Nuclear Instruments and Methods in Physics Research B 356–357 (2015) 129–134

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

SAXS investigation of latent track structure in HDPE irradiated with high energy Fe ions

Yang Hai [a,b], Can Huang [a,b], Mingwang Ma [a,c], Qi Liu [a], Yuzhu Wang [a], Yi Liu [a], Feng Tian [a], Jun Lin [a], Zhiyong Zhu [a,*]

[a] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Institute of Electronic Engineering, CAEP, Mianyang 621900, China

ARTICLE INFO

Article history:
Received 29 November 2014
Received in revised form 28 April 2015
Accepted 28 April 2015
Available online 14 May 2015

Keywords:
Ion irradiation
High density polyethylene (HDPE)
Small-angle X-ray scattering (SAXS)
Ion track

ABSTRACT

Semi-crystalline high density polyethylene (HDPE) samples were irradiated with 1.157 GeV ^{56}Fe ion beams to fluences ranging from 1×10^{11} to 6×10^{12} ions/cm^2. The radiation induced changes in nano/microstructure were investigated with small angle X-ray scattering (SAXS) technique. The scattering contributions from HDPE matrix and ion tracks are successfully separated and analyzed through tilted SAXS measurements with respect to the X-ray beam direction. Lorentz correction, one-dimensional correlation function calculation, fractal nature analysis of the isotropic scattering pattern reveal that HDPE long period polymeric structures are damaged and new materials, possibly clusters of carbon-rich materials, are formed inside the ion tracks. Least square curve fitting of the scattering contribution from the ion track reveals that the track is composed of a core of about 5.3 nm in radius, characterized by a significant density deficit compared to the virgin HDPE, surrounded by a shell of about 4.3 nm in thickness with less density reduction.

1. Introduction

High density polyethylene (HDPE) has wide applications in industry [1], agriculture [2] and biomedical [3] area due to its excellent physical and chemical properties as well as its low production cost. It is a typical semi-crystalline polymer, composed of periodically stacked lamellar crystals and entangled amorphous polymeric chains in between forming the so-called semi-crystalline state [4]. Irradiation with electrons, gamma rays and ions has been proven to be very efficient in modifying materials for various uses. A review about electron and gamma ray irradiation effects in PE has been given by Ungar [5]. The radiation effects induced by swift heavy ions are very different from those induced by electron and gamma ray irradiation [6,7]. In addition to the chain scission and cross-linking processes which are the most commonly observed effects in irradiated polymeric materials, a highly modified zone called latent track [6] can be formed along the ion path due to the extremely high electronic stopping power $(dE/dx)_e$ of swift heavy ions in materials. It is found that in polymeric materials latent tracks are usually composed of a track core and a track halo [8]. In the track core the material is severely degraded and carbonized [9] due to the high dense energy deposition and in the track halo molecular chains are cross-linked to some extent depending on the polymer structures.

One non-destructive technology used to detect the ion track structure of irradiated polymer is small angle X-ray scattering (SAXS). The basic detection principle of the SAXS technique is rooted in the X-ray scattering in small angles induced by electronic density variation inside materials. Through analysis of electron density changes obtained from SAXS measurements not only the structure variation of the base material induced by irradiation can be provided but also the ion track size and track structure can be evaluated. In 1985, Albrecht et al. [10] carried out a systematic investigation on the ion track structure in mica, polyethylenterephtalet and polystyrol irradiated with various swift heavy ions by using SAXS. Since then a series of SAXS investigations on ion track structures have been conducted with various models being developed [11–14].

In this paper, we present the results of the structure study on high energy Fe ion irradiated HDPE foils by using SAXS. Through tilted SAXS measurements with respect to the X-ray beam direction the scattering contributions from HDPE matrix and from ion tracks are successfully separated and analyzed. In this way possible errors from measurements and data processing can be greatly

* Corresponding author.
E-mail address: zhuzhiyong@sinap.ac.cn (Z. Zhu).

http://dx.doi.org/10.1016/j.nimb.2015.04.075
0168-583X/

minimized since all information is from one measurement that is conducted on the same sample.

2. Experimental

2.1. HDPE sample preparation

High density polyethylene (HDPE) samples were prepared from HDPE particles of about 80% in crystallinity and 0.95 g/cm^3 in density. The particles were stirred at 190 °C and then compressed into foils of about 1 mm in thickness at 150 °C under a pressure of 15 MPa. The final prepared samples used for irradiation were cut into 10×10 mm^2 squares with a thickness of about 1 mm and a density of about 0.95 g/cm^3.

2.2. Irradiation

Three HDPE samples were irradiated under normal incidence, in vacuum and at room temperature, with 1.157 GeV ^{56}Fe at the irradiation terminal of heavy ion research facility in Lanzhou (HIRFL). The flux was around 2×10^8 ions/(s cm^2) to avoid extra heating of samples and the fluence was continuously monitored during irradiation. The irradiated fluences are 1×10^{11}, 5.1×10^{11}, and 6×10^{12} ions/cm^2. The energy loss values and the range of the irradiated ions in the material were calculated by the SRIM code [15] with the displacement threshold energy being set at 15 eV (as estimated by SRIM). As shown in Fig. 1, the electronic energy loss processes are the main processes that determine the energy deposition inside the sample and have values ranging from 1.6 to 5 keV/nm before the end of the projected range (~492 μm). As only about half of the sample across the sample thickness was irradiated, the samples were thinned from the backside to remove the unirradiated layer in order to cancel the influence of the unirradiated part as well as the implanted layer at the end of the project range. The thinned samples have thicknesses ranging from 300 to 470 μm.

