TRACKS OF HIGH-ENERGY IONS IN POLYIMIDE: I. PROPERTIES OF POLYIMIDE IRRADIATED BY HIGH-ENERGY IONS

A.I.Vilensky, V.A.Oleinikov, Yu.V.Tolmachyova, N.G.Markov, E.P.Dontzova

Institute of Crystallography Russian Academy of Sciences
Moscow, 117333, Leninsky pr.,59

Abstract. Properties of polyimide irradiated by high-energy ions of Ar (the energy 40 MeV) and Kr (the energy 210 MeV) were investigated. It was found that as a result of high energy ions irradiation destruction of imide rings with formation of amide groups and intermolecular bonds takes place. The dichroism of bands in polyimide spectra and also dependence of chemical resistance on surface density of polymer irradiation were studied.

1. INTRODUCTION

Nowadays nuclear filters (track membranes (TM)) are perspective materials for membrane technique. These structures are made by means of the irradiation of initial material by high-energy ions beam and following development of formed latent tracks in this material [1,2].

Track membranes made on the base of polyethyleneterephthalate and polycarbonate are manufactured in a number of countries. But applications of these membranes have some limitations which are defined by physico-chemical properties of TM materials. Therefore intensive research in the field of TM creation on the base of another materials have been performed. For this purpose polyimide (PI) is the most perspective polymer because of its great thermal and radiation resistivity.

Important step in the way of polyimide TM creation is the investigation of the interaction of high-energy charged particles with this polymer and the change of PM structure as a result of action of high-energy ions with energies enough for the formation of pores in PM films (the energy more than 1 MeV/nucleon).

The influence of ions beams with significantly less energy (0.05-0.2 MeV) on the PM was studied [3-6].

Investigations concerning the influence of varions types of irradiations on PM were performed for:

- UV irradiation (the wave length 185 nm) [7,8];
- irradiation (more than 2000 Mrad) [7,9];
- ions beams H^+, He^+, Kr^+, Xe^+, with energies from 0.5 to 2 MeV [3-6];

as well as low temperature plasma discharges of various types.

The typical results of these irradiations are:

- The destruction of imide cycles takes place. It was noted in some papers [6,11] that the number of aromatic cycles does not change.
- The gases eduction (O_2, N_2, CO) appears[7,12].
- The increase of adhesion activity of surface and their hydrofilization is observed.
- There is an increasing of electroconductivity, probably connected with polymer grafitization [3,4,8].

In present work the investigations of

influence of high-energy ions (the energy 1-2 MeV/nucleon) on the PM were performed. The alterations of polymer structure as a result of ions irradiation (imidization and macromolecules orientation) as well as changes of chemical resistance and physical-mechanical properties of ions-irradiated PI were studied.

2. EXPERIMENTAL

PI films were prepared by means of deposition of the polyamide acid (PAA)solution on the forming surface. PAA was synthesized on the base of pyromellitol dianhydrite (PMDA) and 4,4-diaminodiphenyl ester (DADFE) in dimethyl formamide (DMFA) with the following thermoimidization. The residual solvent content was estimated as the weight loss of sample as a result of the thermotreatment of samples at 400°C, for 40 min, with the use of the firm "Dupont" device.

PI films in thickness of 10±1 and 20±1 μm were studied. The residual solvent content (DMFA) was 1.1% and 1.3%, respectively. After thermotreatment at 320°C, for 2 hours, the content of DMFA was decreased to 0.6%. Thus, these foils and the foils "Kapton" ("Du Pont") or "Upilex" (Ube Industries Co. Ltd.) are similar.

Physico-mechanical properties of both initial and irradiated by Kr ions PI films (the longitudinal strength and breaking elongation) were measured.

PI films were irradiated by Ar ions with the energy 40 MeV (1MeV/nucleon), using cyclotron in A.F. Ioffe Physics-Technical Institute (St.Peterburg, Russia), and by Kr ions with the energy 210 MeV (2,6 MeV/nucleon) in the cyclotron U-400, G.N.Flerov Laboratory of Nuclear Reactions of Joint Institute of Nuclear Research (Dubna, Russia).

The irradiation density was controlled by the count of holes number in the samples after their treatment in acidify $KMnO_4$ solution at 80°C, during 5 hours [13].

The IR spectra were recorded using spectrophotometer Specord M80 with cycle measurements program with the same wave number (0.21 start, slit 12.1/T=10, expx 20). The optical density was calculated as an average of the least three measurements for each sample. The errors connected with thickness variations of PM films were excepted by averaging of optical densities for 7-10 samples.

