Polymer modifications due to absorption of different ionizating radiations

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Abstract

In the last years, an useful collaboration developed between the material engineers and the physicians of Messina University. The study of the intimate structure of a material, before and after its modification induced by an external ionizing radiation source (electrons, ions, gamma) requires the simultaneous presence of specialist in Chemistry, Physics and Engineering in order to define the best modification conditions and the consequent features of the new synthesized material. In particular the polyethylene, employed in different fields, such as microelectronics and biomedicine, was chosen as an important target to modify its properties through ions and electron beam irradiations. Ion beams, with energy of the order of some hundred keV and doses of the order of $10^{14}/cm^2$, are able to improve the polyethylene surface properties without change the pristine bulk. Instead, electron beams with energy of about 5 MeV and high dose, improve significantly bulk properties of the polymer. The effects of the ion and electron modifications were investigated with several physics characterization methods, as will be discussed in the following.

INTRODUCTION

Ultra-high-molecular-weight-polyethylene (UHMWPE) is employed in the biomedical field due to its peculiar properties, such as the biocompatibility, chemically inertia, electrical insulation, high mechanical resistance and lightness. Some fixed and mobile prosthesis are based on UHMWPE; the antifriction bearings of shoulder prostheses, the vertebral hip and knee (Fig.1) and discs are some examples [1].

In order to improve the already appreciable chemical and physical aspects, surface treatments by means of ion implantation and bulk treatments by means of the electrons treatment were investigated [2-4].

The *ions implantation* have been carried out with 3 different ion types: N^+, Ar^+ and Xe^+. It was demonstrated that the treatment with ions increases the UHMWPE wear resistance and decreases the permeability to the liquids [5-6].

The *electrons treatment* have been employed with high doses, of the order of the MGy, in oxygen presence. It induces an increase of the wear, the Young modulus and the tensile strength with the increasing of the electron dose.

The *goals of the our research* have been the following:

- to estimate the induced effects due to the Ar^+, N^+, Xe^+ ions on the UHMWPE in terms of surface wear resistance;
- to estimate the induced effect due to the electrons on the UHMWPE in terms of bulk compressive, traction and wear resistance.

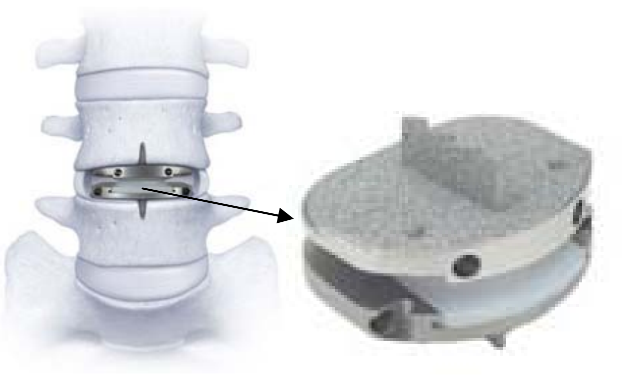


Fig. 1. An example of UHMWPE application to the intervertebral disk prostheses.

EXPERIMENTAL SETUP

Material modification

Two modification methods were applied at the UHMWPE (GUR 1020, supplied by TICONA) in order to study and compare their effects:

1) Modification by means of ion implantation with N^+, Ar^+, Xe^+ at 300 keV energy, with an implant current of 3 μA, in an ion implanter sta-

tion supplied by the University of Catania (Fig.2) at 400 keV. Ion implantation is performed in high vacuum conditions (10^{-7} mbar).

2) Modification by means of the electron use at 5 MeV energy and a current of 40 mA produced by a LINAC supplied by the Physics Department of Messina University (Fig. 3).

Electron irradiation is performed in air (1 atm).

Fig. 2. The ion Implanter.

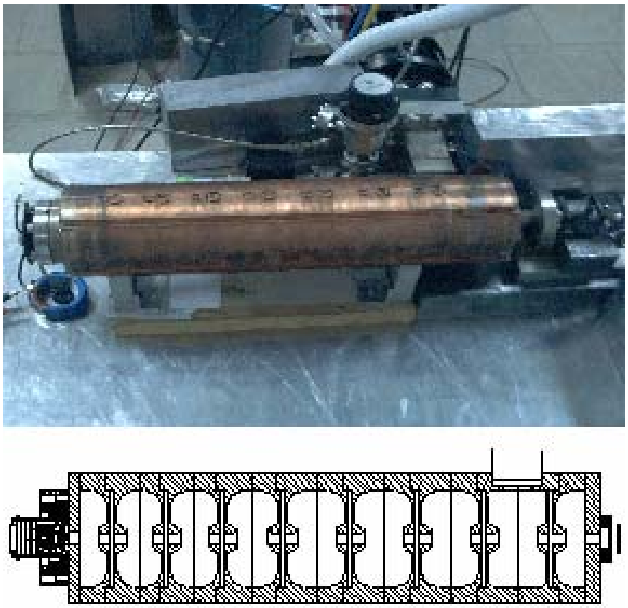


Fig. 3. The LINAC.

