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FABRICATION OF PSF AND AC-CEL ULTRAFILTRATION MEMBRANES USING PHASE INVERSION METHOD

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This study focused on the polymeric membrane fabrication via immersion precipitation using phase inversion techniques. The membranes were prepared by bleeding polyvinylpyrolidone (PVP) and polyethylene glycol (PEG) with polysulfone/cellulose acetate in N-methyl-2-pyrrolidone (NMP). The morphology, thermogravimetric analysis and water flux permeation of these membranes were characterized. Two different coagulation solutions were used in the experiments. In comparison with the polymeric membrane fabrication, a commercial 50 kDa polysulphone membrane was tested. For all membranes tested the ultrapure deionized water flux increases with the increase in working pressure. Exception to this rule was the Ac-Cel2 membrane, which recorded a decrease in flux by increasing the pressure from 4 bar (Jmed = 816.44 L/m^2 h) to 5 bar (Jmed = 784.72 L/m^2·--h).

Keywords: polymeric membranes, phase inversion, ultrafiltration, water flux

1. Introduction

A membrane can be described as a thin layer of material that is capable of separating materials as a function of their physical and chemical properties when a driving force is applied across the membranes [1, 2].

Ultrafiltration membranes can be made from both organic (polymer) and inorganic materials (zirconia, glass, metal and alumina) [3, 4]. There are several

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polymers and other materials used in the manufacturing process of the ultrafiltration membrane. The choice of a given polymer as a membrane material is based on very specific properties such as molecular weight, stereoisomerism properties, chain flexibility and chain interaction. The main advantages of asymmetric polymer membranes include their flexibility, durability and ease of production [3].

The most common preparation methodology for producing synthetic ultrafiltration membranes is phase inversion via immersion precipitation, coating, sintering, stretching, sol-gel process, vapor deposition, solution coating, and track-etching [3, 4]. However, the techniques usually used for the preparation of a UF membrane are mainly phase-inversion and sol-gel process. Phase inversion membranes can be prepared from a wide variety of polymers, such as polysulfone, polyethersulfone, sulfonated polysulfone, polyvinylidene fluoride, polyvinyl chloride, polyacrylonitrile, cellulosics, polyimide, polyetherimide, aliphatic polyamides, and polyetherketone [3, 5-6]. The polymers used in this method must be soluble in a solvent or in a solvent mixture. During the process, a thermodynamically stable polymer solution is transformed from a liquid into a solid state, in a controlled manner [7]. The process consists of three main stages:

- dissolving the polymer in a suitable solvent or mixture of solvents;
- film coating of the polymer solution, on a flat or tubular surface of glass, metal, Teflon, textile;
- precipitation of the polymer by treatment with an insolvent (actual phase inversion).

The characterization method of the porous membranes can be performed based on the structure-related parameters (determination of pore size, pore size distribution, top layer thickness, surface porosity) and the permeation-related parameters (cut-off measurements) [3]. The main characterization tests in membrane techniques are: bubble pressure, gas and liquid displacement methods (GLDP-LLDP), mercury porosimetry (MP), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), flux and retention measurements [8].

The main objective of this paper was fabrication of the polymeric membrane (polysulfone and cellulose acetate) via immersion precipitation using phase inversion techniques.

2. Experimental

2.1. Materials and reagents

The polymeric membranes used in the experiments were made through the phase inversion process, immersion-precipitation technique, using the following materials:

- Polysulfone (Psf), transparent pellets, Mw = 35000 g/mol, ρ=1.24g/cm^3, (Aldrich, USA);
- Cellulose acetate (Ac-Cel), powder, Mn = 50000 g/mol, ρ=1.3g/cm^3, (Sigma-Aldrich, USA);
- N-methyl-2-pyrrolidone (NMP), liquid, C_5H_9NO, GC purity-99.5%, ρ=1.032g/cm^3, (Merck, Germany);
- Polyvinylpyrrolidone (PVP) K30, powder, M=40000 g/mol, purum, (Fluka, USA);
- Polyethylene glycol (PEG) 4000, HO (C_2H_4O) nH, M = 3500-4500 g / mol, (Scharlau Chemie SA, Spain);
- Ultrapure deionized water, obtained using the Elix Technology Inside system (Milli-Q Integral 15, Merck, Millipore, France) with a resistivity of at least 15 MΩ·cm (equivalent to a conductivity less than 5.6×10^{-5} mS/cm);
- Ethyl alcohol, 96%, Chimreactiv SRL, Bucharest;
- Glycerin, 99.5%, ρ = 1.261g / cm^3, Chempur, Poland.

