



IMPROVED SELECTIVITY OF A POLYSULFONE MEMBRANE BY SURFACE GRAFTING OF A VINYL ACETATE MONOMER

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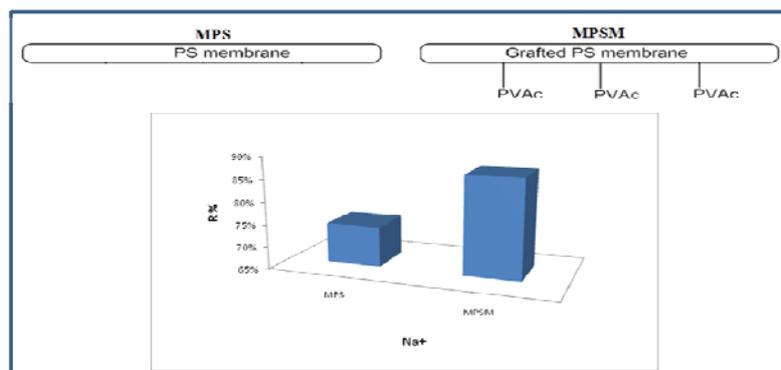
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The current investigation involved the chemical modification of a commercial Polysulfone PS membrane by grafting vinyl acetate monomers onto the surface to evaluate the removal of the Na⁺ ion. Graft polymerization on the membrane surface was developed under reflux in ethanol; several moles of monomer/initiator were used to examine PS-grafting-PVAc membranes. The modified protocols and the progression of the polymerization reaction were studied by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle, and X-ray photoelectron spectroscopy (XPS). An application with a frontal filtration module was explored to confirm the enhancement of selectivity and retention rates for the seawater. The findings showed that the surface modification of the polysulfone membrane improved both the properties and the performance of the non-grafted membrane.



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INTRODUCTION

Membrane technology has many benefits and is consistent with worldwide strategies in materials as well as energy management. Although membrane fouling affects all membrane separation processes. The durability of such processes has often been decreased as a result of the fouling.¹ Pollutants accumulating on the surface of the membrane or within the porous network, leads to a reduction in the productivity of the membrane. To minimize mem-

brane fouling and enhance membrane performance, the modification of the membrane surface properties without affecting the transfer characteristics is a promising technique.²

To avoid or minimize the fouling, butting the membrane surface allows new separating functions by reducing undesirable interactions and thus improving the rejection.³ Owing to excellent mechanical properties, good resistance against thermal aging and high chemical stability, polysulfone PS membranes have been used in a

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wide range of applications. As a result of the hydrophobic character of the PS material, conventional PS membranes have a fouling problem and thus a low permeation flux, which is undesirable in the reverse osmosis filtration process. PS membrane surface modification has been an efficient way to improve the properties and reduce fouling of PS membranes. Such surface modifications target to change the hydrophobicity and the roughness of surface by creating a thin layer via interracial polymerization on the membrane surface.⁴

Several different types of modifying agents have been used for membrane surface modification by carboxylation, sulfonation, amination, and peroxylation.⁵ PS membranes can generally be modified through coating with additional surface layer, such as polyethylene glycol (PEG) or lyophilic polyvinyl alcohol (PVA), or by cross-linking hydrogels which have shown a significant enhancement in fouling resistance.⁶ There are some examples of coatings used for surface modification of PS membranes, such as polyethylenimine on the surface of PS membrane as well as PEG in sodium alginate. These coatings have concurrently improved the membrane flux.⁷ For the chemical grafting, membrane surfaces contained chemical groups that could be exploited in the grafting reaction. Functionalization of the membrane surface and the initiation of the polymerization reaction are achieved by creating radicals that promote the attachment of modifying agents to the membrane surface. PS membranes can be grafted by plasma treatment, UV irradiation or chemical surface modification.⁸

