Available online at www.sciencedirect.com
ScienceDirect
Radiation Physics and Chemistry 76 (2007) 123–128
Radiation Physics and Chemistry
www.elsevier.com/locate/radphyschem

Positron annihilation and ion beam analysis of ion-bombardment-induced hydrogen release and oxidation of ultra high molecular weight polyethylene

I.Y. Al-Qaradawi[a,*], N.K. Madi[a], A. Turos[b,c], A.M. Abdul-Kader[b,c]

[a]Physics Department, College of Science, University of Qatar, Doha, Qatar
[b]Institute of Electronic Materials Technology, ul. Wolczynska 133, 01-919 Warsaw, Poland
[c]The Andrzej Soltan Institute for Nuclear Studies, ul. Hoza, 69, 00-681 Warsaw, Poland

Abstract

Ultra high molecular weight polyethylene was bombarded with He^+ and Ar^+ ions to fluences ranging from 10^{13} to 2×10^{16} ions/cm^2. Rutherford backscattering and nuclear reaction analysis were applied to study mechanism of oxygen uptake and hydrogen release induced by ion beam bombardment. The influence of ion bombardment on positron annihilation lifetime parameters is also discussed. Hydrogen release was observed with increasing ion dose and was correlated to the ion stopping power. An important effect observed, was the rapid oxidation of samples after exposure to air.

Keywords: Positron lifetime; Polymers; Ion bombardment; Oxidation; Surface modification; Ion beam analysis

1. Introduction

In the contemporary total joint arthroplasty, in which the total diseased joint has been replaced, metal-on-UHMWPE total joint replacement is an international standard (Kurtz et al., 1999). Despite the recognized success, a major obstacle limiting the lifetime of implants is osteolysis induced by wear debris produced in the form of microparticles from the surface of ultra high molecular weight polyethylene (UHMWPE) component. Microparticles are typically released from the microcracks generated by dynamical loads on the joint. The best solution of the problem will be the modification limited to the top surface, leaving the bulk of material intact (Abdul-Kader et al., 2005). In such a case the hardened top surface layer can transfer load to the soft bulk, the load will be absorbed and distributed over a large bulk area preventing elastic deformation.

Because of the large stopping power and easily adjustable penetration depth, ion bombardment seems to be a very promising tool for this purpose (Chen et al., 2000; (Valenza et al., 2004). Bombardment of polymers by energetic ions produces dramatic changes due to disruption of original chemical bonding (Dong and Bell, 1999), eventually producing cross-linking and chain scission. Koizumi et al. (1996) have found that the radical yield is constant at lower dose and decreases with increasing ion fluence. Abdul-Kader et al. (2005) have studied the changes of the surface layer composition produced by different ion bombardment of polyethylene and isotactic polypropylene. They have observed important hydrogen release with increasing ion dose and

*Corresponding author. Tel.: +974 5813023; fax: +974 4852221.
E-mail address: ilham@qu.edu.qa (I.Y. Al-Qaradawi).

0969-806X/$ - see front matter
doi:10.1016/j.radphyschem.2006.03.016

they have correlated it with linear energy transfer (LET). Another important effect they have observed was the rapid oxidation of samples, which apparently occurred after exposure of bombarded samples to air. Hama et al. (2001) studied the oxidative degradation for high-density polyethylene irradiated with different ion beams. Mackova et al. (2005) and Djourelov et al. (2004) studied ion implantation using positron annihilation and RBS.

The aim of this paper was to investigate in detail the hydrogen release and oxygen uptake process using NRA and RBS techniques. Positron annihilation lifetime spectroscopy (PALS) was used to show the influence of ion bombardment of UHMWPE on PAL parameters.

It is believed that hydrogen release and oxidation are principal constraints in the application of ion beams for polymer modification.

