

Structure and Mechanical Properties of Ultrafiltration Membranes Modified with Langmuir–Blodgett Films

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Abstract—The structure and local mechanical properties of the surface of polysulfone(PS-100)- and polyacrylonitrile(PAN-100)-based source ultrafiltration membranes and ones modified with thin films of polyvinylpyridine (PVPyr) or latex particles applied by the Langmuir–Blodgett (LB) method and by the formation of a PVPyr/sodium polystyrene sulfonate polyelectrolyte complex have been studied using atomic force microscopy. It has been found that the application of a PVPyr layer on the PS-100 membrane results in a two-fold decrease in the membrane pure water flux from 250–360 L/(m² h), while a substantial increase in the rejection coefficient is observed: the nominal molecular weight cut-off limit is reduced from 100000 to 10000 Da. For the PAN membrane a 10% increase in water permeability was found, and the rejection coefficient for PVP K-30 increases from 55 to 65%. Modification with latex particles results in a sharp decrease in the membrane performance. Comparative analysis of the topography and the local elasticity modulus of the samples indicates almost complete blocking of the porous structure of the source membranes in the case of their modification with latex particles, as well as the destruction of the PVPyr layer with the formation of globular structures upon contact with water. The surface energy of the samples after the modification increases. Layer-by-layer applying of PVPyr and sodium polystyrene sulfonate results in a twofold decrease in the pure water flux of the PAN-100 membrane and in an increase in the rejection coefficient due to the formation of a polyelectrolyte complex. In addition, for the PAN/PVPyr/PSS membrane a substantial decrease in the degree of fouling after filtration of a model calibrant solution was detected. It was shown that depending on the type of the source matrix and the polymer used for the surface modification by the horizontal precipitation (LB) method, it is possible to produce membranes with a predetermined pore size, mechanical and transport properties; at the same time, the density and permeability of the modifying layer are determined by the physicochemical properties and the surface structure of the source membrane.

Keywords: ultrafiltration membranes, Langmuir–Blodgett films, fouling, specific productivity, rejection coefficient, atomic force microscopy, local elasticity modulus, surface energy

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INTRODUCTION

Membrane separation techniques such as ultra- and microfiltration have been widely used for the treatment of water for drinking and technical needs, wastewater treatment, separation of liquids in biotechnology, chemical, pharmaceutical, food and other industries [1]. One of the main problems limiting the use of membrane technologies is the membrane fouling during operation [2]. Membrane fouling is a complex of phenomena at the membrane/feed solution interface resulting in a sharp, in some cases irreversible decrease in the performance of the membranes caused by the deposition of components of purified liquids in pores or on the surface of the membrane. Depending on the nature of foulants, the following types of fouling are distinguished: inorganic (precipitation of spar-

ingly soluble salts), organic (fouling by dissolved proteins, polysaccharides, and humic substances), colloidal (fouling by colloid particles of iron, silicon, and heavy metal oxides and hydroxides and organic compounds), and biofouling (formation of a biofilm with microorganisms, fungi, bacteria and viruses). The basic approach to minimize membrane fouling is to prevent undesired adsorption interactions between foulants or microorganisms and the membrane surface. This is achieved by modifying the membrane selective layer in order to increase its hydrophilicity; impart a charge; and decrease the membrane surface roughness, which determines its interaction with foulants and microorganisms [2, 3]. One of the ways to change the physicochemical properties of the surface is to apply a thin “skin” layer on the surface. Selective layers can be applied using various methods: by phys-

Table 1. Properties of ultrafiltration membranes

Membrane type	Nominal cut-off, kDa	Pure water flux (J), L/(m ² h)	Rejection factor (R)*, %
PAN-100	100	190–230	55
PS-100	100	250–360	24

* Determined using 0.2% polyvinylpyrrolidone K-30 ($M_w = 40000$) solution as a calibrant.

ical adsorption [2, 4] with immobilization, in some cases, of the adsorbed layer by heat treatment or cross-linking [2]; phase transfer polycondensation [5]; plasma-enhanced deposition [3]; combined casting or extrusion of two polymer solutions [6]; and layering of polyelectrolytes according to the Langmuir–Blodgett (LB) technique [7, 8]. The advantage of the LB method is the ability to prepare LB layers of nanometer thickness. This method also makes it possible to vary the permeability of the modifying layer within wide limits depending on the task.

A promising method for studying the structure and local mechanical properties of the surface of membrane selective layer is atomic force microscopy (AFM).

