Весці Нацыянальнай акадэміі навук Беларусі. Серыя фізіка-тэхнічных навук. 2023. Т. 68, №3. С. 234–241
Proceedings of the National Academy of Sciences of Belarus. Physical-technical series, 2023, vol. 68, no. 3, pp. 234–241

ISSN 1561-8358 (Print)
ISSN 2524-244X (Online)
https://doi.org/10.29235/1561-8358-2023-68-3-234-241
UDC 678

Original article

Galina B. Melnikova[1,3*], Aliaxander E. Salamianski[2], Tatyana N. Tolstaya[1], Victorya M. Akulova[2], Sergei A. Chizhik[1], Ilya V. Korolkov[3,4,5], Indira B. Muslimova[3,4], Nurdaulet N. Zhumanazar[3,4], Maxim V. Zdorovets[3,4,5]

[1]A. V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, 15, P. Brovka Str., 220072, Minsk, Republic of Belarus
[2]Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus, 36, F. Skaryna Str., 220141, Minsk, Republic of Belarus
[3]L. N. Gumilyov Eurasian National University, 2, Satbaev Str., 1000, Astana, Republic of Kazakhstan
[4]The Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan, 1, Ibragimov Str., 050032 Almaty, Republic of Kazakhstan
[5]Ural Federal University, 19, Mira Str., 620002, Ekaterinburg, Russian Federation

HYDROPHOBIZATION OF PETF-SURFACES FOR WATER-IN-OIL EMULSIONS SEPARATIONS

Abstract. The technique of poly(ethylene terephthalate) track-etched membranes (PETF TMs) modification to increase of water-in-oil emulsions separations is developed. The water-in-oil emulsions separations by using PETF TMs with regular pore geometry and pore sizes 200 and 350 nm is described in the article. PETF TMs were modified with octadecyltrichlorosilane by spin-coating method to increase their hydrophobic properties. The results of changes in the pore diameters and the contact angle after PETF TMs modification are presented. The obtained samples were characterized by AFM, SEM and gas-permeability test. Chloroform–water and n-hexadecane–water emulsions have been used as a test liquid for water-in-oil emulsions separations. At an operating vacuum of 700 mbar, the specific filtration performance of chloroform: water emulsions were 51.5 and 932.0 l/(m^2 · h), hexadecane: water were 46.1 and 203.4 l/(m^2 · h) for PETF-200 / OTS and PETF-350 / OTS, respectively. The degree of purification of emulsions by modified membranes according to the refractive index is of 100 %. Obtained membranes can be used to separate oil-water emulsions in order to prevent the corrosion of pipelines and changes of crude oil viscosity, as well as the treatment of water purification from oil industry waste.

Keywords: track-etched membranes, octadecyltrichlorosilane, atomic force microscopy, contact angle, free surface energy, hydrophobicity

Acknowledgements: the work was carried out within the framework of the Belarusian Republican Foundation for Fundamental Research (grant no. T22MS-029) and the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (grant no. AP09 057 934).

Conflict of interest: the authors declare that there is no conflict of interest.

Information about the authors: *Galina B. Melnikova*[*] – Cand. Sci. (Engineering), Associate Professor, Senior Researcher at A. V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus. https://orcid.org/0000-0003-4891-7523. E-mail: galachkax@gmail.com; *Aliaxander E. Salamianski* – Cand. Sci. (Chemistry), Leading Researcher at Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus. https://orcid.org/0000-0001-8355-8867. E-mail: solasy@gmail.com; *Tatyana N. Tolstaya* – Researcher at A. V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus. E-mail: tolstaya.tn@yandex.ru; *Victorya M. Akulova* – Junior Researcher at Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus. https://orcid.org/0000-0003-3883-2921. E-mail: SinSagi@outlook.com; *Sergei A. Chizhik* – Academician of the National Academy of Sciences of Belarus, Dr. Sci. (Engineering), Professor, Chief of the Laboratory of Nanoprocesses and Technologies at A. V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus. https://orcid.org/0000-0002-5301-0195. E-mail: chizhik_sa@tut.by; *Ilya V. Korolkov* – Ph. D. (Chemistry), Associate Professor, Senior Researcher of the Technological Laboratory of Track-Etched Membrane at Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan. https://orcid.org/0000-0002-0766-2803. E-mail: i.korolkov@inp.kz; *Indira B. Muslimova* – Master of Chemistry, Researcher of the Technological Laboratory of Track-Etched Membrane at Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan. https://orcid.org/0000-0002-0923-5506. E-mail: bazarbaykyzy@list.ru; *Nurdaulet N. Zhumanazar* – Master of Chemistry, Engineer of the Technological Laboratory of Track-Etched Membrane at Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan. E-mail: nurdauletzhumanazar@gmail.com;

[*] Corresponding author / Автор, ответственный за переписку.

