



Modification of Thin-Film Polymer Membranes by Microwave Radiation in Ammonia Medium

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Abstract

In this paper, we aimed to modify thin-film microfiltration membranes of nylon and polytetrafluoroethylene (PTFE) with ultrahigh-frequency (UHF) radiation within the decimeter wave band in ammonia vapor medium. It has been found that the treatment of a nylon membrane in ammonia leads to the membrane capacity decrease from 79% to 70.8% and to membrane weight decrease by 0.52%. And they observed the decrease of membrane weight by 0.24% from the original. In general, the treatment of membranes with microwave radiation in ammonia medium leads to specific productivity increase. They revealed the decrease of emulsion separation degree after the nylon membrane treatment by microwave radiation in ammonia environment. And when the oil emulsion is separated using PTFE-treated membranes, the degree of purification from oil increases by 3.6%, and the size of the separated oil particles also decreases from 118 nm to 49 nm.

Keywords: Oil-in-water emulsion, microfiltration, PTFE, nylon, particle size, modification, microwave radiation, ammonia vapors.

1. Introduction

Recently, the electromagnetic radiation of the microwave (UHF) range is used widely for the processing of polymeric materials. As is known, microwave radiation has several advantages in comparison with other physical fields (ultrasonic frequency range vibrations, infrared radiation, vibration treatment): it intensifies the energy exchange in a substance by converting the radiated energy into the kinetic energy of molecular vibrations; it provides the uniform processing of a substance in the irradiated volume, and there is no need to use additional ingredients to transform the substance structure, the high stability of the energy flow due to the lack of inertia at its power varying [1].

The treatment of polymer membranes with electromagnetic radiation leads to the changes of their surface properties [2-4]. The processing of membranes by electromagnetic radiation of the microwave range is carried out in gaseous media of air, nitrogen, helium, argon, in the vapors of hydrocarbons and solvents. The literature has the works on the modification of polymer membranes by the treatment in low-temperature plasma and in ammonia vapors [5-6], and there is no data on the treatment of membranes with microwave radiation within the decimeter wavelength range in ammonia vapor environment.

During the processing of membranes in inert gas plasma, a slight etching of the surface layer takes place due to physical spraying [7], whereas the etching rate is several times higher in air, nitrogen and oxygen under similar conditions [8-11].

The etching rate of the membrane surface depends on the nature and the degree of polymer crystallization, the etching rate of the amorphous regions is higher. This is related to the lower density and the greater diffusion of the reaction gases [1,8,9,12].

During the processing of polymer membranes in nitrogen plasma or ammonia vapors, in addition to surface etching and the

formation of macroradicals, they observe the introduction of nitrogen-containing groups into the surface layers of the membrane with the formation of nitrogen-carbon chemical bonds [13-17]. In the case of ammonia or its mixture use with hydrogen, nitrogen-containing groups (amino-, amido-, imido-, imino-) appear on the surface [18].

In [19], they obtained cellulose acetate membranes by synthesizing cellulose carbamate via microwave radiation. They studied the effect of urea concentration and the reaction time on nitrogen content development in the membrane. The determination of membrane pore size has shown the tendency of urea increase, observed under a scanning electron microscope of field emission.

On the basis of the stated above, it seems relevant to study the mechanism of exposure to microwave radiation in ammonia vapor environment on the structure and the physicochemical properties of polymer membranes made of nylon and polytetrafluoroethylene (PTFE) in order to increase the efficiency of oil emulsion separation.

2. Methods

In order to improve the performance and the degree of oil emulsion separation, the thin-film microfiltration membranes made of nylon and polytetrafluoroethylene (PTFE) were modified with ultrahigh-frequency radiation within the decimeter wavelength range without heat, using MC-6 laboratory microwave system. During the processing, the following parameters of MC-6 device were established: power - 750–1500 W, operating frequency - 2450 MHz, temperature - 24 °C, processing time - from 10 to 60 min.

To assess the effect of microwave radiation on membranes, they determined the membrane weight before and after treatment, using the analytical balance with the accuracy of 0.00001 g.

