

Impacts of Heat Treatment Medium on Performance of Aliphatic-aromatic and Aromatic-aromatic based Thin-film composite (TFC) polyamide Reverse Osmosis (RO) Membrane

A.K. GHOSH^{*} AND R.C. BINDAL

Membrane Development Section, Chemical Engineering Group, Bhabha Atomic Research Centre, Trombay, Mumbai – 400 085, India,

ABSTRACT

In this study, we report the impact of heat treatment medium (hot air, hot water & steam) on structure and performance of aliphatic-aromatic and aromatic-aromatic types thin-film composite (TFC) polyamide reverse osmosis (RO) membranes prepared by in-situ interfacial polymerization. Aliphatic-aromatic polyamide membranes were prepared using polyethylene imine (PEI) & isophthaloyl chloride (IPC) and aromatic-aromatic polyamide membranes were prepared using m-phenylene diamine (MPD) & trimesoyl chloride (TMC). Thin film coating of polyamide was given over laboratory synthesized microporous polysulfone supports. TFC membranes prepared using three different heat treatment media were characterized in terms of water permeability, separation of NaCl solute, water contact angle and atomic force microscopy studies. It was found that different heat treatment media produced TFC polyamide membranes with widely varying water fluxes, salt rejections, and surface properties under identical coating conditions and it has different impacts on aliphatic-aromatic and aromatic-aromatic type polyamide composite membrane performances. The surface hydrophilicity of the steam and hot water-cured membranes increased more than that of hot air cured membranes for aromatic-aromatic type TFC-RO membrane. Heat treatment in hot water and steam media results TFC membrane with the more permeates flux and salt rejection for both aliphatic-aromatic and aromatic-aromatic type.

KEY WORDS : *Membrane, Thin-film composite, Reverse osmosis, Heat curing medium, Performance enhancement*

INTRODUCTION

Thin Film Composite (TFC) type reverse osmosis (RO) membranes are typically consists of a thick, porous, nonselective layer of polysulfone or polyethersulfone which is subsequently coated with an ultrathin barrier layer of polyamide on its top surface^[1]. The membrane prepared in first step is called support membrane and the ultrathin polyamide layer formed on the surface provides the controlling properties such as semipermeability. Support membrane is prepared by phase inversion technique whereas polyamide active layer in TFC membranes is prepared by the in-situ interfacial polymerization of amine aqueous solution and acid chloride organic solution. After the interfacial polymerization reaction, heat treatment is applied to complete polycondensation reaction and stabilize the nascent polyamide film^[2]. Two most successful thin-film composite (TFC) based RO membranes in past are - (a) NS-101 membrane prepared using polyethylene imine (PEI) and isophthaloyl chloride (IPC) & (b) FT-30 membranes using *meta*-phenylenediamine (MPD) and trimesoyl chloride (TMC)^[3].

An ideal successful RO membrane should have maximum permeate flux with adequate salt rejection properties. The structure, morphology, and performance of such TFC membranes prepared by *in-situ* polycondensation reaction are influenced by number of factors namely, support membrane structure and chemistry^[4], monomer selection and concentration^[5], polar and apolar solvent selection^[6, 7], catalysts and other additives^[8], reaction temperature and time, treatment temperature and time^[9], and other post-treatments. Then most of the research was

directed towards improvements in performance of these TFC polyamide RO membranes in terms of increasing membrane productivity and selectivity by changing new monomeric systems^[10, 11], by adding extra additives with the reactants^[12], by surface treatments etc.^[13, 14]. Later on, the concept of a mixed-matrix membrane was introduced for development of advanced nanocomposite RO membranes, where a small filler material is dispersed throughout the entire polymer matrix to have improved mechanical, chemical, and thermal stability alongwith the enhanced separation and sorption capacity^[15-18]. Hence, an easy approach with minor change in any of the preparation process would be more acceptable keeping all chemical compositions and process parameters unaltered. The heat treatment is one such step which affects both polysulfone support layer as well as the top polyamide film layer of TFC membranes. It is well known that with increase in treatment time, the porosity of the polyamide film decreases by promoting cross-linking reactions leads to decrease in water flux with increase in salt rejection. So, the structure and properties of TFC membranes can be affected by the heat treatment medium also alongwith the treatment time & temperature. Detailed investigation on the effect of treatment medium on aliphatic-aromatic and aromatic-aromatic types TFC polyamide type RO membrane performance is not available in the literature.

In the present study, the effect of heat treatment medium (hot air, hot water & steam) on structure and performance of PEI-IPC (aliphatic-aromatic) and MPD-TMC (aromatic-aromatic) based TFC polyamide reverse osmosis (RO) membranes

was fully investigated. Concentration of amine & acid chloride alongwith the time of reaction was optimized for both types TFC membrane independently and then heat treatment in three different media (hot air with ambient humidity, steam with a relative humidity of 90% and hot water). The performance of the TFC membranes was evaluated under brackish water RO test condition.

EXPERIMENTAL

Materials

Polysulfone(PSf) in bead form were obtained from M/s. Solvay Specialities India Pvt. Ltd., India. The reagent grade N,N-dimethyl formamide (DMF) was procured from M/s.Sisco Research Laboratories, India and used as solvent for making polysulfone support membranes. Polyethylene imine (PEI) as a 50% aqueous solution were obtained from Fluka A.G. 1, 3-phenylene diamine or m-phenylene diamine (MPD), 1,3- benzene dicarbonyl chloride or isophthaloyl chloride (IPC) and 1,3,5- benzene tricarbonyl chloride or trimesoyl chloride (TMC) of M/s. Sigma-Aldrich, India make were used without further purification.

