion force between the sample surface and the AFM probe were the average of the measurements made in three different areas of each sample. Moreover, surface potential or contact potential difference (CPD) was determined by the Kelvin probe force microscopy (KPFM) technique. Probes used in this study were conductive Pt/Cr coated silicon probes (Budget Sensors, ElectriMulti75) with nominal first resonant frequency of 75 kHz, 3 N/m spring constant, 225 μm length, and tip radius lower than 25 nm. Polycrystalline gold film was used as a reference of the CPD measurements. According to the literature, the electronic work function of gold film is in the range of 5.30–5.34 eV; for KPFM measurements a value of 5.3 eV in gold film as a reference is typically used [23].

To analyze the chemical changes in the PET surfaces samples, XPS measurements were performed using an Alpha 110 instrument of Thermo Electron (East Grinstead, UK) equipped with a monochromatic Al- $K_{\alpha 1}$ source, photon energy of 1486.7 eV and a seven-channel hemispherical detector, assembled by Intercovamex with a pass energy of 15 eV.

Force–distance curves have been used for the study of materials properties and the characterization of surface forces. Values of the adhesion force between the sample surface and the tip of the probe can be obtained from these curves. The force–distance curves show a discontinuity, i.e., a jump-off-contact occurs when the tip of the probe withdraws off the sample. This behavior is produced when the cantilever elastic force is larger than the adhesive forces. The difference between minimum cantilever deflection before cut-off and the deflection of the relaxed probe is used for the estimation of the adhesive force. The force–distance curves measured in this work were obtained for different points in the sample surface.

3. Results and discussion

3.1. Surface chemical changes

In order to analyze the surface chemical changes in PET films produced by ion beam treatment (2.5 keV and 5.0 keV) XPs measurements were performed and compared with pristine sample. Fig. 1a shows the C1s spectra of untreated PET deconvoluted in three characteristic peaks located at 284.9 eV which correspond to phenyl carbons ($-\text{C}_6^*\text{H}_4-$), 286.6 eV corresponding to methylene C atoms bonds to one oxygen ($-\text{C}^*\text{H}_2$) and a peak located at

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