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NOVEL TYPES OF NUCLEAR TRACK MEMBRANES

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Nuclear track membranes (or nuclear (track) filters) are produced by irradiating a variety of plastic films, mainly polycarbonate (PC) and polyethylene terephthalate (PET), with heavy ions and subsequent etching with appropriate etchants [1]. Since the seventies heavy-ion accelerators are used for the production of nuclear track membranes from PET at JINR (Dubna, U.S.S.R.) [2]. Nuclear track membranes (NTM) have some significant advantages over conventional ones. However, certain characteristics of the NTM (such as chemical resistivity, permeability, etc.) need to be improved.

This review summarises the results of developing the nuclear track method to produce membranes with new structural and chemical properties.

POLYPROPYLENE MEMBRANES

The membranes are obtained from biaxially oriented polypropylene (PP) films 10 μm thick, by irradiation with accelerated heavy ions followed by chemical etching in a solution containing sulphuric acid and Cr(VI). The film "torayfan" (Toray, Japan) and the film produced in the USSR (further called as PP1 and PP2, respectively) were used. The major advantages of polypropylene compared with PET are: (1) high chemical resistance; (2) polypropylene films do not contain inorganic compounds (like TiO_2, kaolin) and, hence, the membrane matrix should be cleaner. Trace element analysis of the PP films was performed by neutron and gamma activation. It was found that PP1 contains Cu (0.01 %) and PP2 contains Ca (0.01 %), Ti (0.003 %), and Cl (0.0003 %). Probably, these are the traces of polymerization catalysts. It should be noted that there is no detectable amount of Sb in the polypropylene while the Sb contamination is always present in PET and stands in the way of element microanalysis of precipitations retained by the membrane.

According to the infrared spectroscopy data, the PP films are anisotropic and characterized by the degree of crystallinity of about 65 and 80 % (the average values for the foils PP2 and PP1, respectively). The large content of the isotactic polymer fraction and the high degree of crystallinity result in a good resistivity of the PP films in organic solvents. The long treatment (36 hr) of the foils in boiling hexane and heptane leads to the weight loss not exceeding 5 %.

Figures 1 - 4 show the electron micrographs of the PP nuclear track membranes obtained. Because of the anisotropy of the PP films the cross section of pore channel is elliptic in shape (see fig. 3). The large axis of the ellipse is always oriented normally to the direction of longitudinal stretching of the PP film. The pores consist of two cones (the shape of a "sandglass", see fig.5).

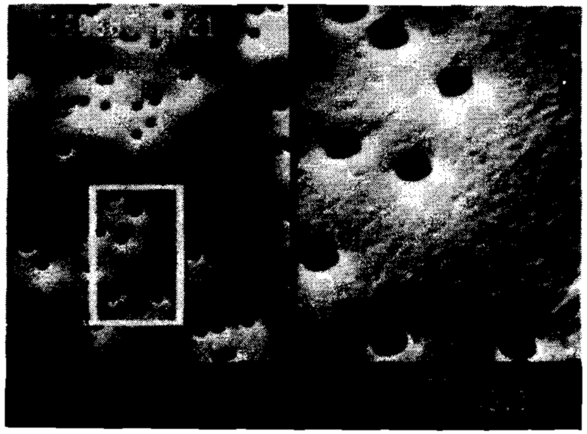


Fig. 1. SEM-photograph of the surface of a NTM made of "torayfan" irradiated with Xe ions. The etching conditions: 16 N H_2SO_4, 50 g/ℓ $K_2Cr_2O_7$, 80°C, 3hr.

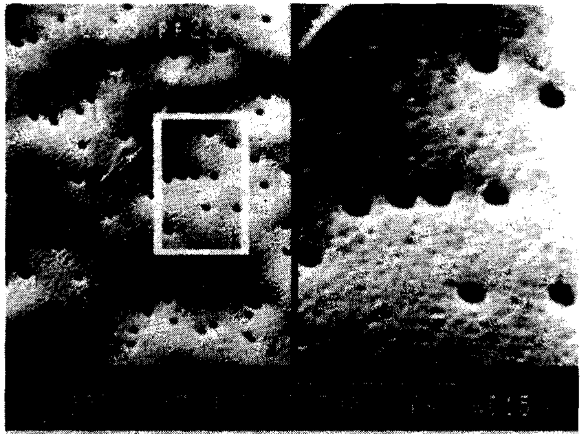


Fig. 2. SEM-photograph of the surface of a NTM made of the PP2 film.

