PHYSICO-CHEMICAL CHANGES IN HEAVY IONS IRRADIATED POLYMER FOILS BY DIFFERENTIAL SCANNING CALORIMETRY

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1. INTRODUCTION

Heavy ions irradiation induces chemical and physical changes in thin polymer foils [1]. Selective dissolution of material in tracks leading to pores creation, is possible due to increment of reactivity of material in tracks in comparison to polymer matrix material. Although methods of PTM production have been elaborated for some polymer foils and influence of different factors on pore creation process have been examined, little is known about the inner structure of latent tracks.

The chemical as well as physico-chemical methods have been applied in track structure studies [2 - 6]. The scission and cross-linking of polymer chains as well as new chemical species have been discovered.

At present we have applied differential scanning calorimetry (DSC) in studies of physico-chemical changes occurring after heavy ion irradiation in thin polymer film. The results obtained for poly(ethylenetherephtalate) (PETP) are presented and related to structural changes confirmed by wide angle X-ray scattering (WAXS). Some preliminary DSC results obtained for heavy ions irradiated polycarbonate (PC) and polyimide (PI) films are also presented.

2. EXPERIMENTAL

2.1. Materials and irradiations

Poly(ethylenetherephtalate) 19 μm thick foil Hostaphan, polycarbonate 30 μm thick foil Makrofol and polyimide 25 μm thick foil Kapton were irradiated at UNILAC accelerator in G.S.I., Darmstadt.

PETP foil was irradiated using Dy ions with energy 13 MeV/u through a honey-comb structured mask having transmission c.a. 90 %. The applied ion fluence was about $5x10^{10}$ ions/cm^2 and 1 - $5x10^{11}$ ions/cm^2. PC and PI foils were irradiated using ion fluence $5x10^{10}$ ions/cm^2.

2.2.Methods

DSC measurements were carried out in nitrogen stream using Perkin Elmer heat flow DSC7 calorimeter installed in University of Antwerp. Measurements were performed with heating rate 2 and 3^{o}C/min for PETP foils and with 10^{o}C/min and 3^{o}C/min for PC and PI foils.

WAXS measurements were performed using X-ray powder Diffractometer HZG4-C. The CuK_{α} (Ni filtered) radiation was employed. The measurements were carried out in the

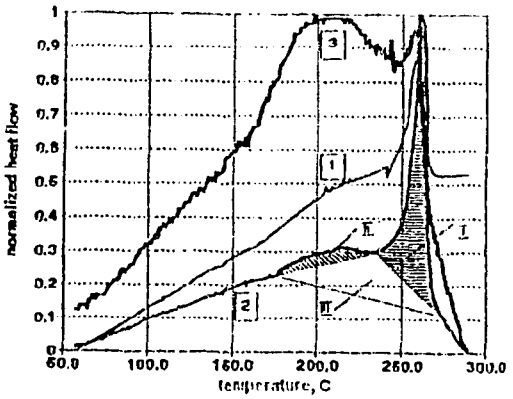

Fig. 1. Normalized DSC curves of 19 μm thick PETP foil recorded with heating rate 2 °/min: initial foil (curve 1), foil irradiated with Dy ions using ion fluence $5x10^{10}$ ions/cm^2 (curve 2) and 1 - $5x10^{11}$ ions/cm^2 (curve 3). On curve 2 there area distinguished on DSC traces due to melting and premelting processes are shown

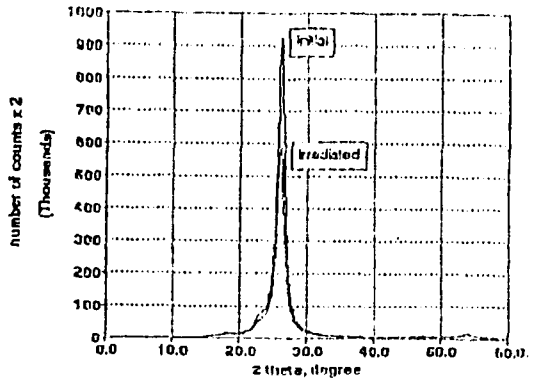

Fig. 2. X-ray scattering curves recorded for PETP 19 μm thick: *initial, Irradiated using fluence* 1 - $5x10^{11}$ ions/cm2

range 2Θ 4.5 - 60 degrees.

3. RESULTS AND DISCUSSION

3.1. Poly(ethylenetherephtalate)

DSC curves recorded for 19 μm thick PETP foil: initial and irradiated with 13 MeV/u Dy ions using two different ion fluences are shown in Fig.1. These curves are normalized to 1.

In the case of an initial sample, single endothermal effect of PETP melting with maximum at 261°C has been recorded (curve 1). In the case of irradiated samples (curves 2, 3) an additional broad endotherm appeared in the temperature range below the melting temperature characteristic for the initial PETP. This endotherm is connected with the premeltingof poly(ethylenetherephtalate) [7,8]. The premelting effect is related to the presence of disordered phase in PETP. It became more distinct while PETP foil was irradiated with larger ions fluence of 1 - 5 x 10^{11} ions/cm^2 (curve 3). Simultaneously heat of fusion associated with the main melting effect became smaller. For foil irradiated with large ions fluence the maximum of melting endotherm was observed at lower temperatures (257°C as compared to 261°C for unirradiated foil). The results indicated on diminution of the crystalline phase content after irradiation.

