



On the comparison of changes induced in crystallinity and surface nanomechanical properties of ultra high molecular weight polyethylene by γ and swift heavy ion irradiations



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ABSTRACT

In this work the influence of two different irradiation techniques on the degree of crystallinity and nanomechanical properties of a medical grade UHMWPE is compared. One technique, widely used in the production of components for total joint replacement, is comprised by γ -irradiation followed by a thermal treatment above the melting temperature of UHMWPE and thus modifies the material's bulk. The other one, an alternative modification technique that affects only the near surface layers of UHMWPE, is swift heavy ion (SHI) irradiation. The effect of two types of ion beams (nitrogen and lithium) with different energies (33 and 47 MeV) and fluences (10^{11} to 10^{13} ions/cm²) is investigated. Changes in degree of crystallinity are investigated by DSC and Raman spectroscopy while the nanomechanical properties – elastic modulus and hardness – are evaluated by nanoindentation tests. The γ -irradiated and remelted sample exhibits lower degree of crystallinity than the pristine material due to the hindered recrystallization process of the crosslinked chains. Concomitantly, this sample shows a reduction in hardness and elastic modulus of the bulk. On the other hand, SHI-irradiated samples display a large increase in degree of crystallinity and surface mechanical parameters with respect to pristine UHMWPE. The modification is confined to the ion target depth. The layer affected by the ion beam shows constant mechanical properties that appeared to be slightly influenced by the fluence in the studied range (around the optimum). Despite the changes induced by both techniques are completely different, they are able to enhance the wear performance of UHMWPE due to the beneficial change in elastic to plastic properties. Among SHI-irradiated samples, the N-ion (33 MeV and 1×10^{12} ions/cm²) exhibits the better combination of nanomechanical properties.

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1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is the preferred polymer for the acetabular component in hip prostheses or tibial insert and patella component of knee prostheses, owing to its excellent mechanical properties, bio-compatibility and chemical stability. However, wear of UHMWPE releases fine wear particles (debris) which exert serious adverse reactions on living tissues. Those reactions finally induce osteolysis and thus failure of prosthetic joint components [1]. It is known that wear debris generates mostly by the rupture of polymeric fibrils formed by large strain plastic deformation and orientation of the surface under multidirectional motion [2].

Near the end of the 90's, it was shown that the wear resistance of UHMWPE could be significantly improved by crosslinking of

polymeric chains by low ionizing particles such as gamma irradiation (γ) and electron beam irradiation (e-beam) [2–4]. Ionizing radiation passes through the component and affects homogeneously the material's bulk. Ionizing radiation cleaves C–C and C–H bonds of UHMWPE creating free radical that recombines to form crosslinks. The wear rate of UHMWPE decreases with increasing crosslinking density [2,3]. Usually, radiation crosslinking is followed by a thermal treatment above the melting temperature of UHMWPE to avoid the oxidation effects caused by the presence of non-recombined free radicals [2]. Components prepared from crosslinked and remelted UHMWPE have been clinically implanted in more than 2 million patients around the world. The disadvantage of this technique is that it produces the detriment of other relevant properties such as strength, fracture toughness and fatigue crack propagation [1]. Low fracture and fatigue resistance are now recognized as the main causes of UHMWPE components failure in the long term [5]. An alternative strategy to improve wear resistance of UHMWPE

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without compromising the other mechanical properties is by modifying only its surface layers. In this sense ion beam irradiation constitutes an attractive technique since ions only penetrate several micrometers in the polymer [6–10]. If the physico-chemical transformation induced by ion beam irradiation is effective, the wear resistance of the surface could be improved while the subsurface mechanical properties remain intact [1].

It has been shown that ion beam implantation and plasma-based ion implantation techniques resulted in improved wear resistance of UHMWPE [11–18]. In these techniques, ions are implanted into the polymer substrate with energies in the order of keV and fluences ranging from 10^{14} to 10^{17} ions/cm². The thickness of the affected layer varies from a few nanometers to 1 μ m, depending on ion type and energy [11,12]. In polyethylene, the physico-chemical changes associated with ion implantation are chain scission, cross-linking, formation of double and triple bonds, dehydrogenation of the surface layers and creation of carbonaceous aggregates especially at high fluences [19,20]. The improvement in wear resistance is attributed to crosslinking but also to stiffening and hardening of the surface due to the formation of a diamond like carbon (DCL) layer [20,21].

An alternative to ion implantation and plasma-based ion implantation is swift heavy ion (SHI) irradiation provided by high energy accelerators. SHI beams can reach up to hundreds of micrometers into polymers and the fluence required to generate structural changes in polymers is within 10^{11} to 10^{13} ions/cm² [6,10,22–25]. This technique involves ion beams with energies in the order of MeV. It is distinguished from ion implantations by its very high electronic stopping power $(dE/dx)_e$ that dominates the energy deposition mechanism and reaches up to some tens of keV/nm. Another characteristic of SHI irradiation is that the deposited energy is very inhomogeneous. As the interactions between ions and polymer chains depend strongly on the special distribution of the deposited energy, the effects induced by SHI irradiation are considerably different from those induced by low ionizing particles. SHI irradiation produces complex physical and chemical modifications in polymers that are the result of inelastic collisions between ions and target atoms that leads to ionization of the atoms and excitation of target electrons [6]. Studies carried out in low density polyethylene (LDPE) and high density polyethylene (HDPE) films showed that SHI irradiation can induce crosslinking, formation of in-chain double bonds, hydrocarbon gas release and creation of vinyl, alkyne and allene groups [7,9]. The effect of SHI irradiation on LDPE and HDPE depends on $(dE/dx)_e$ and is very sensitive to radical migration so it also depends on time and temperature [9].

