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Dose and Dose-rate Dependence of Polyethylene Irradiation with Electron Beams "in Air"

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The chemical and physical properties of ultra-high-molecular-weight-polyethylene (UHMWPE) can be modified by high absorption dose of ionizing radiations. Energetic electron beams, 5 MeV in energy, with a penetration depth higher than 1 cm, can be used to deposit electron energy in thick UHMWPE. Different doses and different dose-rates have been employed at room temperature to irradiate the polyethylene samples in air. Mechanical measurements of tensile strength, wear resistance and hardness were performed on the pristine and electron-irradiated polymers. Results suggested the better irradiation conditions in order to optimize the mechanical properties of the polymer. Special medical applications of the electron-irradiated UHMWPE are presented and discussed.

Keywords electron beam, dose-rate, mechanical characterization, polyethylene modification

1. Introduction

The radiation effects induced in polymers by energetic particles find special interest because they can improve the chemical and physical properties of the irradiated materials. Medicine, engineering, food industry and microelectronics are using more frequently energetic ion and electron beams to modify the properties of polymers in a controllable manner.

Particularly interesting appears the use of the hydrogenated polymers, such as polyethylene, which is employed in many scientific fields. The $–CH_2–$ long chains confer high mechanical and chemical resistance to the polyethylene and the ultra high molecular weight UHMWPE species finds application in high stress devices, such as load prosthesis (hip and knee prosthesis), low friction surfaces, fluids containers highly resistant to pressure and chemical agents, etc. (Ref 1, 2).

Treatments with ionizing radiations, such as ion, electron and gamma beams, are finding many interest to modify the mechanical properties of UHMWPE irradiated both in vacuum and in gas environments (Ref 3).

Thanks to their high penetration range, energetic electron beams can be used to modify the bulk properties of thick polymers. For instance, 5 MeV electrons have a penetration range of about 2.5 cm in polyethylene and, by using tens mA/cm^2 current densities, the beams may modify depth layers of the polymer in fast times (Ref 4).

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In order to reduce the cost and the time of the treatments, the electron irradiation can be performed directly in air, without the use of expensive vacuum chambers and pump systems. In this case, chemical reactions of the excited species may generate oxides and nitrides and develop peculiar macroscopic properties of the treated polymer. Recent investigations have demonstrated that the electron irradiation of UHMWPE in air modifies strongly the polymer as a function of the temperature and absorbed dose (Ref 5). Optical spectroscopy indicated that high-absorbed doses of energetic electrons produce a strong dehydrogenation and cross-link of the polymer. This effect increases with the temperature of the irradiating polymer and with the electron dose absorbed by the polymer (Ref 6).

In this article the macroscopic effects of the mechanical properties of UHMWPE, due to 5 MeV electron irradiation in air and at room temperature, are reported and discussed as a function of the absorbed dose and dose-rate. Results suggest the optimal dose and dose-rate values in order to enhance the polymeric material performance.

2. Materials and Methods

A Ticona GUR 1020 UHMWPE resin, with an average molecular weight of 3×10^6 g/mol, without calcium stearate addiction, with a density of 0.93 g/cm^3, was employed to obtain 10 cm × 10 cm surface and 1-mm thick sheets. UHMWPE was prepared by compression molding in a laboratory press. The polymer powder was kept in a box at 200 °C for 30 min at 20 MPa pressure. The homogeneity of the polymer sheet was controlled by light transmission analysis. The characteristics of the used polymer, so obtained, are reported in a previous work (Ref 7).

In order to use the test-stress machines for the characterization of the polymeric material, the samples have been built with the classical engineering shape so called "bone-dog" according to the ASTM 638 M-3 international protocols (60 mm total length, 10 mm useful length, 2.5 mm minimal width, 1 mm

thickness). Samples were shaped by using the manual cutter press "DGT system".

A 1 kW auto-focusing LINAC of the Physics Department of Messina University provided to accelerate 5 MeV electrons, with a max peak current of 200 mA. All the irradiation treatments on polyethylene were performed in air, at a stable 20 °C temperature, with 60 mA peak current and 3 Hz repetition rate.

The electron charge deposited on the polyethylene was monitored "on line" by a Faraday cup, which can be placed in front of (or behind) the irradiated specimen. The current measurements have been correlated to the effective dose absorbed by the polyethylene. Calibration measurements of dose, as a function of the electron current, were performed with a thin Markus ionization chamber.

