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Effect of Surface Modifying Macromolecules Stoichiometric Ratio on Composite Hydrophobic/Hydrophilic Membranes Characteristics and Performance in Direct Contact Membrane Distillation

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The stoichiometric ratio for the synthesis components of hydrophobic new surface modifying macromolecules (nSMM) was altered systematically to produce three different types of nSMMs, which are called hereafter nSMM1, nSMM2, and nSMM3. The newly synthesized SMMs were characterized for fluorine content, average molecular weight, and glass transition temperature. The results showed that fluorine content decreased with increasing the ratio of α,ω-aminopropyl poly(dimethyl siloxane) to 4,4′-methylene bis(phenyl isocyanate). The synthesized nSMMs were blended into hydrophilic polyetherimide (PEI) host polymer to form porous hydrophobic/hydrophilic composite membranes by the phase inversion method. The prepared membranes were characterized by the contact angle measurement, X-ray photoelectron spectroscopy, gas permeation test, measurement of liquid entry pressure of water, and scanning electron microscopy. Finally, these membranes were tested for desalination by direct contact membrane distillation and the results were compared with those of commercial polytetraflouroethylene membrane. The effects of the nSMM type on the membrane morphology were identified, which enabled us to link the membrane morphology to the membrane performance. It was found that the nSMM2/PEI membrane yielded the best performance among the tested membranes. In particular, it should be emphasized that the above membrane was superior to the commercial one. © 2009 American Institute of Chemical Engineers *AIChE J*, 55: 3145–3151, 2009

Keywords: direct contact membrane distillation, desalination, hydro-phobic/-philic composite membranes, surface modifying macromolecules, polyetherimide

Introduction

Membrane Distillation (MD) is well documented and explained in many review articles.[1–8] Briefly, MD is a physical separation process where the membrane acts as a

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Table 1. Materials Used in this Work

Material Description	CAS Number	Source
4,4′-Methylene bis(phenyl isocyanate) (MDI, 98%)	101-68-8	Sigma-Aldrich, Inc., St. Louis, MO, USA
α,ω-Aminopropyl poly(dimethyl siloxane) (PDMS) of average molecular weight 900	106214-84-0	Shin-Etsu Chemical Co. Ltd., Tokyo, Japan
Zonyl BA-L$^{\text{TM}}$ (BAL) of average M_n 443 and 70 wt % fluorine	678-39-7	DuPont product supplied by Aldrich Chemical Company, Inc., Milwaukee, WI, USA
N,N-Dimethylacetamide (DMAc, anhydrous 99.8%)	127-19-5	Sigma-Aldrich, Inc., St. Louis, MO, USA
1-Methyl-2-pyrrolidinone (NMP, anhydrous 99.5%)	112-14-1	Sigma-Aldrich, Inc., St. Louis, MO, USA
γ-Butyrolactone (GBL, 99+%)	96-48-0	Aldrich Chemical Company, Inc., Milwaukee, WI, USA
Tetrahydrofuran (THF, HPLC grade 99.9%)	109-99-9	Aldrich Chemical Company, Inc., Milwaukee, WI, USA
Polyetherimide (PEI, Ultem 1000, Natural Pallet) Specific gravity: 1.27	61128-46-9	General Electric Co., Pittsfield, MA, USA

physical support separating a hot feed solution from a cooler chamber that contains either a liquid or a gas. When the cooler chamber uses a flowing liquid to condense and recover the migrated vapor through the membrane pores from the hot feed solution side, the MD configuration is called direct contact membrane distillation (DCMD).[1–7]