Preparation of membranes

Membrane preparation was carried out in two steps. In the first step, PSf support membrane was cast followed by the thin film coating of polyamide over the support by in-situ polycondensation reaction in second step. For support membrane preparation, in an airtight glass bottle, 16.5gm of PSf was taken and then 83.5gm of the DMF was added. The solution was kept agitated for several hours for complete dissolution. A mild vacuum was applied for removal of trapped air bubbles in the polymer casting solution. Then this polymer solution was spread over a non woven polyester spun bonded fabric support (Viledon grade H1006 obtained from M/s. Freudenberg Nonwovens India Pvt. Ltd.) using a knife edge. The membrane, after casting is immersed in a demineralized water bath maintained at a room temperature. The thickness of the membrane was

controlled by varying the thickness of adhesive tapes at the sides of glass plate. The size of the membrane prepared was typically of 20cm length and 12 cm width. The membranes were made in the environment of controlled temperature (typically 25°C) and humidity (typically 40%RH). The membrane obtained after gelling was repeatedly washed with demineralized water and stored in refrigerator cooled water (~6°C) till further use. These PSf membranes are inspected for pinholes and good areas are chosen for subsequent TFC membrane preparation.

For TFC membrane preparation, wet PSf support membrane was kept in air vertically to remove surface droplets of water and then immersed subsequently in aqueous solution of amine for predetermined time. Excess amine solution was removed from the support membrane surface by squeezing through soft rubber roller till the surface looked free of amine solution. Subsequently, it was immersed in hexane solution of known concentration of IPC or TMC for predetermined time. A thin layer of polyamide film is formed over support membrane. This composite polyamide membranes obtained are heat cured in different media (hot air, hot water & steam) independently.

Characterization of membranes

The porosity of both support and TFC-RO membrane was calculated using equation: $P (\%) = (Q_0 - Q_1)/Ah \times 100$ where P is the porosity of membrane, Q_0 the wet sample weight, Q_1 the dry sample weight, A the square of membrane and h is the thickness of membrane. The TFC polyamide membranes were characterized in terms of pure water flux and percentage (%) rejection of NaCl in a tangential flow type test cell at 225 psig (1551 kPa) pressure. The feed water was pumped across a given specimen using a reciprocating pump. The schematic details of the experimental set up and the test cell were given in our previous paper [19]. Flux is calculated by taking the average of three readings taken at a regular time interval. The flux values obtained as (mL/min.) were reported as $L \cdot m^{-2} \cdot d^{-1}$ (LMD). Intrinsic water permeability or pure water permeability constant ($A = Jv/\Delta P \cdot A_m$; Jv is the volumetric permeate flux, ΔP is the applied hydraulic pressure, A_m is the surface area of membrane

in the test cell) is determined from the measured de-ionized water flux at a given externally applied pressure. The solute separation data were collected using feed concentration of 2000 ppm of NaCl. The solute separation was computed using feed and permeates concentrations. The solute concentration was measured from specific conductance measurements.

Hydrophilicity of composite polyamide membranes was qualitatively provided by measuring pure water contact angles using the sessile drop method on a standard drop shape analysis system (DSA100, KRUSS GmbH, Germany). Average roughness of the surface of the composite polyamide films was measured using an atomic force microscope, AFM (NT-MDT-Multimode 3, Ireland), equipped with standard silicon nitride cantilever. As membranes are soft materials, tapping mode was used for scanning.

RESULTS & DISCUSSIONS

Aliphatic-aromatic polyamide composite membranes were prepared using PEI/IPC system and aromatic-aromatic polyamide membranes were prepared using MPD/TMC system over same polysulfone support membranes. In order to get salt rejection properties in same range with PEI/IPC system, TMC was chosen as acid chloride with MPD as IPC gives relatively lower rejection. The reaction scheme of polyamide thin film formation

from PEI/IPC and MPD/TMC systems were given in Fig. 1.

Optimization of concentration of reagents & reaction time for preparation of TFC-RO membranes

In polycondensation reaction, the concentration of both the reactants and time are two variables which directly influence the reaction rate and the degree of polymerization. In our previous study^[20], we have found that 2.0% (w/v) aqueous solution of para-phenylene diamine (PPD) with 0.2% (w/v) of TMC solution was optimum for aromatic-aromatic (PPD/TMC) type membranes whereas 2.0% (w/v) aqueous solution of PEI with 0.3% (w/v) of IPC solution was optimum for aliphatic-aromatic (PEI/IPC) type TFC-RO membranes. The dipping time in amine was 120 sec. whereas reaction time in acid chloride was 60 sec. As a reference, the similar concentration range of the reagents was chosen in the present study. From previous studies^[4, 5, 7, 9], it was evident that 2.0% amine solution is optimum for most of the amines used for TFC membrane suitable for preparation of brackish water RO membrane. However, optimum concentration of TMC can be different for MPD (in present study) than found in our

TABLE 1. Separation performances of MPD/TMC based TFC membranes as a function of concentration of acid chloride in organic solution.

Conc. of TMC (% w/v)	MPD/TMC	
	PWP (LMD)	NaCl rej. (%)
0.05	1040	90.0
0.10	960	96.4
0.15	936	97.0
0.20	912	97.3

Heat curing: 90°C hot air in oven for 4 minutes.

