Formation of hydrophobic polymer coatings on the track-etched membrane surface

L I Kravets¹, M A Yarmolenko², R V Gainutdinov³, V Satulu⁴, B Mitu⁴ and G Dinescu⁴

¹ Joint Institute for Nuclear Research, Flerov Laboratory of Nuclear Reactions, 141980, Dubna, Russia
² Francisk Skorina Gomel State University, 246019, Gomel, Belarus
³ Shubnikov Institute of Crystallography of FSRC “Crystallography and Photonics” of RAS, 119333, Moscow, Russia
⁴ National Institute for Laser, Plasma and Radiation Physics, 077125, Bucharest, Romania

E-mail: kravets@jinr.ru

Abstract. Methods of forming coatings on the hydrophilic poly(ethylene terephthalate) track-etched membrane surface by means of plasma polymerization of organic compounds, magnetron sputtering and electron-beam dispersion of polymers in vacuum are considered. It is shown that the usage of compounds with low surface energy as pristine materials to coatings application allows to obtaining hydrophobic coatings on the membrane surface. The resulting composite membranes with hydrophilic and hydrophobic layers can be used in membrane distillation processes for desalination of seawater.

1. Introduction

Modification of polymer materials, including membranes, is a universal approach that allows varying their physical, chemical, mechanical and working properties in a wide range. One of the modern methods of modifying membranes is applying thin polymer films to their surface. Such modification leads to the formation of composite membranes (CM) consisting of a porous substrate (initial membrane) and a deposited polymer layer. Of greatest interest is the development of methods for creating bilayer composite membranes (BCM), in which one of the layers has a highly porous hydrophilic base, and the second thin microporous layer has hydrophobic properties. Membranes of this type are used in membrane distillation processes for desalination of seawater. The usage of a thin hydrophobic layer in combination with a thick hydrophilic sublayer can increase the condensate flux through the membrane by reducing the resistance to mass transfer [1, 2].

There are different strategies for applying polymer coatings to the surface of products. The most interesting approach is the formation of coatings from the active gas phase, which includes two groups of the methods. The first group of these methods involves the coating deposition on the surface of solid substrates as a result of plasma polymerization reactions of adsorbed low-molecular organic compounds (precursors) and activated under the influence of electrons, ions or UV radiation [3]. The second group of the methods encompass the coatings formation on the surface of the substrate due to sputtering a target (polymer or oligomer) as a result of exposure to a concentrated energy flow, such as
electrons, ions, laser radiation [4]. A feature of the second approach is the simultaneous occurrence of two main stages, namely, the stage of formation of volatile products and the stage of their activation. These methods are more technologically advanced as they allow to easily adjusting the structure and composition of the deposited layers. To obtain hydrophobic coatings, materials with low surface energy are usually used. These materials primarily include compounds based on silicon and fluorine.

The aim of this paper is to study the surface morphology and wettability of nanoscale polymer coatings deposited on the surface of poly(ethylene terephthalate) track-etched membranes (PET TMs) by means of plasma polymerization of organic precursors, as well as by the methods of radio-frequency (RF) magnetron sputter deposition (MSD) and electron-beam dispersion (EBD) of polymers in vacuum.

2. Experimental details

In the present experiments, samples of PET track-etched membranes with an effective pore diameter ranging from 65 to 250 nm obtained on the basis of polymer film Lavsan (Russia) having a nominal thickness of 10.0 μm were used. In order to produce the membranes, a poly(ethylene terephthalate) film was irradiated by krypton positive ions accelerated in the cyclotron (with energy about 3 MeV/nucleon) with a fluence ranging from 2×10⁸ to 3×10⁹ cm⁻². The irradiation is carried out under vacuum (0.15 Pa) at room temperature. The irradiated films were kept in air under normal conditions. Chemical etching of the irradiated PET films was performed in aqueous solution of sodium hydroxide using a standard procedure [5]. The irradiated films were treated with UV radiation (the maximum wavelength of the emission spectrum was 310-320 nm) before etching to increase the selectivity of tracks etching.