The tables I and II show some data relatives to the type of ion and electron implantation, respectively. The effects of the ion implantation depend on the atomic number, energy, dose and dose-rate of the ion. The effects of the electron irradiation depend on the energy, dose and dose-rate of the electrons. Observing the data of the two tables, it's evident that the two methods produce a great difference in the deepness of penetration, which is of the order of hundred of nanometres for ions and centimetres for electrons.

The total stopping power of the electrons is, instead, very lower than that of the ions. The ion stopping power is nuclear, while the electron stopping power is electronic. The consequence is a lighter effect of the electron beam in the polymeric material with respect of that of the ion beam.
In the tables 1 and 2 are shown data relatives to the ion and electron implantation, respectively.

Table I.

Ion type	Ion energy (keV)	Total stopping power (keV/μm)	Range (nm)
N^+	300	390.4	926
Ar^+	300	656.0	460
Xe^+	300	1662	212

Table II.

Energy e (MeV)	Total stopping power (keV/100μm)	Range (mm)
0.5	18.0	2.8
1	14.5	6.9
5	12.8	39.0

Wear test

The traditional system "pin on disc" was realized with the aim to measure the wear resistance of the pure and radiation modified UHMWPE samples [7]. It's composed of a motor, a speed meter, a guide and a fix a tip made of steel AISI 316L. The vertical force of the tip can be increased adding a know weight in order to apply a know pressure. In our system, the pressure produced by the tip on the polymer surface was maintained at 8.50 MPa by using a spherical with a tip roughness of 50 nm. The wear measurements were performed with samples immersed in a bath containing distilled water at room temperature (23°C).

Tensile and compressive tests

In order to estimate the change, of the property of the polymer bulk due to electron irradiation, tests of traction and compression of the electron modified UHMWPE samples were performed. Such investigations use an universal test machine (LLOYD INSTRUMENTS LR10K) which can be used at temperatures ranging between room temperature (23 °C) and 60 °C. For the tensile tests was used a cross-head speed of 1 mm/min, according to ASTM 638 protocol. For each radiation dose, 10 specimens were analyzed. The tensile sample length, width and thickness were 60 mm, 10 mm and 1 mm, respectively. Compression tests were performed according to ASTM D 695M protocol. Samples shape was cylindrical with a high of 20 mm and a base diameter of 10 mm. The mechanical tests permitted to measure the elastic module of the polymer (E), the yielding stress (σ_y), the elongation at break (ε_r) and the ultimate strength (σ_r) of the pristine and irradiated samples.

FTIR and DSC analysis

FTIR (transformed of Fourier to the Infra Red) spectra have been record with a Perkin Elmer 2000 spectrometer equipped with a MCT detector. *ATR* spectroscopy was performed in polymeric films before and after the ion irradiation. Special attention was devoted to investigate in the wave number range 600 – 3000 cm^{-1} containing information about the main C-H and C-C chemical bond absorption peaks.

Differential Scanning Calorimeter (DSC) analyses of a pristine and irradiated polymer have been performed using the mod. TA DSC-2920 instruments at a heating rate of 10 °C/min. The analysed sample weights varied in the range 10 ÷11,5 mg.

CONCLUSION AND RESULTS

The macroscopic modifications caused by the two particle irradiation techniques (ion and electron beams) in the UHMWPE cause an optical effect clearly visible in the following photographs of Fig. 4 and Fig. 5. The photos of UHMWPE samples N^+ ion implanted and electrons beam irradiated vs. doses show a progressive darkening with respect to the pure un-irradiated polyethylene. The electron beam do not completely darkens the polymer, although the employed high energy produces high absorbed dose. This result is in agreement with the data of the tables upper discussed and it is due to the electrons which reach high deep into the polymer dilute their energy density along their long track. On the contrary, ions have high stopping power and release their energy in the first superficial layers depositing high energy-density. Furthermore, in the case of the ion beam, the color intensity let to define an ionic dose of threshold beyond which the sample is totally blackened (~ $3x10^{15}$ N^+/cm^2). At this threshold dose, all the material is full modified.