The aim of the work is to study the structure and local mechanical properties of the surface of modified membranes by atomic force microscopy and examine changes in their transport properties.

EXPERIMENTAL

The objects of study were ultrafiltration (UF) membranes based on polyacrylonitrile (PAN-100) and polysulfone (PS-100) produced by the Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus (TU BY 100185198.091-2008). The test membrane properties are listed in Table 1.

In addition, to practice modification modes and to study coating stability in an aqueous medium, porous PS matrix prepared by coating a glass substrate with a 20 wt % PS solution in dimethylacetamide followed by precipitation into water, washing to remove the residual solvent, and drying were used.

The modification of the membrane surface with monomolecular polymer films was carried out from an aqueous solution by the horizontal precipitation technique using an LT-103 (ODO Microtestmachines, Belarus) device. Solutions of poly-4-vinylpyridine (PVPyr, $M \sim 73000$; Sigma-Aldrich) in chloroform at a concentration of 1 mg/mL and these of latex particles based on a commercial polyacrylate WB-125 adhesive in isopropyl alcohol were used. A procedure for the preparation of latex particles with a diameter from 30 up to 100 nm is described in [9]. A PVPyr film was applied at a pressure of 15 mN/m; latex particles, at 40 mN/m.

The choice of materials for modification was motivated by differences in their physicochemical properties (hydrophilicity, thickness). PVPyr is a thin film

5 nm in thickness with moderately hydrophobic properties, latex particles are 30 nm in diameter and are hydrophilic.

To assess the stability of the coatings formed by PVPyr and latex particles the samples of the matrix were aged in distilled water for 60 h, and then analyzed.

In order to stabilize the PVPyr coatings on the membrane surface, an additional processing of the membrane with a sodium polystyrene sulfonate (PSS, $M \sim 70000$; Sigma-Aldrich) aqueous solution was conducted after the application of a PVPyr monolayer, which led to the formation of a polyelectrolyte complex.

The determination of the filtration properties of the membranes was performed on a membrane filter of the FM02-200 type at $P = 0.1$ MPa and 25°C.

The value of the water flux of the membranes was calculated using the formula:

$$J = \frac{V}{St}, \quad (1)$$

where V is volume of liquid (m³) passed through the membrane during time t (s) and S is the membrane area (m²).

To determine the rejection coefficients of the membranes (R), a 0.3% aqueous solution of K-30 polyvinylpyrrolidone (PVP) ($M_r = 40000$; Fluka) was used.

The value of the rejection coefficient (R) was calculated by the formula:

$$R = \left(1 - \frac{C_f}{C_0}\right) \times 100\%, \quad (2)$$

where C_f is the calibrant concentration in the filtrate and C_0 is the calibrant concentration in the feed solution.

Concentrations of PVP in the feed solution and filtrate were measured with an ITR-2 interferometer.

The degree of membrane fouling after the filtration of the PVP solution was determined by the following formula:

$$F = 1 - \frac{J_{fin}}{J_0}, \quad (3)$$

where J_0 is the pure water flux of the initial membrane, J_{fin} is the pure water flux after filtration of the PVP solution.

The structure of the samples was studied on an NTh-206 atomic force microscope with standard silicon cantilevers with a stiffness of 3 N/m (MicroMash, Estonia). Surface topography was studied in the static and dynamic AFM modes. The coating thickness was measured by nanoscratch testing [10]. The elastic properties were evaluated by static force spectroscopy. The modulus of elasticity (E) of the materials was calculated by the Hertz model [11], and the surface energy (γ) was found from the values of cantilever deviation upon the separation of the probe tip from the sample surface according to the Johnson–Kendall–Roberts model [12]. The average standard deviation of the results measuring the elastic modulus and surface energy of the sample did not exceed 5%.

The study of the initial structure and the determination of the thickness of monomolecular films were performed by applying them to silicon plates (111). The thickness of the modifying layer of latex particles on silicon was 30 nm; PVPyr layer, 5 nm.

RESULTS AND DISCUSSION

The experimental procedure for coating by the LB method included the steps of washing the initial films in water, contacting them with an organic solvent upon a horizontal coating deposition, and drying in air at room temperature. These treatments are generally not used in the case of ultrafiltration membranes because of capillary contraction of pores and irreversible change of the structure. In this regard, a preliminary study of changes in the structure and properties of the surface of PS matrix having no through porosity (their hydraulic permeability is zero) after treatment in water and subsequent drying was carried out.