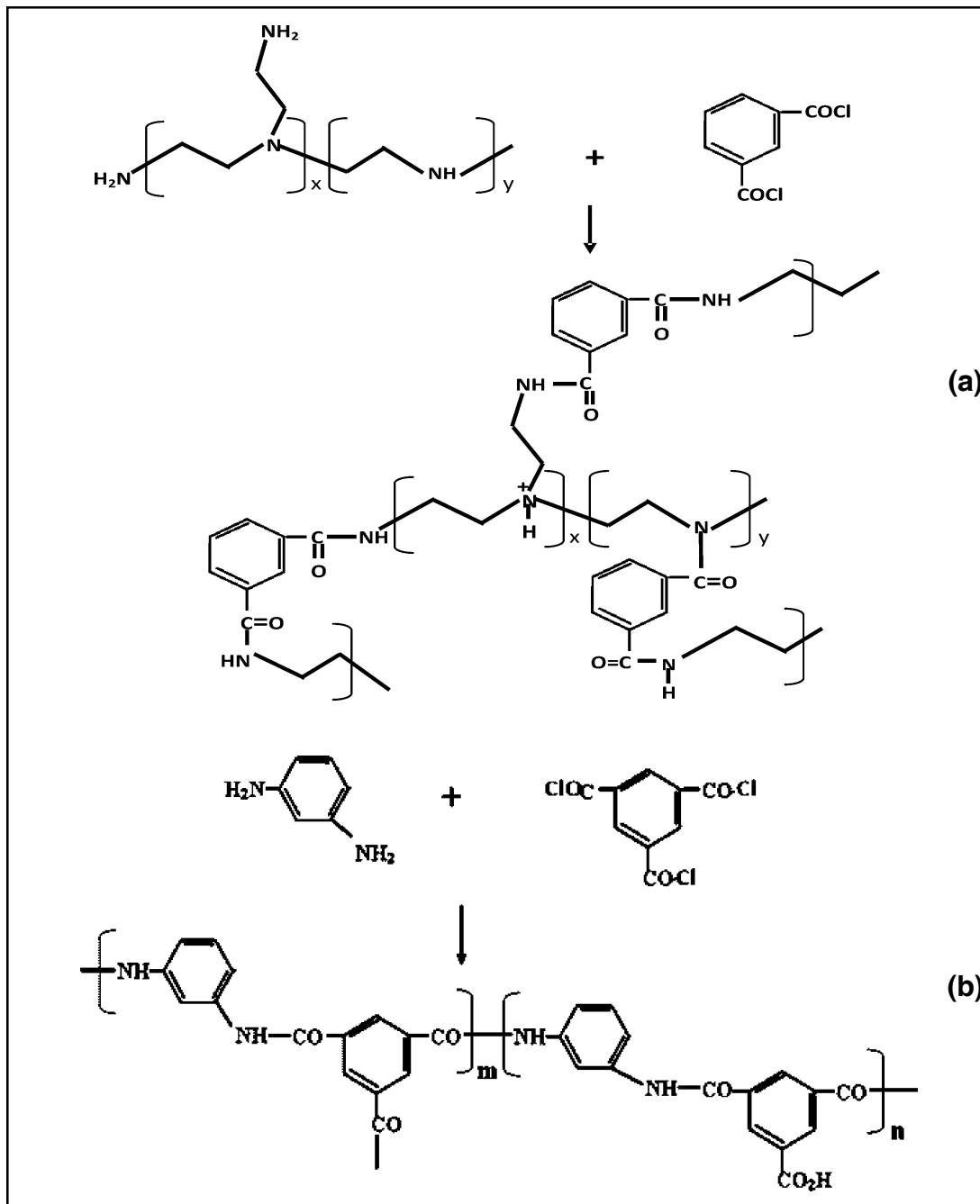


Fig. 1. Reaction schemes of polyamide thin film formation from (a) PEI/IPC, (b) MPD/TMC systems

previous study using PPD. Hence, concentration of TMC was optimized by preparing TFC membranes using 2.0% MPD and four different concentration of TMC varying within the range of 0.05 – 0.2% w/v. Separation performance of TFC membranes with respect to pure water permeability (PWP) and % NaCl rejections as a function of concentration of TMC was given in Table 1. Then effect of varying time of reaction was also studied using optimized amine and acid chloride concentration in hot air oven to get RO membranes with better performance and the results were given in Fig. 2. It was found that with increase in the

concentration of TMC, salt rejection of TFC membranes increases with decrease in PWP. At lower concentration of TMC, the TFC membrane formed shows very high PWP with relatively lower salt rejection (~90%). Flux reduction and salt rejection increase due to change of TMC concentration from 0.05% to 0.1% is higher than that of change from 0.15% to 0.2%. As concentration of TMC increases, the PWP decreases with increase in salt rejection which indicates that 0.05% TMC is not enough to form complete thin-film polyamide layer but 0.1% gives compact film with 96.4% salt rejection and it gets almost saturated at

