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Influence of temperature during irradiation on the structure of latent track in polycarbonate

P. Yu. Apel[a,*], I.V. Blonskaya[a], T.W. Cornelius[b,1], R. Neumann[b], R. Spohr[b], K. Schwartz[b], V.A. Skuratov[a], C. Trautmann[b]

[a] Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, Joliot-Curie Str. 6, 141980 Dubna, Russia
[b] Materials Research, Gesellschaft für Schwerionenforschung, Planckstr. 1, Darmstadt, Germany

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ABSTRACT

Stacks consisting of several layers of polycarbonate foils 10 μm thick were irradiated with U, Sm and Ni ions at the UNILAC (GSI, Darmstadt) and with Kr ions from the U-400 cyclotron (JINR, Dubna). The energy of the ions varied from 1 to 11 MeV/u. The irradiation with each ion species was performed at room temperature (RT) and at low temperatures (80 K or 15 K). The irradiated samples were etched with aqueous NaOH solutions in a conductometric cell. The effective pore diameter as a function of the etching time was calculated assuming cylindrical geometry of the etched out channels. The conductometric curve consisted of three parts which we identified as the track core, track halo and bulk etching. Radii of both track core and halo increased with increasing ion mass, and were consistent with the power-law energy-loss dependence. The size of the track core was found to not depend on the temperature during irradiation. Since this result was obtained in experiments performed at two different accelerator facilities and with four different projectiles of various energies, it can be considered as the one of high confidence level. In contrast, the radius of the halo tended to decrease with decreasing irradiation temperatures. However, reproducibility of the track halo radius estimates was quite poor which might be caused by some uncontrolled experimental factors influencing post-irradiation chemical reactions.

1. Introduction

A study of track etching in a polymer irradiated with charged heavy particles at different temperatures is of interest for two main reasons. First, etching of ion tracks in polymer foils is widely used for the production of membranes and templates with micro- or nanopores (Fleischer et al., 1975; Spohr, 1990, 2005). Reproducible fabrication of precisely defined structures requires the detailed knowledge of factors determining the properties of narrow pores resulting from ion track etching. Secondly, the track etching is a tool that can help to shed light on mechanisms responsible for the track formation. Since the discovery of etchable tracks in insulators (Young, 1958), several theoretical models have been proposed to explain the appearance of tracks induced in matter by the slowing down of energetic ions in the electronic stopping power regime (Fleischer et al., 1975; Young, 1997). But nowadays, the formation process is still not completely understood and relevant processes are controversially discussed. The most prominent track formation mechanisms are the Coulomb explosion and the thermal spike. The thermal spike model has been significantly developed and refined in recent years (Toulemonde et al., 1994, 2000; Szenes et al., 2000; Klaumünzer, 2004) which made it possible to confirm relevance of the thermal spike model to track formation.

When etching ion tracks, changes of the local etch rate with increasing pore radius reflect the spatial distribution of chemical and physical modifications of the polymer. Previous studies showed that ion tracks in polymers have a narrow core (easily etched out damage zone) surrounded by a halo of much larger radius. In polyethylene terephthalate (PET), the etch rate of the polymer in the halo is lower than the etch rate of pristine PET (Apel et al., 1998) indicating that cross-linking takes place. For ion tracks in polycarbonate (PC), the behavior of the local etch rate in the halo was found either similar (Apel et al., 1989; Francisco et al., 2004) or different (DeSorbo, 1979; Guillot and Rondelez, 1981) than in PET. Cross-linking in PC was shown to occur in ion tracks by using solubility and solution viscosity measurements (Apel et al., 1989). However, the etching curves obtained by Guillot and Rondelez (1981), Schnoor et al. (1982), Ferain and Legras (1994), did not show

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* Corresponding author. Tel.: +7 49621 63544; fax: +7 49621 28933.
E-mail address: apel@nrmail.jinr.ru (P.Yu. Apel).

[1] Present address: European Synchrotron Radiation Facility (ESRF), BP 220, 6 rue Jules Horowitz, 38043 Grenoble Cedex, France.

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any indication of a reduced etch rate in the halo. The controversial results could be caused by different contributions of chemical reactions leading to scission or to cross-linking of macromolecules. Since the balance between scission and cross-linking depends on the temperature at the moment of irradiation, it is important to investigate ion tracks formed at low temperature, i.e. under conditions when the mobility of radiolysis intermediates is significantly reduced.

So far, most of the experiments on nanopore etching in PC were performed using alkaline etchants containing surfactants (DeSorbo, 1979; Guillot and Rondelez, 1981; Schnoor et al., 1982; Ferain and Legras, 1994). Surface-active substances are normally used to improve wetting and obtain more uniform etching. However, it was recently shown that the presence of a surfactant significantly alters the shape of etching curves (Apel et al., 2001, 2006b, 2008; Man et al., 2007) which might lead to wrong conclusions about the distribution of the damage in the tracks. In the present work we therefore employed a surfactant-free etching solution.

