INFLUENȚA NANOPARTICULELOR DE TiO_2 ŞI ZnO ASUPRA PROPRIETĂȚILOR DE PERMEABILITATE ALE MEMBRANELOR PSf

INFLUENCE OF THE TiO_2 AND ZnO NANOPARTICLES ON THE PERMEATION PROPERTIES OF PSf MEMBRANES

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The influence of the TiO_2 and ZnO nanoparticles on the permeation properties of PSf membranes was studied at 32 wt.% PSf and 0.125 wt.% nanoparticles. The membranes were prepared by phase inversion method using 1-methyl-2-pyrrolidone (NMP) and deionized water as coagulant. The influence of TiO_2 and ZnO nanoparticles on the permeation properties was determined using dead-end filtration equipment at a constant pressure of 10 bars. Membranes hydrophilicity was investigated using contact angle method and the morphology were studied by SEM analysis. The addition of nanoparticles increase the permeability and the hydrophilicity of the PSf membranes, the optimum results for permeation properties were obtained using ZnO nanoparticles.

A fost studiată influența nanoparticulelor de TiO_2 şi ZnO asupra permeabilității membranelor PSf la o concentrație de 32 wt.% PSf şi 0,125 wt.% nanoparticule. Membranele au fost fabricate prin inversie de faze utilizând 1-methyl-2-pyrrolidone (NMP) şi apă distilată ca şi coagulant. Influența nanoparticulelor de TiO_2 şi ZnO asupra permeabilității a fost determinată utilizând pentru filtrare un modulul dead-end la o presiune constantă de 10 bari. Hidrofilicitatea membranelor a fost determinată utilizând metoda unghiului de contact iar morfologia a fost studiată prin analiză SEM. Adaosul de nanoparticule creşte permeabilitatea şi hidrofilicitatea membranelor PSf, rezultatele optime pentru proprietățile de permeabilitate obținându-se adăugând nanoparticule de ZnO.

Keywords: *TiO_2, ZnO, nanoparticles, PSf, membranes*

1. Introduction

In the last years, the membranes used in filtration processes were improved by incorporating inorganic additives in the polymer material. Nanoparticles used to change polymeric membranes are SiO_2, Al_2O_3, Fe_3O_4, ZrO_2, ZnO and TiO_2 [1].

The nanoparticles, with unique physical and chemical properties that differ from the bulk material, are of great interest in the production of the membranes to achieve a high degree of control over membrane fouling and the ability to produce the desired structure and functionality. The fouling of the membrane is the main problem that limits the use of the membranes in a wide range of applications, economically or technically. Nanoparticles can provide a key to solve this problem [2].

In search of the necessary properties of membrane filtration processes were highlighted in particular nanoparticles of TiO_2, ZnO and SiO_2.

To achieve composite membranes, various processes can be put into practice such as coating, spinning, self-assembly, deposition, and interfacial polymerization. Widely, the most used methods of manufacturing composite membranes are Coating and interfacial polymerization [3].

The process for obtaining composite membranes by interfacial polymerization is used because it exceeds the barriers traced to asymmetric membranes obtained by phase inversion [4, 5].

Currently composite membranes are among the most widely used and available nanofiltration membrane used in the membrane process. They present a selective layer on top of the membrane. To obtain this layer membranes are made using interfacial polymerization [1].

Composite membranes possess excellent morphology and composition vary depending on variables such as the concentration of the reactants, the reactivity of the reactants, the solubility of the polymer, diffusion of the reactants [6]. Composite membranes ensure a high flux and selectivity of solutes at low pressures [7, 8].

The polymer solution was poured into a thin layer and immersed in a bath of non-solvent (water). The non-solvent (water) layer broadcasted in the film and broadcast solvent solution in coagulation bath. Thus causing precipitation of the polymer and membrane formation [9].

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2. Experimental

2.1 Materials

The polymer used was polysulfone supplied by Solvay (Belgium). As solvent 1-methyl-2-pyrrolidone (NMP, 99.5%) was used. TiO_2 and ZnO nanoparticles with a size smaller then 100nm were used.

2.2 Membrane preparation

Blended polysulfone membranes were manufactured using the phase inversion induced by immersion precipitation. Membranes were manufactured at 32 wt.% of PSF and 0,125 wt.% nanoparticles in N-Methyl-pyrrolidone (NMP) as solvent. The homogeneous casting solution, represented schematic in Figure 1, was obtained by adding ZnO or TiO_2 nanoparticles into the NMP and mixed on the mechanical stirring at 200 rpm at room temperature. The polysulfone was added after 5 hours to the solution and stirred for 24 hours at 500 rpm.

A thin film with a thickness of 250 µm was cast with a filmograph (K4340 Automatic Film Applicator, Elcometer) on the support at room temperature and 40 % relative air humidity. For the precipitation, the membrane was immersed in a non-solvent bath and kept for 15 minutes. To obtain true values of membranes properties, three different solutions were made for every type of membrane.