Hexamethyldisiloxane (HMDSO), hexamethyldisilazane (HMDSN) and 1,1,1,2-tetrafluoroethane (TFE) produced by Aldrich Chemical Co. (USA) were served as precursors for membrane modification by plasma polymerization. In the experiments, we used a RF-discharge plasma chemical setup with a frequency of 13.56 MHz. The polymer deposition from HMDSN and HMDSO vapors was carried out at a pressure of 0.7 Pa and a discharge power of 100 W, and from TFE at a vapor pressure of 32 Pa and a discharge power of 20 W. Argon was used as the carrier gas. Only one side of the membranes was exposed to the plasma. The setup scheme and the processing procedure for treatment are described in detail in [6].

The powders from ultra-high molecular weight polyethylene (UHMWPE) with an average molecular weight of 5×10⁶ g/mol and density of 0.93 g/cm³ (Foresight Global FZE, UAE), polytetrafluoroethylene (PTFE) with a density of 2.15 g/cm³ (Aldrich, USA), isotactic polypropylene (PP) with an average molecular weight of 9.7×10⁴ g/mol and a density of 0.91 g/cm³ (Polypropylene Co., Japan), high-pressure polyethylene (HPPE) and polymethylphenylsiloxane (PMFS) from Russia without additional drying before application were used as pristine substances to form coatings on the PET track-etched membrane surface by magnetron sputter deposition and electron-beam dispersion. Installation schemes and coating deposition techniques are described in detail in [7, 8].

The membrane surface morphology was studied with atomic force microscopy (AFM) on a NT-MDT NTEGRA Prima Spectrum Instrument (Russia). Imaging was performed in a tapping mode using a HA_FM silicon cantilever (Tipsnano, Estonia). The scanning area was 1×1 μm² with a resolution of 512×512 lines. The surface roughness (root-mean-square deviation of surface profile relative from the mean plane), the main parameter obtained from the measurements, was calculated taking into account all the data points of an AFM image. For each sample, AFM images were acquired in five different regions, and the values obtained for Rrms were averaged. The scans of smaller area without pores were studied to exclude the influence of pores on the determination of surface roughness.

The changing of the membrane surface wettability was evaluated by static contact angle measurements at room temperature based on the sessile drop method using Easy Drop DSA100 (Kruss, Germany) equipped with a digital camera, and the images were acquired using the Drop Shape Analysis Software V.1.90.0.14. Double distilled water was used as a test liquid.
3. Results and discussion

The formation of polymer coatings on the surface of PET track-etched membrane by the methods of magnetron and electron-beam sputter deposition of polymers in vacuum is illustrated in figure 1. This figure shows two-dimensional AFM micrographs of the surface layer of the composite membranes, which were formed in these processes. From the presented data, it follows that as the thickness of the deposited polymer layer increases, the pore diameter on the membrane surface decreases more significantly. Herewith the diameter of the pores on the back side of the composite membranes remains unchanged. This indicates that the polymer deposition occurs only on the modified side of the membrane. The application of coatings on the surface of PET track-etched membranes by magnetron and electron-beam sputter deposition of polymers in vacuum leads, thus, to the formation of bipolar composite membranes having an asymmetric pore shape—the pore diameter on the untreated side of the membrane does not change, and on the modified side it decreases. We obtained similar data in the study of the modification of PET track-etched membranes by the method of plasma polymerization [6].

The study of the morphology of the composite membranes surface layer shows a certain difference in the deposition processes of coatings by the studied methods. When studying the process of applying polymer coatings by the plasma-chemical method, we observed smoothing of the surface layer of the initial membrane [6]. The value of the standard deviation of the surface profile ($R_{ms}$), as shown by our experimental data, decreases. Deposition of UHMWPE and PTFE coatings on the surface of the track-etched membrane by magnetron sputtering also leads to smoothing of structural inhomogeneities of the surface layer (figures 1(a), (b), (c) and (d)). So, for the initial membrane with a pore diameter of 65 nm, the $R_{ms}$ value on the pore-free surface is 5.4 nm. The deposition of the UHMWPE coating with a thickness of 75 nm causes a decrease in $R_{ms}$ to 2.8 nm (figure 1(a)). When the thickness of the deposited layer increases to 100 nm, the surface roughness is 3.5 nm (figure 1(b)), i.e., in this case, the $R_{ms}$ value also is lower than that of the initial membrane.