To investigate possible changes in polymer macromolecules orientation after PI films irradiation, the method of dichroism ratio measurements was used. The absorption of polarized IR-radiation in dependence on the PI films orientations was measured. Samples were oriented both normally and with tilt 45o with respect to incidence ray [14,15].

The estimation of chemical resistance of ions-irradiated PI films was carried out by measuring of PI etching rate in 5% NaOH solution at 90°C. The etching rate was determined by sample weight change with the accuracy of 0.1 mg.

The results were processed by mathematical statistics methods, where confidence coefficient was 0.95 [16].

3. RESULTS AND DISCUSSION

Dependencies of intensity of typical PI absorption bands on track density in the samples were studied. Decreasing of 1380 cm^{-1}, 1720 cm^{-1}, 1776 cm^{-1} bands (oscillation of groups contained in imide rings), 1244 cm^{-1}, 1180 cm^{-1} 1290 cm^{-1} bands (ester groups oscillations), 1020 cm^{-1}, 1512 cm^{-1} bands (benzene rings oscillations), 726 cm^{-1}, 885 cm^{-1} ones (amorphous sensitive bands) [7] was observed. The dependencies were nonlinear: the more tracks density (10^9), the more decreasing of absorption bands.

The dependencies of optical density D_{726} of 726 cm^{-1} band (deformation oscillations of C=O bonds of imide rings) on surface density of ions irradiation (both for thermotreated PI and without one) are presented in Fig. 1. It is known [7], that the treatment of PI films at the high temperature gives the partial destroy of imide rings with formation of intermolecular bonds, therefore D_{726} is decreased for thermotreated polymers in comparing with the non-thermotreated one. The decrease of D_{726} for ions-irradiated PI points that the destruction of imide rings is takes place in this case. It should be noted that for

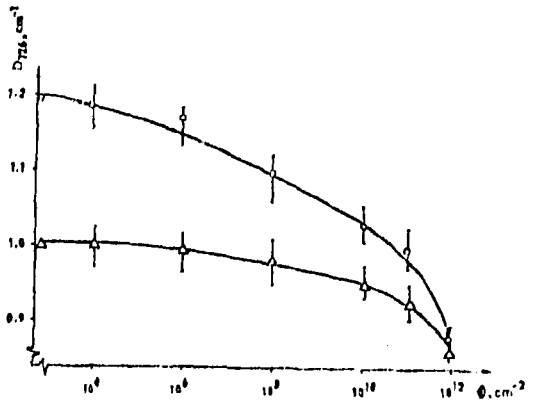

Fig. 1. The dependencies of D_{726} optical absorption density (deformation oscillations of C=O bonds of imide rings) as a function of surface density of PI irradiation by Ar ions: 1 — termotreated film; 2 — non-termotreated film

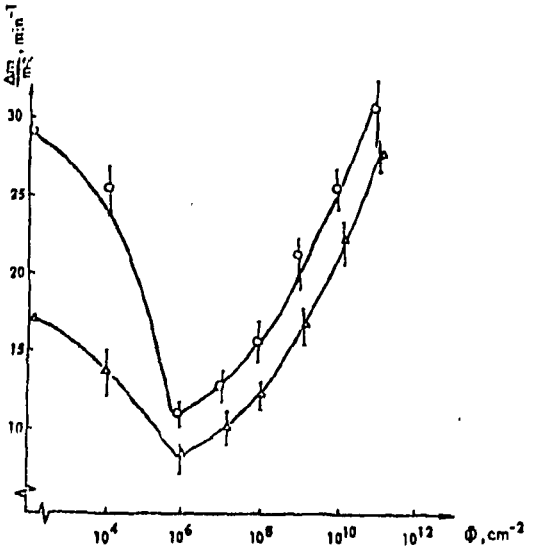

Fig. 2. The dependencies of PI film etching rate in 5% NaOH solution (90°) as a function of surface density irradiation by Ar ions: 1 — termotreated film; 2 — non-termotreated film

thermotreated PI (Fig. 1, curve 2)D_{726} practically does not depend on irradiation density up to 10^9-10^{10} cm^{-2}. This phenomenon is connected with high radiation resistivity of PI.

