Journal of Fundamental and Applied Sciences

ISSN 1112-9867

Available online at http://www.jfas.info

Research Article

Special Issue

DYNAMIC MEMBRANES OF NYLON-PTFE FOR SEPARATION OF WATER-OIL EMULSIONS

D. D. Fazullin*, G. V. Mavrin, I. A. Nasyrov, I. G. Shaikhiev

Kazan Federal University, Naberezhnye Chelny Institute

Published online: 15 February 2017

ABSTRACT

For the separation of water-oil emulsions, this paper deals with the promising methods for modifying the surface of a microfiltration membrane by applying a dynamic layer of PTFE, which allows changing the surface properties of these materials and separating efficiently water-oil emulsions. Dynamic membranes of "nylon-polytetrafluoroethylene" (nylon-PTFE) are obtained by applying polytetrafluoroethylene particles of 0.9 to 262 nm on the nylon membrane surface. An increase in the membrane contact angle measured with a distilled water drop was from 59.6º to 115.6º as a result of the applying PTFE particles on the surface of the initial membrane. It was determined that the membrane surface becomes hydrophobic after the modification. After applying a layer of PTFE on the surface of the nylon membrane, the specific productivity of the latter decreases 6 to 10 times due to the intensive accumulation of PTFE particles in the pores and surface of the membrane. It was also revealed that the specific productivity of the nylon-PTFE membrane after washing with the detergent solution recovers better as compared with the initial values than the original membrane, due to hydrophobic property of the surface. Modification of the membrane leads to an increase in the degree of removal of petroleum products from the oil-in-water emulsion up to 53%, based on the amount of PTFE applied to the surface.

Keywords: Emulsion, petroleum products, ultrafiltration, dynamic membranes, nylon, polytetrafluoroethylene.

Author Correspondence, e-mail: denr3@yandex.ru

doi: http://dx.doi.org/10.4314/jfas.v9i1s.794

1. INTRODUCTION

Wastewater containing emulsified oils and petroleum products is formed practically at all machine-building enterprises as a result of application of lubricating-cooling liquids, as well as at oil production enterprises, at large oil depots, in river and sea ports, at gas transportation enterprises.

Emulsions are characterized by high kinetic and thermodynamic stability; their purification by traditional methods such as flotation, sedimentation, coagulation, is ineffective, and in some cases even impossible.

The membrane technology is one of the most promising branches of chemical technologies, which makes it possible to separate water-oil emulsions. Membrane methods are based on the separation of homogeneous or heterogeneous mixtures consisting of two or more components by means of membranes, under the influence of the driving force applied to the system [1].

The processes of emulsion separation often involve the application of polymeric membranes with a high degree of separating ability. Disadvantages of polymer ultrafiltration membranes in the separation of water-oil emulsions are: low permeability, reduced specific productivity due to the formation of a gel layer on the surface of membranes, insufficient mechanical strength, and high operating pressure. One of the ways for solving the aforementioned shortcomings of membranes is the use of dynamic membranes.

The degree of separation in dynamic membranes is provided by the formation of a thin layer of colloidal particles formed on the surface of the substrate and in the pores of membranes by filtration of liquid through membranes containing these components [2]. Colloidal particles, neutral organic polymers, organic and inorganic polyelectrolytes are suitable for the formation of dynamic membranes. Dynamic membranes are formed on porous bases of microfiltration and ultrafiltration membranes with a pore size of 0.01 μm to 5 μm on a variety of materials such as porous metals, ceramics, polymer films [3-8].

Filtering properties of membranes are mainly determined by their polymer composition. Nylon membranes are positively charged groups that ensure enhanced binding of negatively charged molecules such as lipids [9]; they have large and hydrophilic surface [7]. PTFE-films can change their hydrophobic surface to hydrophilic by simple preliminary surface treatment with alcohols or acetone.

2. METHODS

This paper describes for the first time the method of obtaining dynamic nylon-polytetrafluoroethylene (nylon-PTFE) membranes intended for separation of waste water-oil

emulsions and oil emulsions formed as a result of petrochemical, oil-producing and machine-building industries.