Hydrophobic porous membranes made of polytetraflouroethylene (PTFE), polypropylene (PP), and poly(vinylidene fluoride) (PVDF) have been often used in MD experiments, though these membranes were marketed for microfiltration and ultrafiltration processes.[1,2] Recently, more attention has gone into preparing membranes specifically for the MD applications. Most of these attempts are summarized in a recent MD review article.[1,2] One of the most promising attempts is the concept of hydrophobic/hydrophilic composite membranes for MD, which was firstly proposed by Khayet et al. in a series of publications.[8–15] In this concept; the surface modifying macromolecules (SMMs) were synthesized and blended with the host polyetherimide (PEI) hydrophilic polymer to prepare composite membranes. Those membranes were further tested for desalination by DCMD. The SMMs were prepared from methylene bis-(*p*-phenyl isocyanate) (MDI), dihydroxy diphenyl sulfone (DPS), and oligomeric fluoroalcohol, Zonyl BA-L$^{\text{TM}}$ of average molecular weight 443 (BAL). The stoichiometric molar ratio for SMMs synthesis was 3(MDI):2(DPS):2(BAL).

Suk et al.[16] later developed new surface modifying macromolecule (nSMM), in which DPS in the earlier work was replaced by α,ω-aminopropyl poly(dimethyl siloxane) (PDMS) using 3(MDI):2(PDMS):2(BAL) molar ratio. They used these nSMM together with the host polyethersulfone (PES) to prepare membranes for vacuum membrane distillation (VMD). More recently, we have synthesized nSMM containing 3(MDI):2(PDMS):2(BAL) molar ratio and tested the blended membranes for DCMD.[17] It is worth mentioning that blending DPS-based SMM yielded better DCMD fluxes than blending nSMM.[14,16,17]

In this study, further improvement of the DCMD membranes performance was attempted by changing the nSMM structures. To this end, the stoichiometric molar ratio of nSMM components was altered systematically in nSMM synthesis:

(1) nSMM1: 2(MDI):1(PDMS):2(BAL)
(2) nSMM2: 3(MDI):2(PDMS):2(BAL)
(3) nSMM3: 4(MDI):3(PDMS):2(BAL).

Furthermore, the newly developed nSMMs were blended with PEI host polymer to prepare composite hydrophobic/hydrophilic membranes. This was done in a single casting step by the phase inversion method.

The membranes were characterized using gas permeation test, measurement of the liquid entry pressure of water (LEPw), scanning electronic microscopy (SEM), and contact angle (CA) measurement. The effects of the nSMM type on the membrane morphology were identified, which enabled us to link the membrane morphology to the membrane performance.

The membranes were further tested by DCMD for desalination of 0.5 M NaCl solution and the results were compared with commercial polytetraflouroethylene (PTFE) membranes (FGLP 1425, Millipore Corporation, Billerica, MA). A better and instructive understanding of hydrophobic/hydrophilic membrane performance in DCMD has been obtained by finding the relationship between membrane morphology and membrane performance. This will open a wide avenue to the rational development of novel membranes for membrane distillation.

Experimental

Materials

All chemicals used in this work and their chemical abstract service (CAS) number are enlisted in Table 1. The weight average molecular weight (M_w) of the PEI is 15 kDa and its glass transition temperature (T_g) is 216.8°C. 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.

SMMs synthesis

The SMMs were synthesized using a two-step solution polymerization method.[16,17] The solvent *N,N*-dimethylacetamide (DMAc) was distilled at about 25°C under a pressure of 133.3 Pa. Methylene bis(*p*-phenyl isocyanate) (diphenylmethane diisocyanate, MDI) was also distilled at 150°C under 66.7 Pa (0.5 Torr). α,ω-aminopropyl poly(dimethyl siloxane) (PDMS) and Zonyl BA-L$^{\text{TM}}$ low fraction (or 2-(perfluoroalkyl)ethanol) (BAL) were degassed for 24 h under 66.7 Pa. The first polymerization step was conducted for 3 h at 45–50°C in a solution of DMAc with a predetermined composition to form polyurea for the reaction of MDI with PDMS as a prepolymer. In the second polymerization step, which last for 24 h at 45–50°C, the prepolymer was end-

Table 2. The Preparation Composition of nSMM

nSMM	MDI: PDMS: BAL (Molar Ratio)	MDI (gm) in 50 ml DMAc	PDMS (gm) in 100 ml DMAc	BAL (gm) in 50 ml DMAc
nSMM1	2:1:2	5	9	8.86
nSMM2	3:2:2	7.5	18	8.86
nSMM3	4:3:2	10	27	8.86

capped by the addition of BAL, resulting in a solution of nSMM in DMAc. The molar composition of nSMMs was presented in Table 2. The prepared polymer solution was precipitated in water and then dried in an air circulation oven at 120°C for 5 days. The prepared nSMMs are named hereafter as nSMM1, nSMM2, and nSMM3, respectively, based on the stoichiometirc molar ratio. The general chemical structure of the synthesized nSMMs is shown in Figure 1. The chemical name of the nSMM is poly(urea-dimethylsiloxane-urethane) where both ends are capped by BAL.