The wear resistance of the pure un-treated and ion implanted UHMWPE samples has been expressed like weight loss of material as a function of the tip covered travel-space (L). Fig.5 shows the wear behavior of the pure and ion implanted UHMWPE. All the ion implanted samples show a better wear resistance with respect to the pristine UHMWPE. The polymer implanted with lighter ion (N^+) show a better wear resistance on long times with respect to the sample implanted with heavy ions (Ar^+ and Xe^+).

The wear resistance of the pristine and electron beam modified UHMWPE samples decreases with increasing the dose (Fig.6). Only the samples irradiated with low electron dose (0.1 MGy) show a better wear resistance than the pristine ones. This unexpected result could be due to the oxygen presence during the irradiation and/or to a too high absorbed dose. Mechanical wear test suggests that the ion effect upon the wear resistance is better than that of the electron beam. Particularly, light ions, as the N^+ ions, are preferred to the heavy ones for their effect on longer stress times.

The mechanical tensile and compressive tests have been performed at two different temperatures: 23 °C and 60°C. Measurements give: the tensile and the compressive modules E_t and E_c; the tensile and the compressive yield strength, σ_{ty} and σ_{cy}; the

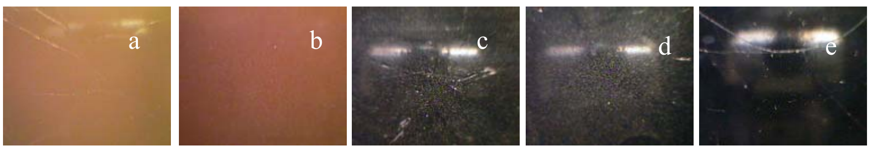


Fig. 4. UHMWPE implanted with a dose of: (a) $0.5x10^{15}$ N^+/cm^2 ; (b)$1x10^{15}$ N^+/cm^2; (c) $3x10^{15}$ N^+/cm^2; (d) $6x10^{15}$ N^+/cm^2; (e)$10x10^{15}$ N^+/cm^2 .

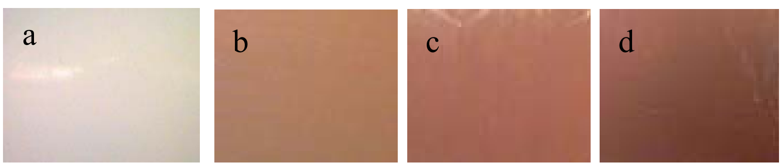


Fig. 5. HMWPE irradiated with electron beam at a dose of: (a) 0 MGy ; (b) 0.8 MGy; (c) 1.6 MGy ; (d) 3.2 MGy.

ultimate tensile strength, σ_r; the elongation at break, ε_r (table III). The measurements were performed in order to give the average value on 8 independent tests. The E_t and E_c modulus were plotted as a function of the absorbed dose and of the two temperatures in the Fig 7. Results indicate that the material stiffness increases with the irradiation dose with respect to the pristine UHMWPE stiffness. This dependence, for the tensile and the compressive modulus, is stronger at lower temperature (23 °C) with respect to the higher temperature (60°C).

These results suggest that the radiation damage increases the mechanical properties in terms of elastic modulus, for compressive and tensile stresses. Unfortunately, the material becomes more fragile, as demonstrated by the decreasing of the rupture charge to elongation and compressive stress (Table 3). In order to improve the mechanical properties of the polymer without increase excessively its fragility, it's very important to irradiate the material with an optimal electron dose. The dose of 0.8 MGy could be considered the value at which the polymeric properties are well improved maintaining low the fragility. The ion implanted UHMWPE samples are mechanically improved only on the polymer surface, as demonstrated by the microhardness measurements [7].