In the performed experiments, additionally to the membranes obtained in the laboratory, imported membranes with the following characteristics were also tested: polyethersulfone (PES) with an exclusion molecular weight of 50 kDa (Sartorius Stedim Biotech GmbH, Germany).

2.2. Preparation and characterization of polymeric membranes

Four experiments were performed in the laboratory in order to obtain the polymeric membranes. Three membrane types from the polymer Psf (coded Psf1) and Ac-Cel (coded Ac-Cel1) respectively, were obtained in the first set of two experiments were obtained. The matrix of the polymer solution from which the two types of membranes were made was identical and includes:

- polymer concentration (Psf or Ac-Cel): 13%;
- PVP concentration: 1.86%;
- PEG concentration: 1.86%;
- solvent: NMP.

For this first set of experiments, a coagulation solution was used with the composition:

- ultrapure deionized water: 97% (volumetric percentages);
- glycerin: 1% (volumetric percentage);
- ethyl alcohol: 1% (volumetric percentage);
- NMP: 1% (volumetric percentage).

In the second set of experiments, three membranes were also obtained from the polymer Psf (coded Psf2) and Ac-Cel (coded Ac-Cel2) respectively, using the same polymeric solution described above, the difference being the composition of the coagulation liquid. Thus, for this experimental stage the coagulation of the membranes was performed using only ultrapure deionized water.

The technical conditions for the realization of all membranes (from both experimental sets), specific to the phase inversion process by immersion-precipitation were identical, namely:

- filming tool: cylindrical stainless-steel shooter „Doctor Blade” with a slot of 300 µm;
- film support: glass;
- film speed: 1m/minute;
- quick immersion in the coagulation bath;
- coagulation time: 3-5 minutes;
- washing under a stream of cold water;
- conditioning/storage until use in 10% ethyl alcohol solution (volumetric percentages).

2.3. Ultrafiltration installation

The membranes created were characterized by point of structural view, both before and after the ultrafiltration process, by scanning electron microscopy (SEM) using a SEM Quanta FEG 250 equipment, Thermo Fischer Scientific and by thermogravimetric analysis, using a STA 409 PC equipment, produced by Netzsch (Germany).

The hydrodynamic characteristics of the membranes (flux of ultrapure deionized water) were determined in tangential flux regime, using a LABCELL-CF1 Koch Membrane System, described in other works [9]. The installation was equipped in each experiment with a circular membrane, of 76 mm diameter and an effective active area of 28 cm^2.

For the hydrodynamic characterization, the ultrapure deionized water flux was determined for each membrane in the UF experiments using equation 1:

$$J = \frac{V}{t \times S} \tag{1}$$

where:

J = flux of liquid through the membrane (L/m^2 h);
V = volume of liquid (L) passing through the membrane during time (t);
t = time (h) in which the volume V of liquid is collected;
S = membrane area (m^2).

3. Results and discussion

The ultrapure deionized water flux for the four membranes obtained were analyzed according to equation (1) mentioned in subchapter 2.3.

The variation of the average ultrapure deionized water fluxes for the five membranes, determined at 5 working pressures (1, 2, 3, 4 and 5 bar respectively) were presented in Fig. 1. It was found that for all membranes, the flux increases with the increase in working pressure. Exception to this rule was the Ac-Cel2 membrane, which recorded a decrease in flux by increasing the pressure from 4 bar (Jmed = 816.44 L/m^2 h) to 5 bar (Jmed = 784.72 L/m^2·h). This decrease denotes the deformation (shrinkage) of the pore diameter under the effect of pressure on the membrane's surface and its elasticity.