For membrane separation, they used the model oil emulsion, which was obtained by carbonic oil dispersion in distilled water with the addition of sodium dodecyl sulfate. The concentration of petroleum products in the initial emulsion was 212 mg/dm³. They used microfiltration polymer membrane of nylon and PTFE with an average pore size of 0.45 µm and the diameter of 47 mm as the initial membrane for modification. The nylon membrane is hydrophilic, and the PTFE membrane is hydrophobic. Therefore, the surface was wetted with acetone in order to improve the wettability of the hydrophobic PTFE membrane, before the emulsion separation.

The particle size of oil-in-water emulsion dispersed phase was determined using the dispersed phase particle size analyzer "Nano Brook Omni". To study the characteristics of oil emulsions, the device is configured according to the following parameters: solvent - water; viscosity - 0.89; scattering angle - 90°; measurement time - 3 min.

In order to assess the effectiveness of membrane treatment with microwave radiation in ammonia vapors, the following parameters were considered before and after the treatment of membranes: specific productivity and the degree of model oil emulsion separation. The degree of model oil emulsion separation was determined by the oil content in the original emulsion and in the filtrate which was measured by IR spectrometry.

The process of emulsion separation by microfiltration was carried out as follows: the original emulsion, containing the particles of oil and anionic surfactants as the dispersed phase, is pumped to the membrane module. Under the action of the working pressure, the emulsion is separated into a filtrate and a concentrate. In the process of distilled water and emulsion separation, the working pressure of 0.1 MPa was applied, the temperature of the liquid was 24 °C.

3. Results and discussion

The change of polymer membrane weight after the microwave treatment in ammonia vapor medium is presented on Table 1.

Table 1: The decrease of membrane weight after microwave processing in ammonia vapors

№	Membrane name	Treatment period, min.	Membrane weight, g.		Membrane weight decrease Δ, %
			до	после	
1	nylon	10	0,0969	0,0964	0,10
2		30	0,0986	0,0984	0,20
3		60	0,0988	0,0987	0,52
4	PTFE	10	0,0846	0,0845	0,12
5		30	0,0931	0,0929	0,21
6		60	0,0828	0,0826	0,24

After 10 minutes of membrane treatment with microwave radiation in ammonia vapor medium, the weight of nylon membranes decreases by 0.10% of the initial mass, with the processing time increase up to 60 minutes, the membrane weight is decreased by 0.52%. During the processing of PTFE membranes from 10 to 60 minutes, there is the decrease of membrane weight by 0.12% to 0.24% from the initial weight. During the processing by microwave radiation in ammonia vapors, nylon membranes lose more weight.

In order to determine the change of membrane surface wettability after microwave treatment, the moisture capacity of the original and modified membranes was measured using an "A & MD" moisture analyzer. The results on membrane water capacity are presented in table 2.

Table 2: The change of membrane moisture capacity after the treatment with microwave radiation in ammonia vapors.

№	Membrane name	Treatment period, min.	Moisture capacity, %	
			before	after
1	nylon	10	73,5	71,8
2		30	79,0	70,8
3		60	70,8	70,8
4	PTFE	10	0,6	2,5
5		30	0,6	3,7
6		60	0,6	4,0

1	nylon	10	79,0	73,5
2		30		71,8
3		60		70,8
4	PTFE	10	0,6	2,5
5		30		3,7
6		60		4,0

According to research results, when the processing time of microwave radiation is increased, the moisture capacity of the nylon membrane is decreased from 79% to 70.8%. And after the processing of PTFE membrane, the reverse increase of moisture capacity is observed from 0.6% to 4% is observed during the processing for 60 minutes. Microwave radiation in ammonia environment also affects the wettability of membrane surface with distilled water, PTFE membrane hydrophilicity is increased, and the hydrophobicity of nylon membrane is also increased.

The membranes modified by microwave radiation were used for the separation of oil model emulsion of "oil in water" type with the oil content of 212 mg/dm³.

The specific productivity was determined by distilled water and model oil emulsion in the initial and modified nylon and PTFE membranes (table 3).

