

USE OF TRACK MEMBRANES AS TEMPLATES FOR SYNTHESIS OF NANOMATERIALS BASED ON POLYMERIC COMPOSITIONS

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Abstract

A new approach has been developed by us for preparing of nanomaterials on the basis of polymeric compositions. This approach entails filling by polymeric compositions within the pores of the poly(ethylene terephthalate) track membranes (PET TM) with the help of an impregnation method. Depending on the variation of parameters of the template synthesis process allows obtaining of a big assortment of nanostructural materials (nanotubules and nanowires as well as nanomembranes) with a wide spectrum of characteristics. This type nanomaterials can be used for creation of electronic nanodevices. They can be also used for production of chemical sensors.

1. Introduction

Interest to the problem of producing nanostructural materials with use of porous materials as a template has grown essentially recently [1, 2]. The essence of the method consists in filling the pores of the template with a desired material using various physicochemical methods. These investigations are of major practical and scientific importance, as they allow obtaining of a wide spectrum of nanomaterials with unique properties which find their application in many areas of modern science and technologies – nanoelectronics, photonics, chemotronics, biotechnologies, etc. Two types of nanoporous membranes, the aluminum membranes and polymeric track membranes are often used as templates. Aluminum membranes are obtained via anodization of aluminum foil in acid media and track membranes are produced by irradiation of polymeric films with a beam of high energy heavy ions, followed by a subsequent chemical etching of latent tracks of these particles. Both type membranes have cylindrical pores with a narrow distribution over the diameter that gives an opportunity for synthesis of nanowires, nanotubules as well as nanomembranes. In the case when the pore area is completely filled by a desired material, nanowires are produced. If the used material is deposited only on the pore walls, nanotubules are formed. In order to fill the pores of template, various materials can be used: metals [3-5], carbon [6, 7], semiconductors [8, 9], polymers [10-12]. The nanostructures can remain inside the pores of the template or they can be freed from the membrane. In order to produce nanowires and nanotubules as an ensemble of free particles, one dissolves porous matrix by a suitable solvent and then they can be collected on a substrate after filtration. If the nanowires and nanotubules are attached to the substrate surface and the membrane is removed, an ensemble of nanostructures like the bristles of a brush can be obtained. Synthesized nanotubules can be left inside the pores of template, the

composite nanomembranes are produced in this case, their properties can vary under the influence of external factors, such as solution pH, electric current, ionic force of the solution [13-15]. For obtaining of the nanostructural materials with porous membranes as templates, various methods are applied: electrolytic deposition, chemical or electrochemical polymerization of organic monomers, deposition of polymers by plasma, etc.

In the present paper a new approach for obtaining of nanostructural materials (nanowires and nanotubules as well as nanomembranes) on the basis of polymeric compositions has been developed. As a template for synthesis of nanomaterials, the track membranes on the basis of poly(ethylene terephthalate) developed and produced at the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research were used. Study of the mechanism of formation of these materials as well as the research of their structure and properties were performed. An impregnation method was used for obtaining of the polymeric nanomaterials.

2. Experimental

As a template for synthesis of nanostructural materials, the PET track membranes with the thickness of 10.8 μm and an effective pore diameter of 1.0 μm (pore density was $1.5 \times 10^7 \text{ cm}^{-2}$) as well as with the thickness of 19.8 μm and an effective pore diameter of 3.0 μm (pore density was $1.0 \times 10^6 \text{ cm}^{-2}$) were used. In order to produce the membranes, poly(ethylene terephthalate) films were irradiated by krypton positive ions, accelerated at the energy $\sim 3 \text{ MeV/nucleon}$ in the cyclotron, and then subjected to chemical etching using the technique [16]. As a precursor for obtaining of nanomaterials the polymeric compositions were used. These polymeric compositions were obtained by radical copolymerization of styrene and butylmethacrylate (in ratio of 50:50 mol %) and styrene, butylmethacrylate and 4-aminostyrene (in ratio of 20:50:30 mol %) as described in [17]. Toluene was used as a solvent for dissolving of polymeric compositions. The concentration of polymeric compositions in the solvent was varied from 0.5 to 20 %. The membranes were covered with a solution of polymeric compositions with the help of an impregnation device of "meniscus" type (see Fig. 1).