Maxim V. Zdorovets – Cand. Sci. (Physics and Mathematics), Professor, Director of the Astana Branch at Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan. https://orcid.org/0000-0003-2992-1375. E-mail: mzdorovets@inp.kz

Contribution of the authors: *Galina B. Melnikova* – concept description, experimental research design, research planning, data collection and systematization, comparative analysis, manuscript text writing; *Aliaxander E. Salamianski* – prepare the techniques of modification membranes; *Tatyana N. Tolstaya* – analysis and synthesis of literature data; *Victorya M. Akulova* – prepare samples of modification; *Sergei A. Chizhik* – interpretation of research results, manuscript text editing; *Ilya V. Korolkov* – instrumental research, data collection and systematization, manuscript text editing; *Indira B. Muslimova* – prepare of PERT TMs; *Nurdaulet N. Zhumanazar* – work with graphic material; *Maxim V. Zdorovets* – formulation of conclusions.

For citations: Melnikova G. B., Salamianski A. E., Tolstaya T. N., Akulova V. M., Chizhik S. A., Korolkov I. V., Muslimova I. B., Zhumanazar N. N., Zdorovets M. V. Hydrophobization of PETF-surfaces for water-in-oil emulsions separations. *Vestsi Natsyyanal'nai akademii navuk Belarusi. Seryya fizika-tekhnichnykh navuk = Proceedings of the National Academy of Sciences of Belarus. Physical-technical series*, 2023, vol. 68, no. 2, pp. 234–241. https://doi.org/10.29235/1561-8358-2023-68-2-234-241

Received: 02.05.2023
Approved for publication: 07.09.2023
Signed to the press: 21.09.2023

Оригинальная статья

Г. Б. Мельникова[1,3*], А. Е. Соломянский[2], Т. Н. Толстая[1], В. М. Акулова[2], С. А. Чижик[1], И. В. Корольков[3,4,5], И. Б. Муслимова[3,4], Н. Н. Жуманазар[3,4], М. В. Здоровец[3,4,5]

[1]Институт тепло- и массообмена имени А. В. Лыкова Национальной академии наук Беларуси, ул. П. Бровки, 15, 220072, Минск, Республика Беларусь
[2]Институт химии новых материалов Национальной академии наук Беларуси, ул. Ф. Скорины, 36, 220141, Минск, Республика Беларусь
[3]Евразийский национальный университет имени Н. Гумилева, ул. Сатбаева, 2, 1000, Астана, Республика Казахстан,
[4]Институт ядерной физики Министерства энергетики Республики Казахстан, ул. Ибрагимова, 1, 050032, Алматы, Республика Казахстан
[5]Уральский федеральный университет, ул. Мира, 19, 620002, Екатеринбург, Российская Федерация

ГИДРОФОБИЗАЦИЯ ПЭТФ-ПОВЕРХНОСТЕЙ ДЛЯ РАЗДЕЛЕНИЯ ЭМУЛЬСИЙ ТИПА «ВОДА В МАСЛЕ»

Аннотация. Разработана модификация поли(этилентерефталатных) трековых мембран (ПЭТФ ТМ) для увеличения разделения водомасляных эмульсий. Описано разделение эмульсий типа «вода в масле» с использованием ПЭТФ ТМ с правильной геометрией пор и размером пор 200 и 350 нм. Мембраны модифицированы октадецилтрихлорсиланом методом спин-коатинга для повышения их гидрофобных свойств. Представлены результаты изменения диаметров пор и угла смачивания после модификации ПЭТФ ТМ. Структура образцов изучена методами атомно-силовой и сканирующей электронной микроскопии. Методом газопроницаемости определен размер пор мембран. Эмульсии хлороформ–вода и н-гексадекан–вода использовали в качестве тестовой жидкости для разделения эмульсий типа «вода в масле». При вакууме 700 мбар удельные показатели фильтрации эмульсий хлороформ : вода составляли 51,5 и 932,0 л/(м^2·ч), гексадекан : вода – 46,1 и 203,4 л/(м^2·ч) для ПЭТФ-200/ОТС и ПЭТФ-350/ОТС соответственно. Степень очистки эмульсий модифицированными мембранами по показателю преломления составила 100 %. Полученные трековые мембраны могут применяться для разделения водонефтяных эмульсий с целью предотвращения коррозии трубопроводов и изменения вязкости нефти, а также при очистке воды от отходов нефтяной промышленности.

Ключевые слова: трековые мембраны, октадецилтрихлорсилан, атомно-силовая микроскопия, угол смачивания, свободная поверхностная энергия, гидрофобность

Благодарности: работа выполнена в рамках гранта Белорусского республиканского фонда фундаментальных исследований (грант № Т22МС-029) и гранта Комитета науки Министерства образования и науки Республики Казахстан (грант № AP09057934).

Конфликт интересов: авторы заявляют об отсутствии конфликта интересов.

