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Effect of Ar ion on the surface properties of low density polyethylene

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ABSTRACT

In this paper, low-density polyethylene (LDPE) was irradiated by argon ion with different fluences up to 10^{15}ions/cm^2. The optical, chemical and hardness properties have been investigated using UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and micro-indentation tester, respectively. The results showed the ion beam bombardment induced decreases in the transmittance of the irradiated polymer samples. This change in transmittance can be attributed to the formation of conjugated bonds i.e. possible formation of defects and/or carbon clusters. The indirect optical band gap decreased from 3.0 eV for the pristine sample to 2.3 eV for that sample irradiated with the highest fluence of the Ar ion beam. Furthermore, the number of carbon atoms and clusters increased with increasing Ar ion fluences. FTIR spectra showed the formation of new bands of the bombarded polymer samples. Furthermore, polar groups were created on the surface of the irradiated samples which refer to the increase of the hydrophilic nature of the surface of the irradiated samples. The Vicker's hardness increased from 4.9 MPa for the pristine sample to 17.9 MPa for those bombarded at the highest fluence. This increase is attributed to the increase in the crosslinking and alterations of the bombarded surface into hydrogenated amorphous carbon, which improves the hardness of the irradiated samples. The bombarded LDPE surfaces may be used in special applications to the field of the micro-electronic devices and shock absorbers.

1. Introduction

In recent years, the polymeric materials have been grown in their properties. The modified polymers now play an important role in different applications [1], like forming new types of sensors, nanowires or nanotubes. Furthermore, the combination of polymers and lithography can be used to form different types of novel transistors, micro-capacitors, micro-magnets, micro-transformers and miniaturized magnetic field sensors. In addition, polymers can be used in sterilizing foils for medicine and the packing industry [2]. Various studies of the effect of ionizing radiation on the properties of polymers have shown that there is an improvement in the polymer properties such as electrical, optical and mechanical properties as well as the properties of the polymer surface [3–7]. It was found that the main factors causing the modification of these properties is the creation of unsaturated bonds, the chain scission, cross-linking, formation of volatile fragments and creation of clusters of carbon atoms [8–16].

One of these polymers is low-density polyethylene (LDPE). It is thermoplastic and not reactive at room temperature with the exception of strong oxidizing agents and some solvents. This polymer has distinct characteristics such as light weight, flexibility, resistance to chemicals, and shrinking property which makes it suitable for many applications [17]. The modified polymer by radiation can be used in various applications such as biomedical applications (artificial joint), electrical (light emitting diodes, solid state battery and electrical bio-sensing), membrane filters, and rubber products, as well as the pharmaceutical industry (drug delivery) [18].

It is well known that the energetic ions can deposit an enormous amount of their energy in local regions over electronic excitation. The interaction of the ion beam with polymers leads to several complex phenomena viz., bond breaking, intermolecular cross linking, main chain scission, radical composition, loss of volatile fragments and creation of unsaturated bonds [19–22]. All of these processes induced defects inside the polymeric material which are responsible for alteration in optical, electrical, mechanical and structural properties of the irradiated polymers [23]. The strength of these alterations produced in the irradiated polymer predominantly depends on the ion beam parameters (energy, LET, ion fluence, mass, charge, etc.) and the nature of the polymer material itself [19,22,24].

Many investigations have been reported to the use of low linear energy transfer like gamma ray and electron beam as well as high linear energy transfer like heavy ion bombardment for modifications of polymer properties [25–28]. However, the effect of radiation is continuously being studied to determine its role in improving the properties of polymeric materials. The technique of ion beam bombardment is very efficacious in the enhancement of polymer surfaces comparable with low linear energy transfer radiation due to its high stopping power and

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easily controls its parameters such as ion fluence and energy and penetration depth inside the materials [29]. Within the limits of our knowledge, a few works have been performed on the argon-ion bombardment to improve the properties of polyethylene blend [30,31]. In our study, we focus on the effect of Ar ion on the surface properties of low density polyethylene.

The main purpose of this paper is to study the damage and optical, chemical and hardness properties of the bombarded low density polyethylene to deepness of knowledge about the effects of Ar ion beam bombardment on the surface properties of LDPE. Furthermore, this study focuses on the modification of the optical, chemical and hardness properties of bombarded LDPE to increase its use in several applications.

2. Experimental

2.1. Materials

Low density polyethylene (LDPE) pellets having a density of 0.935 g cm^{-3} and crystallinity ratio of about 45% were produced by Exxon Chemical Company. The isotropic films were obtained by compression molding at 433 K and 15 MPa, with 1 mm thickness and 1 cm × 1 cm size.