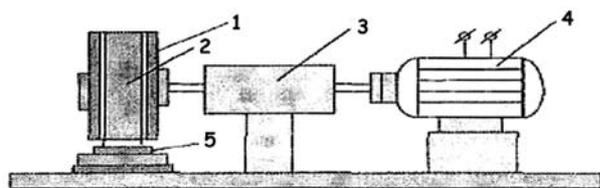


Fig. 1. Scheme of the impregnation device: 1 – drum; 2 – membrane; 3 – reducer; 4 – reversible engine; 5 – bath with solution of polymeric composition.

The essence of the technique for the polymeric composition drawing on the surface of membranes consisted in the following. The membrane, as a flexible basis, is fixed on a rotating drum of a diameter of 50 cm. The drum begins its movement with the help of reversible engine. The bath with a solution of the polymeric composition is placed on a horizontal little table under the drum. As far as the bath approaches the drum, the solution is uniformly distributed over the membrane surface and then the solvent is subjected to evaporation at room temperature. Full drying of the samples was carried out in the clean (free of dust) chamber at increased temperature.

The characteristics of the initial membrane and membranes with a deposited layer of the polymeric compositions were determined through a number of complementary procedures.

The amount of the polymeric composition on the membrane surface, determined by the relation

$$Q_g = (m_g - m_o) \cdot 100 / m_o,$$

where m_o is the mass of initial membrane and m_g is the mass of membrane with the layer of polymeric composition. The changing of the surface properties of the membranes was performed by the contact angle measuring. For this purpose the sessile drop method using a horizontal microscope equipped with a goniometer was applied. Water (doubly distilled) was used as a test liquid. Six measurements were made at different places on the membrane surface and averaged. The change of the membrane thickness was measured using an electronic counter of thickness "Tesa Unit" (Austria), the precision of the measurement being $\pm 0.1 \mu\text{m}$. The gas flow rate through the membranes – a flow of gas (air) passing the membrane of 1 cm^2 was determined at a pressure drop of 10^4 Pa . Gas consumption was measured by float-type flow meter. On the basis of the values obtained according to these experiments the gas-dynamical pore diameter (an effective pore diameter) was determined as described in [18]. The study of the sample microstructure as well as the definition of the pore diameter on the membrane surface was carried out by SEM using the JSM-840 (JEOL). Before scanning, a thin layer of gold was deposited using JEOL JFC-1100 ion sputter.

3. Results and discussion

Research on the process of synthesis of the nanomaterials by the impregnation method with use of TM as a template has shown that for both type membranes with increasing concentration of the polymeric compositions in the solvent one observes a gradual growth in the mass of the samples (Table 1) connected with formation of a polymeric layer on their surface. Moreover, while increasing the sample weight, one can observe increase in the thickness of the membranes and decrease of their effective pore diameter. This means that the formation of the polymer occurs both on the membrane surface and on the pore walls. The essential reduction (up to 100 %) of the effective pore diameter of the membranes in comparison with insignificant increase (up to 4 %) in their thickness allows us to make a conclusion that the formation of the polymer inside the pores prevails its formation on the membrane surface. At small concentration of the polymeric compositions in the solvent, the pore diameter on the membrane surface, determined with the help of electronic microscopy, practically does not differ from the pore diameter on the surface of the initial membrane (Fig. 2). Besides, the research on the cross-sections of these membranes shows that the formation of the polymer on the pore surface occurs uniformly. It means that the formation of the polymer on the pore surface occurs uniformly. In other words, in case of using low concentrations of polymeric compositions in the solution, a formation of nanotubule membranes takes place. The structure of these membranes is preserved. A nominal pore diameter of the membranes of this type is determined by the size of the pore diameter on their surface. It is obvious that the choice of concentration of a polymeric composition in the solvent at formation of nanotubule membranes is determined by the pore diameter of the initial membrane. So, for PET TM with a pore diameter of $1.0 \mu\text{m}$, the formation of membranes this type occurs if concentration of the polymeric compositions is in a range from 0.5 up to 1.0 %. For PET TM with a pore diameter of $3.0 \mu\text{m}$, the formation of nanotubule membranes is observed at concentration of the polymeric compositions in a range from 2.0 up to 5.0 %.