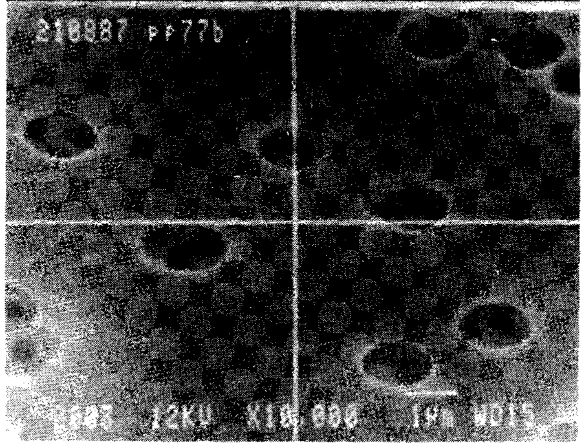


Fig. 3. SEM-photograph of the etched holes in a polypropylene NTM. The vertical line coincides with the direction of the longitudinal stretching of the film (PP2).

The conical shape of pore channels is caused by the low selectivity of the track etching in polypropylene. The cone angle depends on the linear energy transfer (LET) of the bombarding particle as it is shown in fig.5. The heavier the ion the smaller is the cone angle and the more cylindrical are the pore channels. In addition, one can control the pore shape to a certain degree by choosing the appropriate etching conditions. From the statistical analysis of the electron micrographs the standard deviation of the pore size d was found to be equal to about 0.04 μm.

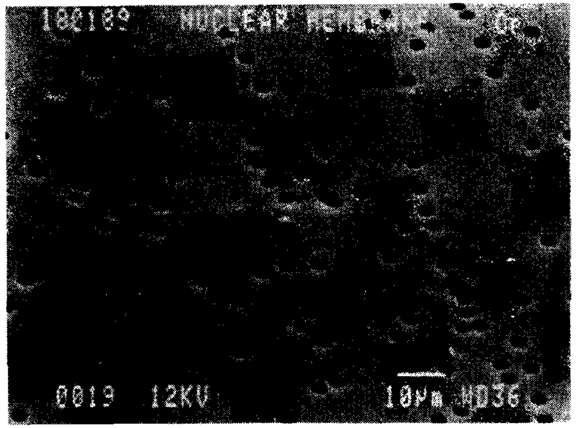


Fig. 4. SEM-photograph of the surface of a polypropylene NTM with large holes (D = 3 μm).

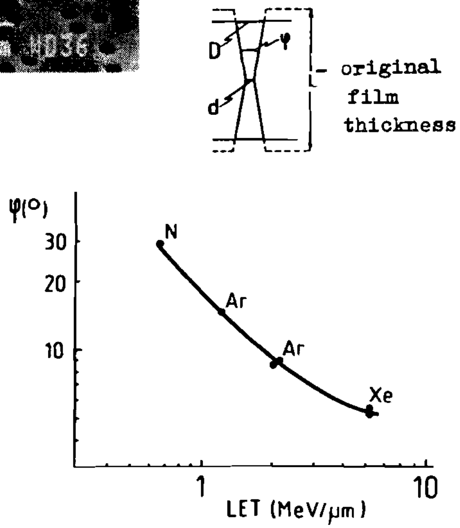


Fig. 5. Schematic diagram of the parameters used to characterize micropores in NTM of polypropylene and the LET-dependence of the cone angle φ of the pores in membranes made of the films irradiated with N, Ar and Xe ions.

Since the membrane has a regular pore structure the through-put of gaseous or liquid media through the PP NTM can be easily calculated using the known formulas for the capillaries of conical shape [3,4]. The calculated values are close to the data measured experimentally. For instance, the flow rate of gaseous nitrogen through a membrane 10 μm thick and having pores with d = 0.2 μm and a pore density of 8.10^7 cm^{-2} is equal to 2.10^4 $m^3/(m^2$ hr MPa).

The preliminary examination showed that the NTMs made of polypropylene are stable in media with high pH. The treatment in

a 20 % KOH solution at 80°C during 24 hr does not change the permeability, bubble point and mechanical strength of the membranes. The NTMs of polypropylene can be used in microfiltration processes for cleaning and analysing agressive chemical species.

