J. Applied Membrane Science & Technology, Vol. 11, June 2010, 1–8

Effect of Casting Conditions on SMM Blended Polyethersulfone Hydro-Phobic/-Philic Composite Membranes: Characteristics and Desalination Performance in Membrane Distillation

M. Qtaishat[1*], M. Khayet[2], T. Matsuura[3] & K.C. Khulbe[4]
[1]Chemical Engineering Department, University of Jordan, Amman 11942, Jordan
[2]Department of Applied Physics I, Faculty of Physics, University Complutense of Madrid, Av. Complutense s/n, 28040, Madrid, Spain
[3&4]Industrial Membrane Research Laboratory, Department of Chemical Engineering, University of Ottawa, 161 Louis Pasteur, P.O. Box 450, Stn. A, Ottawa, Ontario K1N 6N5, Canada

ABSTRACT

This study aims at further improvement and development of the novel hydro-phobic/-philic composite membranes which are made specifically for membrane distillation (MD). This was attempted by studying the effect of the casting conditions during the membrane preparation process by the phase inversion method. Two variables were chosen to study, which are the evaporation time before gelation and the gelation path temperature. Some of the membranes were allowed to evaporate at room temperature for 2 or 3 minutes to study the effect of evaporation time. The temperature of the gelation path was varied to 4°C, 20°C or 60°C in order to study the gelation path temperature effect. The prepared membranes were characterized using gas permeation test, measurement of the liquid entry pressure of water (*LEPw*), X-ray photoelectron spectroscopy (XPS), contact angle measurements and atomic force microscopy (AFM). The effects of the casting conditions on the membrane morphology were identified, which enabled us to link the membrane morphology to the membrane performance. The membranes were then tested for desalination of 0.5 M NaCl solution by direct contact membrane distillation (DCMD) and the results were compared to commercial polytetraflouroethylene (PTFE) membrane. It was found that the membrane which was prepared with no evaporation time produced better flux than those with evaporation time. Regarding the gelation path temperature; the membrane prepared with gelation path temperature of 4°C was better than those prepared with gelation path temperature of 20 or 60°C. It should be emphasized that the DCMD flux of the membranes prepared with no evaporation time or with a gelation path temperature of 4°C was superior to the commercial one. Furthermore, all the prepared membranes were tested successfully for the desalination application. In other words, no NaCl was detected in the permeate.

Keywords: Membrane distillation, desalination, hydro-phobic/-philic composite membranes, surface modifying macromolecules, polyethersulfone

1.0 INTRODUCTION

Membrane distillation (MD) is an emerging non-isothermal separation process where a porous hydrophobic membrane acts as a physical support separating a hot feed solution from a cooling chamber containing either a liquid or a gas [1–6]. Direct contact membrane distillation (DCMD) is the oldest and the most widely used MD configuration [6] in which a cold liquid solution is allowed to flow through the permeate side of the membrane in order to condense the vapor that has migrated through the membrane pores from the hot feed solution.

---

[*] *Corresponding to:* M. Qtaishat (email: mrasool78@yahoo.com)

Despite all of the reported MD advantages [1], the process has not been commercialized yet for large scale desalination plants. The reason is the relatively lower MD flux compared to the production of the well established commercialized desalination processes such as reverse osmosis. In other words, this is a result of the inadequate design of the MD membranes, which should have low conductive heat flux (i.e. low heat loss by conduction through the membrane matrix) and high mass transfer flux.

Generally, microfiltration and ultrafiltration membranes made of hydrophobic material such as polypropylene (PP), polyvinylidenefluoride (PVDF) or polytetrafluoroethylene (PTFE), have so far been used in MD experiments. Recently, more research attention has gone into preparing membranes specifically for MD [7]. One of the most promising attempts is the composite hydro-phobic/-philic membranes.

