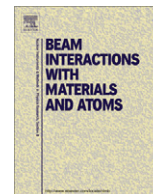




Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimbStoichiometry evolution of polyethylene terephthalate under 3.7 MeV He⁺ irradiationM. Abdesselam^{a,*}, J.P. Stoquert^b, M. Djebara^a, C. Cerruti^b, A.C. Chami^a, P. Montgomery^b^a Faculté de Physique, Université des Sciences et de la Technologie d'Alger, BP32, El Alia, 16111 BEZ, Algeria^b Institut d'Electronique du Solide et des Systèmes, UMR7163, 23 rue du Loess, BP20, F-67037 Strasbourg Cedex02, France

ARTICLE INFO

Article history:

Received 24 June 2010

Received in revised form 30 September 2010

Available online 13 October 2010

Keywords:

Polymers irradiation

Mass loss

Polyethylene terephthalate

Elastic recoil detection

Rutherford backscattering spectrometry

ABSTRACT

A 3.7 MeV He⁺ ion beam was simultaneously used for Polyethylene Terephthalate (PET) film degradation and characterization. To enhance the potentialities of the characterization method, a multi-detector Ion Beam Analysis (IBA) technique was used. The stoichiometry change of the PET target following the irradiation is quantified at a beam fluence varying between 7×10^{13} and 1.8×10^{16} He⁺ cm⁻². The damage induced in PET films by He⁺ bombarding was analyzed *in-situ* simultaneously through Rutherford Backscattering Spectrometry (RBS), Particle Elastic scattering Spectrometry (PES) and Hydrogen Elastic Recoil Detection (ERD).

Appropriate experimental conditions for the observation of absolute changes in composition and thickness during irradiation were determined. The oxygen and carbon content evolution as a function of the ion fluence was monitored by He⁺ backscattering whereas the hydrogen content was measured by H(α ,H) α collisions in which both the scattered He⁺ ions and the recoiling H could be observed. The present study reveals that, at the highest fluence 1.8×10^{16} He⁺ cm⁻², the PET films have lost approximately 15% of the carbon, more than 45% of the hydrogen and 85% of the oxygen of the amount contained in the pristine sample. The energy shift of recoiling H⁺ ions at a forward angle 45° was followed in order to study the mass loss effect.

The experimental results are consistent with the bulk molecular recombination model. Based on the results, hydrogen, oxygen and carbon release cross sections are determined. For hydrogen, comparison with deuteron irradiation indicates a cross section linear dependence on the stopping power.

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1. Introduction

Polymer materials with improved mechanical, optical or electrical properties play an increasing role in a variety of industrial applications, such as in high technology composites for aerospace, radiotherapy and the space satellite industry. Ion beam polymer irradiation has been little studied with heavy ions [1,2], in order to change their chemical and physical properties. The changes are the consequence of irreversible modifications in polymers owing to processes such as main-chain scission, intermolecular cross-linking, morphology change, creation of unsaturated bonds, and loss of volatile fragments. These intricate degradation processes are still incompletely understood and fundamental questions related to the basic ion-collision phenomenon remain unsolved [3]. When striking a polymer, swift ions induce irreversible damage in the structure and the chemical composition within a small volume surrounding the ion trajectory [4] in which the deposited energy density can reach several keV/nm³ and destroy bonds inside the track core. The nature of these changes depends on the

properties of the polymer, such as its composition, chemical bounds, molecular weight and on the mass.

The degradation efficiency is related to the stopping cross section [5]. In the MeV energy range, helium projectiles deposit their energy mainly via electronic interactions and the transferred energies often largely exceed the primary ionization and excitation energies required to cleave any bond of the polymer. Volatile degradation products, typically hydrogen, oxygen and low mass hydrocarbon molecules, escape from the irradiated material. For polyethylene terephthalate (branded as PET, Mylar or Melinex) the dominant gaseous degradation products are H₂, O₂, CO, CO₂ and hydrocarbons C_xH_y [6,7]. IBA and other complementary spectroscopic techniques such as Fourier transform infrared (FTIR), Raman spectroscopy and residual gas analysis can follow the variation of elemental composition or the atomic bounds of the irradiated polymer [8–10].

