Nitrogen-PBII modification of ultra-high molecular weight polyethylene: Composition, structure and nanomechanical properties

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Abstract

Plasma based ion implantation of nitrogen was performed on mechanically polished UHMWPE model samples by applying 27.13 MHz RF energized low pressure N_2 plasma with 15–30 kV pulses and fluences up to $5 \cdot 10^{17}$ ions/cm^2. Surface compositional and structural alterations and nanomechanical property changes were investigated by XPS, Raman and by nano-indentation and nano-scratch techniques. The implanted N amounted up to 13–20 at.% (N/C=0.18–0.30), while a significant amount of oxygen could also be detected on the surface. Three types of chemical states of the incorporated nitrogen were detected, related to linear sp^2 C≡N–C and to planar and non-planar sp^3 type C–N bonds. The applied PBII treatment led to severe dehydrogenation of the polyethylene resulting in conversion of the surface into a nitrogen-containing DLC type structure. Up to four-fold increase of the hardness at 50–100 nm depth was measured compared to the untreated samples. The scratch volume, characterising the wear resistance, decreased also significantly down to 25–35% of the original value.
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1. Introduction

Wear and wear debris induced limitation of the service life of ultrahigh molecular weight polyethylene (UHMWPE, further PE) hip and knee joint components is of great concern at the biomedical implant application of this material. Numerous attempts have been made for improving the wear properties of PE, mostly using electron beam or gamma radiation and also conventional line-of-sight ion implantation. Only a few attempts were published on the PBII treatment stating enhancement of the mechanical and tribological properties [1–6]. In spite of these promising results, to our best knowledge, comprehensive studies of the dependence of the properties on the treatment parameters are still lacking. Also, there are only very few studies on the compositional and structural changes involved [3,5,6]. Considering all this we performed nitrogen plasma based ion implantation (N-PBII) modification of UHMWPE in this work and studied the induced compositional, structural and nanomechanical changes in a relatively broad parameter domain. Implan-

tation energy and ion dose dependence of the nanohardness, elastic modulus and scratch (wear) resistance are presented. Manifold enhancement of these properties is pointed out.

2. Experimental

Medical-grade UHMWPE (type GUR4150 HP, supplied by Poly Hi Solidur/Menasha, molecular weight $3.5 \cdot 10^6$ g/mol, density 0.932 g·cm^{-3}, crystallisation degree 50%) was used in this study. The machined surface of the samples was grinded and polished.

The PBII treatment was performed in high purity (5N5) nitrogen plasma, produced by a Cesar 273 RF generator (Dressler, Germany) at 27.13 MHz with 50–150 W power by using a high voltage pulser (ANSTO, Australia). Pulses of 15–30 kV with 12–30 μs length and 20–100 Hz frequency were applied, while the ion doses varied from $0.25 \cdot 10^{17}$ cm^{-2} to $3 \cdot 10^{17}$ cm^{-2}.

XPS (ESCA) studies were performed by a Kratos XSAM 800 spectrometer using Mg K$\alpha_{1,2}$ excitation, with fixed analyser transmission of 40 eV pass energy and 0.1 eV step size for the high-resolution spectra. The spectra were referenced

to the C1s line set to a binding energy of 284.4 eV. The accuracy of binding energy determination was ±0.2 eV or better. Data acquisition and processing were done with the Kratos Vision 2, while quantification by the XPS MultiQuant [7] programs.

The Raman scattering spectra were recorded on a Renishaw 1000 B micro-Raman spectrometer. The 488 nm line of an argon ion laser and a diode laser with wavelength of 785 nm served as excitation sources sampling a volume of ∼1 μm in diameter.

The nanomechanical properties including nanohardness and scratch volume were measured by a NanoTest 600 (MicroMaterials Ltd., UK) instrument. For depth-sensing nanohardness tests a Berkovich type indenter head was used. Indentations were made in depth-control mode in 50–100 nm range with loading/unloading rate of 0.02 mN·s^{-1}. Linear fit [8] was applied for data evaluation with the accuracy of ±5%. Five-pass wear tests were performed by a Rockwell type diamond head (tip radius of 25 μm, scanning velocity of 2 μm·s^{-1}, track distance 300 μm, 20 mN load). The scratch volume was calculated from the residual wear groove depth and the tip geometry.

