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MODIFICATION OF TRACK MEMBRANES STRUCTURE BY GAS DISCHARGE ETCHING METHOD

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Introduction

The track membranes (TM) produced by irradiation of the polymeric films by high-energy ions beam and subsequent physicochemical treatment [1, 2] stand sharply against the filtering materials of others types due to their advanced features. The main of them is a pore size homogeneity (the pores are cylindrical channels running through the membrane). This feature provides the basic advantage of the TM, their high separation selectivity. The track membranes have gone disadvantages. For instance, their relatively low porosity (down to 10%) does not provide the needed high-performance of the processes in a number of cases. Increase of the TM porosity at the expense of growing up the pore density leads to decreasing selectivity because of a probability of putting the pores. Thus, the development of methods for producing the top-quality TM is of great practical interest.

There exist different ways for solving this problem. One of them is to change the pore geometry in the process of production, i.e. to create asymmetric TM. Under special etching conditions (etchant concentration is different at various film's sites), the pores can be produced in form of frustum of a cone [3]. Giving a conical shape to the membrane's pores leads to improving the performance of the filtration process at the expense of growth of the volume porosity. However, the production of such membranes is complicated enough and meets some technological difficulties.

By using some specialized irradiation procedures, one can obtain the TM with a thin filtering layer [4]. In doing so, the formation of the filtering layer occurs together with the creation of well-shaped deepenings. In this case the efficiency of TM increases at the expense of decreasing the filtering layer's thickness.

Another trend is more promising, to our opinion. It is a modification of a TM structure. It is known that if treating the polymers, for example polyethyleneterephthalate (PET), in plasma of non-polymerized gases the surface is etched [5, 6] together with the lessening of the mass and the emitting of gaseous products. As shown in Ref. [7], the treatment of PET TM in a smouldering discharge can be utilized as a non-reagent method of etching the pores. The authors watched out that the etching was uniform (steady) along the whole length, the cylindrical form of the pores remaining the same. Increase of the pore diameter leads to growing up the efficiency and at the same time to decreasing the separation selectivity.

The objective of this paper is to modify a TM porous structures by a gas-discharge etch method without loosing the selectivity properties of the membranes. The basic task is the choice of the etch mode. This work is devoted to determination of plasma discharge parameters leading to the formation of the track membranes possessing an optimal structure.

Experimental

PET track membranes with the thickness of 10 μm and the pore size of 0.2 μm (pore density is $2 \cdot 10^8$ cm^{-2}) produced by irradiation of polyethyleneterephthalate films with accelerated krypton ions with the energy 3 MeV/nucleon were the objects of the investigation. The irradiation was performed on the cyclotron U-400 in the Flerov Laboratory of Nuclear Reactions JINR. The measurement of the IR-spectra of the membrane samples [8] has shown 40% crystallinity of the polymer.

The plasma treatment was performed with a plasma chemical facility, which provided the RF-magnetron discharge at a frequency shift of 13.56 MHz. The membrane samples of the size of 10×10 cm were placed on a flat holder which served as an electrode. The plasma affected the membrane on one side. The air was used as plasma-forming gas. Discharge parameters (air pressure, discharge power) and treatment time were varied. The treatment procedure and the scheme of the plasmochemical setup are detailed in [9].

Different parameters of the membranes obtained by the discharge etch method were tested with the help of some mutually complementary methods. The thickness of the membrane were registered with the help of the optical caliper IKV-3. The gas flow rate (flow air passing through the membrane) were measured at the pressure overfall 0.1 bar. The effective pore size was calculated from the flow rate by an appropriate computer program [10]. The pore size distribution and the mean pore diameter (MFP) were measured with the Coulter porometer (Coulter Electronics Ltd). The surface and pore structure of PET TM were tested with a scanning electron microscope JSM-840 (JEOL). The burst strength were estimated as a pressure which damages the sample placed in the holder with a round hole of 1 cm^2 size. The water flow rate was measured as mentioned above and by using distilled water, preliminary purified by filtering through TM with the pore size of 0.1 μm.

The results of the measurements were processed with the help of mathematical statistic methods, the fiducial interval corresponds to the reliability value 0.95 [11].

Results and discussions

The PET TM samples were treated in the plasma RF-discharge at different discharge power and plasma-forming gas (air) pressure during 10 min. The effect of the treatment in plasma and the change of the basic properties of the membranes were studied (namely, thickness, pore diameter, burst strength). The duration of the treatment was selected in order to obtain measurable changes of the TM properties. The results are tabulated. Fig. 1 and 2 illustrate the general data.

One can observe the decrease of the thickness and the mechanical strength as well as the increase of the effective pore diameter.

