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Modification of Surface Morphology of UHMWPE for Biomedical Implants

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Abstract

Ultra High Molecular Weight Polyethylene (UHMWPE**)** samples were implanted with metal and metal-gas hybrid ions (Ag, Ag+N, C+H, C+H+Ar, Ti+O) by using improved MEVVA Ion implantation technique [1,2] . **An extraction voltage of 30 kV and influence of 1017 ions/cm2 were attempted in this experiment**. to change their surface morphologies in order to understand the effect of ion implantation on the surface properties of UHMWPEs. Characterizations of the implanted samples with RBS , ATR - FTIR, spectra were compared with the un-implanted ones . Implanted and unimplanted samples were also thermally characterized by TGA and DSC. It was generally observed that C–H bond concentration seemed to be decreasing with ion implantation and the results indicated that the chain structure of UHMWPE were changed and crosslink density and polymer crystallinity were increased compared to unimplanted ones resulting in increased hardness. It was also observed that nano size cracks (approx.10nm) were significantly disappeared after Ag implantation, which also has an improved antibacterial effect . Contact angle measurements showed that wettability of samples increased with ion implantation. Results showed that metal and metal+gas hybrid ion implantation could be an effective way to improve the surface properties of UHMWPE to be used in hip and knee prosthesis.

1. Introduction

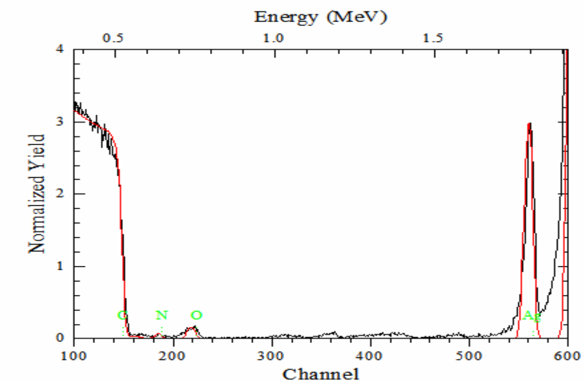
Ultra High Molecular Weight Polyethylene (UHMWPE**)** has been commonly used for acetabular cup of total hip joint replacement as it has densely packed linear polyethylene chains, which gives improved mechanical properties. However the wear of UHMWPE against the articulating metal part and wear debris generated at the surface is recognized as the major cause of loosening and failure of the total joint replacement. Recent studies show that increasing the cross-linking in the polyethylene significantly reduces wear leading to more durable acetabular components and increasing the lifetime of an implant . Increasing the cross-link density of UHMWPE in which UHMWPE is irradiated in air at an elevated temperature with a high-dose-rate electron beam or a common approach is to cross-link the polymer by gamma irradiation, which improves markedly the wear resistance of the polymer but with changed bulk properties [3]. In this work, we tried to change the surface morphology of UHMWPE by low energy metal and metal+gas hybrid ion implantation by MEVVA , with an expectation of improving surface mechanical properties, and promoting antibacterial effect without changing the bulk properties of UHMWPE .

