MORPHOLOGY AND WETTABILITY OF POLYTETRAFLUOROETHYLENE-LIKE FILMS DEPOSITED ONTO TRACK-ETCHED MEMBRANE SURFACE IN VACUUM

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Abstract. The surface morphology and wettability of nanoscale polytetrafluoroethylene-like films deposited onto the surface of the poly(ethylene terephthalate) track-etched membrane by RF-magnetron and electron-beam sputtering of polytetrafluoroethylene in vacuum have been studied. It was shown that the morphology of films formed with the use of these coating techniques varies considerably. This is due to the size of the deposited polymer nanostructures. The nanostructures produced by the electron-beam sputtering of polytetrafluoroethylene are much bigger in size. Investigation of the surface properties of the composite membranes obtained in these processes showns that the deposition of the polytetrafluoroethylene-like film onto track-etched membrane leads to hydrophobization of its surface. The water contact angle for the composite membranes significantly increases.

Keywords: RF-magnetron sputtering of polymer, electron-beam dispersion of polymer, polytetrafluoroethylene, composite membranes.

1. Introduction

Membrane processes have found wide application in many areas of science and technology, such as gas separation, desalination of water, pervaporation, separation and isolation of individual solutes, and purification and concentration of biologically active substances [1]. Prominent among the variety of the membranes used in these processes are polymer membranes. However, the properties of existing membranes are frequently inconsistent with the requirements of industrial processing technologies, since the range of polymers suitable for the manufacture of membranes is limited. To extend the application area of commercial membranes, research works on the modification of their properties are performed. The most popular technique used for this purpose is the treatment of membranes by low-temperature plasma [2, 3]. An important advantage offered by this process is the possibility for modifying a thin surface layer, which alters membrane properties, namely, the adsorption, transport, and selectivity properties [4, 5]. This possibility substantially extends the application area of membranes. The bulk of the membrane matrix remains intact in this case, which is undoubtedly very important from the viewpoint of retention of its mechanical and physicochemical properties.

Another modern method for membrane modification is the application of thin polymer coatings on their surface, which leads to the formation of composite membranes consisting of a porous substrate – the initial membrane and a deposited polymer layer. There are various methods of coating deposition on the membrane surface [6]. The greatest interest is the formation of coatings from active gas phase using polymer dispersion in the result of the energy impact, such as RF-magnetron discharge, laser irradiation or the beam of accelerated electrons. These methods are technological and allow regulating the structure and composition of the deposited layers.

The present paper focuses on a comparative study of the surface morphology and wettability of nanoscale coatings of polytetrafluoroethylene-like deposited onto the surface of poly(ethylene terephthalate) track-etched membrane using RF-magnetron and electron-beam sputtering of polymer in vacuum. The track-etched membrane was used as a substrate because it has excellent material properties and is characterized by the hydrophilic properties. Besides, the membranes of this kind stand sharply against the filtering materials of other types due to their advanced features. The main advantage is the pore size homogeneity (the pores are cylindrical channels running through

Parameters	Initial PET TM	Modified by MSD method	Modified by EBD method
Relative increase in the mass, %	—	1.9	1.6
Thickness of deposited layer, nm	—	90	80
Air flow rate at $\Delta P = 2 \times 10^4$ Pa, ml min^{-1} cm^{-2}	155	115	1.5
Effective pore diameter, nm	95	85	25
Water contact angle, deg	65	110	120
Surface roughness (R_{ms}), nm	7.9	4.0	14.4

Table 1. Change of the PET TM characteristics after deposition of a PTFE-like layer.

