DEPOSITION OF DOUBLE-LAYER COATINGS FOR PREPARING COMPOSITE MEMBRANES WITH SYPERHYDROPHOBIC PROPERTIES

L. Kravets[1], M. Yarmolenko[2], A. Rogachev[2], R. Gainutdinov[3], N. Lizunov[1]

[1]Joint Institute for Nuclear Research, Flerov Laboratory of Nuclear Reactions, Joliot-Curie Str. 6, 141980 Dubna, Russia
[2]Francisk Skorina Gomel State University, Sovetskaya Str. 104, 246019 Gomel, Belarus
[3]Shubnikov Institute of Crystallography of FSRC "Crystallography and Photonics" Russian Academy of Sciences, Leninskii pr. 59, 119333 Moscow, Russia
E-mail: kravets@jinr.ru

The present paper describes the possibility of double-layer superhydrophobic coating formation on a porous substrate by the electron-beam sputter deposition of the polymers. As a porous substrate a poly(ethylene terephthalate) track-etched membrane (PET TM) with a thickness of 9.5 μm and pore diameter of 250 nm (pore density of 2×10^8 cm^{-2}) was used. Ultra-high molecular weight polyethylene (UHMW-PE) was used for sputtering to form the first hydrophobic layer on the membrane surface and polytetrafluoroethylene (PTFE) was used for sputtering to form the second superhydrophobic layer.

The electron-beam generator with filamentary cathode which allows to form beams with current density of 0.01-0.03 A/cm^2, energy E = 0.8-1.6 keV is used as the electron source. The deposition process of coatings was produced at initial pressure of residual gas in the vacuum chamber $\approx 4\times10^{-3}$ Pa. The growth rate in the deposition process was monitored by quartz crystal microbalance. Powders from UHMW-PE ($M_w = 5\times10^6$; density = 0.93 g/cm^3, Foresight Global FZE) and PTFE (density = 2.15 g/cm^3, Aldrich) were used as target materials without additional drying before application.

The characteristics of the original membrane and membranes with the deposited polymer coatings were determined by different procedures. The amount of the deposited polymer on the membrane surface was defined by the gravimetric method. The gas flow rate through the membranes was determined at an adjusted pressure drop by a float-type flow meter. From the obtained data, the effective pore diameter was calculated using the Hagen-Poiseuille equation. The microstructure of membrane samples was studied by a scanning electron microscope Hitachi SU-8020 (Japan). Morphology of the membrane surface was studied by an atomic force microscope NTEGRA Prima (NT-MDT, Russia). The surface properties were characterized by values of the contact angle measured with an Easy Drop DSA100 instrument (KRUSS, Germany) and the software Drop Shape Analysis V.1.90.0.14 using deionized water as a test liquid.

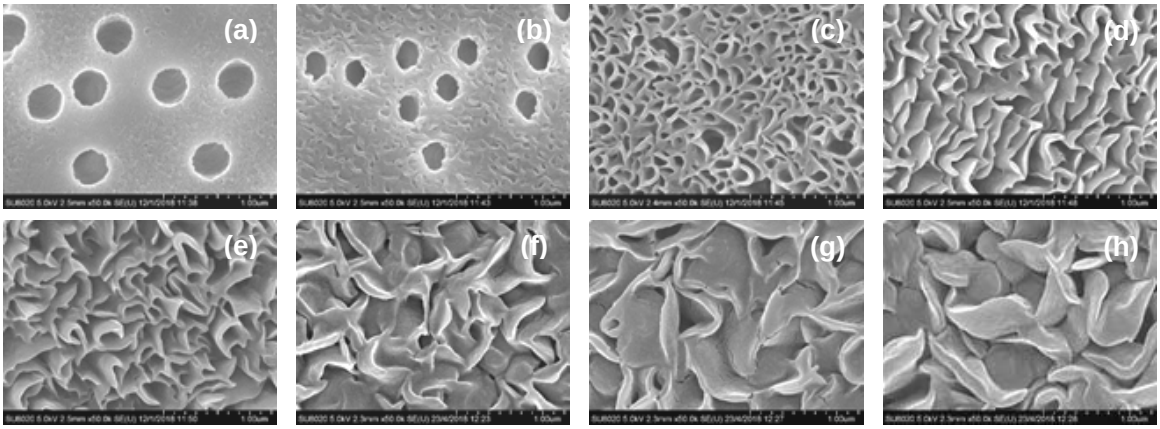

Fig. 1 – SEM images of the (a) original PET TM and membranes with applied coating of UHMW-PE with a thickness of (b) 100, (c) 200, (d) 300, (e) 500, (f) 700, (g) 900 and (h) 1200 nm