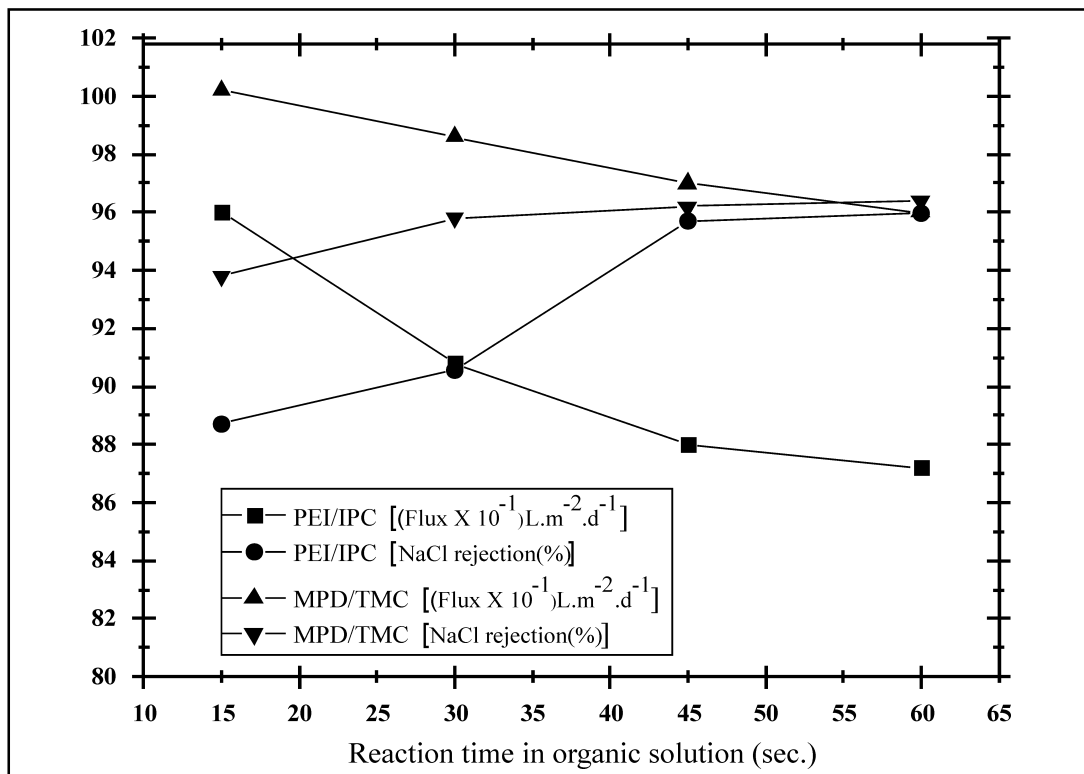


Fig. 2. Separation performances of TFC membranes as a function of time of reaction (dipping time in acid chloride solution)

TABLE 2. Separation performances of TFC membranes as a function of time of heat curing in different heating medium.

Curing media	Time (min.)	PEI/IPC (2.0%/0.3%)			MPD/TMC (2.0%/0.1%)		
		PWP (LMD)	A ($\mu\text{m}/\text{MPa}\cdot\text{s}$)	NaCl rej. (%)	PWP (LMD)	A ($\mu\text{m}/\text{MPa}\cdot\text{s}$)	NaCl rej. (%)
Hot air	2	977	7.19	89.0	1045	7.69	91.0
	3	912	6.71	90.8	991	7.29	94.3
	4	876	6.45	95.5	960	7.07	96.4
	5	862	6.34	96.0	944	6.95	96.5
	6	842	6.20	95.4	934	6.87	96.2
Hot water	2	1018	7.49	90.0	1020	7.51	96.0
	3	976	7.18	95.5	996	7.33	96.2
	4	947	6.97	95.8	988	7.27	96.3
	5	932	6.86	96.0	984	7.24	96.5
	6	926	6.82	96.0	980	7.21	96.5
Steam	2	1012	7.45	91.2	1053	7.75	92.4
	3	984	7.24	95.5	1032	7.60	95.8
	4	956	7.04	95.7	1002	7.37	96.0
	5	947	6.97	95.9	995	7.32	96.2
	6	940	6.92	96.0	990	7.29	96.2

Feed: 2000ppm NaCl ; Applied pressure: 1551 kPa.

higher concentration of TMC (0.15% & 0.2%). So, for fixed MPD concentration (2%), the optimum concentration of TMC is found as ~0.15% where TFC membrane gives optimum performance in terms of PWP and salt rejection. It is obvious for any TFC based membranes that some minimum time is needed to form the thin film of polymer over the support membrane. But once a layer of polyamide formed over the support membrane, it acts as a barrier for amine to diffuse through it and then come in contact with acid chloride in organic medium. This optimum time can

be predicted from the solute separation data by checking whether it is close to the saturation value i.e. highest separation achieved. For the PEI/IPC based composite membrane, the time is around 45 second whereas for the MPD/TMC based membrane it is 30 second.

Effect of heat treatment medium and time on performance of TFC-RO membranes

After formation of polyamide thin layer over polysulfone support membrane, evaporation of

the organic and aqueous solvents from the nascent polyamide layer and polysulfone support layer plays a crucial role in the resulted TFC-RO membrane performance. It is obvious that the solvents evaporation is controlled by the heat treatment environment in addition to the treatment time and temperature. So, using optimum conditions for concentration of reagents and time of in-situ polycondensation reaction, TFC-RO membranes were prepared as a function of time of heat treatment in three different heating medium viz. hot air, hot water and steam. Separation performances alongwith the pure water permeability constant, A of TFC membranes prepared as a function of time of heat treatment in different heating medium was given in Table 2. The time of the heat treatment was varies within 2 - 6 mins. as this is the typical timings used for heat treatment of TFC membranes at 90 -100°C. It was found that with increase in heat treatment time the water flux decreases with increase in salt rejection irrespective of treatment medium. It is revealed in the literature that during heat treatment, the cross-linking takes place in polyamide layer in addition to evaporation of the organic and aqueous solvents from the polyamide [21]. In addition, the pores of polysulfone membrane got shrinked if kept in dry condition and hence it always kept either in moist condition or under water. The results showed that heat treatment affect the polyamide cross-linking degree and pore shrinkage, leading to decrease in water flux and increase of salt rejection within optimum time and temperature. Exposure to high treatment temperatures or long treatment times can causes annealing of the microporous polysulfone support also, which tends to decrease the water flux. In present