The irradiations were performed at two different dose-rates, 60 and 275 Gy/s, by varying the absorbed dose in the range between 100 and 500 kGy.

Mechanical tests have been performed on the pristine and on the electron-irradiated samples in order to compare and to characterize the polymer properties as a function of the absorbed dose and dose-rate. A mechanical tensile-stress machine and a Vickers-Hardness instrument allowed to measure the UHMWPE elasticity and hardness, respectively. Measurements were performed at 25 °C with a LLOYD LR 10K universal testing machine with a cross-head speed of 1 mm · min. For each irradiation dose and for different dose-rate values, ten specimens were tested and the average measurements were compared. The data have given the values of the following parameters: the tensile and compressive modules, E_t and E_c (MPa), respectively; the tensile yield strength, σ_y (MPa); the ultimate tensile strength, σ_u (MPa) and the elongation to break, ε_u (%).

Hardness measurements, in Vickers units (VH), were performed with a Shimatzu DUH-200 instrument, equipped with a pyramidal shape diamond tip. The average HV values have been reported on ten measurements, as results of the following relationship:

$$\mathrm{HV} = \frac{0.7564F}{(d_1 + d_2)^2} \qquad \text{(Eq 1)}$$

where F represents the applied load (N) and d_1 and d_2 the two diagonal lengths (mm) of the pyramidal print produced by the diamond tip on the polymer surface.

Wear tests, of pure and electron-irradiated UHMWPE samples, were performed on a "pin on disc" test machine used to evaluate the wear rate as a function of the absorbed dose. The wear measurements were performed by using the friction of a metallic pin (Stainless steel, 10 g in weight and 1 mm diameter) on a rotating UHMWPE disk (5 cm radius) prepared as above reported. The speed of the rotating disk was 0.057 m · s and the contact pin pressure of 7.50 MPa. The wear rate was calculated from the weight difference measurements before and after the wear action of the metallic probe versus time. More details on the wear tests are reported in a previous paper (Ref 8).

3. Results

Figure 1 shows a photo of UHMWPE samples set submitted to tensile stress. Samples were deformed proportionally to the applied stress. From the pristine (*a*) to the lengthened for traction (*b*, *c*, *d*, *e*) to the break sample (*f*), the relative strain was 200% for the sample *b*, 400% for the sample *c*, 600% for the sample *d* and of 800% for the sample *e*.

Figure 2 shows the tensile module, E_t, which increases exponentially with the absorbed dose. The measurements are performed at the dose-rates of 275 and 60 Gy/s. The tensile module increases significantly at low doses, below 200 kGy,

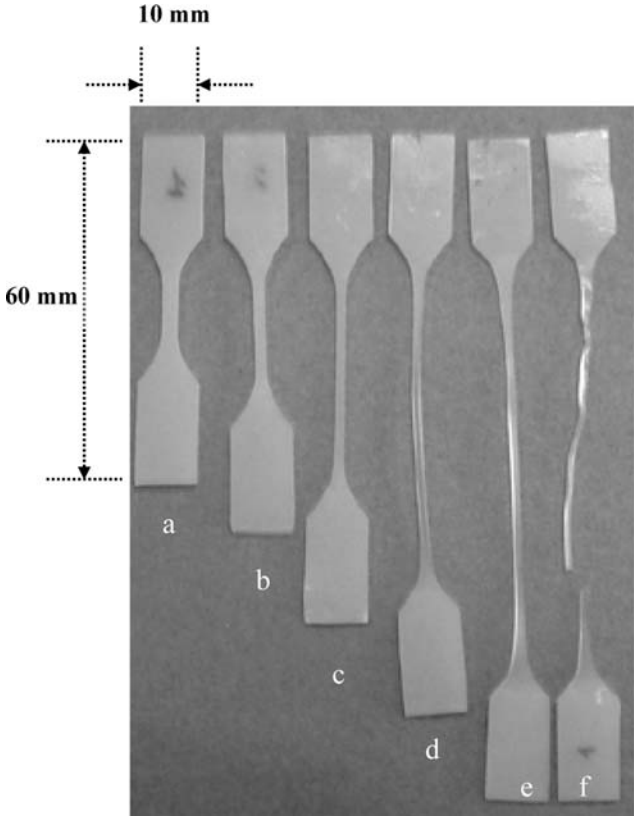

Fig. 1 Photo of a set of UHMWPE samples submitted to tensile stress: pristine (a), after a strain of 200% (b), after a strain of 400% (c), after a strain of 600% (d), after a strain of 800% (e) and the sample broken for high tensile stress application (f)