The microfiltration polymer membrane made of nylon (manufacturer - "Phenex Filter Membranes", 0.45 μm pore size) was used as the initial substrate, onto which surface the dynamic layer was applied [10]. The dynamic layer was obtained by forming a semipermeable layer on the surface of the porous substrate from the suspension of suspended PTFE microparticles present in the filtered isopropanol solution in dynamic equilibrium with the solution. To prepare the suspension, PTFE powder and an anionic surfactant (ASA) were added to isopropanol. After stirring, the suspension was filtered through a "blue tape" paper filter. The percentage of PTFE in the dynamic membrane was determined by the gravimetric method by the membrane weight before and after the modification.

The particle size of the dispersed phase of the emulsions and suspensions was determined by dynamic light scattering (DLS), and the ζ potential by the phase analysis light scattering (PALS) using a NanoBrook Omni analyzer.

The wettability of the test membrane samples was measured using a Kruss DSA 20E apparatus, which allows determining the contact angle on the membrane surface wet with a distilled water drop.

A change in the surface structure of the membranes was recorded with a Jeol JSM-6390 LA scanning electron microscope.

To identify the presence of silver in modified membranes, the elemental composition of the surface was studied by X-ray fluorescence analysis using a Jeol JSM-6390 LA scanning electron microscope with an EX-230**BU energy-dispersive system.

The specific productivity and the degree of separation of the water-oil emulsion, which was calculated as the ratio of the content of petroleum products (PP) in the emulsion before and after separation, determined with the help of the KH-3 concentrate meter, was considered as the main parameters of the emulsion membrane separation.

For membrane separation, a 1% emulsion of the freshly prepared Inkam-1 coolant fluid was used as the model water-oil emulsion (WOE). During the separation of distilled water and emulsions, the applied working pressure was 0.1 MPa, the liquid temperature - 25°C.

3. RESULTS AND DISCUSSION

Figure 1 shows the distribution diagram of the particle size of the PTFE suspension dispersed phase in isopropanol.

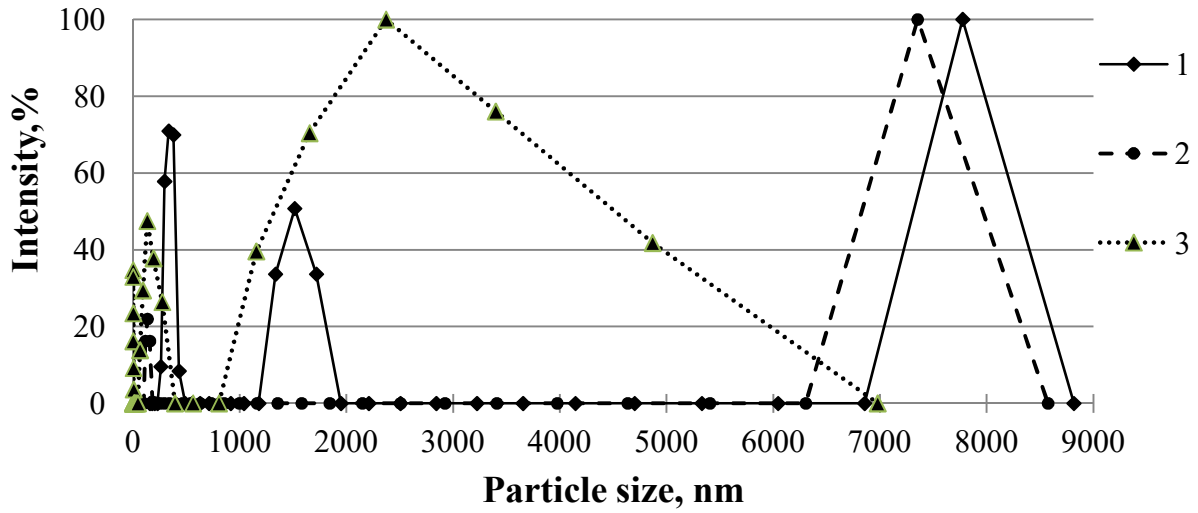

Fig.1. Distribution diagram of the particle size of the PTFE suspension dispersed phase in isopropanol (1 - PTFE in isopropanol after filtration, 2 - PTFE in isopropanol + APAV, 3 - PTFE in isopropanol + APAV).

Table 1. Average values of the particle size and the ζ-potential of the dispersed phase of the suspension.