The concept of hydro-phobic/-philic composite membrane for MD was firstly proposed by Khayet *et al.* [8,9]; where surface modifying macromolecules (SMM) were synthesized then blended into the host hydrophilic polyetherimide (PEI) to prepare composite SMM/PEI membranes. The principle of preparing hydro-phobic/-philic composite membrane by the phase inversion method is based on the hydrophobic SMM migration to the air/polymer interface during the membrane gelation since they have lower surface energy; consequently the membrane's top surface becomes hydrophobic while the bottom surface is kept unaltered, i.e. hydrophilic [7–9]. Suk *et al.* [10] later developed new surface modifying macromolecules (nSMM), which was then blended with the polyethersulfone (PES) to develop SMM/PES membranes for MD. It is worth mentioning that the performance of SMM/PEI membranes in MD was better than that of the nSMM/PES membranes [8–10].

The earlier studies [7–10] focused either on developing new types of SMM or on studying the effect of the membrane casting solution composition on the membrane performance and characteristics. However, the effect of membrane casting conditions has not been studied articulately.

In this study, the nSMM was used to prepare SMM blended PES composite membranes. The membranes were prepared by a single casting step via the phase inversion method as described in an earlier study [7].

The main objective of this work is to study the effect of the membrane casting conditions on the membrane characteristics as well as its DCMD performance when distilled water or 0.5 M NaCl solution was used as a feed and to compare the DCMD fluxes of the prepared membranes to those of the commercial PTFE membrane. Another sub-objective is to link the newly developed composite hydro-phobic/-philic membranes' characteristics to their performance in DCMD. To this end, two major casting conditions were chosen; the evaporation time prior to the gelation step and the gelation path temperature.

2.0 METHODS

2.1 Materials

The hydrophilic polymer used in this work is PES (Amoco Polymer Inc., Alpharetta, Georgia, USA) of weigh average molecular weight (M_w) of 30.8 kD. 1-Methyl-2-pyrrolidinone (NMP, anhydrous 99.5%, Sigma-Aldrich, Inc., St. Louis, MO, USA) was used as solvent to prepare the polymer dope solution. Ethanol (anhydrous, 99+%, Aldrich Chemical Company, Inc., Milwaukee, WI, USA) was used as non-solvent additive. nSMM was used as surface modifying macromolecules. The chemical structure of the nSMM is shown in

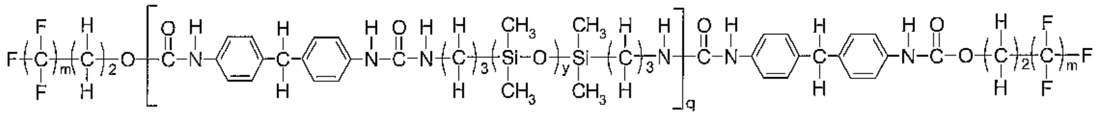


Figure 1 Chemical structure of nSMM

Figure 1. The nSMM synthesising procedure together with its characteristics are shown elsewhere [7]. The commercial membrane used is polytetrafluoroethylene, PTFE, (FGLP 1425) having a porosity of 0.70 and a nominal pore size of 0.25 μm supplied by the Millipore Corporation, Billerica, MA, USA.

2.2 Membrane Preparation

SMM modified PES membranes were prepared in a single casting step by the phase inversion method [7]. 12 wt% of PES was dissolved in a NMP/Ethanol mixture. The amount of non solvent additive (Ethanol) was maintained at 10 wt%. The added SMM concentration was 1.5 wt%. The resulted mixtures were stirred in an orbital shaker at room temperature for at least 48 h. prior to their use; the resulted polymer dope was filtered through a 0.5 μm Teflon® filter and degassed at room temperature. Then, the polymer dope was cast on a smooth glass plate to a thickness of 0.30 mm using a casting rod. Some of the membranes were allowed to evaporate at room temperature for 2 and 3 minutes to study the effect of evaporation time. Subsequently, the cast film together with the glass plate was immersed for 1 h in distilled water (gelation path). The temperature of the gelation path was varied to 4°C, 20°C or 60°C in order to study the gelation path temperature effect. It was noticed that the membrane peeled off from the glass plate spontaneously during gelation. All the membranes were then dried at ambient conditions for 3 days. Table 1 shows the prepared membranes, their materials of construction and preparation conditions.