(a)   *(b)*   *(c)*
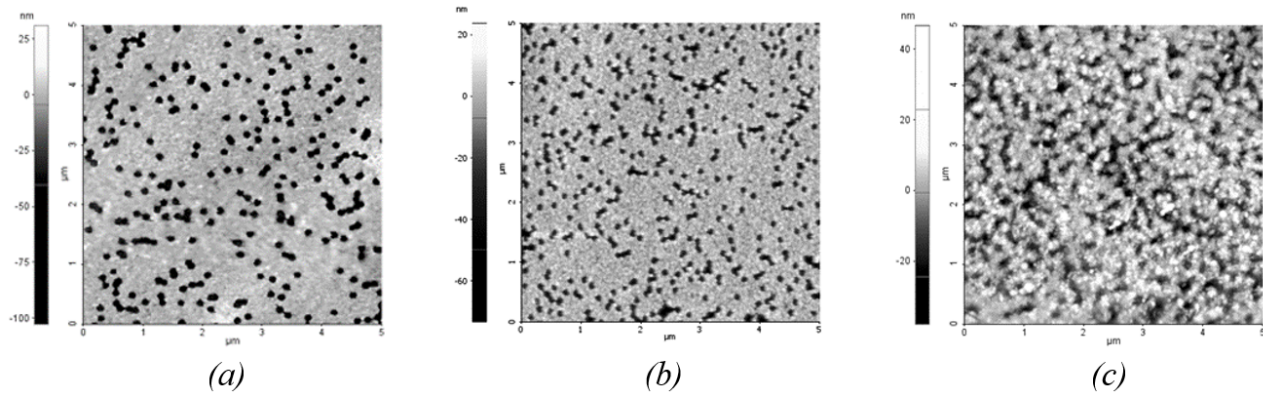
Figure 1. AFM images of the surface of the (a) initial PET TM and the membranes after deposition of the PTFE-like layer by (b) MSD and (c) EBD methods; scan area is 5×5 μm^2.

the membrane). Polytetrafluoroethylene was chosen for sputtering due to the possibility of obtaining a hydrophobic polymer coating.

2. Experimental

In the present experiments, poly(ethylene terephthalate) track-etched membrane (PET TM) with an effective pore diameter of 95 nm and pore density of 1.3×10^9 cm^{-2} was used. To produce the membrane, PET foil with a thickness of 10.0 µm (Lavsan, Russia) was irradiated by krypton positive ions, accelerated to energy of 3 MeV per nucleon at the cyclotron of the Flerov Laboratory of Nuclear Reactions. Then the ion-irradiated film was additionally sensitized with UV irradiation with the maximum emission intensity at 310 nm. The chemical etching process was performed in the NaOH aqueous solution (3.0 mol L^{-1}) at 75 °C for up to 7 min according to a standard procedure [7]. The membrane samples were cut in circular form with diameter of 10 cm prior the experiments.

The nanoscale layers of polytetrafluoroethylene (PTFE-like) coatings were deposited on the membrane surface from an active gas phase by RF-magnetron (MSD) and electron-beam (EBD) sputtering deposition of the polymer in a vacuum. PTFE-like coating deposition onto PET TM support by the MSD method was conducted in a spherical stainless steel vacuum chamber evacuated by a turbomolecular pumping system down to a base pressure of 10^{-2} Pa. The pressure

in the chamber was monitored by a Pfeiffer gauge and the gas flow rates are controlled by electronic mass flow controller (Bronkhorst Instrum.) [8]. The chamber is equipped with a magnetron sputtering source (Kurt J. Lesker) and a second capacitively-coupled plasma source, as well with other ports for various plasma diagnostic systems. The magnetron source was mounted at 45° and of 6 cm distance in respect to the substrate holder, which serves also as grounded electrode. The substrate holder is rotating during the deposition in order to insure thickness uniformity over large area. The PTFE target mounted in the magnetron is sputtered by igniting a discharge in argon flow (100 sccm) at RF power of 50 W and working under pressure of 6.8×10^{-1} Pa. The deposition rate of the PTFE coating was 6 nm/min. In order to insure various thicknesses of the PTFE-like layers, the deposition time was varied. The determination of PTFE layers thickness was controlled by contact profilometry method by using a Tenkor profilometer.