To the author's knowledge, the first studies on the application of SHI irradiation technique towards improving the wear performance of UHMWPE were made in CNEA using C, I, N, S, Li and He ion beams in the 1–100 MeV energy range [10,22,23,26]. These investigations showed that a considerable improvement in wear resistance (~85% reduction in volume loss) with minor changes in the nature of UHMWPE could be achieved after SHI irradiation. Studies also showed that for a given ion type and energy, there exists an optimum fluence that minimizes the wear damage [22]. The optimum fluence appears to decrease with increasing the average $(dE/dx)_e$ of the ion beam independently of the ion type [22,26]. In a later work, it was shown that irradiation with N ion, enhances elastic and plastic properties of UHMWPE surface layers, reduces friction and improves nanowear resistance and creep behavior [24].

Ambitioning to confirm the viability of using SHI irradiation to improve the wear resistance of UHMWPE components, the aim of the presented work is to determine the changes in nanomechanical surface properties and degree of crystallinity induced in UHMWPE by SHI irradiation and to compare them with those promoted by the widely used modification treatment (γ -irradiation followed by remelting). To this aim, different SHI-irradiated samples with fluences around the optimum a γ -irradiated and thermally treated sample and a pristine UHMWPE sample are prepared and evaluated through nanoindentation, DSC and Raman experiments.

2. Experimental

2.1. Pristine material and irradiated samples' preparation

The pristine material used in this investigation was a medical grade UHMWPE (GUR 1050, Poly Hi Solidur). Two types of radiations were applied to UHMWPE: γ -rays and SHI beams. γ -irradiation procedure was conducted in CNEA (Ezeiza, Buenos Aires) and SHI irradiation was carried out in the Tandem Accelerator of CNEA (San Martín, Buenos Aires).

Cubic samples of about $(10 \times 10 \times 10 \text{ mm}^3)$ were machined from the original block and remained unmodified to use as reference samples. They were polished using 1, 0.3 and 0.05 μ m alumina particle size aqueous suspensions to reach the adequate surface roughness level for nano-mechanical characterization. Pristine UHMWPE samples are denoted hereafter as UH samples.

2.1.1. Preparation of γ -irradiated UHMWPE samples

A block of pristine UHMWPE ($100 \times 50 \times 11 \text{ mm}^3$) was γ -irradiated at room temperature in vacuum for 5 hours at 19.03 kGy/h, the minimum dose received was 95.13 kGy and the maximum 98.47 kGy to induce polymer crosslinking. The selected radiation dose was chosen because it is the highest value used in the fabrication of total joint components [2,27–29]. It has been shown that the crosslink density increases linearly with increasing radiation level until 100 kGy beyond which the rate of increase in crosslink density slows down [2,3]. γ -irradiated UHMWPE was kept in nitrogen atmosphere until it was thermally treated above its melting temperature. The thermal treatment allows completing chain crosslinking and therefore prevents material oxidation due to the presence of free radicals [2,30,31]. γ -irradiated UHMWPE block was melt at 170 °C under nitrogen atmosphere for 2 hours and cooled down to room temperature at a rate of 10 °C/min [3]. Cubic samples ($1 \times 1 \times 1 \text{ mm}^3$) were machined and polished. Samples submitted to γ -irradiation are named γ -UH, whereas the samples submitted to γ -irradiation followed by the thermal treatment described above are denominated hereafter as γ -TT-UH samples.

2.1.2. Preparation of SHI-irradiated samples

Cubic blocks of pristine UHMWPE ($10 \times 10 \times 10 \text{ mm}^3$) were subjected to ion beam irradiation at room temperature under vacuum conditions. The face of the block exposed to SHI radiation was first polished in the same way than UH samples. A series of five Li ion irradiated samples with an energy of 47 MeV and different fluence ranging from 1×10^{11} to 4.3×10^{12} ions/cm² were prepared. In addition, one N ion irradiated sample with an energy of 33 MeV and a fluence of 1×10^{12} was prepared.

SHI-irradiated sample denomination is given in Table 1 together with the characteristic ion beam irradiation parameters. Calculation of average electronic stopping power and projected ion range in polyethylene was conducted using the Stopping and Range of Ions in Matter software (SRIM©-2013) [32].

The energy and fluence values used in SHI irradiations were selected on the basis of previous studies [10,24,26]. The fluence used for N-UH sample irradiation was the optimal value found for wear improvement

Table 1

Denomination and ion beam characteristic parameters of prepared SHI-irradiated samples.