SMMs characterization

The elemental analysis of fluorine content in the three prepared nSMMs was carried out using standard method (ASTM D3761). An accurate weight (10–50 mg) of sample was placed into oxygen flask bomb combustion (Oxygen Bomb Calorimeter, Gallenkamp). After pyro-hydrolysis, the fluorine (ion) was measured by an ion chromatography (Ion Chromatograph, Dionex DX1000, Sunnyvale, CA). The analysis for silicon content in the HSMM was performed by oxygen flask bomb combustion same way as fluorine analysis, followed by acid digestion and then analyzing for silicon by inductively coupled plasma—atomic emission spectrometry (ICP-AES, Varian Liberty 110, Varian, Palo Alto, CA).

The glass transition temperature (T_g) was examined by differential scanning calorimeter (DSC) equipped with universal analysis 2000 program (DSC Q1000, TA Instruments, New Castle, DE). About 10 mg of polymer was crimped into aluminum pan. The SMMs were annealed at 280°C for 10 min, then quenched to -50°C and scanned at a heating rate of 10°C/min. The T_g value was recorded at the midpoint of the corresponding heat capacity transition.

The number average molecular weight (M_n) and the polydispersity index (PDI) of the synthesized SMMs was measured by gel permeation chromatography (GPC) using Waters Associates GPC chromatograph equipped with Waters 410 refractive index detector. Three Waters UltraStyragel^{TM} packed columns were installed in series. The tetrahydrofuran (THF) was filtered and used at 40°C and a flow rate of 0.3 ml/min. First, the calibration of the system was performed using polystyrene (Shodex, Tokyo, Japan) standards with different molecular weights between 1.3×10^3 and 3.15×10^6 g/mol. The standards and nSMM samples were prepared in a THF aqueous solution (0.2 w/v %) and filtered before injection through 0.45 μm filter to remove high molecular weight components. Millenium 32 software (Waters) was used for data acquisition.

Membrane preparation

nSMM-modified PEI membranes were prepared in a single casting step by the phase inversion method.[8,9] γ-Butyrolactone (GBL) was used as a nonsolvent additive. A predetermined amount of PEI was dissolved in a NMP/GBL mixture. The PEI concentration in the casting solution was maintained at 12 wt %, while the amount of GBL was maintained at 10 wt %. Three different types of nSMMs, nSMM1, nSMM2, and nSMM3 were added to the PEI solution in a concentration of 1.5 wt %. The resulted mixtures were stirred in an orbital shaker at room temperature for at least 48 h. Before their use, all the resulted polymer solutions were filtered through a 0.5 μm Teflon? filter and degassed at room temperature. The polymer solutions were cast on a smooth glass plate to a thickness of 0.30 mm using a casting rod at room temperature. The solvent was then evaporated at ambient temperature for a predetermined period before the cast films together with the glass plates were immersed for 1 h in distilled water at room temperature. During gelation, it was observed that the membranes peeled off from the glass plate spontaneously. All the membranes were then dried at ambient conditions for 3 days. Table 3 shows the prepared membranes, their materials of construction, and preparation conditions.

Membrane characterization

Measurement of Gas Permeation test and Liquid Entry Pressure of Water. Measurement of liquid entry pressure of water (LEPw) and the gas permeation test were carried out for the prepared surface-modified PEI membranes. The gas permeation test was performed before the measurement of LEPw. The details of the methods are described elsewhere.[18] The product of average pore size and effective porosity per unit effective pore length ($r\varepsilon/L_p$) of the prepared membranes was determined by the gas permeation test. This ratio takes into account the tortuosity of the membrane pores.

