THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 1 – 2011, ISSN 1453 – 083X

INFLUENCE OF THE NANOPARTICLES SIZE ON THE PERMEATION PROPERTIES OF THE POLYMERIC MEMBRANES

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ABSTRACT

In this study, polyethersulfone (PES) membranes blended with zinc oxide nanoparticles (ZnO) were manufactured by diffusion induced phase inversion in N-Methyl-pyrrolidone (NMP) as solvent and deionized water as coagulant, in view of increasing the properties of the polymeric membranes. Neat PES membranes were modified by dispersing ZnO nanoparticles with two different sizes in a PES casting solution. Four different concentrations of nanoparticles was studied between 0.035 to 1 wt.% for four different concentration of PES (25, 27, 30 and 32 wt.%). The influence of the ZnO nanoparticles size on the permeation performances of PES/ZnO membranes were investigated with contact angle and filtration experiments. The results show an important improvement of the neat membranes properties, permeability and flux, by adding ZnO nanoparticles with two different size even at a smaller concentration, less than 0.5 wt.%. The influence of the nanoparticles size is obvious, decreasing the nanoparticles size, the permeation properties of the polymeric membranes increase.

KEYWORDS: nanofiltration, ZnO nanoparticles, membrane synthesis

1. Introduction

Polyethersulfone is one of the most common polymers used in nanofiltration (NF). PES membranes are applied in the treatment of wastewater in industry [1-3] and in the production of drinking water [4-5] because they have a high retention of multivalent ions and organic molecules with a molecular weight above 300 Da. One of the main problems of the nanofiltration is the fouling phenomenon, this is attributed to the organic adsorption on the membrane surface. Membrane fouling leads to diminished the membrane performance, seriously deficient production, and excessive operating costs [6,7]. Because of the fouling, the dyes rejection [8-10] and the permeation properties [11-13] of the membranes decrease due to a higher hidrophobicity of the membrane surface. Membrane fouling depends on the membrane characteristics [14-17] and on the filtration mode (cross-flow or dead-end filtration) [18].

In view of improving the fouling resistance and other properties of polymeric membranes like permeation, thermal stabilities, and mechanical properties, many types of nanoparticles have been used to prepare composite membrane recently, and their application fields have covered microfiltration [19,20], ultrafiltration [21–27], gas separation [28,29], as well as pervaporation [30].

The composite membranes are in general prepared by dispersing the nanoparticles in the casting solution and prepare the membrane via phase inversion [31-37] or by dipping the prepared membrane in a suspension with nanoparticles [38, 39]. The advantage of the first method is that the nanoparticles are more stable in the polymer matrix in comparison with the second method but with a lower efficiency of the nanoparticles use.

The effects of nanoparticles as additive on the preparation of polyethersulfune (PES) blend nanofiltration membranes were investigated in terms of water pure flux and hydraulic membrane resistance (permeability). In this study, a polyethersulfune (PES) membrane was modified by dispersing two different nano-sized zinc oxides particles in a PES solution with N-Methyl-pyrrolidone (NMP) as solvent.

2. Experiment

2.1 Materials

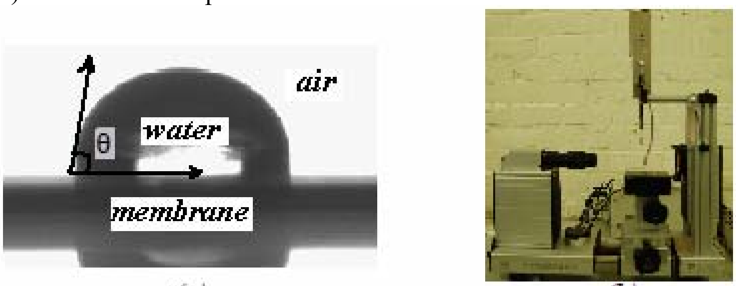
The support layer, Viledon FO2471, for the membrane manufacturing was obtained in Freudenberg (Weinheim, Germany). The polymer used was Polyethersulfone, provided by Solvay (Belgium) and like solvent was chosen 1-Methyl-2-pyrrolidone (NMP, 99.5%). ZnO nanoparticles, and it was provided by Sigma-Aldrich (St. Louis, MO).

