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Optimization of PET Ion-Track Membranes Parameters

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Abstract: Nowadays polymer ion-track membranes are used for a wide range of practical applications, which include various levels of filtration (micro-, ultra-, nanofiltration and osmosis), the creation of flexible electronic circuits and sensors based on polymer substrate, and using as templates for shape-controlled nanostructures synthesis. New applications demand clear understanding of the processes that occur during track membranes formation. For high-precision control of the end-product parameters, it is necessary to establish the correlation between etching conditions and track membranes characteristics (pores dimensions, porosity and membranes thicknesses). For this purpose, in the paper it is considered the technique of membranes formation with 10 nm – 10 μm cylindrical pores and correlation between their parameters and processing modes is studied.

Keywords: ion-track membranes, polyethyleneterephthalate (PET), etching.

1. Introduction

Track membranes (TMs) on the basis of polymers are widely used as nanoporous material with a predetermined size of pores. Depending on the pores parameters TMs could be used for micro-, ultra-, nanofiltration, forward and reverse osmosis, membrane evaporation, dialysis, diffusion, gas separation and template synthesis of nanostructures (NSs) [1–8]. Due to the small thickness, precisely defined structure, simplicity of regeneration and relatively low cost, TMs have advantages over other types of membranes [5]. TMs are obtained in three steps technological process such as thin polymer films irradiation by swift heavy ions, UV-sensibilization and chemical etching.

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Managing modes of processing TMs with pores diameters in the range of 10 mn – 10 μm with fluence 10^4 to 10^{10} cm^{-2} could be obtained [9,10].

At the present time, TMs are well known commercial product, but new applications demand new properties of TMs: dimension, shape, hydrophility and ect. One of the most popular polymers is polyethyleneterephthalate (PET). Pores geometry of PET TMs could be controlled by varying the technological modes [11]. It allows obtaining pores with different shapes (cylindrical, conical and "hourglass") and small pores sizes deviation from the average values. Also PET TMs could be easy functionalized by polymers, metals and inorganic materials for practical applications. In our paper, the formation features of PET TMs with different pore sizes and density are considered, and the effect of the formation modes on TMs characteristics is analyzed.

2. Methods

PET films with thickness of 12 and 23 μm of the Hostaphan® type manufactured by Mitsubishi Polyester Film (Germany) were irradiated on the DC-60 cyclotron with Kr ions with energy of 1.75 MeV/nucleon and fluence in the range of from 10^4 to 10^9 cm^{-2}. All samples before etching were sensibilized by UV-lamp (UV-C lamp with a wavelength of 253.7 nm) for 30 minutes on each side. Chemical etching was carried out in 2.2 M NaOH solution [12]. After etching, TMs were washed in neutralizing solution (1.0% acetic acid and deionized water) and distilled water. The surface and cross-sections of TMs were studied by using of scanning electron microscope JEOL-7500F (SEM). The cross-section was obtained by shearing films previously frozen in liquid nitrogen. At least 50 pores were measured on each sample for a set of statistics.

3. Results and discussions

Well-known [5,9,10] that TMs characteristics are strongly dependent on polymers type, parameters of irradiation by swift heavy ions, sensibilization and etching modes. Schematic illustration of this factors influence on the characteristics of TMs is presented on Fig. 1.

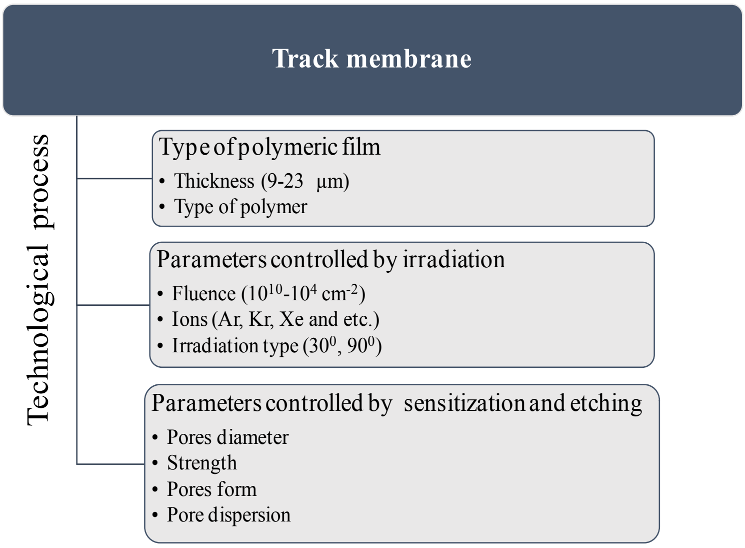

Fig. 1. Factors affecting on the characteristics of TMs.