Sample denomination	Ion type	Fluence (ions/cm ²)	Energy (MeV)	$[(dE/dx)_e]$ (MeV cm ² /mg)	Projected ion range (μ m)
Li-UH-1	Li	7×10^{11}	47	3.73 ^a	454.94
Li-UH-2	Li	1×10^{12}			
Li-UH-3	Li	2×10^{12}			
Li-UH-4	Li	3×10^{12}			
Li-UH-5	Li	4.3×10^{12}			
N-UH	N	1×10^{12}	33	10.21*	37.86

^a Average $(dE/dx)_e$ calculated from the surface up to 10 μ m depth.

[23]. The fluence range used to prepare the Li-UH series was around the optimal value determined following Chappa et al. analysis ($\sim 2 \times 10^{12}$ ions/cm²) [26]. The larger energy used in Li-UH series compared with N-UH sample was intended to enlarge the depth affected by the ion beam. This allowed exploring the profile of nanomechanical properties along the ion target depth. The average electronic stopping power was higher in N-UH sample than in Li-UH samples (Table 1), but both radiation conditions stand on the Bethe–Bloch region so energy deposition mechanism was dominated by $(dE/dx)_e$.

SHI-irradiated samples were kept in vacuum and darkness until testing to minimize aging effects.

2.2. Nanoindentation tests

Nanoindentation tests were carried out in a Triboindenter (TI 750 series from Hysitron Inc.) at room temperature in order to determine the surface nanomechanical properties (elastic modulus and hardness) of the different samples. Tests were performed using a Berkovich tip under load control conditions. A trapezoidal loading function with 9 mN of maximum load, 0.9 mN/s of loading rate of a holding time at maximum load of 30 s, was used. The holding time was applied to minimize the creep effect during unloading. Raw tip displacement data were corrected by thermal drift according to the Hysitron recommended procedure: before the indentation test is started, the system leaves the tip on the sample and monitors any displacement of it, then, a “drift rate” is calculated as the slope of the displacement vs. time data. The drift rate is assumed constant during the indentation test. At least 36 indentations in different locations of the samples' surface were carried out. For the SHI-irradiated samples, indentations were performed on the irradiated face of the block.

In order to determine nanomechanical properties' profiles along depth affected by the ion beam in SHI-irradiated samples, one of the samples (Li-UH-3) was included in an epoxy block, cut by the middle plane to expose the depth of the affected layer and polished to reach adequate surface roughness conditions for nanoindentation experiments. Then, several grids of aligned indentations starting in the epoxy resin region and advancing towards the bulk sample passing through the modified layer were performed.

Reduced elastic modulus (E_r) and hardness (H) values were determined following the well-known Oliver–Pharr approach [33] and considering the correction for viscoelastic effects introduced by Ngan et al. [34]. According to the Oliver–Pharr method, E_r was calculated from the contact stiffness, S , which is the slope of the measured load–depth (P – h) curve at unloading initiation, and the calibrated contact area A_c , as:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_c}} \quad (1)$$

A_c was indirectly obtained from a set of indentations performed on a standard sample (of known E_r). H was determined at the point of maximum applied load P_{\max} , as:

$$H = \frac{P_{\max}}{A_c} \quad (2)$$

Following the post-experiment correction proposed by Ngan et al. [34], the value of S in Eq. (1) was replaced by the corrected contact stiffness, S_e , given by:

$$\frac{1}{S_e} = \frac{1}{S_u} + \frac{\dot{h}}{\dot{P}_u} \quad (3)$$

where S_u is the apparent contact stiffness at the onset of unloading, \dot{h} is the tip displacement rate at the end of the load hold just prior to unloading and \dot{P}_u is the unloading rate.

2.3. Differential scanning calorimetry analysis

UH, γ -UH and γ -TT-UH samples were analyzed by differential scanning calorimetry (DSC). Tests were performed on a Shimadzu calorimeter under nitrogen atmosphere at a heating rate of 10 °C/min and using 5 mg weight samples. The melting enthalpy (ΔH_m) and peak melting temperature (T_m) of the samples were determined. The degree of crystallinity (X_c) was calculated via the total enthalpy method, according to the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_0} \times 100 \quad (4)$$

where ΔH_0 is the melting enthalpy for 100% crystalline polyethylene (291 J/g [3]).

2.4. Raman spectroscopy analysis

Micro-Raman spectroscopy was used to analyze the surface crystallinity of all samples. Spectra in the 1800–600 cm^{−1} wavelength range were obtained using an InVia Reflex confocal Raman microprobe (Renishaw) using a 50× objective. Excitation was provided with the 514 nm emission line of an Ar⁺ laser. Under the operation conditions the depth probe size was about 5–8 μm. The power of the laser was reduced to 50% to prevent damage by heating. For this power level, no thermal damage was observed. Raman spectra were taken averaging three acquisitions of 5 s each.