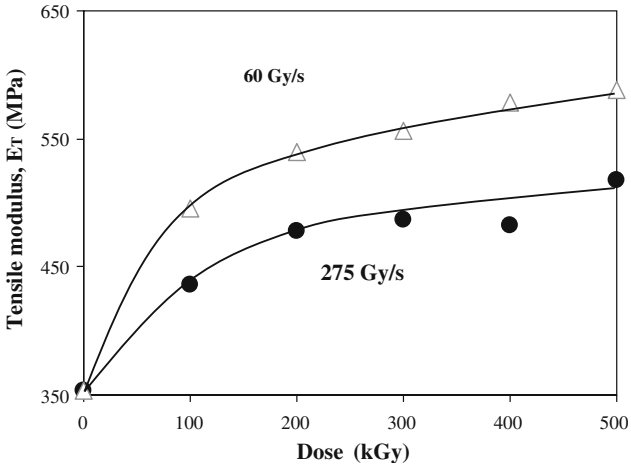

Fig. 2 Tensile modulus as a function of the dose at two dose-rates (60 and 275 Gy/s)

while at higher doses the module remains about constant. The increment is higher at low dose-rates. Thus, in order to maintain high the tensile module, it is necessary to choose a total absorbed dose higher than 200 kGy and to use a low dose-rate irradiation, for example of the order of 60 Gy/s. This choice (300 KGy and 60 Gy/s) will permit to reinforce the polymer to tensile stress, up to about 55% with respect to the pristine value, in a time of the order of 1.4 h.

Figure 3 shows the results relative to the tensile yield strength, σ_y. This parameter increases also exponentially with the dose, reaching a saturation region at doses higher than about 200 kGy. Its value increases up to about 24% with respect to the pristine value. Results indicate that the tensile yield strength depends only on the absorbed dose and not on the dose-rate. Also in this case the tensile yield strength reinforcement will be obtained in about 1 h of irradiation.

Figure 4 reports the experimental data on the ultimate tensile strength, σ_u, for the pristine and the irradiated UHMWPE. This parameter depends strongly on the absorbed dose. Its value increases only for doses lower than 100 kGy while decreases for doses higher than about 120 KGy. Both increasing and decreasing are about exponential with the dose. Thus, in order to reinforce the ultimate tensile strength, it is important do not exceed the "critical dose" of 100 KGy, otherwise irreversible polymer modifications occur. At the critical dose the ultimate tensile strength increment is of about 20% with respect to the pristine value. This increment does not depend on the dose-rate. However, the decrement observed at doses higher than the critical one shows a dependence on the dose rate, as reported in the Fig. 4.

Figure 5 shows the experimental data on the elongation at break, ε_u, of the UHMWPE samples. This parameter decreases exponentially with the dose, indicating that the polymer elasticity decreases and that a more fragile material is generated at high-absorbed doses. The decrement is strongly dose dependent and little dose-rate dependent. Low dose-rates permit to reduce the decrement. At an absorbed dose of 100 kGy and dose-rate of 60 Gy/s the elongation at break decrement is contained within −13% with respect to the pristine value. This low elasticity decrement can be accepted with respect to the other mechanical properties increments due to the absorbed doses but it indicates that, in order to improve all the polymer mechanical qualities, it is necessary not to exceed a dose of about 100 kGy, in agreement with the "critical dose" obtained by the ultimate tensile strength measurements. Figure 6 reports the experimental data relative to the Vickers hardness, HV, of the UHMWPE polymer. The hardness increase with the dose demonstrates that absorbed dose has hardened the polymeric material. The increment reaches the 25% with respect to the pristine value at a dose of about 500 kGy. It is limited to about 16% at an absorbed dose of 100 kGy. The hardness dependence is slow at low dose-rates with respect to the high ones.

Results presented in Fig. 2-6 indicate that the best electron irradiation conditions to improve the global mechanical properties of UHMWPE irradiation in air are limited to the use of an absorbed dose of 100 kGy and an irradiation dose-rate of 60 Gy/s. Thus the treatment of the polymer lasts about 27 min. More reduced or prolonged irradiations can be ineffective or even detrimental for the mechanical improvement of the polymer.