Dimensions and shape of pores are determined by latent track parameters and composition of etching solution as well as its concentration and temperature [13]. On the base of results presented in [6] the transformation of the latent track into pores occurs in the main two stages. First the etching of latent track region takes place. Polymer irradiation leads to the break of chemical molecular bonds and modification of substance in the latent track. This fact can explain the increasing of the dissolution rate of the region along the track. Thus, the ratio $V_t > V_b$ characterizes the process, i.e. the etching rate of the substance in the track (V_t) will always be higher than the etching rate of polymer outside the irradiated region (V_b). For PET the latent track region is about 5-10 nm and could be etched less than in 3 seconds. At the second stage the etching of bulk material occurs with the ratio $V_t \sim V_b$. On this stage pores are etched with less velocity, which is equivalent to the etching velocity of membrane surfaces. This important fact should be considerate as a reason of TMs thinning till its completed destroying.

Control of TMs characteristics (pores dimensions and shape, porosity, TMs thicknesses) is possible by varying of both irradiation parameters and etching modes. For speed-up irradiated material etching process it is useful to apply the UV sensibilization, which leads to photooxidation of the polymer in latent track. As a result, the amount of carboxyl groups increases, which, considerating of their acidic properties, contributes to the acceleration of etching by alkalis (NaOH, KOH). Selectivity of etching is determined by this factor. During the chemical etching process the damaged zone of latent track is removed and transformed into hollow channel. The typical SEM image of surface and cross-section of TMs with diameter of 110 nm and pore density of 10^9 cm^{-2} are presented on Figure 2.

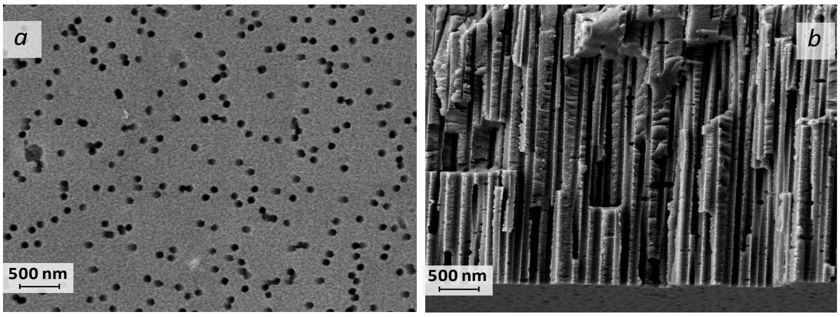

Fig. 2. (a) Example of SEM images of the surface and (b) cross-section of the PET template.

Pores are randomly distributed, which could be explained by the statistical nature of the distribution of ions in the irradiation beam. The appearance of pore overlapping zones is obvious (Fig. 2*a*), but isn't critical. Manage the number of the overlapping zones is possible by varying of pores dimensions and irradiation fluence. In this concern, it is important to correctly choose pores surface density. The choice of required irradiation fluence makes it possible to form track membranes with optimal characteristics for practical applications. In this regard, during formation of pores with required diameters, it is necessary to select appropriate irradiation fluence. Some peculiarities of irradiation fluence (Φ) choice for the formation of membranes with a pore density up to the percolation threshold are given in [14]. Interrelation of percolation threshold and required diameter (*D*) can be calculated with the equation:

$$D = 2\sqrt{\frac{\eta_c}{\pi\Phi}} \tag{1}$$

The percolation threshold η_c is the ratio of all pores total area to the area of the occupied surface. The equivalent critical area was determined with high accuracy and has the value $\eta_c = 1.128$.

In this work, we consider the range of fluence from 10^4 to 10^9 cm^{-2}. It should be mentioned, that in practice overlapping zones appear, when the pore diameter/fluence ratio significantly less than theoretical percolation threshold. Porosity (*П*) is one of the main characteristic of membranes could be presented as:

$$П = \frac{\Phi * S_{pore}}{S_{sumple} * 10^{-4}} * 100\% \tag{2}$$

On the basis of our experience the optimal porosity at a given diameter was found: the balance between the strength of the membrane and its efficiency was observed in the range of 5-15%. The theoretical and experimental dependencies of overlapping zones formation on irradiation fluence, as well as limit of effective porosity are shown on Fig. 3.

