Comparison of Surface Modifications Induced by Ion Implantation in UHMWPE

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This research is a study on ultrahigh molecular weight polyethylene (UHMWPE-GUR 1020) implanted with 100–300 keV ions in order to modify its surface chemical, physical, and mechanical properties. Boron, nitrogen, argon, and xenon ions, at doses between 10^{12} and 10^{16}/cm², have been employed to irradiate polyethylene in high vacuum. Roughness, hardness, wear resistance, and wettability represent some of the superficial properties that are modified by the ion irradiation versus dose. Results highlight the modification depth and surface property dependence on the ion specie and dose. The material wear resistance after the ion implantation has been improved up to about 70%.

INTRODUCTION

The radiation effects induced in polymers by energetic particles are of special interest because they can change the chemical and physical properties of the irradiated material. Medicine, engineering, the food industry, and microelectronics are using more and more ion, electron, and gamma beams to modify, in a controllable manner, the properties of many polymeric species.

Treatments with ionizing radiations, such as ion, electron, and gamma beams, are finding interest for modifying the mechanical properties of ultrahigh molecular weight polyethylene (UHMWPE) in both vacuum and gas environment.[1] UHMWPE has been the choice for bearing material for many devices, such as total joint replacement prostheses, owing to such excellent properties as high elasticity, biocompatibility, chemical stability, and mechanical integrity.[2] Improvements in UHMWPE surface properties can be accomplished with the ion implantation technique.

The fast ion energy released to the polymeric chains produces breaking of the chemical bonds, radical production, molecular excitation, and de-excitations.

The chemical reactions of the excited species may generate radicals, hydrates, carbons, and CH-groups that can react, giving rise to scissions and carbonization effects inside the polymer.[3] Macroscopically, reactions may develop peculiar properties on the treated polymer surface.[4,5]

Recent investigations have demonstrated that the electron and gamma beam irradiation of UHMWPE strongly modifies the polymer as a function of the temperature and absorbed ion dose.[6] Free radicals produced by the irradiation lead to carbon atom cross links that make polyethylene harder and wear resistant but brittle due to losing elastic-plastic character.[7] In order to keep the polyethylene mechanical properties after irradiation, the best solution seems to be to limit the modifications to the surface layers of the polymer, leaving intact its bulk ability for stress relaxation. Ion bombardment seems to be a good candidate to modify the surface layers of the UHMWPE. Generally, ion implantation is very interesting since at high ion doses it may induce polymer carbonization with formation of graphite-like layers that are very hard, wear resistant, highly biocompatible and have low friction properties.[3]

Several authors have already studied the ion implantation of polyethylene. Bielinski et al.[7,8] Chen et al.[9,10] Turos et al.[11] and Del Grosso et al.[12] have correlated the property modification induced by different ion beams irradiating polyethylene with a different macromolecular structure depending on the absorbed ion dose. Those works highlighting ion implantation show an optimal dose useful to significantly improve the wear resistance of the modified surface layers while leaving the bulk unchanged.

In our work, we studied the surface modification induced in UHMWPE by 100–300 keV B^+, N^+, Ar^+, and Xe^+ implantation with ion doses ranging from 3×10^{12} to 10^{16} ions/cm^2. In particular, the implantation with boron and nitrogen ions represents two experiments performed using high electron stopping powers and low nuclear stopping power, i.e., using particles producing relatively low collisional atomic events but high ionization effects. In contrast, argon and xenon ions, having high nuclear stopping powers, induce high collision events with high probability of breaking the polymer chain scissions and de-hydrogenation. These reactions form reactive species that rearrange in carbon-like structures that increase the polymeric wear resistance.

EXPERIMENTAL SETUP

A Ticona UHMWPE resin GUR 1020 (average molecular weight of 3×10^6 g/mol, density of 0.93 g/cm^3, without calcium stearate) was compression molded by a laboratory press at the Engineering Faculty, Messina University. The polymer powder was kept at 200°C for 20 min at 20 MPa pressure in order to obtain sheets with 1 mm thickness and 2 cm × 2 cm surface.[13]

Polymeric modifications were induced by means of ion implantation with B^+, N^+, Ar^+, and Xe^+ atoms at 100–300 keV kinetic energy, with doses ranging from 3×10^{12} to 10^{16} ions/cm^2. Ion implantations were performed at the MT-LAB-IRST of Trento using about 3 μA ion current in a high vacuum chamber (10^{-7} mbar) at room temperature. The irradiation beam was tilted at 7° with respect to normal to the sample. The samples were maintained at room temperature under vacuum for 30 min.