In this paper, the permeation flux of air through each dry membrane was measured at various transmembrane pressures, in the range of 10–100 kPa. In general, the gas permeance, B, for a porous medium contains both a diffusive term and a viscous term, the contribution of which depends on the applied pressure as reported by Carman[19]:

$$B = \frac{4}{3}\left(\frac{2}{\pi MRT}\right)^{0.5}\frac{r\varepsilon}{L_p} + \frac{P_m}{8\mu RT}\frac{r^2\varepsilon}{L_p} \tag{1}$$

where R is the gas constant, T is the absolute temperature, M is the molecular weight of the gas, μ is the gas viscosity, P_m is the mean pressure within the membrane pore, r is the

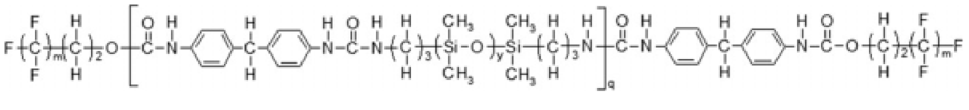

Figure 1. Chemical structure of the prepared nSMM.

Table 3. Prepared Membranes' Codes and the Type of nSMMs used*

Membrane Code	nSMM Type
M0	No nSMM
M1	nSMM1
M2	nSMM2
M3	nSMM3

*PEI concentration: 12 wt %; GBL concentration: 10 wt %; NMP solvent: 76.5 wt %; nSMMs: 1.5 wt %; gelation bath temperature: 20°C; evaporation time: 0 min.

membrane pore radius, ε is the porosity, and L_p is the effective pore length.

Throughout all the conducted gas permeation experiments, it was noticed that the gas permeance was independent of pressure (P_m). Therefore, diffusive mechanism seems to dominate the gas transport through the membrane pores revealing the fact that the prepared membranes in this study have small pore sizes. Accordingly, the gas permeance is described by ignoring the viscous term of Eq. 1 as[10,11]:

$$B = \frac{4}{3}\left(\frac{2}{\pi MRT}\right)^{0.5}\frac{r\varepsilon}{L_p} \tag{2}$$

This test was therefore useful in evaluating the ratio ($r\varepsilon/L_p$). Some of the gas permeation experiments were duplicated using different membrane sheets made from the same casting solution batch in order to evaluate the variance of the obtained values from batch to batch. Moreover, for each membrane, the measurement of the gas flow rate was made three times at a given gas pressure and the data were averaged to obtain the membrane permeance value.

The measurements for the LEPw were then carried out as explained elsewhere.[18] The experiment was done three times using three different sheets made from each casting solution batch. The results were averaged to obtain the final LEPw value of each membrane.

Scanning electron microscopy

The cross-section of the SMMs-blended PEI membranes was observed by scanning electron microscopy, SEM, (JSM-6400 JEOL, Japan). The membranes were cut into pieces (3 mm width and 10 mm length) and subsequently immersed in liquid nitrogen reservoir for 5 s. Although keeping the pieces in the liquid nitrogen, those were broken into two pieces by pulling from both ends. One of the broken pieces was mounted on metal plate with carbon paste and gold-coated before use. The cross-section of the membranes at the broken parts was finally examined by SEM.

X-ray photoelectron spectroscopy

The elemental composition at the surface of each SMM-blended membrane was determined by X-ray photoelectron spectroscopy (XPS, Kratos Axis HS X-ray photoelectron spectrometer, Manchester, UK). Each membrane was cut into samples of 1 cm^2 from random positions of the membrane. Monochromatized Al K$_\alpha$ X-radiation was used for excitation and a 180° hemispherical analyzer with a three channel detector was used. The X-ray gun was operated at 15 kV and 20 mA. The pressure in the analyzer chamber was 1.33×10^{-4} to 1.33×10^{-5} Pa. The size of the analyzed area was about 1 mm^2. All the membrane samples were analyzed for fluorine content at both top and bottom sides.