2.3. Small angle X-ray scattering measurements and analysis

SAXS experiments were performed at the beam line station BL16B1 at the Shanghai Synchrotron Radiation Facility (SSRF) in transmission geometry with an X-ray energy of 10 keV (corresponding to a wavelength λ of 1.24 Å) and a distance from sample to the detector of approximately 1.98 m. Samples were mounted on a 3-axis goniometer which allowed alignment of the ion tracks with respect to the X-ray beam direction. Measurements were taken with the sample surface tilted by 20° with respect to the incoming X-ray beam. Additionally, scattering was measured from an unirradiated sample for comparison. All images were taken with an exposure time of 40 s.

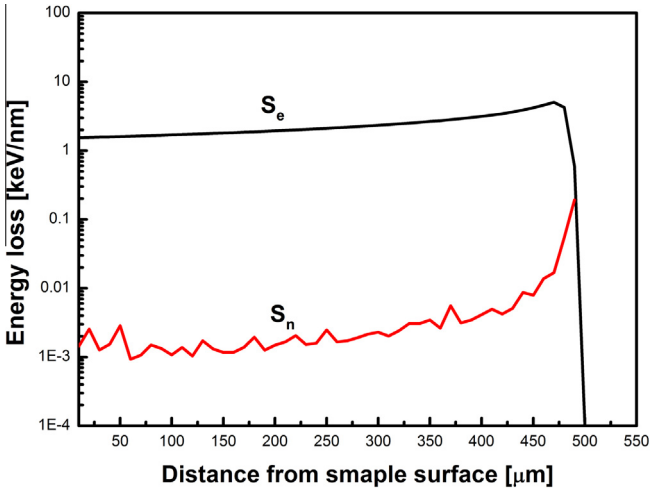

Fig. 1. Electronic energy loss (black line) and nuclear energy loss (red line) values along the projected ranges of 1.157 GeV ^{56}Fe ions in HDPE (SRIM calculation [15]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As shown in Fig. 2, the scattering pattern is composed of isotropic rings overlapped with a slightly curved anisotropic streak. The isotropic rings come from scattering of the HDPE homogeneous background and of the radiation induced new materials inside the ion track area. The anisotropic scattering streak is due to the non-alignment of the ion track, which has a high aspect ratio, with respect to the X-ray beam direction. In order to separate the scattering contribution of ion tracks from the whole scattering pattern, two arcs of the same size from the scattering image that include (area A in Fig. 2) and exclude the anisotropic streak (area B) were selected and the intensities were extracted. Through subtraction of the intensity of area A from that of area B the pure scattering contributions from the ion tracks were obtained. The pure scattering values of ion tracks were then analyzed under the assumption that the ion track is cylindrical in shape with a depleted core surrounded by a shell. All SAXS data of the irradiated samples at three fluence values and one virgin HDPE sample were treated in the same way with all data being corrected for sample thickness and incoming light intensity before analysis.

In order to quantitatively analyze the isotropic scattering pattern (area B) we applied Lorentz correction, one-dimensional correlation function calculation and fractal nature analysis to the measurements. In the Lorentz correction [16] the scattering intensity is multiplied by a factor of q^2 which helps in revealing the peak corresponding to the periodic microstructure of the material. The one-dimensional correlation function $\gamma(r)$ is calculated from the SAXS measurements by using the following equation:

$$\gamma(r) = \frac{\int_0^\infty q^2 I(q)\cos(qr)dq}{\int_0^\infty q^2 I(q)dq} \quad (1)$$

The function gives a more direct impression of the density variation in real space [17,18] which helps in recognizing the microstructure of the material. As an example shown in Fig. 3, the long average period L of HDPE can be estimated from the position of the first maximum of the correlation function curve. The thickness of the amorphous layer L_a for materials with crystallinity larger than 50% can be obtained [19] from the intersection of the extrapolated linear part close to the zero position and the baseline that crosses the first minimum. The thickness of the crystalline layer L_c is equal to $L - L_a$.

It is believed [20] that for a fractal system the scattering intensity follows an inverse power law dependence on the scattering vector, i.e., $I(q) \sim q^{-D}$, with index of D being smaller than 4. Therefore from the double log plot of I vs q one can extract D value for analyzing the variation of the fractal nature of the material induced by irradiation.

3. Results and discussion

Pure HDPE is a semi crystalline and white translucent material. The irradiated HDPE samples were becoming yellow even darken at the high ion fluence. This is commonly believed to be due to the carbonization of the material under irradiation as a result of polymeric chain scission and gas atoms such as hydrogen or hydrocarbons escaping from the bulk material [21,22]. The enrichment of carbon atoms leads to the formation and clustering of carbon particles. It has been found that the carbonization processes