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MODIFICATION OF POLYMER FILMS BY THE NUCLEAR TRACK METHOD

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The nuclear track method is a contemporary nuclear-physical method for modifying substance structure. An accelerated heavy ion beam is a precise instrument allowing to set new properties of materials and extending the fields of their applications in solving various technical and industrial problems. One of the traditional applications of the nuclear track method is the production of membranes based on thin polymer films irradiated with nuclear fission fragments [1]. The possibilities of the method are substantially extended when the accelerated heavy ion beams from cyclotrons are employed [2]. A high beam intensity, controlled particle energy and particle mass as well as the angle of incidence onto the polymer surface assure additional advantages when forming microporous structures with the reguired properties.

In the Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research [Dubna] the nuclear membranes are made on the base of polyethylene terephthalate [lavsan] films 5 - 10 μm thick. The lavsan film has a good chemical and thermal stability as well as high mechanical strength. Unfortunately the nuclear membranes have rather low porosity (less than 10%) due to the necessity of providing mechanical strength. This feature of the nuclear membranes and a high ratio between the length and diameter of pores (100 - 500) reduce the membrane permeability. It does not always satisfy the specific requirement. One can solve this problem by reducing the effective thickness of membrane and by the optimization of the pore geometry.

So it was proposed to produce biporous structure in a monolithic polymer film of which the thin selective layer should be the bottom of the holes in the matrix having "honeycomb-like"shape

[3] .The polymer film is irradiated by heavy ions from a cyclotron through a metallic mask with through holes (fig. 1). The mask moves together with the film during irradiation. The formation of an ion beam with two values of energies is provided by a degrader foil with a slit. The ions, after passing through the degrader, have a

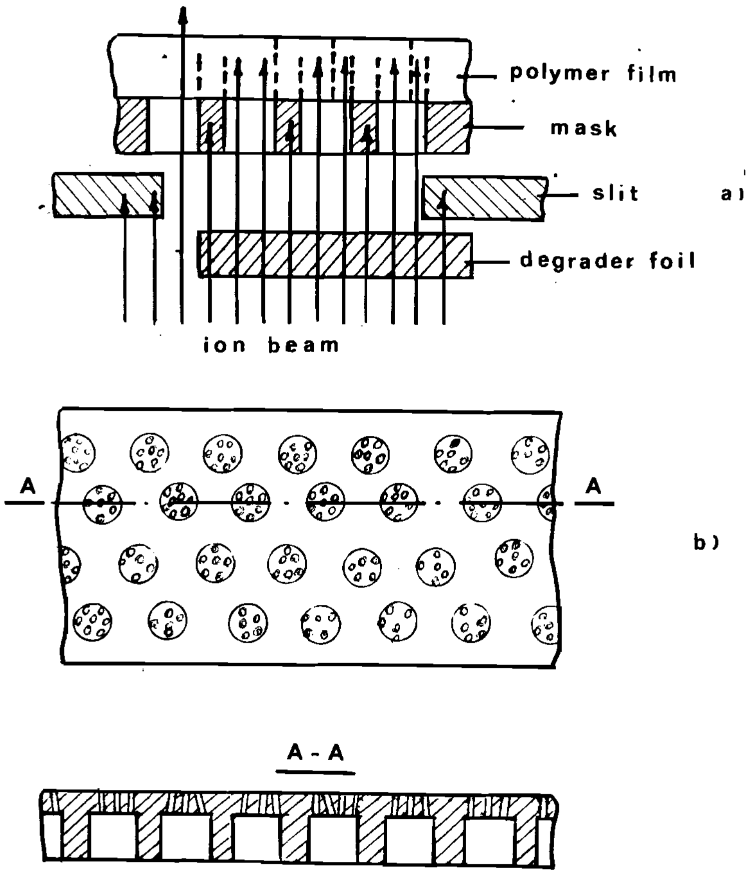

Fig.1. Schematic diagram of producing nuclear membranes with biporous structure:

a) schematic diagram of the irradiation of polymer film with accelerated heavy ions,

b) schematic representation and cross-section of a nuclear membrane with biporous structure.