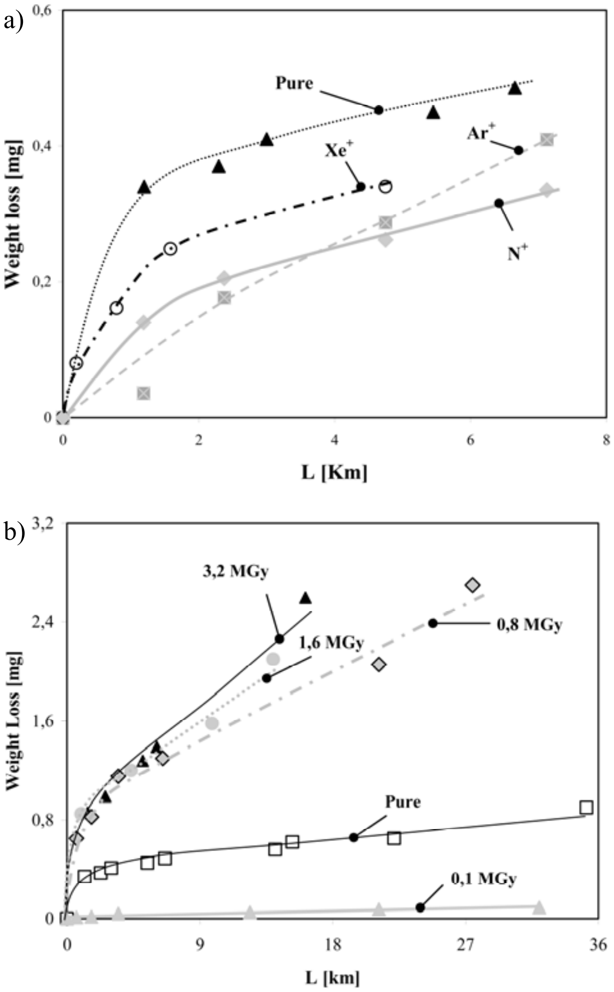


Fig. 6. Wear measurements in water of ion implated specimens (a) and electron beam irradiated ones (b).

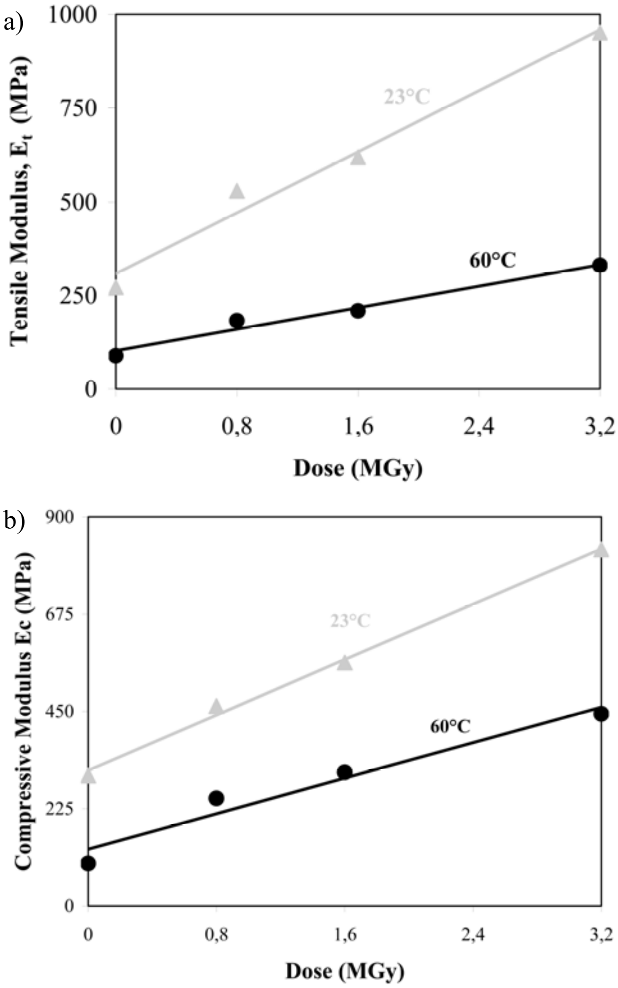


Fig. 7. Tensile (a) and compressive (b) mechanical parameters of electron beam modificated UHMWPE.

FTIR spectra of the electron implanted UHMWPE samples show the trans-vinyl bond formation at ~ 960 cm^{-1} at high electron beam doses (a), the C=C bond at ~ 1462 cm^{-1} due to a cross linking formation process (b) and the characteristic peaks in the range 1700- 1750 cm^{-1} due to oxidation process due to the electron beam irradiation in air presence (Fig.8) [8]. These peaks are well evidenced at high electron beam doses (400 kGy) while are little evidenced at lower electron beam doses (100 kGy) and they are completely absent in the pristine samples The FTIR analysis shows a

Dose (MGy)	T (°C)	E_t (MPa)	σ_{ty} (MPa)	σ_{tr} (MPa)	ε_r (MPa)	E_c (MPa)	σ^*_{cy} ,σ_r (MPa)
0	23	271.4	22.2	22.7	276.9	301.1	48.7*
0.8	23	529.3	-	26.2	33.0	462.4	52.3
1.6	23	619.4	-	27.9	19.3	562.7	55.5
3.2	23	951.3	-	28.9	14.7	825.0	69.0
0	60	88.7	14.0	15.5	360.8	98.4	-
0.8	60	182.6	-	18.7	61.5	248.8	-
1.6	60	208.4	-	21.3	44.5	308.6	-
3.2	60	330.1	-	22.1	22.5	444.2	-