SRIM simulation code was employed to calculate the ion penetration range in UHMWPE, electronic and nuclear stopping powers, ion distribution, ionization and collisional events, recoil energy, damage events, energy and range straggling of the used ion beams.[14]

Wear Measurements

Wear measurements were performed by a "pin on disc" test machine in order to evaluate the volume lost due to polymer friction effects with a metallic moving pin, cylindrically shaped, with diameter of 1.8 mm that gives a load of 22 N. The samples were placed on a rotating plate and a stainless steel AISI 316 L pin (whose roughness was 50 nm) was pressed against the polymer surface generating a circular track at a pressure 8.5 MPa, in dry conditions and at room temperature.

The loss mass, M_L, was calculated from the measure of the depth (h) and width (b) of the wear track, which has an approximate triangular profile as follows:

$$M_L = \rho \cdot b \cdot h \cdot \pi r \tag{1}$$

where ρ is the polymer density (0.93 g/cm^3) and $r = 5$ mm is the radius of the circular pin track. The track profile was measured with the Tencor P10 surface profiler (1 nm depth sensitivity). The duration of the wear test was 10 min and the pin speed was 120 rpm. In such conditions the carried out pin distance was about $L = 40$ m.

Hardness Measurements

Hardness measurements were performed using a Shore D instrument (PCE HT 210), with a 0.1 Shore resolution and ±1 Shore precision, according to DIN 53505, ISO 7619, and ASTM D 2240 international protocols.

Scratch Test

The scratch test was obtained by imprinting micrometric tracks by a stainless steel tip on the polymeric surface with a constant force of a 0.5 N and measuring the track width through SEM investigation.

SEM

Scanning electron microscopy (SEM) analyses were carried out with a JEOL JSM 5600 LU microscope. Polymer samples were coated in vacuum with a very thin gold film to make them electrically conductive. Generally, the electron acceleration voltage was 10 kV and the photo magnification within 50× and 200×.

Roughness Test

The polymer roughness was measured with the profiler Tencor P10, which moves a micrometric point along a single direction recording the surface depth profile with a 1 nm depth resolution. It is assisted "on line" by an optical microscope.

Generally, roughness measurements were performed by using a tip force of 1 mg, a scansion length of 1 mm, and a scan speed of 100 μm/s in different places of the same surface. Average values were calculated.

Contact Angle

Contact angle measurements were carried out by a contact angle micrometer instrument with a CCD camera. A micro-syringe permits depositing 1 μL drop of pure distilled water, at 20°C, on the polymer surfaces.[5] The contact angle θ was measured through the photo of the drop shape on the flat surface, using an optical image with $10 \times$ magnification and the following equation:

$$\theta = 2\arctan\left(\frac{H}{r}\right) \tag{2}$$

where H is the height of a droplet and r is the radius of the droplet's circular base. For each sample, the average value was calculated for 10 drop measurements.

IR Spectroscopy

The horizontal attenuated total reflectance (HATR) infrared spectra were registered with a PerkinElmer Spectrum 2000 instrument equipped with a mercury cadmium tellurium (MCT) detector. Twenty scans were accumulated in the $4000–400\,cm^{-1}$ wave number region for each studied sample.

RESULTS AND DISCUSSION

The effects of ion implantation depend mainly on the ion specie and energy, on the kind of irradiated material, and on the implanted dose and dose rate. The ion stopping power gives information on the ion energy deposited per unit of trajectory length in the irradiated target. Electronic and nuclear contributions of the ion energy loss in the polymer indicate different regimes of energy release, at low and high density, respectively, giving rise to different microscopic modifications. Light ions, such as H^+ and B^+, have low electronic stopping powers and high ranges and produce mainly ionization effects with generation of energetic electrons along the ion tracks. Such ion beams do not induce significant nuclear recoil effects, as deducible from the data listed in Table I, which shows a comparison of the stopping powers and ranges of some ion beams irradiating UHMWPE.

Heavy ions, such as Ar^+ and Xe^+, have high electron and nuclear stopping powers and produce not only ionization effects but also many collision events along the ion track, with consequent breaking of the chemical bonds of the polymer chains, vacancy production, chain scissions, and nuclear recoils. The Xe^+ nuclear stopping powers for example, are about two orders of magnitude higher than the B^+ ones. This demonstrates that the modification effects induced by Xe^+ ions in the polymer are significantly higher than those induced by B^+ ions.

Figure 1 shows the results of some SRIM simulation code[15] comparisons of the ionization events due to the primary incident ions and to the secondary recoil atoms, produced by collisional events, as a function of the depth between B^+, N^+, Ar^+, and Xe^+ ions at 300 keV energy implanted in UHMWPE.