Polyethylene has been described by a three phase model composed by an orthorhombic crystalline domain, an amorphous phase and an intermediate anisotropic disorder phase [35]. According to this model, the fraction of orthorhombic crystalline domains was estimated by the following equation [35]:

$$X_{c|\text{orth}} = \frac{I_{1416}}{0.46 \times I_{1295+1305}} \times 100 \quad (5)$$

where I_{1416} represents the area of the Raman band located at 1416 cm^{−1} associated with the orthorhombic crystalline phase; $I_{1305+1295}$ is the area of the internal standard band group (CH₂ twisting); and 0.46 is the normalizing coefficient derived from a fully crystallized sample of polyethylene.

To calculate $X_{c|\text{orth}}$, all spectra were baseline corrected and normalized by the intensity of the peak at 1295 cm^{−1}. The fitting was performed using commercial software and Lorentzian functions.

3. Results

3.1. Surface nanomechanical properties

Fig. 1 shows typical load, P , vs. indentation depth, h , curves obtained in nanoindentation experiments for every sample studied. All curves exhibited load hysteresis due to irreversible deformation and indentation creep as evidenced by the increase in depth during the holding period. The penetration depth reached by the indenter in SHI-irradiated samples was much lower than the predicted ion projected range (Table 1), so that the differences observed in the indentation response were due to structural changes induced by the ion beam.

Overall, γ -irradiation followed by thermal treatment above the melting temperature modified the indentation response of UHMWPE in a larger extent than SHI irradiation, as judged by the difference in the shape of indentation curves. The maximum penetration depth achieved by the tip was higher for γ -TT-UH than for UH sample, which in turn was higher than for Li-UH and N-UH samples. The energy and ion type used in SHI irradiation also influenced the indentation response.

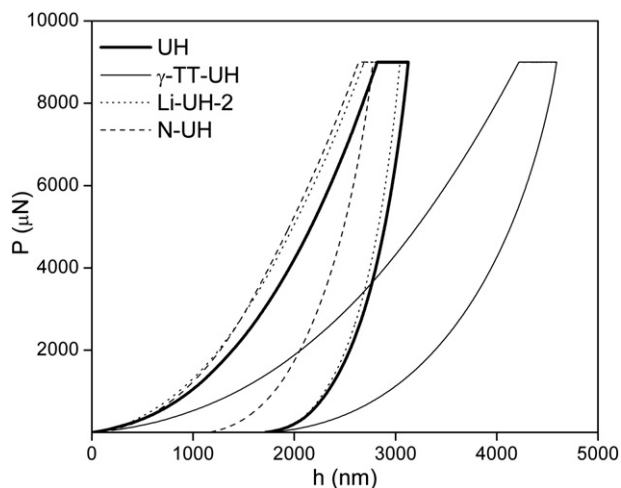


Fig. 1. Typical force–displacement curves obtained in nanoindentation experiments for UH, γ -TT-UH, Li-UH-2 and N-UH samples.

Nanomechanical properties determined from indentation curves taken at different locations of the samples' surfaces are shown in Table 2. In agreement with the changes observed in the shape of the indentation curves (Fig. 1), γ -irradiation followed by remelting caused a decrease in elastic modulus and hardness with respect to pristine UHMWPE. On the contrary, SHI irradiation produced an increase in both nanomechanical properties (Table 2).

For the Li-UH series, mechanical properties appeared practically unaffected by the ion beam fluence (Table 2). Li irradiated samples exhibited an elastic modulus of about 1.75 GPa and a hardness of 59 MPa. On the other hand, ion type and energy (and therefore electronic stopping power) had a strong effect on the resulting mechanical properties. The N-UH sample exhibited larger hardness than Li-UH samples but lower elastic modulus. This fact is better illustrated in Fig. 2, where the relative changes in elastic modulus and hardness of UHMWPE after SHI irradiation are plotted as a function of fluence and ion beam. Clearly, N ion irradiation slightly increased elastic modulus ($\sim 10\%$) but largely improved its hardness ($\sim 65\%$). Li ion irradiation caused an increase in elastic and plastic properties in the same extent ($\sim 50\%$).

Joslin et al. [36] postulated that the P_{\max}/S^2 ratio, which is proportional to H/E_r^2 , is a mechanical parameter that represents the material resistance to permanent deformation. This parameter is independent on contact area and therefore it is not influenced by possible changes in surface roughness induced by SHI irradiation. H/E_r^2 values were included in Table 2. It was observed that γ -TT-UH was the most resistant sample to permanent damage. N-UH was more resistant to permanent deformation than pristine UHMWPE due to the extension of the elastic deformation and the limitation of plastic deformation capabilities. On the contrary, Li-UH was less resistant to permanent deformation than pristine UHMWPE because the increase in surface stiffening is accompanied by a relative hardening.