2.2 Membrane preparation

Neat Polyethersulfone membranes and blended with ZnO nanoparticles were manufactured at different concentrations of polymer (25, 27, 30 and 32 wt.%) and nanoparticles with two different size, 50nm and 80 nm, in N-Methyl-pyrrolidone as solvent using the phase inversion induced by immersion precipitation. Four different concentrations of ZnO nanoparticles, for both sizes, were used: 0.250, 0.500, 0,750, and 1 wt.%. The casting solution was obtained by adding ZnO nanoparticles into the solvent and mixed through mechanical stirring at 200 rpm and room temperature. After three hours the polymer was added to the solution and stirred for 24 hours at 40^{0}C and 500 rpm. A thin film of the polymer solution with a thickness of 250 µm was cast on a polyester support with a filmograph (K4340 Automatic Film Applicator, Elcometer) in an atmosphere with relatively controlled air humidity, at room temperatures. After casting the membrane was immersed in a non-solvent coagulation bath for precipitation. After 15 minutes, to remove the excess of solvent, the membrane were repeatedly washed and stored in distilled water. For every type of membrane, two different solutions were made and from every solution three membranes was manufactured and tested to obtain the true values of retention and permeation properties of the membranes.

2.3. Water contact angle

To study the hydrophilicity/hydrophobicity of the membranes was used a Drop Shape Analysis System DSA 10 Mk2. On the cleaned and dry membrane surface was placed a distillate water droplet of 2 µl and the contact angle between the membrane surface and the droplet was calculated (figure 1). The final value of the contact angle for every type of membranes was the average 21 measurements, seven determinations for three different membranes.



(a) (b)

Fig. 1. *Contact angle measurements: (a) the principle and (b) the setup*

2.4. Filtration experiment

To determine the pure water flux, have been tested all the membranes for a long time in a cross flow installation (figure 2b). In all experiments the temperature was 24 ^oC and the applied pressure was 8 bars. The membranes surface area was 0.0059m^2 and the time for every experiment was 24 hours.

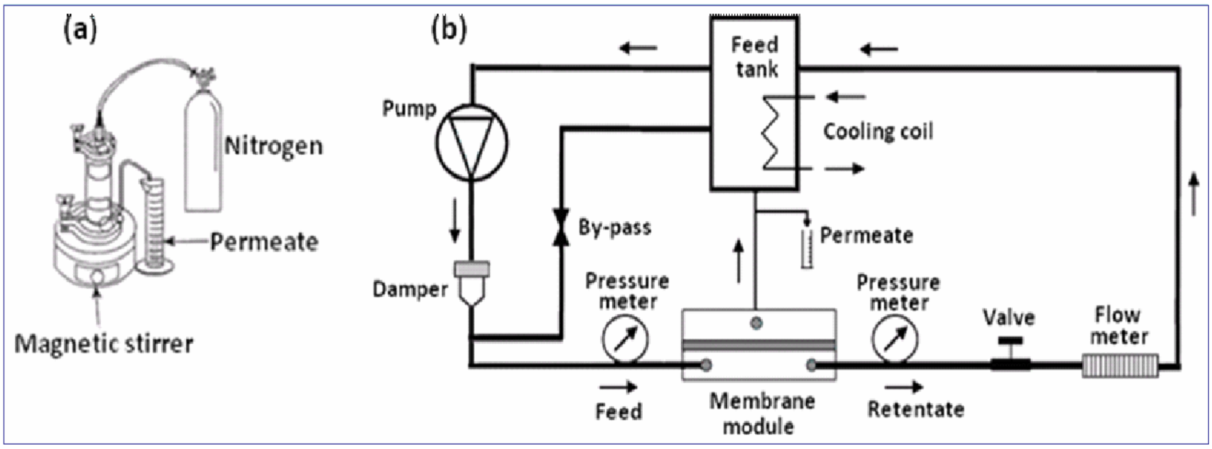


Fig. 2. *Filtration equipment: a) dead-end and b) cross flow*

The pure water flux and permeability of the prepared membranes were studied using a dead end filtration device (figure 2b).

All experiments were made at the room temperature at desirable pressure on the Sterlitech HP4750 Stirred Cell to keep a homogeneous solution inside of the dead end device. The pressure was realized with a nitrogen cylinder with a pressure regulator, connected to the cell. A wide range of membranes were tested, five samples for six different membranes.

The final results are the average of 30 experimental values. The solution volume was 250 ml and the permeate was collected in a graduate cylinder. The pure water flux was determined at 10 bar pressure and the time was measured at every 5 ml of permeate.

To determine the pure water permeability (*PWP*), the water flux (J_w) was measured at six different pressure (ΔP) from 5 to 20 bar. The *PWP* was calculated by the following equation:

$$PWP = \frac{J_w}{\Delta P} \qquad (1)$$

3. Results and discussions

3.1. Pure water flux and permeability

It was observed that the polymer concentration has a negative influence on the permeation properties of membranes. Increasing the concentration of PES the pore size decrease and in consequence the pure water flux (figure 3) and permeability (figure 4) decrease. Membranes with 25% of PES have a good permeability but because of the weaker mechanical resistance, they have an important instability of flux in time. For 30 and 32% of PES the improvement is not so evident in comparison with membranes at smaller concentration of polymer. For this reason and because of the membranes instability at 25% of PES, the membranes at 27% were chosen for future studies.

