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Nuclear Instruments and Methods in Physics Research B 218 (2004) 294–299
NIM B
Beam Interactions with Materials & Atoms
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Thermal regression of latent tracks in the polymer irradiated by high energy heavy ions

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Abstract

The influence of heat treatment (85–180 °C) on latent tracks (LTs) in poly(ethylene terephthalate) (PET) films irradiated by Xe ions with energy of 1 MeV/nucleon was studied. The kinetics of the alkaline etching (layer-by-layer technique) was investigated. Thermal annealing rises the time of through-pore formation. The etching of through pores, investigated by Hagen–Poiseuille and atomic force microscopy (AFM) methods, was found to be nonlinear: steps were discovered at the etching diagram. They were associated with earlier detected zones of high chemical stability around the track (with the diameters of approximately 10 and 20 nm). Using the AFM method an appearance of surface craters after the irradiation was found. After the annealing the shape of these defects changed to the hillock form.

From the analysis of the Raman and electron paramagnetic resonance (EPR) spectra it is supposed that the polymer structure in the LT area was changed towards carbonaceous phase with graphite-like inclusions, which are evolving under the annealing and affecting the sequential etching process.
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Keywords: Polymer; Ion implantation; Radiation damage; Etching; Annealing; Atomic force microscopy; Raman scattering spectroscopy; Electron paramagnetic resonance

1. Introduction

Swift heavy ion irradiation produces tracks in polymers which are cylindrical zones of radiation-induced damage. Subsequent etching creates pores which is used for polymer membrane production. Hence, this field of research is of a great practical importance. The track etching process was investigated earlier, for example in [1], and explained by the destruction of radiolysis products and their removal from the tracks.

It is known that heat treatment of irradiated polymer strongly affects the track structure and the result of such a treatment depends on the sample temperature [2]. It was shown that low-temperature (below glass-transition point) annealing could accelerate the sequential etching process of the tracks in PET, the so-called sensitisation effect.

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doi:10.1016/j.nimb.2003.12.066

For example, it was found [3] that annealing of the irradiated PET films at the temperatures of 30–80 °C considerably changed the etching kinetics due to the desorption of air components from the tracks. Annealing of irradiated polymer at the temperatures higher than the glass-transition temperature leads to disappearance of LTs (''healing'') or to the reduction of their detectability. This effect is probably caused by thermal motion of macro-molecule fragments and decay of active centres [2,4].

Heavy ion tracks were found to have a complex structure: different radial areas were discovered to show different properties [5]. It was also shown that due to this texture the first period of etching had complicated character including various processes such as diffusion of different components, swelling of the track area, etc. It might be supposed that the changes of the track structure during the annealing would affect the kinetics of further etching. Therefore, the aim of this work is to study the effect of annealing on both the track structure formed in PET film by heavy ions and the etching rate of these tracks for pore formation.

2. Experimental

Biaxially oriented PET films 10 μm thick were irradiated by Xe ions with the energy of 1 MeV/nucleon in the fluence range of 10^9–10^{11} cm^{-2} at the U-300 cyclotron (JINR, Dubna). Annealing of the irradiated polymers was carried out in air at the temperatures between 60 and 220 °C for 1–3 h. Then the samples were etched in aqueous 0.25 M KOH solution, at the temperature of 75 °C. The etching process was studied in detail for samples irradiated with a fluence of 10^9 cm^{-2}. For determination of the etching rate the accumulation of terephthalate ions was measured by a Specord-UV–vis spectrophotometer (wavelength region of about 240 nm).

An atomic force microscope Solver P-47 (NT-MDT, Russia) operated in the resonance regime (''tapping'' mode) [6,7] was used for investigation of sample surfaces. The unit was completed with silicon cantilevers NT-MDT with a curvature radius of the tip of 10 nm. The diameters of the through-etched tracks (pores) were measured using the flow-rate method, namely, the flow of distilled water through the pores under applied trans-membrane pressure ($\Delta P = 10^6$ Pa) and the calculation according to Hagen–Poiseuille's equation (''flow-rate method'') [8]. Pore diameters on the surface were determined with AFM. Raman spectra were registered by an U-1000 spectrometer (Jobin–Yvon) with a microscope allowing to choose homogeneous surface areas and to minimise heating by a laser beam [9]. An Ar-laser ($\lambda =$ 488 nm) with the focused beam (diameter 20 μm) was used. The device resolution was about 1–5 cm^{-1}. EPR spectra were obtained using X-band Varian E112 spectrometer at room temperature.