Suspension	Particle size, nm	ζ-potential, mV
PTFE in isopropanol	>38,000	-0.11±0.01
PTFE in isopropanol after filtration through a "blue tape" paper filter	260-431; 1,336-1,718; 7,775	-0.54±0.05
PTFE in isopropanol + ASA	116-157; 7,353	-2.7±0.3
PTFE in isopropanol + ASA + filtration through a "blue tape" paper filter	0.9-5.2; 65-274; 1,155-4,870	-7.9±0.8

The particle size of the dispersed phase of the PTFE suspension in isopropanol according to Table 1 is over 38,000 nm, and after filtering the suspension through the "blue tape" paper filter, there is a decrease observed in particle size of the dispersed phase from 260 to 7,775 nm, as well as increase n the absolute value of ζ-potential of the disperse phase, and removal of large coalescent fluoroplastic particles.

To obtain a dynamic layer, the particle size of the PTFE particles in the slurry should be less than the average pore size of the nylon membrane used (450 nm). Therefore, ASA – sodium dodecyl sulfate – was added to the suspension for its dispersion. According to Fig. 1 and Table 2, after adding ASA to the suspension, there was decrease in the particle size of PTFE and an increase in the absolute value of the ζ-potential from -0.54 to -2.7 mV. And after filtering the resulting suspension through a "blue tape" paper filter, the particle size of the dispersed phase of the suspension was reduced to a range from 0.9 to 4,870 nm.

The results of the wettability of the test membrane samples are shown in Figure 2.

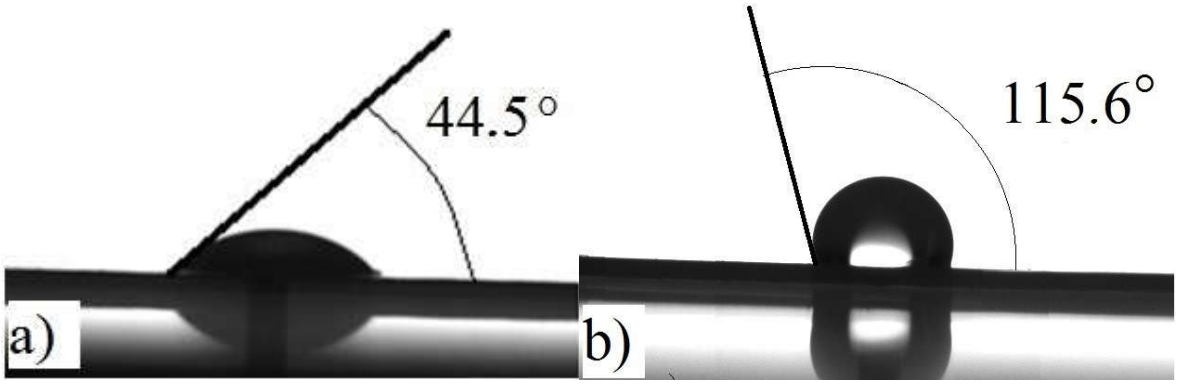

Fig.2. Images of the wettability of a drop of distilled water membrane: a) the original of nylon; b) dynamic nylon-PTFE.

As can be seen from the images in Figure 2, the application of a layer of PTFE on the surface of the nylon membrane contributes to an increase in the contact angle from 44.5º to 115.6º, which indicates an increase in the hydrophobic property of the nylon-PTFE membrane. This circumstance results from changes in the chemical structure of the surface of the modified membrane.

Table 2 shows the results of the study of the elemental surface composition of the initial and modified membranes by X-ray fluorescence analysis using a scanning electron microscope.

Table 2. Element composition of the surface of the initial and modified nylon-PTFE membranes

Element	Weight content, %	
	nylon	nylon-PTFE
Carbon (C)	43.7	45.5
Nitrogen (N)	38.3	35.3
Oxygen (O)	18.0	13.8
Fluoride (F)	-	5.4
TOTAL	100	100

After the modification of the nylon membrane by applying the PTFE dynamic layer, fluoride appeared on the membrane surface, and the carbon content also increased. In addition, it is obvious that as a result of the formation of a PTFE layer on the membrane surface, the oxygen and nitrogen content decreased.

The image of the 300 times scaled-up surface of the initial and modified membranes is shown in Figure 3.