The mechanical improvement obtainable from the electron irradiation of UHMWPE was investigated through wear tests results for dose-rates of 60 and 275 Gy/s as a function of the adsorbed dose. The wear decreases in irradiated UHMWPE

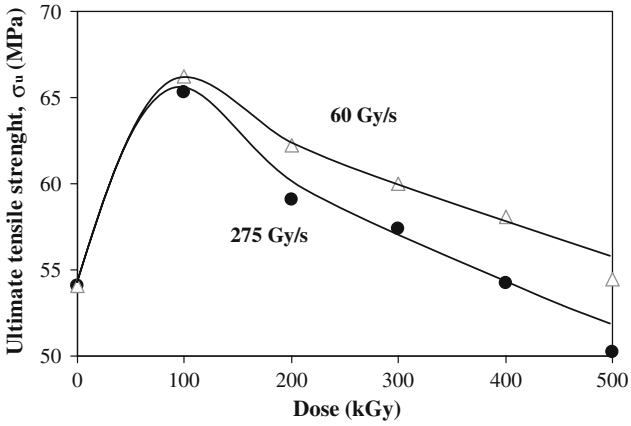

Fig. 4 Ultimate tensile strength as a function of the dose (60 and 275 Gy/s)

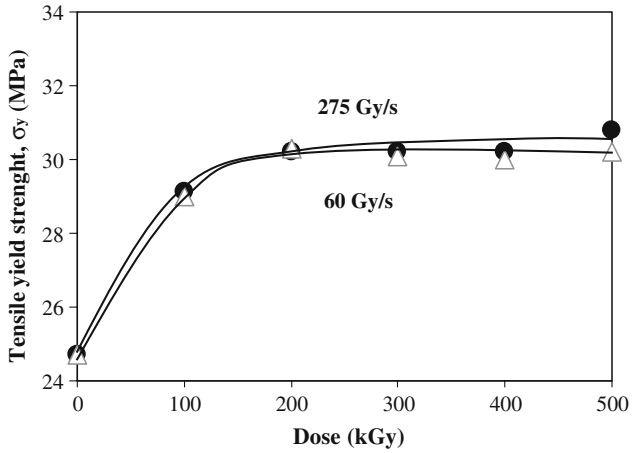

Fig. 3 Tensile yield strength as a function of the dose (60 and 275 Gy/s)

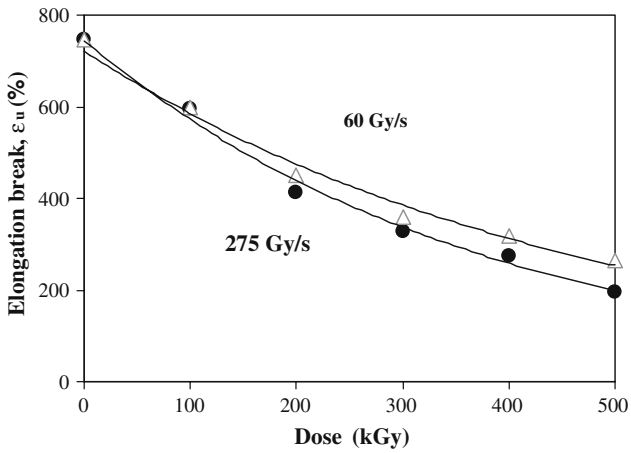

Fig. 5 Elongation at break as a function of the dose (60 and 275 Gy/s)

samples with respect to the pristine ones. A significant wear rate decrement of −32% is obtained at 300 kGy and 60 Gy/s while a decrement of −15% can be obtained at 100 kGy and 60 Gy/s, as reported in Fig. 7. At doses higher that 300 kGy the wear increases strongly demonstrating a bulk damage of the whole polymer.

4. Discussion and Conclusions

The microscopic modifications induced by in air irradiation of UHMWPE with electron beams are complex and indicate that chemical reactions occur (radical production and chemical bonding breaking, with hydrogen lost, new C–C chemical bonds generation and oxides and nitrides structures incorporation in the material), as reported in literature (Ref 9-11).

This article reports the macroscopic mechanical properties of irradiated UHMWPE, which can be improved only by the optimization of the absorbed dose and dose-rate. Low doses do not change significantly these mechanical properties while high doses modify significantly the polymer but they may deteriorate some characteristics.