2. Experimental

Samples with medical grade GUR 1020 - Type 1 - Ultra High Molecular Weight Polyethylene (UHMWPE - , Hipokrat Co.) with a density of 945 kg/m^3 were used . Disk samples with a diameter of 30mm and thickness of 4mm were polished down to about surface roughness of 95 (nm) Ra. Samples were implanted with Ag, Ag+N, C+H, C+H+Ar, Ti+O ions by using MEVVA ion implanter with a fluence of 10^{17} ion/cm^2 and extraction voltage of 30 kV. ATR- FTIR chemical characterization analysis was used to see if any new chemical bonds formed 2 microns deep at the surface. Thermo Nicolet Nexus 670 model FTIR with Smart DuraSamplIR 3 Bounce diamond HATR (3 reflection diamond ATR) and OMNIC software were used. DSC (Differential Scanning Calorimeter) SHIMADZU DT-50 and the TGA (Thermo Gravimetric Analyzer) SHIMADZU DT-51 were used for thermal analysis of implanted and unimplanted samples. The analyses were performed in a dry nitrogen atmosphere. Aluminum cells were used for analysis of the polymers. The temperatures of the sample cells were increased by 10 ^{0}C/min. The total heat of melting ΔH (the area under the endotherm-DSC) was determined and, knowing the total heat of fusion of 100% crystalline UHMWPE (ΔH_f = 293.6 J/g), the percentage crystallinity was calculated as 100($\Delta H/\Delta H_f$) [4]. Scanning electron microscopy (Philips XL-305 FEG – SEM) was used to examine the surfaces of unimplanted and Ag and Ag+N implanted samples. Atomic force microscopy (AFM) was used to investigate the surface morphology of unimplanted and implanted UHMWPE. A Digital Instrument- MultiModeSPM apparatus was used to determine the surface roughness. The durometer hardness test was used to measure the relative hardness of the samples. The test method is based on the penetration of a specified indenter forced into the material under specified conditions. A Shore hardness tester ZWICk/Roell (HPE) under 50N force was used. The contact angle of wateron unimplanted and implanted UHMWPE surfaces was measured with a Krüss-G10 goniometer. The antibacterial activities of unimplanted and Ag implanted UHMWPE samples of 5mm diameter and 3mm thickness were examined against “Staphylococcus Aureus” by "Agar Disk Diffusion Method". After 24 hours bacteria reduction was100%.

3. Results and Discussions

RBS graphs, are used as an analytical tool to measure some of the implanted elements (C, Ag, Ti, N, O) concentration of the sample surfaces. For example, Figure 1,2 show Ag, Ti, C , N and O ions, which can be detected up to 42 +15 nm underneath the surface. All spectra show an O peak, which is believed to be caused by oxidation and some small peaks by the residual air in the Vacuum chamber. Oxygen uptake takes place once the ion bombarded polymer sample was exposed to the air [5].



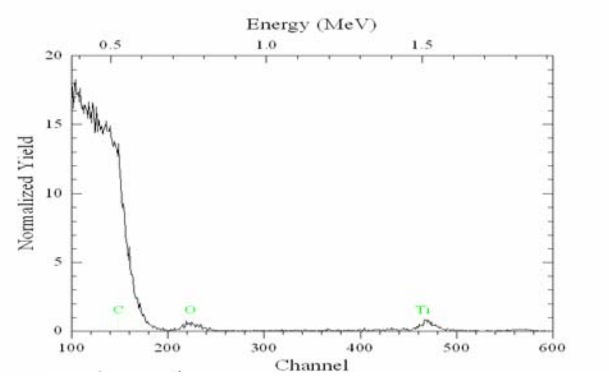


Figure.1 RBS Spectrum of Ag + N Implanted UHMWPE

Figure.2 RBS Spectrum of Ti + O Implanted UHMWPE

The characteristic absorption bands for the CH_2 bonds appear in the 2900–2840, 1460–1370 and 740–720 cm^{-1} regions [6]. The transmission ATR analysis of the unimplanted and implanted samples confirms the C–H bond breaking since the C–H stretching (at 2847 cm^{-1}) bond peaks of the pure UHMWPE sample disappear after ion implantation (figures. 3,4,5).