Table 1 Membrane preparation details[a]

Membrane code	Evaporation time (min)	Gelation path temperature (°C)
M1	0	20°C
M2	2	20°C
M3	3	20°C
M4	0	4°C
M5	0	60°C

[a] PES conc.: 12 wt%; Ethanol conc.: 10 wt%; NMP conc.: 78 wt%; SMM conc.: 1.5%

2.3 Membrane Characterization

The prepared membranes were characterized using a wide variety of characterization techniques including; gas permeation test, measurement of the liquid entry pressure of water (*LEPw*), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and contact angle measurements (CA). A detailed description of the used characterization techniques are available elsewhere [7,11]

2.4 DCMD Experiments

The prepared SMM blended PES membranes were tested by the DCMD setup described in a previous study [8]. The experiments are conducted first for pure water to determine the water vapour permeability of the membranes. Subsequently, aqueous solution of 0.5 M sodium chloride is employed as feed.

The experiments are carried out under a temperature difference between the feed and permeate of 10°C. When distilled water was used as feed, the mean temperature was varied from 20 to 45°C. When 0.5 M NaCl solution was used as feed, the mean temperature was 45°C. The concentration of both feed and permeate solutions is determined by a conductivity meter (712 ΩMetrohm). The solute separation factor, α, is calculated using the following expression:

$$\alpha = \left(1 - \frac{C_p}{C_f}\right) * 100\% \tag{1}$$

Where C_p and C_f are the NaCl concentration in the permeate and in the bulk feed solutions, respectively.

3.0 RESULTS AND DISCUSSION

3.1 Membrane Characteristics and Morphology

The resulted contact angle (CA) data and the fluorine content of the prepared SMM/PES membranes are shown in Table 2. It was observed that the CA of the top side of the prepared membranes is higher than their bottom side. The CA of the top side was nearly equal to or higher than 90° indicating that the top layer is sufficiently hydrophobic. In contrast, the CA of the membranes' bottom side was lower than 90° indicating the hydrophilicity of the bottom layer. This is an evidence of the formation of composite hydrophobic/hydrophilic membranes by the phase inversion method through blending hydrophobic nSMM into a hydrophilic polymer. Furthermore, the CA data agrees with the reported fluorine content from the XPS test. It was further shown that increasing the evaporation time and the gelation path temperature increased the fluorine content in the top side of the membrane. This is logical, since the SMM migration toward the membrane top surface is enhanced by increasing both evaporation time and gelation path temperature.

Table 2 Top and bottom contact angles (CA) and fluorine contents of the prepared membranes

Membrane	CA ($\theta°$)	F (mass conc. %)
M1	Top: 89.76 ± 3.34 Bottom: 62.69 ± 3.82	Top: 7.32 Bottom: 17.12
M2	Top: 97.35 ± 2.82 Bottom: 61.45 ± 3.12	Top: 8.90 Bottom: 16.15
M3	Top: 104.36 ± 2.43 Bottom: 63.89 ± 3.23	Top: 10.71 Bottom: 18.19
M4	Top: 88.79 ± 2.67 Bottom: 69.56 ± 3.08	Top: 6.67 Bottom: 20.42
M5	Top: 98.62 ± 3.18 Bottom: 61.42 ± 4.28	Top: 9.53 Bottom: 8.89

Interestingly, the CA and the Fluorine content of M1 membrane showed the presence of the SMM, even when the evaporation time was zero. This trend might be explained by the fact that SMM were present at the membrane surface from the very beginning and the hydrophobic tails of the SMM could be oriented towards air at the air/solution interface even before the SMM migration began to take place. This indicates the fast migration of the SMM as was previously reported in [10].