Table 3: The specific performance of the membranes treated with microwave radiation in ammonia vapors

Membrane name	Microwave treatment period, min.	Membrane specific productivity, dm ³ /m ² · hour	
		By distilled water	By oil emulsion
nylon	-	3099	701
	10	3243	716
	30	3403	969
	60	3519	985
PTFE	-	2943	443
	10	4613	463
	30	5190	466
	60	5323	578

The processing of PTFE and nylon membranes by microwave radiation in ammonia leads to specific productivity increase. This circumstance is connected, apparently with the increase of membrane pore size. In addition, there are the structural changes in the material, the increase of roughness and wettability. With an increase of processing time, the membrane performance is increased. During the separation of the oil emulsion, the specific productivity is reduced by an order as compared with the filtration of distilled water.

In order to restore the initial performance of the membranes after the emulsion filtering at the volume of 500 cm³, the membranes were washed by backwashing with a 5% sodium dodecyl sulfate solution and then they were washed with distilled water.

The results of the model emulsion separation by the original membrane and the membrane processed by microwave radiation from petroleum products are presented in Table. 4.

Table 4: The degree of model oil emulsion separation

Membrane name	Microwave treatment period, min.	Oil product concentration, mg/dm ³		Treatment degree, %
		Initial	After treatment	
nylon	-	212	8,4	96,0
	10		9,5	95,5
	30		28,8	86,4
	60		45,0	78,8
PTFE	-	212	68,0	67,9
	10		65,7	69,0
	30		62,0	70,8
	60		60,5	71,5

The efficiency of emulsion purification from petroleum products with the original membrane of nylon is higher by 28% as compared with PTFE membrane. After the processing of nylon

membrane by microwave radiation in ammonia, the degree of purification from petroleum products is decreased, with the processing time increase up to 60 minutes, the degree of purification is decreased by 17%.

And when the oil emulsion is separated using PTFE membranes modified by microwave radiation in ammonia medium for 60 minutes, the degree of purification from oil is increased by 3.6%. Figure 1, 2 shows the graph of dispersed phase particle size distribution from model oil emulsion and its filtrates by the original and the treated membranes. Table 5 presents the particle size ranges and ζ -potentials of the original emulsion dispersed phase and its filtrates.

Table 5: Particle size and ζ -potential of emulsion and emulsion filtrate dispersed phase

Emulsion	Particle size, nm	ζ -potential, mW
Model Oil Emulsion	198 - 260, 877 - 1510	-95,7
Nylon filtrate	30,6 - 48,5	-28,1
Microwave Nylon Filtrate (10 min)	37-64	-30,1
Microwave Nylon Filtrate (30 min)	39-108	-31,3
Microwave Nylon Filtrate (60 min)	49-114	-36,7
PTFE filtrate	118-179; 630-957	-36,5
PTFE microwave filtrate (10 min)	92-249; 450-1211	-34,1
PTFE microwave filtrate (30 min)	90-143	-28,6
PTFE microwave filtrate (60 min)	49-174	-20,9

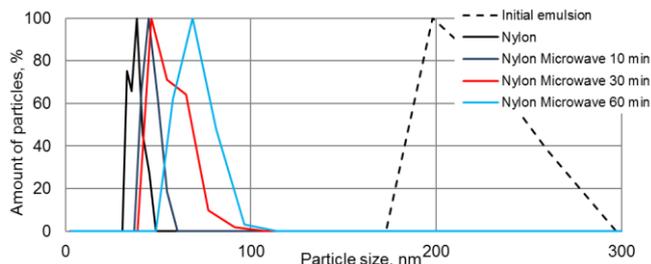


Figure 1: The graph of particle size distribution of the emulsion dispersed phase and its filtrates by original and treated in ammonia vapor environment nylon membranes.

According to Figure 3, the initial emulsion is a polydispersed system with the particle sizes from 198 to 1510 nm. By the value of ζ -potential which is -95.7 mV, it can be said about the stability of the dispersed system. The minimal size of the cut-off particles by the original membrane made 31 nm. After the membrane processing with microwave radiation for 10 minutes, the size of the cut-off particles is increased from 39 nm, after the processing for 60 min the particles with the sizes from 49 nm are cut off. The absolute value of ζ -potential is decreased after the separation, which indicates the emulsion destruction.