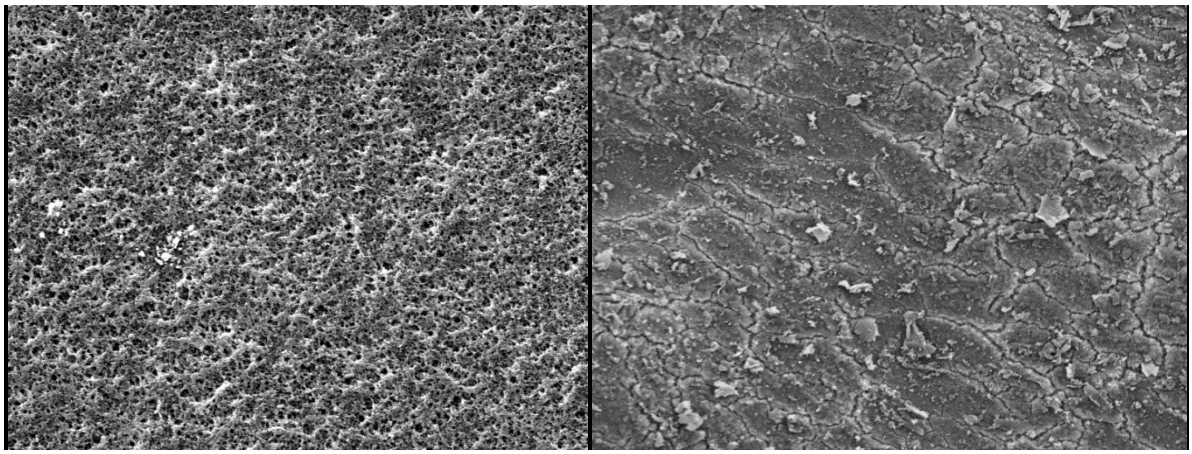

Fig.3. Morphology of the surface of the original nylon membrane increased 300 times (left) and the modified nylon-PTFE membrane increased 300 times (right).

As follows from the images, the morphology of the surface of the original membrane undergoes changes after treatment. If the initial membrane (Figure 3, left) is an aggregate of pores of 0.4 to 5 μm, then after modification, the surface of the membrane is covered with a layer of PTFE with 0.01 to 0.2 μm wide cracks throughout the surface. It is also obvious that the pore size after modification decreased.

The specific productivity of the initial and dynamic nylon-PTFE membrane was determined for distilled water and for 1% WOE (Table 3).

Table 3. Specific productivity of membranes

Membrane	PTFE content, % (by weight)	Specific productivity of membranes, $cm^3/cm^2 \cdot min$	
		for distilled water	for 1% WOE
Nylon	-	9.3	0.27
Nylon-PTFE	2.3	1.5	0.12
Nylon-PTFE	5.5	0.6	0.05

After applying a layer of PTFE on the surface of the nylon membrane, the specific productivity of the latter decreases 6 to 10 times due to the intensive accumulation of PTFE particles in the pores and surface of the membrane, and an increase in the PTFE content in the membrane results in a decrease in the specific membrane productivity. The maximum productivity of the initial and dynamic membranes is observed when flowing distilled water through the membranes.

To recover the initial productivity of the membranes after filtering the 500 cm^3 emulsion, the membranes were backwashed with a 5% solution of sodium dodecyl sulfate and then rinsed with distilled water.

It is determined that, on average, the specific productivity of the initial membrane was 90% recovered from the original values, and the specific productivity of the dynamic membrane of nylon-PTFE - 96%, due to the hydrophobic surface.

The obtained nylon-PTFE dynamic membranes are similar in the specific performance to the polysulfonamide membranes "UPM-100" (0.02-0.07 $cm^3/cm^2 \cdot min$) [11] and cellulose acetate membranes "UAM-150" (0.09 $cm^3/cm^2 \cdot min$) [12].

The results of the emulsions from petroleum products separation are shown in Table 4.

Table 4. Degree of separation of petroleum products from 1% water-oil emulsion

Membrane	PTFE content, % (by weight)	Concentration of petroleum products, mg/dm^3		Purification degree, %
		initial	purified	
Nylon	-	11,070±1,107	6,910±680	37.6
Nylon-PTFE	2.3		3,041±304	72.5
Nylon-PTFE	5.5		1,012±101	90.9

As can be seen from Table 4, the degree of removal of petroleum products from the emulsion when using the original nylon membrane is significantly lower than in the separation with the use of the dynamic nylon-PTFE membranes. After applying the PTFE layer, the surface and pores of the nylon membrane were coated with polytetrafluoroethylene particles of 0.9 to 262 nm, the pore size decreased, which is confirmed by the reduced specific productivity of the modified membranes and the increased degree of separation of petroleum products from the 1% WOE up to 53%.