Research in the surface properties of tubular membranes shows that formation of polymers of a mixture of monomers selected for the research leads to hydrophobization of the membrane surface – the water contact angle (Θ) for all the membranes raises. So, if for initial

PET $\Theta = 65^\circ$, then for treated membranes the value of water contact angle, irrespective of the concentration of the polymeric compositions in the solvent, is $80\text{--}82^\circ$ in case using copolymer from styrene and butylmethacrylate and is 95° in case using terpolymer from styrene, butylmethacrylate and 4-aminostyrene. The identical values of water contact angle in both cases for all modified membranes allows us to conclude that the polymeric compositions, even at low concentration in the solvent, completely cover the membrane surface and they uniformly distribute over the membrane surface. The particular value of the water contact angle of the membrane surface is determined by the properties of the polymeric compositions, their chemical structures can be expressed by the formulas given in Fig. 3.

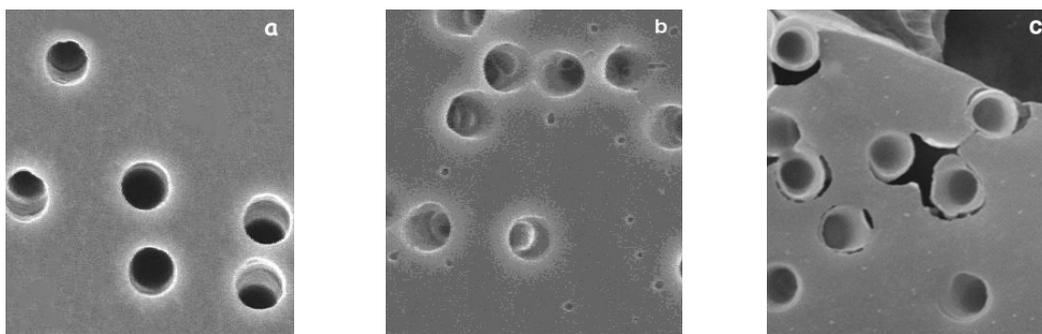


Fig. 2. SEM images of the surface of the initial membrane with a pore diameter of $3.0\ \mu\text{m}$ (a), with layer of a polymeric composition from styrene and butylmethacrylate (b) and after deformation of layer of polymeric composition (c). Concentration of polymeric composition in a solvent was 2 %.

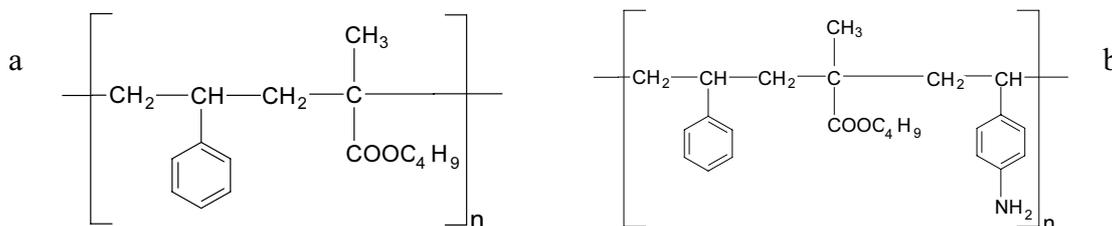


Fig. 3. Chemical structures of copolymer from styrene and butylmethacrylate (a) and terpolymer from styrene, butylmethacrylate and 4-aminostyrene (b).