The plasma treatment was used to covalently bind hydrophilic polymers like PEG and polyacrylic acid (PAAc) and polymers with amine moieties covalently to the surface of PS membranes. UV-initiated grafting of polyethylene glycol methacrylate (PEGMA), acrylic acid (AAc), and acrylamide (AAm) reduces fouling and enhances water permeability of PS membranes.⁹ As for molecular weight-based modifications, the polymers were grafted to the membrane surface by atom transfer radical polymerization (ATRP). This grafting justified the introduction of hydrophilic polymers and consequently the anti-fouling properties of PS membranes are improved.¹⁰ The chemical grafting polymerization is one of the high-quality surface modification methods, such as distinctive properties for a new separation of functions. This method is fairly easy to carry out,

inexpensive since the low cost monomer has been closed for the polymerization process staples.¹¹

MATERIALS AND METHODS

1. Starting materials

PS commercial membrane supplied by an american industrial specialized in reverse osmosis manufacturer has been employed (LENNECH, reference BW 30-4040). Moreover, benzoyl peroxide provided by Sigma-Aldrich (801641) Benzoyl peroxide (with 25% H₂O) for synthesis, CAS 94-36-0, molar mass 242.23 g/mol. Finally, vinyl acetate provided by Sigma-Aldrich (803184) Vinyl acetate (stabilised) for synthesis, CAS 108-05-4, pH 7 (20 g/L, H₂O, 20 °C).

2. Chemical reactions occurring during vinyl acetate grafting

The surface of the PS membrane studied can be chemically modified by the use of benzoyl peroxide as initiator to cleave the C-S bond. The degradation of benzoyl peroxide leads to the formation of two types of free radicals on the membrane surface. The formation of the R* radical causes the initiation of the grafting reaction on the PS membrane surface. The order of addition of the initiators and the monomer avoids a competition between two possible reactions: one on the vinyl monomers and the other on the sulfoxyl function SO₂. After formation of free radicals on the surface of the membrane, the introduction of vinyl monomers into the reactive medium leads to the initiation of the polymerization reaction of vinyl acetate on the surface of the PS membrane (Fig 1).

The presence of a medium rich in vinyl acetate allows the propagation of chains and the formation of macromolecules exhibiting very large dimensions.¹²

3. Experimental procedure and grafting parameters

In this paper, we will study the effect of the variation of two parameters on the grafting of vinyl acetate monomers on the PS membrane surface. These two parameters are the ratio monomer/grafting initiator and the function carried by the grafted polymer unit. We have opted to

work on all grafting reactions in organic medium in the presence of ethanol as solvent because it is less toxic than other organic solvents and at low temperature, the choice of a low temperature can help us to control the length of the grafted chains and thus avoid quite important kinetics that lead to the formation of quite long macromolecules. The length of the grafted chains can affect the properties of the membrane. To avoid the effect of this parameter, we tried several monomer/initiator ratios to vary the length of chains attached to the active sites of the PA membrane. The ratios studied are $R_1 = 28135$, $R_2 = 2813$ and $R_3 = 28$.

4. Characterization of the modified surface of membrane

The modifications of the surface of membranes have been highlighted by different characterization

methods such as ATR-FTIR (Fourier-Perkin Elmer-FTIR 2000), SEM (JEOL JSM IT300 LV and FEG 450 QUANTA FEI), AFM (AGILENT TECHNOLOGIE AC mode III AGILENT 5500 LS), contact angle technique (CONTACT ANGLE METRE MODEL DIGIDROP) and XPS (AXIS ULTRA DLD). The hydrophilicity, the membrane surface roughness and the uniformity of the modification are the crucial factors to evaluate our modification procedure. The modification of the hydrophobicity of the membrane surface can be estimated by measuring the values of the contact angle or by changes of the Zeta potential, the roughness and the surface uniformity are parameters could be evaluated by AFM thus images and morphological sections of the modified PS membrane surface were characterized by SEM scanning electron microscopy.