3. Results and discussion

3.1. Investigation of track etching rate

It is known that the decrease of D_{988}/D_{873} (where D_{988} and D_{873} are the absorbances at the corresponding wave lengths, respectively) indicates the crystallization process in PET [10]. The dependence of D_{988}/D_{873} ratio on the temperature for PET film after thermal treatment is shown in Fig. 1. Irradiation with swift heavy ions leads to amorphization of the polymer (see also for example [11]). On the other hand, heat treatment results in crystallization of both control and irradiated

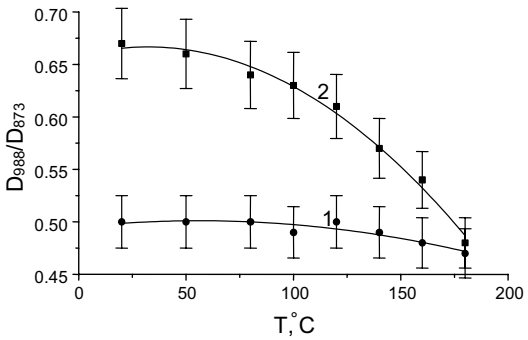

Fig. 1. Dependence of PET absorbance (D_{988}/D_{873}) on temperature (Thermal treatment during 3 h) 1. Control sample; 2. Irradiated sample.

samples. It must be mentioned that the crystallization process for ion-irradiated sample began at lower temperature than for the virgin (non-irradiated) sample. This difference is possibly connected with the porous structure of the tracks and therefore with a lower density of the irradiated polymer. Due to extra free volume, the crystallization (i.e. ordering) of macromolecules is facilitated around track zones.

A detailed study on the behaviour of LTs using UV-spectroscopy of solution during etching is presented below.

The effect of annealing temperature on the total etching velocity v is shown in Fig. 2. (In order to determine the etching velocity we estimated the slope of the absorbance versus time function ($v = \mathrm{tg}\alpha = D/\Delta t$). The part of the graph corresponding to radial etching of the pores was used – for example, for pores radii between 10 and 100 nm.) One can see that the etching velocity increases with annealing temperature, becomes maximal for the samples treated at the temperature about 75 °C and drops down for higher temperatures. These results on etching dynamics are in good agreement with the earlier published data. More information about the etching velocity was obtained using optical spectroscopy. The dependence of absorbance of the etchant (alkali solution) in the UV spectral range on etching time for the irradiated and sequentially annealed PET films is shown in Fig. 3. The latent period of etching, covering an interval from the beginning of the etching to the moment of through pores

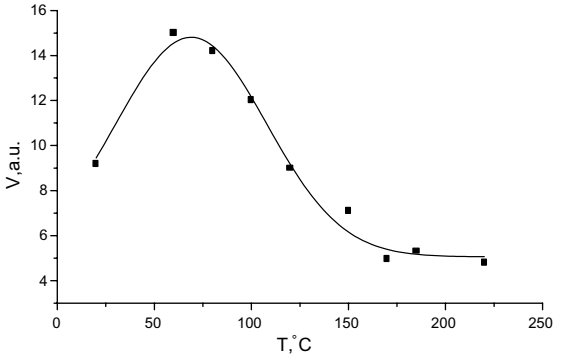

Fig. 2. The dependence of total etching velocity (arbitrary units) on annealing temperature.

