ARTICLE

STUDY OF CHANGES IN THE SURFACE LAYER OF THE MEMBRANE UNDER THE EFFECT OF MICROWAVE RADIATION

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ABSTRACT

Studies of the surface layer of membranes have been carried out using FTIR spectroscopy, scanning electron microscopy, NMR analysis, chromatography-mass spectrometry and other methods to identify changes in the properties of membranes processed in various physical media. The processing by microwave radiation in air leads to a loss of mass of the membranes due to the etching of the surface layer. With an increase in processing time in air up to 60 minutes, the water capacity of the nylon membrane decreases from 79% to 70.4%. Nylon 66 is usually characterized by absorption bands within the range of 650–3500 cm –1, which correspond to a peptide bond. An increase in the intensity of the absorption bands within the entire range of 650–3500 cm–1 of IR spectra after the membrane was treated by microwave radiation in air was established. New absorption bands of 2340 and 2358 cm -1 were also found, what can be attributed to the vibrations of the bonds in the amine salts R 2 C = NH + - or the diazonium salts –N 2 +.Changes in the composition of the membrane, identified by IR spectrometric studies, is associated with oxidation of atomic nitrogen contained in the air. An increase in the pore size in some areas of the membrane to 2 μm after treatment with microwave radiation in air is revealed. The increase in membrane pores is also confirmed by an increase in the specific performance of the membranes.

KEY WORDS
Surface layer of membranes, pores, FTIR

INTRODUCTION

In recent years, electromagnetic super high-frequency (UHF) range radiation has become rather widely used for processing polymeric materials [1].

To detect changes in the chemical composition, physical properties, and surface structure as a result of microwave radiation, the following methods are used: measuring the rate of mass loss (gravimetric method) [2], FTIR spectroscopy, scanning electron microscopy, NMR spectroscopy, methods for determining the wettability of the membrane surface and others [3-6].

The change in the mass of the membranes after treatment with microwave radiation characterizes the speed of the etching process. The change in the mass of the membranes is determined by the gravimetric method: they measure the mass of the membranes before and after treatment, taking into account the processing time.

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To obtain data on the composition and structure of the surface layer of a polymer, IR spectroscopy methods are used. The method of IR- spectroscopy allows obtaining data on the chemical structure (group, bond) of the surface and in the surface layer before and after etching or polymerization. The use of modern devices (FTIR spectrometers) allows not only to obtain high resolution absorption bands, but also to fix concentration profiles in certain structures to a depth of 10 nm. The method allows establishing the formation of functional groups of different chemical nature or change their number (for example, structures containing nitrogen, oxygen, fluorine, chlorine and others), fix the detachment of molecules and crosslinking in the surface layer, as well as inoculating a new layer on the surface [7]. Literature data, and reference books are used for the assignment of absorption bands [8-9].

The method of electron- microscopy (SEM) which is widely used to establish the surface scanning structure of membranes [6, 10], allows obtaining important results in the study of thin polymer layers applied on a surface by microwave polymerization. Using SEM, one can confirm the fact of a change in the surface

structure of membranes as a result of etching the surface, applying a new polymer layer on a substrate. The method also allows for control the presence of powdered polymer in the structure of the deposited coating. The SEM also makes it possible to record changes in the roughness profile and the supramolecular structure of polymers when they are etched by microwave radiation.

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In this work, microfiltration membrane made of nylon is subjected to microwave radiation. Nylon 66 is a polyhe xamethylene adipamide which belongs to the group of synthetic polyamides. The molecular formula of nylon is: [—HN (CH 2NHOC (CH 2) 4 CO—] n. The structural formula of nylon 66 is shown in [Fig. 1].

In the crystalline regions, the nylon macromolecules have a flat zigzag conformation with the formation of hydrogen bonds with neighboring molecules between carbonyl oxygen atoms and the neighboring amide groups of hydrogen atoms. Therefore, nylon has a higher physical and mechanical properties than polyesters and polyalkenes, a higher degree of crystallinity (40-60%), and glass transition and melting temperatures.