A question now arises about how representative of the modified layer were the nanomechanical properties determined in SHI-irradiated samples: do they vary throughout the ion beam affected layer? To answer this question additional nanoindentation experiments were performed in the specially prepared Li irradiated sample described in Section 2.2. The resulting hardness and reduced elastic modulus profiles

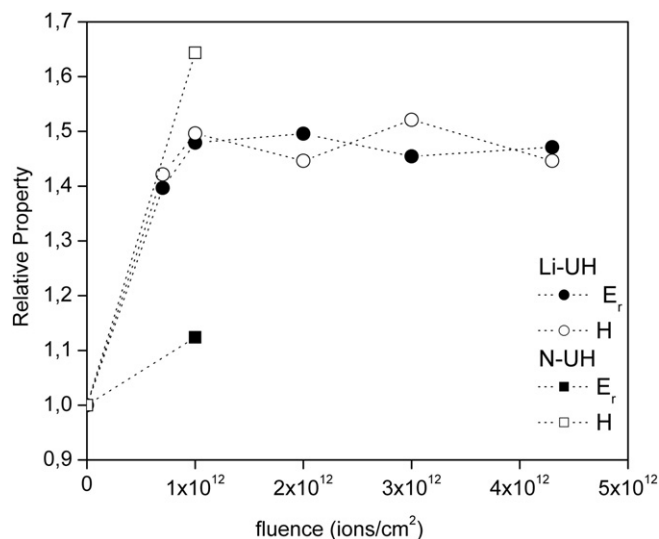


Fig. 2. Surface nanomechanical properties of SHI-irradiated samples related to pristine UHMWPE properties as a function of fluence. Dot lines are a guide to the eye.

are shown in Fig. 3 together with an optical image of the post-experiment sample surface. The marks left by the Berkovich indenter were visible on the surface (Fig. 3). Three different regions could be optically distinguished on the tested sample: a white zone corresponding to the epoxy resin; a light gray zone of about $500 \mu\text{m}$ in thickness that starts at the surface originally exposed to ion beam irradiation; and a gray zone that corresponds to unaffected material. The thickness of the light gray region coincided with the projected ion target depth predicted by SRIM©-2013 (Table 1), so it can be thought that it corresponds to the zone affected by the Li ion beam. The difference in color between the affected and non-affected regions (optical image of Fig. 3) was due to the difference in hardness that induced different surface roughness and hence different light reflection.

Nanomechanical properties remained almost constant along the depth affected by the Li ion beam (Fig. 3). The affected layer exhibited higher elastic modulus and hardness than the unaffected UHMWPE and average values were in good agreement with those reported in Table 2 for Li-UH samples within the error bands. Therefore, it could be confirmed that nanomechanical properties reported in Table 2 were essentially those of the modified layer.

The constancy in nanomechanical properties throughout the modified depth also suggested that structural changes induced by Li-irradiation were homogeneous. This may be due to the fact that $(dE/dx)_e$ decreased in a shallow depth and then remained almost constant until it vanished, as predicted by SRIM©-2013 for Li-polyethylene interactions (47 MeV).

3.2. Degree of crystallinity

DSC is the most common technique used to measure thermal properties of UHMWPE and provides the melting temperature (T_m), heat of fusion (ΔH_m) and degree of crystallinity (X_c). DSC analysis was used to investigate changes in thermal properties of UHMWPE induced by γ -irradiation and by the subsequent thermal treatment above the melting temperature because these treatments affect the material's bulk.

Table 2
Nanoindentation test results: Surface nanomechanical properties of UH, γ -TT-UH, Li-UH and N-UH samples.

Sample	UH	γ -TT-UH	Li-UH-1	Li-UH-2	Li-UH-3	Li-UH-4	Li-UH-5	N-UH
E_r (GPa)	1.21 ± 0.05	0.54 ± 0.03	1.69 ± 0.10	1.79 ± 0.06	1.81 ± 0.11	1.76 ± 0.09	1.78 ± 0.06	1.36 ± 0.04
H (MPa)	40.1 ± 3.0	22.1 ± 0.5	57.0 ± 5.0	60.0 ± 3.2	58.0 ± 4.0	61.0 ± 5.0	58.0 ± 2.1	65.9 ± 2.6
H/E_r^2 (GPa^{-1})	0.027	0.076	0.019	0.019	0.018	0.019	0.018	0.0356

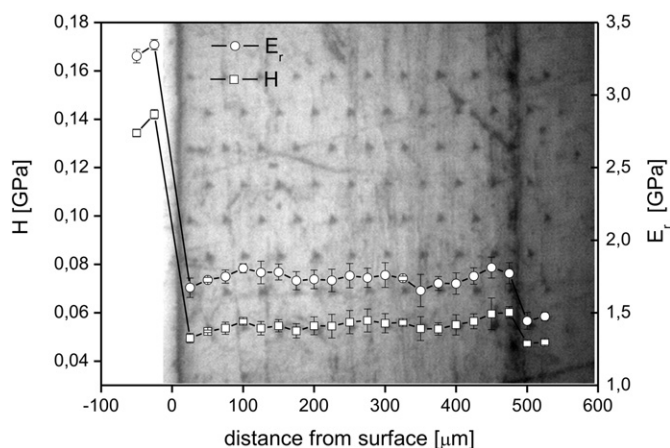


Fig. 3. Elastic modulus and hardness values determined along the distance from surface for a specially prepared Li-UH-3 sample embedded in an epoxy block (details of sample preparation are given in Section 2.2). The background is the optical image of the tested sample.