Информация об авторах: *Мельникова Галина Борисовна*[*] – кандидат технических наук, доцент, старший научный сотрудник Института тепло- и массообмена имени А. В. Лыкова Национальной академии наук Беларуси. https://orcid.org/0000-0003-4891-7523. E-mail: galachkax@gmail.com; *Соломянский Александр Ефимович* – кандидат химических наук, доцент, ведущий научный сотрудник Института химии новых материалов Национальной академии наук Беларуси. https://orcid.org/0000-0001-8355-8867. E-mail: solasy@gmail.com; *Толстая Татьяна Николаевна* – научный сотрудник Института тепло- и массообмена имени А. В. Лыкова Национальной академии наук Беларуси. E-mail: tolstaya.tn@yandex.ru; *Акулова Виктория Максимовна* – младший научный сотрудник Института химии новых материалов Национальной академии наук Беларуси. https://orcid.org/0000-0003-3883-2921. E-mail: SinSagi@out-

look.com; *Чижик Сергей Антонович* – академик Национальной академии наук Беларуси, доктор технических наук, профессор, заведующий лабораторией нанопроцессов и технологий Института тепло- и массообмена имени А. В. Лыкова Национальной академии наук Беларуси. https://orcid.org/0000-0002-5301-0195. E-mail: chizhik_sa@tut.by; *Корольков Илья Владимирович* – кандидат химических наук, доцент, старший научный сотрудник технологической лаборатории трековых мембран Института ядерной физики Министерства энергетики Республики Казахстан. E-mail: i.korolkov@inp.kz; *Муслимова Индира Базарбаевна* – магистр химических наук, научный сотрудник технологической лаборатории трековых мембран Института ядерной физики Министерства энергетики Республики Казахстан. https://orcid.org/0000-0002-0923-5506. E-mail: bazarbaykyzy@list.ru; *Жуманазар Нурдаулет Нуртайулы* – магистр химических наук, инженер технологической лаборатории трековых мембран Института ядерной физики Министерства энергетики Республики Казахстан. E-mail: nurdauletzhumanazar@gmail.com; *Здоровец Максим Владимирович* – кандидат физико-математических наук, профессор, директор филиала в г. Астана Института ядерной физики Министерства энергетики Республики Казахстан. https://orcid.org/0000-0003-2992-1375. E-mail:mzdorovets@inp.kz

Вклад авторов: *Мельникова Галина Борисовна* – обоснование концепции, разработка дизайна экспериментального исследования, написание текста рукописи; *Соломянский Александр Ефимович* – разработка методики модификации мембран; *Толстая Татьяна Николаевна* – анализ и обобщение данных литературы; *Чижик Сергей Антонович* – интерпретация результатов исследования, редактирование текста рукописи; *Корольков Илья Владимирович* – проведение инструментальных исследований, сбор и систематизация данных, редактирование текста рукописи; *Акулова Виктория Максимовна* – проведение модификации образцов; *Муслимова Индира Базарбаевна* – подготовка ПЭТФ трековых мембран; *Жуманазар Нурдаулет Нуртайулы* – работа с графическим материалом; *Здоровец Максим Владимирович* – формулировка выводов.

Для цитирования: Гидрофобизация ПЭТФ-поверхностей для разделения эмульсий типа «вода в масле» / Г. Б. Мельникова [и др.] // Вес. Нац. акад. навук Беларусі. Сер. фіз.-тэхн. навук. – 2023. – Т. 68, № 3. – С. 234–241. https://doi.org/10.29235/1561-8358-2023-68-3-234-241

Поступила в редакцию: 02.05.2023
Утверждена к публикации: 07.09.2023
Подписана в печать: 21.09.2023

Introduction. According to UNESCO data the pollution of wastewater with oil products is the ten numbers of dangerous. The separation of water-in-oil emulsions is also important in particular for prevention the corrosion of pipelines and changes of crude oil viscosity [1]. The wettability of membranes is a key property that determines the separation of an oil/water emulsion. The membrane performances in contact with liquid depend on surface energy, pore size, pore density and roughness [2]. Track-etched membranes (TMs) have a record narrow pore size distribution. Modification of their surface in order to regulate wettability can improve properties of separation water/oil emulsions or gases [3]. The most of the above polymers, membranes have oleophilic properties [4], but the actual problem is their modification in order to form surfaces with controlled wettability. Regulation of the membrane surface wettability is achieved both by physical methods, by modifying the surface layer, and by chemical methods, at the stage of obtaining membranes [5]. The modification of TMs surfaces allows formation of hydrophobic properties and significantly expands the area of their possible application due to a significant change in the surface characteristics of membranes, hydrophilic properties and the possibility of changing the pore size under the influence of external conditions.

Superhydrophobic-superoleophilic membranes allow oil droplets from an oil/water emulsion to wet the membrane surface and pass through the pores without passing water. However, the surfaces of membranes intended for the separation of water/oil emulsions are easily polluted and the pores are clogged with oils, since it is not yet possible to achieve the limiting requirements for oleophilic properties. Oil contaminants due to the high viscosity are difficult to remove and affect the separation performance of the membranes when they are reused. Currently, to clean water sources from accidental oil spills, membranes are used that separate oil pollution in the aqueous phase (membranes operating under water) [6]. The use of materials with low surface energy and hierarchical micro/nanostructure can contribute to the formation of superhydrophobic surfaces [7–9]. In addition, it is possible to change the properties of the medium (pH, temperature, exposure to light, the influence of electric and magnetic fields) to expand the spectrum of separable impurities [8]. Janus membranes are an emerging class of materials with opposite properties at the interface. Most of them are asymmetric in terms of wettability: one side has superhydrophilic properties (to protect against oil fouling), while the other side has superhydrophobic properties (self-cleaning) [10]. Polymeric materials (for example, polyacrylonitrile, polyvinylidene fluoride, polyethersulfone, polyvinyl alcohol, polyvinyl chloride, polyethylene, polypropylene, polyamide, chitosan, etc.) [2, 10, 11] are of the most interest in the field of filtration and separation membranes due to their mechanical strength, chemical stability and elasticity.