Table I. Comparison of stopping powers and ranges of the used ions for UHMWPE implantation

Ion beam	Energy (keV)	Stopping power (keV/μm)			Range (nm)
		Electronic	Nuclear	Total	
Hydrogen	100	98.7	0.15	98.9	1140
	200	74.3	0.08	74.38	2310
	300	58.4	0.06	58.46	3830
Boron	100	231	21.7	252.7	458
	200	277	13.3	290.3	817
	300	321	9.9	330.9	1130
Nitrogen	100	254	44.9	298.9	355
	200	134	28.4	162.4	658
	300	369	21.4	390.4	926
Argon	100	315	325	640	161
	200	398	247	645	311
	300	454	202	656	460
Xenon	100	271	1210	1481	91
	200	383	1240	1623	153
	300	449	1213	1662	212

It can be observed that the depth range is about 1.3, 0.93, 0.46, and 0.21 μm for the four ion species, respectively. For boron, the number of recoil ionization events is negligible with respect to the ionization induced by primary ions; moreover, the maximum value of the energy loss is about 30 eV/Ångstrom. For nitrogen, the recoil component increases about 14% with respect to the ionization induced by primary ions, and the maximum value of the energy loss increases to about 35 eV/Ångstrom. For argon, the recoil component increases about 37% with respect to the ionization induced by primary ions, and the maximum value of the energy loss increases to about 45 eV/Ångstrom. For xenon, the recoil component increases up to about 200% with respect to the ionization induced by primary ions, and the maximum value of the energy loss, nuclear in this case, increases to about 80 eV/Ångstrom.

The number of collision events of the incident ions with the atoms of the polymer chains increases with the atomic number and atomic mass of the ion, and for xenon it reaches such high values that high damage per unit of depth is obtained. The number of collisions between the xenon ion and C and H atoms of the polymer is by a factor of about 13 higher than that with boron, as calculable from SRIM simulations at 300 keV implanted energy. However, for Xe^+ ions, the ion range in UHMWPE is below or comparable to 1 micron depth, and, consequently, only very superficial polymeric modifications can be induced at the used ion energy.

The macroscopic modifications produced by the ion implantation cause a surface polymer darkness whose color depends on the deposited ion dose and on the implanted ion specie. The photos of the ion-implanted UHMWPE samples versus doses show a progressive darkening with respect to the pure polyethylene, as seen in Figure 2. This result indicates the color intensity that defines an ionic threshold dose above which the sample is totally blackened. This threshold corresponds to approximately 10^{16}/cm^2, 10^{15}/cm^2, and 10^{14}/cm^2 for B^+, N^+, and Xe^+, respectively. As discussed in a previous paper,[3] the darkening effect is due to the C–H bond
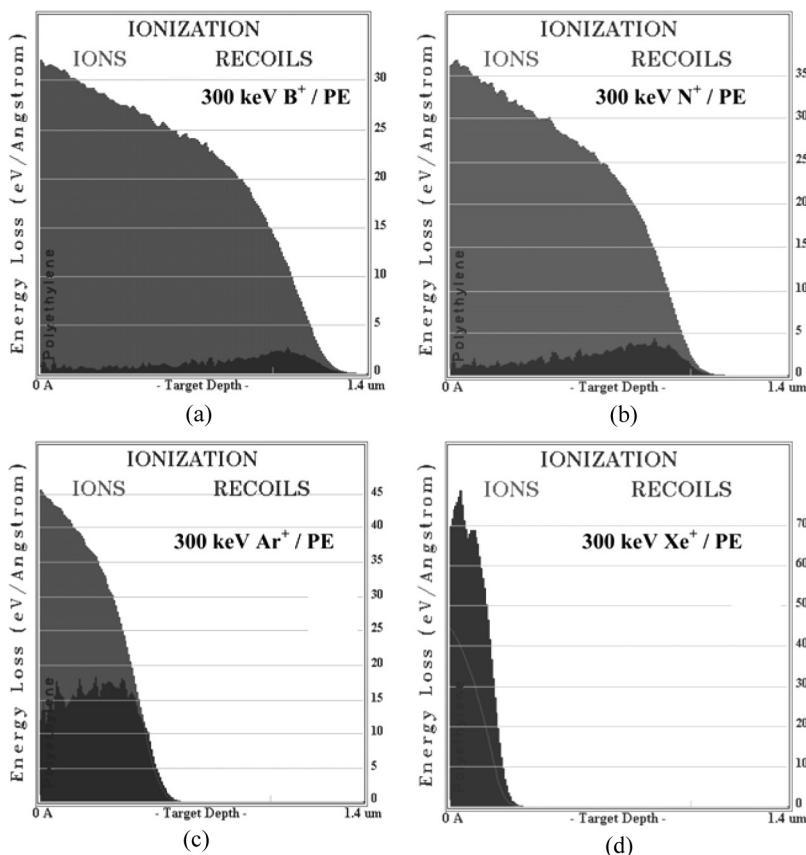
Figure 1. SRIM simulation of the energy loss vs. UHMWPE depth for 300 keV implantation with B^+ (a), N^+ (b), Ar^+ (c), and Xe^+ (d) ions.

breaking and C–C bond formation. This process is faster with increase of the nuclear stopping power of the ions.