On the contrary, the deposition of polymer coatings by the electron-beam deposition method causes a rise in roughness with an increase in their thickness (figures 1(e), (f), (g) and (h)). For example, when forming a PTFE coating with a thickness of 100 nm, the $R_{ms}$ value is 9.6 nm (figure 1(g)).
the coating thickness increases to 300 nm (figure 1(h)), the surface roughness increases and becomes equal to 16.4 nm. The observed difference in the morphology of the surface layer of bipolar composite membranes formed using these coating methods can be primarily related to the size of the deposited polymer nanostructures. Nanostructures formed on the track-etched membrane surface during the dispersion of polymers under the action of an electron beam are, as a rule, significantly larger than nanostructures formed during magnetron sputtering of polymers [9].

The study of the wettability of the initial membrane and composite membranes formed during the deposition of coatings on its surface indicates a certain difference in their surface properties (figures 2 and 3). If the PET track-etched membrane is characterized by a water contact angle (\(\Theta\)) of 65°, then for PET track-etched membrane with a thickness of 50 nm UHMWPE coating obtained by magnetron sputtering of a pristine polymer, the value \(\Theta\) is 78°. For a membrane with a 75-nm-thick UHMWPE layer \(\Theta = 82°\). An increase in the thickness of the applied polymer layer to 100 nm leads to an increase in the water contact angle up to 94° (figure 2(b)). Deposition of the polymer layer obtained by magnetron sputtering of PTFE leads to a more noticeable hydrophobization of the initial track-etched membrane surface. The value of the water contact angle for the composite membranes in this case is on average 111°. This is due to the lower surface energy of PTFE in comparison with UHMWPE. Thus, for PTFE, the surface energy is 18.3 mJ/m², and for UHMWPE this value is 33.0 mJ/m². It should be noted that the values of the contact angles for these coatings are lower than for UHMWPE and PTFE coatings obtained by electron-beam dispersion (figure 2(a)). For example, the value of the water contact angle of the UHMWPE coating, depending on its thickness, increases from 92° to 125°, and for the PTFE coating, the \(\Theta\) value varies from 130° to 155°. Such a change in the wettability of coatings with hydrophobic properties is due to an increase in the roughness of their surface with a growth in the thickness of the deposited polymer layer [10]. The difference in the wettability of coatings formed by magnetron and electron-beam sputter deposition of polymers in vacuum can be also caused by a difference in the chemical structure of the deposited polymers. A comparison of experimental data on the study of coatings deposited by the methods of magnetron and electron-beam sputter deposition of polymers shows that the coatings obtained by the electron-beam deposition method are more similar in chemical composition to the original polymers. In addition, a significantly lower concentration of oxygen-containing groups is observed on the surface of these coatings than on the surface of coatings obtained by the magnetron sputter deposition method [7, 8].

![Figure 2](image_url)

**Figure 2.** Changing the water contact angle values for coatings obtained by (a) electron-beam and (b) magnetron sputter deposition of polymers in a vacuum as a function of their thickness.

The usage of the plasma polymerization method to obtain hydrophobic polymer coatings showed that their surface contains a significant amount of oxygen-containing, including carboxyl groups, the formation of which is associated with oxidation during the removal of samples to the air, as well as with the presence of residual oxygen in the vacuum reaction chamber [3, 6]. It is with the formation of
oxygen-containing groups in the surface layer of the deposited polymers that insufficiently high values of the contact angles are associated. The water contact angle of the deposited coatings at the using silicon- and organofluorine compounds as precursors, as shown by the conducted studies, does not exceed 100° (figure 3).

4. Conclusions
Thus, the application of coatings on the PET track-etched membranes surface by plasma polymerization of xamethylidisilazane, hexamethyldisiloxane and 1,1,1,2-tetrafluoroethane, as well as by magnetron and electron-beam sputter deposition of ultra-high molecular weight polyethylene, polytetrafluoroethylene, polypropylene, polyethylene and polymethylphenylsiloxane leads to the formation of composite membranes consisting of two layers. One of them is the initial poly(ethylene terephthalate) track-etched membrane, characterized by an average level of hydrophilicity. The second layer is hydrophobic in nature. The water contact angle of this layer varies depending on its thickness. Membranes of this type can be used in membrane distillation processes for desalination of seawater.

Acknowledgment
This work was supported by a bilateral contract (no. 4648-5-17/2021) between JINR (Dubna) and NILPRP (Bucharest).

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