In this paper, we report on the results of the irradiation of the polyethylene terephthalate (PET) films with helium ion beams in order to study the evolution of the hydrogen, carbon and oxygen contents versus the fluence. Three characterization methods [11,12], i.e. Rutherford Backscattering Spectrometry (RBS), Particle Elastic scattering Spectrometry (PES) and hydrogen Elastic Recoil Detection (ERD) are used in the appropriate geometrical conditions

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to follow thoroughly the PET's atomic absolute composition and thickness variations as a function of the fluence for hydrogen, carbon and oxygen.

A helium beam was used at the same time for irradiation and analysis. Some RBS, PES and ERD informations being redundant, cross-linked data analysis allows for internal checking of result-consistency.

2. Experimental set up

Commercially available PET ($C_{10}H_8O_4$) films (Somar International, Inc.) of $3.6 \mu\text{m}$ thickness were irradiated with a 3.7 MeV He^+ ion beam. The irradiation was performed at the 4 MV Van De Graaff Accelerator of the InESS laboratory in Strasbourg, France. The fluence ranged from 7×10^{13} to $1.8 \times 10^{16} \text{ He}^+ \text{ cm}^{-2}$. The pressure in the beam line and the target chamber were below 10^{-4} Pa . Normal incidence irradiation was carried out at room temperature. A defocalized ion beam was used to insure fluence uniformity of the irradiated spots. At the entrance of the target chamber, at 15 cm from the impact point on the target, a circular collimator constrained the beam spot "footprint" to a diameter of 1 mm. A Faraday cup positioned downstream from the target recorded the transmitted ions and monitored the beam current during irradiation. The beam current was kept at approximately 3 nA to avoid polymer thermal degradation. A schematic diagram of the experimental arrangement is given in Fig. 1, where the relevant quantities for RBS, ERD and PES geometries refer to the laboratory coordinate system.

The ion fluence was determined by using a current integrator delivering a digital pulse at each increment of 7×10^{13} incident ions, which was sent to a multiscale analyzer (MCS) in the "time" mode. In this way, the fluence interval was stored as channel content during each constant time interval (corresponding to a MCS channel). The accuracy of the current measurement was 3%. In order to minimize sample modification during a run, time intervals of 60 s were chosen for the first half an hour of irradiation. Then the measurements were performed each 120 s. IBA spectra of the different runs have been renormalized based on the corresponding fluence interval.

The PET thicknesses have been checked by energy loss measurements from 2.0 to 2.6 MeV He^+ ions backscattered on an Au foil [13] and their homogeneity and uniformity checked by scanning their surface using the Nuclear Reaction Analysis (NRA) method. In our experimental conditions, the number of recoiling nuclei concerned by collisions was always negligible in comparison with the total number of atoms involved in the polymer deterioration.

Charged particle spectroscopy was performed by two similar data acquisition systems consisting of a silicon surface barrier detector, a charge sensitive preamplifier, a spectroscopy amplifier,

an analog-digital converter and an acquisition card in the computer. One detector was positioned in the backward direction at a scattering angle $\theta_{\text{RBS}} = 160^\circ$. A large surface detector (300 mm^2) was used to compensate the oxygen and carbon low backscattering differential cross sections. To reduce geometrical straggling a rectangular slit ($7 \times 18 \text{ mm}^2$) was mounted in front of the detector.

The recoil protons and forward scattered alpha particles were collected by a surface barrier detector (25 mm^2) at a scattering angle $\theta_{\text{PES}} = 45^\circ$. A 3 mm diameter collimator was placed in front of this detector to reduce the acceptance angle in the scattering plane.