Measurement of contact angle

The contact angle (CA) of the SMMs-blended membranes was measured to study their hydro-phobicity/-philicity. The CA measurements were executed using the VCA-Optima (AST products, MA). Samples of 4 cm^2 area (2×2 cm) at random positions were prepared from each membrane. The samples were then placed on the glass sample plate and fixed with scotch tape. The equipment syringe filled with distilled water was installed to stand vertically. Two microliters of water was deposited on the membrane surface. The CA was measured at five different spots on each membrane sample for both top and bottom surfaces.

DCMD experiments

The prepared SMMs-blended PEI membranes were tested by the DCMD setup shown in a previous study.[17,20] The performance of each membrane was compared with that of the commercial PTFE membrane in terms of water vapor flux and NaCl separation factor. The membrane modules are a system of three circular stainless steel cells each composed of two cylindrical chambers. Each cell has an O-ring to prevent water leakage, one inlet and one outlet at the feed side and one inlet and one outlet at the permeate side, respectively. The diameter of each cell is around 10 cm, which results in a total effective area (of three cells), of 235.6 cm^2. Each cell has two supportive compartments with a thickness of 2.5–3 cm. The feed chamber is connected to a heating system through its jacket to control the temperature of the liquid feed. The permeate chamber is connected to a cooling system to control the temperature of the permeate side stream. The membranes were placed between the two chambers (feed side and permeate side). The feed and permeate flow rate were held constant at 1 l/min for each cell (the total flow rate was 3 l/min). The inlet and outlet temperatures of both the feed and permeate solutions were measured, after the steady state was reached, using thermocouples connected to a digital meter with an accuracy of ±0.05°C. The MD module cells together with all tubes were insulated to prevent heat loss. The permeate flux was measured by monitoring the water level in both the feed and permeate cylindrical-graduated container. The loss in the amount of water in the feed container should be equal to the gain in the amount

Table 4. SMMs Characterization Results

nSMM	F (wt %)	Si (wt %)	M_n (10^4 g/mol)	PDI	q
nSMM1	16.21	12.82	1.62	1.82	13.10
nSMM2	11.75	11.52	1.28	2.12	10.14
nSMM3	10.06	11.48	1.55	2.13	12.49

Table 5. Contact Angle (CA) and Fluorine Content from the XPS Results of the Prepared Membranes for Both Top and Bottom Sides

	CA (θ°)		F (wt %)	
Membrane	Top Surface	Bottom Surface	Top Surface	Bottom Surface
M0	80.04 ± 4.55	72.83 ± 2.62	0.00	0.00
M1	93.55 ± 1.054	62.84 ± 3.05	30.80	4.62
M2	91.93 ± 0.52	67.76 ± 3.29	28.93	7.68
M3	100.17 ± 3.62	73.80 ± 4.08	5.82	4.89

of water in the permeate container when there is no leakage of water in the DCMD setup.

Different sets of DCMD experiments were carried out using distilled water and 0.5 M NaCl aqueous solution as feed. When distilled water was used as feed, the feed temperature was varied from 35 to 65°C, while the permeate temperature was maintained at 11–15°C. When 0.5 M NaCl solution was used as feed, the feed temperature was 65°C and the permeate temperature was 15°C.

Results and Discussion

SMMs characterization

The fluorine and silicone content in the nSMMs are presented in the Table 3. The glass transition temperature (T_g) of those nSMMs is above 280°C. The precise T_g values could not be obtained for the nSMMs (nSMM1, nSMM2, and nSMM3) as the samples could be heated only up to 280°C due to the limitation of the equipment to achieve higher temperatures. According to the nSMMs chemical structure presented in Figure 1, the value of m, the number of the CF_2 repeating unit was calculated from the molecular weight of (BAL) which is 7.58. The value of y, the number of the PDMS repeating unit was calculated from the average molecular weight of PDMS which is 9.81. The values of q, the number of the urea repeating unit was estimated for each nSMM using number average molecular weight are given in Table 4.