ASYMMETRICAL MEMBRANES

To increase the permeability of the membrane while retaining its mechanical strength, the method of forming "honeycomb-like" structure is developed [5, see also the contributions to the present Symposium]. The PET film 20 μm thick is initially irradiated through a metallic mask with regularly distributed holes by ions with a path length in the polymer less than the thickness of the film. The film is then irradiated by ions with a path length greater than the film thickness. In addition, the ion flux of the second irradiation is one order of magnitude lower than that of the first irradiation. The subsequent etching converts the irradiated areas into cells having thin porous bottoms. For asymmetric membranes the throughput of gaseous nitrogen is at least 3 times higher than that for conventional nuclear membranes.

The properties of membranes with conical pores were also investigated. The conical pores are obtained by etching the irradiated film on one side. It is shown that the maximum permeability of a membrane of a fixed porosity is achieved for a certain shape of pores, namely, the optimum ratio of the channel radii on one and the other side of the membranes lies in the range of 1.5 to 4. One can control the pore dimensions and pore shape by choosing the appropriate irradiation and etching conditions.

NUCLEAR MEMBRANES MODIFIED BY RADIATION-INDUCED GRAFTING

Such membranes have been prepared by the radiation-induced grafting of monomer compounds (styrene, vinylpyridine, vinylpirrolidone) onto PET nuclear membranes. Three methods of grafting are used: simultaneous irradiation and grafting, preirradiation in a vacuum, and preirradiation in the air [6]. Some properties of grafted membranes have been investigated [7,8]. The relative gas permeability has a tendency to decrease with increasing degree of grafting (relative increase of membrane mass after grafting) [6].

The new direction of extraction - membrane extraction - has been developed recently. The method of extraction is characterized by using the matrix for an extragent solution in the form of membranes. One of the basic problems in the membrane extraction is the time stability of an impregnated membrane.

For investigating the problem we used nuclear membranes with different pore diameters and surface properties. The first set of membranes is the nuclear membranes made of PET and the second one is nuclear membranes modified by radiation grafting of polystyrene (PS). Both sets of nuclear membranes have cylindrical pores and a thickness of 10 - 12 μm. We used the cell which is divided by the impregnated membrane into two chambers with stirrers. All permeation experiments were carried out at room temperature. The feed solution was HNO_3 (1 mol/l) and the downstream solution was water. The membrane was impregnated by CCl_4 (ρ = 1,595 g/cm^3) or by mixture a of CCl_4/C_6H_6 = 1/5 by vol. (ρ = 1 g/cm^3) without a carrier. We measured the change of pH of the downstream solution.

The results of the modification of the nuclear membrane surface properties are presented in Fig. 6 which shows the water contact angle as a function of the relative mass of PS grafted onto a nuclear membrane with a pore diameter of 0.1 μm. The contact angle increases with an increase in the relative mass of PS by up to 8 - 10 %.

The change of pH of the downstream solution with working time of impregnated membrane is shown in Figs. 7 and 8. Nuclear membranes with different pore diameters after grafting of PS have a tendency

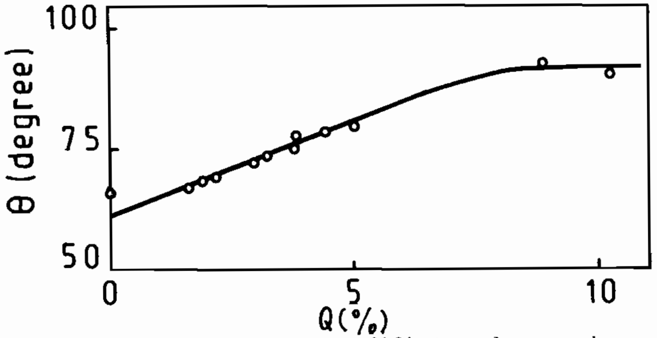
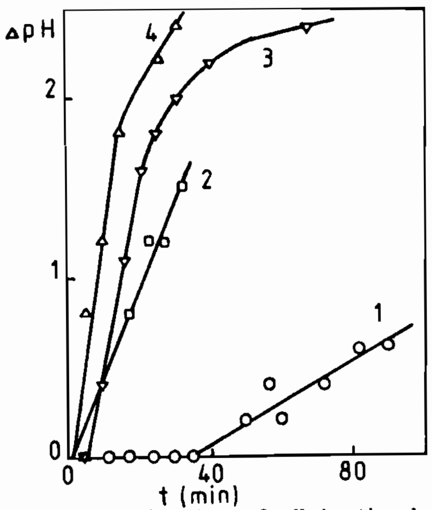


Fig. 6. Contact angle of water on modified nuclear membrane with a pore diameter of 0.1 μm as a function of the relative mass of grafted PS.