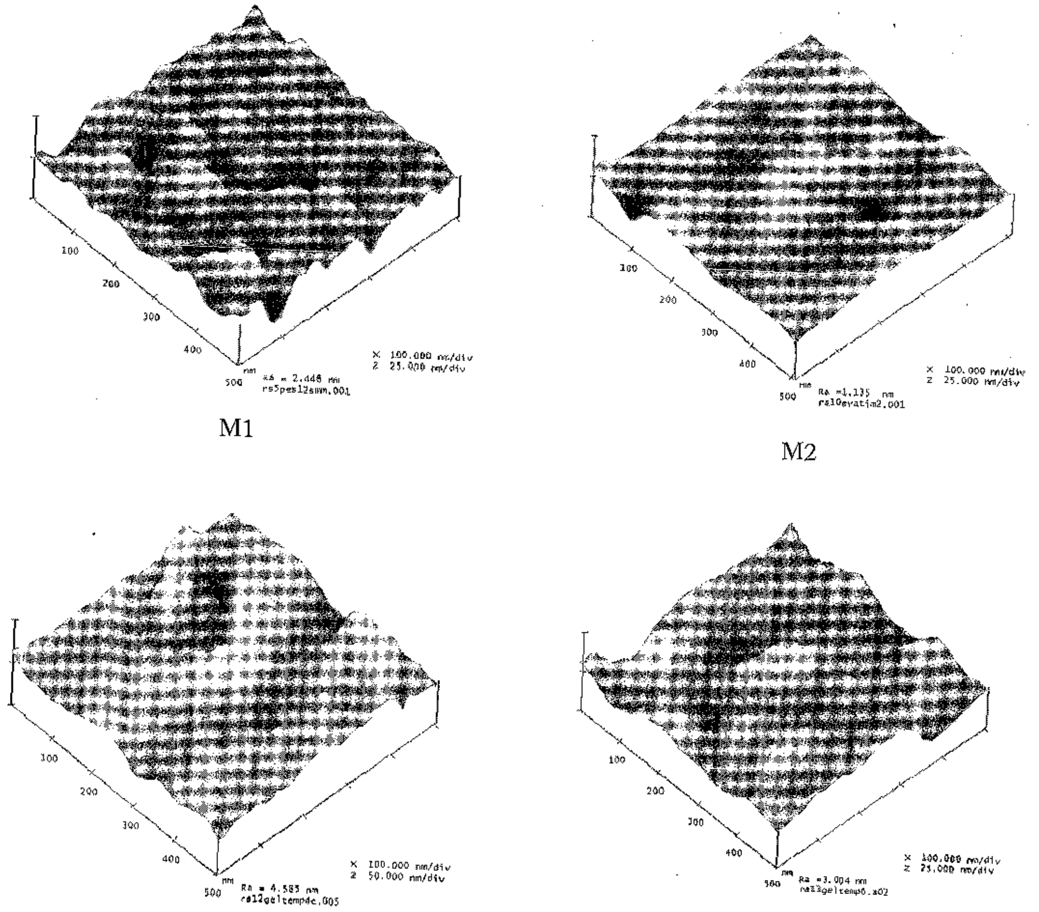
Table 3 shows the prepared membranes' top surface characteristics from the AFM analysis, including the mean pore size (d_p, *nm*), the surface roughness (*R*, *nm*), the mean nodule size (*N*, *nm*) and the geometric standard deviation (σ_p), in addition to the data for the *LEPw* and product of average pore size and effective porosity per unit effective pore length ($r\varepsilon/L_p$) from the gas permeation test.

AFM images of the SMM/PES top side membranes are shown in Figure 2. The bright side is the highest point (nodule) and the dark region is the lowest point (pore). For analyzing the top surface characteristics, AFM image analysis program was used. As shown in Table 3 M1 (no evaporation time) membrane exhibited smaller mean pore size and nodule size compared to that of M2 membrane (evaporation time is 2 minutes). On the other hand, M4 membrane which was prepared at 4°C gelation path temperature exhibited higher mean pore size than those membranes prepared at higher gelation path temperature, i.e. M1 and M5.