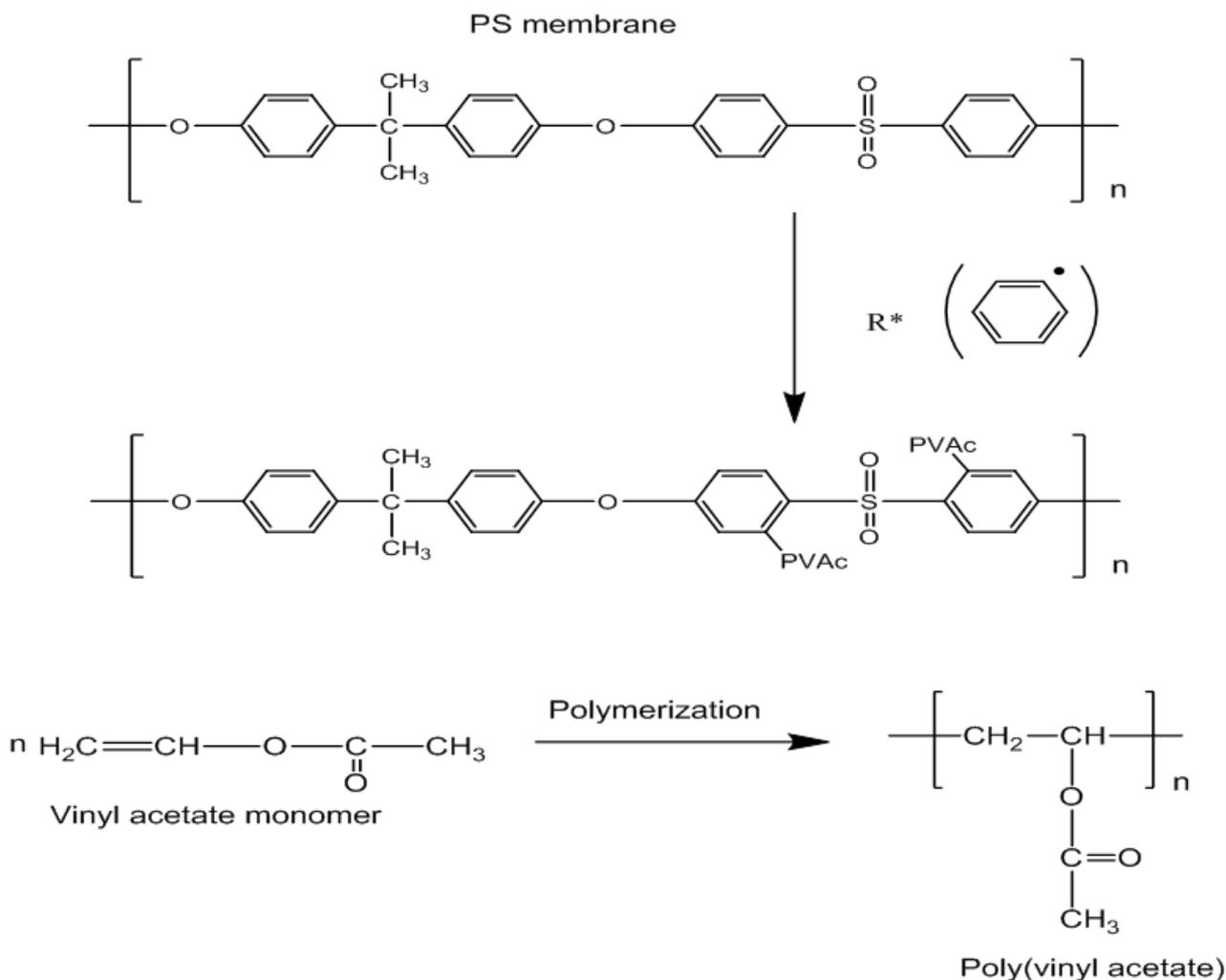


Fig. 1 – Grafting reaction of PVAc on the surface of the PS membrane.

RESULTS AND DISCUSSION

1. Characterization of membranes modified by ATR-FTIR

The ATR-FTIR spectra of PS membrane modified by chain grafting of polyvinyl acetate (MPSMR1) showed modifications at the levels characteristic bands of the commercial PS membrane (MPSNM) (Fig. 2). As expected, the commercial PS membrane (MPSNM) showed a typical spectra of PS, *i.e.*, the band at 3050 cm^{-1} correspond to a valence vibration of the group CH, the band at 2969 cm^{-1} correspond to a valence vibration of CH_3 , the band at 1350 cm^{-1} correspond to a valence vibration of the SO_2 bond, and the band at 700 cm^{-1} correspond to a valence vibration of the CS bond. That spectra revealed a very weak band at $3400\text{--}3600\text{ cm}^{-1}$ that is associated with the OH stretching of water molecules. There is no OH band in the PS structure but some researchers consider that the presence of remaining poly (vinylpyrrolidone) in the membrane structure and its high tendency to water may cause a band in the area of OH stretching.¹³ On the other hand, porous materials can retain a small amount of water in their pores that, in practical terms, are almost impossible to remove. The infrared spectra of PS membranes modified by chain grafting of polyvinyl acetate (MPSMR1) show the absorption bands observed at 3445 and 2850 cm^{-1} are