PTFE-like layers deposition onto membrane surface was applied also by the electron-beam sputtering deposition of the polymer. The electron source was a filament electron gun, which could produce beams with a current density of 5–100 A m^{-2}, an electron energy of 0.5–2 keV, and a cross-sectional area of $(5 - 10) \times 10^{-4}$ m^2. The initial pressure of residual gases in the reaction chamber was ~10^{-3} Pa; the substrate surface temperature was ~300 K; the emis-
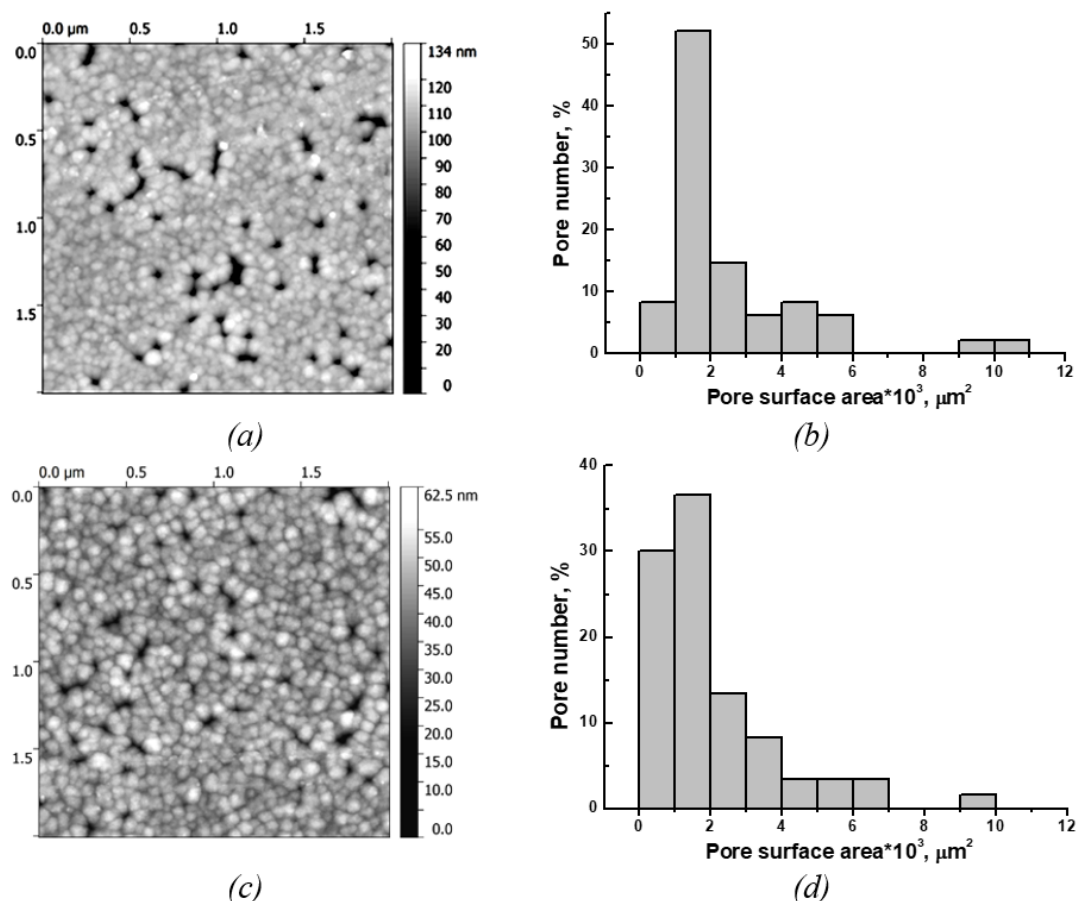
Figure 2. AFM images of the PET TM surface after deposition of the PTFE-like layer with a thickness of (a) 60 and (c) 180 nm by the MSD method and the corresponding histograms of the surface pore area distribution (b, d); scan area is 2×2 μm².

sion current, 10 mA; and the electron energy, 1.2 keV. The target was a PTFE plate of 10 mm in thickness and 35 mm in diameter (Plastopolymer, St. Petersburg). The deposition rate of the PTFE coating was 10 nm/min.The time of the sputtering deposition also was varied. The schematic of the setup and the treatment procedure are described in detail in our previous work [9].