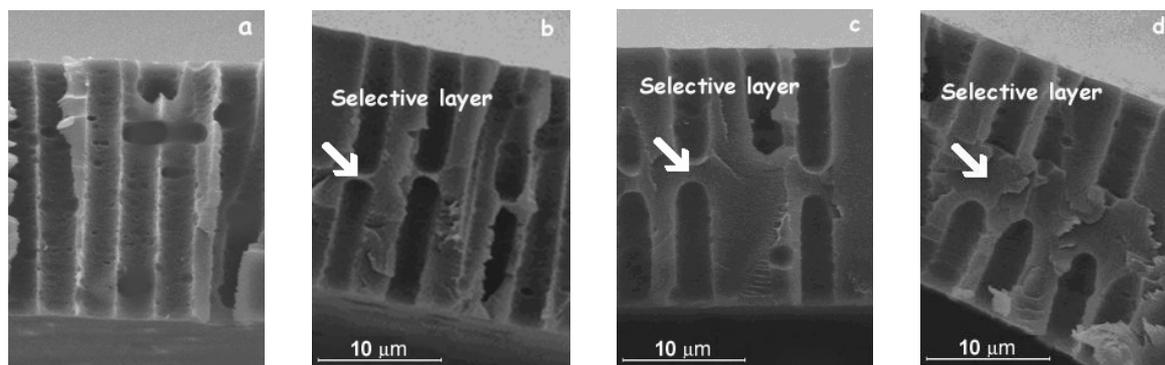


Fig. 4. SEM images of the cross-sections of the initial membrane with a pore diameter of $3.0\ \mu\text{m}$ (a) and composite membranes with various thickness of the selective layer. Concentration of polymeric composition from styrene and butylmethacrylate in a solvent was 5 % (b), 10 % (c) and 15 % (d).

Table 1. Change of the membrane characteristics during a process of template synthesis.

Concentration of composition* in solvent, %	Relative increase in the mass, %	Thickness, μm	Relative increase in the thickness, %	Air flow rate at $\Delta P=10^4$ MPa, ml/min·cm ²	Effective pore diameter, μm	Relative decrease in the effective pore diameter, %
Control	–	10.8	–	3200	1.00	–
0.5	1.7	10.8	0.50	965	0.74	26.0
1.0	2.4	10.9	0.95	525	0.62	38.0
2.0	3.6	11.0	1.85	185	0.47	54.0
2.5	4.0	11.1	2.75	90	0.38	63.2
Control	–	19.8	–	6600	3.00	–
2.0	1.8	20.0	1.0	4650	2.70	7.2
5.0	4.3	20.2	2.0	1200	1.90	38.4
10.0	7.4	20.4	3.0	180	1.15	60.3
15.0	9.4	20.6	4.0	0	0	100

*The polymeric composition of styrene and butylmethacrylate in ratio of 50:50 mol % was used in these experiments.

Increasing concentration of the polymeric compositions in solvent, one observes essential reduction of the effective pore diameter (Table 1). If so, the pore diameter on the membrane surface in some cases practically does not change. This means that the pores of such membranes are corked up at a depth from the surface. Electronic microscopic research of the membrane cross-sections confirms this conclusion. As it is seen from the microphotographs in Fig. 4, in membrane pores upon completing the treatment, a layer of polymer is formed. I.e., in this case, the formation of nanomembranes with a selective layer takes place. Moreover, the concentration of the polymeric composition in solvent essentially influences the thickness of the selective layer. The structure of these membranes in this case changes – pores get an asymmetric form. The nominal pore diameter of these membranes is determined by the pore diameter of the polymeric layer. Choosing a significant concentration of the polymeric composition in solvent one observes a full corking of the pores. So, when drawing a composite mixture with concentration of 15 % on the surface of initial PET TM with a pore diameter of 3.0 μm , its effective pore diameter decreases down to zero. Research on the cross-sections of this membrane by electron microscope shows, however, that in this case a nanomembrane with a selective layer is formed (Fig. 4d), i.e. full corking of pores occurs only in part of pore channels.