This observation indicates that the dose necessary to strongly modify the superficial optical properties of the polymer decreases with the nuclear stopping power of the used ion specie. As a consequence, the lowest darkening threshold is obtained in the samples implanted with the Xe^+ ions and the highest threshold with the B^+ ions.

Measurements of surface roughness demonstrated that the polymer surface becomes less rough with ion irradiation. The pristine average roughness of about 35 nm, in fact, decreases with the implanted dose and the decrease is stronger when increasing the nuclear ion stopping power. A $10^{15}/cm^2$ Xe^+ dose reduces the pristine roughness to about only 5 nm, as reported in Figure 3. The figure inset shows a typical surface profile of the untreated polymer surface. The reduction of surface roughness upon irradiation is due to the atomic collision of the used ion species. This effect is more consistent with increasing ion heaviness and its dose since it better breaks the surface atoms, smoothing the surface.
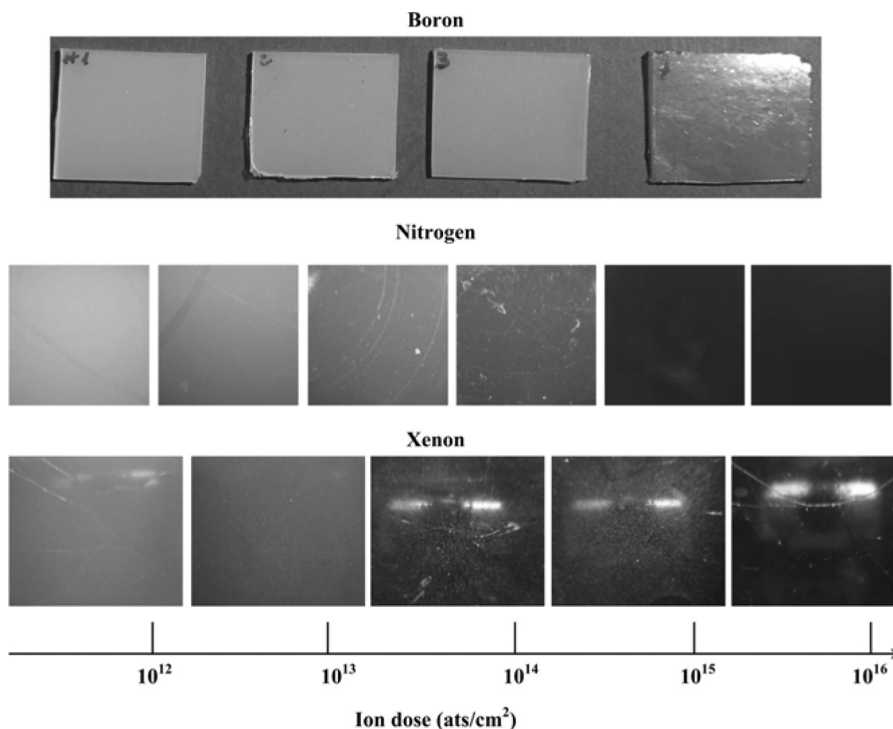
Figure 2. Photos showing the color of the UHMWPE sheets implanted with different doses of B^+ (first line), N^+ (second line), and Xe^+ (third line).