3. Results and discussion

3.1. Estimated thickness of the implantation

Calculation for ion penetration was performed using the SRIM-2003 program for estimation of the maximum thickness of the modification at the highest applied acceleration (pulse) voltage of 30 kV. Taking into account that in our conditions the major ion species in the plasma are N_2^+, each implanted N atom, will have, as an average, only half of the energy acquired by the molecular ion from the electric field. Thus the calculation was performed for 15 keV N^+, resulting in 64 nm for the mean projected ion range. The distribution curve shows that practically all implanted N stops in a depth below 100 nm thickness. This calculation does not take into account, however, that the PE surface is gradually transforms into a carbonaceous, densified
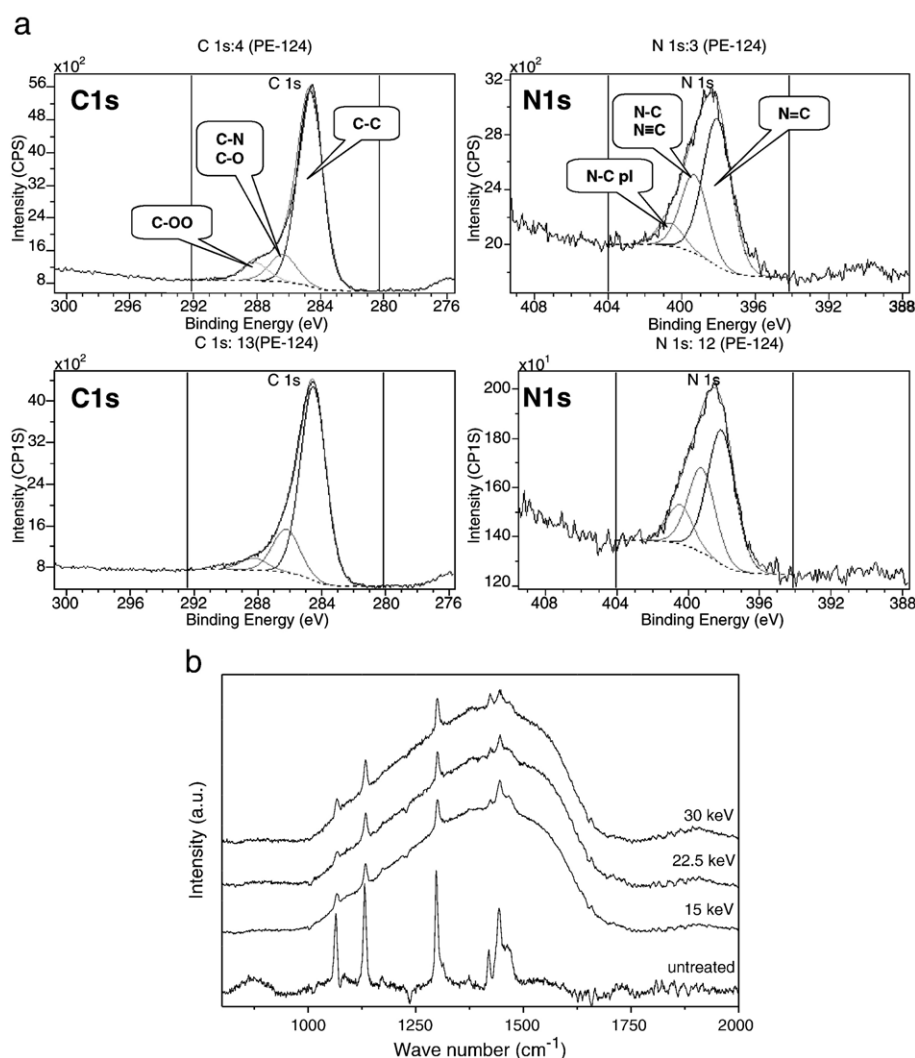

Fig. 1. Chemical structure characterisation of PBII treated UHMVPE samples: (a) XP spectra of C1s and N1s lines of the PE-124 sample in as-treated condition and after Ar$^+$ ion etch, showing three different chemical states, (b) Raman spectra of untreated and N-PBII treated (at indicated energy) samples, recorded with 785 nm excitation wavelength.

layer exhibiting higher obstacle to the penetration and, as a result, decreasing the above calculated range of the implanted ions.

3.2. Composition and chemical structure

The surface composition representative for the top 5–8 nm shows, in addition to the 13–15 at.% implanted nitrogen, also the presence of 10–14 at.% oxygen. This amount of oxygen is far above the value of 0.9 at.% measured on the untreated PE. A 'light' (1.5 keV, <1 μA·cm^{-2}, 5 min) Ar$^+$ ion etch removes the majority of the oxygen. From this fact it can be concluded that the active sites created by the PBII treatment and left behind on the surface are reacted by oxygen (or water) after the treatment. Another conclusion is that the majority of oxygen is situated at the near surface region of the samples. Water chemisorption may be the cause of the observed further increase of oxygen at storage in ambient.