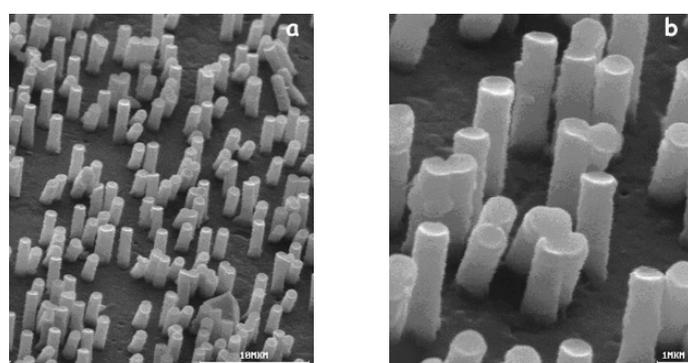
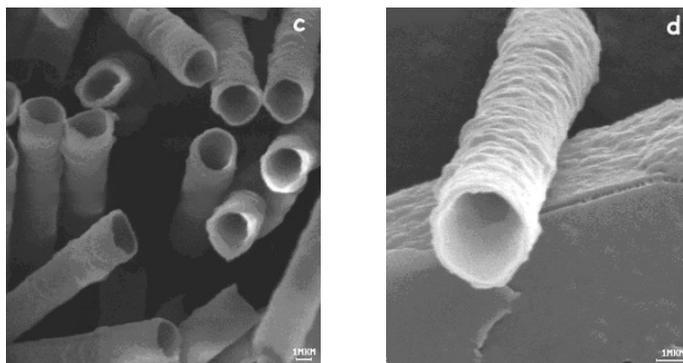


Fig. 5. SEM images of the polymeric microwires that were obtained using PET TM with a pore diameter of 1.0 μm as a template. Concentration of polymeric composition of styrene, butylmethacrylate and 4-aminostyrene in a solvent was 20 %.

Fig. 6. SEM images of the polymeric microtubules that were obtained using PET TM with a pore diameter of $3.0\ \mu\text{m}$ as a template. Concentration of polymeric composition of styrene and butylmethacrylate in a solvent was 5 %.



At further increase of the polymeric composition concentration in solvent, the full corking of pores occurs over the full length of pore channels. So, as electronic-microscopic research shows, at drawing a composite mixture with concentration 20 % on the surface of the initial PET TM with a pore diameter of $1.0\ \mu\text{m}$, the pore area is completely filled by a composite polymer. Dissolution of the matrix of the membrane in water solution of alkali with concentration of 20 % in this case leads to formation of nanostructural objects – nanowires (Fig. 5). The matrix of the membrane can be also dissolved in the case of formation of nanotubule membranes. Its removal leads to formation of nanotubules (Fig. 6) which then can be easily collected on the substrate after filtration.

4. Conclusion

The performed investigations have allowed us to make the following conclusions. Research on the process of formation of nanomaterials by the impregnation method with the use of track membranes as templates has shown that depending on the concentration of polymeric compositions in the solvent it is possible to form both nanomaterials (nanotubules or nanowires) and nanomembranes. For obtaining of nanowires and nanotubules, the pore region of the initial membranes was filled with a polymeric composition, then the membrane matrix was dissolved in water solution of alkali and the synthesized nanoobjects were accumulated on the substrate after filtration. In the first case the pore region was filled fully with polymeric composition, while in the second case the polymeric composition was formed only on the pore walls. In order to obtain nanomembranes, polymeric compositions after deposition were left inside the pores of the initial membranes. The research in the mechanism of nanomembrane formation shows that depending on concentration of polymeric compositions in the solvent, it is possible to obtain tubular membranes, in which the deposition of the polymeric layer on the walls of the pores occurs along its full length, as well as nanomembranes with a selective layer, in which the deposition of polymeric composition occurs along a part of the pore channel.

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