Available online at www.sciencedirect.com
ScienceDirect
Nuclear Instruments and Methods in Physics Research B 261 (2007) 711–714
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Polymeric thermal analysis of C + H and C + H + Ar ion implanted UHMWPE samples

N. Kaya [a,*], Ahmet M. Oztarhan [a], E.S. Urkac [b], D. Ila [c], S. Budak [c], E. Oks [d], A. Nikolaev [d], A. Ezdesir [e], F. Tihminlioglu [b], Z. Tek [f], S. Cetiner [g], C. Muntele [c]

[a] *Department of Bioengineering, Ege University, Izmir/Bornova 35100, Turkey*
[b] *Chemical Engineering, IYTE, Izmir/Urla 35430, Turkey*
[c] *Alabama A&M University, Center for Irradiation of Materials, P.O. Box 1447, Normal, AL 35762, USA*
[d] *High Current Electronics Institute, Tomsk, Russia*
[e] *Department of R&D, Petkim, Aliaga/Izmir, Turkey*
[f] *Department of Physics, Celal Bayar University, Manisa, Turkey*
[g] *R&D, Hipokrat A.S., Pinarbasi/Izmir, Turkey*

Available online 14 April 2007

Abstract

Chemical surface characterization of C + H hybrid ion implanted UHMWPE samples were carried out using DSC (differential scanning calorimeter) and TGA (thermal gravimetric analysis) techniques. Samples were implanted with a fluence of 10^{17} ion/cm^2 and an extraction voltage of 30 kV. The study of TGA and DSC curves showed that: (1) Polymeric decomposition temperature increased, (2) T_m, ΔC_p and ΔH_m values changed while ΔC_p and ΔH_m increased. T_g value could not be measured, because of some experimental limitations. However, the increase in ΔH_m values showed that T_g values increased, (3) the branch density which indicated the increase in number of cross-link (M_c) decreased in ion implanted samples and (4) increase in ΔH_m values indicated increase in crystallinity of implanted surface of UHMWPE samples.
Published by Elsevier B.V.

PACS: 65.40.Ba; 61.25.Hq; 61.41.+e; 68.47.Mn; 68.60.Dv; 71.20.Rv; 79.60.Fr; 68.37.Ps

Keywords: Heat capacity (ΔC_p); Melting temperature (T_m); Cross-link; Melting enthalpy (ΔH_m); Branch; Glassy transition temperature (T_g)

1. Introduction

UHMWPE (–CH2– ln monomer) is a very important polymer in different fields such as medicine, engineering and biology. A special application of this polymer in biomedical concerns the interface of hip joints prostheses, where the friction can be a significantly reduced using intermeddled sheet of UHMWPE [1]. The acetabular cup part of the hip joint is generally covered or produced by UHMWPE, because of its wear resistance. Covering something by polymer is possible only with thermoplastics which are melt – able polymers. UHMWPE is a semi-crystalline polymer so it has lots of thermal behaviors. Generally, the percentage of the crystallinity of the polymer changes with the molecular mass of the polymer, tip of monomers of atoms, an irradiation, ion implantation, number of cross-links and additives. Thermal behavior changes of polymers could be seen with the changes in the number of cross-links and the changes in the density of side of the branches of the polymer. If the number of cross-links of a polymer is known, an assumption can be made about the percentage of crystallinity of the semi-crystalline polymer. In the chemistry of the polymer, the crystallinity of polymer measurements with some chemical–thermal analysis's could be used for the characterization and the qualification of the polymers. UHMWPE

* Corresponding author. Tel.: +90 505 3551711; fax: +90 232 3744289.
E-mail address: nnusrettersunn@gmail.com (N. Kaya).

0168-583X/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.nimb.2007.04.098

and all the other thermoplastic polymers have typically displays of the endotherms of the broad melting and glass transitions (T_g) as a major analytic features associated with their properties. If those properties of the polymer are changing by the same chemical or physical applications, the all thermal behaviors of the polymer will change. The MEVVA (metal vapor vacuum arc) ion implantation technique could be used to change the properties of the polymers by an accelerated metal and gas ions. For example, the glass transition temperature, T_g, is defined as the temperature where the polymer changes its phase. After the ion implantation is introduced, the amorphous phase of the all of the polymers turns to the phase of the crystallinity. The melting point, T_m, is the another important point for the polymers. At the melting point, the phase of the crystallinity of the all of the polymers reduces to the amorphous phase. The melting enthalpy of a polymer value could be calculated from the data of the thermal analysis. The last important parameter for a polymer is the heat capacity (ΔC_p) at a constant pressure. Since all of the polymers have different heat capacity constants at constant pressures, the heat capacity is very important for the characterization and the identification of a polymer.

