TRACKS OF HIGH-ENERGY IONS IN POLYIMIDE: II. ETCHING OF TRACKS. PRODUCTION OF POLYIMIDE TRACK MEMBRANES

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Abstract. The processes of high-energy ions tracks etching in polyimide (PI) were studied. Comparison between characteristics of etchants with various compositions was made. A new etchant (concentrated hydrogen peroxide) with high selectivity and high enough etching rate was suggested. The etchant is accessible and ecologically clean. PI track membranes for ultra and microfiltration were created.

1. INTRODUCTION

At present one of the most widely used technological proccesses of separating of complex mixtures is the membrane filtration [1]. Among those materials, which are used in this process, track membranes (TM) fill a highly important place. TM are made by polymer film irradiation by a beam of high-energy ions with the further development of the tracks up to the through pores formation [2-4].

Polyimide is promising as a material for manufacturing of chemical, thermal- and radiation-damage stable membranes. The composition for the tracks etching in PI ($KMnO_4$ in H_2O_2) was first suggested in the work [5]. In [6,7] conic or cylindrical pores in this polymer were obtained by etching of irradiated PI of specification "Upilex" of the Ube Industries Co. Ltd., with thickness of 25 μm in 25% $KMnO_4$ solution at 90°C with the following washing off manganese oxides by chloride acid.

For reagent $KMnO_4$ mixed with $HClO_3$ or $KMnO_4$ mixed with H_2O_2 was also suggested [6,7]. Saturated solution of $K_2Cr_2O_7$ in 12N, 16N, 24N H_2SO_4 as well as 4.5N NaOH were also used for PI [8]. For the tracks etching one can also use the PI solvents, such as solutions based on hydrasinhydrate and ethylendiamine [9,10], base solutions of ethanol or propanol [11].

In the present work the known methods of tracks etching in PI were evaluated and compared (the PI films used were identical, irradiated under the same conditions). The information about design and investigation of new methods of TM producing from PI is provided.

2. EXPERIMENTAL PROCEDURE

As the subject of investigation we used the manufactured PI film of 10 and 20 μm thickness. To investigate the influence of residual solvent content on the etching process of the irradiated polymer, a part of the film was thermotreated at 320°C during two hours, with the residual solvent content (RSC) reduced up to 0.6%, what corresponds to the RSC in PI film of "Kapton" or "Upilex" marks.

The PI film was irradiated by ions of argon, krypton, wolfram and by fragments of uranium fission:

- the Ar ions irradiation (energy 1 MeV/nucleon) was conducted in the cyclotron in Ioffe Physics-Technical Institute (St. Petersburg); the film of 10 μm in thickness was used;

- the irradiation by Kr-ions (energy 0.3 MeV/nucleon) - in the cyclotron U-400 (Flerov Laboratory Nuclear Reactions, Dubna), film of 20 μm in thickness;

- the irradiation by W-ions (energy 0.3 MeV /nucleon) - in the accelerator in the Institute of Theoretical and Experimental Physics (Moscow);

- the irradiation by fragments of uranium fission - in the Karpov Physicochemical Science Research Institute (Obninsk).

The essential difference of the latter kind of irradiation from the irradiation in accelerators is wide range of ions tracks directions, what is a result of a relative close position of PI film and the fission fragments source. Let us note that for irradiation by means of accelerators the ion tracks are practically perpendicular to the PI film surface.

The energies of Ar and Kr ions were high enough to make through tracks. The range of W ions tracks account for 10 μm of length. This is enough to obtain deadended tracks in initial films of 20 μm in thickness. The surface density of irradiation was varied between 10^7 and 10^9 ions/cm^2. This range of values for tracks density allowed to produce membranes as for micro-(pores diameters 0.05-2.5 μm) so also for ultrafiltration (pores diameters below 0.05 μm). The etching of irradiated films was carried out at the temperature of 20-100^{0}C.

The film thickness during the treatment has changed, approximately of 1 μm. The pores diameters were defined by a hydrodynamic method by the distillated water flow through a membrane at a given differential pressure (square of membrane amounted to 0.55×10^{-3} m^2, differential pressure - $5 \cdot 10^6$ Pa) [1], and also by the scanning electron microscopy of surface and break of membranes. The etching rate of non-irradiated films was defined by a method of weight and by the film thickness change determination by electron microscopy. To obtain breaks, membranes were cooled to the liquid nitrogen temperature, the conducting layer was deposited by Au or Cu evaporating in vacuum. The scanning electron microscope BS 340, TESLA, was used.