assigned to the vibrations of OH and CH_2 , respectively. Compared to commercial PS membrane (MPSNM), PS membranes modified (MPSMR1) shows two new absorption bands at 1090 and 1040 cm^{-1} , which are ascribed to the symmetric and asymmetric stretching vibrations of SO_2 .

2. Characterization by SEM of the surface of grafted membranes

Scanning electron micrographs were used to visualize the morphologies of the membrane surface before and after grafting. The scanning electron microscopy image of the unmodified PS membrane surface is shown in (Fig. 3). Surface morphological imaging showed some parallel bands on the membrane surface not observed on the modified PS membrane.¹⁴ After grafting, the attached polymer film significantly changed the surface appearance as shown in (Fig. 3).

Based on Figure 4, it can be observed that the cross-sectional morphology of the PS membrane surface is a porous surface with a well-structured underlayer. After the modification, there is no significant change in the underlay, which indicates that the grafting of PVAc did not require any deep underlay and grafting only occurs on the surface of the PS membrane and that the change on the top layer can be easily observed.¹⁵

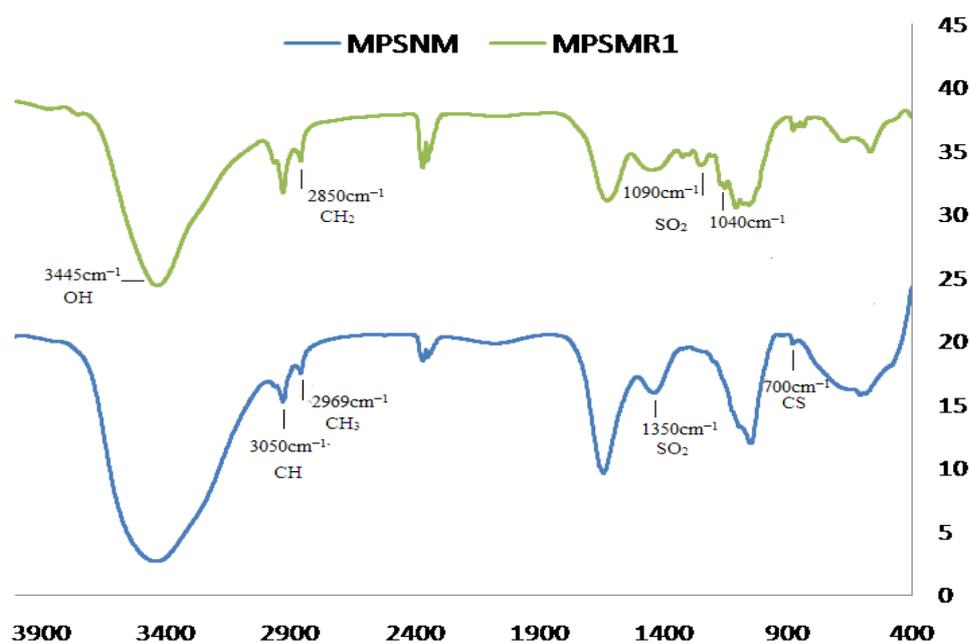


Fig. 2 – IR spectrum of the MPSNM and MPSMR1.