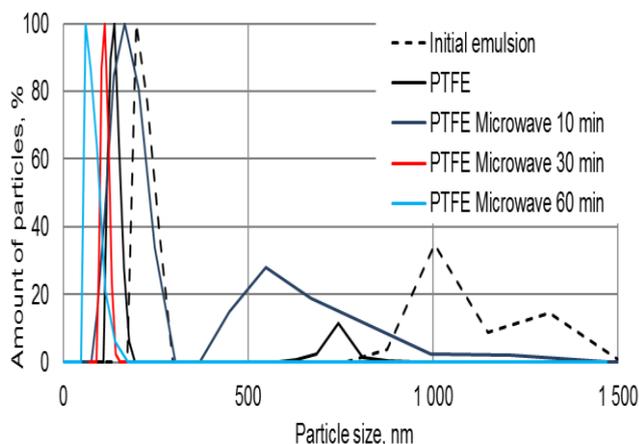


Figure 2: The graph of the particle size distribution during the dispersed phase of the emulsion and its filtrates by the original and PTFE-treated membranes.

The initial PTFE membrane cuts off oil particles with the minimal size of 118 nm. After the membrane treatment with microwave radiation in ammonia vapors within 10 minutes, the size of the removed particles decreases and makes at least 92 nm, after 30 minutes of processing the size of the separated particles makes 90 nm at least, and 49 nm after 60 minutes.

4. Summary

The processing by microwave radiation in ammonia environment leads to the loss of membrane weight, during the processing of the membrane made of nylon for 60 minutes, the weight loss makes 0.52%, during the processing of PTFE membrane for 60 minutes, the membrane weight loss makes 0.24%. The membrane weight is reduced by the surface layer etching. The etching rate of the membrane surface depends on the nature and the degree of polymer crystallization, the etching rate of the amorphous regions is higher, this is due to the lower density and greater diffusion of the reaction gases [1,8,9].

With the processing time increase in the ammonia environment, the moisture capacity of the nylon membrane is decreased from 79% to 70.8%, and after the treatment of the PTFE membrane for 60 minutes, the reverse increase of moisture capacity is observed from 0.6% to 4%. The decrease of nylon membrane moisture capacity as the result of processing is associated with the crystallization of polymer, and the increase of moisture capacity in PTFE membrane is apparently due to surface roughness increase because of surface etching and the destruction of membrane surface layer defective areas.

The specific productivity of the membranes after the treatment with the microwave radiation in ammonia medium increases. When the oil emulsion is separated by a nylon membrane, the productivity is increased by 29%, and by 23% with PTFE membrane. This circumstance is related apparently with the membrane pore size and roughness increase; the increase of wettability also takes place.

After the processing of the nylon membrane by microwave radiation in ammonia, the degree of purification from petroleum products is reduced. And when the oil emulsion is separated via PTFE-treated membranes, the purification degree from oil is increased by 3.6%, and the size of the separated oil particles is also decreased from 118 nm to 49 nm.

5. Conclusions

The modification of the microfiltration membrane of nylon by microwave radiation in ammonia increases the specific productivity of the membranes, and with the processing time increase, the productivity is also increased, but with the productivity increase the degree of oil emulsion separation decreases. The increase of membrane performance is associated with the membrane pore size increase due to the etching of the surface layer with microwave radiation and the destruction of membrane surface defective areas, which is confirmed with the membrane weight decrease by 0.52% from the original.

The result of PTFE membrane processing by the microwave radiation is the specific performance of the membrane increase, which is associated with the membrane surface wettability increase by water. Also the degree of emulsion separation is increased by 3.6% as compared with the original membrane. The treatment of membranes with microwave radiation in ammonia medium leads to a positive result — the increase of membrane specific productivity at the separation of oil emulsions.

It is advisable to treat thin-film PTFE membranes with microwave radiation within the decimeter wavelength range to hydrophilize the surface, as well as to increase the specific productivity and the degree of emulsion separation.

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