A compromise had to be found between sufficient counting statistics and peak shift with film thickness decrease. RBS complementary information on the loss ($^{16}\text{O} + ^{12}\text{C}$) has also been gathered in this detector. RBS and ERD spectra were accumulated simultaneously, and all peaks normalized to the fluence intervals, and to their pristine hydrogen, carbon or oxygen content, respectively. The experimental errors on the atomic content loss quantification depend on the precision of the He^+ charge measurement and on statistical errors of peak areas. The cumulated uncertainty is estimated to be better than 10%. The latter is due to the low backward elastic cross section. Moreover there is no experimental data for $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ cross section for $\theta_{\text{PES}} = 45^\circ$, so instead calculated values were used [14–16].

3. Results and discussions

3.1. Procedure

A multistep data analysis procedure was developed to extract the atomic concentration changes with the irradiation fluence ϕ . The same notations as in Ref. [17] were used, the oxygen and hydrogen contents being expressed with respect to the carbon amount respectively by:

$$\gamma_{\text{O}}(\phi) = n_{\text{O}}(\phi)/n_{\text{C}}(\phi) \quad \text{and} \quad \gamma_{\text{H}}(\phi) = n_{\text{H}}(\phi)/n_{\text{C}}(\phi), \quad (1.a)$$

where n_{C} , n_{O} and n_{H} represent the carbon, oxygen and hydrogen atomic densities (atoms/cm³). Thus the PET's total atomic density is given by:

$$n(\phi) = [1 + \gamma_{\text{O}}(\phi) + \gamma_{\text{H}}(\phi)]n_{\text{C}}(\phi). \quad (1.b)$$

Within this description, the PET's "pseudo molecule" writes as $C_1H_{\gamma_{\text{H}}O_{\gamma_{\text{O}}}}$ with $\gamma_{\text{H}}(0) = 0.8$ and $\gamma_{\text{O}}(0) = 0.4$ before irradiation. Assuming a homogenous PET composition of the irradiated region at a given fluence ϕ , the peak area for each type i of detected particles (i stands for O, H or C) is given by:

$$A_i(\phi) = \frac{\Delta\phi s}{\cos\theta_{\text{in}}} \left[\frac{d\sigma_i}{d\Omega}(\phi) \Delta\Omega \right] [\gamma_i(\phi)n(\phi)X(\phi)], \quad (2)$$

where $\Delta\Omega$ is the detector solid angle, s the beam spot area, $\Delta\phi$ the fluence interval, $X(\phi)$ the geometric film thickness, and θ_{in} the incident angle relative to the normal of the sample (0° in our measurements). The mean differential cross-sections $\frac{d\sigma_i}{d\Omega}(\phi)$ is calculated in the laboratory system for a given fluence ϕ as the exit energy $E(\phi)$ is fluence dependent. The mean differential cross-section is given by:

$$\frac{d\sigma_i}{d\Omega}(\phi) = \frac{\int_{E_0}^{E(\phi)} \left(\frac{d\sigma_i(E)}{d\Omega} \Delta\Omega \right) \frac{dE}{\frac{dE}{dx}(E)}}{\int_{E_0}^{E(\phi)} \frac{dE}{\frac{dE}{dx}(E)}}, \quad (3)$$

where E_0 is the incident energy.

Since the measurements are mainly in the Bethe region, the stopping power is approximately proportional to $1/E$. So, the mean cross section is:

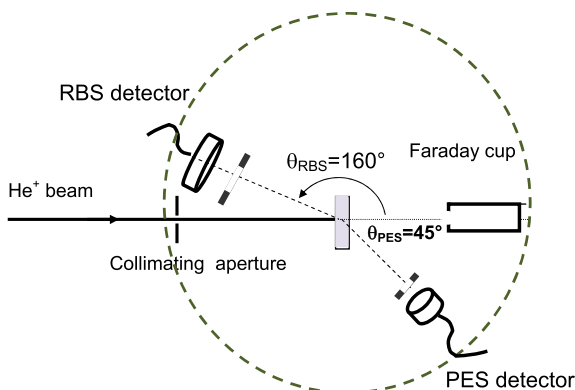


Fig. 1. Geometry and schematic view of the reaction chamber.

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