Fig. 4 shows the DSC thermograms obtained for UH, γ -UH and γ -TT-UH samples while the extracted thermal properties are listed in Table 3.

It was observed that the heat of fusion and melting temperature of UHMWPE increased after γ -irradiation and decreased after the subsequent thermal treatment below their initial values. Therefore, samples exposed to the combined technique (γ -TT-UH) exhibited a slight reduction in crystals size as well as a marked decrease in crystalline fraction. The explanation for this behavior is well documented in literature [2, 37–39]. When UHMWPE is exposed to low energy ionizing radiation, chain scission and crosslinking occur by the formation and recombination of free radicals primarily in the amorphous phase. The increase in X_c and T_m after γ -irradiation (Table 3) is due to chain scission, which permits polymer chains in non-crystalline regions to fold and further crystallize. The free radicals generated in the crystalline domains remain trapped owing to the reduced mobility of the chains. During the subsequent thermal treatment over the melting point of UHMWPE, radicals are released from crystalline domains, the mobility of the chains increases and then radical are able form new crosslinks. During cooling to room temperature, molecular organization and chain folding capability are hindered by the presence of crosslinks in comparison to unirradiated UHMWPE. Therefore, as a consequence of the crosslinks hindering effect, the recrystallization of γ -irradiated UHMWPE led to a polymer

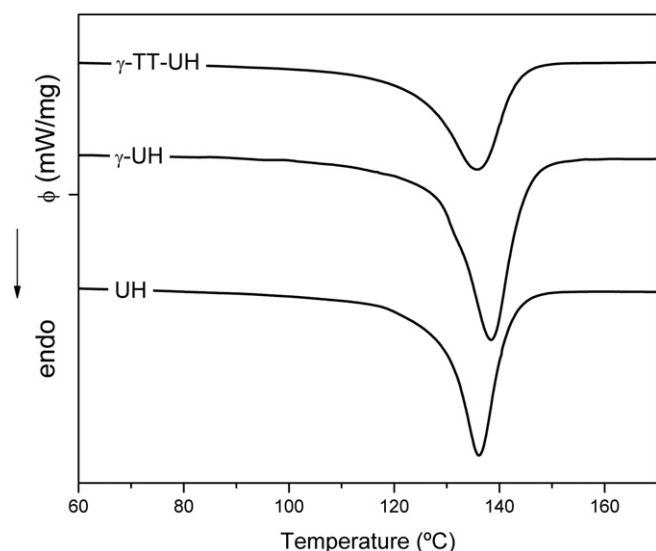


Fig. 4. DSC thermograms obtained for UH and γ -UH and γ -TT-UH samples (first heating).

Table 3
DSC results: thermal properties and degree of crystallinity of UH, γ -UH and γ -TT-UH samples.

Sample	T_m (°C)	ΔH_m (J/g)	X_c (%)
UH	136	159	54.5
γ -UH	141.3	174	59.7
γ -TT-UH	135.5	139	47.7

(γ -TT-UH sample) that displayed a lower crystalline fraction and smaller sized crystals than pristine UHMWPE.

The X_c determined for γ -TT-UH sample was in excellent agreement with the value reported for GUR1050 γ -irradiated and thermally treated in equivalent conditions (46.2%) [40].

Thermal properties of SHI-irradiated samples could not be determined by DSC because the minimum mass required to perform feasible calorimetric experiments exceeded that of the modified layer. Therefore, Raman spectroscopy in the 900 to 1600 cm^{-1} wavelength range was used to determine the crystalline fraction in N-UH and Li-UH samples. For comparison, UH and γ -TT-UH samples were also analyzed. As no significant differences were observed in nanomechanical properties of Li-UH samples only the Li-UH-2 sample was tested as representative of the series.

Fig. 5 shows the Raman spectra obtained for UH, γ -TT-UH, Li-UH and N-UH samples. The characteristic Raman sharp bands associated to polyethylene vibrational modes such as those located at 1060, 1127, 1295, 1416, 1440 and 1460 cm^{-1} remained after SHI-irradiation and after γ -irradiation followed by remelting [16,29,41–43]. SHI-irradiation enhanced the effect of photoluminescence in the Raman spectra as shown in Fig. 5 by the shift of the base line of the N-UH and Li-UH samples to higher intensities. This effect was previously reported for UHMWPE after nitrogen plasma immersion ion implantation and attributed to an increase of defects in the polymer crystals caused by energetic ions [44]. Li-UH and N-UH spectra did not show a broad peak around 1600 cm^{-1} which is associated to the development of a dehydrogenated diamond-like carbon layer, as observed after plasma immersed ion implantation of UHMWPE [19,20,44]. In addition, the concomitant change in surface color from shining white to brownish yellow reported for ion implantation and plasma based ion implantation of UHMWPE was not observed at all [13,19].