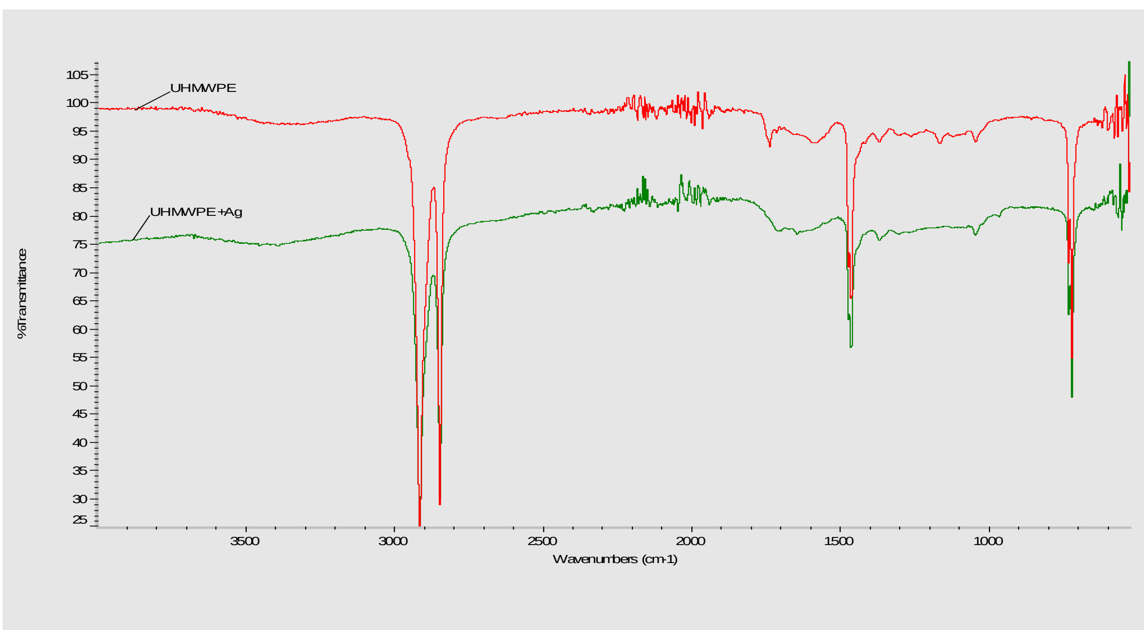


Figure.3 FTIR spectra of Ag Implanted UHMWPE

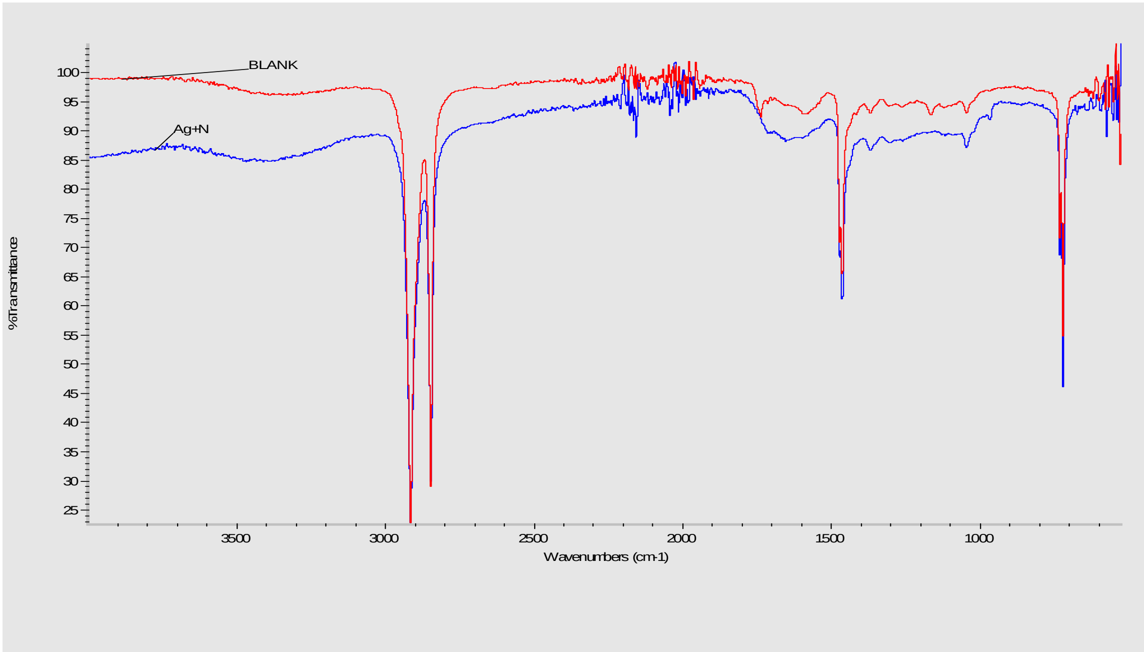


Figure.4 FTIR spectra of Ag+N Implanted UHMWPE

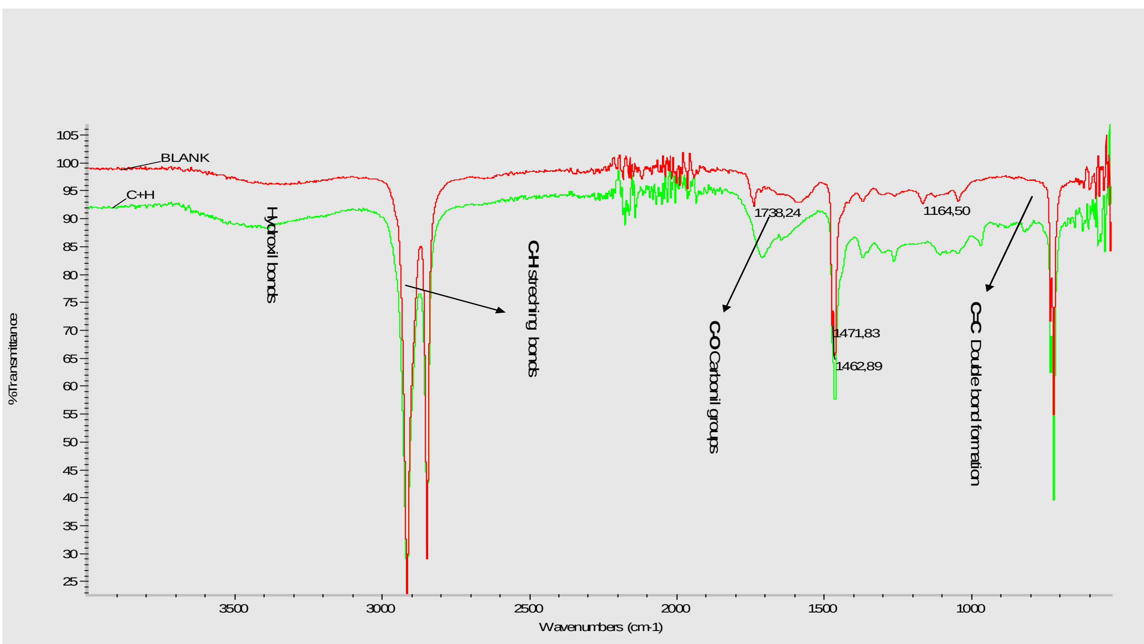


Figure.5 FTIR spectra of C+H Implanted UHMWPE

Increase in the absorption bands in the 800 and 1738.4 cm^{-1} regions , due to the implantation, has been attributed to the creation of unsaturated C=C bonds and carbonyl group formations respectively [7] . One of the main products of the ion bombardment is the chemical change resulting the C=C formation, and its stretching vibration is clearly observed in the spectra by an absorbance peak at 800 cm^{-1}. The presence of this peak suggests that after ion implantation, the polymer surface becomes poor of hydrogen and rich of unsaturation which is susceptible to crosslinking and oxidation. Oxidation causes carbonyl groups formation which is observed at around 1740 cm^{-1}. DSC (Differential Scanning Calorimeter) was used to measure the energy change of the polymer by increasing the temperature in inert N_2 gas atmosphere. DSC determines thermal properties of the polymer such as T_m, ΔH_{fus}. ΔH_{fus} is defined as the fusion enthalpy which is calculated by taking an integration of the area of the melting peak. The crystallinity of UHMWPE (unimplanted and implanted) percentage is shown in table.1, tohether with roughness, hardness, contact angle, ΔH_{fus} and T_m . The detailed calculation of the crystallinity percentage of the polymer could be found in the literature [4] . DSC Analysis of un implanted UHMWPE, Ag and Ag+N, and C+H+Ar and C+H ion implanted UHMWPE samples are shown in figures 6 and 7.