2.3. Membrane characterization

2.3.1. Filtration experiments

Sterlitech HP4750 Stirred Cell was the divorce used to study the water flux and the permeability of the composite membranes. A constant pressure of 10 bars was used to study the water flux and to determine the permeability differential pressure between 2 and 15 bar was used.

2.3.2. SEM

To study the membrane structure scanning electron microscopy (SEM) was used; a Philips XL30 FEG instrument was used with an accelerating voltage of 20 KeV. Membrane samples were prepared by fracturing the membranes in liquid nitrogen, to keep the pore structure. The samples were sputtered with gold to have a clear image of the membrane structure.

2.3.3. Water contact angle

To explain the differences in permeation properties between the composite and neat membranes the hydrophilicity which is an important properties were studied. A Drop Shape Analysis System DSA 10 Mk2 was used and for every type of membranes was determined the contact angle for 10 surface points and the average value was used.

3. Results and discussion

3.1. The influence of TiO_2 and ZnO nanoparticles on the permeation properties

The influence of the TiO_2 and ZnO nanoparticles on the membranes permeability is shown in Figure 2.

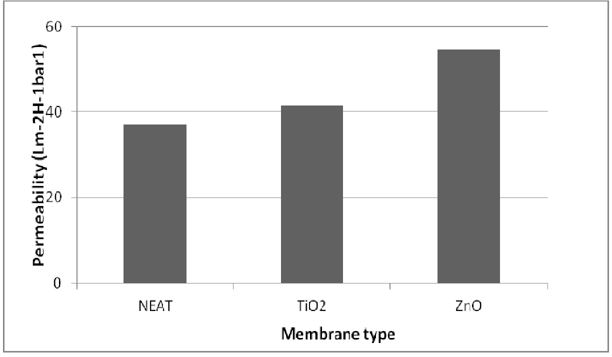

Fig. 2 - Influence of the TiO_2 and ZnO nanoparticles on the membrane permeability / *Influența nanoparticulelor de TiO_2 şi ZnO asupra permeabilității membranelor*

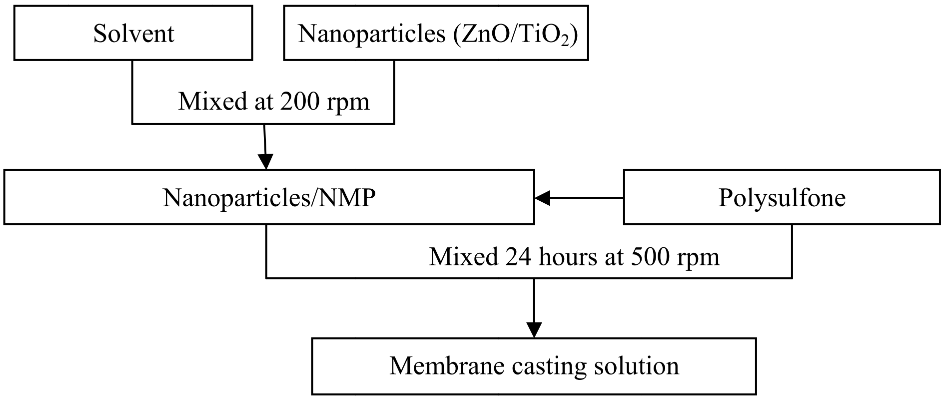

Fig. 1- Schematic diagrams for the preparation of PSf/ZnO/TiO_2 nanocomposite membranes / *Digrama schematică a preparării membranelor nanocompozite PSf/ZnO/TiO_2.*