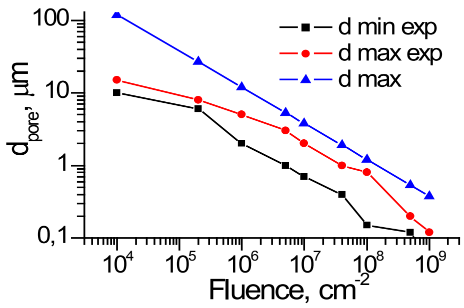

Fig. 3. Comparison of the percolation threshold curve, the experimentally obtained maximum ratio of fluence and diameter at which pores overlapping occurs and minimum ratio with minimum track membranes effectiveness.

This graph could be used to determine the irradiation fluence for production of TMs with required pores diameters. Diameters are controlled by etching time and can be chosen from the dependence shown on figure 4*a*. It should be mentioned, that deviation from average diameters value is high at the low etching times. At times more over 100 seconds it almost does not depend on time and less than 5%. This fact shows the high quality of TMs. Dependence of pore diameters (*d*) as well as deviation from average diameters value (*Delta*) on etching time are shown in figure 4.

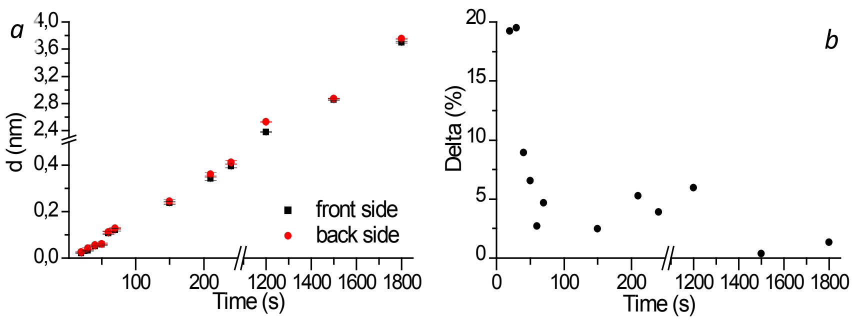

Fig. 4. (a) Dependence of the pore diameter and (b) deviation from average diameters value on the etching time.

In literature sources the TMs thicknesses changes are almost not taken into account, because it can be neglected at short etching time. During formation of pores with large diameter (up to 10 µm), the films thickness is important, and this parameter must be controlled. Investigation of the dependence of membrane parameters, such as thicknesses (*h*) and pores diameters (*d*), on the etching conditions (temperature and time) are represented in figure 5.

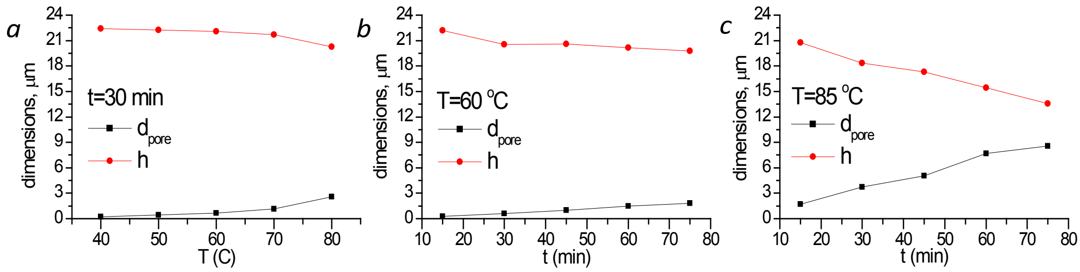

Fig. 5. Dependences of pores diameters and thicknesses of TMs: (a) on etching temperature at etching time 30 min; (b) dependence of pores diameters on etching time at temperatures 60 °C and (c) 85 °C.

The etching rate strongly depends on temperature (Fig. 5*a*) and increases dramatically at temperature range about 70-80 °C. It is due to factors such as PET transition into plastic state (glass transition temperature of 70-80 °C) and the increasing of convective flows intensity in solution. The increasing of temperature leads to significant rising of the process rate (Fig. 5*b,c*). At pores diameters more than 1 µm the membrane thinning due to surface etching is evidence. The thinning process occurs at the almost same rate as pore diameter rising, that is corresponding to the ratio $V_t \sim V_b$. Our study makes it possible to determine the minimum initial PET film thickness for production of TMs with micro-sized pores.

4. Conclusions

PET films with thickness of 12 and 23 µm irradiated with swift heavy ions at fluence in the range of from 10^4 to 10^9 cm^{-2} were studied to define the main technological aspects of resulting ion-track membranes formation. Cylindrical pores with diameters 10 nm – 10 µm were obtained. Influence of irradiation fluence and pore diameter on the optimum porosity without overlapping zones was discussed. The effect of etching time and temperature dependence of pores parameters was considered. In addition, the experimental results of ion-track membranes thicknesses after the etching process were analyzed.

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