Structural and Thermal Characterization of Ti+O Ion Implanted UltraHigh Molecular Weight Polyethylene (UHMWPE)

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Abstract. In this work, Metal-Gas Hybrid Ion Implantation technique was used as a tool for the surface modification of Ultra High Molecular Weight Polyethylene (UHMWPE). Samples were Ti + O ion implanted by using Metal-Vapour Vacuum Arc (MEVVA) ion implanter to a fluence of $5x10^{16}$ ion/cm^2 for each species and extraction voltage of 30 kV. Untreated and surface treated samples were investigated by Rutherford Back Scattering (RBS) Spectrometry, Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) Spectroscopy, Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Results indicate that Ti + O ion implantation can be applied on UHMWPE surfaces successfully. ATR-FTIR spectra indicate that the C-H concentration on the surface decreased after Ti + O implantation. Thermal characterization with TGA and DSC shows that polymeric decomposition temperature is shifted after ion implantation.

Keywords: UHMWPE, Ti, O, MEVVA, Ion Implantation, RBS, ATR-FTIR , DSC, TGA
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1. INTRODUCTION

Synthetic polymeric materials have been widely used in medical disposable supplies, prosthetic materials, dental materials, implants, dressings, extracorporeal devices, encapsulants, polymeric drug delivery systems, tissue engineered products, and orthodoses like those of metal and ceramics substituents [1].

Although hundreds of polymers are easily synthesized and could be used as biomaterials only a few polymers are mainly used in medical device applications from disposable to long-term implants. UHMWPE has been used for orthopedic implant fabrication, especially for load-bearing applications such as an acetabular cup of a total hip joint and the tibial plateau and patellar surfaces of knee joints [1,2].

In this work, Ti + O ion implantation of UHMWPE surfaces using a metal-gas co-implantation technique were performed. The effects of implantation on the structural and thermal properties were investigated.

2. MATERIAL AND METHOD

Samples with medical grade GUR 1020 - Type 1 - Ultra High Molecular Weight Polyethylene (UHMWPE - , Hipokrat Co. $–CH_2–|_n$ monomer) with a density of 945 kg/m^3 were used. Ti and O ions were implanted by using a MEVVA ion implanter to a fluence of 5×10^{16} ion/cm^2 for each species and extraction voltage of 30 kV. Mixed Ti and O ion beams were generated by a magnetic field, which was obtained through a magnet coil located in front of anode plate and by adding gas in the discharge region. This modified system was used to form burried layers of mixed metal-gas species such as Ti and O.

RBS measurement was performed using 2.1 MeV He+ ions in an IBM scattering geometry with the particle detector placed at 170° from the incident beam to study elemental constituents in the W+C ion implanted UHMWPE sample.

ATR- FTIR analysis was used to see if any new chemical bonds formed 2 microns of the surface. Thermo Nicolet Nexus 670 model FTIR with Smart

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DuraSamplIR 3 Bounce diamond HATR (3 reflection diamond ATR) and OMNIC software were used. Scans were done in the wave number range of 500 - 4000 cm^{-1}.

Thermal analysis of untreated and Ti + O ion implanted UHMWPE samples were conducted by using Shimadzu Differential Scanning Calorimeter (DSC, 50) and Shimadzu Thermal Gravimetric Analyzer (TGA, 51). The measurements were carried out at temperatures between 20°C – and 500 °C for DSC analyses, and 20 °C – 510°C for TGA analyses , at heating intervals of 10 °C/min.

3. RESULTS AND DISCUSSION

RBS spectra, such as shown in Fig. 1, were used to measure elemental constituents in the UHMWPE samples after surface modification. As seen in Fig. 1, Ti and O ions could be detected underneath the surface after implantation.

In the IR region, the characteristic absorption bands for the CH_2 bonds appear in the intervals 2900–2840, 1460–1370 and 740–720 cm^{-1} [3,4]. The transmission ATR analysis of the unimplanted and Ti+O implanted samples confirms the breaking of bonds [4-7].

As seen in Fig. 2 the increase in the absorption bands in the 1600 and 1750 cm^{-1} regions after implantation has been attributed to the creation of unsaturated C=C bonds and the beginning of polymer oxidation [7,8].

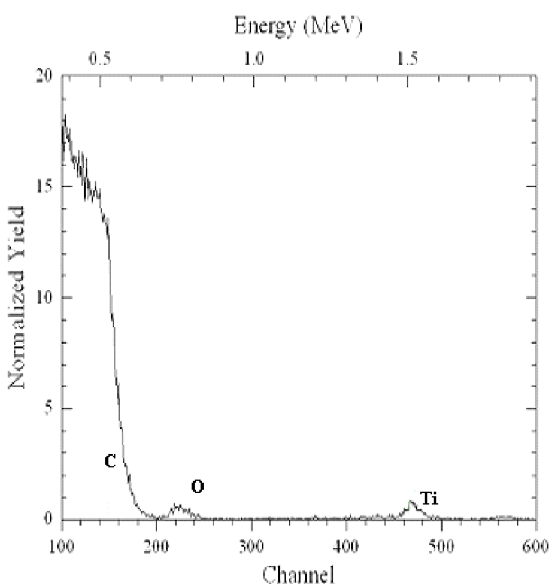

FIGURE 1. RBS Spectrum of Ti+O implanted UHMWPE

One of the main products of the ion implantation induced chemical changes is the C=C formation, and its stretching vibration, is clearly observed in the spectra by an absorbance peak at 1594-1630 cm^{-1}. The presence of this peak suggests that after Ti+O implantation, the polymer surface becomes hydrogen-poor, and cross-linked structure.

