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Short communication

Improved wear resistance of ultra-high molecular weight polyethylene by plasma immersion ion implantation

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Abstract

Surface modification of ultra-high molecular weight polyethylene (UHMWPE) has been explored using the novel non-line-of-slight plasma immersion ion implantation (PIII) with nitrogen. The modified surfaces were characterised by SEM and a Nano Test 600 testing machine. The tribological behaviour of PIII treated UHMWPE sliding against AISI 316L stainless steel counterfaces was evaluated using a pin-on-disc tribometer under water lubricated conditions. The experimental results show that PIII is a very promising surface engineering technique to improve such surface mechanical properties as surface hardness and elastic modulus of UHMWPE. As a result, the wear resistance of UHMWPE was significantly enhanced by a factor of three following PIII treatment, as compared with untreated material. It was found that the significantly improved wear resistance of PIII treated UHMWPE can be mainly attributed to ion bombardment induced cross-linking, and thus surface hardening. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ultra-high molecular weight polyethylene (UHMWPE); Plasma immersion ion implantation (PIII); Sliding wear

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) has been the principle material of choice for total joint replacement prostheses (TJR) (e.g. acetabular cups and tibial components) for many years [1]. However, the wear of UHMWPE and the resultant wear debris induced osteolysis is now recognised as one of the major causes of premature failure of total joint replacement [2]. Therefore, many attempts have been made to enhance the wear resistance of UHMWPE with a view to increasing the life span of total joint replacements involving UHMWPE articulating surfaces. These include (i) optimising the design via mathematic modelling [3] and tribological analysis [4]; (ii) modifying polymer structure such as chain length [5], molecular weight and crystallinity [5,6], cross-linking [7], and fibre reinforcement [8]; and (iii) selecting or engineering the counterfaces [9,10]. For example, our previous work has demonstrated that the tribological properties of UHMWPE can be significantly improved by surface engineering the Ti₆AL4V alloy counterfaces using a novel thermal oxidation (TO) treatment [11].

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In recent years, there is an ever-increasing interest in enhancing the tribological behaviour of polymers via advanced surface engineering techniques. Ion beams have been used to improve the tribological properties of polymers [12]. However, it is very difficult, if not impossible, to achieve uniform ion implantation of complex shaped components, such as acetabular cups, without using sophisticated manipulating devices. Having been developed to address this problem [13], plasma immersion ion implantation (PIII) is a novel surface engineering technique that offers a substantially uniform surface modification of components owing to easing the light-of-sight restriction of conventional ion implantation.

Until very recently, little attention has been paid to the PIII surface modification of polymers [14]. However, no results have been reported for the tribological behaviour of PIII surface modified UHMWPE. Therefore, the present study was directed towards improving tribological behaviour and interrelated surface mechanical properties of UHMWPE employing the PIII treatment technique. In additional, the wear mechanisms operating were also investigated.

2. Experimental details

2.1. Materials

The medical grade UHMWPE (GUR 4150 HP) used in this study was supplied by Poly Hi Solidur Ltd. (UK), in the

Table 1 Plasma immersion ion implantation parameters

Designation	Voltage (kV)	Repetition rate (Hz)	Pulse length (µs)	Dose (ions per cm ²)
PE1	20	100	60	$1 \times 10^{17} \text{ N}^+$
PE2	20	100	60	$2 \times 10^{17} \text{ N}^{+}$
PE3	20	100	60	$4 \times 10^{17} \text{ N}^{+}$

form of 12.5 mm diameter, extruded and annealed rod. The crystallinity of the as-received UHMWPE was estimated to be about 50% using X-ray diffraction method (X, Pert Pw 3040, Philips). The density of homogeneous material and average molecular weight, quoted by the manufacture, are $0.932\,\mathrm{g/cm^3}$ and $3.6\times10^6\,\mathrm{g/mol}$, respectively. The sample surfaces were ground with 2400[#] grit SiC abrasive paper and polished on alumina paste to an average surface roughness value R_a of about $0.02\,\mu\mathrm{m}$. The counterpart material was commercial AISI 316L stainless steel. The nominal composition of the steel is as follows (in wt.%): $0.03\mathrm{C}$, $2.0\mathrm{Mn}$, $17\mathrm{Cr}$, $13\mathrm{Ni}$, $10\mathrm{Si}$, $2.5\mathrm{Mo}$ and balance Fe. Discs of approximately $100\,\mathrm{mm}$ in diameter and $10\,\mathrm{mm}$ in thickness were ground to $1200^{\#}$ SiC grit paper and polished on diamond paste to a surface roughness value R_a of $0.015\,\mu\mathrm{m}$.