As known, XPS is unable to detect hydrogen, but combined RBS-ERDA analysis, performed outside of this study, revealed that N ion implantation led to preferential removal of the hydrogen from the near-surface region of the PE [9].

The chemical state of C and N in the modified layer is depicted in Fig. 1(a) for a representative sample in as-prepared condition and after Ar$^+$ ion etch. The broad and asymmetric shape of these C1s and N1s lines demonstrates at least 3 different components corresponding to 3 different chemical states. As seen the majority of carbon is in C–C bonding state (predominant peak at 284.4 eV). Components at 286.1 eV and at about 288 eV can be assigned to C–O, C–N or disordered C–C and to –COO (carboxylic C), respectively [10]. The assignment N1s peak components can be done based on the overwhelming, although controversial, chemical shift data published for carbon-nitride (CN$_x$, C$_3$N$_4$) ([11–14], and references therein). In accordance to our previous data the peak at 398.3 eV represent nitrogen bonded to two sp^2 carbon atoms as C–N=C [11,13]. The component at 400.7 eV was assigned to N single bonded to three sp3 type carbon (N–C) [11–13]. The peak at about 399 eV is assignable also to N–C of none-planar geometry [13], but small amount of nitril –C≡N or type units may not be excluded either. After Ar$^+$ ion etch, in connection with elimination most of the surface oxygen, significant decrease of the intensity of 288 eV (COO) peak is detected. A small increase of the 286 eV (C–N) peak is connected with a slight increase of the surface N-content. A small redistribution in the ratio of the chemical states of N can also be observed showing an increase of sp^3 N–C and decrease of sp^2 N=C components. Such ion bombardment induced transformations were observed also at argon bombardment of the CN$_x$ layers [14].

Significant hydrogen loss due to N-PBII treatment detected by RBS-ERDA, was further supported by Raman spectra shown in Fig. 1(b). While the vibrational spectral lines characteristic for the pristine UHMWPE sample are still visible, the spectra of the treated samples dominated by the broad D and G bands at about 1341 cm^{-1} and 1527 cm^{-1} respectively. These bands are characteristic features for amorphous carbon or DLC. Consequently these spectra give evidence for the evolution of DLC

type chemical structure on the surface of the UHMWPE at the applied N-PBII treatment. Detailed analysis (curve-fitting) of similar spectra revealed also the presence of two low intensity bands at 1063 and 1173 cm^{-1} tentatively related to the distorted C–C skeleton vibrations of sp^3 hybridised carbon [15]. At increasing the implantation energy of the treatment the position of the G band shifts to lower wave numbers together with the decrease of the D band intensity. These changes suggest that the
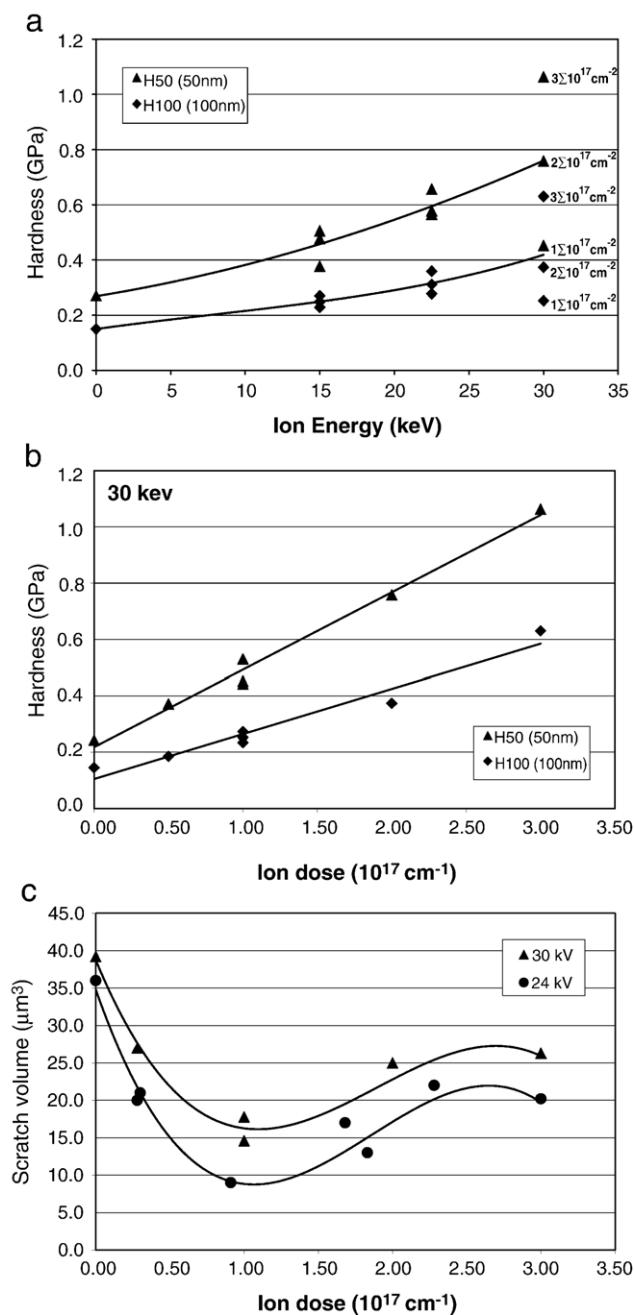