The highest flux values were recorded for the Psf1 membrane and the lowest for the the Ac-Cel2 membrane. This demonstrates the different behaviors of the two polymers (polysulfone and cellulose acetate, respectively) in the process of obtaining membranes by phase inversion. The flux characteristics closest to the import membrane (PES) are those of the Psf2 membrane. For all membranes, it is found that the optimal working pressure was that of 3 bar, taking into account both the variation of the flux from one pressure to another but also considering technical-economic reasons.

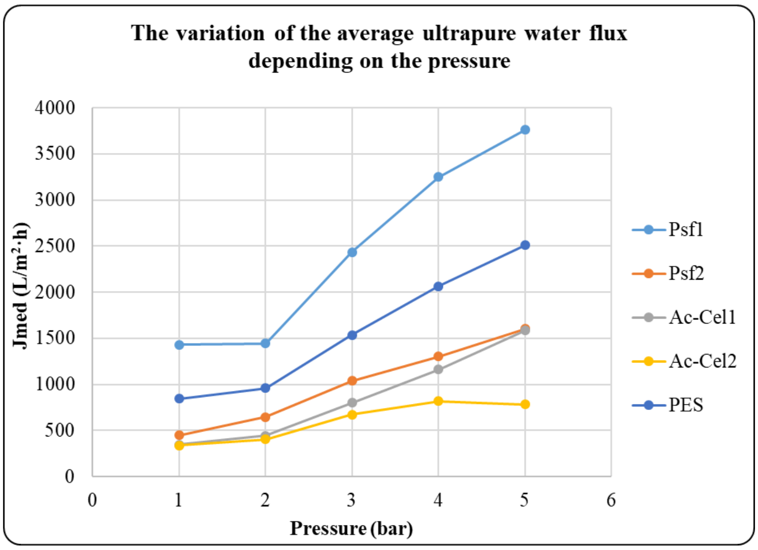
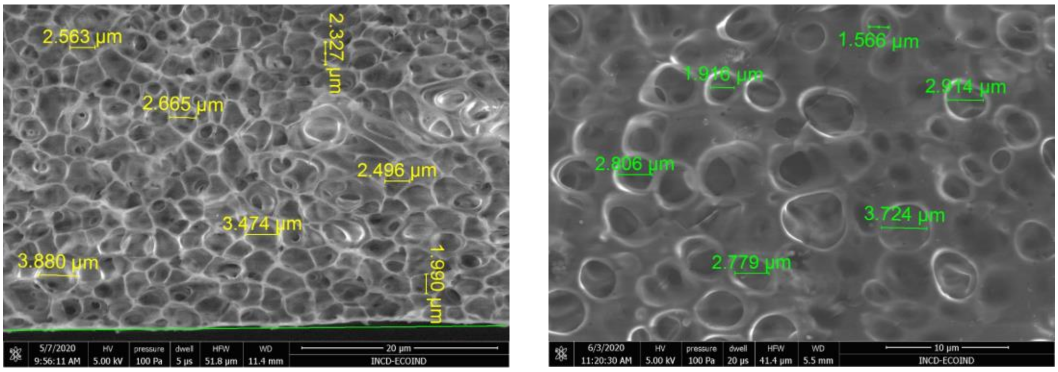


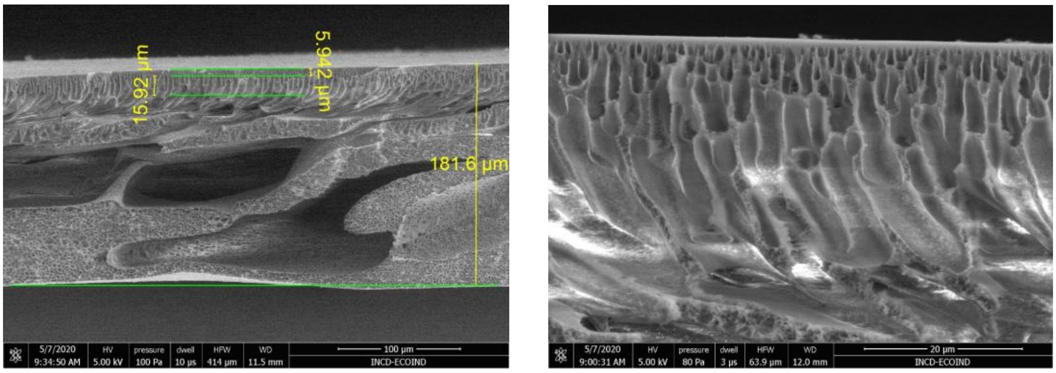
Fig. 1. Variation of membrane fluxes with pressure.