case, exposure to 6 minutes of heat treatment in hot air tends to decrease both water flux and salt rejection in TFC-RO membranes prepared from PEI/IPC as well as MPD/TMC systems. But in the humid atmosphere (hot water and steam), chances of annealing of the microporous polysulfone support is less and hence decrease of water flux is much less compare to hot air cured membrane for both types of membranes. Heat treatment of the TFC membrane in hot air from 5 to 6 minutes results decrease in water flux of 20LMD for PEI/IPC based membrane and 10 LMD for MPD/TMC based membrane. But in similar condition, heat treatment in hot water and steam results much less decrease in water flux for both PEI/IPC based (6-7LMD) and MPD/TMC based (4-5 LMD) TFC-RO membranes. The optimum time of treatment with respect to achieve optimum TFC membrane performance is different for different heat treatment medium and also sometime it is different for PEI/IPC based membrane than MPD/TMC based membranes. In case of hot air treatment, the optimum time found as around 5 minutes for PEI/IPC and 4 minutes for MPD/TMC based TFC-RO membranes. Similarly, in case of hot water treatment, the optimum time found as around 3 minutes for PEI/IPC and 2 minutes for MPD/TMC based membranes. But in steam treatment, the optimum time is 3 minutes for both PEI/IPC and MPD/TMC based TFC-RO membranes. The optimum separation performances of TFC membranes in three different heating medium is given in Fig. 3. In general, aromatic-aromatic type MPD/TMC based membrane is more permeable than the aliphatic-aromatic type PEI/IPC based membranes irrespective of

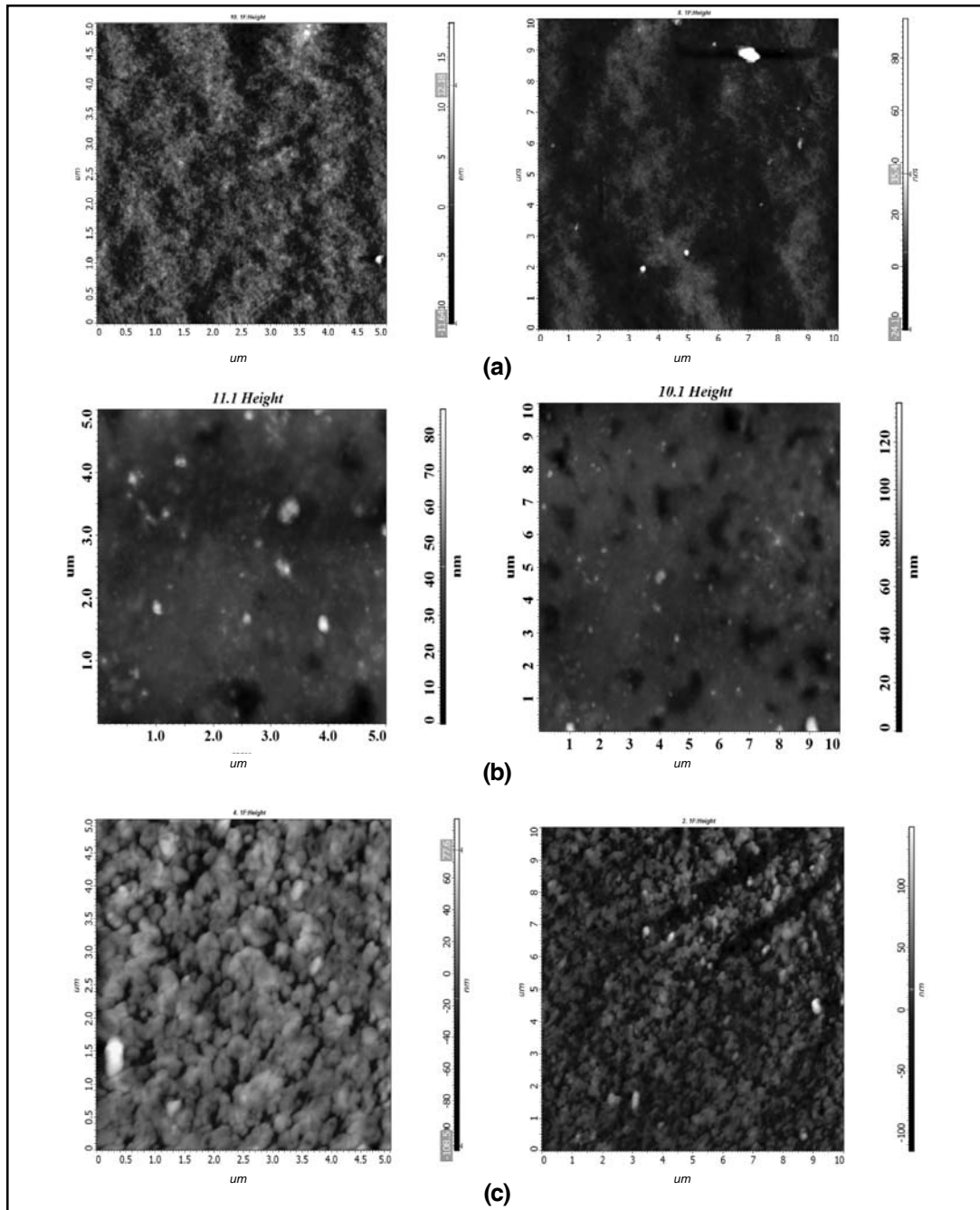


Fig. 3. 2-D AFM images of (a) PSf support, (b) PEI/IPC based TFC and (c) MPD/TMC based TFC membranes.

medium of heat treatment. Overall, water flux of hot water and steam cured TFC membranes are more than the corresponding hot air cured membranes. For better understanding, porosities of TFC membranes in different

heating medium prepared with optimized treatment time is given in Table 3. It indicates that humid atmosphere does not allow to shrink the support layer of the TFC membranes.