3. RESULTS AND DISCUSSION

The results of tracks etching in PI investigations by solutions of different compositions are tabulated in Table 1.

The results given in [6,7] are not reproduced. In PI films irradiated by Ar-ions and treated by 25% [7] and 19% solutions $KMnO_4$ in H_2O (Table 1, p. 1-2), there are not etched tracks though this solution destroys PI surface quickly enough (let us note that the $KMnO_4$ solution in H_2O at 100^{0}C accounts for 19%). These results were not explained though the film types used in the research were alike to ones used in [6,7] and Cu and S-ions by their weight and energy were alike to Ar ions. Because of this, they carried out investigation of influence pH value of KMnO solution on selectivity of tracks etching in PI. At pH > 7 the selective etching of tracks does not happen. If the solution is acidified the etching becomes selective; the etching selectivity (that is the ratio of rate of etching along track to radial etching rate) exceeds 10^3. Let us note that in such conditions the oxidant potential of MnO_4^- ions is at its maximum.

In the oxidant mixtures, offered in [7] (Table 1, p.4-6), the pores etching rate is superior to acidified solutions of $KMnO_4$, but the selectivity is much worse.

The tracks etching in chrome mixtures (Table 1, p.7) passes quick enough (3-6 min). However, the etching selectivity is not high, the intensive surface etching is well seen.

As for base etchants (5% KOH in water, hydrasinhydrate and etylendiamide solutions) in some cases there are a through pores formation, but the etching selectivity is not sufficient. For each studied mixture the etching rate of thermotreated films was a little bit lower than the one of non-thermotreated films. Analyzing the results we can conclude that the examined compositions do not suit well for practical use in technological process of TM manufacturing on PI basis. Basic etchants are not selective enough. The etchants on the basis of oxidants give pore structure, but they are highly

Table 1. Etching of polyimide by solutions of different composition. Films thickness is 10 μm; Ar ions energy is 1 MeV/nucleon; fluence 10^9 cm^{-2}

No	Composition of etching solution	Temperature, °C	Etching time, hour	Thickness after etching, μm	Average pores diametr, μm
1.	25% sol. $KMnO_4$	100	4.5	5	absence of pores
2.	19% sol. $KMnO_4$	100	8	9.9	absence of pores
		100	12	6.8	absence of pores
3.	25% sol. $KMnO_4$ acidified by H_2SO_4	90	4.5		0.1
		90	8.5		0.2
4.	25%H_2O_2+75%$KMnO_4$	100	15	2-3	0.4-0.6*
		100	15	2-3	0.5
5.	50%H_2O_2+50%$KMnO_4$	100	15	5	0.33-0.35
		100	15	9	0.5
6.	75%H_2O_2+25%$KMnO_4$	100	15	9	0.2*
		100	15	9	0.3
7.	24N H_2SO_4+$K_2Cr_2O_7$	90	0.08	4	0.15
8.	5% solutionKOH	90	0.08	6.6	0.1
9.	0.1N sol. KOH in	60	15	13	absence of pores*
10.	5% sol. KOH in ethanol	70	0.16	4	absence of pores
11.	5% sol. KOH in 10% ethanol	80	0.16	8	0.08
12.	5% sol. KOH in 50|% ethanol	70	0.05	3	0.08
13.	25% p-p hydrasinhydrate	70	0.05	6	0.1

* PI films were thermotreated (at 320°C, for 2 hours).