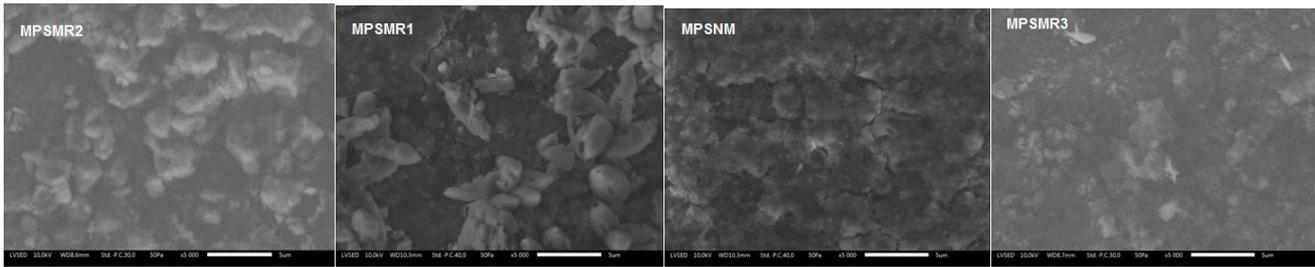


Fig. 3 – SEM of MPSNM, MPSMR1, MPSMR2 and MPSMR3.

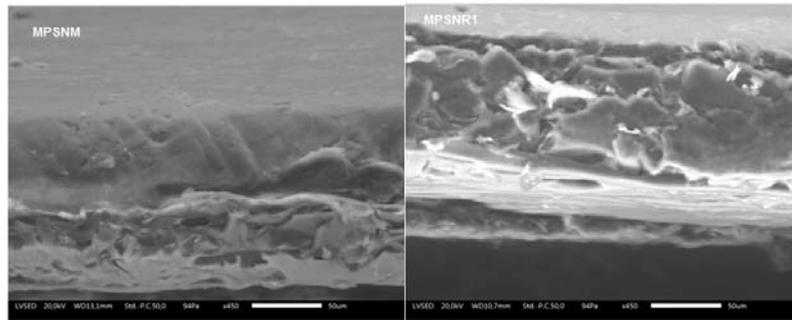


Fig. 4 – Cross sectional morphology of MPSNM and MPSMR1.

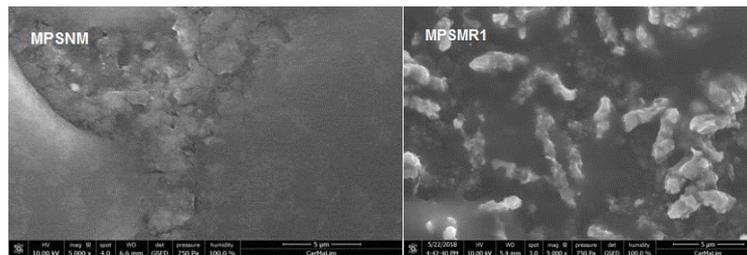


Fig. 5 – SEM environmental of MPSNM and MPSMR1 at wet condition.

Moreover, we can claim that the pore size becomes smaller after the surface modification of the PS membrane, such that the surface of the modified membrane becomes porous but is smooth. This is probably due to the partial or total penetration of the PVAc graft polymer into the pores of the top layer of the PS membrane, which is a hydrophobic one, which leads to a smooth and hydrophilic surface for the modified PS membrane, as shown in the environmental SEM images (Fig. 5).¹⁶

3. Characterization by AFM of the surface of grafted membranes

The findings obtained by AFM characterization for the surface topography was generally coherent with the SEM observations. AFM images revealed that the surface of the MPSNM membranes was flat and uniform. Although, the roughness of the modified membranes is almost double that of unmodified ones and the modified surface is still bright and smooths (Fig. 6). The smooth surface

can provide the membrane with promising anti-fouling properties. The smooth surface of the PS modified membrane can be responsible for improving the antifouling property.¹⁷

4. Surface damping property

The contact angle technique involves the values of a liquid drop deposited on the membrane surface. The (Fig. 7) shows the contact angle of the water with the PS membrane and PS modified membrane with different monomer / initiator ratio on the surface layer of the membrane.

The PS membrane has contact angle values of 93.4° whereas modified PS membranes have lower contact angle values. The decreasing values of the contact angle indicate a higher wettability of the membrane surface, which promotes the formation of a layer of water on the membrane surface which inhibits the attachment of impurities on the membrane surface during filtration.¹⁸