2.2. PIII treatment and characterisation

The UHMWPE samples were surface treated using a Mark 1 PIII system at the Technical University of Clausthal, Germany, in a nitrogen working gas at a pressure of 1.7×10^{-1} Pa. Detailed treatment conditions and the specimen designation are summarised in Table 1. Following PIII treatment, surface morphology was examined using SEM (JEOL 5410). The nanohardness and elastic modulus of the PIII-treated UHMWPE were studied employing a NanoTest 600 machine with a Berkovich diamond indenter because of the ultra-thin modified layers and very soft substrate. The conditions used for measuring nanohardness and elastic modulus are detailed in Table 2.

2.3. Tribotesting

Tribological properties of the PIII modified UHMWPE pins sliding against 316L austenitic stainless steel counterfaces in distilled water were investigated employing a conventional pin-on-disc tribometer at a constant speed of 0.25 m/s and a contact stress of 5 MPa in a dust-free environment. The schematics of the tribometer, test configuration

Table 2
The detailed conditions of nanoindentation tests

Maximum load (mN)	1	
Initial load (mN)	0.02	
Loading rate (mN/s)	0.02	
Maximum depth (nm)	250	
Dwell time (s)	10	

and test pin are given in Fig. 1. Friction coefficient data were acquired from conversion of the friction force collected by the computer. The wear pins were truncated cylindrical in order to offer a substantial foundation for the wear surface.

Before wear testing, the discs were degreased with acetone and polymeric pins were ultrasonically cleaned to remove any loose particles, and were then immersed in distilled water for 2 days in order to pre-soak them. After each test period of about 21 km, the wear pins were removed and any adhering debris attached to the trailing edge of the wear surfaces was wiped away. Subsequently, the pins were ultrasonically rinsed, dried and weighed on a balance with accuracy to 0.01 mg. In view of the water absorption by polymer pins, a control pin of the same material and size was used to account for and monitor the rate of water absorption during the testing period. The experiments were terminated after reaching a sliding distance of about 110 km. Wear volume loss was calculated from the weight loss by assuming the density of UHMWPE to be 0.932 g/cm³. The average specific wear factor of UHMWPE was calculated using the following formula:

Wear factor =
$$\frac{\text{volume loss}}{\text{sliding distance} \times \text{load}}$$

where the wear factor is measured in mm³/m N, volume loss in mm³, sliding distance in meters and load in Newton.

2.4. Post-test microanalysis

Optical microscopy and scanning electron microscopy (SEM, JEOL 6300) were used to examine the wear morphologies of the UHMWPE pins and wear tracks on the 316L counterfaces. To detect any UHMWPE transferred onto AISI 316L stainless steel counterface, ultra-thin window EDX, attached to the JEOL 6300 SEM was also used.

Microstructure analysis was carried out using a high resolution Hitachi S-40000 field emission gun (FEG)-SEM. It was necessary to etch the tested surfaces in order to reveal representative lamellar reconstruction in UHMWPE during water lubricated sliding wear. Etching was carried out at room temperature for about 17 h, under constant agitation using a permangnic reagent consisting of 0.5 wt.% potassium permanganate in a mixture of 50 vol.% concentrated sulphuric acid and 50 vol.% orthophosphoric acid [15]. After being etched, samples were washed successively with two parts sulphuric acid and seven parts water in v/v cooled to -20°C with dry ice, hydrogen peroxide in concentration of

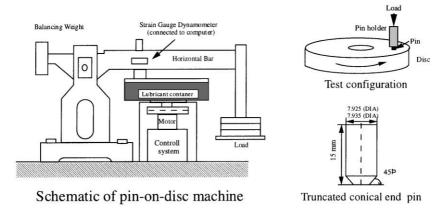


Fig. 1. Schematics of the tribometer, test configuration and test pin.