4. CONCLUSIONS

Dynamic membranes of "nylon-polytetrafluoroethylene" (nylon-PTFE) are obtained by applying polytetrafluoroethylene particles of 0.9 to 262 nm on the nylon membrane surface. An increase in the membrane contact angle measured with a distilled water drop was from 59.6º to 115.6º as a result of modifying the surface of the initial membrane. It was determined that the membrane surface becomes hydrophobic after the modification. After applying a layer of PTFE on the surface of the nylon membrane, the specific productivity of the latter decreases 6 to 10 times due to the intensive accumulation of PTFE particles in the pores and surface of the membrane. Modification of the membrane leads to an increase in the degree of removal of petroleum products from the oil-in-water emulsion up to 53%, based on the amount of PTFE applied to the surface.

5. ACKNOWLEDGEMENTS

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

6. REFERENCES

1. Cheryan M., Rajagopalan N. Membrane processing of oily streams. Wastewater treatment and waste reduction. Journal of Membrane Science,1998, Vol. 151, № l. P. 13-28.

2. Dukhin S.S., Knyaz'kova T.V. Kolloidnyi zhurnal. 1980. V. 42. №. 1. P. 31 – 42.

3. Rudenko L.I. Research adsorbent properties of silicon yerhanichnoho “KREOSORB” / Rudenko L.I., Dzhuzha O.V., Khan V.E., Koval'chuk S.I. / Reports of the National Academy of Sciences of Ukraine. 2007. № 6. P. 139 – 143.

4. Savitskaya T.A. Dynamic Membranes based on poly (N-isopropylacrylamideco-heptadecyl vinyl ketone): preparation and properties / Savitskaya T.A., Epshtein O.L., Kulinkovich O.G. / Colloid J. 2000. № 62. P. 746–750.

5. Eduardo F. Barbosaa. Nanoscale characterization of synthetic polymeric porous membranes: Scrutinizing their stiffness, roughness, and chemical composition / Eduardo F. Barbosaa, Luciano P. Silva / Journal of Membrane Science. 2012. Vol. 408. P. 128–135.

6. Wagner E.M.V. Freeman Surface modification of commercial polyamide desalination membranes using poly(ethylene glycol) diglycidyl ether to enhance membrane fouling resistance / E.M.V. Wagner, A.C. Sagle, M.M. Sharma, Y.H. La, B.D. Freeman Journal of Membrane Science. 2012. Vol. 367. P. 273–287.

7. Ulbricht M. Advanced functional polymer membranes. / M. Ulbricht / Polymer. 2006. Vol. 47. P. 2217–2262.

8. Fazullin, D.D. Separation of petroleum products from aqueous emulsion sewage using a modified nylon–polyaniline membrane. / Fazullin, D.D., Mavrin, G.V., Shaikhiev, I.G., Haritonova, E.A. / Petroleum Chemistry. 2016. Vol. 56. Issue 5. P. 454-458.

9. Zaluzec E.J. Direct matrix-assisted laser desorption ionization mass spectrometric analysis of proteins immobilized on nylon-based membranes / E.J. Zaluzec, D.A. Gage, J. Allison, J.T. Watson / J. Am. Soc. Mass Spectrom. 1994. Vol. 5. P. 230–237.

10. Fazullin D.D. Infrared spectroscopic studies of the PTFE and nylon membranes modified polyaniline / Fazullin D.D., Mavrin G.V., Shaikhiev I.G., Sokolov M.P. / Modern Applied Science. 2015. Vol. 9. №. 1. P. 242-249.

11. Fazullin D.D. Modified PTFE–PANI membranes for the recovery of petroleum products from aqueous oil emulsions / Fazullin, D.D., Mavrin, G.V., Shaikhiev, I.G. / Petroleum Chemistry. 2017 Vol. 57. Issue 2. P. 165-171

12. Sedysheva S.A. Development of the liquid emulsifying technology with the use of ceramic membranes. Author's abstract for Cand. Chem. Sciences. Moscow, 2011. p. 18.

How to cite this article:
Fazullin D D, Mavrin G V, Nasyrov I A, Shaikhiev G I. Dynamic membranes of nylon-ptfe for separation of water-oil emulsions. J. Fundam. Appl. Sci., 2017, *9(1S), 1441-1449.*