The glass transition and melting point are strongly dependent on the processing conditions of the polymers and the dispersion in the structural and chemical properties of plastics. If the heat capacity of a polymer changes, it might be caused by MEVVA. Characterization of polymers requires a detailed analysis of these characteristic thermal transitions using either the differential scanning calorimeter (DSC) technique or the differential thermal analysis (DTA) technique. Moreover, the weight loss with heating is a common phenomenon for polymers due to the degradation and the loss of the residual solvents and monomers [2]. Weight loss on heating is studied using the thermal gravimetric analysis (TGA) technique. Complete thermal analysis of a plastic sample results in the inferential information concerning the chemical composition and the structure of the material.

In this study, we investigated the thermo-chemical changes on the C + H and C + H + Ar implanted UHMWPE and unimplanted UHMWPE samples. The MEVVA ion implantation technique changes the surface crystallinity and the number of the cross-links of the polymer. We tried to see and observe those thermal–chemical changes using the chemical–thermal analysis equipments.

2. Experimental

2.1. Material

Medical Grade GUR 1020-Type 1 – ultra high molecular weight polyethylene (UHMWPE $-CH_2-|_n$ monomer) with a density of 945 kg/m^3 was used. The disk-like specimens having 30 mm of a diameter and 6 mm of a thickness were chosen. Surface roughness was nearly the same at the all of the disk-like samples before the ion implantation. Ultra high molecular weight polyethylene (UHMWPE) samples were implanted using MEVVA ion implantation technique with C + H and C + H + Ar hybrid ions at the fluence of 10^{17} ion/cm^2 and the extraction voltage of 30 kV to improve its chemical and thermal properties.

2.1.1. Characterization techniques

We used two different kinds of equipments. One of them is DSC (differential scanning calorimeter) SHIMADZU DT-50 and the other one is TGA (thermo gravimetric analyzer) SHIMADZU DT-51. DSC and TGA were used in N_2 atmosphere. N_2 flow rate was 50.00 ml/min. Aluminum cells were used for analysis of the polymers. The temperatures of the sample cells were increased by 10 K/min. The weights of the all of the samples were nearly 5.00 ± 1.00 mg.

3. Results and discussions

This work showed the change of the surface thermal behaviors of UHMWPE before and after the ion implantation. DSC (differential scanning calorimeter) was used to measure the energy change of the polymer by increasing the temperature in inert N_2 gas atmosphere. The reason for choosing the N_2 atmosphere is that the polymers never give any reactions by increasing the temperature in the N_2 atmosphere. Generally, many of the polymers give oxidation reactions in the air atmosphere. Thus, the oxidation of the polymer would change the chemical characteristics of the polymer. Thus, the measurements could not give the correct data about the thermal properties of the polymer. DSC focused on the thermal properties of the polymer like T_g, T_m, ΔH_{fus} and ΔC_p. T_g is the temperature where the polymer changes its state through glass. This temperature is called glassy transition temperature [3]. Up to this temperature, the all polymers are crystalline. After T_g is reached the crystalline structure of the polymer starts to be semi-crystalline. Semi-crystalline polymers have an amorphous phase. The melting temperature of polymer, T_m, is important for polymer industry due to the extrusion process of thermoplastics. Thermoplastic materials are melt-able polymers and all kind of thermoplastic polymers have different melting points and glassy transition temperatures. Glassy transition temperatures might be identified by DSC. DSC instrument gives some important data from its thermographs about ΔH_{fus} and ΔC_p values. ΔH_{fus} is defined as the melting enthalpy of the polymers or the fusion enthalpy of the polymers. The measurement can be done by taking an integration of T_m over the area of the peak. In the integration, the lower limit is nearly starting of melting temperature and final limit is the finishing temperature of melting. ΔC_p value is seen as a small half peak in Fig. 1 and it can come before or after T_m value in the DSC thermograph. The height of this peak gives ΔC_p. If the polymeric structure changes, the new structure should have a different ΔC_p value. Table 1 shows the thermal data of UHMWPE before and after the ion