The water wetting measurements demonstrated that the contact angle increases with the implanted ion dose and stopping power, as reported in Figure 4. The figure insets show two typical photos of the water drops on the polymer surface. The pristine polymer has a contact angle of 67°, which increases up to about 87° after xenon ion irradiation at doses higher than $10^{15}/cm^2$. At these dose values an abrupt change in the wetting angle occurs, demonstrating that microscopic effects on the surface characteristics significantly increase the UHMWPE hydrophobic property. Generally, wettability changes of a material surface can be ascribed to the processes generated by ion irradiation, such as free radical formation and the following rearrangements that eventually lead to the oxidation of the irradiated layers.[13] Although our experiments were performed in high vacuum, we have evidence of small amounts of oxidized specie (like the $C=O$ one; see the Fourier transform-infrared (FT–IR) results discussed below). Anyway, wettability properties seem to be mainly due to the surface carbonization and to the smoothing process, rather than to oxidation, which can be considered negligible. In fact, all the surfaces contain oxidized species but the B^+ion implanted surface is smoothed, poor in carbon structures, and the most hydrophilic among the three ions investigated. Instead, the surfaces implanted with Xe^+ or the N^+ ions are highly smooth, particularly rich in carbon structures (especially at high implantation dose), and highly hydrophobic compared to that implanted with the B^+ ion.
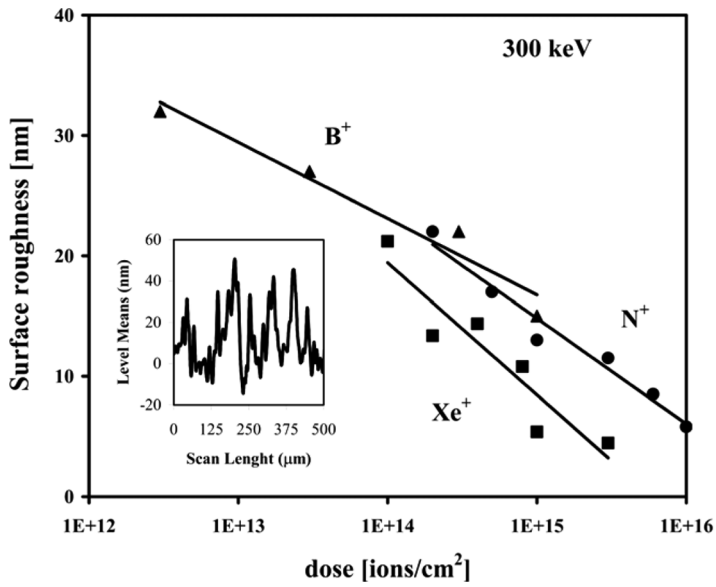
Figure 3. Roughness measurement of UHMWPE implanted with 300 keV B$^+$, N$^+$, and Xe$^+$ ions vs. dose.
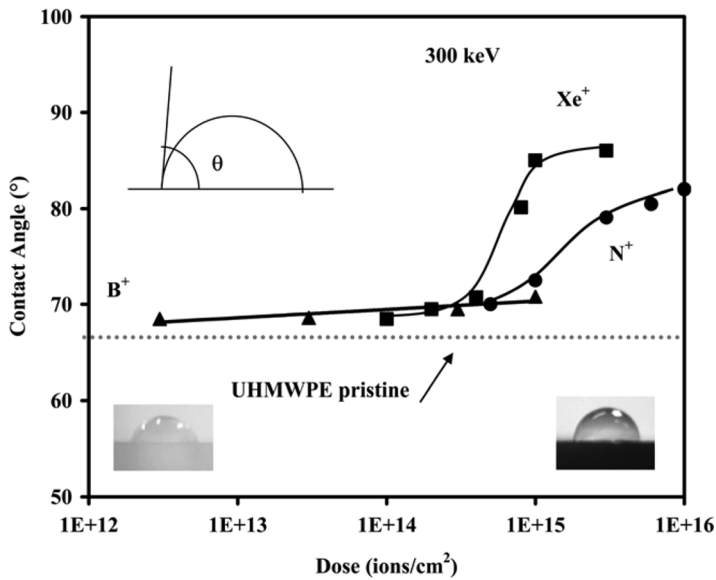

Figure 4. Water contact angle measurement of UHMWPE implanted with B$^+$, N$^+$, and Xe$^+$ ion vs. dose.

These results highlighted that the wettability increases with surface roughness, while it decreases with the formation of carbon-like structures.

The wear resistance of the pure and ion-implanted UHMWPE samples has been expressed as mass loss of material for a length $L = 40\,m$ of space covered by the tip. Figure 5(a) shows the wear behavior tests of the pure and ion-implanted UHMWPE samples. The figure inset shows the pin-on-disc machine photo. All the ion-implanted samples have better wear resistance than the pristine ones, in fact, their mass loss is below the value of 0.64 mg of the untreated surface. The wear resistance of the pristine and ion beam–modified UHMWPE samples increases with increasing ion dose and ion stopping power. For example, using 300 keV ions at the dose of $10^{15}/cm^2$ the mass loss is about 0.55 mg due to B^+ implantation, 0.40 mg for N^+, 0.30 mg for Ar^+, and 0.19 mg for Xe^+. Figure 5(b) shows a typical comparison between the track profile obtained in pristine polymer and in B^+ implanted polymer (300 keV, $10^{15}\ B^+/cm^2$).

These results highlight that the B^+, N^+, Ar^+, and Xe^+ 300 keV ion implantation, at the dose of $10^{15}/cm^2$, improved the UHMWPE wear resistance by about 14%, 38%, 53%, and 70%, respectively. By increasing the implanted doses the wear improvement increases further.

The measurements demonstrate that the polymer implanted with the lighter ion (B^+) shows better wear resistance at long times than the samples implanted with heavy ions (Ar^+ and Xe^+), which highly increase the short-time wear resistance. This result can be explained on the basis of the ion range, which is too superficial for heavy ions at 300 keV ion energy, and, consequently, for long times it can be removed by wear and the effect of the ion implantation can be cancelled.