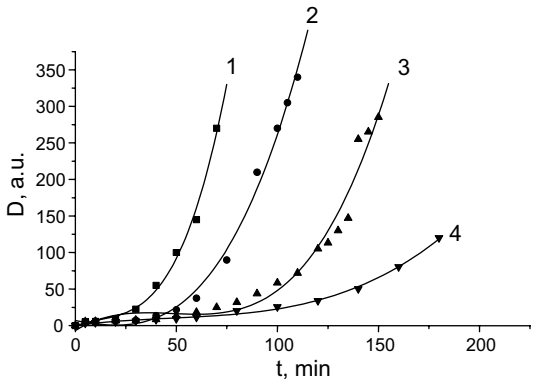

Fig. 3. Dependence of absorbance (D) of solution for Xe-irradiated and annealed PET (in UV-range) on etching time for different annealing temperatures: 1. Control (without annealing); 2. 120 °C, 3. 160 °C, 4. 180 °C.

formation, rises with annealing temperature. After the latent period, the etching process becomes faster and weakly depends on the annealing temperature. It could be also seen that the etching velocity decreases for the annealed samples in comparison with the as-irradiated ones. It is necessary to note that for the as-irradiated PET the absorbance of the etchant is a linearly increasing function of the etching time and the dependences are only slightly different for various annealing temperatures.

For comparison, the etching rate is determined from the pore diameter measurements by the Hagen–Poiseuille method. Fig. 4 demonstrates the dependence of the through-etched pore diameter on the etching time for different annealing temperatures. The latent period of etching increases for the annealed samples and the etching speed decreases with increasing of annealing temperature. A step-like shape of the curves is supposed to be connected to the complex track structure, namely to ring-like areas within the LT, with different radiation-induced changes depending also on the annealing process.

To our opinion at least two zones of polymer around the track axis (with diameters around 10 and 20 nm) with different etching rates could be detected. For the annealed samples this rate is lower than that for the as-irradiated PET. This might be explained by structural alteration of the

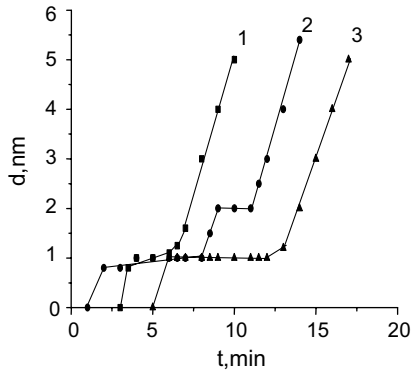

Fig. 4. Dependence of through-etched tracks diameters (pores), d, on etching time for different annealing temperatures: 1. Control (without annealing); 2. 90 °C; 3. 130°C.

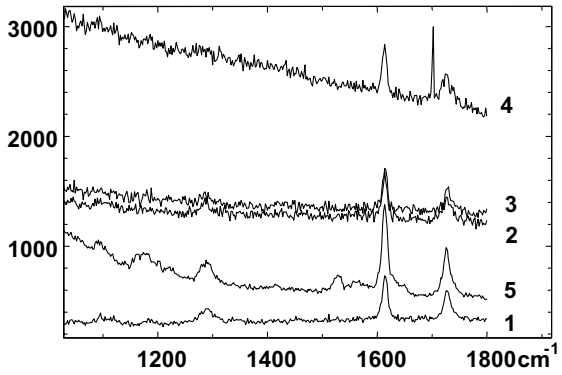

Fig. 5. The Raman spectra (intensity in arbitrary units versus reciprocal wavelength) of the samples after different types of treatment: 1. Control (initial) sample; 2. Irradiated sample (irradiation fluence 10^{11} ions/cm^2); 3. Sample after irradiation and annealing at 100 °C; 4. Sample after irradiation and annealing at 150 °C, 5. Sample after irradiation, annealing and etching of the pores up to 30 nm diameter.

radiation-modified area around the track, in particular, by additional cross-linking of the polymer macromolecules or the formation of a conjugated carbon systems under the annealing. At the same time no significant difference of the etching rate for the as-irradiated and irradiated + annealed samples were found in the case of etched pores with diameters larger than 20 nm.