It was found that the aging the initial PS matrix in water for 60 h followed by drying results in a change in the surface structure (Fig. 1). The change is manifested as a reduction in size of the structural elements on the matrix surface and is associated with the capillary contraction and shrinkage of the sample during drying.

The surface of the PS matrix was modified with LB films formed by PVPyr and latex particles. The application of PVPyr films results in covering the surface and smoothing its topography occur. In the case of latex particles, the morphology of the initial matrix is conserved to a greater extent. However, after aging in water and drying of the samples, substantial differences in the surface structure are observed. A quite uniform PVPyr coating is altered to form islet globular structures. For latex particles, the surface profile is smoothed and the formation of globules is less expressed. To clarify the nature of changes in the sur-

face properties, the surface elasticity modulus of the samples was determined (Fig. 2).

The values of the elasticity modulus of the initial PS matrix and the samples modified with latex particles are similar. After applying the PVPyr film, the values of E decrease, but holding in water and subsequent drying make them nearly the same as E for the initial PS matrix. This change indicates the degradation of the applied PVPyr layer by water and is consistent with the AFM data, since the area free of conglomerates, which is the initial surface of the PS matrix, is indented during the measurement of E .

For the PS matrix modified with latex particles, a substantial decrease in the surface elasticity modulus was observed after water treatment, a change that suggests the complete blocking of the polysulfone surface by latex after contact with water and can be associated with the degradation of the film of latex particles during the contact and the formation of a continuous coating formed by the adsorbed polymer.

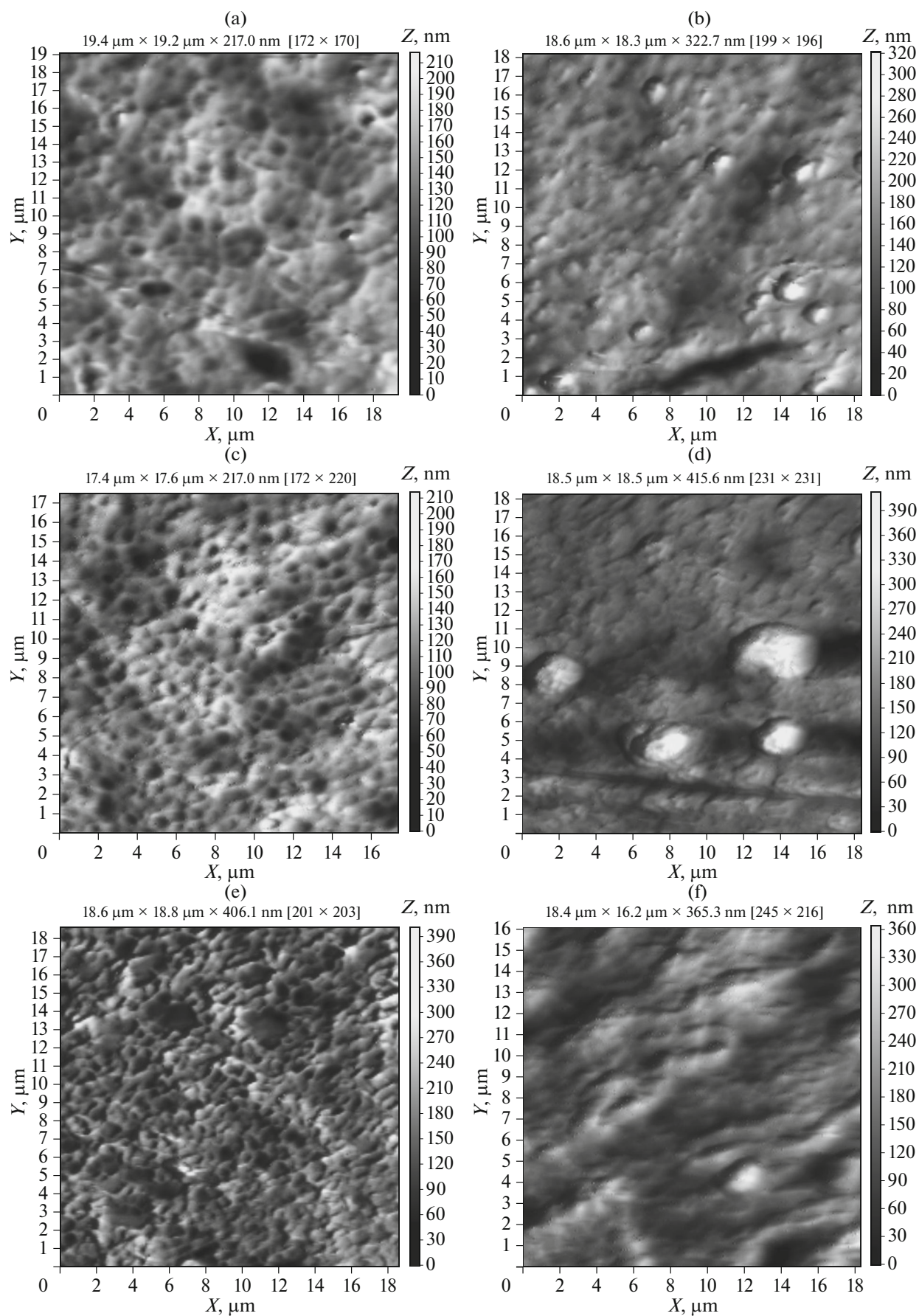
A different picture was observed for the modified ultrafiltration membranes differing in the type of polymer and having a developed porous surface. The values of elasticity modulus and surface energy for the initial and modified membranes were determined.