The polymeric surface mechanical resistance increase depends strongly on the ion stopping power, as demonstrated by the measurements of mass loss as a function of the total stopping power of boron ions at energies ranging between 100 and 300 keV and at a constant implanted dose of 3×10^{14} ions/cm^2, as reported
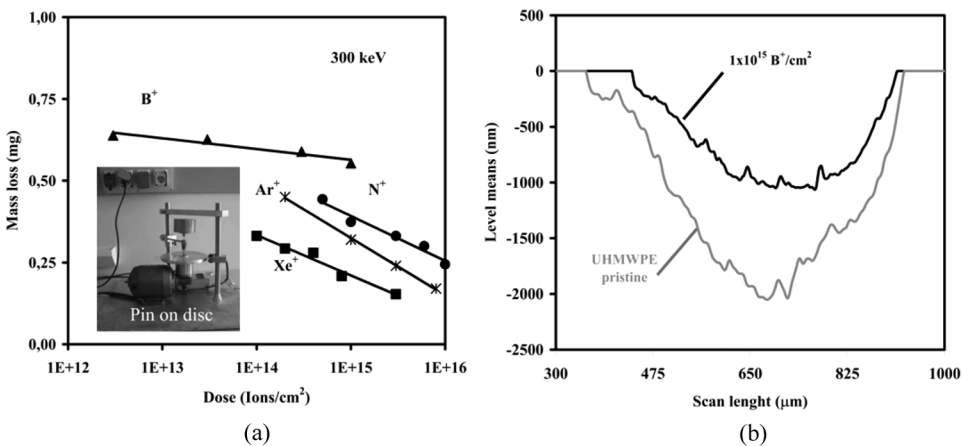
(a)

(b)

Figure 5. Mass loss of UHMWPE implanted with ion B^+, N^+, Ar^+, and Xe^+ ions vs. dose (a) and comparison of the wear profiles between pristine and 300 keV, $10^{15}/cm^2$ B^+ ion-implanted surfaces (b).
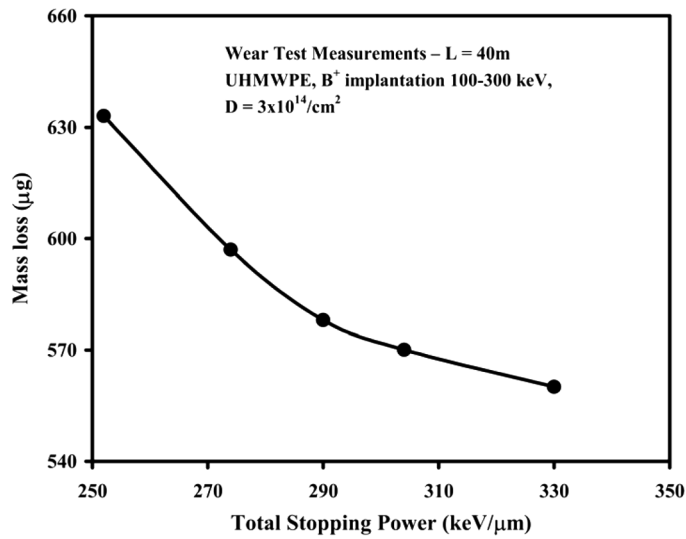
Figure 6. Mass loss measurement of UHMWPE implanted with ion B^+ vs. total stopping power.

in Figure 6. A total stopping power increase of 32% (from 250 to 330 keV/μm) produces an 11% mass loss reduction.

Surface hardness was measured accurately using light pressure forces on the polymer surface with a Shore scale. The pristine polymer micro-hardness is about 62.5 Shore D units. This parameter increases with the ion dose and ion stopping power, as reported in Figure 7. The figure inset shows the photo of the Shore instrument. The maximum micro-hardness of 71 Shore D is obtained after 300 keV xenon ion irradiation at a dose of 3×10^{15}/cm^2.
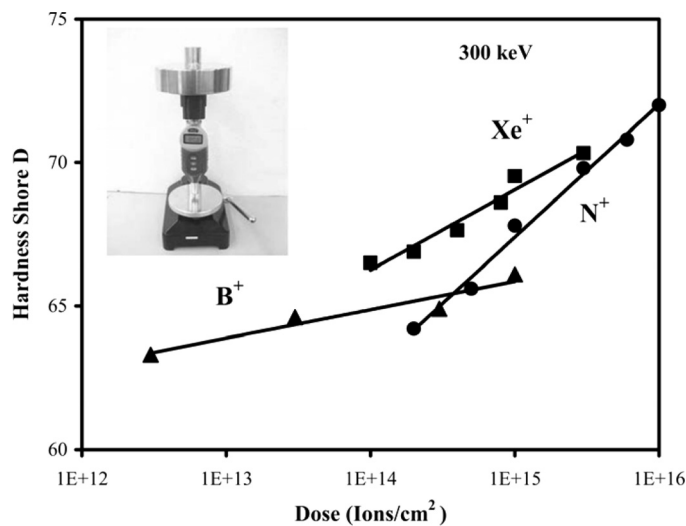

Figure 7. Hardness Shore D measurement of UHMWPE implanted with B^+, N^+, and Xe^+ ions vs. dose.