Fig. 7. Reduction of pH in the downstream solution vs. operation time in the system: 1M HNO_3 - CCl_4 - H_2O; 1 is a nuclear membrane with a pore diameter of 0.1 μm containing 6.8 % of grafted PS (abbreviated as 0.1-F-gr-PS(6.8 %); 2 is a nuclear membrane with a pore diameter of 0.1 μm (abbreviated as 0.1-F); 3 is 0.35-F-gr-PS(7.2 %); 4 is 0.35-F.



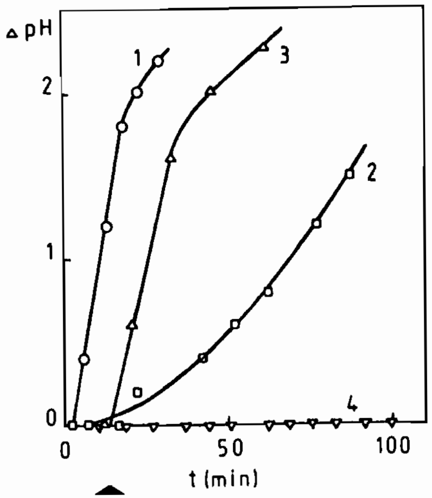


Fig. 8. Reduction of pH in the downstream solution vs. operation time in the system: 1M HNO_3 - CCl_4/C_6H_6 = 1/5 (by vol.) - H_2O; 1 is 0.35-F; 2 is 0.35-F-gr-PS(8.4 %); 3 is 0.1-F; 4 is 0.1-F-gr-PS(10.4 %).

to increase the stability of the impregnated matrix. For both types of membranes, i.e. those made of PET and containing grafted PS, the delay time increases and the flux of H^+-ions decreases with a decrease in the pore diameter. The smaller the difference between the densities of the extragent solution and water phases, the higher is the stability of the impregnated membrane. As a result of an increase in porous matrix hydrophobity one can refuse the necessity of an increase in the extragent solution viscosity because the last parameter decreases the ion permeability through an impregnated nuclear membrane [9]. Thus the grafting of PS prolongs the working time of modified nuclear membranes in the extraction process compared to ungrafted ones.

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Новые типы ядерных трековых мембран

Приведены результаты развития метода ядерных треков для производства мембран с новыми структурными и химическими свойствами. Приводятся данные о структуре пор, о распределении их размера и о проницаемости полипропиленовых (ПП) мембран, а также о содержании примесей в материале мембраны. Поры в ПП мембране состоят из двух конусов (форма "песочных часов").С целью увеличения проницаемости мембраны при сохранении ее механической прочности разработана сотоподобная структура. Изучены также свойства мембран с коническими порами. Методом радиационной прививочной полимеризации мономерных соединений на ПЭТФ ядерных мембранах были получены модифицированные мембраны. Показано, что удержание раствора экстрагента в объеме пор повышается по мере роста содержания привитого полистирола в мембране.

Работа выполнена в Лаборатории ядерных реакций ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1989

Flerov G.N. et al. E18-89-723
Novel Types of Nuclear Track Membranes

The results of the developing nuclear track method to produce membranes with new structural and chemical properties are summarized. The data on pore structure, the straggling of pore size, the permeability of polypropylene (PP) membranes and on the content of impurities in membrane matrix are presented. The pores in PP membranes consist of two cones (the shape of "sandglass"). To increase the permeability of the membrane while retaining its mechanical strength, the method of forming "honeycomb-like" structure is developed. The properties of the membranes with conical pores were also investigated. Modified membranes have been prepared by radiation-induced grafting of monomer compounds onto PET nuclear membranes. It is shown that extragent solution retention within the pore volume increases with polystyrene content in the membrane.

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

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