30 vol.% (to reduce any manganese dioxide or permanganate present), distilled water and acetone. The technology of permangamic etching preferentially removed the amorphous regions whilst leaving the crystalline regions relatively intact [16].

3. Experimental results

3.1. Characteristics of PIII treated UHMWPE

It was found by visual observation that the surface colour of the PIII modified samples had changed from shining ivory-white to shiny brownish yellow. This is believed to be caused by separate processes involving, i.e. thermal effect and dehydrogenation. As highly energetic ions pass through the UHMWPE surface during PIII processing, some of their energy is dissipated onto the treated surface as heat. Meanwhile, the removal of hydrogen from polymeric surface facilitated the formation of a series of conjugated double bonds, to which the surface colour is sensitive. It is worth noting that no tarnished brown colour was observed up to a dose of 4×10^{17} ions per cm², indicating that no serious dehydrogenation generally occurred at ion implanted polymer with high dosage. The modified surfaces, as observed by optical microscopy, looked featureless, except for occasional scratches. However, SEM examination (Fig. 2) revealed some regular patterns or surface relives on samples of PE2 and PE3, which were thought to be a result of ion beam bombardment of energetic ions or so-called ion etching effects.

3.2. Mechanical properties

As illustrated in Fig. 3, the PIII modification has a pronounced hardening effect on UHMWPE and the degree of hardening is increased with increasing ion fluence used. The hardening factor was found to be 2, 2.1 and 2.2, for PE1 (1×10^{17} ions per cm²), PE2 (2×10^{17} ions per cm²) and PE3 (4×10^{17} ions per cm²), respectively, as compared to the untreated material. Fig. 4 presents the enhanced

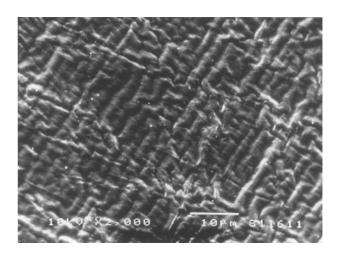


Fig. 2. A SEM image showing a regular pattern or surface relief occurred at the modified PE2 $(2 \times 10^{17} \text{ ions per cm}^2, 20 \text{ kV})$ and PE3 $(4 \times 10^{17} \text{ ions per cm}^2, 20 \text{ kV})$ samples.

elastic moduli of all the PIII modified UHMWPE samples. The detailed surface hardness and elastic modulus of the PI-III treated UHMWPE at a maximum depth of 250 nm are compiled in Tables 3 and 4, respectively.

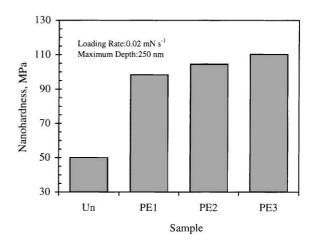


Fig. 3. Nanohardness of untreated and PIII treated UHMWPE.

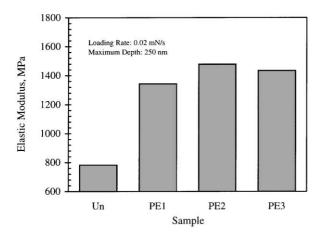


Fig. 4. Elastic modulus of untreated and PIII treated UHMWPE.

Table 3
The results of nanohardness

Designation	Mean (MPa)	S.D. (MPa)	S.E. (%)
Un	50.24	3.42	4.3
PE1	98.32	6.17	6.3
PE2	103.96	7.3	7.0
PE3	110.14	5.91	5.4

3.3. Tribological properties

Fig. 5 depicts the wear behaviour of PIII modified UHMWPE, coupled with untreated samples for comparison, sliding against 316L stainless steel to a distance of 110 km. Some notable characteristics can be drawn from Fig. 5. Firstly, the shapes of the wear curves for all PIII treated pins are similar to that for the untreated one. All these wear curves show two regions: a high initial wear rate corresponding to the 'running-in' stage (region 1) followed

Table 4
The results of elastic modulus

Designation	Mean (MPa)	S.D. (MPa)	S.E. (%)
Un	782	4.7	0.4
T32	1343	137	7.8
T33	1478	137	7.0
T34	1435	58.7	3.1