Table III

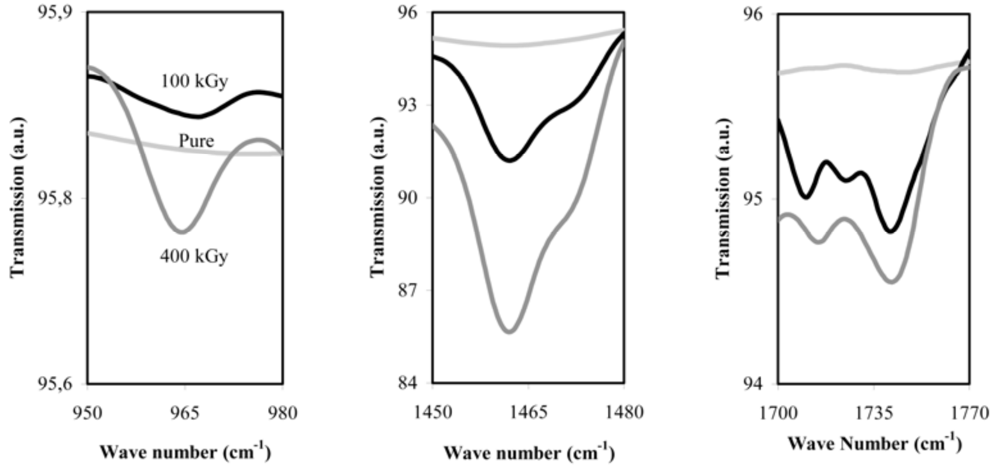
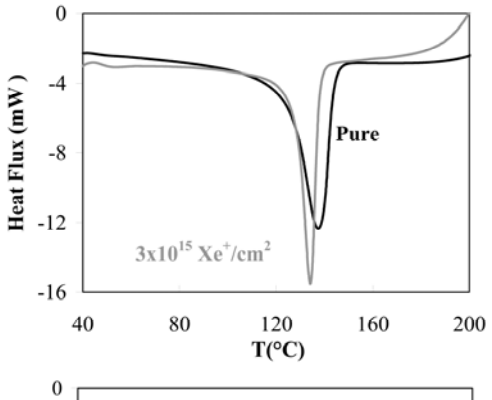


Fig. 8. FTIR of electron implanted UHMWPE.

difference between the two kind of modifications due to ions and electrons. High ion doses modify the UHMWPE samples producing cross links on the surface chains and darkening the surface colour. The electron beam modification is less strong than that observed for ion implantation and its use in air produces vinylic double bonds and oxidized species not completely cross linked. Electron irradiated surface appears not completely dark but it is modified in deep, up to about 2-3 centimeters.

DSC measurements confirms that UHMWPE modifications occur with both the irradiations and that a different result is induced by the two kind of charge particle. The melting temperature of the pure polymer decreases after the ion implantation (Fig.9a) and increases after the electron beam irradiation (Fig. 9b), changing also the polymer crystallinity. Ion implantation and electron beam irradiation are two physical techniques capable to modify the polyethylene material in a different way since they modify the surface and the bulk properties of UHMWPE, respectively.

a)



b)

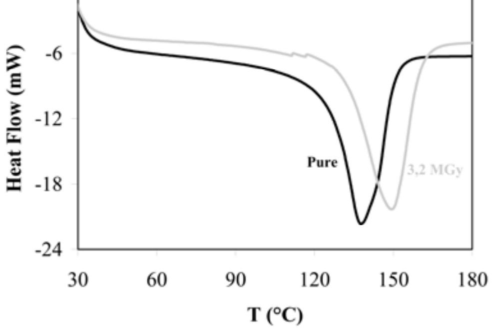


Fig. 9. DSC analysis of ion implanted (a) and electron beam modificated (b) UHMWPE.

The visible effect is a progressive darkening of the initially white polymer which becames brown after the electron beam exposure and completely black only after the high ions doses implantation.

The ion implantation process modifies the UHMWPE surface in terms of an increasing of its wear resistance. The weight loss generally decreases with increasing the ion dose used to implant the polymer. Furthermore, the UHMWPE implanted with lighter ions shows a better wear resistance than the heavier ones over longer wear simulation times.

The ion implantation increases the wear resistance better than the electron beam irradiation. The not good wear resistance of the electrons modified samples can be due probably to the oxygen presence during the irradiation and to the too low deposited electron density. The electron beam increases the bulk mechanical properties of the UHMWPE in terms of stiffness and ultimate strength.

Further studies will be carried out on UHMWPE samples modified with electrons in inert atmosphere and in vacuum by using at low doses with the final aim to increase the bulk wear resistance properties of this interesting polymeric material.

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