Appearance of 1680 cm^{-1} and 1550 cm^{-1} absorption bands (amide$_1$ groups oscillations) and 1680 cm^{-1} ones (intermolecular bonds) confirms the imide groups destruction in PI exposed by Ar ions with density of irradiation 10^8-10^{10}cm^{-2}. It may be explained by the amide groups formation (1680 cm^{-1} - Amide-1 and 1550 cm^{-1}- Amide-2) [7,14], and also by the crosslinkage bonds creation (1660 cm^{-1}) [7].

Besides, both 726 cm^{-1} and 885 cm^{-1} bands are amorphous sensitive [17]. Therefore the decreasing of D_{726}(Fig.1) and D_{885}, as well simbath increasing of crystal sensitive band D_{800} tells about the structural changes in polymer. It is likely, these changes are caused by regulating of polymer chains as the result of imide rings destruction and crosslinkage bond formation [7,9,17].

The decrease of bands intensities in the range 900-1500 cm^{-1} points out the destructions of multiester groups and simple ester bonds with removing aromatic molecules fragments as a result of the ions irradiation. The same changes are observed in PI films after their thermotreatment at temperatures above 400°C [18].

Investigations of additional orientation of polymer due to their exposition to high-energy ions beam were carried out by measuring of dichroism of 726 cm^{-1}, 1380 cm^{-1}, 1512 cm^{-1}and 1776 cm^{-1} bands for films oriented both normally to the incident IR-ray and with the tilt 45°. The results are shown in Table 1.

The films normally oriented to the falling IR-ray are practically isotropic. It is true for both inital and irradiated by Kr ions films. In the case of film oriented with the tilt 45° the dichroism ratio increases with increasing surface density of ions irradiation. This fact points out to the additional orientation of polymer macromolecules along the track axis.

The mechanism of this orientation is not clear now. It can be connected with processes, which take place in polymer due to tracks formation.

In Fig. 2 curves of relative etching rates of PI films in 5% NaOH solution at 90°C as a function of Ar ions irradiation density are shown. The etching rate of thermo-treated polymer is less than the etching rate of the initial one. Probably, it is caused by the additional intermolecular linkage formation in thermal treatment process.

At increasing the surface density of ions irradiation the number of intermolecular linkages increases. It is defined by the

Table 1. Dichroism of PI absorption spectra (PI films thickness is 20 μm, non-thermotreated, PI was irradiated by Kr ions)

R — films were normally oriented to fallen IR-ray;

R* — angle between normal and IR-ray direction is 45°

Wave number	R/R*			
	Surface density of irradiation, cm^{-2}			
cm^{-1}	0	10^7	10^8	10^9
726	1.00/0.91	1.09/0.95	1.04/1.17	1.06/1.17
1380	0.94/0.96	0.94/1.20	0.97/1.20	0.97/1.25
1512	0.91/0.90	1.01/1.47	1.07/1.35	1.05/1.50
1776	1.05/1.05	1.02/0.97	1.11/1.16	1.10/1.20

rising of PI chemical resistivity. But for the fluence higher than 10^9 cm^{-2}, the part of destructing polymer in cores of ions tracks is increased. Thus, there is a minimum on the curve of the function of etching rate versus fluence.

However, the decrease of PI etching rate for low fluence cannot be explained on the base of intermolecular bonds created in the zone of ions passing only. It is true, if we use the size of changing structure zone for PETP estimated by means of conductometry [19] or layer by layer etching method [20]. The size of this zone is 50-70 nm. Thus, the part of sewed volume (volume with higher density of intermolecular bonds) is 10^{-3}% when fluence is 10^6 cm^{-2}. Therefore, it should be supposed that the ion acting zone is significantly extended. The same "long distance effect" when a ion passes through the substance was theoretically found in the work [21] and was experimentally discovered, by means of investigation of DMFA absorption the irradiated Xe ions PETP [22].

The results of investigations of the high-energy ions influence on the physical and mechanical characteristics of PI show that the irradiation of film by Kr ions in range 10^7-10^9 ions/cm^2 practically has no influence on both breaking elongation and longitudinal strength.

4. CONCLUSION

As a result of PI films irradiation by ions with energy 1-2 MeV/nucleon the imide rings destruction with amide groups and intermolecular linkages formation in ions action zone take place. The dichroism ratio changes in the samples oriented with the tilt to incident IR ray was also observed.

The rise of these ratio points out that additional macromolecules orientation have occurred in the process of tracks formation. Decrease of etching rate of PI is observed for surface density of irradiation 10^6-10^8 ions/cm^2. It can be explained by "long distance effect". Surface density of ions irradiation in the range up to 10^9 cm^{-2} practically has no influence on physical and mechanical characteristics of PI.

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