It was found that the elasticity modulus for the test membranes is substantially different. For polyacrylonitrile membranes, the value of E is nearly two times that for polysulfone membranes. After modifying the PAN-100 membrane with PVPyr, the values of E become almost tenfold lower, whereas the elasticity modulus of the PS-100 membrane increases by one and a half times (Fig. 3), unlike in the case of nonporous PS matrices.

The result of membrane modification with both PVPyr and latex particles is a substantial increase in the surface energy. Thus, the membrane modification with the LB films makes it possible to impart hydrophilic properties to the membrane surface, even after applying one monomolecular layer of polyelectrolyte or latex particles.

The marked changes in the values of E and surface energy caused by the modification of the test membranes are due to the difference in the structure of their surface (Fig. 4). The initial membranes have a porous surface with a pore diameter of ~ 100 nm. No substantial changes in the surface structure have been detected after PAN-100 membrane modification with PVPyr. The mean square roughness of the PAN/PVPyr membrane surface was not changed substantially and made 3–4 nm. A different pattern is observed for the PS-100 membrane. Application of PVPyr results in the formation of a dense structure indicating the formation of a PVPyr monolayer on the

Fig. 1. Structure of (a, b) the initial PS matrix and the matrix modified with (c, d) PVPyr LB film or (e, f) latex particles: (a, c, e) before and (b, d, f) after holding in water.



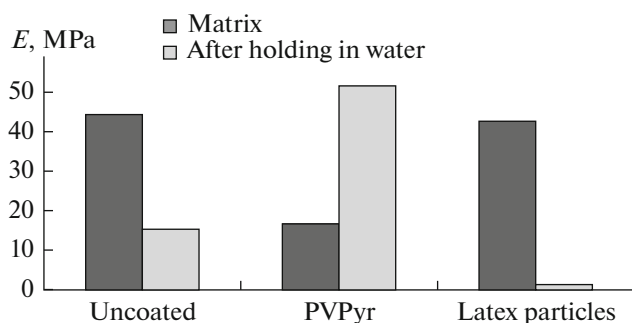


Fig. 2. Modulus of elasticity for the initial PS matrix and the matrix modified with PVPyr and latex particles before and after holding in water.

surface of the source membrane. The thickness of the PVPyr LB film coating is ~ 15 nm, which is slightly higher than that for silicon wafers, and the mean square surface roughness was 6 to 6.5 nm.

As a result of applying latex particles layer a dense film is formed on both membranes. The described differences in the structure of the LB layers on the initial membranes affect the transport properties of the modified membranes.

As a result of applying a layer of latex particles on the PS-100 membrane, a sixfold reduction in the pure water flux values occurs. This indicates almost complete blocking of the porous structure of the membranes by latex, which is confirmed by the results of the membranes surface topography study (Fig. 4f) and correlates with results obtained using the PS-matrices. Therefore, further experiments on the modification of polysulfone membranes using latex particles were discontinued.

For the polyacrylonitrile membrane a decrease in the performance after modification with latex was less pronounced and made $\sim 20\%$. Thus, in the case of latex particles the density of the modifying layer is determined by physicochemical properties and the structure of the membrane surface.