The decrease in the flux of the Psf2 membrane compared to that of the Psf1 membrane indicates the importance in the composition of the coagulation solution. The existence of components such as glycerin, ethyl alcohol and especially NMP (polymer solvent) in the coagulation solution was reflected in the delay of the coagulation process and the formation of pores with larger diameters than in the case of the membrane coagulated in ultrapure deionized water. In the case of Ac-Cel1 and Ac-Cel2 membranes made under similar conditions, the coagulation solution acts in the opposite way. Delaying the coagulation process of the solution with glycerin, ethyl alcohol and NMP (Ac-Cel1 membrane) results in obtaining pores with smaller dimensions than the coagulated membrane in ultrapure deionized water (Ac-Cel2 membrane).

Important aspects regarding the correlation between the morphological structure of the studied membranes and their fluxes are highlighted by the SEM analyzes shown in Fig. 2 and Fig. 3.



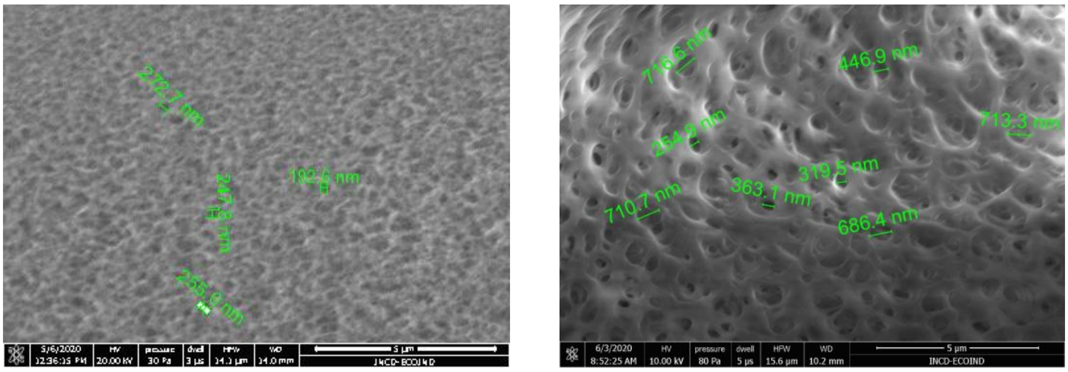
a) Psf1 - Surface view b) Psf2 - Surface view



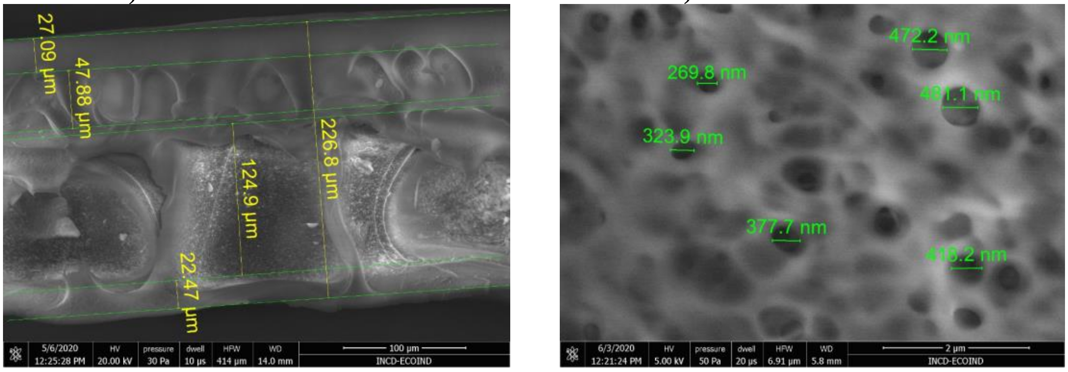
c) Psf1 - Section view (1) d) Psf1 - Section view (2)

Fig. 2. Views of Psf1 and Psf2 membranes obtained by SEM analysis.