Existing methods used to fabricate PTFE membranes and PTFE-modified materials are either limited by complex manufacturing equipment or relatively expensive, and are also not applicable to modifying substrates. To solve these problems, *Asadi et al.* [12] used the Layer-by-Layer method: this is an inexpensive method that allows the formation of multifunctional coatings of controlled thickness at the nanoscale on almost any substrate.

Another method for the production of superhydrophobic-superoleophilic or superoleophobic-superhydrophilic porous materials for separation of oil and water emulsions is the laser ablation method, which forms micro-/nano-sized structures with a certain roughness and increases the contact angle to 155.5° ± 1.5° without chemical modification [13].

One of the widely used methods for the formation of hydrophobic and superhydrophobic nanoscale coatings on the surface of a porous substrate is the method of electron beam dispersion of polymers in vacuum [14].

For water filtration PETF TMs membranes are often used. The resistance to oil population is an important criterion for membranes used for oil/water emulsion separation, since oil can easily accumulate on the top surface of the membranes, resulting in a significant reduction in flow.

In addition, there is a limited number of studies in the literature devoted to establishing a relationship between the membrane morphology and physicochemical phenomena occurring on the membrane surface [15]. A correlation was established between membrane surface roughness factors, pore diameters, and membranes with high surface porosity, low microroughness, relatively high tortuosity and a small radius of pore curvature in depth, wide and relatively dense and evenly distributed density surface features, "defects" (understood as fibers, knots or even pores) are most preferred in the formation of hydrophilic/oleophobic membranes [16, 17].

In this article, we present the results of PETF TMs hydrophobization by octadecyltrichlorosilane via simple spin coating method. Prepared hydrophobic PETF TMs were tested in separation of chloroform–water and hexadecane–water emulsions.

Materials and Methods. In the work, polyethylene terephthalate track-etched membranes (PETF TMs) were obtained by the Astana branch of the Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan. To obtain membranes, a PETF film of the trademark Hostaphan® RNK-12 was used, which was irradiated with $^{84}Kr^{15+}$ ions with an energy of 1.75 MeV/nucleon at a DC-60 heavy ion accelerator; the irradiation density was $1 \cdot 10^8$ cm^{-2}. After chemical etching in 2.2 M NaOH at 85 °C [18], membranes with pore diameters 200 (PET-200) and 350 nm (PET-350) were obtained.

Preparation of the coating. OTS coating (Sigma-Aldrich, 98 % purity) was formed on PETF TMs (square of the sample is of 4.9 cm^2) and silicon monocrystalline substrates (size of the sample is of 2.5 to 2.5 cm) from solution of OTS in hexane (Sigma-Aldrich, ≥ 97.0 % purity) with a concentration of 1 mM by spin-coating method. All reagents were used without additional purification.

OTS solution of volume of 1 ml was applied on substrates during 10 minutes they were centrifuged at a speed of 3000 rpm for 2 min. Then OTS-modified substrates were sequentially washed with hexane and isopropyl alcohol for 1 min to remove excess OTS inside the pores.

Silicon monocrystalline substrates (111) were previously hydrophilized in water solution of hydrogen peroxide and ammonium solution during 10 min at 80 °C. The volume ratio of mixture NH_3 (26.9 % water solution) : H_2O_2 (30.8 % water solution) : distilled water is of 1 : 1 : 5 respectively.

In these experiments all reagents were used without additional purification.

Study of the surface structure and mechanical properties of PETF TM. The structure of the membrane surface was studied using an atomic force microscope (NT-206, ALC "Microtestmashiny", Belarus) using standard FMG 01_SS silicon cantilevers (TipsNano, Estonia) with average rigidity of 3 N/m (accordingly passport data) and a curvature radius of no more than 10 nm. Changes in the pore diameter of PETF membranes before and after modification were estimated from the surface topography by constructing a surface profile along the image scanning line. The average value was calculated for 15 randomly selected pores.

The structure was studied by SEM using a JEOL JSM-7500F high resolution electron microscope (Jeol, Germany) with a cold (field emission) cathode. Before the study, the samples were sputtered with gold 15–20 nm thick on a JFC-1600 magnetron.

Surface wettability analysis. The contact angles were measured using a DSA 100E (KRUSS, Germany) by the sessile drop method. Distilled water and diiodomethane (Sigma-Aldrich, 99 % pure) were used as test liquids. Based on the CA values, the free surface energy was calculated according the OWRK method, according to which the energy of the surface layer of a solid includes two components: dispersive and polar.