2. Experimental

Polycarbonate foils Makrofol KG (10 μm thick) were irradiated with U, Sm and Ni ions (initial energy of 11.1 MeV/u) at the UNILAC (GSI, Darmstadt), both at room temperature (RT) and at 15 K. The use of stacks consisting of 12–15 samples made it possible to gradually vary ion energies and energy losses. The irradiation experiments at low temperature (LT) were performed in a cryostat installed at the beamline. The polycarbonate specimens were mounted on a thick copper holder using indium foils for reliable thermal contact (Schwartz et al., 2008). Irradiation of the samples with Kr ions (energy of 2.5 MeV/u) was performed on the U-400 cyclotron at the Flerov Laboratory of Nuclear Reactions (JINR, Dubna). The sample holder was kept either at room temperature or cooled down with liquid nitrogen (Skuratov et al., 1999). To reduce the total number of tracks in a sample, the stacks were covered with a diaphragm having a small aperture (1–3 mm). This measure enabled us to avoid errors stemming from low resistance of the foil during the conductometric etching. Typical track densities in the samples ranged from 10^5 to 10^6 cm^{-2}. The irradiated samples were sensitized with ultraviolet light and etched with aqueous NaOH solutions in a conductometric cell. A LabView-controlled HIOKI RCL-meter was employed to monitor ohmic resistance of the cell in the range of 10^{10} down to 10 Ω. To avoid polarization effects on the electrodes sine voltage with an amplitude of 1 V and a frequency of 2 kHz was applied to the cell. The number of tracks in the samples was carefully counted in a scanning electron microscope (JSM-840, JEOL) with a statistical error (2σ) not exceeding ±6%. All etching experiments were performed using 5 M NaOH at 40 °C. The specific conductivity of the etchant was 0.54 Ω^{-1} cm^{-1}. The effective pore diameter d_{eff} as a function of the etching time t was calculated assuming cylindrical geometry of the etched pores.

3. Results and discussion

The dependence of the effective pore diameter (curve *a*) and its derivative (curve *b*) on the etching time in 5 M NaOH solution is shown in Fig. 1. The evolution of d_{eff} as a function of etching time t consists of three parts which we interpret as follows: The first stage (part I) starts at the moment of breakthrough which takes typically a few minutes. The fast pore growth ($t \leq 5$ min) up to 10–20 nm in diameter is ascribed to the dissolution of the track core. At the border between stage I and II, the derivative attains a minimum (see curve *b*) that is assigned to cross-linking. Part II is a concave segment with gradually increasing slope which may be associated with a decrease in density of cross-links between macromolecules. In part III, the radial etch rate decreases again. At larger radii, the radial etch rate V_r is expected to evolve towards a constant value corresponding to the etch rate of the non-irradiated matrix material. However, we observed that even at pore diameters as large as 2–4 μm, i.e. far beyond the damage zone, the radial etch rate V_r does not become constant (Apel et al., 2006a). We have also found that the shape of part III does not directly correlate with the mass and energy of the ion but rather depends on the alkali concentration and temperature of the etchant. As recently shown by Fink et al. (2000), etching of polycarbonate is accompanied by a "compaction" of the polymer which leads to a decrease in susceptibility of the material to chemical attack. In addition to the compaction effect, accumulation of etching products and their adsorption on the polymer surface can also induce a slow decrease of the etch rate at large pore radii (Cornelius et al., 2007). Therefore we conclude that stage III of the pore evolution is bulk etching with permanently changing rate.

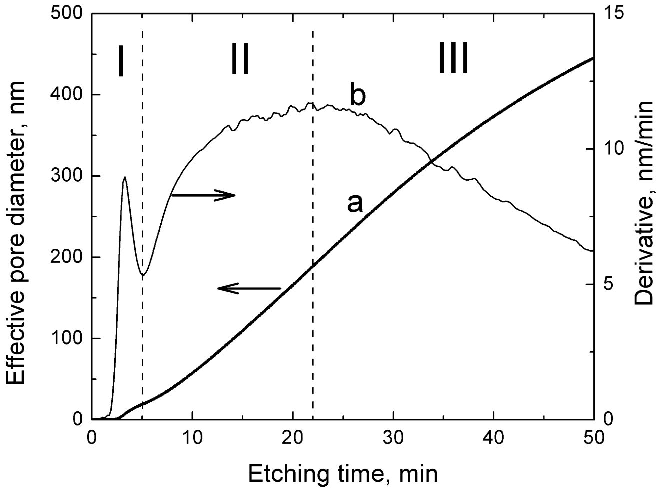

Fig. 1. Etching of Makrofol KG irradiated at RT with 2.8 MeV/u U ions (3.8×10^5 cm^{-2}, 3400 tracks per sample) using 5 M NaOH at 40 °C. Curve (*a*) shows the effective pore diameter d_{eff} as a function of etching time. Curve (*b*) is the derivative thus illustrating the change of the doubled radial etch rate, $2V_r$, in stages I, II, and III.

Based on the arguments adduced above, we defined the diameters of the track core d_c and the halo d_h as the points of inflection of the d_{eff} –vs–t curve that manifest transitions between phases I, II, and III. Minima and maxima on the derivative curve in Fig. 1 correspond to the d_c and d_h values. Their positions can be determined quite accurately by sequential procedures of smoothing and differentiation. Core and halo diameters of low-temperature and RT irradiations in the energy-loss range from 3.6 keV/nm to 18.4 keV/nm are presented in Fig. 2. There is evident correlation between *dE/dx* and the typical track diameters derived from the etching curves. Both d_c and d_h increase with increasing *dE/dx*. This is a clear indication that phases I and II reflect the structural characteristics of latent track. The d_c and d_h values were fitted by a power-law function to quantitatively describe the transversal dimensions of the damage zone depending on the energy loss:

$$\mathrm{d}_{c,h} = A(\mathrm{d}E/\mathrm{d}x)^b \qquad (1)$$

where A and b are fitting parameters. For the four series of experimental data d_c (RT), d_c (LT), d_h (RT), d_h (LT) the parameter b was found to vary in a relatively narrow range of 0.30–0.38. The data for the track core diameters were best described with b values that differed only slightly from each other (0.30 for LT and 0.31 for RT). This enabled us to fix the parameter $b = 0.31$ for the two series of d_c data and repeat the fitting procedure with only one fitting