The characteristics of the initial membrane and membranes with the deposited polymer layers 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. Gas consumption was measured by a float-type flow meter. From the obtained data, the effective pore diameter was calculated using the Hagen-Poiseuille equation [10]. Surface topography of the membranes was studied using a NTEGRA Prima (NT-MDT, Russia) atomic force microscope (AFM). Measurements were made in the dynamic mode to obtain a three-dimensional images; the scan area for each sample was 5×5 μm². The main determined parameter was the surface roughness – a root-mean-square deviation of the surface profile (R_{ms}), calculated over all scan points. In determining the surface pore area

distribution for the membranes after deposition of the PTFE-like layer the scan area was 2×2 μm². The surface properties were characterized by values of the static contact angle (Θ) 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 (error ±1°).

3. Results and discussion

The results of measurements of the characteristics for the initial PET TM with an effective pore diameter of 95 nm and composite membranes (CMs) obtained by applying a polymer layer using RF-magnetron and electron-beam sputtering deposition of PTFE are shown in the Table 1, in which each experimentally obtained value is the result of averaging of at least three measurements. From these data it follows that the deposition of the PTFE-like layer leads to an increase in mass of the membrane samples; their thickness increases, and the effective pore diameter decreases. The greatest decrease in the effective pore diameter is observed for the membrane with PTFE-like layer obtained by EBD method. The thickness of the coating in this case is slightly lower than for the membrane with PTFE-like layer applied by the MSD method.
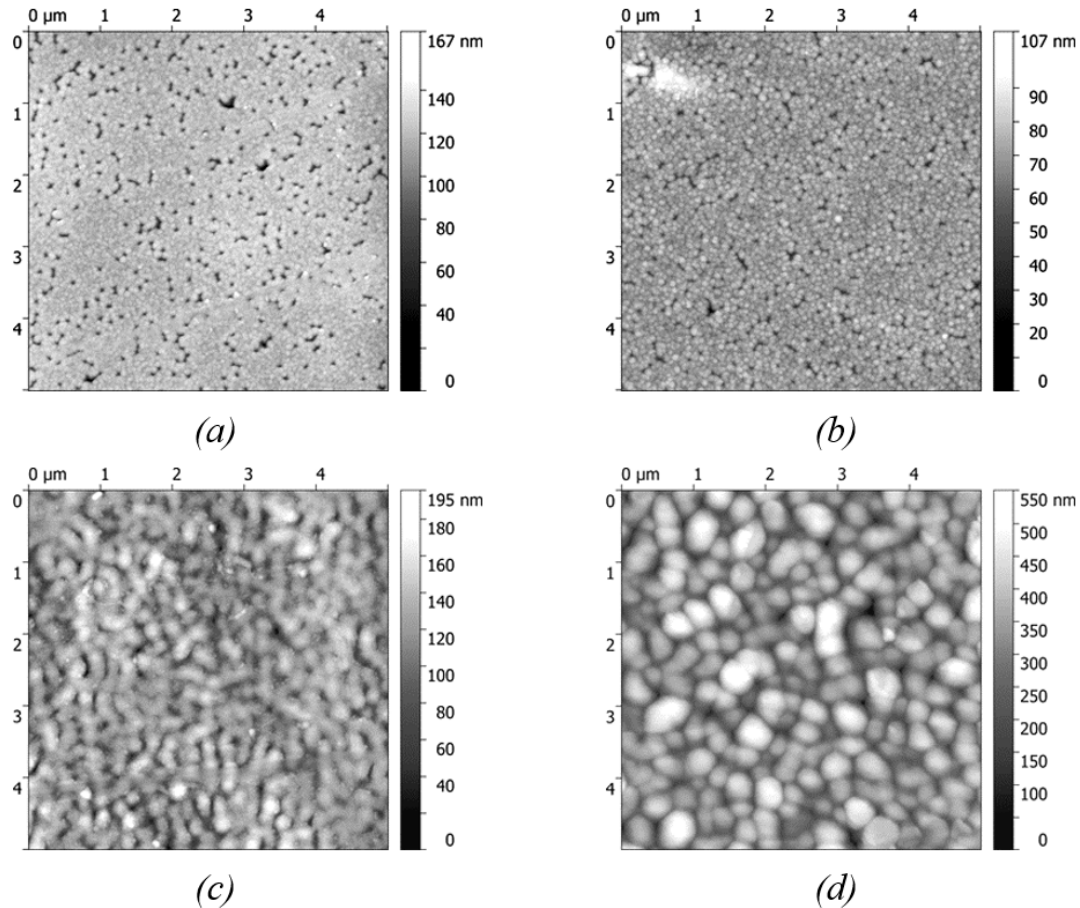
Figure 3. AFM images of the PET TM surface after applying PTFE-like layer by the MSD method with the thickness of (a) 60 and (b) 180 nm and after applying PTFE-like layer by the EBD method with the thickness of (c) 200 and (d) 500 nm; scan area is $5 \times 5 \ \mu m^2$.