The image in Fig. 2 (a) shows that the pore sizes at the surface of the Psf1 membrane was in the range of 1.99 - 3.88 µm, compared to 1.566 - 3.724 µm recorded in the case of the Psf2 membrane (Fig. 2 (b)). Visually, it was observed that the number of pores on the surface of the Psf1 membrane was much higher than those on the surface of the Psf2 membrane. There were whole inactive areas between the pores on the surface of the Psf2 membrane, while the pores on the surface of the Psf1 membrane were united, there was no inactive areas. These aspects argue with the large flux differences of the two membranes, generated by the change of the coagulation solution. Fig. 2 (c) and Fig. 2 (d) show the morphological structure of the Psf1 membrane, corresponding to a membrane obtained by the phase inversion process, in accordance with literature data [10]. Fig. 2 (c) shows that the active layer of the Psf1 membrane has a thickness of 5.942 µm, the intermediate layer was 15.92 µm and the total thickness of the membrane was 181.6 µm. Practically, in this case there was a decrease in coagulation in thickness from 300 µm (the thickness of the polymer film generated by the slit of the „Doctor Blade” device) to 181.6 µm. The fact that the final membrane has a small thickness was demonstrated by the large fluxes at any pressure values. As it can be seen from Fig. 2 (d), in depth, the membrane was very well structured on the three areas: active layer, intermediate layer and support layer.



a) Ac-Cel1 - Surface view a) Ac-Cel2 - Surface view



b) Ac-Cel1 - Surface view c) PES – Surface view

Fig. 3. Views of Ac-Cel1, Ac-Cel2 and PES membranes obtained by SEM analysis.

Regarding the membranes made of cellulose acetate polymer through the two coagulation solution variants (Ac-Cel1 and Ac-Cel2, respectively), SEM analyzes showed that the pores on the surface of the Ac-Cel1 membrane, in the range 192.6 - 255 nm (Fig. 3 (a)) are smaller than those on the surface of the Ac-Cel2 membrane, in the range 254.9 - 713.3 nm (Fig. 3 (b)). However, the fact that the Ac-Cel1 membrane has a higher flux of deionized water than that of the Ac-Cel2 membrane (as shown in the graphs shown in Fig. 1) was explicable by the higher number of pores on the Ac-Cel1 surface compared to those of the Ac-Cel2 membrane (visible from the comparison of the views made at the same resolution of 5 µm - Fig. 3 (a) and Fig. 3 (b). The morphological structure of the Ac-Cel1 membrane highlighted in the section (shown in Fig. 3 (c) was totally different from that of the Psf1 membrane (Figs. 2c and 2 d). Thus the thickness of the active layer of the Ac-Cel1 membrane was 27.09 µm, compared to 5.942 µm in the case of Psf1; the thickness of the intermediate layer of Ac-Cel1 was 47.88 µm, compared to 15.92 µm of Psf1; the total thickness of the Ac-Cel1 membrane was 226.8 µm compared to 181.6 µm of Psf1. All this argues for the large difference between the deionized water flux of Psf1 and that of Ac-Cel1. The same structural differences explain the flux variations between Psf2 and Ac-Cel2. Fig. 3 (d) shows a view of the surface of the PES import membrane. This highlights the fact that the pore diameters (269-481 nm) are comparable to those of the Ac-Cel1 membrane pores and almost an order of magnitude smaller than that of the Psf2 membrane pores. However, the deionized water flux of the PES membrane was higher than that of both the Ac-Cel1 membrane and the Psf2 membrane (to a lesser extent). The explanation was given by the existence of a larger number of pores on the surface of the PES membrane than the other two (Fig. 3 (d) shows a view with a resolution of 2 µm compared to those of the membrane Ac-Cel1 - 5 µm, Fig. 3 (a) and 10 µm respectively for Psf2, Fig. 2 (b).