Obtained results indicate that the goal to improve the UHMWPE by using in air irradiation can be reached by using an absorbed dose of 100 kGy and a dose-rate of 60 kGy. In such conditions the modifications increase the mechanical resistance of the polymer, probably due to a high density of the chain cross-links effects, without the production of macroscopic polymer degradations.

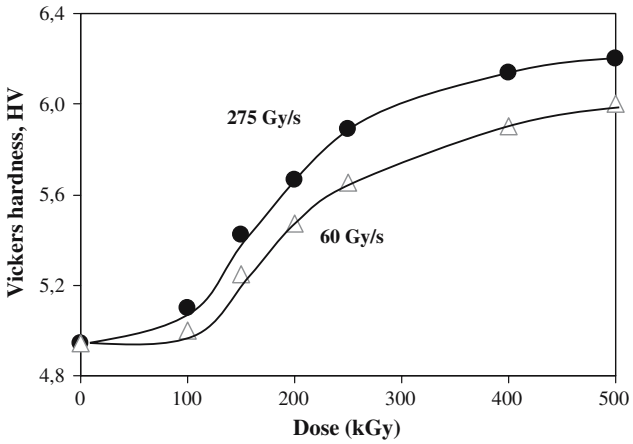

Fig. 6 Vickers hardness as a function of the dose (60 and 275 Gy/s)

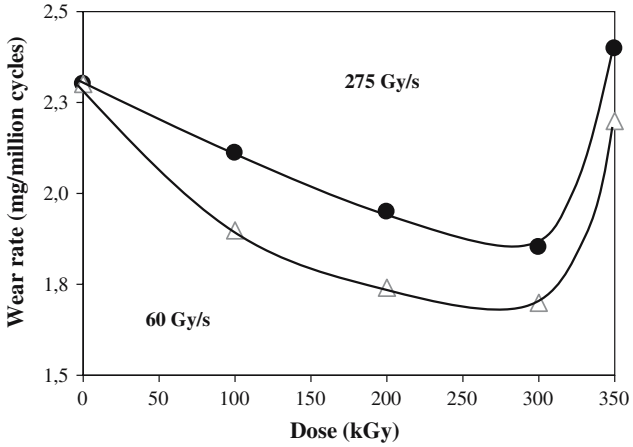

Fig. 7 Wear rate as a function of the dose (60 and 275 Gy/s)

It is not possible to use high dose-rates, because the structure has a proper relaxation time. Probably, at high dose-rate a three-dimensional cross-linking network is produced too fast inside the polymer. The causes of this effect can be due to the electron tracks overlap due to the high electron current. In these overlap regions the high density of released electron energy promotes many excitations, ionizations and reactive radical generation. The consequent fast chemical reaction kinetics induce a three-dimensional cross-linking network and many scission effects which alters the whole bulk properties with worsening of the global properties.

The uses of low dose-rates, instead, permits to the chains to re-organize a structure during the electron irradiation. The slow chemical reaction kinetics preserves the existence of long chains which may cross-link strengthening the mechanical properties of the polymer.

Preliminary measurements of mechanical properties in UHMWPE as a function of the temperature are demonstrating that at 60 °C the dose necessary to modify the mechanical properties of the polyethylene decreases of about a factor 30% with respect to that necessary at 20 °C temperature.

In conclusions, the treatment in air and at room temperature of polyethylene with 5 MeV electrons, doses of 100 kGy and dose-rates of 60 Gy/s permits to improve the mechanical properties of UHMWPE while different values of dose and dose-rate may produce a worsening.

Such results can be advantageous for many application fields. For example, in the field of biomedical devices, an improvement can be obtained for the acetabular cup of UHMWPE used in the hip prosthesis or for the planar disk employed to amortize the loads on the knee prosthesis (Ref 11, 12). Another interesting application of the electron treated polyethylene can be found in the industrial production of pipes for transport of fluids (liquids and gases), which, after treatment, can operate at higher pressure without rupture risk (Ref 13).

The irradiation in air produces improvements in the macroscopic UHMWPE mechanical properties. However, more investigations are needed to understand the microscopic changes due to chemical reactions between specific radicals groups of the polymer. Complex ionized species, molecular groups, peroxides groups, nitride groups and dehydrogenation effects will be investigated in a next experiment.

The in vacuum treatments, on the contrary, producing more stable species and stable cross-linking, may find a better macroscopic improvement of the material. Work is in progress to investigate the comparison of the microscopic aspects occurring during the in air and in vacuum UHMWPE irradiation.

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