TABLE 3. Porosities of TFC membranes in different heating medium prepared with optimized curing time.

Curing media	PEI/IPC		MPD/TMC	
	Curing time (min.)	Porosities (%)	Curing time (min.)	Porosities (%)
Hot air	5	50.6±3.1	4	55.0±2.6
Hot water	3	57.1±2.5	2	59.3±2.1
Steam	3	56.2±2.7	3	58.5±2.0

*Porosity of PSf support membrane: 68±2.6%

Effect of heat treatment medium and treatment time on surface characteristics of TFC-RO membranes

During heat treatment, it is expected that the surface roughness and hydrophilicity of TFC membranes may change while changing the heating medium and varying the heat treatment time. So, TFC-RO membranes were prepared as a function of time of heat treatment in three different heating medium viz. hot air, hot water and steam and using optimum concentration of reagents and time of in-situ polycondensation reaction. 2-D AFM images of polysulfone support and hot air cured PEI/IPC and MPD/TMC based TFC membranes are given in Fig. 4. It is very clear that support membrane has very smooth surface but TFC membrane prepared out of support membrane has much rougher surfaces. In order to understand the changes of surface hydrophilicity and surface roughness on changing heating medium, water contact

angles and surface roughness of top layer of TFC membranes were measured and the results are given in Figs. 5 & 6 respectively. The summary of the water contact angle and average roughness data of TFC membranes in different heating medium prepared with optimized treatment time is given in Table. 4. It was found that different heating media produce TFC polyamide membranes with widely varying surface properties with respect to hydrophilicity and average surface roughness when prepared under identical coating conditions. In addition, it has different impacts on aliphatic-aromatic and aromatic-aromatic type polyamide composite membranes surface properties. In general, with increase in time of heating, the water contact angle of TFC membranes decreases upto a certain time. At lower treatment time, the formation of full cured cross-linked polyamide layer could not be completed and there is a possibility of exposure of polysulfone layer in some places which has higher water contact value (72-74°).

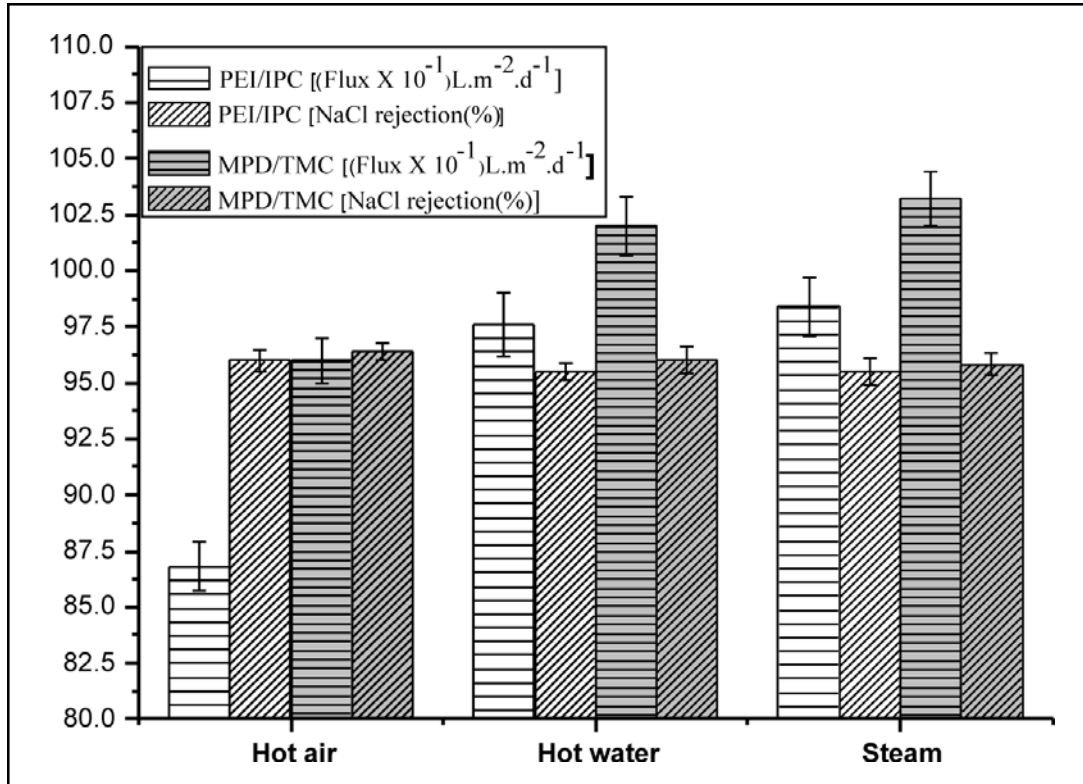


Fig. 4. Optimum separation performances of TFC membranes in three different heating medium

The surface hydrophilicity of the steam and hot water-cured membranes is more (lower water contact angle) than that of hot air cured membranes but the effect is more for MPD/

TMC (aromatic-aromatic type) and less for PEI/IPC (aliphatic-aromatic) based TFC-RO membrane. In case of TFC-RO membrane prepared using MPD/TMC based system, 3

Table 4. Water contact angle and average surface roughness of TFC membranes in different heating medium prepared with optimized curing time.