The investigation of the deposition process of UHMW-PE coating on the PET TM surface shows that, as the thickness of the deposited polymer coating increases, the effective pore diameter decreases. Reduction of the effective pore diameter of composite membranes (CMs) means that the pore diameter in the deposited polymer is less than the pore diameter of the original PET TM. Electron microscopic examination of the CMs surface (Fig. 1) has shown that for the membrane with the UHMW-PE coating of 100 nm (Fig. 1b) there is a slight decrease in the pore diameter on the surface. The surface of the deposited polymer coating has a slightly pronounced roughness. As the thickness of the deposited UHMW-PE coating increases, the pore diameter on the membrane surface decreases. So, the decrease in the pore diameter for the membrane with a coating thickness of 200 nm (Fig. 1c) is more significant. The deposited coating of the polymer thus acquires a mesh shape and becomes more roughness. Further increase in the thickness of the applied UHMW-PE coating leads to the formation of an ordered rough morphological structure on the membrane surface (Figs. 1d-1h). The effective pore diameter of the CMs is significantly reduced in these cases. From the electron microscopic data, it also follows that the pore diameter on the backside of the composite membranes remained unchanged, thereby implying that the polymer is not deposited in part of the pore channels. The electron-beam sputter deposition of a UHMW-PE coating on the PET TM surface thus leads to the formation of CMs having an asymmetric (tapered) shape of pores; the pore diameter remains unchanged on the untreated side of the membrane and significantly decreases on the modified side. This result correlates with the data obtained in our study of the modification of track-etched membranes by plasma polymerization /1, 2/.

Study of the morphology of CMs surface using AFM confirms the conclusion that during the UHMW-PE coating deposition on the PET TM surface there is a development of its roughness. Thus, for the original

membrane, the mean square deviation (R_{ms}) surface profile calculated for all scan points with an area of 5×5 μm^2 equal to 58.9 nm. The relatively high value of roughness is due to the presence of pores on the membrane surface, and the method of manufacturing the track-etched membranes, including chemical etching. The presence of pores has a more noticeable effect on the value of roughness. This is indicated by the determination of such parameters as the average height of the peak of the roughness (R_{pm}) and the average depth of the cavity of the roughness (R_{vm}) of the middle line of the surface profile. Evaluation of these parameters for the original membrane leads to the following results. The R_{vm} value is 52.1 nm, while the R_{pm} value is 30.8 nm, which is much lower.

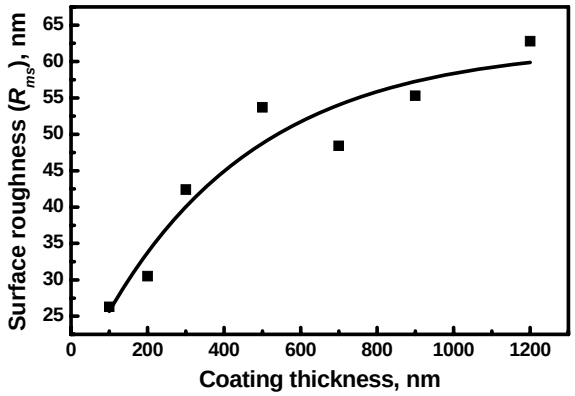

Fig. 2 – Plot of surface roughness of deposited UHMW-PE coating as a function of its thickness

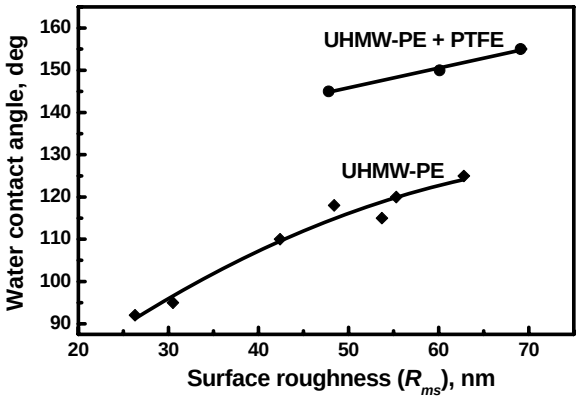

Fig. 3 – Plot of contact angle values of the CMs surface as a function of coatings roughness

Deposition of UHMW-PE coating on the surface of PET TM leads to a change in its surface roughness. The studies show that at the coating thickness of 100 nm surface smoothing is observed. The R_{ms} values decreases for this CM. This result is explained by the formation of a polymer in the pore channels at a certain depth from the entrance and the overlapping of pores on the membrane surface. However, the increase in coating thickness leads to increased surface roughness (Fig. 2). The R_{ms} values for the CMs markedly grow. The increase of R_{ms} value of the membrane surface during deposition indicates that the UHMW-PE coating has a more developed surface compared to the surface of the original track-etched membrane and the value of the surface roughness depends significantly on the duration of the deposition process.