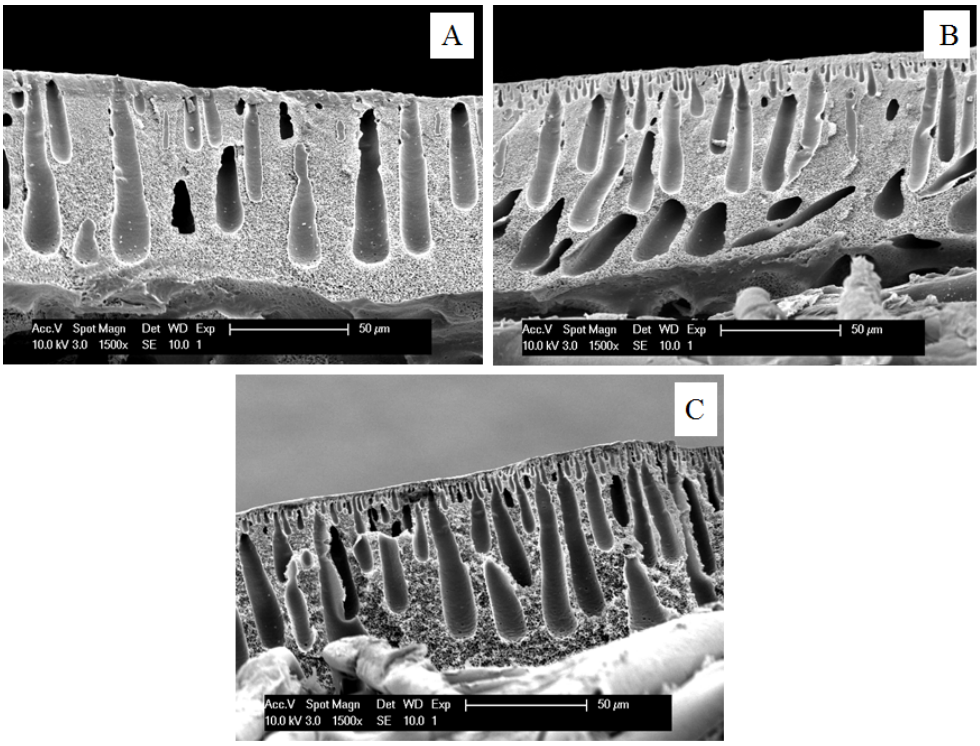

Fig 3 - Cross-sectional SEM images of membranes A) NEAT, B) TiO_2, C) ZnO / *Imagini SEM în secţiune a membranelor:A) NETE, B) TiO_2, C) ZnO.*

Adding nanoparticles, the permeability increase from 37.03 *$Lm^{-2}H^{-1}bar$* for neat membranes to 41.59 *$Lm^{-2}H^{-1}bar$* for membranes with TiO_2 and to 54.51 *$Lm^{-2}H^{-1}bar$* for membranes with ZnO. This effect of nanoparticles on the membranes permeability is similar with the results obtained by others authors in the case of TiO_2 nanoparticles [10] and ZnO nanoparticles [11, 12]. Increasing of permeability for membranes with TiO_2 and ZnO nanoparticles is in agreement with the membrane structure, Figure 3, where is shows the improvement of macrovoids formation.

3.2. SEM analysis

The influence of the addition of TiO_2 and ZnO nanoparticles to the membrane morphology is shown in Figure 3.

By adding TiO_2 nanoparticles the numbers of pores from the membrane surface increase in comparison with neat membranes but the macrovoids from the membrane structure are similar. Adding ZnO nanoparticles in PSf membranes have an important impact on the membrane structure. The number of macrovoids from the membrane structure and the porosity increase. An important influence of adding ZnO nanoparticles is on the thickness of the top layer, or separation layer, which became thinner. This effect of ZnO nanoparticle was observed and for other polymer type, for example for PPSU, adding 0.015 wt.% the size and number of macrovoids increase [13].

3.3. The influence of TiO_2 and ZnO nanoparticles on the membranes hydrophilicity

The addition of TiO_2 and ZnO nanoparticles the membranes hydrophilicity increases due to the high affinity of nanoparticles to water. The contact angle results for all types of membranes studied is shown in Figure 4.

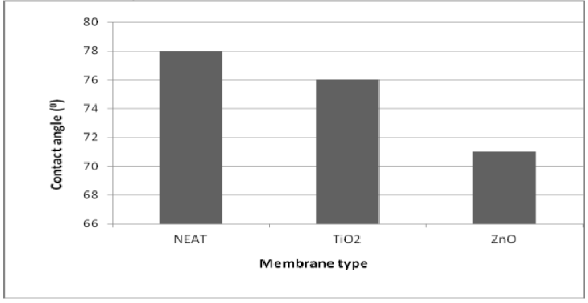

Fig. 4 - Infuence of the TiO_2 and ZnO nanoparticles on the membranes hidrofilicity / *Influenţa nanoparticulelor de TiO_2 şi ZnO asupra hidrofilicităţii membranelor .*

The results of membranes hydrophilicity are in concordance with the permeation properties. Adding TiO_2 nanoparticles the hydrophobicity decrease and the permeability increase. The same effect but more evident is when ZnO nanoparticles are added in the membrane structure. The contact angle is lower the porosity increase and a large fraction of water diffuses trough the membrane structure.

4. Conclusion

The results of this study show that the addition of nanoparticles has a positive influence on the permeation properties of membranes. Membranes blended with ZnO nanoparticles have a better improvement of water flux comparing with neat membranes and with membranes blended with TiO_2 nanoparticles. This was observed at the same concentration of polymer, 0.125 wt.% and 32 wt.% PSf. Membrane porosity increase for the both type of composite membranes but the thickness of ZnO composite membranes is smaller, explained the permeation results. The improvement of blended membranes may lead to new applications of membranes in the forthcoming years due to the attractive properties of nanoparticles in general and of ZnO in particular.

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