Table 5
Coefficients of wear and friction

Designation	Coefficient of wear (mm ³ /N m)	Coefficient of friction
Un	19.6×10^{-9}	0.060-0.063
PE1	14.1×10^{-9}	0.066-0.068
PE2	8.45×10^{-9}	0.065 - 0.066
PE3	6.51×10^{-9}	0.060 – 0.070

by a moderate steady wear test (region 2) for the rest of test. Secondly, PIII modification can significantly improve the wear resistance of UHMWPE. As summarised in Table 5, the average wear coefficients calculated from at least two wear tests were reduced by 1.36, 2.3 and 3 times for PE1, PE2 and PE3, respectively, compared with the untreated material. Clearly, the wear behaviour of the PIII modified UHMWPE is closely related to the N⁺ ion fluence used.

As illustrated in Fig. 5, after sliding for 24 km, the wear curves of PE1 pins $(1 \times 10^{17} \text{ ion per cm}^2)$ are almost parallel with those of untreated samples. This indicates that both samples produce virtually identical steady wear rates. By contrast, the steady-state wear rate of PE2 $(2 \times 10^{17} \text{ ions per cm}^2)$ and PE3 pins $(4 \times 10^{17} \text{ ions per cm}^2)$ was much lower than that of PE1 and the untreated pins. Thus, it can be deduced that the full potential of PIII treatment can only be realised by optimising the treatment conditions.

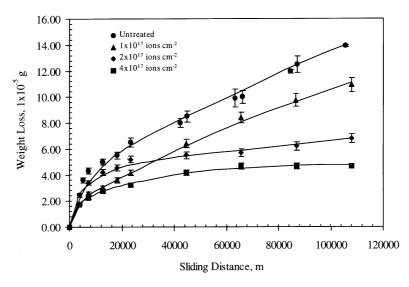


Fig. 5. Variation of weight loss with sliding distance for untreated and PIII treated UHMWPE sliding against AISI 316L stainless steel.

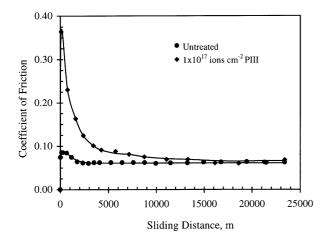


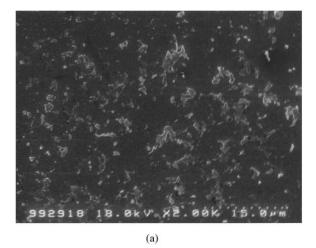
Fig. 6. Coefficient of friction vs. sliding distance of untreated and PIII treated UHMWPE sliding against AISI 316l stainless steel to a distance of 24 km.

Likewise, it was observed that the friction curves for all the UHMWPE samples, whether PIII surface modified or not, were characterised by an initial peak, which reduced gradually and finally reached a constant value. As typified in Fig. 6, the PIII surface modified UHMWPE differs in initial frictional behaviour from the untreated material. The initial frictional peak of the PIII modified material PE1 pin is much higher than that of the untreated one. This friction behaviour could be attributed to the roughened surface of PIII-modified UHMWPE. The corresponding coefficients of friction at steady-state are listed in Table 5, and it can be seen that the steady frictional coefficients of the surface modified pins are comparable to those found for the untreated ones.

3.4. Microscopic characterisation

Fig. 7a shows the wear morphologies of the untreated UHMWPE pins after sliding for 24 km. As can be seen, irregularly-shaped white marks are scattered on the smooth surface. Close examination revealed that microcracks were initiated beneath these marks (Fig. 7b). After sliding for 110 km, a series of faint wave-like patterns normal to the sliding direction, together with observable microgrooves, became the main wear morphologies of the tested surface (Fig. 8). By contrast, the wear morphology of PE3 (4×10^{17}) ions per cm²) after 110 km sliding was, as shown in Fig. 9a, characterised by white fibril-like marks distributed on the very smooth, featureless wear surface. A close observation under high magnification revealed some micro-cracks initiated at the edges of the raised marks (Fig. 9b). It is clear from Fig. 10 that the delaminated zones (Fig. 10a) display micro shearing plastic flow in nature (Fig. 10b).

