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SCANNING ELECTRON MICROSCOPY (SEM) IN THE ANALYSIS OF THE STRUCTURE OF POLYMERIC NANOFILTRATION MEMBRANES

Key words

Scanning electron microscopy, nanofiltration, polymeric membranes.

Abstract

The authors examined the possible use of a scanning electron microscope (SEM) for polymeric nanofiltration membranes testing. The analysis of results allowed us to conclude that SEM technique is useful for the determination of the construction of “skin” and the support layer of nanofiltration polymeric membranes and that Energy-dispersive X-ray spectroscopy (EDS, EDX) provides “average” data from both layers.

Introduction

Nanofiltration (NF) is one of the latest pressure membrane techniques. This technique allows for retention of molecules with a molecular weight above 200 g/mol, which correspond to a molecule of 10 Å in diameter [1, 2].

Currently, asymmetric thin-film composite membranes are commonly used for nanofiltration. They are composed of “dense” 0.1–1.0 µm thick “skin” layer, disposed on a support layer having a thickness of 50–150 µm (Fig. 1). In these types of membranes, the support layer is a porous ultrafiltration membrane usually made of polysulfone [3, 4]. Its task is to take over the mechanical loads and protect the “skin” layer, while the “skin” layer is usually made of polymers such as polyamide or poly(piperazine-amide) [5–7]. It acts as a permeation layer and thus determines the separation properties of an asymmetric composite membrane. The small thickness allows for high hydrodynamic permeability, whereas the density determines the selectivity [8, 9].

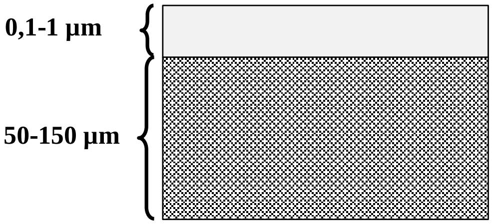

Fig. 1. The construction of asymmetric thin film composite membrane, based on [8, 9]

Nanofiltration has been successfully used for the treatment of surface and groundwater, primarily for their softening [10–13], the reduction of the salt concentration and the removal of low molecular weight organic compounds [14–16], for treatment of industrial waste, including the separation of metal ions [17, 18], the separation of mono and multivalent ions [19, 20], and the removal of dyes [21, 22]. Nevertheless, a major limitation to the widespread use of nanofiltration is the declining efficiency of the process caused by fouling and/or scaling of membranes [10, 23]. These phenomena depend primarily on the properties of the nanofiltration membranes. The main role is played by charge in the membranes, which depends on the functional groups present in their structure [24, 26]. The charge of nanofiltration membranes may vary due to conditions in treated solutions and cleaning baths [27, 28]. The tendency of scaling in membranes depends on the type and density of the charge and also on the structure of the surface which can be examined by the means of atomic force microscopy (AFM) [10, 29, 30]. According to the test results shown in [10, 23], membranes which have a lower surface roughness are much less prone to the formation of fouling and scaling. This is connected with the surface roughness, which causes local perturbations of the low rate, which promote the contact of particles present in the feed with the surface of the membrane, which leads to the formation of intermolecular interactions and chemical bonds with the surface of the membrane. For this reason, the membrane surface should not be too rough. The authors propose the use of scanning electron microscopy (SEM) for visual observation of changes taking place on the surface and the structure of membranes. SEM allows performing various types of image analysis and direct quantitative determination of details of examined objects [10, 31].

The aim of this study was elemental analysis of the surface of nanofiltration membranes as well as their morphology by means of scanning electron microscopy and X-ray microanalysis. Furthermore, the possibility of identifying the types of membranes by using these techniques was tested. During the studies, SEM images of the surfaces and cross section of polymeric nanofiltration membranes were taken, and the EDX technique was used to determine the elemental composition.

1. Experimental

A HITACHI S3500N scanning electron microscope with a Schottky type thermal field emitter (SU-70 model) was used to record the SEM images of the microstructure of the membranes surfaces and their cross section. The analysis was carried out in vacuum conditions ($1x10^{-8}$ Pa) at an accelerating voltage of 15 kV and a secondary electron reception angle of 30.4°. The membrane samples were coated with a layer of gold approx. 2 nm thick using BAL-TEC SCD 050 Sputter Coater from Quorum Technologies. The elemental composition of the surface of nanofiltration membranes were examined by a Thermo Scientific X-ray microprobe, coupled with a Hitachi scanning electron microscope.

