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Hydrophilization of the polyethyleneterephthalate ion track membrane surfaces

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Abstract. Results of polyethyleneterephthalate ion track membranes hydrophilization by (Chytozan/Dextran)₄ multilayers with using Layer-by-Layer method and by Nafion monolayer with using Langmuir – Blodgett and spin-coating methods are presented in articles. The structure, contact angles and polar component of specific surface energy of modified membranes has been researched.

1. Introduction

Track membranes (TM) are widely used in the processes of separation and purification of liquid and gaseous media, for microfiltration processes in biotechnology, medicine, microbiology and virology. A number of practical problems require a targeted improvement of the hydrophilic properties of membranes in order to increase their water permeability, change the surface properties, etc. [1, 2]. The degree of hydrophilicity of membranes significantly determines a number of important operational parameters, such as selectivity, efficiency, and regeneration capacity. A change in the wettability of the membranes surface can be achieved at the stage of their preparation by plasma-chemical treatment of the finished materials surface [1], deposition of additional components [2], simultaneous copolymerization of amphiphilic polymers on a porous surface, modification with thin polymer layers by Layer-by-Layer deposition (LBL), Langmuir – Blodgett (LB), spin-coating (SC) in this case without changing the membrane matrix, which is important at the point of view of preservation their mechanical and physicochemical properties [3]. The surface layer modification leads to a change in a number of their properties, namely: adsorption, selective, filtration, which makes it possible to form membranes with hydrophilic properties, which is important for wastewater treatment.

The aim of this work is development of methods for polyethyleneterephthalate ion track membranes surface modification by coatings based on polymers, amphiphilic organic compounds and analysis of their structure to improve their performance.



2. Materials and methods

To obtain the membranes, we used Hostaphan® RNK-12 polyethyleneterephthalate (PET) film, which was irradiated with ${}_{84}\text{Kr}^{15+}$ ions with an energy of 1.75 MeV/nucleon on a DC-60 heavy ion accelerator, after chemical etching in 2.2 M NaOH at 85°C membranes with pore diameters of 150 and 200 nm were obtained. The irradiation density was $1 \cdot 10^8 \text{ cm}^{-2}$. Then, chemical treatment was carried out in a sodium hydroxide solution [4].

The formation of Nafion films (Sigma-Aldrich, 5% solution (density 0.874 g/cm^3) polymer in higher aliphatic alcohols and water) carried out by LB and SC methods. The surface pressure of the LB-film formation was 25mN/m, which corresponds to the phase state of the Langmuir layer “solid film” [5]. Commercial Nafion solution was diluted with 96% ethyl alcohol to 0.05% Nafion solution and 10 μL was dropped onto the surface of a rotating substrate at a speed of 3000 rpm for 2 min to form films by SC method.

The membranes were treated in low-temperature plasma of a dielectric barrier discharge (PDBD) for cleaning and activation of their surface before the modification. Processing in PDBR was carried out for 30 sec to prevent the destruction of the polymer film. The power of the plasma source is 10–30 W. Distance from source to sample 15 mm [6].

The surface modification of PETF TM with coatings based on chitosan (Chit) and the sodium salt of dextran sulfate (DS) was carried out by the LBL method using Chit solutions ($M_w \sim 310\text{--}375 \text{ kDa}$, concentration in 1 wt.% aqueous solution of acetic acid is of 1 mg/ml) and DS ($M_w \sim 500 \text{ kDa}$, concentration in water is of 1 mg / ml). The cycle of formation of the Chit/DS bilayer consisted of: immersion of PET TM for 3 min in Chit solution; washing in 1 wt.% acetic acid solution for 2 min; air drying for 10 min; immersion of PET TM, modified with a Chit layer in a DS solution for 3 min; then washing in water for 2 min and air drying for 10 min. The procedure for the formation of the Chit/DS bilayer repeated 4 times in the aim of increasing the uniformity coating and of the charge distribution over the TM surface.

To control the change in the hydrophilic properties of the membrane surface, the values of the contact angles (CA) were measured on a DSA 100E device (KRUSS, Germany) by the sessile drop method. Distilled water and diiodomethane (Sigma-Aldrich, 99% pure) were used as test liquids. The values of the free surface energy (γ) and its specific polar component (γ^p) were calculated based on the CA values using the Owens, Wendt, Rabel and Kaelble method.

The structure of the membrane surface was studied using an atomic force microscopy (AFM, NT-206, ODO “Microtestmashines”, Belarus) method with standard FMG 01_SS silicon cantilevers (TipsNano, Estonia), with a force constant of 3 N/m and a radius of curvature of no more than 10 nm. The pore diameter of PET membranes before and after modification were measured using surface topography by plotting the profile on the line of surface scan. The average values were calculated for 15 randomly selected pores.

The performance measured at a pressure of 900 mbar. To create a pressure difference, a vacuum pump LVS 210 T was used. Distillation water, chloroform and o-xylene used as test liquids. The measurement of effective pore diameter provided by gas permeability method at pressure difference of 20 kPa.

IR spectra of the studied samples were recorded on an Infracum FT-08 spectrophotometer using an ATR-GladiATR (PIKE) ATR attachment, in the range $400\text{--}4000 \text{ cm}^{-1}$, resolution 2 cm^{-1} , number of scans 25.

3. Results and discussion

On the base of the research by the AFM-method, it was shown that the pore diameter, the values of the arithmetic mean (R_a) and root-mean-square roughness (R_q) of the modified TM surface change insignificantly within the confidence interval (figure 1). However, the values of pore diameter measured by gas permeability were decreased on 50 nm compared with initial PET membranes, that is associated with methodological features of two used methods.