Table 3 *LEPw*, $\varepsilon r/L_p$ and AFM top surface analysis of the prepared membranes

Membrane	LEP_w (bar)	$\varepsilon r/L_p{}^a$	$d_p{}^b$ (nm)	R^b (nm)	N^b (nm)	$\sigma_p{}^b$
M1	3.1	6.97 10^{-5}	20.1	2.446	23.1	1.1086
M2	3.6	8.24 10^{-6}	62.2	1.135	32.1	1.2153
M3	4.0	2.20 10^{-6}	N/A[c]	N/A	N/A	N/A
M4	3.0	7.91 10^{-5}	38.5	4.585	29.0	1.2132
M5	4.1	2.86 10^{-6}	23.5	3.004	23.6	1.1956

[a] Adopted from the gas permeation test [7]
[b] Adopted from the AFM analysis
[c] AFM analysis was not performed to M3



M1

M2

M4

M5

Figure 2 AFM images of the top surface of the selected SMM/PES membranes

From the mean pore size (d_p) and the geometric standard deviation (α_p) data, the pore size distribution of the laboratory made membranes can be expressed by the probability density function [12]

$$\frac{df(d_i)}{d(d_i)} = \frac{1}{d_i \ln(\sigma_p)\sqrt{2\pi}} \exp\left[-\frac{(\ln di - \ln d_p)^2}{2(\ln \sigma_p)^2}\right] \quad (2)$$

The pore size distribution of M1, M2, M4 and M5 membranes are shown in Figure 3. As can be seen, M1 (nSMM/PES) membrane exhibited the narrowest pore size distribution.

3.2 Membrane Performance

Figure 4 shows the DCMD fluxes of the prepared SMM/PES membranes along with those of the commercial membrane (FGLP 1425). Figure 4a shows the DCMD flux versus the average temperature of feed and permeate solutions (T_m) when distilled water was used as feed, while Figure 4b shows the DCMD flux of the same membranes when using 0.5 M NaCl aqueous solution as feed.

It is well known that temperature is the operating variable that affects the MD flux the most due to the exponential increase of vapor pressure with temperature according to the Antoine equation [1–7]. As shown in Figure 4a; both the

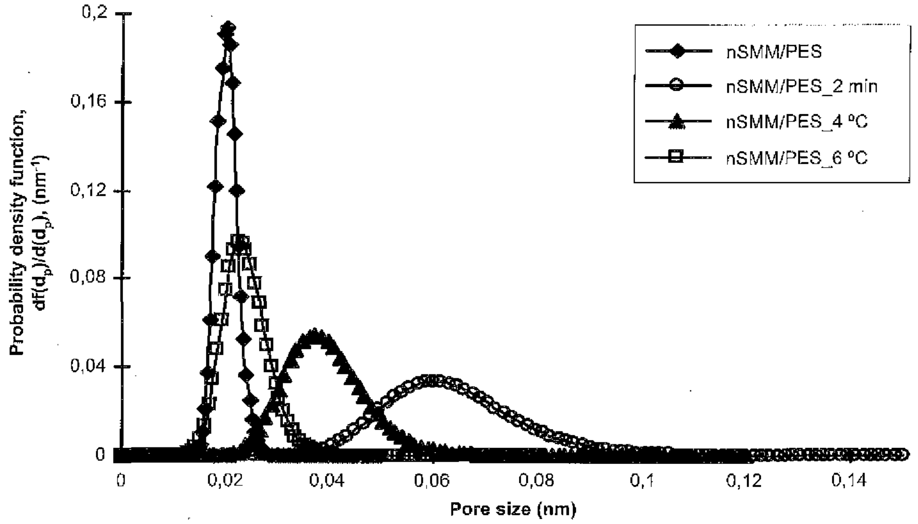
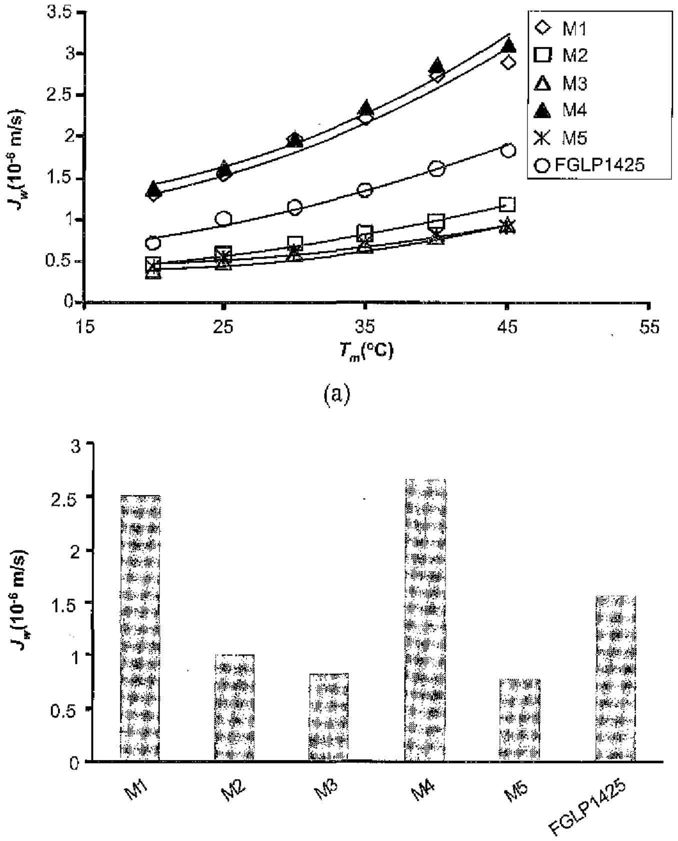