The study involved two types (HL and DL) of flat nanofiltration thin film composite membranes from GE Osmonics, which are used for similar applications. These membranes were chosen for comparison because of their similar physicochemical and filtration properties (Table 1), and taking into account previous research [32] influenced the choice. The common characteristics of the tested membranes is their “skin” layer, which is made of poly(piperazine-amide) [5, 7]. This means that their surfaces have both carboxyl and amide groups. Both DL and HL type membranes stop divalent ions (Table 1), and the monovalent ion permeability depends on the concentration and composition of the feed [28, 32].

Table 1. Characteristics of nanofiltration membranes [28, 32]

	DL	HL
Retention of $MgSO_4$, [%]	98	98
Cut-off, [g mol^{-1}]	150–300	150–300
pH range	2–11	3–9
Max temperature, [°C]	90	50
Max pressure, [bar]	40	40

2. Results and discussion

The morphology of the membranes was assessed based on SEM images. Figure 2 presents SEM images of membranes surfaces of DL and HL types at a magnification of 10000x. SEM images show that the surface structures of the "skins" of both membranes are significantly different. The surface of the HL type membrane is more homogeneous than is the DL membrane. Single spheres of diameters less than 0.2 µm are present on the HL type membrane surface. Similar microstructures cover the entire surface of the DL type membrane. Differences in the structure of the "skin" layer of the membranes suggest different structures of the support layer as well, indicating that their manufacturing technologies vary widely. Figure 3 shows the cross section of the "skins" and support layers of DL and HL membranes.

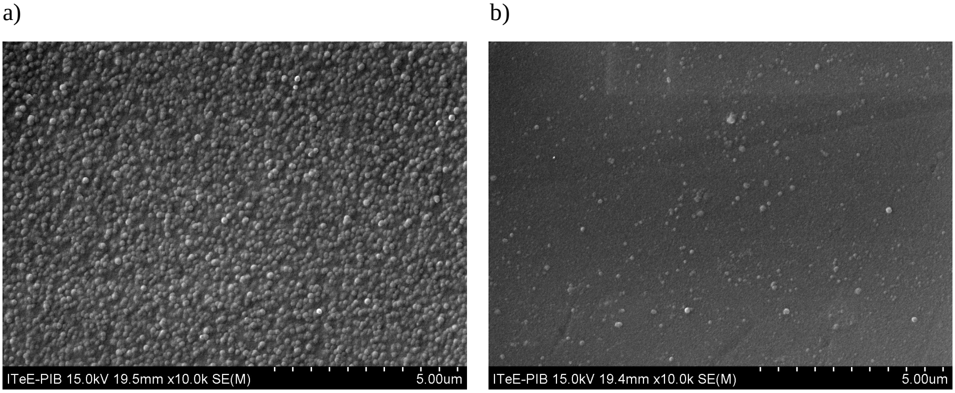

Fig. 2. SEM images of the DL (a) and HL (b) membranes surface

SEM images of the cross sections of the tested membranes (Fig. 3) show that the support layers of the two types of membranes have a similar thickness, but a radically different structure. The support layer of the DL membrane is porous (Fig. 3a), while the HL membrane has a cellular structure (Fig. 3b). As a result, the HL membrane has a thinner "skin" layer than does the DL membrane. Therefore, the HL membrane has a higher coefficient of the filtration of demineralized water than does the DL membrane [28, 32]. According to research conducted by Tang et al. [5, 7], the "skin" layer of tested membranes is made of poly(piperazine-amide) located on a support of polysulfone. Therefore, differences in the structure result from the different manufacturing technologies of DL and HL membranes. However, despite the different structures of the support layer, both membranes have a similar selectivity [28].