Curing media	PEI/IPC (2.0%/0.3%)			MPD/TMC (2.0%/0.1%)		
	Curing time (min.)	Water contact angle (o)	Av. surface roughness (nm)	Curing time (min.)	Water contact angle (o)	Av. surface roughness (nm)
Hot air	5	63.2	45.1	4	67.0	62.0
Hot water	3	60.0	56.7	2	52.0	70.3
Steam	3	60.4	46.6	3	58.6	64.4

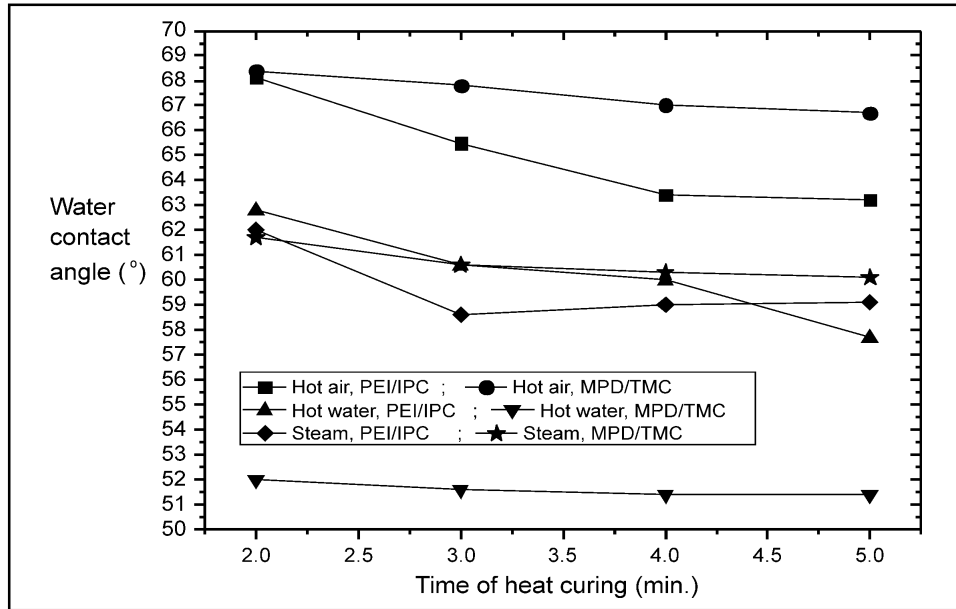


Fig. 5. Water contact angles of TFC membrane surfaces as a function of time of heat curing in different heating medium

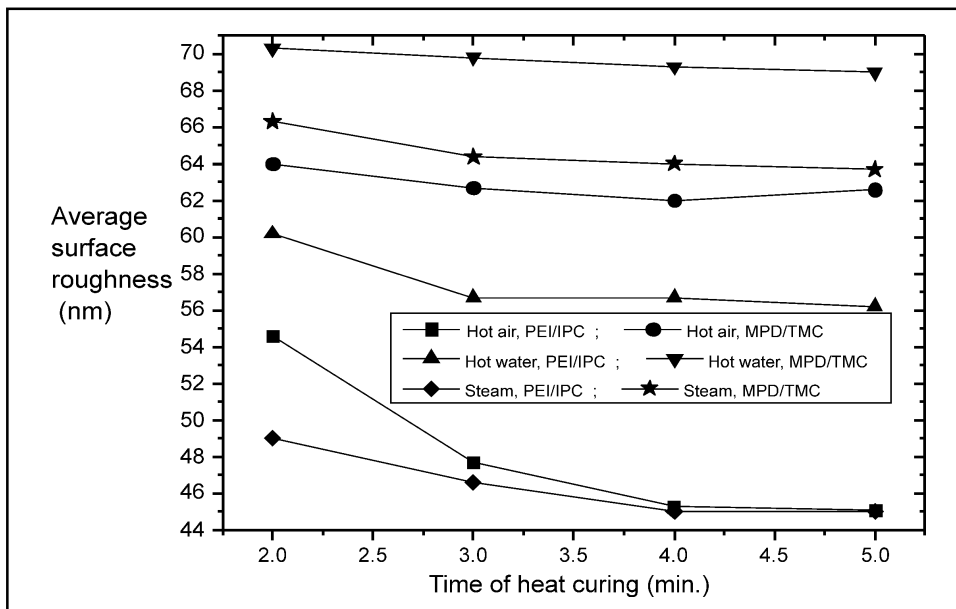


Fig. 6. Surface roughness of TFC membranes as a function of time of heat curing in different heating medium

carboxylic acid chloride groups (-COCl) of TMC is available to react with 2 amino groups (-NH₂) of MPD in-situ at the interface of aqueous & organic medium and form polyamide layer over polysulfone support membrane. It has been reported that some of the unreacted third acid chloride group got hydrolysed and remain as carboxylic acid group (-CO₂H) in polyamide thin film (Fig. 1). The chances of getting carboxylic acid group in polyamide thin film are much more when heated in humid atmosphere of hot water and steam than the hot air. Due to the stronger H-bonding between water and carboxylic pendant group, the surface hydrophilicity of the steam and water-treated membranes increased significantly.