Figure 3 Probability density function generated for the pore size measured from the AFM images for M1, M2, M4 and M5



(a)

(b)

Figure 4 DCMD flux result: (a) mean temperature effect on DCMD flux of distilled water feed solution; (b) water vapor flux of 0.5 M NaCl feed solution at T_m of 45°C commercial membrane and the SMM blended PES membranes exhibit an exponential increase of the DCMD flux with an increase in T_m.

When considering the evaporation time effect; both Figure 4a and 4b showed that the order in the DCMD flux is M1 > FGLP 1425 > M2 > M3. On the other hand, for the gelation path temperature effect, the DCMD flux order was M4 > M1 > FGLP1425 >M5.

According to Table 3; the decreasing order of the ratio ($r\varepsilon/L_p$) is M1 > M2 > M3 for evaporation time effect and M4 > M1 > M5 for gelation path temperature effect. Moreover, Table 3 shows that the *LEPw* of those membranes under investigation followed the order of M5 > M1> M4 (gelation path temperature effect) and M3 > M2 > M1 (evaporation time effect). This indicates that the order of the maximum pore size, according to Laplace equation, should follow the opposite trend of the *LEPw* [7]. It can be therefore concluded that the membrane exhibiting higher ($r\varepsilon/L_p$) ratio and/or lower *LEPw* will have higher DCMD flux. This is expected since an increase in the ratio ($r\varepsilon/L_p$) means an increase in either the porosity and/or pore radius or a decrease in effective pore length.

According to the AFM data (see Table 3), M1 membrane exhibited smaller mean pore size compared to M2 membrane. One can say that this contradicts the reported permeate flux result. But according to ($r\varepsilon/L_p$) values then this flux enhancement is due to the increase of the effective porosity ratio, ε/L_p, which is greater for M1 membrane.

Most importantly, some of the prepared SMM/PES membranes exhibited higher flux than the commercial PTFE membrane. In particular, the DCMD flux of the membranes M1 and M4 was found, on average within the tested temperatures, to be 65% and 73%, respectively, higher than that of the commercial membrane as shown in Figure 4a.