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Fig. 1: The structural formula of nylon 66.

In subsequent studies, the surface layer of nylon membranes was studied using IR spectrometry and scanning electron microscopy.

In the work [6], the authors studied the effect of functionalized multi-layer carbon nanotubes of sodium dodecyl sulfate on the characteristics and performance of polyacrylonitrile (PAN) membranes. Mixed matrix membranes were obtained by mixing solutions and with the use of phase inversion methods. After acidification, the membranes then were functionalized with an amino group using microwave radiation. The resulting membranes were examined by SEM, field emission electron microscopy (FESEM), atomic force microscopy (AFM), measurement of the wetting angle with a drop of water, and FTIR spectroscopy. The hydrophilicity and

productivity as to distilled water increased with the addition of additives. The results showed that both supplements improve the performance parameters of the PAN membrane.

In [11], nylon fibers were modified with 2-acrylamido-2-methylpropanesulfonic acid (AMPS), and the polymerization was carried out using microwave radiation. The obtained nylon fibers were investigated by infrared Fourier spectroscopy, and with the use of SEM. Chromatographic properties were also studied, including permeability, and the degree of separation of proteins. The modified phase of the fiber showed an increase in the dynamic filtration rate during the polymerization by microwave radiation.

Using microwave radiation, the authors of the work [12] obtained the cation-exchange phase of nylon-COOH for ion chromatography. Polyacrylic acid was grafted onto nylon fibers by radical polymerization with microwave radiation. The surface of the obtained fibers was investigated by the method of infrared Fourier spectroscopy and SEM. The obtained IR spectra contained an absorption band of 1722.9 cm -1 corresponding to the vibrations of the –COOH group. The authors concluded that polymerization under the effect of microwave radiation has great potential as a generalized methodology for modifying the surface of polymers.

In [13], the authors modified the membrane made from nylon by microwave radiation, which was used to filter nitrogen. The radiation power was 100 Watts. The authors investigated changes in the physical properties of the surface using scanning electron microscopy. The authors found that the transmittance of nitrogen atoms is 20% after treatment of the membrane with microwave radiation for 1 minute. After increasing the processing time of microwave radiation up to 30 minutes, the transmittance of nitrogen atoms has become to 50%. According to the results of SEM studies, the authors found an increase in the pore sizes of membranes from 5 to 10 microns depending on the processing time. The results of FTIR spectroscopy confirm the formation of C-N bonds by etching the surface.

In the above work, methods of IR- FTIR spectroscopy, scanning electron microscopy, methods of NMR analysis and weight methods were used to establish the changes in the composition and properties of the surface layer of membranes, after treatment with microwave radiation. The processing of polymer membranes with microwave radiation led to an increase in the pore size, an increase in the specific productivity, a change in the wettability of the surface, and an increase in the level of crystallization of the polymer.

METHODS

To improve the performance and degree of separation of oil emulsions, we modified thin-film microfiltration membranes made of nylon by microwave radiation in the decimeter wavelength range without heat exposure using the MS-6 laboratory microwave system. During processing, the following parameters of the MS-6 installation were established: power 750–1500 W, operating frequency of 2450 MHz, temperature 24 ° C, processing time from 10 to 60 min.

A microfiltration polymer membrane of nylon with an average pore size of 0.45 μm and a diameter of 47 mm was used as the initial membrane for modification.

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

The moisture capacity of the initial and modified membranes was determined using a brand A & MD moisture analyzer.

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The study of the infrared spectra of the samples was carried out on the infrared Fourier spectrometer "InfraLUM FT-02". IR Fourier spectrometer allows obtaining a high resolution of the absorption bands. The method allows for the formation of functional groups of different chemical nature or a change in their number to identify. The reference book [10] was used to assign absorption bands.

A change in the surface structure of the membranes was recorded using a LEO-1430 VP scanning electron microscope manufactured by Carl Zeiss. The samples were glued onto aluminum plates, the surface of the membranes was sprayed with gold, using the method of cathode sputtering in argon and viewed in the high vacuum mode.