After the spectra were baseline corrected and normalized, changes in the relative intensities of several bands associated with degree of crystallinity of the samples, with respect to the pristine UHMWPE, were observed. Fig. 6 shows an example of the peak deconvolution

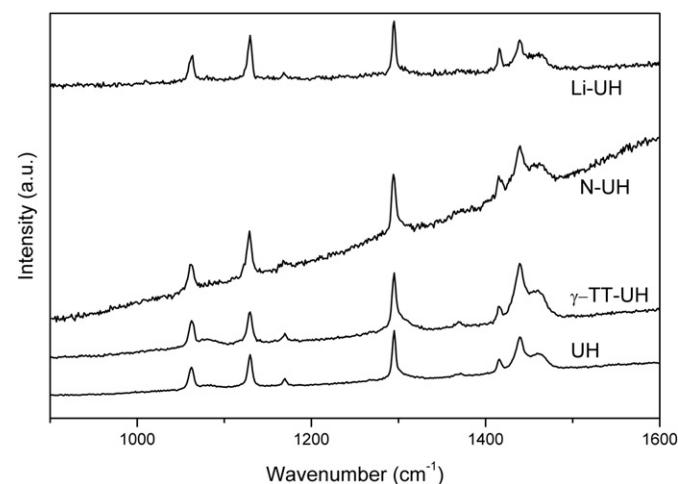


Fig. 5. Raman spectra in the 600 to 1800 cm^{-1} range obtained for UH, γ -UH, Li-UH-2 and N-UH samples.

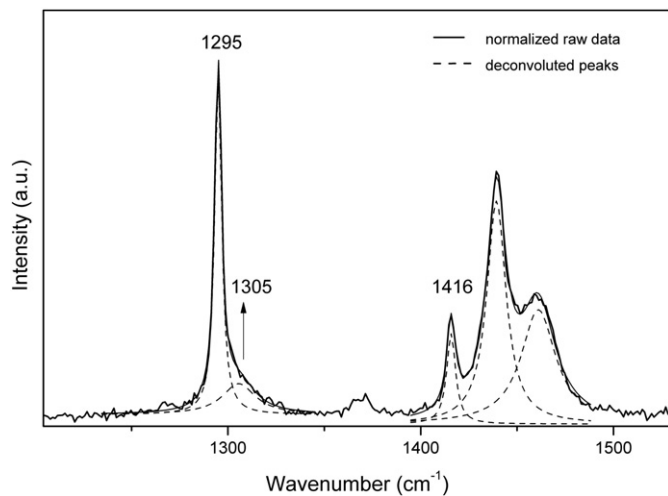


Fig. 6. Example of orthorhombic crystalline fraction determination from deconvolution of Raman spectra (UH sample spectra).

procedure used to evaluate the orthorhombic crystalline fraction according to Eq. (5). The $X_{c|orth}$ values are listed in Table 4.

As expected, γ -TT-UH sample exhibited lower orthorhombic crystalline fraction than pristine UHMWPE [2,35,38,39]. On the contrary, SHI irradiation induced an increase in $X_{c|orth}$, which was more pronounced in Li-UH than in N-UH samples.

3.3. Degree of crystallinity-nanomechanical properties correlation

When comparing the shape of the indentation curves (Fig. 1) with the orthorhombic crystalline fraction (Table 4) of all tested samples, it emerged that the indentation response depended on the crystallinity level. For example, the γ -TT-UH sample, which exhibited the most different degree of crystallinity presented the most different indentation curve.

Nanomechanical properties were plotted as a function of $X_{c|orth}$ in Fig. 7. An exponential correlation between E_r and $X_{c|orth}$ was found, indicating the strong dependence of the elastic response of the surface with UHMWPE crystalline level. The increase in elastic modulus with increasing crystallinity has been widely reported in literature for polyethylene polymers including UHMWPE [2,45–47]. Crystallinity level and interlamellar thickness have been assigned as the main variables affecting elastic modulus of polyethylene [45].

It is also known that hardness is proportional to yield stress [48,49]. The increase in hardness and yield stress with degree of crystallinity has been widely reported [45,50,51]. The dependence of yield stress with microstructure is more complex than elastic modulus, and depends on the structure of crystallites and associated regions [45]. A similar exponential correlation between H and $X_{c|orth}$ was found in this study with the exception of the N-UH sample.

The difference between the change in properties of UHMWPE after being irradiated with Li ions and N ions is still not fully understood. The larger increase in H/E_r in N-UH with respect to Li-UH samples could be related to another structural change, which may depend on

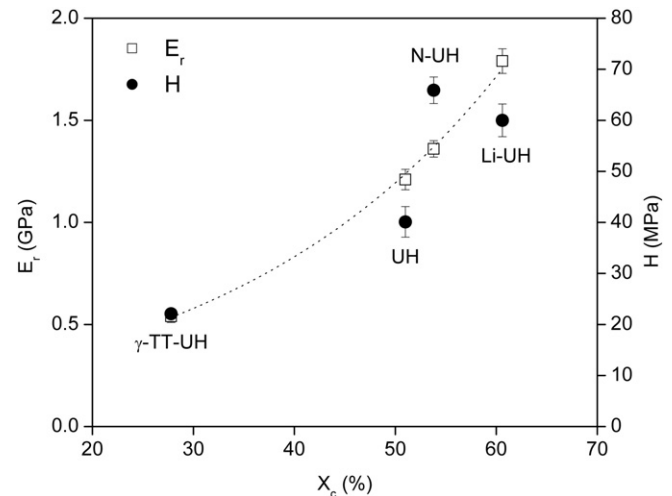


Fig. 7. Elastic modulus and hardness values obtained in nanoindentation tests plotted against orthorhombic crystalline fraction measured by Raman spectroscopy.