Table gives the contact angle and roughness results together with the other measured properties. It seems that the wettability increased with ion implantation and that hidroxil bonds and carbonil bonds have dominant effect on wettability

	Roughness (Ra-nm)	**Hardness (Shore-D)**	**Contact Angle(°)**	**ΔH_f J/g)**	**Tm (C^0)**	**Crystallinity (DSC - %)**
Untreated	124	58	56	115.07	141	39,5
Ag	30	66.4	45	116.52	137	40
Ag+N	74	63.4	32	119.67	140	41
C+H	69.5	64,2	37.5	115.82	135.2	39,9
C+H+Ar	101	66,1	47.5	117.57	131.8	40,5

Table 1 . Over all results

Table.1 Over all results

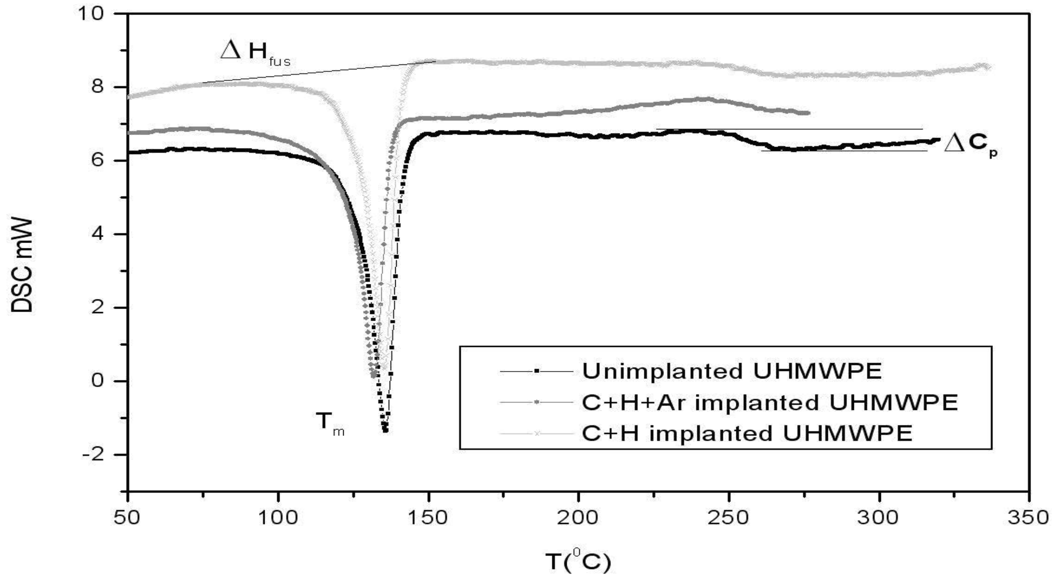


Figure .6. DSC Analysis of unimplanted UHMWPE, C+H+Ar and C+H ion implanted UHMWPE samples.