Filtration characteristics. The pore size (r, m) was measured by the gas permeability method at a vacuum difference of 20 kPa [18]. The effective pore sizes of the membranes were estimated by gas permeability using equation:

$$r^3 = \frac{Q \cdot 3l}{\sqrt{\frac{2\pi}{R \cdot T \cdot M}} \cdot \Delta p \cdot 4n},$$

Q – air permeability, $m^3/(c \cdot m^2)$; l – film thickness, m; Δp – applied vacuum, Pa; R – universal gas constant, J/(mol · K); M – molar mass of air, g/mol; n – irradiation density, J/m^3; T – temperature, K.

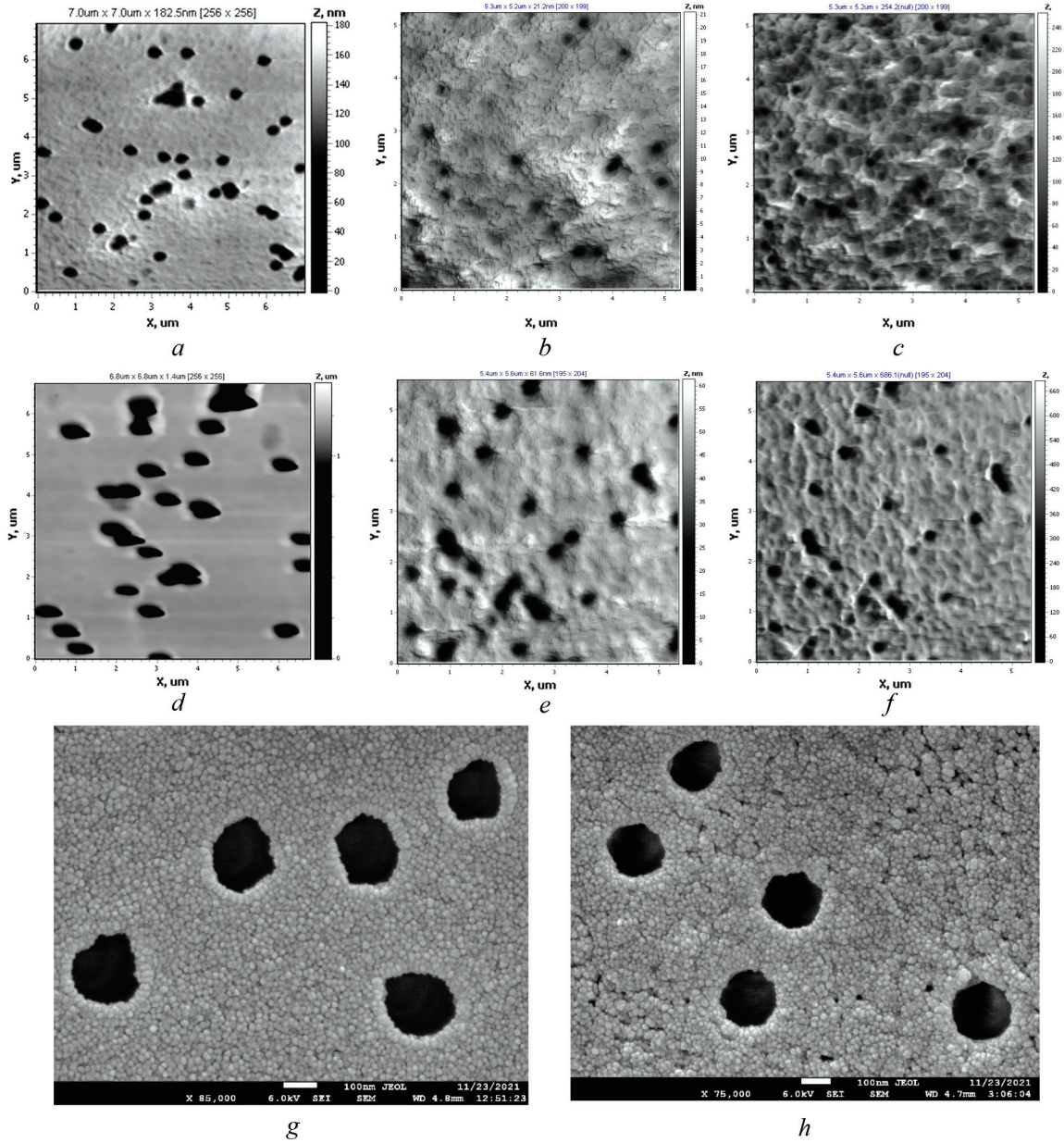

Figure 1. AFM (*a–f*) and SEM (*g*, *h*) images of the morphology of PETF TMs (*a*, *d*) and modified with OTS (*b*, *c*, *e*, *f*, *g*, *h*). PETF TMs with pore diameters 200 nm (*a–c*, *g*) and 350 nm (*d–f*, *h*), AFM Topography (*a*, *b*, *d*, *e*) and Torsion (*c*, *f*) regimes