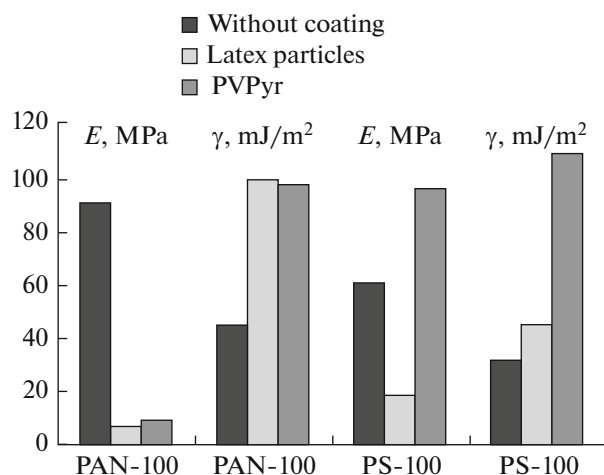


Fig. 3. Values of the elasticity modulus and surface energy for the initial PAN-100 and PS-100 membranes and the membranes modified with latex particles and polyvinylpyridine.

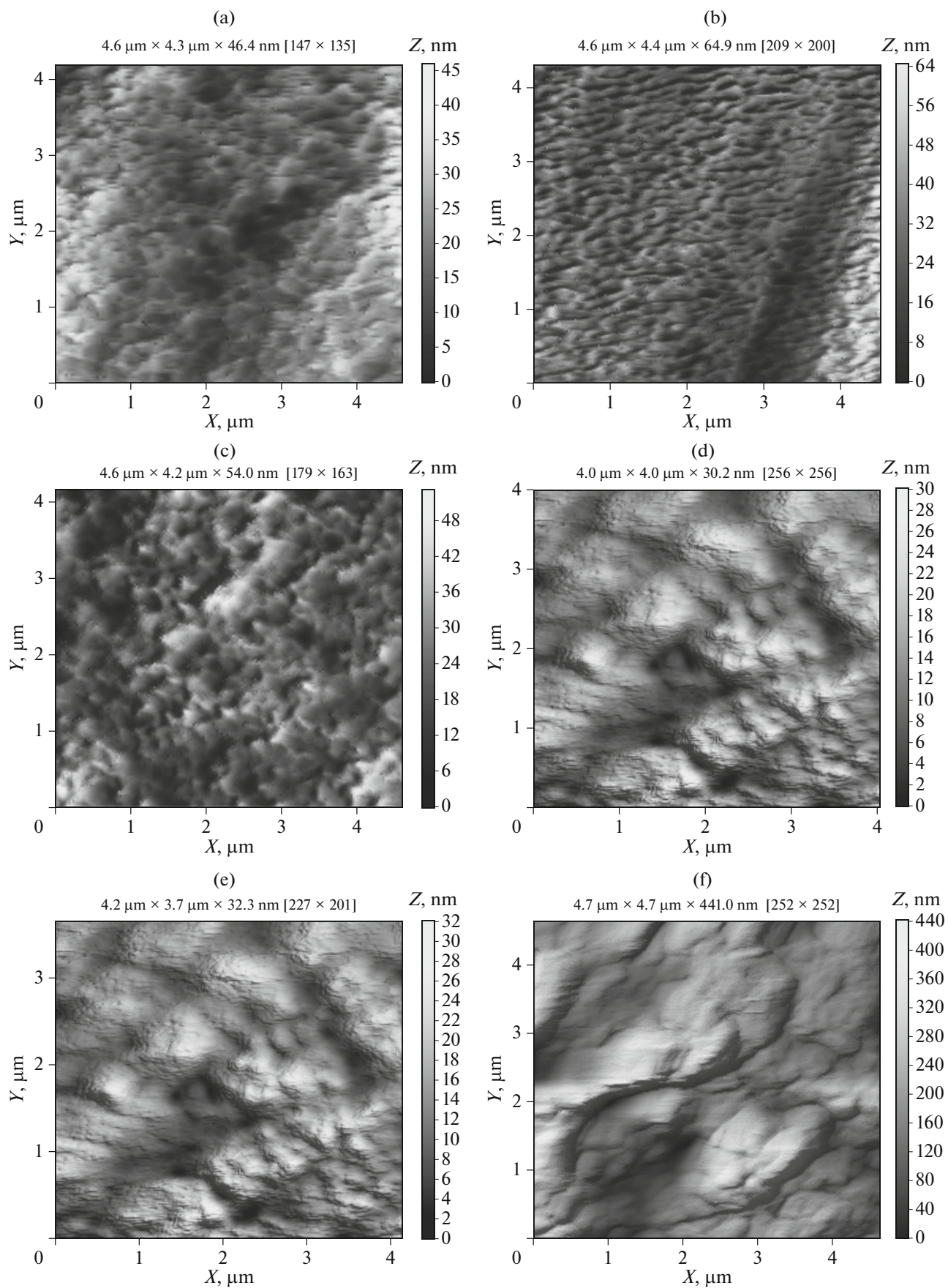
The application of a PVPyr layer on the PS-100 membrane decreases its pure water flux twofold from 250–360 L/(m² h) and substantial increases the rejection coefficient (Table 2). Under DIAFLO catalog [13], the rejection coefficient of membranes for PVP K-30 in the range of 70–85% corresponds to the nominal molecular weight cut-off of 10000 Da, i.e., the cut-off of the membranes is reduced by a factor of 10. These data indicate that despite the contact with water, only partial removal of the modifying PVPyr layer occurs.