2. Experimental

The studied UHMWPE was supplied by Goodfellow Ltd. (UK). Processing characteristics: $M_w = 120\,000$ g/mol, $M_w/M_n = 3.4$, $T_m = 132\,°C$, $T_c = 112\,°C$, density $d = 0.95\,g/cm^3$. Polymer samples used were flat, rectangular wafers of 1 mm thickness.

Ion bombardment was carried out in vacuum at room temperature by means of commercial Balzers MPB 202 RP ion implanter at the Institute of Electronic Material Technology (ITME), Poland. Beam density was maintained below $0.1\,\mu A/cm^2$ in order not to let the sample temperature rise. The following ion beams were applied for modification:

(a) 130 keV He fluence range from 1×10^{14} to $2\times10^{16}\,cm^{-2}$,
(b) 160 and 300 keV Ar fluence range from 1×10^{13} to $1\times10^{15}\,cm^{-2}$.

Hydrogen concentration was determined by means of nuclear reaction. A sharp resonance of the cross-section at 6.385 MeV was applied for hydrogen depth profiling. Typical value for the $^{15}N^{2+}$ ion beam current from the 5 MV tandem accelerator at Forschungszentrum Rossendorf (FZR) was about 5 nA. It was focused on a spot of $10\,mm^2$. Gamma rays with the energy of 4.43 MeV were detected by a bismuth germanate scintillation detector (4″ x 4″ BGO crystal) located outside the vacuum about 1.5 cm behind the sample. The incident beam was monitored by the RBS signal from a beam chopper in front of the sample.

RBS for determination of oxygen concentration was performed using 2 MeV ^{4}He-ion beam from Van de Graaff accelerator Lech at the Institute for Nuclear Studies, Poland. Since polymers are usually very sensitive to ion bombardment, to reduce the incident ion fluence necessary and to obtain large enough count rate of the spectra instead of a conventional RBS arrangement, annular detector covering the solid angle of 0.16 sr with an average scattering angle of 160° have been employed. The energy resolution was 20 keV.

PALS measurements were performed using an automated fast–fast coincidence system with a timing resolution of 240 ps. Two identical samples, 1 mm thick, were placed on either side of a ^{22}Na source. The sample–source sandwich was placed between two plastic detectors. Positron lifetime spectra of about 2 million counts were collected for all samples under study.

3. Results and discussion

3.1. NRA analysis

The mechanism of hydrogen release induced by ion irradiation was proposed by Adel et al. (1989) in the frame of statistical molecular recombination model (MRM). This model is based on the fact that atomic hydrogen is produced by cleavage of C–H bonds. Once formed hydrogen atoms are usually trapped by neighbouring dangling bonds and cannot diffuse over large distances. However, if two hydrogen atoms have a chance to encounter and recombine to form H_2 molecule this specie can easily diffuse out. Walker et al. (1998) developed further the model of Adel et al. (1989) scaling the release cross-section with the stopping power of incident beam.

Fig. 1 shows hydrogen release profiles, i.e. the number of H atoms that were released from the 100 nm depth interval located at the given depth for 160 keV Ar ions. Also shown are the electronic LET (ionization) and the density of displaced atoms (damage) as calculated using the SRIM code (Ziegler et al., 1985). In the case of heavy ion bombardment, the effects produced by ionization and atomic displacements cannot be directly separated (Abdul-Kader, 2005). The observed release curves resulted from the interplay between the production of mobile hydrogen atoms (ionization) and formation of trapping centers by breaking the polymer backbone (displacements). Since in the region of maximum nuclear stopping power (150–250 nm) the trap density is apparently very high, hydrogen is released only from the near surface region. The hydrogen release holds with increasing ion fluence and until saturation is reached. The loss of hydrogen as a function of ion fluences for UHMWPE bombarded with 130 keV He-ions is shown in Fig. 2. Here the retention curve, i.e. average concentration of remaining hydrogen in the modified layer versus ion fluence is plotted (solid curve). Also shown, the same results (filled circles) as calculated with MRM (Adel et al., 1989). Evidently, the solid curve fits