The formation of polymer coatings on the PET TM surface is illustrated in Figure 1 by AFM images which present the surface layer of the (a) initial and (b, c) modified membranes. It is seen that the deposition of the coating causes a decrease in the pore diameter on the surface of the CMs formed, and their shape changes from round to irregular. However, the membrane pores on the surface are not completely closed by the polymer layer. The histograms obtained using the SPIP program to determine the pore surface area distribution for membranes after applying of PTFE-like layer by the MSD method are shown in Figure 2. The number of pores as well as their area can be extracted from this figure. So, for the membrane with the 60 nm PTFE-like layer, the largest number of pores has a surface area in the range from 10^{-3} to $2 \times 10^{-3} \ \mu m^2$, their diameter varies from 36 to 50 nm (Figure 2b). The surface porosity of the membrane is reduced up to 3.1%. Note, for the initial membrane with a pore diameter of 95 nm a pore area is $7.2 \times 10^{-3} \ \mu m^2$, and its porosity at the pore density of $1.3 \times 10^9 \ cm^{-2}$ is 9.2%. Deposition of the 180 nm polymer layer leads to more closing the pores on the membrane surface. The pore fraction with diameter from 36 to 50 nm some decreases herewith, and the

pore fraction with diameter less than 36 nm increases (Figure 2d). The surface porosity of the membranes is reduced in this case up to 2.9%.

It should be noted, according to the AFM data, the pore diameter on the untreated side of the composite membranes remains unchanged. This means that the polymer deposition occurs only on the modified membrane surface. The applying PTFE-like layer onto the surface of PET TM by MSD and EBD methods leads, thus, to the formation of CMs having an asymmetric (conical) pore shape. 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 earlier study on the modification of track-etched membranes by plasma polymerization [11, 12].

In addition, during the deposition of the coating there is a change in the surface roughness. For the initial membrane, the standard deviation of the surface profile with respect to the baseline R_{ms} is 7.9 nm. So, the deposition of PTFE-like coating on the membrane surface by the MSD method leads to smoothing irregularities (Figure 1b). For a typical scan area of $5 \times 5 \ \mu m^2$, the R_{ms} value of the modified membrane markedly decreases and is 4.0 nm at a coating

thickness of 90 nm. This result is explained by the formation of a polymer layer in the pore channels at some depth from the entrance and the overlap of pores on the membrane surface. In contrast, the deposition of PTFE-like coating by the EBD method (Figure 1c) leads to increase in surface roughness. A value of R_{ms} increases up to 14.4 nm at the formation of the film with a thickness of 80 nm. The observed difference in the morphology of the surface layer of CMs formed by using these methods may be due primarily to the size of the deposited polymer nanostructures. The nanostructures produced by the deposition of PTFE under the action of the electron-beam (Figures 3c and 3d) are significantly greater in size than the nanostructures produced by RF-magnetron sputtering of polymer (Figures 3a and 3b). Such difference is due to the peculiarities of the impact of the flow of particles falling on the target, leading to the destruction of the polymer and the deposition process itself. The energy impact on the target in the magnetron discharge is more significant. The decomposition at magnetron sputter materials is reached under bombardment with Ar^+ ions. Various atoms, ions and radicals based on C and F atoms from the PTFE target are present in the reaction chamber and after reaching the substrate the film growth is taking place. The decomposition of electron-beam sputter materials is reached under bombardment of electrons. When exposed to the flow of electrons on the surface of the polymer processes are occur, leading to the destruction of macromolecules. As a result, low-molecular fragments are formed in the reaction chamber. The polymer film growth on the membrane surface in this case takes place from polymer fragments as a result the formed nanostructures have more large size.