2.2. Ion beam bombardment

Ion bombardment of LDPE sheets was carried out in vacuum (in the order of 10^{-4} Pa) at room temperature with a 320 keV Ar fluence range (1×10^{13} – 1×10^{15} Ar/cm^2). The beam density was maintained below 0.1 μA/cm^2 to avoid raising the temperature of the samples. The bombardment was carried out by means of a commercial Blazers MPB 202 RP ion implanter at the Institute of Electronic Material Technology (IEMT), Warsaw, Poland.

2.3. SRIM calculations

SRIM is a specialist software program that calculates the stopping power and range during ion interaction with the target material [32]. In addition, there are common parameters that the user calculates: (1) "ion distribution and quick calculation damage" and (2) "detailed calculation with full damage cascades". Besides the calculation of the stopping power and range of the ions within the target, the SRIM program produces a number of output files which contain a table of values as a function of distance from the surface of the material with a unit described in Table 1.

The range R of the 320 keV Ar ion, nuclear energy loss (S_n) and electronic energy loss (S_e) in 1 mm of the LDPE sample are calculated by SRIM 2008 [32] and are equal to 486.5 nm, 196 eV/nm and 466.5 eV/nm, respectively.

2.4. Characterization techniques

2.4.1. UV–Vis spectroscopy

The UV-Vis spectra in the transmission mode for the pristine and bombarded LDPE polymers were investigated using a UV-Visible double-beam spectrophotometer JASCO V-630 in the wavelength range of 190-1100 nm having a resolution of 0.1 nm. The LDPE samples have been carrying on a metal holder after being cleaned with distilled water and all samples have the same thickness and dimensions in all techniques. Air was kept as a reference.

Table 1
Common SRIM output files relevant to damage calculations.

File name	Contents	Units
e2recoils.txt	Energy transferred from incident ions to target atoms and energy absorbed by target atoms	eV/Å/ion
Ioniz.txt	Energy absorbed in electronic stopping by target atoms from incident ions and recoil atoms	eV/Å/ion
Vacancy.txt	Vacancies created	Vacancies/Å/ion
Collision.txt	Table of all ion/target atom collisions which lead to target damage	

2.4.2. FTIR spectroscopy

The FTIR spectra of pristine and argon bombarded LDPE films were detected using an FTIR spectrophotometer model Nicolet 6700 FTIR spectrometer (Thermo Scientific). All samples were scanned in the wavenumber range of 400 – 4000 cm^{-1} with accuracy better than ± 4 cm^{-1}, keeping air as a reference.

2.4.3. Surface morphology

The surface morphology of the pristine and bombarded LDPE films was studied with a scanning electron microscope (SEM) of type JSM-5600-LV.

2.4.4. Vicker's micro-indentation tests

The indentation hardness test penetrates a permanent deformation on the sample surface using an indenter of a diamond or rigid body and determines the hardness of the sample based on the load used to generate the deformation and dimensions of the generated deformation. In the present work, Vickers hardness is calculated based on the test load used when penetrating a Vickers indenter on the sample surface and the indentation area calculated from the indenter diagonal length. The tip of the indenter shall be a diamond in the form of a right pyramid with a square base having the angle between the opposite faces at the vertex of 136°.

The micro-indentation measurements were performed at room temperature by a Shimadzu HMV-1000micro-hardness tester with an applied load of 98 mN. For each load, the duration time of etch indentation was 50 s and three indentations were done at different places on the sample surface. The Vickers hardness (VH) was determined by the relation [33]:

$$VH = \frac{1.854\ L}{d^2} \tag{1}$$

where VH is the Vicker's hardness, L is the test load (mN) and d is the mean of the indentation diagonal length (mm).

3. Results and discussion

3.1. Damage calculations in SRIM

Fig. 1 illustrates the affected region in the irradiated polyethylene by 320 keV Ar ions calculated with SRIM code. The argon ions penetrate the surface polymer film and interact with the components of the polyethylene (carbon and hydrogen atoms) and they recoil. Tree collisions were formed due to the collision between recoiled atoms (receive energies high enough to leave their sites in the molecular structure) and other carbon/hydrogen atoms [34].

The depth distribution of the displaced atoms (damage) in the LDPE bombarded with 320 keV Ar ions at three different fluences calculated with SRIM code is shown in Fig. 2. It is clear from the figure that the damage increases with an increase in ion fluences. This increase may be attributed to the formation of defects and leads to destruction of surface chemical species [35,36] due to an increase in the energy deposited through electronic energy loss.

Fig. 3 shows the ion energy lost due to the ionization interaction with the LDPE films. The ionizing process starts immediately when the ions enter under the surface. The penetrating ion movement in the polymer causes collisions with atoms and electrons of the polymer molecules. As a result of these collisions, the atoms and electrons can be shifted from their equilibrium positions, leading to the excitation of vibrational modes and the resulting phonons propagate to dissipate the