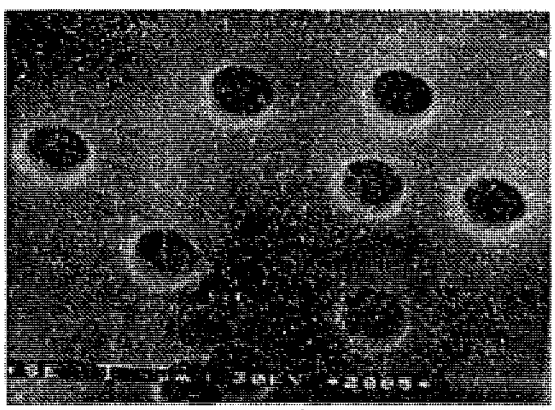

Fig. 1a. Microphotograph of surface of PI track membranes. PI film was irradiated by Kr-ions

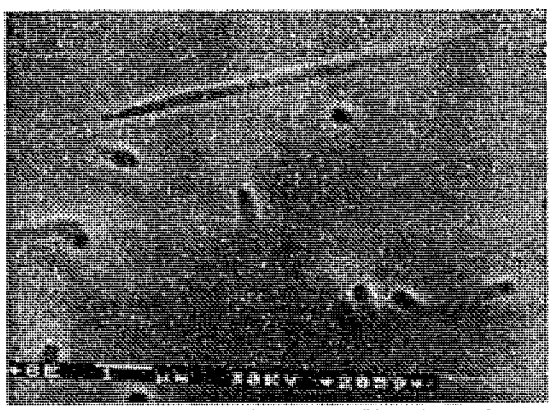

Fig.1b. Microphotograph of surface of PI track membranes. Irradiation by fragments of uranium fission

Table 2. Etching of polyimide by hydrogen peroxide at 90°C

Irradiation	Etching time, hours	Average diameter of pores, μm
Ions Ar, $5x10^7$ cm^{-2} Energy of 1 MeV/nucleon, non-thermotreated	5	0.15
	10	0.35
Ions Kr, $1x10^7$ cm^{-2} Energy of 2.6 MeV/nucleon, non-thermotreated	5	0.25
	10	0.45
Ions W, $4x10^7$ cm^{-2} Energy of 0.3 MeV/nucleon, non-thermotreated	5	0.85
Ions Ar, 5x107 cm-2 Energy of 1 MeV/nucleon, thermotreated	5	0.15
	10	0.35

corrosive, toxic, and need a long washing to remove products of etching. Besides wastes of the process are ecologically dangerous.

We consider the PI treatment by 30% solution of hydrogen peroxide is more perspective etching process [2]. PI treatment with the suggested etchant goes quickly and does not need careful washing. The process of pores etching in this way is charactized by high selectivity. The results of investigation of PI treatment in H_2O_2 are tabulated in Table 2. (The etching results of inital and heat treated PI films of 10 and 20μm in thickness, irradiated by Ar, Kr and W ions).

The tracks etching rate in PI increases with the loss of specific energy of ions mount. So, for Ar, Kr and W average value of radial rate of etching (in 30% H_2O_2 solution at 90°C) is egual to 15, 23 and 60 nm/h, respectively. For these pores, which diameters are below 0.4 μm, the radial etching rate values practically do not depend on the thermal treatment of a film, while the etching rates of non-irradiated films amount in the same conditions - for initial - to 60 nm/h, for thermotreated - to 30 nm/h. This discrepancy shows that for small diameters of pores the radial etching rate depends essentially on the tracks structure.

Figure 1 shows the SEM pictures of characteristic surfaces of PI films which were etched in 30% solution of H_2O_2 at 90°C during 10 hours. In comparison to surfaces of TM etched in others reagents, the surfaces of these membranes are smooth, pores outlines are sharply identified. The angles of ions directions are well seen.

Figure 2 illustrates replicas of TM surfaces of PI and PETP (irradiation by Ar-ions). Surfaces of TM pores of PI are significantly smoother than surfaces of TM pores of PETP, which have many defects.

4. CONCLUSION

Different ways of etching of TM on PI base were studied. It was established that the etchants given in literature are not enough suitable for pore structure formation in this polymer. A new etchant suggested in this work (hydrogen peroxide solution of 30% concentration) possesses high selectvity and proper etching rate comparable with the other ones. After hydrogen peroxide treatment filtres do

not need long washing for etching products removal. The etchant is accessible and is less toxic in comparison with other etchants. It is possible to use this etchant in the technological process of PI track membranes manufacturing.

Using above results, filters for ultra- (diameters of pores below 0.05 μm) and microfiltration (diameters of pores 0.05-2.0 μm) are being realized.

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