Membrane characterization

The resulted contact angle (CA) data of all membranes are shown in Table 5. It was observed that the CA of the top side of the prepared membranes was higher than their bottom side. The higher CA of the top surface of the membranes M1 and M3 when compared with that of the membrane M2 prepared under the same conditions indicates that the top surface hydrophobicity of the prepared membranes with nSMM1 (M1) and nSMM3 (M3) is greater than that of the membrane prepared with nSMM2 (M2). The surface hydrophobicity of the nSMM-blended membrane is determined by the interplay of the nSMM chemical formula and the nSMM migration rate in the casting solution. Hence, it is difficult to find a simple relationship between the CA and the chemical formula of nSMM. It should also be noted that the hydrophobicity of nSMMs comes also from the urea prepolymer, because it contains hydrophobic dimethylsiloxane group.

The results of the XPS analysis for both PEI and nSMMs-blended PEI membranes are also presented in Table 5. Fluorine was not detected in the PEI membrane. This is expected

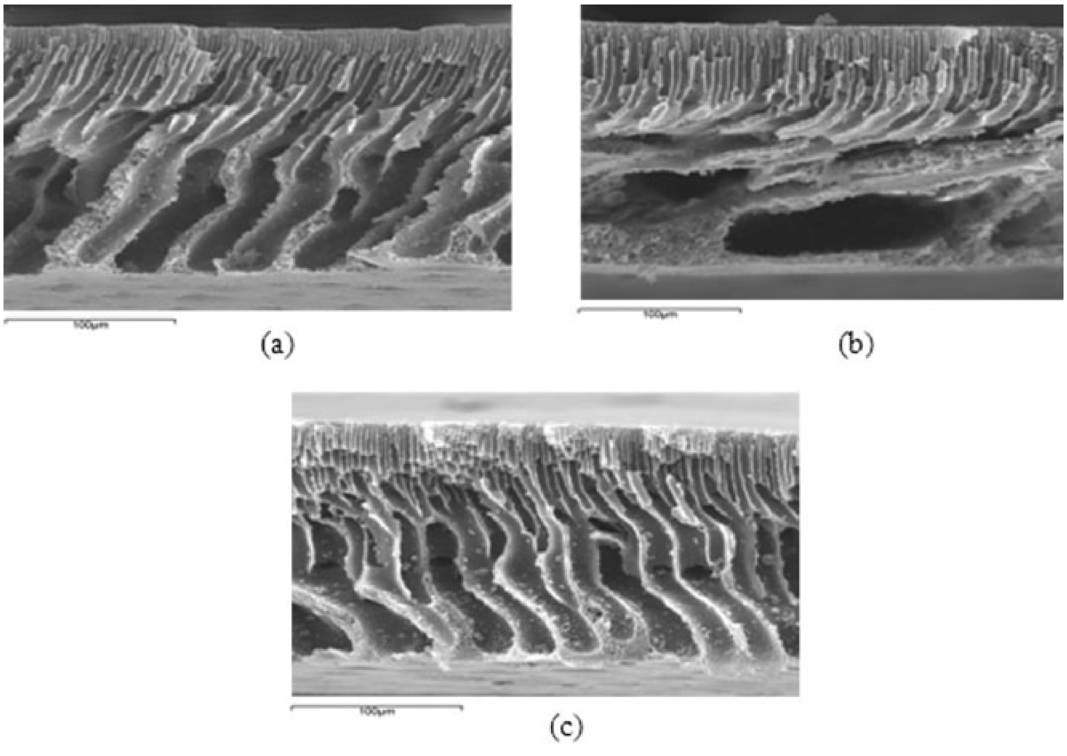

Figure 2. Cross-sectional SEM pictures of the prepared PEI/nSMM membranes: (a) M1; (b) M2; (c) M3.