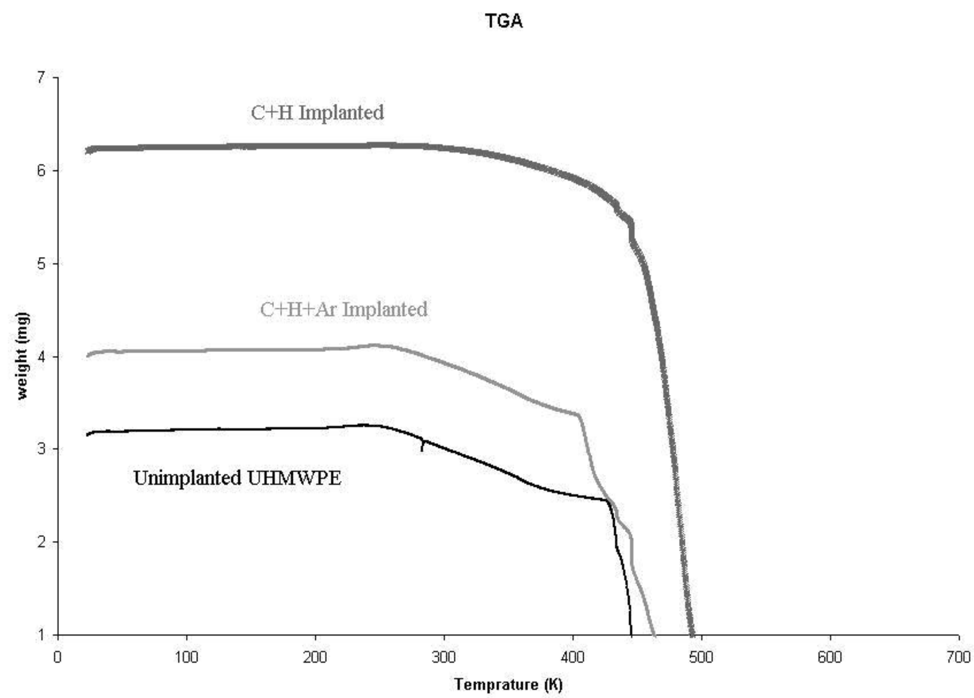


Figure .7. DSC Analysis of Untreated, Ag and Ag+N Implanted UHMWPE Samples

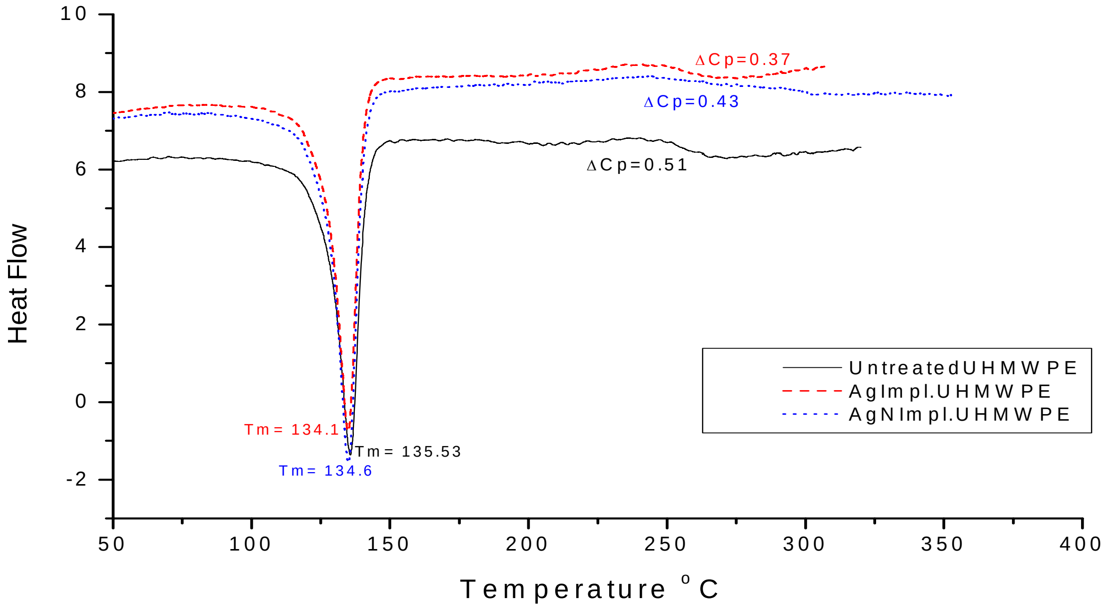


Figure . 8. TGA curves of the samples of UHMWPE before and after the ion implantation with C+H, C+H+Ar ions.