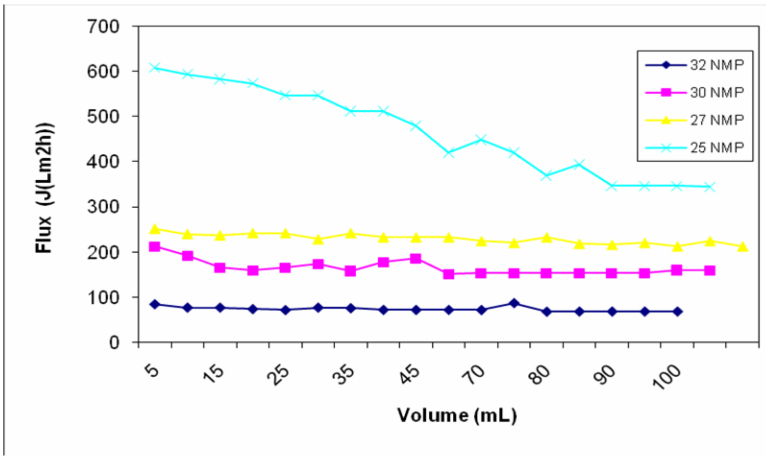


Fig. 3. *Pure water flux of neat membranes at different concentrations of PES*

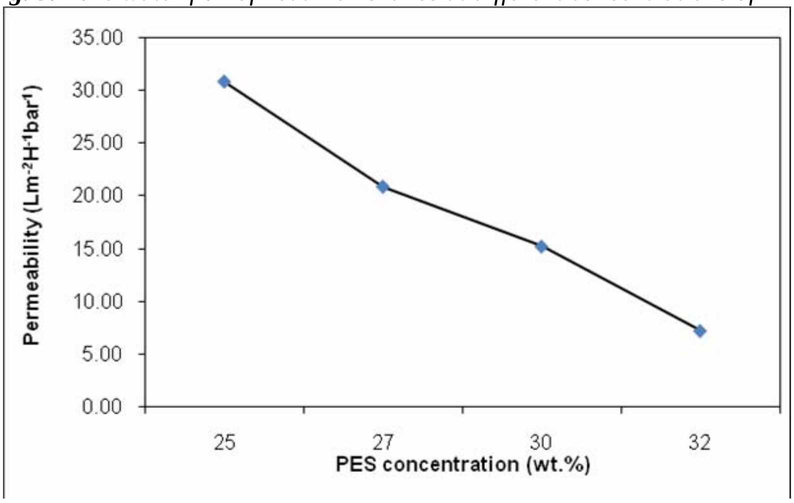


Fig. 4. *Permeability of neat membranes at different concentrations of PES*

The addition of a small amount of nanoparticles with 80nm size, 0.250 wt.%, increases both pure water flux and permeability.

Decreasing the nanoparticles size until 50nm, the permeability and pure water flux increase.