Three areas can be distinquished in DSC curves. They are displayed in Fig. 2, (curve 2). For results presented in Fig. 1 the following values of heat (in J/g) can be estimated for these areas

curve\area	I	II	III
1	59	5	132
2	52	13	140
3	21	63	176

The structural examinations of PETP foils were carried out by the WAXS method. The measurements were performed for initial PETP and for product irradiated with heavy ions using fluence 1- 5x 10^{11} ions/cm^2).

Diffractograms are presented in Fig. 2. Due to orientation of biaxially stretched film, only few reflections are recorded. Only the (100) reflection (2Θ c.a. 26.0°) shows very high intensity. In diffractogram of irradiated sample the intensity of the very strong (100) reflection is smaller in absolute units but the background intensity is relatively higher as compared to the diffractogram of the unirradiated foil. The absolute intensity of the (100) reflection measured for irradiated product is equal to about 2/3 of that measured for initial foil under the same conditions (Fig. 2). The attenuation of sample ordering occurring after heavy ions irradiation can be concluded on the basis of the above results.

3.2. Poly(imide) and poly(carbonate)

The results obtained for PC and PI films are presented in Figs. 3, 4, 5.

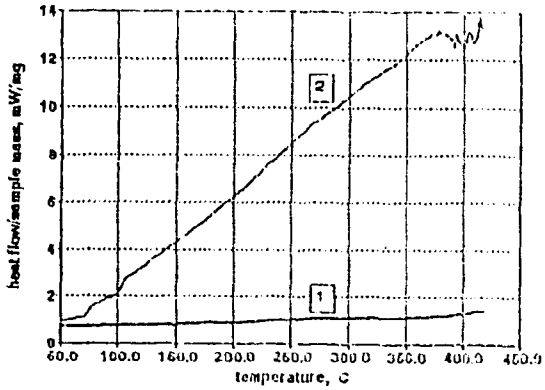

Fig. 3. DSC curves of 30 μm PC foil Makrofol recorded with a heating rate 10 °/min: initial (curve 1) and irradiated (curve 2)

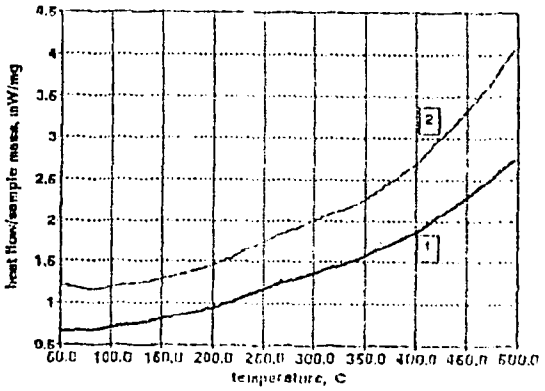

Fig. 4. DSC curves of 25 μm thick PI Kapton film recorded with a heating rate 10 °/min: initial (curve 1) and irradiated (curve 2); both products after heating to 500 °C with a rate of 3 °/min

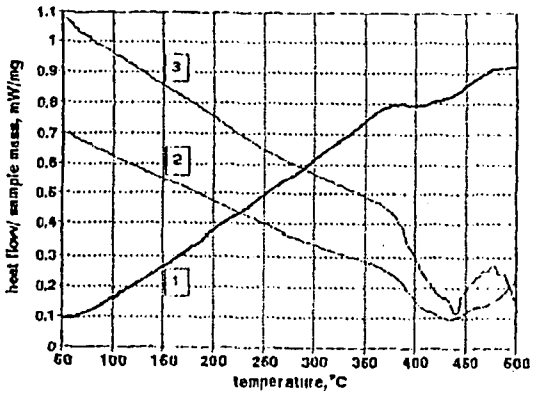

Fig. 5. DSC curves of 25 μm thick PI Kapton film recorded with a heating rate 3 °/min: initial (curve 1) and irradiated (curve 2, 3)

The differences can be observed in slope of DSC curves of both PC and PI recorded for unirradiated and irradiated foils. The slope of DSC curves recorded for the same sample was dependent on the heating rate (10 °/min or 3 °/min).

The decomposition of iradiated PC foil Makrofol starts at lower temperatures in comparison to the initial foil (Fig. 3). The beginning of decomposition was observed at 430°C for initial PC foil but at 360°C for irradiated sample both heated 10°/min.

The degradation effect was not observed for PI Kapton foil heated to 680°C with 10 °/min (Fig 4). However, while PI Kapton foil was heated to 500°C with a small rate 3 °/min a broad exothermal effect was noticed in the temperature range from 364°C to 480°C (Fig.5). The exotherm was larger for irradiated foil than for the initial one. The heat involved during this transformation is equal to 46 kJ/g for the initial foil and 245 J/g for the irradiated foil.

4. CONCLUSION

The differences in DSC traces of unirradiated and heavy ions irradiated polymer foils are brought about by changes in film ordering resulting from heavy ion irradiation. In the case of biaxially oriented PETP film the attenuation in film ordering was found by DSC and WAXS methods. In the case of PC and PI film a decrease of thermal resistivity was found by DSC method.

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