Determination of a size of the polymer nanostructures by the program SPIP shows that the size of the PTFE-like nanostructures deposited by the MSD method varies slightly with the increasing of sputtering time (Figure 4). Whereas at the dispersion of the polymer by EBD method is observed enlargement of nanostructures with an increase in the process time (Figure 5). Thus, the average size of the deposited polymer nanostructures during the process for 6 min is ~300 nm, and their maximum size reaches 500 nm (Figure 5a). During the process for 15 min, the average size of PTFE-like nanostructures is 400 nm, and their maximum value reaches 700 nm (Figure 5b). At the same time, the average size of the polymer nanostructures deposited by the MSD method during the process for 10 min is ~50 nm, and their maximum size reaches 120 nm (Figure 4a). During the process for 30 min, the average size of PTFE-like nanostructures is 60 nm, and their maximum value reaches 130 nm (Figure 4b).

The study of the wettability of CMs has shown that the deposition onto the PET TM surface of the PTFE-like films by MSD and EBD methods leads to substantial hydrophobization. If the initial membrane
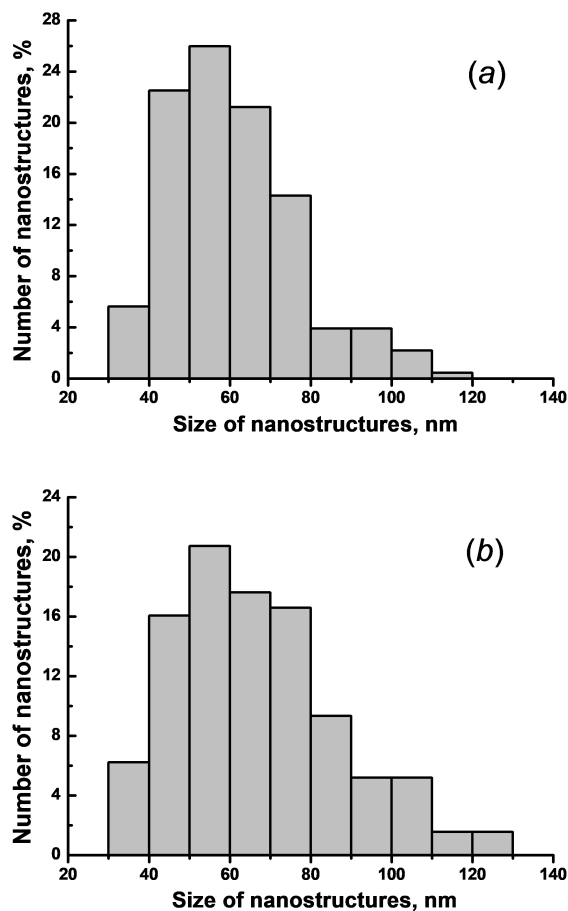

Figure 4. Histograms of the size distribution of nanostructures for PTFE-like layers deposited on the PET TM surface by the MSD method for (a) 10 and (b) 30 min; scan area is $5 \times 5 \ \mu m^2$.