Membrane specific performance (*J*) for water, chloroform, o-xylene and hexadecane were determined by solvent filtration at an overpressure created using an LVS 210 T vacuum pump operating vacuum of 700–900 mbar. An emulsion of chloroform (Merck, ≥ 99.9 % purity) – distilled water was prepared in a volume ratio of 9 : 1, n-hexadecane (Merck) – water in a ratio of 100 to 1. Mixing was carried out using IKA T 18 digital ULTRA-TURRAX dispersant for 3–4 min. The emulsion is a cloudy stable liquid for 2 h. Immediately after dispersion, the emulsion was passed through the membranes. The performance measurement was determined under vacuum from 900 to 700 mbar. After filtration, the refractive index of the solvent was evaluated on refractometer (Isolab GmbH).

Results and Discussion. According to AFM analyze, the differences in the structure of the modified membranes with OTS were established (Figure 1).

In the case of modifying the surface of OTS membranes, the pore diameter for PETF-200 membranes does not change, for PETF-350 – it decreases by 1.5–2 times. The arithmetic mean roughness, R_a, decreased by 2 and 1.5 times for PETF-200 and for PETF-350, consequently (Table 1), the root mean-square roughness values change more significantly: R_q decreased by 3.6 and 1.8 times for PETF-200 and for PETF-350, consequently.

T a b l e 1. **The values of roughness of the modified TM surfaces**

Roughness, nm	PETF-200		PETF-350	
	initial	OTS	initial	OTS
R_a	7.5	3.1	6.2	4.3
R_q	14.2	3.9	11.4	6.8

Gas permeability results and changes of pore size also confirm formation of OTS coating on PETF TMs surfaces (Table 2). Based on this, it can be concluded that the main contribution to the formation of the hydrophobic properties of the surface is made by the nature of modifier layer on PETF TM surface.

T a b l e 2. **Gas permeability results**

Sample	Average effective pore diameter by gas permeability, nm	Diameter of the largest pore, nm
PETF-200	201 ± 9	695 ± 63
PETF-350	354 ± 13	821 ± 73
PETF-200/OTS	127 ± 10	737 ± 15
PETF-350/OTS	286 ± 10	900 ± 50

The changes of the above parameters after modification indicated the formation of a uniform coating, as well as enveloping the membrane pore boundaries with a layer of modifier. The results of hydrophilic properties are presented in Table 3.

T a b l e 3. **Contact angle (CA), specific surface energy (*w*) and polar component of surface energy (γ^p) for hydrophobized membranes**

Sample	Water CA	*w*, mJ/m^2	γ^p, mJ/m^2
PETF-200 (350)	51.0°	63.2	15.86
PETF-200/OTS	99.0°	45.9	0.02
PETF-350/OTS	100.0°	45.1	0.10

Accordingly, the OTS formed more hydrophobic layer on silicon substrate. The diiodomethane CA for PETF TM modified with OTS changed from 49◦ to 9◦ within 1 min, which was due to the passage of a liquid drop through the membrane pores. The low values (γ^p) of the polar component of the specific surface energy for the PETF-200/OTS samples should be noted, which indicates an increase in the oleophilicity of the surface.

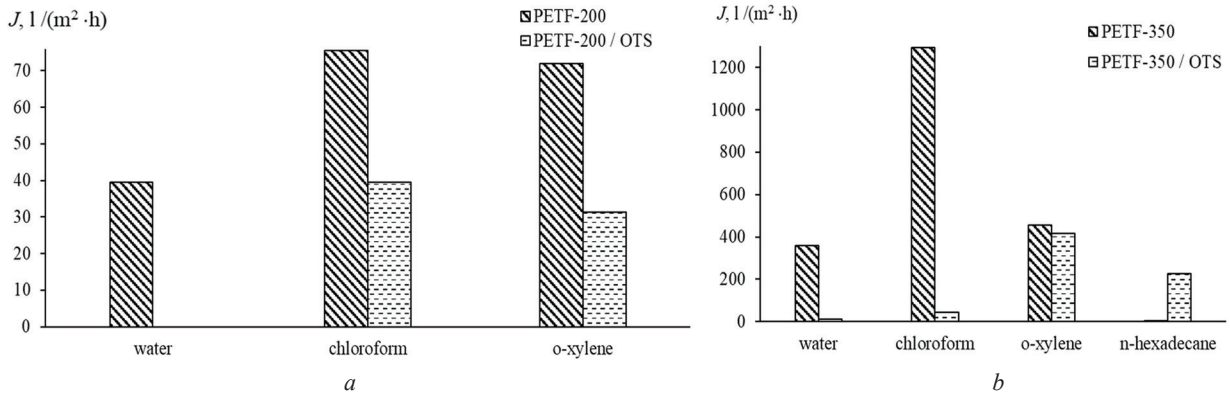

Figure 2. The performance values (*J*) for water, o-xylene and chloroform and n-hexadecane of initial and modified PETF TMs with OTS at operating vacuum 900 mbar; diameters of pores: *a* – 200 nm, *b* –350 nm