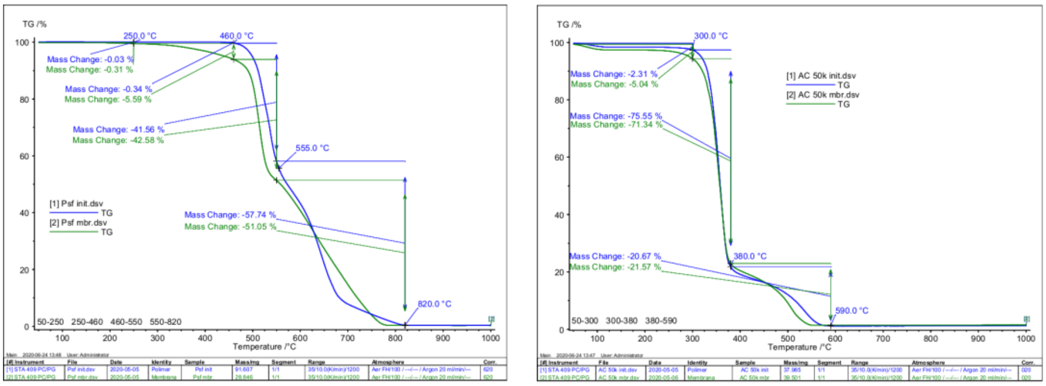
In order to verify the reproducibility of the characteristics of the obtained membranes, deionized water fluxes were determined at a pressure of 3 bar, considered as the optimal value for 3 different samples from the same membrane (Psf2). The values of the obtained fluxes and their deviations for the average value are presented in Table 1.

Table 1

Flux values and deviations obtained for the Psf membrane.

	M1	**M2**	**M3**
Initial flux (L/m^2·h)	1037.12	1010.52	1023.16
Average flux (L/m^2·h)	1023.6		
Deviation (%)	1.32	-1.28	-0.04

In Fig. 4 (a and b) were presented thermograms of polysulfone and cellulose acetate membranes and related polymers. As it can be seen in Fig. 4 (a), there are small differences between mass losses, ranging from 250°C to 820°C. Thus, the mass losses for membranes are lower at a temperature value of about 625°C compared to the original polymer. In regard to Fig. 4 (b), it can be seen that up to a temperature of 300°C, there are small differences in loss between the membrane and the initial polymer.



a) Psf b) Ac-Cel

Fig. 4. Thermograms of polysulfone and cellulose acetate membranes and related polymers.

The differences come from the fact that when fabricating membranes in accordance with the working method, various adjuvants are used to increase the polymer solution such as PVP and PEG [11-13]. After the membrane coagulation process, some of these compounds remain incorporated into the porous structure of the membranes, these being organic compounds that degrade at lower temperatures than polysulfone.

4. Conclusions

In this study membranes for ultrafiltration process were fabricated by phase inversion method from polysulfone and cellulose acetate polymers.

The flux of deionized ultrapure water increases with the increase in working pressure, with a single exception for the Ac-Cel2 membrane. This membrane recorded a decrease in flux by increasing the pressure from 4 bar to 5 bar. The decrease in the flux of the membrane indicates the importance in the composition of the coagulation solution. The flux characteristics closest to the import membrane (PES) are those of the Psf2 membrane. The results showed that the Psf1 membrane was corresponding to a membrane obtaining by phase inversion techniques. The pore sizes at the surface of the Psf1 membrane was in the range of 1.99 - 3.88 µm, compared to 1.566 - 3.724 µm recorded in the case of the Psf2 membrane. The reproducibility of the membranes obtained in the laboratory was demonstrated by the deviations below 5% of the average deionized water fluxes of the three samples from the same type of membranes (Psf2).

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