shorter range than the film thickness whereas the ions passing through the slit retain their initial energy and pierce the polymer film. The ion beam intensity provides fully etched holes under the apertures available in the mask (fig.1). The depth of the holes is equal to the ion range. The width of the degrader slit regulates the pore density in the selective layer (in the bottom of the "honeycomb"). By the following chemical treatment of the irradiated film the biporous structure of the membrane is formed (fig.2). The areas of the film protected by the mask against irradiation create a strong net that adds the mechanical strength to the membrane and plays the role of a support simultaneuosly. The thickness of the selective layer of the membrane is 1/3 - 1/10 of the general membrane thickness and depends on the conditions of irradiation. Experimental research shows that the permeability of the nuclear membranes is 2 - 5 times higher compared with the conventional nuclear membranes having the same pore diameter and porosity.

The accelerated heavy ion beams with atomic number $z > 40$ produce local damages in the lavsan film which allow one to manufacture nuclear membranes with cylindrical pores. It is known that membranes with conical or funnel-shaped pores possess a lower resistance to the fluid being filtered due to an increase in the effective pore diameter and to the optimization of the hydrodynamics of the filtration process [4,5]. We calculated and measured the increase in the throughput of the membranes for certain ratios between the pore radii on the two sides of the membrane. If the membrane has conical pores instead of cylindrical ones, the bulk porosity of the membrane increases, thus leading to a decrease in the mechanical strength of the membrane. Therefore, to keep the mechanical strength of a membrane with conical pores the increasing bulk porosity must be taken into account by using the following relation:

$$V_{co}/V_{cy} = (r_2^3 - r_1^3)/\,3r_1^2\,(r_2 - r_1) = \frac{1}{3}\sum_{i=0}^{2} k^i, \qquad (1)$$

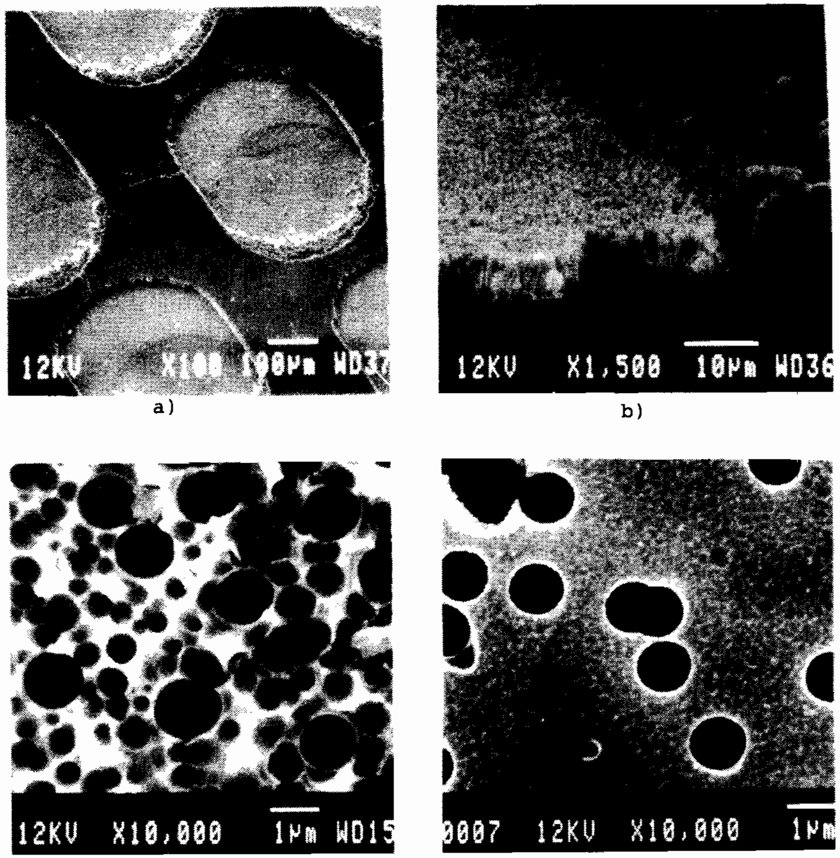

Fig.2. SEM-photographs of the nuclear membrane with biporous structure:

a) the general view of the surface of a nuclear membrane,

b) the cross-section of the nuclear membrane on the "honeycomb" side,

c) the surface of the selective layer of the inside of the "honeycomb",

d) the surface of the selective layer of the outside of the "honeycomb".

where V_{co} is the volume of the conical pore,

V_{cy} is the volume of the cylindrical pore,

r_1 is the radius of the cylindrical pore or the smaller radius of the conical pore,

r_2 is the larger radius of the conical pore,

$k = r_1 / r_2$.

In paper [6] it is shown that permeability through a membrane with conical pores (provided that the cone angle is small if $r_2 - r_1 \ll 1$) can be described by the following relation:

$$Q = (3\pi r_1^4 / 8\mu l) [r_1/r_2 + (r_1/r_2)^2 + (r_1/r_2)^3]^{-1}, \quad (2)$$

where μ is dynamic viscosity,

l is the pore length.

(It is obvious that for $r_1 = r_2$ this formula transforms to the Poiseuille law). Using eq.(2) it is easy to show that the ratio of liquid flow rates for the membranes with cylindrical pores of radius r_1 and for those with conical pores of the smaller radius r_1 can be expressed as

$$Q_{co}/Q_{cy} = 3/\sum_{i=1}^{3} (r_1/r_2)^i \quad (3)$$

The calculations have shown that a 30-50% increase in the permeability of membranes with conical pores is observed in case $r_2 / r_1 = 1.5 - 4.0$ if the membranes have the fixed porosity. If the membranes have the same pore density, the permeability increases 2 - 9 times.

The composite nuclear membrane consisting of a thin selective layer produced by the nuclear track method and of a high porosity support allow one to solve the problem of increasing the permeability of the nuclear membranes. Industrial lavsan film with a thickness of about 1,0 μm presents interest for use as a base for the nuclear membrane with a high permeability. But its use without support creates additional difficulties in work. The possible combination of films with thicker support is a topical problem. The support and the selective layer can be produced using

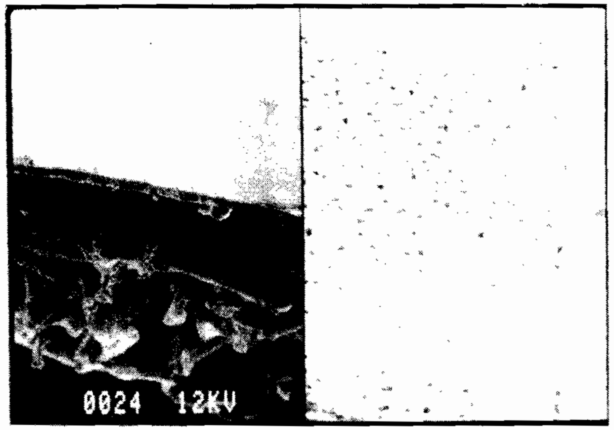

Fig.3. SEM-photograph of the cross-section of a composite membrane (the support is uncloth polypropylene).

the nuclear-physical method and connected with glue or by a thermal method (fig.3). An uncloth lavsan or polypropylene with large-porosity structure can be used as a support. To produce the composite membrane one must calculate correctly the parameters of porous structure. It should not limit the permeability of the selective layer and at the same time, should provide the minimum loss of the useful area of the membrane. Tests have shown that the permeability of the samples of the composite nuclear membrane is 5 and more times higher than that of the conventional nuclear membranes.

Thus, the beam of accelerated heavy ions allows one to modify polymer films locally or on a global scale, depending on the track density, by creating porous structure with the accurately defined parameters.

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