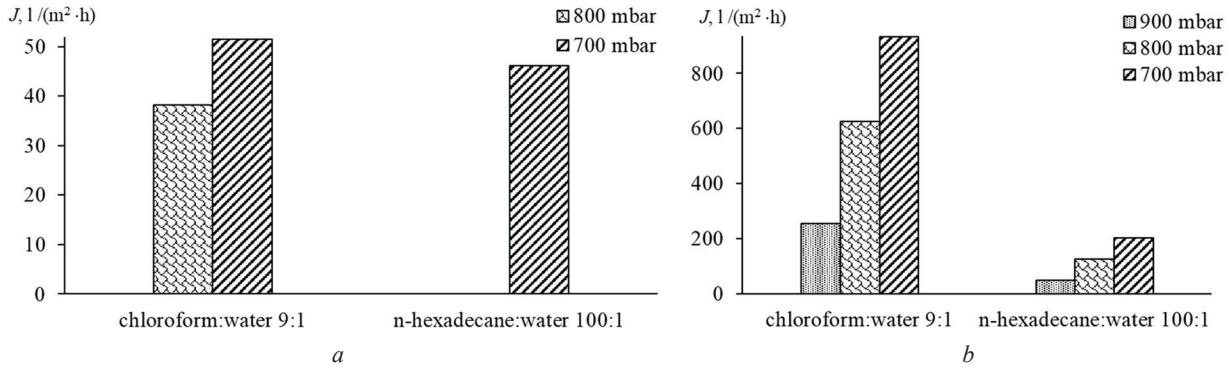

Figure 3. Results of filtration performance of chloroform and hexadecane emulsions in water with PETF-200/OTS (*a*) and PETF-350/OTS (*b*) membranes at difference operating vacuum

PETF TMs performance results. For PETF TMs with a pore diameter of 350 nm the performance values (*J*) for water, o-xylene and chloroform and n-hexadecane are significantly higher (Figure 2, *b*) compared to membranes with a pore diameter of 200 nm (Figure 2, *a*), which is due to the larger pore diameters. For hexadecane, the J values for PETF-200 are close to zero.

It should be noted that a change in vacuum to 800 mbar makes it possible to increase the performance for water of PETF-200 membranes from 0 to 7.9 l/(m^2 · h).

The performance of n-hexadecane (n-hexadecane is a non-polar liquid, the surface tension of which is less than that of most technical oils) for the original membranes is close to zero. The modified membranes filter this solvent, the values J of the membranes modified with OTS are found in the range from 38.2 to 51.5 l/(m^2 · h) at a vacuum of 900 to 600 mbar, respectively. These coatings are promising for the separation of water-oil emulsions.

Chloroform emulsions were used as test solutions and hexadecane in water at volume ratios of 9 and 100 to 1 (Figure 3), respectively. For the original unmodified membrane with a pore diameter of 350 nm (by gas permeability) separation of the emulsion is established, but after the chloroform is filtered out, water also seeps through the pores. Performance is of 716.4 l/(m^2 · h).

An increase in filtration flow with increasing operating vacuum has been established. At a vacuum of 700 mbar, the specific filtration performance of chloroform: water emulsions were 51.5 and 932.0 l/(m^2 · h), hexadecane: water was 46.1 and 203.4 l/(m^2 · h) for PETF-200/OTS and PETF-350/OTS, respectively. The degree of purification of emulsions by modified membranes according to the refractive index is of 100 %. It has been established that for PET-350 membranes, the performance values do not change for five filtration cycles, for PETF-200 – for one cycle.

Conclusions. In this study, we have shown simple and technologically convenient method of PETF TMs hydrophobization with octadecyltrichlorosilane. Thus, the application of spin-coating meth-

od for modifying the surface of polymeric membranes, the complex of studies of surface characterization and the study of their separation selectivity and productivity made it possible to develop new membranes with improved performance properties for the separation of water-in-oil emulsions.

References

1. Xiaoming Luo, Haiyang Gong, Juhang Cao, Haoran Yin, Yaipeng Yan, Limin He. Enhanced separation of water-in-oil emulsions using ultrasonic standing waves. *Chemical Engineering Science*, 2019, vol. 203, pp. 285–292. https://doi.org/10.1016/j.ces.2019.04.002

2. Qing W. Robust superhydrophobic-superoleophilic polytetrafluoroethylene nanofibrous membrane for oil/water separation. *Journal of Membrane Science*, 2017, vol. 540, pp. 354–361. https://doi.org/10.1016/j.memsci.2017.06.060

3. Korolkov I. V., Narmukhamedova A. R., Melnikova G. B., Muslimova I. B., Yeszhanov A. B., Zhatkanbayeva Zh. K., Chizhik S. A., Zdorovets M. V. Preparation of Hydrophobic PET Track-Etched Membranes for Separation of Oil–Water Emulsion. *Membranes*, 2021, vol. 11, no. 8, p. 637. https://doi.org/10.3390/membranes11080637