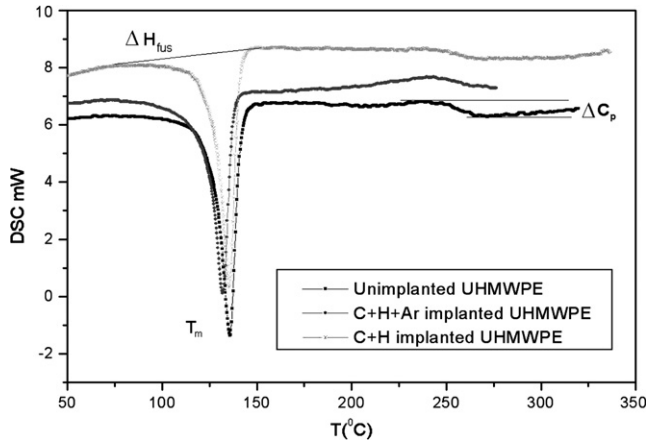

Fig. 1. DSC thermograph of the samples of UHMWPE before and after the ion implantation with C + H, C + H + Ar ions.

Table 1
Thermal data of UHMWPE before and after the ion implantation with C + H, and C + H + Ar ions

SAMPLE	Weight (mg)	ΔH_f (J/g)	ΔC_p (mw)	T_m (C^0)	Crystallinity (%)
Un implanted UHMWPE	5.4	115.07	0.51	135.6	38.1
C + H + Ar implanted UHMWPE	5.0	117.57	0.43	131.8	40.5
C + H implanted UHMWPE	5.2	115.82	0.31	135.2	39.9

implantation with C + H, and C + H + Ar ions. We could discuss the crystallinity of the polymer percentage from Table 1. The detailed calculation of the crystallinity of the polymer percentage could be found in [4]. The crystallinity of the polymer is an important manufacturing gradient for the production process and for the improvement of physical properties of polymeric materials. Increase in the crystallinity of the polymer changes the surface quality of the polymers. We could give the wet ability and surface energy as examples of the surface quality of the polymers.

The purpose of the MEVVA ion implantation is to change the thermal, the chemical and the physical surface properties of UHMWPE samples [5–7]. C + H and C + H + Ar ion implantation changed the melting temperature of the polymer. As seen from Fig. 1, T_m value decreased after the ion implantation of C + H + Ar of UHMWPE sample. The decrease in T_m shows the increase in the numbers of the surface cross-link of UHMWPE samples. The same behavior was seen also in C + H ion implantation. But, this time the increase in the numbers of the surface cross-link was not as much as the case in C + H + Ar implantation. The difference in two cases is coming from Ar ion sputtering. There are locally cross-link parts on the polymer surface. These regions are stable as much as the crystalline parts. When Ar atoms crash to the these locally cross-link parts, they sputter some polymer cross-links and remove from the polymer surface. This event changes the topography of the surface of the polymer. As well as the topography change, one could see the breaking change in main chains. If PE main chains are broken, this will produce radicals. These radicals will make cross-links inside of the crystalline parts of the polymer. Thus, the matrix of the cross-link size will decrease and cross-link density will increase. The change in ΔH_{fus} value is significant for the crystallinity of the polymer. If the surface crystallinity and molecular order increase, ΔH_{fus} value increases. Implantation of C + H and C + H + Ar increased the crystallinity of the polymer. Due to the effect of Ar ion in the implantation, C + H + Ar ion implantation caused more crystallinity effect than C + H ion implantation. We saw different changes in ΔC_p value for both C + H and C + H + Ar implantations.

We thought that the ion implantation changed the main chains and regular bonds of the polymer. Although when we looked at T_g value, we could not see the exact value from Fig. 1. Because the derivatives of T_g values of UHMWPE and PE are nearly at 180–190 K. But, one could could understand or estimate T_g value from T_m value change. While T_m is decreasing, T_g is increasing for the UHMWPE samples, because the ion implantation caused increase in the polymer crystallinity. It can be seen easily from Table 1.