The decrease of the thickness during the treatment in air plasma shows that the TM surface layer is etched. As one can see, the etching rate depends on the discharge parameters (Fig. 1, curves 1 and 2). Besides, the plasma also prompts morphological changes of the surface relief. Numerous craters appear on the initially smooth surface. It becomes rough. If varying the treatment conditions and duration, the sizes of the crates change. This phenomenon is probably caused by different etch rates for crystalline and amorphous regions [12]. No significant changes in the membrane thickness are observed at low discharge parameters (Fig. 1, curve 2). Negligible mass loss of the samples and change of the membranes' surface relief indicate the etching in amorphous regions, the rate of the process being extremely low.

TABLE. Parameters of track membranes subjected to the plasma discharge treatment.

No	Regime of the treatment		Membranes parameters				
	Air pressure, Torr	Power, W	Effective pore diameter, μm	MFP diameter (Coulter), μm	Porosity, %	Air flow rate at ΔP=0.1 bar, ml/min·cm²	Initial water flow rate at ΔP=0.7 bar, ml/min·cm²
1	–	–	0.220	0.195	7.6	200	4.75
2	$8 \cdot 10^{-4}$	70	0.225	0.196	7.9	220	5.45
3	10^{-3}	70	0.23	0.199	8.3	230	5.75
4	10^{-3}	100	0.235	0.204	8.7	260	6.45
5	$2 \cdot 10^{-3}$	70	0.24	0.205	9.0	275	6.95
6	$8 \cdot 10^{-2}$	70	0.255	0.221	10.2	360	9.55
7	$8 \cdot 10^{-2}$	100	0.265	0.239	11.0	445	11.40
8	$8 \cdot 10^{-2}$	150	0.275	0.245	11.9	470	13.30
9	$8 \cdot 10^{-2}$	200	0.295	0.262	13.7	650	17.05

Remark: samples of membranes were treated in the plasma during 10 min.

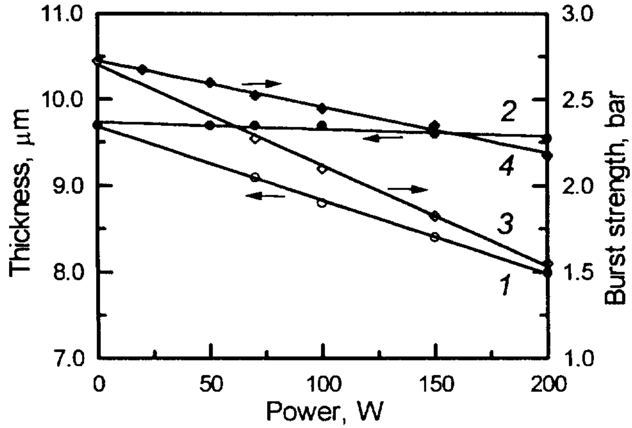

FIG. 1. Dependence of thickness and damaging pressure of PET TM with the pore diameter of 0.2 μm upon the value of the air discharge power at $P_{air} = 8 \cdot 10^{-2}$ Torr (*1* and *3*) and $P_{air} = 10^{-3}$ Torr (*2* and *4*), duration of plasma effect is 10 min.

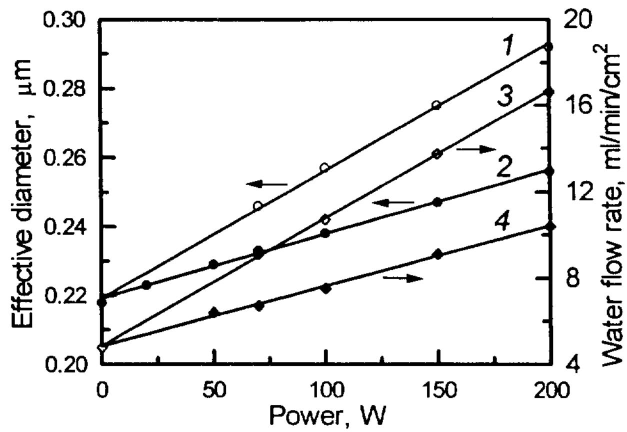

FIG. 2. Dependence of the effective pore diameter and water permeability of PET TM with the pore diameter of 0.2 μm upon the air discharge power at $P_{air} = 8 \cdot 10^{-2}$ Torr (*1* and *3*) and $P_{air} = 10^{-3}$ Torr (*2* and *4*), duration of plasma effect is 10 min.

Besides, the increase of the effective pore size proves that the pore walls are etched, too. The pore surfaces etch rate also depends on the discharge parameters (Fig. 2, curves 1 and 2). The growth of the effective pore diameter means the change of the pore size. As noted in Ref. [7], the treatment of PET TM in smouldering discharge in air does not cause a change of the shape. It is of special interest to figure out if there is a change of the track membranes' shape at high frequency discharge. In order to solve this question, the measurement of the mean pore diameter was performed on the Coulter porometer providing the information about the diameter in the most narrow cross-section of the pore channels.