For membranes modified of the (Chit/DS)₄ system by LBL method, the R_a and R_q values increase from 7.5 and 14.2 nm (for the initial TM) to 11.0 and 19.1 nm, respectively, due to the presence of conglomerates from 200 to 400 nm on the membrane surface. The uniformity of the coating achieved by increasing the number of polymer layers on TM surface applied by LBL method; however, this can lead to the presence of Chit and / or DS compounds in the depth of the pores.

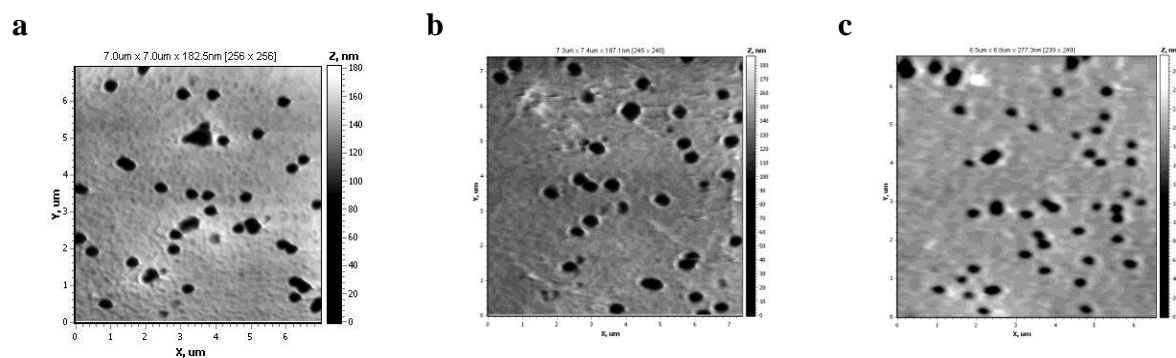


Figure 1. AFM-images of TM surface, scan area 7x7 μm : PET-200 (a), PET-200/Nafion (b), PET-200/(Chit/DS)₄ (c).

The presence of compounds using for PET TM modification on their surfaces has been confirmed by IR-method. For multilayers coatings Chit/DS new peaks appear at 1438 cm^{-1} (CH, CH₂OH), 1614 cm^{-1} (C = O amide I), 1579 cm^{-1} (NH amide II) are shown. A redshift of the band of amide I from 1644 to 1614 cm^{-1} observed, which probably indicates the formation of a hydrogen bond between chitosan and dextran. In the IR spectrum of sample PET/Nafion, we observed the appearance of peaks at 646 cm^{-1} (C-S), 519 cm^{-1} (O-S-O), 1221 cm^{-1} (C-F).

The modification of the PET TM coating (Chit/DS)₄ by the LBL and Nafion by the LB and SC methods allow to improve the hydrophilicity of the membranes (table 1), possibly by increasing the polar groups on the surface.

Table 1. The values of contact angle of initial and modified PET TM.

Sample	Initial TM	Contact angle		
		Nafion	(Chit/DS) ₄	
		LB	SC	LBL
PET TM-150	50°	51°	40°	41°
PET TM -200	51°	37°	43°	32°

Additionally, the values of the specific surface energy of the modified membranes with the best hydrophilization properties were estimated. It was shown that the values of γ as a result of modification don't change compared to the initial membranes (table 2), but its polar component increases, which is correlated with an increase in the number of hydrophilic groups on the PET TM surface.

The most stable coating is (Chit/DS)₄ multilayers. On PET TM with pore diameters of 200 nm, after holding in distilled water for two days and subsequent drying in air, the CA increased to 37°. The pore diameter of the TM samples modified with (Chit/DS)₄ after exposure to water does not change, which indicates about stability of the layers on the membrane surface under these conditions. However, in the case of Nafion modification for the samples kept in water, a significant increase in the CA values to 77° was established, which is probably associated with the swelling of the coating.

Table 2. The specific surface energy (γ) and its polar component γ^p , the value of the flux (J) of initial and modified PET TM.

Sample	γ , mJ/m ²	γ^p , mJ/m ²	J , ml/(m ² sec)		
			water	chloroform	o-xylene
PET-200	63.2	15.9	11.0±2.0	21.0±1.0	20.0±3.0
PET-200/Nafion, SC	63.2	23.2	9.5±0.5	15±1.0	9.5±0.6
PET-200/(Chit/DS) ₄ , LBL	66.5	24.4	8.0±0.5	10.0±0.5	8.0±0.4

Accordingly the results of filtration it was shown, that the values of performance by water of modified membranes by (Chit/DS)₄-multilayers and by Nafion-monolayer have not changed within experimental error (Table 2). In the case of filtration chloroform and o-xylene the values of the flux decreased from 1.5-2.0, that is results hydrophilic properties of modified PET membranes. It should be noted, that the values of the flux by organic solvent in twice as much for the initial membranes. Data of flux are correlating with the changes of polar component of specific surface energy – if the polar component increases (hydrophilic properties is increase), the flux by organic solvent increases. The modified membranes can used for filtration straight type emulsion oil in water.

4. Conclusions

It was shown that thin layers (Chit/DS)₄ and Nafion formed on the surface of PET TM by LBL and spin-coating methods, respectively, increase the hydrophilicity of the surface, which will reduce membrane contamination during filtration of oil-in-water emulsions, proteins solutions, and also to prevent surface at biofouling.

Acknowledgments

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