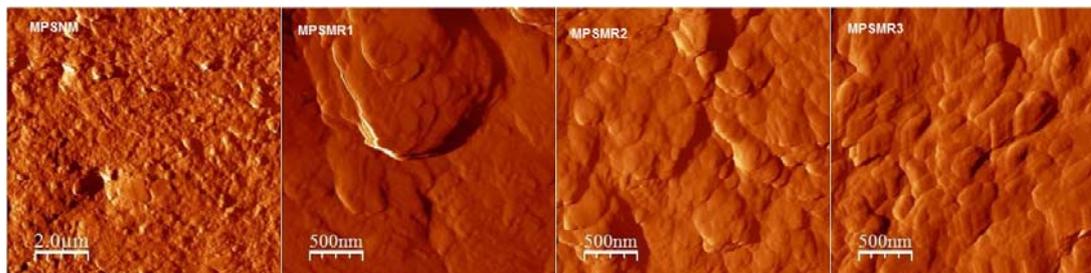


Fig. 6 – AFM of MPSNM, MPSMR1, MPSMR2 and MPSMR3.



Fig. 7 – Angle contact of MPSNM, MPSMR1, MPSMR2 and MPSMR3.

5. XPS Analysis

XPS spectra were performed to analyze the elemental composition of the modified PS (MPSMR1, MPSMR2 and MPSMR3) and the commercial PS membrane (MPSNM). The XPS signals at 286 and 533 eV correspond respectively to the carbon and oxygen elements. This is because there are no new elements to be introduced onto the membrane surfaces during the PVAc grafting (Fig. 8).

The modified samples (MPSMR1, MPSMR2 and MPSMR3) showed a high oxygen content compared with the commercial PS membrane (MPSNM) which is due to the presence of PVAc

on the PS modified membrane surfaces. This confirms the modification of the structure of the surface of the PS membrane by chemical grafting of PVAc on the membrane surface. The result provides a new evidence for the successful grafting of PVAc besides the ATR-FTIR analysis.

The PVAc-grafted membrane which has the highest monomer / initiator ratio (MPSMR1), showed a high oxygen content compared with the commercial PS membrane (MPSNM) and the modified ones (MPSMR2 and MPSMR3). This is because the content of oxygen element in the surface of the grafted PS membranes increases with the monomer / initiator ratio.¹⁹

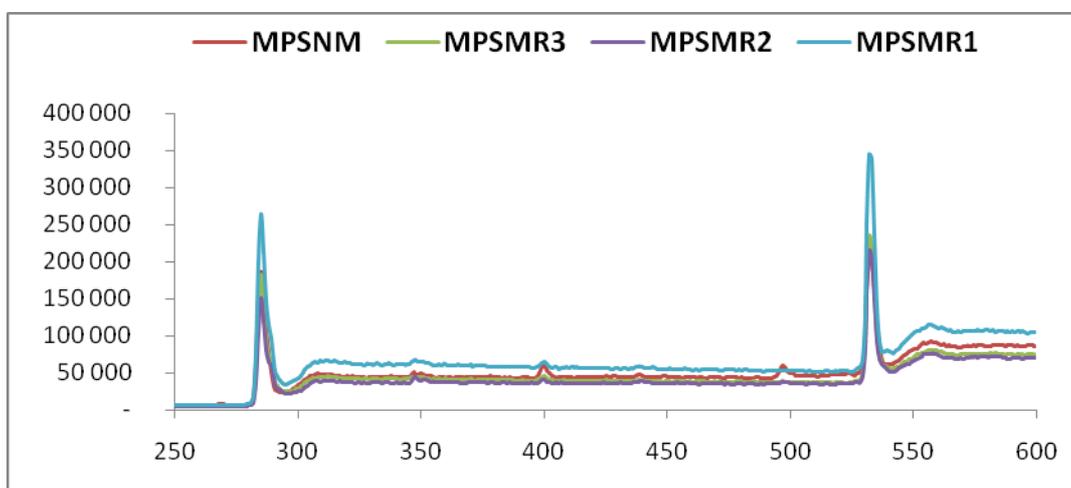


Fig. 8 – XPS of MPSNM, MPSMR1, MPSMR2 and MPSMR3.

PERFORMANCES OF MODIFIED PS MEMBRANE IN SERVICE CONDITIONS

1. Hydraulic permeability

The permeate water flux was determined by measuring the permeate volume collected over a certain period in terms of a liter per square meter per hour (l / m²h) and calculated through the following equation:

$$J_v = \frac{Q_p}{S} = \frac{V_p}{t \times S}$$

where J v is the permeation flow, S is the effective area of the membrane for permeation, Q p is the volumetric permeation rate over a time interval Δt and V p is the volume of permeate recovered.