It should be noted that the difference between the effective pore diameter calculated from the air flow data, and the MFP diameter measured with the Coulter porometer, allows us to suggest that the pore channels in the initial sample are not cylindrical but rather conical (of "egg-timer" shape). The reason for that is a limited etch rate ratio of krypton ions which, in turn, have less energy loss, if comparing to the xenon ions. The increase of both effective and MFP diameters in the plasma-modified membranes shows that the pore size and shape generally change – especially under "hard" plasma treatment conditions. The MFP diameters in samples No 2–5 (see the Table) remain the same, i.e. the size at the narrowest parts of the pore channels is not affected by the plasma. Thus, the etching of the pore walls in these samples occurs only to a certain depth, so part of the pore channel remains of original size and shape. Another part accessible for the plasma, is of a conical shape with a basis on the membrane side subjected to the discharge. Further increase of the discharge power and the gas pressure leads to the etching along the whole pore channel and to the changing of the MFP diameters (see samples No 7–9). In this case the marked difference between the diameters indicated the formation of the pores with trankated cones. Therefore, the treatment of the PET TM with the plasma RF-discharge in air causes the modifications of their pore shape (asymmetry appears), i.e. leads to the modification of the TM structure.

The comparison of the effective (initial sample) and MFP diameters of the membranes' pores modified in plasma, allows one to estimate approximately the etched layer's depth. So, for the membrane No 6 the MFP diameter coincides with the effective pore diameter for test sample. This means that the inner diameter of the channel has grown up, i.e. the etching occurred in the depth exceeding half a thickness of the membrane. In case of samples No 2–5 the MFP diameter is smaller than the effective diameter for the initial sample. Obviously, the etching did not reach half a depth of the membrane matrix in these samples.

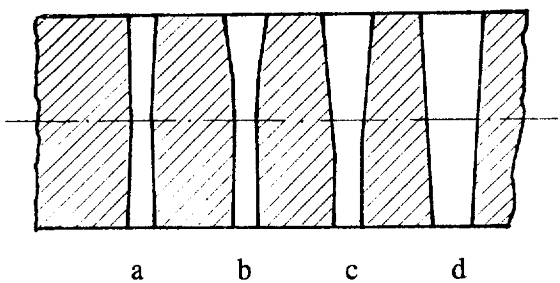

FIG. 3. Pore structure of the initial PET TM (*a*) and the membranes modified in air plasma during 10 min at $P_{air} = 2 \cdot 10^{-3}$ Torr, W = 70 W (*b*); $P_{air} = 8 \cdot 10^{-2}$ Torr, W= 70 W (*c*); $P_{air} = 8 \cdot 10^{-2}$ Torr, W= 150 W (*d*).

Fig. 3 represents schematically the structure of the initial TM (a) and the TM modified by plasma discharge in air (b–d). The treatment in plasma provides the formation of the membranes with asymmetric pore structure. The membranes in which only a part of the pore channels were etched in plasma are of special interest (membrane's b, c). The effective porosity of such membranes is higher than the porosity of the initial membrane and, as a result, the modified membranes have better water flow rate characteristics, if comparing to the initial membrane. This is illustrated by Fig. 2 (curves 3 and 4) and Fig. 4. The initial water flow rate as well as the filtrate volume after a prolonged water flow experiment is higher for the modified membranes. The layer not affected by plasma etching (selective), the structure of which remains the same, will determine the separation properties of the membranes. The separation selective properties do not change, if the initial pore diameter remains the same in this layer. The length of the conical parts of the pore channels and the length of the unaffected layer can be checked up by changing the discharge parameters. This provides a way for producing a wide variety of the track membranes with different properties.

The increase of the effective pore diameter causes the increase of porosity and decrease of their mechanical strength (Fig. 1, curves 3 and 4). The experimentally measured burst strength values for the plasma modified membranes are lower than those for the conventional PET TM with the same porosity. Such a phenomenon can be explained by the presence of a damaged superficial layer on the modified membranes (with a small molecular weight of the macromolecules) forming in the process with the results given in [7], according to which the depth of a similar layer is 10–30 nm, approximately. More significant difference in the mechanical strength of the TM treated at high discharge parameters, if comparing with the samples not treated in plasma, witnesses the formation of the deeper damaged layer (Fig. 5). The loss of their strength is essential. This can be taken into account, if choosing the optimal conditions of plasma etching.

Thus, one can see that the choice of the plasma etch condition has two aspects. First of all, the discharge parameters should provide an increase of the pore diameter in a certain layer and an increase of the flow rate. Secondly, the discharge should be enough to prevent a damage of the membrane. We have come to a compromise when the loss in mechanical strength is of 10-15%, whereas the water and air flow rate are as twice as higher. Such membranes can have a good use in separation and purification processes.