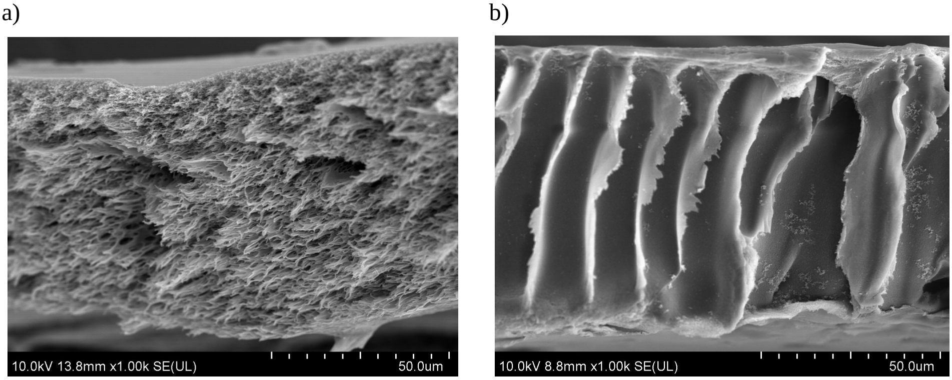

Fig. 3. SEM images of cross section of the tested membranes: (a) DL and (b) HL series

The possibility of using the EDX technique for determining the chemical composition of nanofiltration polymer membranes was tested. Because of the specific construction of composite membranes, which are covered with a few nanometre thick active “skin” layer, the EDX technique provides only "averaged" results from both layers. A further complication in using the EDX technique is the necessity of coating the surface of the membrane with a conductive material, usually gold or graphite, due to the accumulation of charge on the surface. Table 2 presents results from the EDX analysis after calculating and eliminating the influence of gold.

The analysis of data from Table 2 shows that both membrane types have four main elements: carbon, oxygen, nitrogen, and sulphur. There were also small amounts detected of sodium, chlorine, and calcium. Quantitative analysis (Table 2) shows that the mass and atomic shares of these elements are less than 1%. The presence of chlorine may be interpreted as the result of incomplete condensation of the monomers forming the “skin” of the membrane (one of them is trimesic acid trichloride [5, 7]) or incomplete hydrolysis of its free chlorocarboxylic groups. The presence of sodium may be the result of a specific nature of the manufacturing process of the membranes. The presence of calcium is probably a result of a slight surface contamination.

Table 2. Chemical composition (and standard deviation (SD) of the results) of polymer nanofiltration DL and HL membranes determined by the EDX technique

Element	Membrane DL		Membrane HL	
	Concentration [% mass]	SD	Concentration [% mass]	SD
C	38.75	0.72	47.91	0.03
N	3.67	0.48	5.72	0.21
O	33.34	1.47	30.93	0.16
Na	0.37	0.06	0.21	0.05
S	22.73	1.39	14.68	0.18
Cl	1.14	0.05	0.27	0.06
Ca	0.00	0.00	0.28	0.10
Total	100.00	-	100.00	-
Element	Membrane DL		Membrane HL	
	Concentration [% atomic]	SD	Concentration [% atomic]	SD
C	50.99	1.09	58.55	0.03
N	4.14	0.53	6.00	0.22
O	32.93	1.28	28.38	0.15
Na	0.25	0.04	0.13	0.03
S	11.21	0.76	6.72	0.08
Cl	0.51	0.02	0.11	0.02
Ca	0.00	0.00	0.10	0.04
Total	100.04	-	100.00	-

3. Conclusions

Scanning electron microscopy (SEM) coupled with Energy-dispersive X-ray spectroscopy (EDX) was used for the determination of the physicochemical characteristics of polymeric nanofiltration membranes (nonconductive materials). Different types of membranes with comparable filtration properties were tested. As a result of SEM analysis, it was found that the solid “skin” layer of the tested membranes has subtle morphology that is different for each type of membrane. This is connected to the structure of the support layer, which in turn depends on the manufacturing technology of membranes. The EDX technique showed that the “skin” and the support layers have different elementary composition, but this technique has insufficient vertical resolution; therefore, provides "averaged" data from both layers. However, the resolution is sufficient to distinguish membranes. The combination of data obtained with both SEM and EDX techniques allows the identification of membranes.

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Skaningowa mikroskopia elektronowa (SEM) w analizie struktury polimerowych membran nanofiltracyjnych

Słowa kluczowe

Skaningowa mikroskopia elektronowa, nanofiltracja, membrany polimerowe.

Streszczenie

W pracy zweryfikowano możliwość zastosowania skaningowego mikroskopu elektronowego do badania polimerowych membran nanofiltracyjnych. Analiza uzyskanych wyników pozwoliła na stwierdzenie, że SEM może być pomocna w określaniu budowy warstw naskórkowej i wzmacniającej polimerowych membran nanofiltracyjnych, a technika EDX dostarcza „uśrednionych” danych obejmujących obie warstwy.