The water flow of MPSNM raw PS membranes and modified by PVAc grafting to the membrane surface with different monomer / initiator ratios (MPSMR1, MPSMR2 and MPSMR3) were studied with the same frontal filtration module and the results showed that the Water flow decreases with increasing chain length of PVAc grafted onto the surface of the commercial PS membrane (Fig. 9).

As the monomer / initiator ratio increases, the thickness and degree of crosslinking of the grafted PVAc layer on the surface of the grafted PS membranes decreases which also hinders the penetration of water flow through the membrane.

In particular, the modified PS membrane with the lowest monomer/ initiator ratio (MPSMR3) showed a high water flow compared to the other PS membranes modified by the other monomer / initiator ratios (MPSMR1 and MPSMR2). The length of the PVAc polymer chain grafted onto the surface of the PS membrane influences the behavior of these membranes. More the PVAc chain is long, more the clogging phenomenon is favored and the fouling behavior of the grafted PS membranes depends on the monomer / initiator ratio.²⁰

2. Study of the behavior of modified membranes with respect to the element Na⁺

The rejection was evaluated using the following equation:

$$R = (1 - (C_p / C_i)) * 100$$

in which Cp and Ci are the concentrations of ions Na⁺ in permeate and feed.

The study of the retention of the Na⁺ ion shows that the uptake of the commercial polysulfone membrane MPSNM is 74% while the yield of our membrane modified by grafting MPSMR3 is 87%. This study shows an improvement in the case of the membrane modified due to the selectivity of acetate groups vis-à-vis sea water.²¹

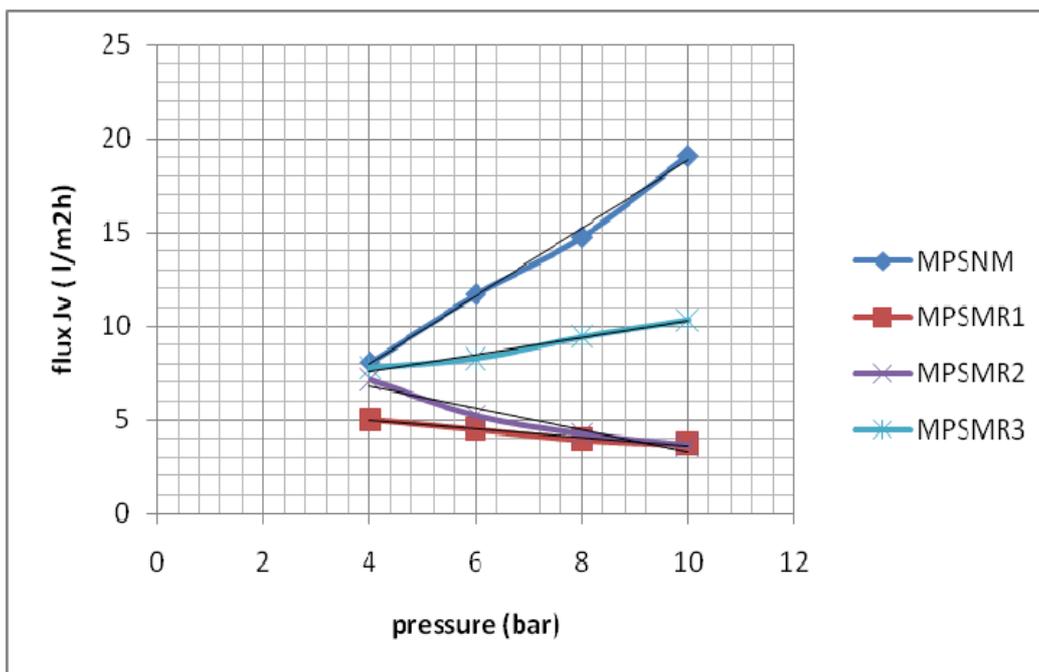


Fig. 9 – Flow water evaluation of PS membranes MPSNM, MPSMR1, MPSMR2 and MPSMR3as a function of the pressure.