Another special technique of the thermal analysis is TGA (thermo gravimetric analysis). TGA is usually used to see the additives and the thermal degradation temperature of the polymers. When the UHMWPE was implanted with C + H and C + H + Ar ions, the thermal properties changed. The implantations of C + H and C + H + Ar ions through the UHMWPE increased the thermal resistant of UHMWPE. If you look at the Fig. 2 and Table 2, you can see branches removing temperature, decomposition temperature and graphitization temperature of UHMWPE before and after the ion implantation with C + H, and C + H + Ar ions. C + H ion implantation gave us very important information about the thermal properties. Its branches number decreased and these branches could make new bonds or could remove from the surface.

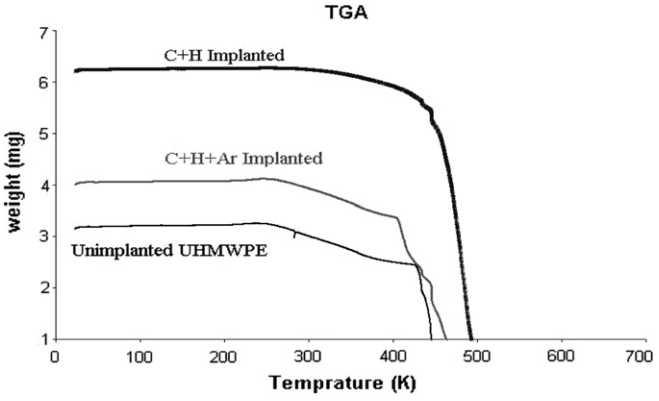

Fig. 2. TGA thermograph of the samples of UHMWPE before and after the ion implantation with C + H, C + H + Ar ions.

Table 2
Some significant temperatures for UHMWPE before and after the ion implantation with C + H, and C + H + Ar ions

SAMPLE	Branches removing $T(C^0)$	Chains decompositions $T(C^0)$	Graphitazion $T(C^0)$
Un implanted UHMWPE	252	429	445
C + H + Ar Implanted UHMWPE	260	(1) 406 (2) 443	463
C + H implanted UHMWPE	305	450	492

When the new bonds are formed, the new cross-links are formed. Thus, this causes the increase in the thermal stability of the UHMWPE samples. If we look at the C + H + Ar ion implanted sample, it is seen that it has two branches removing points. This means that Ar ions could damage the main chain of polymers and shorten the chain length. When the temperature increases, the small parts of these polymer chains remove from the polymer. We could see the parallelism between the numbers of the cross-link and the decomposition temperature. The last point is graphitization point of polymer. At this temperature, the polymer returns to graphite and it's chemical bonds become more stable. Thus, the rigid polymer structure is formed.

4. Conclussion

The thermal characteristics of the UHMWPE samples were improved by C + H and C + H + Ar ions implantations. The C + H and C + H + Ar ions implantations changed the fundamentals of the polymer morphology and the chemistry of the UHMWPE samples. The implantation increased the numbers of the cross-link of the UHMWPE samples. The numbers of the cross-link in the case of the implantation of UHMWPE samples with C + H + Ar ions was higher than the numbers of the cross-link in the case of the implantation of UHMWPE samples with C + H. Ar ions caused damages in the main chains of the polymers and decreased the sizes of the cross-link matrix of the surface of the UHMWPE samples. The increase in the numbers of the cross-link number gives us the improvement in the physical properties of the polymer.

References

[1] T. Suzuki, Y. Ito, K. Velitchkova, E. Hamada, Nucl. Inst. and Meth. B 215 (2004) 83.
[2] Minakshi Maitra, K.C. Verma, Mrinal Sinha, Rajesh Kumar, T.R. Middya, S. Tarafdar, P. Sen, S.K. Bandyopadhyay, Udayan De, Nucl. Inst. and Meth. B 244 (2006) 239.
[3] G. Ehrenstein, G. Riedel, P. Trawiel, Carl Hanser, Thermal Analysis of Plastics, Verlag-Munich, 2004.
[4] Netzsch Applications Laboratory Newsletters 09-2005-03.
[5] T. Ujvari, A. Toth, I. Bertoti, P.M. Nagy, A. Juhasz, Surface Treatment of Polyethylene by Fast Atom Beams, Solid State Ion. 141 (2001) 225.
[6] D.V. Sviridov, Usp. Khim. 71 (2002) 363.
[7] G. Marletta, F. Lacona, In material and processes for surface and interface engineering, in: Y. Pauleau (Ed.), NATOASI Series, Seri E, Applied Science, Vol. 290, Kluwer, Dordrecht, The Netherlands, 1995, p. 597.