Accordingly, the wear tracks on the 316L counterfaces after sliding for a distance of 110 km against the untreated



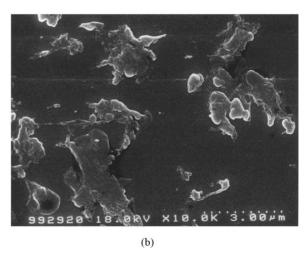


Fig. 7. (a) The surface morphology of the untreated wear pins after sliding against a 316L disc for a distance of 24 km. (b) A close view revealing deep micro-cracks initiated beneath the island-like markings. The wear direction is from right to left.

and the PE3 pins were scattered with patches of transferred UHMWPE, as reflected in Fig. 11a and b, respectively. As can be seen, the transferred UHMWPE as examined by SEM was found to be very thin and non-uniform, however, UHMWPE patches can be readily detected by EDX using a low voltage of 5 kV. For example, Fig. 12a and b show the image of the transferred UHMWPE on the counterface and the corresponding EDX scanning spectra. Clearly, transfer of UHMWPE onto the counterfaces occurred for both untreated and PIII surface modified material. However, it seems that no remarkable difference in the amount of transferred UHMWPE was observed for these two wear tracks.

3.5. Microstructure evolution

In order to investigate the effect of PIII treatment on the reconstruction of the linear polymeric microstructure

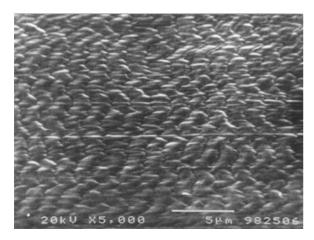
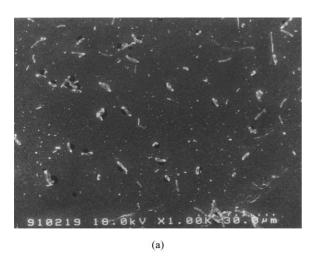


Fig. 8. The surface morphology of the untreated wear pins after sliding against a 316L disc for a distance of $110\,\mathrm{km}$. The wear direction is from right to left.



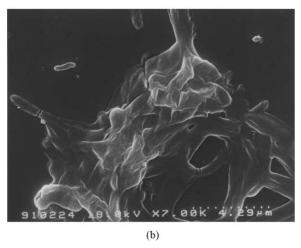
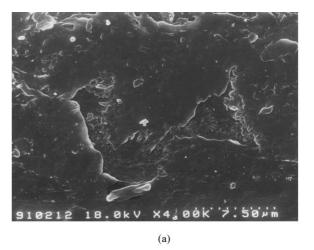


Fig. 9. (a) The surface morphology of the PIII treated PE3 (4×10^{17}) ions per cm², $20\,\mathrm{kV}$ wear pins after sliding against a 316L disc for a distance of 110 km. (b) A close view revealing the partial micro-cracks initiated at the ridge of the raised markings. The wear direction is from right to left.



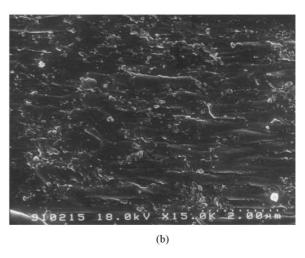


Fig. 10. SEM images showing (a) delaminated zones and (b) micro-shearing flow. The wear direction is from right to left.

during unidirectional sliding wear, evolution of linear molecular chains in the wear surface of the PIII treated PE3 pin and the untreated pin was examined for comparison with sliding wear process. Fig. 13a-c show, respectively, high resolution SEM images of etched untested and wear tested surfaces of untreated and PIII treated PE3 pin surfaces following 110 km sliding. As can be seen from Fig. 13a and b, the untested material is characterised by a randomly distributed microstructure, comprising crystalline lamellae and inter-lamellar amorphous, and microstructures evolved to the remarkably preferred lamellae to the sliding direction occurred in the untreated pin surface after 110 km of sliding. However, no sign of alignment of crystalline lamellae could be identified in the wear surface of the PE3 pin after the same sliding distance (Fig. 13c). It is, thus, deduced that although the fact that reconstruction of the molecular chain structure of the linear polymer occurred in the surfaces during the wearing process, it is not true for the PIII treated UHMWPE. This is presumably due to a modified cross-linking structure being induced by the ion bombardment.