CONCLUSION

The analysis of the structure of the grafted polymer layers on the surface of PS membranes highlights various characteristics. A reduction in roughness was obtained with RO membranes using AFM technique. Thus, if a substantial modification of the surface roughness is required, the grafting procedure described must be improved. SEM analysis of the modified membrane cross-sections reveals a reasonable correlation with the extent of grafting as determined by ATR-FT-IR. Results derived from SEM suggest that a thin layer of hydrophobic polymer may indeed form on the surface of the active layer.

The filling of the pores of the support by the grafted polymer occurs in some cases, especially in high degrees of grafting. This phenomenon should be avoided by optimizing the conditions so that grafting takes place only on the active surface. This optimization must take into account both the chemical factors and the hydrodynamic conditions used in the modification procedure.

REFERENCES

1. Y. Zhang, Y. Wan, G. Pan, H. Shi, H. Yan, J. Xu, M. Guo, Z. Wang and Y. Liu, *J. Appl. Surf. Sci.*, **2017**, *419*, 177–187.
2. J. Nikkola, J. Sievänen, M. Raulio, J. Wei, J. Vuorinen and C. Y. Tang, *J. Membr. Sci.*, **2014**, *450*, 174–180.
3. A. C. Sagle, E. M. Van Wagner, H. Ju, B. D. McCloskey, B. D. Freeman and M. M. Sharma, *J. Membr. Sci.*, **2009**, *340*, 92–108.
4. J. S. Louie, I. Pinnau, I. Ciobanu, K. P. Ishida, A. Ng and M. Reinhard, *J. Membr. Sci.*, **2006**, *280*, 762–770.
5. D. Li D, J. Wu, S. Yang, W. Zhang and F. Ran, *New J. Chem.*, **2017**, *41*, 9918–9930.
6. M. Nyström, *J. Membr. Sci.*, **1989**, *44*, 183–196.
7. F. F. Stengaard, *J. Desalination.*, **1988**, *70*, 207–224.
8. L. T. Duarte, A. C. Habert and C. P. Barges, *J. Desalination.*, **2002**, *145*, 53–59.
9. A. Idrisa, N. M. Zaina and M. Y. Noordin, *J. Desalination.*, **2007**, *207*, 324–339.
10. J. F. Li, Z. L. Xu, H. Yang, L. Y. Yu and M. Liu, *J. Appl. Surf. Sci.*, **2009**, *255*, 4725–4732.
11. M. L. Luo, J. Q. Zhao, W. Tang and C. H. Pu, *J. Appl. Surf. Sci.*, **2005**, *249*, 76–84.
12. N. Maximous, G. Nakhla, W. Wan and K. Wong, *J. Membr. Sci.*, **2009**, *341*, 67–75.
13. A. Khemakhem, M. R. Ben Romdhane and E. Srasra, *J. Surf. Eng. Appl. Electrochem.*, **2020**, *56*, 561–570.
14. A. Higuchi, N. Iwata and T. Nakagawa, *J. Appl. Polym. Sci.*, **1990**, *40*, 709–717.
15. A. Higuchi and T. Nakagawa, *J. Appl. Polym. Sci.*, **1990**, *41*, 1973–1979.
16. A. Higuchi, S. Mishima and T. Nakagawa, *J. Membr. Sci.*, **1991**, *57*, 175–185.
17. M. Di Vincenzo, M. Barboiu, A. Tiraferri and Y. M. Legrand, *J. Membr. Sci.*, **2017**, *540*, 71–77.
18. X. L. Du, J. Q. Meng, R. S. Xu, Q. Shi and Y. F. Zhang, *J. Membr. Sci.*, **2015**, *476*, 205–215.
19. S. Bing, J. Wang, H. Xu, Y. Zhao, Y. Zhou, L. Zhang, C. Gao and L. an Hou, *J. Membr. Sci.*, **2018**, *555*, 318–326.
20. S. Shultz, M. Bass, R. Semiat and V. Freger, *J. Membr. Sci.*, **2018**, *546*, 165–172.
21. Y. T. Hu, K. Lu, F. Yan, Y. L. Shi, P. P. Yu, S. C. Yu, S. H. Li and C. J. Gao, *J. Membr. Sci.*, **2016**, *501*, 209–219.