RESULTS AND DISCUSSION

The change in mass and moisture capacity of nylon membranes after microwave processing in air is presented in [Table 1].

Table 1: Membrane weight loss and moisture capacity reduction after microwave treatment in air

The name of the membrane	Processing time (min)	The decrease in the mass of the membrane Δ,%	Moisture content,%
Nylon	-	-	79.0
	10	0.12	76.5
	30	0.25	73.7
	60	0.33	70.4

After 10 minutes of membrane treatment with microwave radiation in an ammonia vapor medium, the weight of nylon membranes has decreased by 0.12% of the initial mass, and with an increase in processing time up to 60 minutes the membrane weight decreases by 0.33%. With an increase in the processing time of microwave radiation, the water capacity of the nylon membrane decreases from 79% to 70.4%.

[Fig. 2] shows the infrared absorption spectra of the original and processed by microwave radiation in an atmosphere of air nylon membrane.

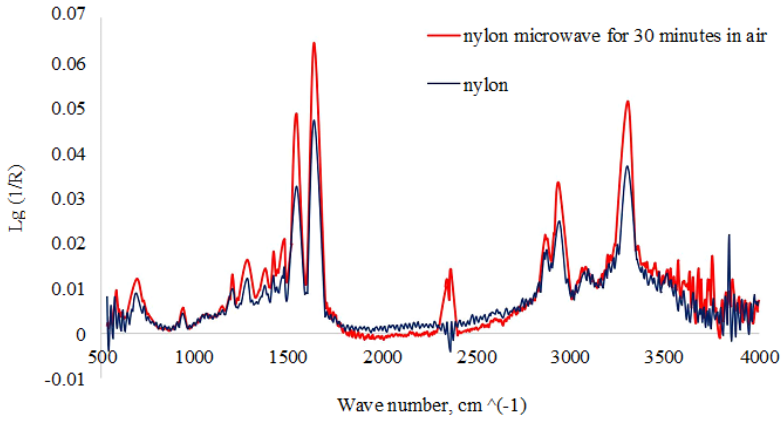

Fig. 2: IR absorption spectra of nylon before and after treatment with microwave radiation in an air environment for 30 minutes.

Nylon 66 absorption bands within the range of 650–3500 cm – 1, corresponding to a peptide bond. The absorption bands of 680 cm -1 , 726 cm -1 , 935 cm -1 correspond to out-of-plane deformation vibrations of the 2.5-substituted C – H bonds. The region of the absorption bands of 1200–1274 cm –1 refers to the vibrations of C – O bond. The absorption bands of 1370 cm -1 , 1475 cm -1 , 2855 cm -1 , 2869 cm -1 correspond to the vibrations of –CH 2 - bond , the absorption band with a wave number of 1640 cm–1 characterizes the deformation vibrations of the carbonyl group, and the 1540 cm –1 band characterizes the deformation vibrations of the N – H bond. The absorption band characterized by a wavenumber of 3050 cm -1 is associated with the deformation vibrations of the N – H bond of the secondary amide, and the absorption band of 3300 cm –1 refers to the stretching vibrations of the N – H bond of the secondary amines R2NH. These absorption bands are also present in the spectra of other compounds containing secondary amide groups, such as proteins, but other bands in the absorption spectrum of nylon 66 are specific only for this class of polymers, which makes it possible to identify them [14].

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After processing the nylon membrane for 30 min in air, an increase in the intensity of the IR spectra is observed in the entire range of the absorption bands of 650–3500 cm – 1. New absorption bands of 2340 and 2358 cm -1 also appear that can be attributed to the vibrations of the bonds of the amine salts R 2 C = NH + -, or the diazonium salts –N 2 + [15].