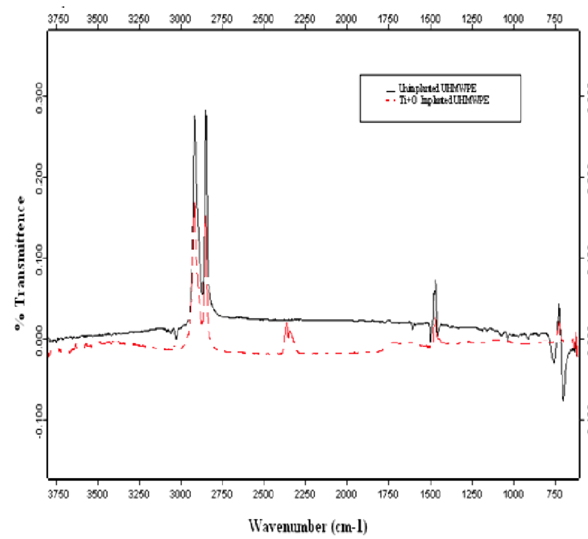

FIGURE 2. ATR FTIR Spectrum of Ti+O implanted UHMWPE, peaks at 2900–2840, 1460–1370 and 740–720 cm^{-1}

Due to oxidative degradation some carbonyl formation was observed at around 1720 cm^{-1}. In particular, C-H characteristic peaks have decreased after Ti+O implantation. It is also seen, in the 2200 cm^{-1}region that triple bond formation occurs after Ti + O implantation.

Fig. 3 shows TGA results of pure and implanted UHMWPE samples. It can be seen that onset degradation for pure UHMWPE is around 260°C. In contrary, the onset degration temperature shifted after implantation to 240°C; moreover, offset degradation temperatures also shifted from 440°C to 400°C after Ti+O implantation which indicates that the crystal structure had changed.

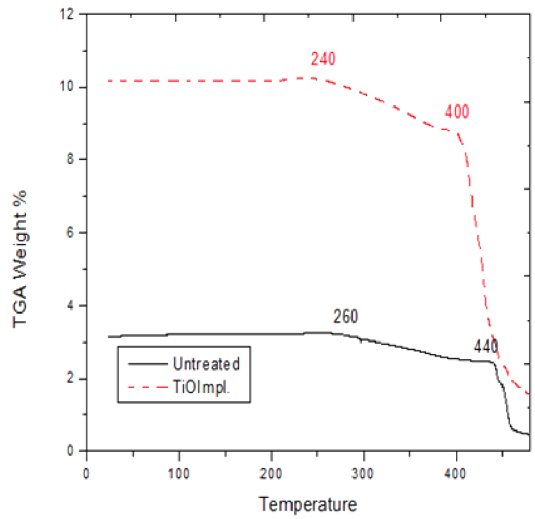

FIGURE 3. TGA graph of unimplanted and Ti+O implanted UHMWPE. The heating rate is 10 °C min–1

As seen in Fig. 4, DSC thermograms for unimplanted and Ti+O implanted UHMWPE exhibited changes in thermal properties after surface modification. In Fig. 4, T_m(Melting Temperature) values are moved from 139°C to 135°C and peak intensities are decreased after Ti+O implantation which means that a significant polymer modification and probably chain reduction was occurred.

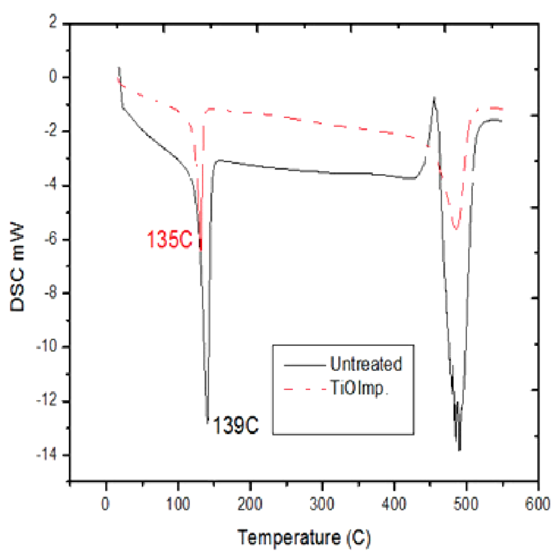

FIGURE 4. DSC thermograms of unimplanted and Ti+O implanted UHMWPE. The heating rate is 10 °C min–1

4. CONCLUSION

In summary, from the RBS and ATR FTIR analysis results, we can infer that a new material was formed after bombardment. The new material has a cross-linked structure which is constituted of conjugated bonds. In TGA and DSC analysis, results can be attributed to the ion bombardment inducing changes in thermal properties of UHMWPE.

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