Table 6. Liquid Entry Pressure of Water (LEPw) and Product of Average Pore Size and Effective Porosity Per Unit Effective Pore Length ($\varepsilon r/L_p$) of the Prepared Membranes

Membrane	LEP_w (bar)	$\varepsilon r/L_p$
M1	4.5	6.02×10^{-6}
M2	4.0	1.53×10^{-5}
M3	4.7	2.74×10^{-6}

because fluorine is associated to nSMMs alone. For all the nSMMs-blended PEI membranes, fluorine contents were found to be higher at the top side than the bottom side indicating nSMMs' migration towards the top side. The nSMM1-blended PEI membrane (M1) exhibits more fluorine than the nSMM2 and nSMM3-blended PEI membrane (M2 and M3), respectively. This is related to the order in the fluorine contents of nSMMs, that is, nSMM1 > nSMM2 > nSMM3 (Table 4). It is worth mentioning that the fluorine content at the top side of nSMM1 and nSMM2-blended PEI membranes was significantly higher than the bottom side. On the other hand, nSMM3-blended PEI membrane exhibited only a small difference between the top and the bottom side. This indicates that the migration of nSMM1 and nSMM2 to the top-layer was much faster than nSMM3. The migration kinetics study of SMM to the top-layer membrane surface is reported in our earlier works.[16,21] In these articles, it was reported that the CA responded immediately to the presence of nSMM. The contact angle of the membranes prepared in Ref. 16 is increased by 20° in the presence of nSMM, even when the evaporation period was zero. This trend was explained by the fact that nSMM were present at the membrane surface from the very beginning and the hydrophobic tails of the nSMM could be oriented towards air at the air/solution interface even before the nSMM migration began to take place. This further support our conclusion of the fast migration of nSMM1 and nSMM2 to the membrane top surface

The SEM images of the membrane cross-sections are shown in Figure 2. As can be seen, all the membranes are of asymmetric structure with a dense top-layer supported by a finger-like structure underneath. However, the bottom parts of the membranes are different. The finger-like structure of the membrane M1 and M3 (Figures 2a,c, respectively) reaches the bottom side, where small macrovoids were formed in vertical direction. On the other hand, for the M2 membrane (Figure 2b), the finger-like structure became more irregular in the middle of the cross-section and large macrovoids were formed in horizontal direction.

The data for the LEPw and product of average pore size and effective porosity per unit effective pore length ($r\varepsilon/L_p$) are summarized in Table 6. The increasing order in LEPw values was M2 (4.0 bar) < M1 (4.5 bar) < M3 (4.7 bar). According to the Laplace equation,[19] the above order should be the same as the order in the decreasing pore size and/or in the increasing hydrophobicity. It is found that both are satisfied when looking into the $\varepsilon r/L_p$ values in Table 6 (M2 (1.53×10^{-5}) > M1 (6.02×10^{-6}) > M3 (2.74×10^{-6})) and the CA data of the membrane top surface in Table 4 (M2 (91.93°) < M1 (93.55°) < M3 (100.17°)).

Membrane performance

Figure 3 shows the DCMD fluxes of the prepared membranes along with those of the commercial membrane (FGLP 1425). Figure 3a shows the DCMD flux vs. feed inlet temperature when distilled water was used as feed. Figure 3b shows the DCMD flux of those membranes when using 0.5 M NaCl aqueous solution as feed. As can be observed, both the commercial membrane and the SMMs-blended PEI membranes exhibit an exponential increase of the DCMD flux with an increase in the feed inlet temperature. Both Figures 3a,b show that the order in the DCMD flux is M2 > FGLP 1425 > M1 > M3. The nSMM2-blended PEI membrane (M2) showed 10% higher permeate fluxes than the commercial membrane. On the other hand, M1 and M3 exhibited lower fluxes than that of the commercial membrane by 42 and 72%, respectively.