The study of the surface properties of composite membranes shows that the deposition of UHMW-PE coating on the PET TM surface leads to substantial hydrophobization. If the original PET TM has the water contact angle (CA) of 65°, whereas the membranes with UHMW-PE coating have the CA from 92° to 125°, depending on its thickness as well as on the surface roughness (Fig. 3). This change is due to the development of roughness of the deposited coating having hydrophobic properties with an increase in its thickness. Therefore, the

application of the UHMW-PE coating on the surface of the PET TM thus leads to the formation of CMs consisting of two layers, one of which is the original PET matrix characterized by a medium level of hydrophilicity. The second layer deposited by means of UHMW-PE electron-beam sputtering in vacuum is hydrophobic in nature.

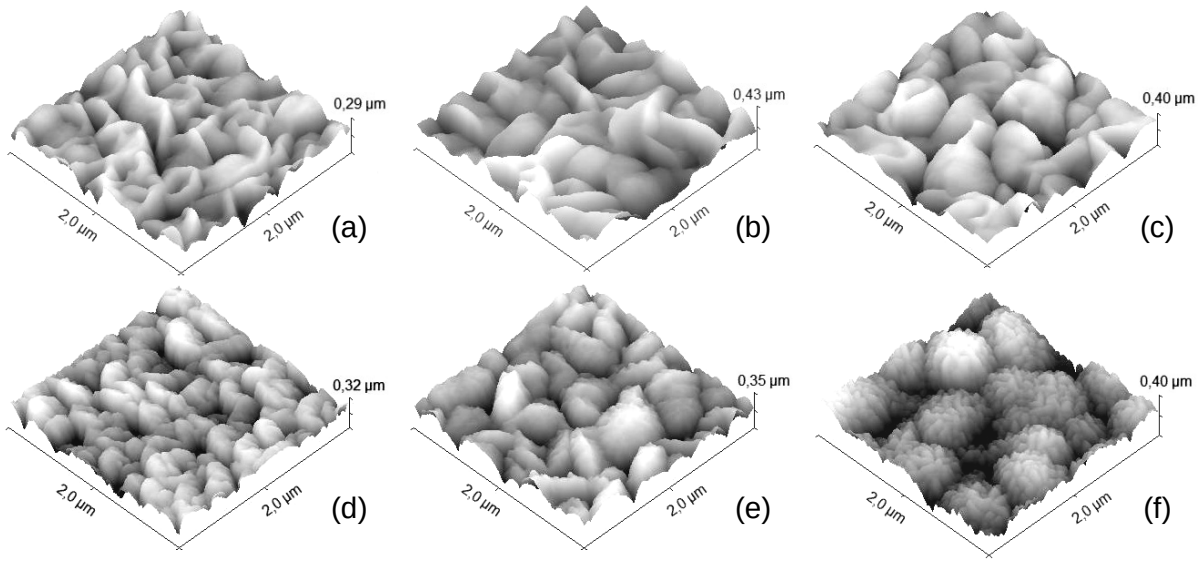

Fig. 4 – AFM scan images (2×2 μm^2 area) of applied on the PET TM surface UHMW-PE coating with a thickness of (a) 700, (b) 900 and (c) 1200 nm; (d-f) the same CMs with additionally applied second PTFE coating with a thickness of 100 nm

Formation on the CMs surface the second layer with a thickness of 100 nm obtained by electron-beam sputter deposition of the PTFE results in formation of superhydrophobic coatings. The values of water contact angle for this type CMs are 145°–155° (Fig. 3). It can be explained by the lower surface energy of the fluoropolymer and also by more significant development of the roughness of PTFE coating (Figs. 4d-4f) compared to the UHMW-PE coating (Figs. 4a-4c). In addition, in this case we observe formation of polymer particles with hierarchical structure (Fig. 4f).

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