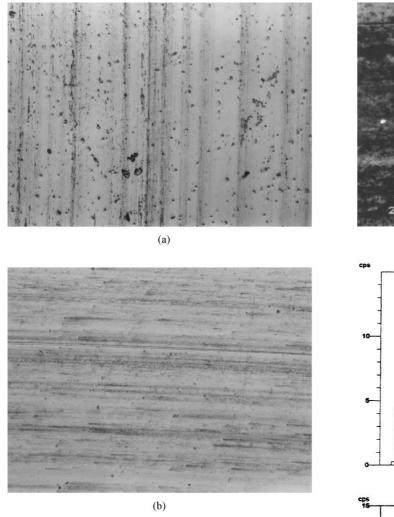


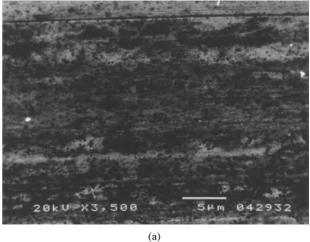
Fig. 11. Optical photographs of the wear tracks on 316L discs sliding against (a) untreated and (b) PIII treated PE3 (4 \times 10^{17} ions per cm², $20\,kV)$ pins.

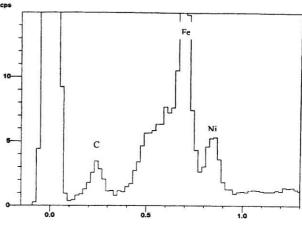
4. Discussion

4.1. Surface modification effect

Notwithstanding the fact that surface modification by PIII is confined to a very thin layer ($<1~\mu m)$ beneath the surface, significantly improved mechanical properties such as surface hardness and elastic modulus were well identified in this study. This pronounced desirable effect could be attributed to the change in structure conferred by PIII induced interaction between the energetic N^+ and the UHMWPE surface.

It is well known that, when high energy ions bombard surface atoms of polymers, the loss of their energy takes place mainly as nuclear stopping (direct collisional displacement of the target atoms) and electronic stopping (electronic ionisation of the target electrons). The former is responsible for permanent degradation, mainly through bond breakage or molecular chain scission by displacing atoms from polymer





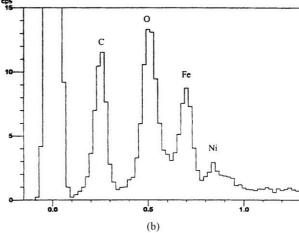
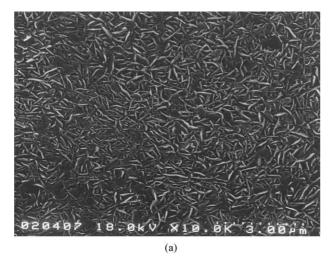
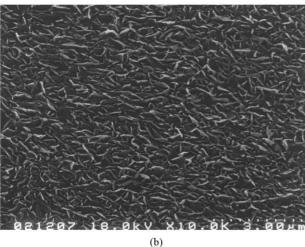


Fig. 12. (a) A SEM image of transferred UHMWPE and (b) as-received and corresponding EDX scanning spectra.

chains. The latter induces activated chemical complexes and subsequent reaction and dissociation, thus leading to free radical formation, molecular emission and cross-linking. Although these two processes usually coexist, electronic stopping prevails for high energy (>10 kV) ion beam





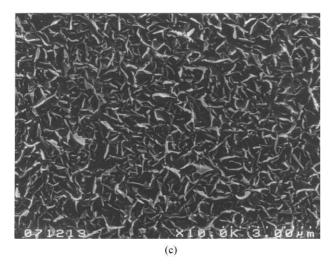


Fig. 13. The microstructure of (a) the untested pin surface; (b) the wear tested, untreated pin surface and (c) PIII treated PE3 (4×10^{17}) ions per cm², (20) kV) pins after sliding for a distance of (110) km. The wear direction is from right to left.

modification. According to the unit structure of UHMWPE and the PIII treatment conditions, it is expected that the UHMWPE surface is modified dominantly through the formation of cross-liked molecular microstructure induced by electronic stopping primarily undertaken by the incident ions. Therefore, weak secondary bonds between long smooth molecular chains in the untreated material are replaced by much stronger covalent bonds at these cross-linked points. As a result, the resultant increased rigidity of backbone structure by anchoring molecular chains significantly decrease mobility (flexibility) of the molecular chain. Therefore, when subjected to an applied force, modified UHMWPE exhibited higher surface hardness and elastic modulus than that of as received materials. Indeed, it is also strongly supported by the evolution of the microstructure during wearing process (Fig. 13). Meanwhile, the dosage dependent hardening effect could be interpreted by the fact that the degree of cross-liking is increased with increasing ion fluence up to the formation of a full three dimensionally networked cross-linked molecular chain structure.