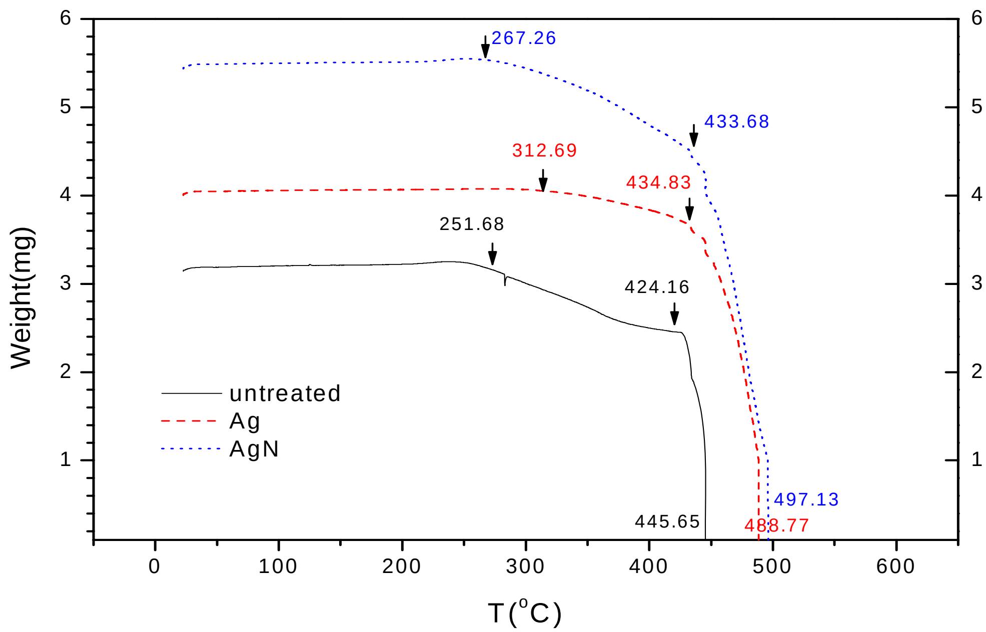


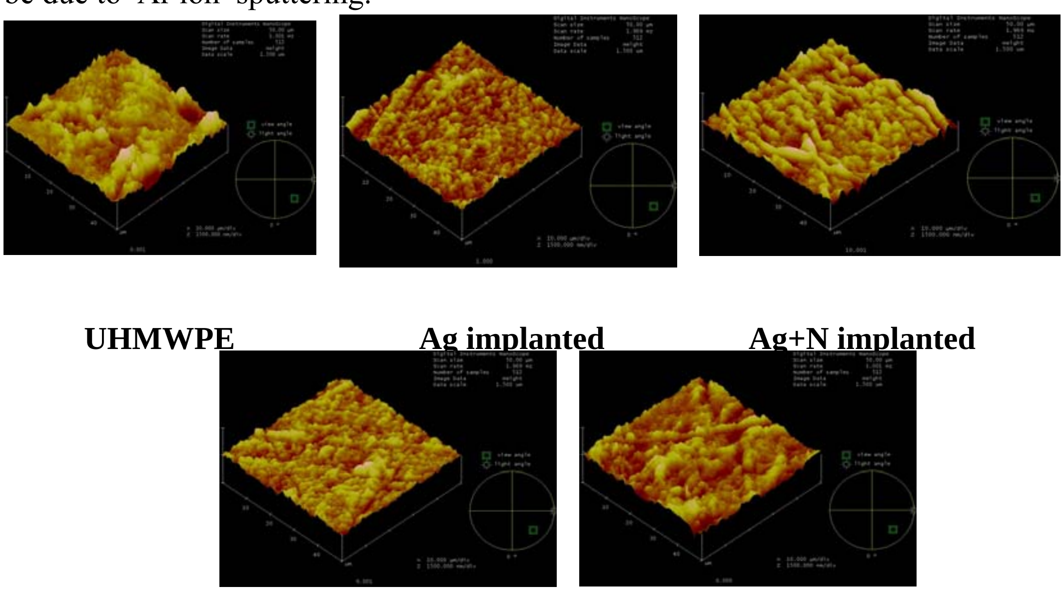
Figure . 9. TGA Analysis of Untreated, Ag and Ag+N Implanted UHMWPE Samples.

In TGA results, onset of degradation starts for untreated UHMWPE is 251.68 ^{0}C. This point shifted after irradiation to higher values for implanted samples (Figures 8, 9). With the same trend total degradation point 424 ^{0}C for untreated UHMWPE sample shifted to higher values for implanted samples. These results can indicate that the thermal stability increased at the surface [8] . Shore-D hardness measurements of unimplanted and implanted UHMWPE samples are given in Table.1 **,** which shows that hardness increases with ion implantation . Hardness is purely a relative term and an increase in hardness is due to the crosslink formation on the surface [9,10]. It was also observed that C–H bond concentration seemed to be decreasing. This might also indicate that C rich surfaces and graphite like structures occurred, resulting in increased hardness.Contact angle and roughness results are given in Table.2 . It seems that the wettability increased with ion implantation and that hidroxil bonds and carbonil bonds have dominant effect on wettability. Rather low contact values for Ag+N could be due to formation of nitride which has an additional effect to oxygen containing groups.