the electronic stopping power of the ion beam, for example the creation of crosslinks and in-chain unsaturations, among other possibilities as reported for LDPE and HDPE [7,9]. It is known that some chemical changes appeared in SHI-irradiated polyethylenes if $(dE/dx)_e$ exceeds a threshold and the used N ion beam had a larger $(dE/dx)_e$ than Li ion beam [9]. In own previous works, the formation of C=C double bonds in a similar N-UH sample was detected by FTIR (ATR mode) analysis [22,24]. FTIR spectra showed the appearance of a band at 965 cm^{-1} characteristic of trans-vinylene groups. Trans-vinylene groups appeared to be stable at room temperature [9] and therefore could be the responsible for the further improvement in hardness. The chemical changes induced in UHMWPE by ion beams of different $(dE/dx)_e$ needs further investigation.

3.4. Implications on wear performance

It is well known that crosslinking induced by γ -irradiation diminishes the chain mobility required for large strain plastic deformation and orientation, retards the fibril formation and hence slows down the wear rate of UHMWPE components [2]. Therefore, in this modification technique, the source of wear resistance improvement relays on the reduction of the polymer strength in the transverse direction, which is the mechanism responsible for wear debris generation in UHMWPE during multidirectional motion [52].

In UHMWPE, stiffness and hardness are mainly dependent on its crystallinity [2,47]. Therefore, it was shown that γ -irradiation itself does not adversely affect these properties, but the melting required after irradiation to avoid oxidation decreases the degree of crystallinity and hence detracts the bulk and surface properties. Despite the observed reduction in elastic modulus and hardness, the crosslinking achieved in γ -TT-UH samples effectively enhanced the resistance to permanent deformation of UHMWPE, as demonstrated by the increase in the H/E_r^2 ratio (Table 2). This result is in good agreement with related literature [2,53,54].

The increase in wear performance observed in UHMWPE after SHI irradiation, reported in [22–24,55], can be attributed to a completely different source. Contrary to γ -TT-UH samples, Li-UH and N-UH samples exhibited harder and stiffer surfaces than pristine UHMWPE primarily due to the large increase in degree of crystallinity of the surface layers. As hardness is proportional to material yield stress, it is expected that its enhancement improves abrasive wear resistance of UHMWPE [56,57] without detriment of the bulk properties. As well, the increase in elastic modulus is presumed to increase both abrasive and adhesive wear resistance [21].

Table 4

Raman spectroscopy results: degree of crystallinity of UH, γ -TT-UH, Li-UH-2 and N-UH samples.

Sample	$X_{c orth}$ (%)
UH	51.0
γ -TT-UH	27.8
Li-UH-2	60.6
N-UH	53.8

The SHI irradiation condition used in N-UH sample yields to a better nanowear performance than the ones used in the Li-UH samples [55]. This may be due to the different relative change in plastic to elastic properties suffered by both types of samples as judge by the H/E_p^2 ratio (Table 2).

4. Conclusions

In this paper, the surface nanomechanical properties and degree of crystallinity of UHMWPE samples exposed to SHI irradiation using Li and N ion beams were compared with those promoted by the traditional treatment of γ -irradiation followed by remelting.

It was shown that SHI irradiation improves hardness and elastic modulus of UHMWPE surface layers while γ -irradiation followed by remelting reduces these properties of the bulk. SHI irradiation enlarges the degree of crystallinity of UHMWPE while the thermal treatment over its melting temperature (170 °C) reduces the crystalline level due to the hindered crystallization process of crosslinked chains. Therefore, the changes in nanomechanical properties are primarily linked to the changes in degree of crystallinity of UHMWPE.

It was observed that the increase in nanomechanical properties as well the relative change in elastic to plastic properties of SHI-irradiated samples depends on the ion type and energy used. The sample irradiated with N ions displays a higher hardness to stiffness ratio than the series irradiated with Li ions. The difference between both irradiation conditions is the higher electronic stopping power of the N-ion beam. Therefore, a beneficial change in the chemical structure that acts improving the resistance to plastic deformation of UHMWPE is probably occurring and it may depend on the electronic stopping power of the ion beam.

It was demonstrated that the layer affected by the Li ion beam exhibits constant nanomechanical properties. Thus, SHI irradiation yields a homogeneous modified layer perfectly attached to the pristine polymer.

It was found that nanomechanical properties remain practically unaffected by the fluence used if it is in a range near the optimum value determined according to Chappa et al. analysis [22,26].

Further work is in progress to verify the usefulness of SHI irradiation to improve the wear resistance of UHMWPE components. The comparison between the performance under conditions similar to those presented in service of pristine, γ -irradiated and remelted and SHI-irradiated UHMWPE is under development.

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