The AFM method was used for testing the sample surface after each stage of treatment. The small craters with diameter of 6–8 nm at the surface of as-irradiated sample were found to be track entries. The thermal treatment of the PET samples in the temperature interval of 100–160 °C leads to the change of the surface topography. Hillocks appeared at the places of craters. These results are in accordance with our data for PET irradiated with Bi-ions (3.5 MeV/nucleon) [12].

After through-pores formation the pore diameters were also measured by AFM and the results obtained coincided with the data derived by the Hagen–Poiseuille method.

3.2. Investigations of track composition

To study the composition of the track area Raman spectroscopy was used. Samples irradiated with different fluences were examined. All obtained spectra have the same character but clearer and more distinct results were obtained for the high fluence of 10^{11} cm^{-2}. Typical spectra are presented in Fig. 5. A few characteristic spectral bands are registered for PET. A slight broadening of the spectral lines after the irradiation is observed and may be associated with the radiation damage. The luminescence background increase is probably caused by carbonisation of the track area and nucleation of the carbon-rich clusters [13]; these particles are known to exhibit intensive luminescence [14,15]. The annealing leads to further increase of the luminescence background. As a result of the etching of through pores, i.e. membrane formation, the Raman spectrum shifts down in the intensity scale close to the spectrum of the initial non-irradiated film. From this fact one can conclude that the spectral changes for the irradiated and annealed samples come from the LT areas only.

EPR spectra show an appearance of the signal with $g = 2.0036 \pm 0.0005$ and linewidth of about 10 G for the irradiated PET films. This signal is well known for graphite and associated with surface defects, namely with π-electrons delocalised on surface states. For irradiated graphite this signal was caused by radiation-induced broken bonds similar to those ones at the surface [16]. Thus, EPR measurements are in good agreement with Raman experiments showing carbonisation of the radiation-damaged areas. Moreover EPR data allow

one to obtain more detailed information; one could assume the formation of graphite-like structures along the LT. This result is different from those ones found on low-energy (tens and hundreds keV) polymer implantation indicating an EPR signal with $g = 2.0025 \pm 0.0005$ corresponding to delocalised π-electrons of the carbon clusters with conjugated bonds [17,18]. The "graphite-like nature" of the signal in our case could be explained by the very high energy transferred to the polymer matrix especially by electronic stopping causing probably extremely high local temperatures favourable for the formation of graphite-like ensembles. Thermal annealing of the irradiated samples does not affect the EPR spectrum which shows the absence of qualitative changes in the electronic system of the LT area. After the etching the signal becomes weaker and broader but does not disappear. Unfortunately, due to the relatively low irradiation fluence the concentration of the registered paramagnetic centres was close to the detectable limit of the spectrometer. That allowed us only qualitative analysis and comparison of the EPR spectra corresponding to the samples after different sorts of treatment. This problem will be under further investigation.

4. Conclusions

It is shown that the annealing at the temperatures higher than 100 °C results in a decrease of the chemical etching rate of the PET films irradiated with Xe ions. The kinetic curve of the film etching is nonlinear. The presence of the steps on this curve allows to suppose that the ring-like zones of different chemical resistance with diameters of about 10 and 20 nm exist in the track region.

It is supposed that sequential annealing of the irradiated samples to the temperatures above glass-transition induces not only "healing" (slow disappearing) of the tracks but also the complex change of the radiation-modified zones. This process probably leads to an increase of density inside of the tracks and to an additional cross-linking which increases the chemical resistivity as compared to the non-annealed samples.

Raman spectroscopy shows a clear evidence of the polymer carbonisation under the implantation. Sequential annealing changing the chemical properties of the radiation-modified areas is also reflected by the Raman spectra. Results of the EPR measurements suggest the formation of graphite-like structures in the tracks as a result of very high energy transferred to the polymer matrix due to the stopping of the MeV ions.

Acknowledgements

The authors thank R.V. Gainutdinov (Shubnikov Institute of Crystallography, Moscow) for making a part of AFM experiments. This work was supported in part by ISTC (grant N 918) and Russian Foundation for Basic Research (grant N00-03-32099).

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