Hardness measurements are in good agreement with scratch tests: SEM micrographs of Figure 8 compare the scratch test width imprinted before (a) and after $3 \times 10^{14}/cm^2$ (b) and $10^{15}/cm^2$ (c) 300 keV B^+ implanted surfaces. The track width is initially about 500 μm (pristine sample) and then decreases up to about 40 μm in the highest dose implanted sample, suggesting a significant surface hardening due to the modifications of the ion irradiation.

Finally, Figure 9 compares the infrared HATR spectrum of pristine polymer with those of different irradiated polymers; the major HATR bands of the pure and hydrogen-implanted samples are listed in Table II; see also Valenza et al.[3] and Silverstein et al.[17]

The infrared analysis of the pure UHMWPE evidences C–H band presence with the peaks at 725, 1470, 2850, and 2920 cm^{-1}. The infrared analysis of the high ion dose–implanted UHMWPEs evidences the C–H band reduction and –C–C– chemical bond with delocalized charge formation (peaks at ~1660 cm^{-1}). These results demonstrate that the polymer surface becomes more and more poor in hydrogen and rich in carbon-like structures when increasing the ion dose.

In literature it was observed that one of the main products of ion implantation modification is the –C–C– formation, whose stretching vibration is clearly observed in the spectra by an absorption peak at 1640 cm^{-1}.[16] Our measurements suggest that the absorbance peak measured at 1660 cm^{-1} can be ascribed to carbonization processes induced by high doses or by high ion stopping powers. In fact, at high
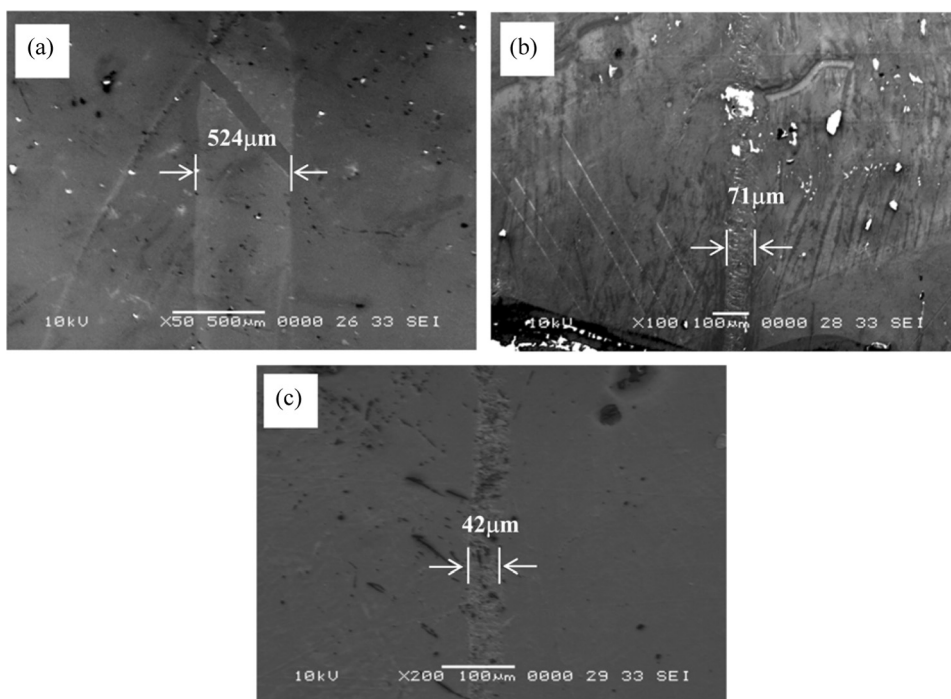

Figure 8. SEM analysis on UHMWPE scratch test in pristine (a), 3×10^{14} B^+/cm^2 (b), and 10^{15} B^+/cm^2 ion implantation (c).
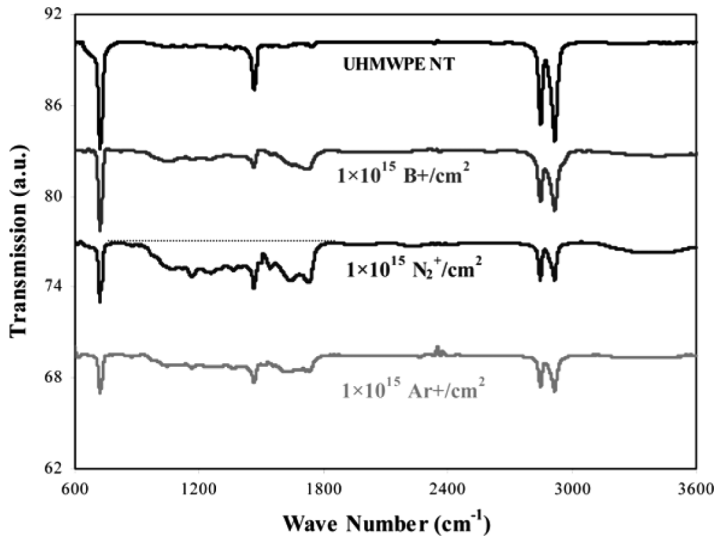
Figure 9. FT–IR spectra of the absorption bands relative to the C–H and to the C–C groups vs. different ion-implanted species with energy of $100\,keV$ and dose of $10^{15}\,ions/cm^2$.