4. Yuzhang Zhu, Dong Wang, Lei Jiang, Jian Jin Recent progress in developing advanced membranes for emulsified oil/water and gas separation. *NPG Asia Materials,* 2014. vol. 6, no. 5, p. e101 (11). https://doi.org/10.1038/am.2014.23

5. Chao-Hua Xue, Peng-Ting Ji, Ping Zhang, Ya-Ru Li, Shun-Tian Jia Fabrication of superhydrophobic and superoleophilic textiles for oil-water separation. *Applied Surface Science,* 2013, vol. 284, pp. 464–471. https://doi.org/10.1016/j.apsusc.2013.07.120

6. Zhongxin Xue, Shutao Wang, Ling Lin, Li Chen, Mingjie Liu, Lin Feng, Lei Jiang. A novel superhydrophilic and underwater superoleophobic hydrogel-coated mesh for oil/water separation. *Advanced Materials,* 2011, vol. 23, no. 37, pp. 4270–4273. https://doi.org/10.1002/adma.201102616

7. Padaki M., Murali R. S., Abdullah M. S., Misdan N., Moslehyani A., Kassim M. A., Hilal N., Ismail A. F. Membrane technology enhancement in oil-water separation: A review. *Desalination,* 2015, vol. 357, pp. 197–207. https://doi.org/10.1016/j.desal.2014.11.023

8. Hao-Cheng Yang, Jingwei Hou, Vicki Chen, Zhi-Kang Xu. Janus membranes: exploring duality for advanced separation. *Angewandte Chemie. Internatonal Edition*, 2016, vol. 55, no. 43, pp. 13398–13407. https://doi.org/10.1002/anie.201601589

9. Mimi Tao, Lixin Xue, Fu Liu, Lei Jiang. An intelligent superwetting PVDF membrane showing switchable transport performance for oil/water separation. *Advanced Materials,* 2014, vol. 26, no. 18, pp. 2943–2948. https://doi.org/10.1002/adma.201305112.

10. Yibin Wei, Hong Qi, Xiao Gong, Shuaifei Zhao. Specially wettable membranes for oil-water separation. *Advanced Materials Interfaces*, 2018. vol. 5, no. 23, pp. 1800576 (27). https://doi.org/10.1002/admi.201800576

11. Bassyouni M., Abdel-Aziz M. H., Zoromba M. Sh., Abdel-Hamid S. M. S. A review of polymeric nanocomposite membranes for water purification. *Journal of Industrial and Engineering Chemistry*, 2019, vol. 73, pp. 19–46. https://doi.org/10.1016/j.jiec.2019.01.045

12. Asadi A., Zinatizadeh A. A., Loosdrecht M. V. Hygienic water production in an innovative air lift bioreactor followed by high antifouling ultrafiltration membranes modified by layer-by-layer assembly. *Journal of Cleaner Production*, 2018, vol. 182, pp. 27–37. https://doi.org/10.1016/j.jclepro.2018.02.037

13. Jiale Yong, Yao Fanf, Feng Chen, Jinglan Huo, Qing Yang, Hao Bian, Guangqing Du, Xun Hou. Femtosecond laser ablated durable superhydrophobic PTFE films with micro-through-holes for oil/water separation: separating oil from water and corrosive solutions. *Applied Surface Science*, 2016, vol. 389, pp. 1148–1155. https://doi.org/10.1016/j.apsusc.2016.07.075

14. Kravets L. I., Yarmolenko M. A., Rogachev A. V., Gainutdinov R. V., Altynov V. A., Lizunov N. E. Formation of hydrophobic and superhydrophobic coatings on the surface of track membranes to create composite membranes for water desalination. *Colloid Journal*, 2022, vol. 84, no. 4, pp. 433–452. https://doi.org/10.31857/S0023291222040085

15. Ho Chia-Chi C., Zydney A. L. Theoretical analysis of the effect of membrane morphology on fouling during microfiltration. *Separation Science and Technology*, 1999, vol. 34, iss. 13, pp. 2461–2483. https://doi.org/10.1081/SS-100100785

16. Guillen-Burrieza E., Servi A., Boor S. L., Hassan A. A. Membrane structure and surface morphology impact on the wetting of MD membranes. *Journal of Membrane Science*, 2015, vol. 483, pp. 94–103. https://doi.org/10.1016/j.memsci.2015.02.024

17. Korolkov I. V., Mashentseva A. A., Guven O., Niyazova D. T., Barsbay M., Zdorovets M. V. The effect of oxidizing agents / systems on the properties of track-etched PET Membranes. *Polymer Degradation and Stability*, 2014, vol. 107, pp. 150–157. https://doi.org/10.1016/j.polymdegradstab.2014.05.008

18. Kaniukov E. Yu., Shumskaya E. E., Yakimchuk D. V., Kozlovskiy A. L., Ibragimova M. A., Zdorovets M. V. Evolution of the polyethylene terephthalate track membranes parameters at the etching process. *Journal of Contemporary Physics*, 2017, vol. 52, no. 2, pp. 155–160. https://doi.org/10.103103/S1068337217020098