is characterized by the value of the water contact angle (Θ) of 65°, whereas the PET TM with a PTFE-like layer on the surface with a thickness of 90 nm obtained by MSD method, has the Θ value 110°. For the PET TM with the 80 nm PTFE-like layer obtained by EBD the $\Theta = 120°$, that is higher than for polymer deposited by the MSD method. The study of the chemical structure of the surface layer of the deposited PTFE-like layer by the EBD using the XPS method showed that this polymer does not contain oxygen and nitrogen atoms, the presence of which is associated with a lower value of Θ for the polymer deposited by the MSD method [13]. The increase in the value of the water contact angle for CMs with PTFE-like layer obtained by EBD method is also due to the greater surface roughness [14]. For example, for CM with 80 nm PTFE-like layer, the surface roughness is 14.4 nm. Deposition of the 200 nm polymer film leads to raising the value of R_{ms} up to 20.2 nm and, therefore, causes an increase in the Θ value to 125°. During the deposition of the 500 nm film, the R_{ms} value is 69.9 nm, and the Θ value increases up to 140°.

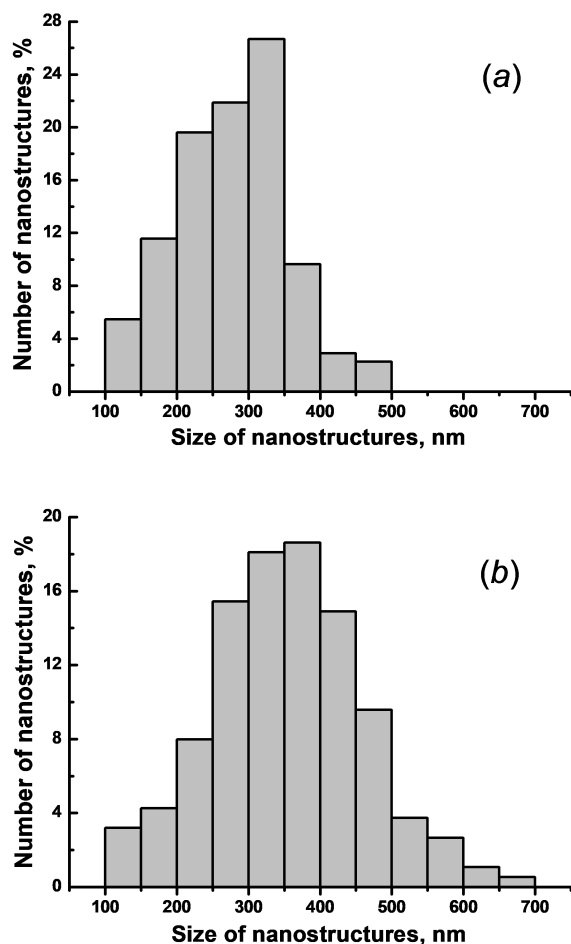Thus, the applying of PTFE-like layers onto the

Figure 5. Histograms of the size distribution of nanostructures for PTFE-like layers deposited on the PET TM surface by the EBD method for (a) 6 and (b) 15 min; scan area is $5 \times 5 \ \mu m^2$.

PET TM surface by the MSD and EBD methods leads to the formation of CMs, consisting of two layers, one of which is the initial track-etched membrane, characterized by an average level of hydrophilicity. The second layer has a hydrophobic nature. The wettability of this layer depends on its thickness. Membranes of such type can be used in various membrane processes, such as desalination of water, pervaporation, reverse osmosis, and nanofiltration.

4. Conclusions

In summary, we can conclude that the formation of a PTFE-like layer onto one side of a track-etched PET membrane by the MSD and EBD methods results in a composite membranes having the hydrophilic and hydrophobic sides. The surface morphology of the PTFE-like films deposited by these methods have some difference. This is due to the size of the deposited polymer nanostructures. The nanostructures produced by the sputtering deposition of PTFE under the action of the electron-beam irradiation are

usually significantly greater in size than the nanostructures produced by RF-magnetron sputtering of polymer. Therefore, unlike MSD, polymer formed by EBD of PTFE results in formation of a polymer film with more advanced relief of a surface. As a result, the CMs with a PTFE-like layer deposited by the EBD method have more hydrophobic properties in comparison to the membranes with a PTFE-like layer deposited by MSD method.

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