4.2. Improved wear resistance of PIII modified UHMWPE

It has been clearly shown that the wear resistance of UHMWPE sliding against smooth ($R_a = 0.015 \,\mu\text{m}$) 316L stainless steel counterfaces under water lubricated conditions can be significantly enhanced by PIII surface modification. PIII-modification with the highest fluence (4×10^{17} ions per cm²) has the most profound effect on improving the wear resistance of UHMWPE. This is, thus, believed to be related to the degree of cross-linked structure and the resultant surface mechanical property improvement.

It can be seen by comparing Fig. 7a with Fig. 9a that although both wear surface were scattered by the white-contrasted marks, the size and morphologies of the marks on the wear surface of the PIII treated pins are different from that on the untreated pins. Although the detailed damage or wear mechanisms operating is still under investigation, it is believed that reconstruction or alignment of lamellar crystallites as revealed by Klapperich et al. [17] may have played an important role in promoting the formation of these island-like marks as observed on the wear surface of the untreated pins (Fig. 7a). The untreated UHMWPE pins are soft and under the action of the applied normal stress and traction caused by friction, semicrystalline UHMWPE is subjected to reconstruction or alignment of lamellar crystallites parallel to the sliding direction and some degree of plastic deformation at real contact areas [17]. As wear process proceeded, micro-cracks formed, cracks propagated beneath the contact surface, and finally, these island-like areas were delaminated as wear debris.

In contrast, the wear surface of the PIII treated material looks very smooth with some fibril-like marks. This could be attributed to the surface strengthening induced by ion beam bombardment via cross-linking. Firstly, increased

surface hardness as a consequence of structural modification could effectively increase the load-bearing capacity of the surface treated surfaces, thus leading to significantly reduced real contact areas and stretching. Secondly, the three-dimensional cross-linked structure converted from a smooth molecular microstructure makes UHMWPE non-susceptible to reconstruction of microstructure.

Indeed, as has been shown in Fig. 13, the wear surface of the untreated pins experienced by re-construction as evidenced by the preferential orientation of crystalline lamellae to the sliding direction. On the other hand, the lamellar crystallites in PIII treated PE3 are randomly distributed even after sliding for 110 km. This cross-linking conferred structure stability may have retarded the initiation of micro-cracks and extension of the localised adhered area.

4.3. Implications and limitations

It is clear from the preceding discussion that the wear resistance of UHMWPE can be significantly improved via advanced surface modification technologies. However, it should be indicated that the present wear test results may not immediately be applicable to total joint replacements since the test configuration (pin-on-disc), type of motion (unidirectional) and lubricant (water) employed in the present study differ from those in human joints. However, some investigators have indicated that the simple tests can give a reasonable simulation of contact conditions, and can serve as a first resort for screening surface treatment parameters [18]. With a view to providing firm technological database for prolonging the lifetime of total joint replacement prostheses via surface engineering of the articulating surfaces, long-term simulator tests with bovine serum and protein containing fluid have been planned and the results will be published in a separate paper in due course.

5. Conclusions

- Plasma immersion ion implantation can significantly improve the surface hardness and elastic modulus of UHMWPE. The improvements in the surface mechanical properties are found to be proportional to the ion fluence used.
- 2. Significant enhancements (up to 230%) in the wear resistance of UHMWPE sliding against 316L stainless

- steel counterfaces under water lubricated conditions are achieved by PIII surface modification with nitrogen.
- Ion beam surface treatment induced cross-linking can effectively retard molecular structure reconstruction or alignment of lamellar crystallites in UHMWPE, thus giving rise to high resistance to initiation and propagation of micro-crack and wear.

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