Fig. 2. Nanomechanical characterisation of PBII treated UHMVPE samples: (a) implantation energy dependence of nanohardness measured at 50 and 100 nm plastic depth; fitted by polynomial trendline, (b) ion dose dependence of nanohardness of 30 keV treated samples measured at 50 and 100 nm plastic depth; fitted by linear trendline, (c) ion dose dependence of the scratch volume of 24 kV and 30 keV N-PBII treated UHMVPE samples; fitted by polynomial trendline.

sp^3 type carbon content may be increased in the modified layer at increasing the energy of the treatments.

3.3. Nanomechanical properties

Dynamic hardness values obtained at 50 nm (H50) and 100 nm (H100) plastic depths were taken as representative ones for characterising the effect of the treatment. Increased nanohardness was measured for all samples treated in the indicated energy and dose domain, as shown in Fig. 2(a) and (b). A super-linear increase was documented at increasing ion energy (Fig. 2(a)) when a high dose of $3 \cdot 10^{17}$ ions/cm^2 was applied. The hardness of the uppermost surface layer, represented by the H50 values, was always higher than that for the deeper layer expressed by the H100 points. The increase of the hardness with the implantation energy is obviously connected with the increase of the thickness of the modified surface layer, in one hand, but in the other, it can also be connected with the increasing sp^3 content concluded from the XP and Raman spectra.

As depicted in Fig. 2(b), a close to linear dependence of the hardness for both 50 nm and 100 nm depths was established at increasing the applied dose in the range $(0.5–3) \cdot 10^{17}$ ions/cm^2 when the treatment was performed at 30 keV N$_2^+$ energy. Less pronounced increase with the dose was measured at treatments with lower, e.g., 15 keV and 22.5 keV implantation energy.

Scratch volume. As represented by the data in Fig. 2(c), the scratch volume on the N-PBII treated samples was always smaller than that for the untreated PE, i.e., the scratch resistance can be increased significantly by such treatment. The dose dependence for samples treated at 30 keV and also at 24 keV indicates a local minimum showing as low as 25–35% of the original value of the untreated samples. The exponential guide-lines fitted to the data indicate that the highest scratch/wear resistance was obtained at doses around $1 \cdot 10^{17}$ ions/cm^2.

4. Conclusions

The applied surface sensitive analytical techniques (XPS, Raman) reveal significant compositional and structural changes of the PBII modified surface layer of UHMWPE. The nanohardness alterations show convincingly implantation energy and dose dependence consistent with the determined structural changes. The hardness data reflects the changes of the top layer. The elastic modulus and the scratch data are representative for a thicker layer. This means that the properties of the fully modified top surface, the partially modified interface and the underlying unmodified bulk can be interpreted as a layered composite structure, as reflected by the dose dependent alterations of the elastic modulus and scratch.

- PBII modification of UHMW PE can be performed at the commonly applied conditions used for treating various types of samples, e.g., metallic ones.

- The implanted N forms predominantly three different chemical states similarly to those found in the different CN$_x$ thin films.
- The PBII treatment results in significant loss of H and conversion of the PE surface to nitrogen-containing DLC.
- Nanohardness increases gradually at increasing of the implantation energy and dose, reaching at 30 kV and $3 \cdot 10^{17}$ cm^{-2} dose about four times higher value than that of the unimplanted PE.
- Scratch volume decreased considerably with ion dose reaching a minimum of 25–35% of the original value at around $1 \cdot 10^{17}$ cm^{-2} dose, representing a significant increase of the scratch (wear) resistance.
- The results of the N-PBII treatment manifest complete chemical and structural alterations of the UHMWPE surface leading to enhanced nanomechanical properties potentially beneficial for biomedical (joint prostheses) applications.

Acknowledgement

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