Similarly, with increase in time of heating, the average surface roughness decreases upto a certain time for both PEI/IPC and MPD/TMC based TFC-RO membranes. At lower treatment time, there is a possibility of exposure of polysulfone layer in some places which make the TFC membrane rough. Once the full polysulfone is covered with heat treated polyamide layer, the average roughness didn't change. The surface roughness of the hot water-treated membranes is more for both MPD/TMC and PEI/IPC based TFC-RO membrane than the hot air and steam treated membranes. Heating at faster rate mostly results rougher film than that of heating at slower rate. In general, MPD/TMC based membranes are more rough than PEI/IPC based membranes irrespective of heating medium used. This is due to the mechanism of polyamide thin film formation by in-situ polycondensation reaction between amine and acid chloride at the aqueous-organic interface created at the

surface of polysulfone support membrane. The amine diffuses from pores of polysulfone support to the surface and reacts with acid chloride available in bulk to form polyamide film over polysulfone. Once a thin film of polyamide forms at the interface (created at the surface of polysulfone support membrane) by reaction of aqueous solution of amine (available inside the pore of the support) and organic solution of acid chloride (available as bulk solution), the amine need to diffuse through the polyamide thin layer to react further with the acid chloride. Hence, the changes in diffusivity of amine from aqueous to organic medium have influence on the rate of the polycondensation reaction and physico-chemical properties of polyamide film and the faster reaction gives rougher film than the slower reaction [22]. PEI is a polymeric amine and hence its diffusion is slow whereas MPD is a monomeric amine with high diffusion rate and hence MPD expected to give faster reaction with rougher film.

CONCLUSIONS

During heat treatment of thin film composite (TFC) reverse osmosis (RO) membranes, alongwith the heating temperature and time, the heating medium plays very important role in surface properties and separation performance. Different heating media produce TFC polyamide membranes with widely varying surface properties with respect to hydrophilicity and average surface roughness and it has different impacts on aliphatic-aromatic and aromatic-aromatic type polyamide composite membranes. TFC membranes prepared using polyethylene imine (PEI)/isophthaloyl chloride (IPC) system show smooth surface with relatively less permeable than that of prepared

using meta-phenylene diamine (MPD)/trimesoyl chloride (TMC) in all three heating medium (hot air, hot water and steam). Overall, water flux of hot water and steam treated TFC membranes are more than the corresponding hot air treated membranes as the humid atmosphere does not allow to shrink the support layer of the TFC membranes. The optimum time of curing to achieve optimum TFC membrane performance is different for different heating medium. The steam and hot water-treated membranes are more hydrophilic than that of hot air treated membranes. In general, MPD/TMC based membranes are more rough than PEI/IPC based membranes irrespective of heating medium used for treated and the hot water-treated TFC membranes have more rough surface than the hot air and steam cured membranes.

REFERENCES

1. R.J. Peterson, *J. Membr. Sci.* **83** (1993) 81.
2. I.J. Roh, A.R. Greenberg, V.P. Khare, *Desalination* **191** (2006) 279.
3. J.E. Cadotte, R.J. Petersen, R.E. Larson, E.E. Erickson, *Desalination*, **32 (1-3)** (1980) 25.
4. A.K. Ghosh, E.M.V. Hoek, *J. Membr. Sci.*, **336** (2009) 140.
5. B. Khorshidi, T. Thundat, B. Fleck, M. Sadrzadeh, *RSC Adv.*, **5** (2015) 54985.
6. T. Kamada, T. Ohara, T. Shintani, T. Tsuru, *J. Membr. Sci.* **453** (2014) 489.
7. A.K. Ghosh, B.-H. Jeong, X. Huang, E.M.V. Hoek, *J. Membr. Sci.* **311** (2008) 34.0
8. L. Zhao, P.C.Y. Chang, W.S.W. Ho, *Desalination*, **308** (2013) 225.
9. A. Prakash Rao, N.V. Desai, R. Rangarajan, *J. Membr. Sci.* **124** (1997) 263.
10. H. Wang, L. Li, X. Zhang, S. Zhang, *J. Membr. Sci.*, **353** (2010)78.
11. L. Li, S. Zhang, X. Zhang, G. Zheng, *J. Membr. Sci.*, **289** (2007) 258.
12. Z. Lin, C.-Y. Philip, W.S. Chang, H. Winston, *Desalination* **308** (2013) 225.
13. X. Lu, S. Castrillon, D. L. Shaffer, J. Ma, M. Elimelech, *Environ. Sci. Technol.*, **47**(2013) 12219.
14. S. Yu, Z. Lu, X. Liu, M. Liu, C. Gao, *J. Membr. Sci.*, **371** (2011) 293.
15. B.H. Jeong, E.M.V. Hoek, Y. Yan, A. Subramani, X. Huang, G. Hurwitz, A.K. Ghosh, A. Jawor, *J. Membr. Sci.*, **294** (2007) 1.
16. A. Mostafa, A. El-Aassara, *Desal. Water Treat.* **55**, (2015) 2939.
17. M.L. Lind, A.K. Ghosh, A. Jawor, X. Huang, W. Hou, Y. Yang, E.M.V. Hoek, *Langmuir*, **25(17)** (2009)10139.
18. M.T.M. Pendergast, A.K. Ghosh, E.M.V Hoek, *Desalination*, **308** (2013)180.
19. A.K. Ghosh, V. Ramachandhran, M.S. Hanra and B.M. Misra, *J. Polym. Mater.* **15** (1998) 279.
20. V. Ramachandhran, A.K. Ghosh, S. Prabhakar and P.K. Tewari, *Sep. Sci. & Technol.* **44** (2009) 599.
21. J.-E. Gu, J.S. Lee, S.-H. Park, I.T. Kim, E.P. Chan, Y.-N. Kwon, J.-H. Lee, *Appl. Surf. Sci.* **356** (2015) 659–667.
22. P.W. Morgan, S.L. Kwolek, *J. Polym. Sci. Part A: Polym.Chem.* **34** (1996) 531-559.

Received: 20-08-2017

Accepted: 26-11-2017