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Surface characteristics changes in polymeric material by swift ion beam



BEAM INTERACTIONS WITH MATERIALS

AND ATOMS

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ABSTRACT

In this work, polyethylene (PE) samples were subjected to 9 MeV Cl⁺² ions with fluences ranging from 1×10^{13} to 5×10^{14} ion/cm². Rutherford back scattering spectrometry (RBS), X-ray diffraction (XRD), ultraviolet–visible (UV–vis) spectroscopy and Vicker's micro-hardness (Hv) techniques were used to investigate the compositional transformation, changes in the structure, optical and surface hardness of bombarded samples. The adhesion parameters were analyzed using the contact angle measurements. The obtained results showed that the ion irradiation caused a decrease in the crystallinity of polyethylene and increase in absorption of oxygen on the polymer surface as well. The absorption edge shifted towards the red shift as Cl-ion fluence increases. It was found that the hardness and adhesion parameters increase with increasing the ion beam fluence.

1. Introduction

Recently, Polymers modification by ion bombardment technique became an important topic in the field of bio-engineering applications. The high wear resistance and relative low cost of the polyethylene (PE) recommend it as a promising material for biomedical and industrial applications. Since hydrophilicity of the polymeric material is one of the parameters enhances its biocompatibility, the industrialization of hydrophilic polymer surfaces has been an important subject attracting a lot of researches. Many methods such as corona treatment [1], flame treatment [2], plasma [3] or irradiations by ion beam [4,5–10] have been used to improve the hydrophilicity of the polymers. Modification of the polymeric material by irradiation is a useful way to amend the surface characteristics of the polymeric materials, including chemical structure and composition [11], free energy surface [12] morphology [13] and electrical properties [14]. Specially, ion irradiation has been shown to be a useful method to alteration the surface characteristics of polymeric material without noticeable variation in the bulk characteristics; beside an improve the bio-compatibility of polymer surfaces [15–17]. Treatment of the polymeric materials using ion irradiation in a controllable way reflects many induced effects e.g. chain scission, sputtering, carbonization, cross linking, ionization and free radicals; which leads to degrade or enhancement the polymer surface properties [18.19].

Meanwhile, irradiation of polymeric materials using ion bombardment leads to a scission the chemical bonds and ultimately to escape of hydrogen molecules [20]. Ion bombardment can also produce defects and amorphous track along the path of its motion in polymeric material [21]. Oxygen uptake that occurs directly as a results of exposure the modified samples to air is another important process, which brings wettability to the polymeric surfaces by formation of oxidized layer and/or hydrophilic groups on the polymer surface. On the other hand, the micro-pores formed due to change of the roughness may leads to increase the surface energy of polymers too [22,23]. The current work aims to depict to what extent the swift Cl-ions beam affects the surface properties of the polyethylene (PE), because thicker modified layer would be beneficial for most of applications. The structural variation, optical properties, wettability, free energy of the surface as well as the surface hardness properties due to ion beam induced compositional transformation and improvement of the polymer surface are presented and discussed.

2. Experimental details

The studied PE samples were manufactured by Goodfellow (UK) product of 1 mm thickness, degree of crystallinity Xc = 65%, density of 0.95 g/cm³ and molecular weight Mw = 150,000 g/mol.

The polymeric samples were treated with 9 MeV Cl⁺² ions to fluence ranging from 10^{13} to 5×10^{14} ion/cm²at room temperature using 3 MV Tandetron accelerator at Forschungszentrum Rossendorf (FZR), Germany. Monte Carlo simulation program SRIM code (version 2012) [24] was used to determine the ion irradiations parameters. Cl- ions penetrate ~6.3 µm in PE sample. The initial electronic (S_e) and nuclear (S_n) stopping power were 2615 and 15.49 eV/nm, respectively. Fig. 1 shows the depth distribution of the deposited energy and damage in PE irradiated with 9 MeV Cl⁺² ions using SRIM code.

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Fig. 1. SRIM calculated the deposited energy (a) and the depth distribution of damage (b) for 9 MeV Cl-ions in PE.

The structural modifications of the samples were evaluated by means of X-ray diffraction, shimadzu diffractometer XD-D1, Japan, with Cu (k α) (λ = 1.54056Ű). The diffraction patterns were recorded in the 2 θ range (4°–90°). The oxygen uptake was conducted using RBS with 2 MeV ⁴He-ion beam at the Institute for Nuclear Studies, Warsaw, Poland. The spectra of the optical absorbance for the un-irradiated and irradiated samples were recorded using JASCO spectrophotometer, V560, Japan, at University College, Umm Al-Qura University, Al-Qunfoza, KSA. The wavelength range was 190–900 nm.

The angle of contact angle for water, glycerol and dimethyl-formamide was measured for obtain the biocompatibility parameters.

The Vickers hardness (Hv) of the PE samples was measured by the micro-hardness tester, Shimadzu HMV-2000, equipped with Vickers diamond pyramid indenter. The hardness indentations of the un-irradiated and the irradiated samples were done at room temperature using load of 0.243 N. The duration time of the hardness indentation was about 60 s for each test. Three hardness indentations measurement were carried out per sample and the mean value was taken for calculation. During perform the experiment test; the specimen was almost kept strictly horizontal and rigid. *Hv* was determined from the relation [25]:

$$Hv = 1.854 \frac{F}{d^2}$$
(1)

where, F is the applied load and d is the diameter of indentation.

3. Results and discussion

3.1. Structural analysis

X-ray diffractograms of the pristine PE sample as well as those treated with Cl-ion are shown in Fig. 2. Three characteristic peaks at $2\theta = 21.455^{\circ}$, 23.803° and 36.105°, respectively, were noticed in the XRD pattern of the pristine sample. After ion bombardment the same



Fig. 2. X-ray diffraction patterns of PE as a function of Cl- ion fluence.

peaks were determined with small shifts towards lower angle; beside decreases in the peak intensity as the Cl-ion beam fluence increases. This shift could be attributed to expansion of lattice perpendicular to the chain direction. The change in the peak intensity may be attributed to destroy the crystalline structure [26]. Thus, the observed decrease in the integral peak intensity may be attributed to decrease in the local order within the polymeric material due to formation of cross-linking of molecular chains that increases with increasing the ion beam fluence [26,27]. Moreover, the crystallite size (L) and interplanar distance (d) were calculated as follows [28,29]:

$$L = K\lambda/(bCos\theta)$$
(2)

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