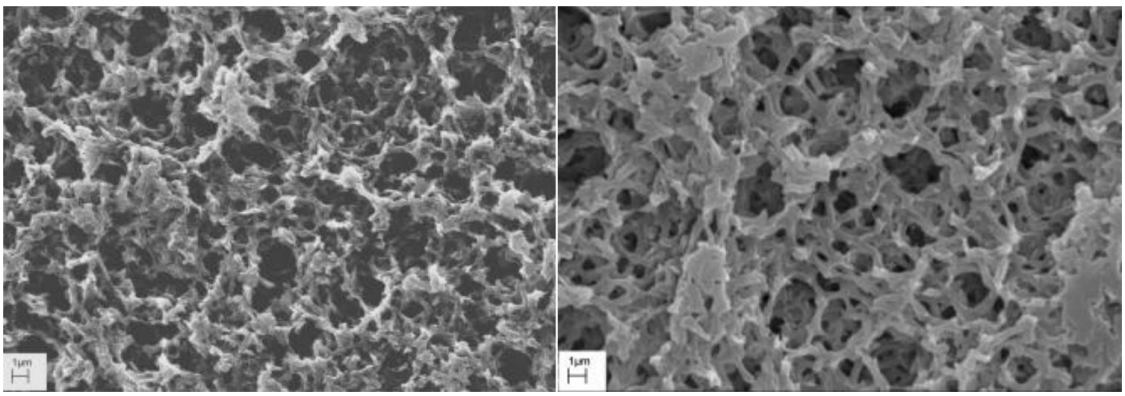

Fig. 3: Image of the surface of the original (left) and microwave treated in air (right) membrane with 3000x magnification.

Images of the original surface and the surface modified by microwave radiation in the air environment for the membranes with 3000x magnification obtained by electron-scanning microscopy are presented in [Fig. 3].

As it follows from the above photographs, the morphology of the original membrane surface undergoes changes after being treated with microwave radiation in air. If the initial membrane ([Fig. 3], left) is a set of pores with sizes from 0.2 to 1 μm, then after modification, the stuck and melted areas could be observed on the membrane surface ([Fig. 3], right). It is also seen from the figures that the pore size in some areas of the membrane after treatment increased to 2 microns.

The processing of microwave radiation in air leads to a loss of mass of the membranes; when processing a membrane made of nylon for 60 minutes, the loss of mass is 0.33%. The mass of the membrane is reduced by etching the surface layer.

The etching rate of the membrane surface depends on the nature and degree of crystallization of the polymer: the etching rate of the amorphous regions is higher, this is due to lower density and greater diffusion of the reaction gases.

With an increase in processing time up to 60 minutes in air, the water capacity of the nylon membrane decreases from 79% to 70.4% when processed within 60 minutes. The decrease in moisture capacity of the nylon membrane as a result of processing is associated with crystallization of the polymer.

An increase in the intensity of the absorption bands in the entire range of 650– 3500 cm – 1 of IR spectra after the membrane has been treated with microwave radiation in air is associated with etching the surface and destroying the defective areas of the surface layer and pores of the membrane. New absorption bands of 2340 and 2358 cm -1 also appear, what can be attributed to vibrations of the bonds in amine salts, R 2 C = NH + -. Either the appearance of these bands in the IR spectrum is associated with the formation of diazonium salts –N 2 +. Changes in the composition of the membrane identified by IR spectrometry studies are associated with oxidation by atomic nitrogen contained in the air.

After processing the microwave radiation of a nylon membrane surface ([Fig. 2], right), stuck together and melted areas are observed. It is also seen from the figures that the pore size in some areas of the membrane has increased after processing. The increase in membrane pores is also confirmed by an increase in the specific performance of the membranes.

CONCLUSION

The results of the study of membrane surfaces by FTIR spectroscopy and electron microscopy showed that as a result of microwave treatment in atmospheric air for 30 minutes, changes are observed in the surface layer of the membranes. The intensity of all the bands within the IR spectrum of the treated membrane increases, and after the treatment, new absorption bands appear that belong to the nitrogen-containing groups. Melted areas on the membrane surface and an increase in the pore size up to 2 μm are observed; that leads to an increase in the specific productivity of the membranes.

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CONFLICT OF INTEREST

There is no conflict of interest.

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FINANCIAL DISCLOSURE

None

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