The permeate flux for the NaCl aqueous solution was 25–30% lower than the distilled water flux, reflecting the lower vapor pressure of the salt solution. Another reason for the decrease in the DCMD flux is the concentration polarization due to the presence of NaCl solute in the feed membrane side.[9] Referring to the experiments with salt solution, the solute separation factor is defined as:

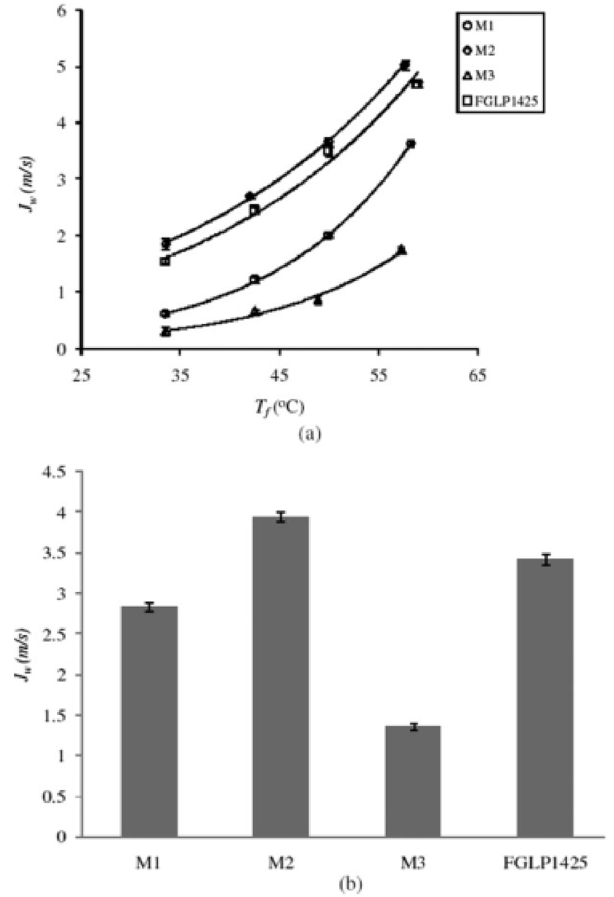

Figure 3. Effect of nSMMs type on membrane performance in DCMD: (a) feed temperature effect on DCMD flux of distilled water feed solution; (b) water vapor flux of 0.5 M NaCl feed solution at T_f of 65°C and T_p of 15°C.

$$\alpha = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

where C_p and C_f are the NaCl concentration in the permeate and in the bulk feed solution, respectively. It was observed that α was above 99% for both the prepared and the commercial membranes. This indicates that the SMMs-blended membranes M1, M2, and M3 are promising MD membranes as reported in the previous studies.[9–11] It is interesting to note that the order in the DCMD flux is M2 $>$ M1 $>$ M3, which is precisely the decreasing order in ($r\varepsilon/L_p$). It can, therefore, be concluded that the higher the $\varepsilon r/L_p$, the higher will be the MD flux. This sounds quite logical, because increasing ($r\varepsilon/L_p$) means an increase in either porosity or pore radius or a decrease in effective pore length, which will naturally lead to a decrease in the barrier resistance. The parallel relationship found between the gas transport and vapor transport is also documented in an earlier study.[18] Furthermore, the reported flux results match well with the LEPw and CA measurements, because the membrane with lowest LEPw and CA exhibited the highest flux due to the fact that it has the largest maximum pore size as discussed earlier.

According to the SEM pictures shown in Figure 2, the macrovoids size of M2 membrane was larger than those of M1 and M3 membranes. This might have reduced the barrier resistance toward mass transfer and enhanced the flux as a result.

Conclusions

The effect of the nSMMs stoichiometric ratio on the nSMMs characteristics and morphology of the composite hydrophobic/hydrophilic PEI composite membranes was clearly identified, which was latter linked to their performance in DCMD.

It was found that increasing the stoichiometric ratio of PDMS to MDI in the nSMM synthesis components decreased the fluorine content of the nSMMs and increased the repeating unit of the polyurea prepolymer (q). Moreover, nSMM2/PEI membrane exhibited the highest flux among the tested nSMMs/PEI membranes due to the fact that it had exhibited higher <i>$r\varepsilon/L_p$, lower liquid entry pressure of water (smaller maximum pore size), and larger macrovoids at the bottom sub-layer.

The nSMMs-blended PEI membranes were tested successfully for desalination application by DCMD, where the separation factor was found to be higher than 99% for all the tested membranes. It was proved that the nSMMs are necessary to produce workable membranes in DCMD.

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