doses a black polymer surface can be obtained, suggesting that a "graphite-like" layer can be produced on the polyethylene surface.[3]

In addition, we can observe a little peak at around $1740\,cm^{-1}$ due to the C=O presence. This peak presence suggests that a small amount of oxidized specie is formed after the ion irradiation. This is probably due to free radical reaction with the small amount of oxygen adsorbed into the polymeric sheets bulk.

Moreover, the N^+ irradiated UHMWPE sample showed a broad band within the 1000–$1700\,cm^{-1}$ range, suggesting the presence of chemical bonds with nitrogen in the polyethylene chains. The broad band could contain the N-H bending signal (generally around $1620\,cm^{-1}$) and the C-N stretching broad band at $1429\,cm^{-1}$.[17]

Table II. Main HATR peaks

Sample	Wave number [cm^{-1}]	Remarks
Pure UHMWPE	725	C–H bending
	1470	C–H bending
	2850, 2920	C–H stretching
Irradiated UHMWPE		
(B^+, $10^{15}/cm^2$)		
(N^+, $10^{15}/cm^2$)	~1660	C–C stretching
(Ar^+, $10^{15}/cm^2$)	~1740	C=O stretching
(N^+, $10^{15}/cm^2$)	~1000–1700	Broad band containing:
		N-H bending
		C-N stretching

This result is in agreement with the literature, since Chen et al.[9] have already observed that injected nitrogen atoms form chemical bonds with the polymer instead of forming precipitates by self-clustering. Nitrogen ion–modified UHMWPE samples showed experimental evidence of possible chemical bonds with this ion, which remains partially entrapped in the macromolecular structure. Anyway, the physical and mechanical results described above seem not to be influenced by the presence of this chemical bond type.

CONCLUSIONS

Ion implantation represents a useful physical technique capable of modifying the polyethylene material surface without damage to the bulk properties. Control of the modified material depth can occur on the basis of the ion range in the polymer. The surface modification quantity of the polymeric chains depends on the ion specie, energy, stopping power, and dose.

Ion implantation increases the wear resistance, micro-hardness, and hydrophobic behavior of the implanted layers. This last property probably is due to a surface roughness smoothing effect produced by ion sputtering. High nuclear stopping power ions, such as heavy ions, induce high sputtering, decreasing the surface roughness and, consequently, decreasing the wettability of the polymer surface.

The visible morphological change of the polymer surface results in the progressive darkening of the initially white color, which becomes brown after the first absorbed doses and completely black at high implanted doses. The microscopic modifications, in fact, are due to a progressive dehydrogenation of the polymer and to the enrichment of the –C–C bonds, as demonstrated by HATR infrared spectroscopy.

The effect of the presence of a small amount of oxidized species and of nitrogen ions bonded in the polymeric samples is negligible compared to that of the smoothing and carbonization processes induced by the ion implantation.

Ion implantation modifies the polymer chains differently depending on the value of the electronic and nuclear stopping powers of the used ions. Light and high energetic ions, with only electronic stopping powers, are generally insufficient to drastically damage the polymer and to induce "graphite-like" structures, such as occurs for H^+ and B^+ implantations. In this case, in fact, the processes of ionization, recombination, and radical formation can be produced significantly but the probability of breaking the long polymeric chains is maintained as low. Heavy ions at low energy, with high nuclear stopping power, instead, strongly damage the polymer chains because many collisional ion-atom events occur. In this case scissions, molecular fragmentations, and high-density radical formation also occur inside the ion tracks, and, consequently, the possibility of generating carbonization effects with the C atoms of the polymeric chains becomes high.

These last phenomena significantly modify the linear polymeric structure, producing new chemical bonds in the polymeric chains. On increasing the ion dose, these groups become more and more enriched in carbon and poor in hydrogen, assuming a graphite-like structure and increasing their intrinsic density. Of course, the low ion energy used in this investigation is relative to modification of the

only very superficial layers, generally sub-micrometric, of the polymeric material. A further investigation will employ light ions with implantation doses higher than 10^{16} ions/cm^2 or higher energies (of MeV order) with the aim to increase both the modified layer thickness and the graphite-like amount.

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