In contrast to PS-100, for the polyacrylonitrile membrane modified with PVPyr a slight (10%) increase in water permeability was detected, and the rejection coefficient increased from 55 to 65%. A possible reason for these differences is the fact that almost complete washout of the PVPyr monomolecular layer occurs in contact with water as a result of its lower adhesion to the PAN-100 membrane surface. As follows from Fig. 4c, PVPyr does not form a continuous layer, but the islet coating “heals” large pores. Because

Table 2. Parameters of the initial and modified UF membranes

Parameter	Membrane					
	PS-100	PS/PVPyr	PS/(PVPyr/PSS)	PAN-100	PAN/PVPyr	PAN/(PVPyr/PSS)
J_0 , L/(m ² h)	249	120	84	204	230	106
R , %	24	86	94	55	65	86
F	0.52	0.61	0.54	0.49	0.55	0.19

Fig. 4 AFM images of surface topography of (a) PAN-100 membrane, (b) PS-100 membrane, (c) PAN/PVPyr, (d) PS/PVPyr, (e) PAN/latex particles, and (f) PS/latex particles.



of surface hydrophilization, the water permeability of the membranes is not reduced.

To stabilize the applied PVPyr coating, the membranes were subjected to additional treatment with a sodium polystyrene sulfonate solution. As follows from the data in Table 2, applying an additional PSS layer results in a twofold decrease in the water flux through the PAN-100 membrane and in a further increase in the rejection factor due to the formation of a polyelectrolyte complex. In addition, a substantial reduction in the degree of fouling after filtration of the calibrant solution was found for the PAN/PVPyr/PSS membrane.

Similar changes in the transport properties of the membranes after treatment with a PSS solution were found for the PS-100 membrane, but the effect of resistance to fouling have not been revealed in this case.

CONCLUSIONS

As a result of the studies of the porous structure and the measurements of the elastic properties of the membrane surface by AFM, it was found that coating with PVPyr or latex particles using the Langmuir-Blodgett technique is an effective way to change the structure and transport properties of ultrafiltration membranes. An increase in the surface energy of the modified membranes indicates the hydrophilization of the initial samples. An analysis of the topography and the results of the measurements of the local elastic modulus the surface revealed structural changes taking place after the deposition of the modifying layer and the subsequent contact of the membranes with water. It was shown that surface modification with monomolecular LB films has a stabilizing effect on changes in the membrane structure after treating with water and drying in the absence of impregnating agents preventing the contraction of the capillary pores. It was found that depending on the type of the source matrix, polymer and the substance used to modify the surface by the horizontal precipitation method, the character of changes in the transport properties of the membranes differs and is determined by the physicochemical and structural properties of the initial membrane surface, i.e., by pore size and surface roughness.

The layer-by-layer deposition of PSS and PVPyr stabilizes the PVPyr coating and leads to a decrease in the membrane pure water flux by a factor of 1.5–2 and an increase in the rejection coefficient, which is caused by the formation of a polyelectrolyte complex. In addition, a substantial reduction in the degree of fouling was found for the PAN/(PVPyr/PSS) membrane after filtration of PVP K-30 model solution.

On the basis of the obtained data, it can be concluded that the decisive factors in the modification of the membrane surface are both the choice of a modifier and the properties of the initial membrane substrate.

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