Contact Angle	**UHMWPE**	**Ag**	**Ag + N**	**C+H**	**C+H+Ar**	**Ti+O**	**Ti+Al+N**
Water	**56.2˚**	**44.8˚**	**32˚**	**37.5**	**47.5**	**30˚**	**48˚**

Table.2 Contact angle measurements with water.

Figure. 10. shows the surface topography of unimplanted and implanted UHMWPE samples obntained by AFM. As seen from the figure surface roughness decreases with ion implantation. This is probably due to rapid melting of the polymer surfaces as a result of ion irradiation. High roughness of C+H+Ar implanted UHMWPE surface could be due to Ar ion sputtering.

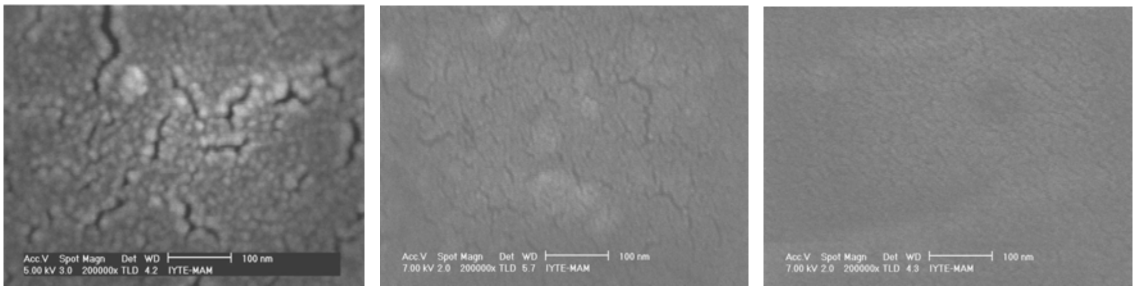


UHMWPE **Ag implanted** **Ag+N implanted**

C+H **C+H+Ar**

Figure. 10. Surface topography of unimplanted and implanted UHMWPE samples obntained by AFM.

SEM micrographs of unimplanted, Ag and Ag+N implanted UHMWPE surfaces were obtained randomly with several measurements are shown in figure 11 . Results represent the surface morphology of UHMWPE before and after implantation. Cracks on the surface are significantly disappeared after Ag and Ag+N implantation. Especially, cracks were totally disappeared with Ag implantation.



(a) (b) (c)

Figure 11. SEM micrographs of (a) unimplanted, (b) Ag+N implanted and (c) Ag implanted UHMWPE samples.

The results proved the Antibacterial effect of Ag implanted in UHMWPE, however, the measurements should be repeated after the wear tests.

Conclusion

The results indicated that the chain structure of UHMWPE were changed and crosslink density increased. There was slight increase in percentage crystallinity but decrease in melting point T_m with irradiation, which may be due to the chain sission of UHMWPE since T_m is closely related to number average molecular weight and also C=C double bond formation as seen in FTIR spectra.
It is believed that slight increase in the crystallinity of the polymer may improve the surface quality of the polymers such as hardness, wear resistance and wettability.
It was also observed that C–H bond concentration seemed to be decreasing. This might indicate that C rich surfaces and graphite like structures occurred, resulting in increased hardness. It was observed that nano size cracks (approx.10nm) significantly disappeared after Ag implantation, however less significant with Ag+N implantation . This is probably due to rapid melting of the polymer surfaces as a result of ion irradiation, which was also thought to be responsible for decreasing in roughness.
Contact angle measurements showed that wettability of samples increased with ion implantation. It is thought that increased in oxygen concentration and formation of carbonyl groups were responsible for this. Rather low contact values for Ag+N could be due to formation of nitride which has an additional effect to oxygen containing groups.
Results indicate that metal and metal+gas hybrid ion implantation could be an effective way to improve the surface of UHMWPE together with antibacterial effect of Ag implantation.

Acknowledgements

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