As can be observed in Figure 5b; smaller permeate fluxes were obtained in the presence of sodium chloride. The flux of both SMM/PES and FGLP 1425 membranes decreased by 13–15% compared to that obtained when distilled water was used as feed. Generally, it is expected to observe a flux decline in presence of NaCl, since the water vapour pressure decreases, which results in lower driving force for vapor transport. Moreover, a boundary layer develops next to the feed membrane surface, where the NaCl concentration increases toward the membrane surface due to concentration polarization. The presence of the concentration boundary layer and the temperature boundary layer together reduces the driving force.

The solute separation factor defined earlier in Eq. (1) was higher than 99.9% (the permeate conductivity was always smaller than 25 μS/cm in all the tested membranes). This indicates that the SMM/PES membranes are considered promising for MD process.

4.0 CONCLUSIONS

The higher product of average pore size and effective porosity per unit effective pore length ($r\varepsilon/L_p$) membranes produced higher fluxes. Membranes with lower *LEPw* (smaller maximum pore size) exhibited higher fluxes. Both evaporation time before gelation and gelation path temperature have a negative effect on the permeate DCMD flux. Overall, some SMM/PES membranes produced higher flux than the commercial PTFE membrane, although they have considerably lower pore size and porosity. This makes them very promising potential MD membranes. Furthermore, it was proved that the SMM are necessary to produce workable membranes in MD.

ACKNOWLEDGEMENTS

The authors are thankful to the SRTD Jordanian/European supporting programme and the Spanish cultural bureau for the grants that supported this study.

REFERENCES

[1] Lawson, K. W., D. R. Lloyd. 1997. Membrane Distillation. *J. Membr. Sci.* 124: 1–25.

[2] Mengual, J. I., L. Peña. 1997. Membrane Distillation. *Current Topic Colloid Interface Sci*. 1: 17–29.

[3] Burgoyne, A., M. M. Vahdati. 2000. Direct Contact Membrane Distillation. *Sep. Sci Technol*. 35: 1257–1284.

[4] Alklaibi, A. M., N. Lior. 2004. Membrane-Distillation Desalination: Status and Potential. *Desalination*. 171: 111–131.

[5] Curcio, E., E. Drioli. 2005. Membrane Distillation and Related Operations - A Review. *Sep. Purif. Rev*. 34: 35–86.

[6] El-Bourawi, M. S., Z. Ding, R. Ma, M. Khayet. 2006. A Framework for Better Understanding Membrane Distillation Separation Process. *J. Membr. Sci*. 285: 4–29.

[7] Qtaishat, M., D. Rana, M. Khayet, T. Matsuura. 2009. Preparation and Characterization of Novel Hydrophobic/ Hydrophilic Polyetherimide Composite Membranes for Desalination by Direct Contact Membrane Distillation. *J. Membr. Sci*. 327: 264–273.

[8] Khayet, M., J. I. Mengual, T. Matsuura. 2005. Porous Hydrophobic/hydrophilic Composite Membranes: Application in Desalination using Direct Contact Membrane Distillation. *J. Membr. Sci*. 252: 101–113.

[9] Khayet, M., T. Matsuura, J. I. Mengual, M. Qtaishat. 2006. Design of Novel Direct Contact Membrane Distillation Membranes. *Desalination*. 192: 105–111.

[10] Suk, D. E., T. Matsuura, H. B. Park, Y. M. Lee. 2006. Synthesis of a New Type of Surface Modifying Macromolecules (nSMM) and Characterization and Testing of nSMM Blended Membranes for Membrane Distillation. *J. Membr. Sci*. 277: 177–185.

[11] Qtaishat, M., K. C. Khulbe, T. Matsuura, M. Khayet. 2009. Comparing the Desalination Performance of SMM Blended Polyethersulfone to SMM Blended Polyetherimide Membranes by Direct Contact Membrane Distillation. *Desalination and Water Treatment*. In Press.

[12] Singh, S., K. C. Khulbe, T. Matsuura, P. Ramamurthy. 1998. Membrane Characterization by Solute Transport and Atomic Force Microscopy. *J. Membr. Sci*. 142: 111–127.