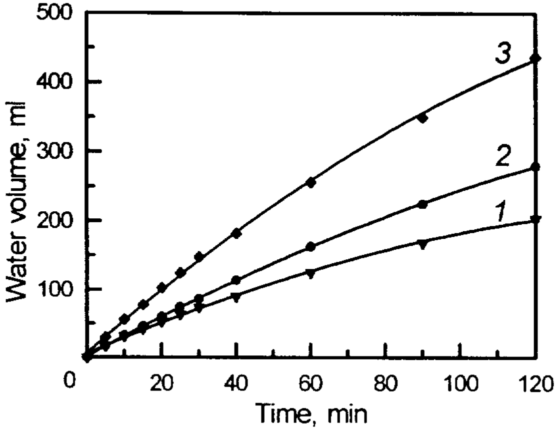

FIG. 4. Dependence of the water volume upon the time filtration of the initial PET TM with the pore diameter of 0.2 μm (*1*) and the membranes modified in air plasma during 10 min at $P_{air} = 3 \cdot 10^{-2}$ Torr, W = 70 W (*2*) and $P_{air} = 8 \cdot 10^{-2}$ Torr, W = 100 W (*3*).

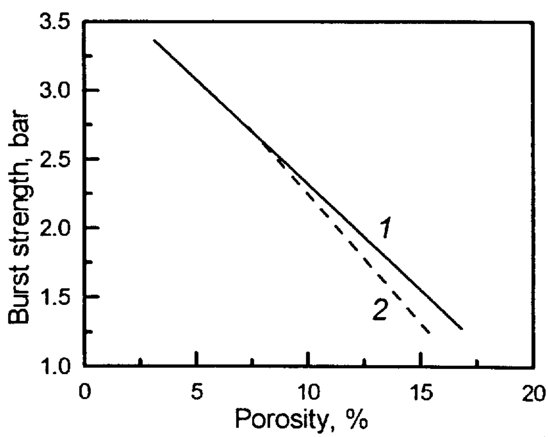

FIG. 5. Dependence of the deteriorating pressure upon porosity for PET TM not treated by plasma (*1*) and exposed to air plasma (*2*).

Conclusion

The performed investigations show that

– the gas discharge etching method makes it possible to change directly the track membrane structure;

– depending on the choice of the discharge parameters, etching can be executed either in a part of the channel or along the whole length of the pore channels; anyway, the asymmetric track membrane possessing higher porosity and flow rate are formed;

– the conditions of plasma treatment have been found which provide the manufacture of the track membranes with a higher flow rate without changing the selective properties of the membranes.

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Дмитриев С.Н., Кравец Л.И., Слепцов В.В. E18-96-292

Модификация структуры трековых мембран с помощью метода газоразрядного травления

Проведено исследование свойств полиэтилентерефталатных трековых мембран (ПЭТФ ТМ), подвергнутых воздействию плазмы ВЧ-разряда в воздухе. Изучено влияние условий обработки в плазме на основные характеристики мембран: размер и форму пор, пористость, механическую прочность. Установлено, что воздействие плазмы воздуха на ПЭТФ ТМ приводит к травлению поверхностного слоя мембран. Размер и форма пор мембран при этом изменяются.

Показано, что с помощью метода газоразрядного травления можно направленно изменять структуру трековых мембран — в зависимости от выбора параметров разряда травление можно производить либо в части канала, либо по всей длине каналов пор. В обоих случаях образуются мембраны с асимметричной формой пор, обладающие повышенной пористостью и удельной производительностью. Использование мембран подобного типа позволяет значительно повысить эффективность процессов фильтрации.

Работа выполнена в Лаборатории ядерных реакций им. Г.Н.Флерова ОИЯИ.

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Dmitriev S.N., Kravets L.I., Sleptsov V.V. E18-96-292

Modification of Track Membranes Structure by Gas Discharge Etching Method

An investigation of the properties of polyethyleneterephthalate track membranes (PET TM) treated with the plasma RF-discharge in air has been performed. The influence of the plasma treatment conditions on the basic properties of the membranes, namely pore size and pore shape, porosity and mechanical strength has been studied. It was arranged that the effect of air plasma on the PET TM results to etching a membrane's surface layer. The membranes' pore size and the form in this case change.

It is shown that it is possible to change the structure of track membranes directly by the gas discharge etching method. Depending on the choice of discharge parameters, it is possible to make etching either in a part of the channel or along the whole length of the pore channels. In both cases the membranes with an asymmetric pore shape are formed which possess higher porosity and flow rate. The use of the membranes of such a type allows to increase drastically the efficiency of the filtration processes.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

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