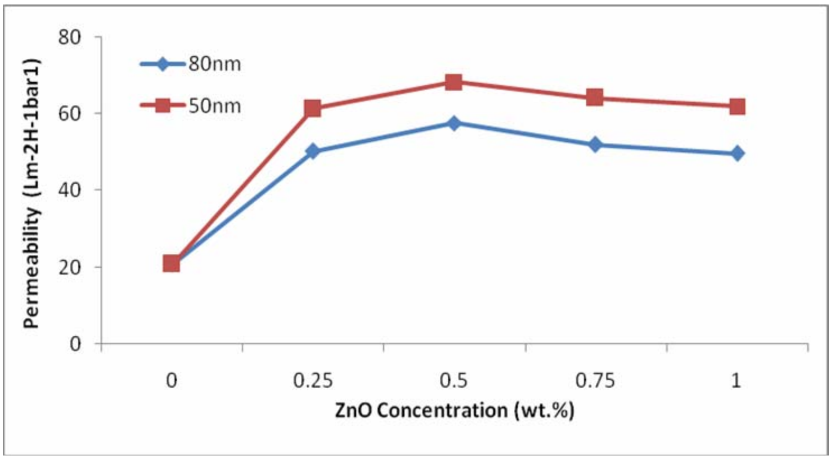


Fig. 5. *Permeability of blended membranes with different size of nanoparticles*

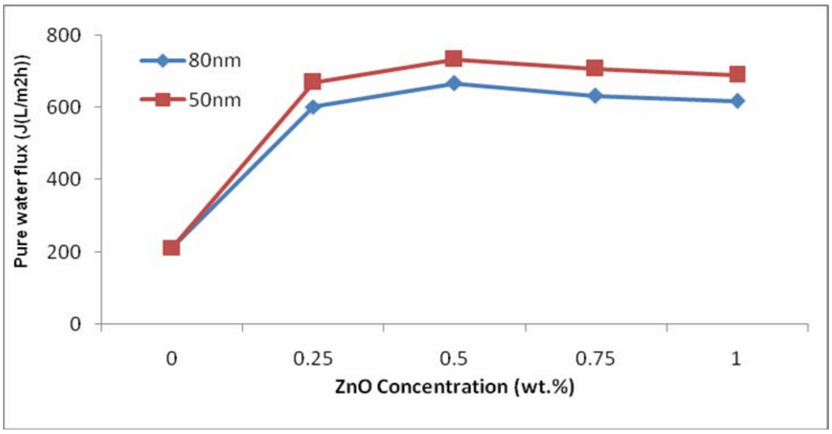


Fig. 6. *Pure water flux of blended membranes with different size of nanoparticles*

The comparison of the results for different sizes of nanoparticles shows the same tendency of the permeability (figure 5) and pure water flux (figure 6) but with an important improvement.

For example the permeability for the membranes with a concentration of 0.250 wt.% of nanoparticles increases from 50.25 for membranes with nanoparticles of 80 nm size up to 61.35 for membranes with nanoparticles of 50 nm size.

These results show an important influence of the nanoparticle size on the permeation properties of the polymeric membranes.

3.2. Hydrophilicity and contact angle

To study the membrane surface hydrophobicity a contact angle experiment was done, knowing that the membranes with a hydrophilic surface have a low contact angle [35].

Figure 7 shows the values of the contact angle for neat and blended membranes at different concentrations and sizes of the nanoparticles. The results show that membranes hydrophilicity increases when id added nanoparticles and in the same time it increases if the size of the nanoparticles decrease. In concordance with permeability the ZnO blended membranes are more hydrophilic than neat PES membranes.

Nanoparticles in comparison with polymer have a higher affinity to water, this can be an explanation for the increases of permeability by addition of nanoparticles.

It can be concluded that in comparison with other types of nanoparticles where the concentration has an important impact on the porosity [30, 36, 37], the concentration of ZnO nanoparticles does not have an important influence. For a large range of concentrations, the porosity is similar.

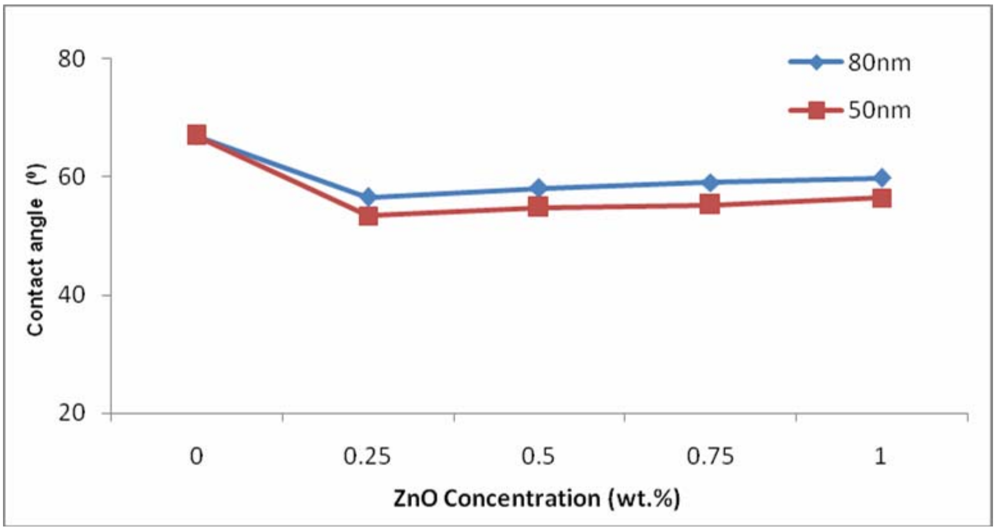


***Fig. 7.** Contact angle at different nanoparticle sizes and concentration*

4. Conclusions

Neat and ZnO blended membranes were prepared via phase inversion by dispersing the ZnO nanoparticles in the PES casting solution. A systematic study of the influence of the polymer and ZnO nanoparticles size and concentration was carried out. Various experiments such as permeability and contact angle were utilized.

ZnO blended membrane showed lower flux decline and a better permeability compared to neat polymeric membrane due to a higher porosity of the ZnO membranes.

The size of the nanoparticles has an important influence on the permeation properties of the membranes. Decreasing the size of the nanoparticles the permeability and pure water flux of the membranes increase.

Acknowledgements

Stefan Balta would like to acknowledge the support provided by the European Union, Romanian Government and Dunarea de Jos University of Galati, through the project POSDRU – 6/1.5/S/15.

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