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Effect of alternation of polyamide selective layers in the formation and performance of thin-film composite membranes

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ABSTRACT

Polyamide thin-film composite membranes were prepared on a reinforced microporous polyethersulfone (PES) support by *in situ* interfacial polycondensation of amic acid diamines (AADs) with 1,3,5-benzenetricarbonyl trichloride and subsequent curing. Water soluble AADs were synthesized by reacting trimellitic anhydride chloride and cyclic/aromatic diamines in dimethylformamide at 5–10°C. Polyamide ultra-thin barrier layer containing different structural modifications were isolated by dissolving the matrix PES support in dichloromethane and characterized for IR, NMR, and DSC techniques. Morphology of membranes by scanning electron microscopy showed the appearance of honeycomb-like structure on the polyamide skin surface and the cross section displayed the presence of nodular structure which arises from the dense polyamide skin. The performances of these membranes were measured by passing the feed solutions containing 2,000 ppm of NaCl and Na_2SO_4 in a reverse osmosis test kit. Membranes exhibited very broad range of separations for NaCl (35–85%) and Na_2SO_4 (40–89%) depending on the chemical nature of the AADs. The glass transition temperature (T_g) of composite membranes with aromatic diamine structures were >220°C, indicating the higher stiffness nature of the polymer chain due to the presence of fully aromatic structural units.

Keywords: Thin-film composite membrane; Polyamide skin layer; Thermal analysis; Glass transition temperature

1. Introduction

Polyamide thin-film composite (PTFC) membrane has been widely used for reverse osmosis or nanofiltration processes for the past few decades. With the development of membrane science and technology, the synthetic process of preparing/modifying TFC members has taken a big change in the commercial market. Currently, they have been prepared by incorporation of various substrates such as nanoparticles [1–3], carbon nanotubes [4,5], amino-functionalized β-cyclodextrins [6–8], and surfactants [9] using different methods such as atomic layer deposition method [10], grafting [11], etc. Conventionally, these membranes are prepared by interfacial polymerization technique, where monomers in two immiscible phases react on the porous substrate surface and thin selective layer is formed *in situ* on top of the substrate. The stability and performance (salt rejection and flux) of these composite

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membranes is mainly dependent on the chemical nature and morphological properties (pore size and its distribution) of the skin layer [12–14]. The advantage in the preparation of composite membranes is the possibility to alter individually both the porous support and the selective layer to meet specific function. The porous support can be optimized for maximum strength with minimum resistance for permeate flux, whereas, the selective layer can be improved for the desired combination of solvent flux and solute rejection. Researchers have explored TFC membranes for different applications, which include pervaporation [15], forward osmosis [16–20], pressure-retarded osmosis [21–23], and osmotic power generators [24,25]. Recently, Meng et al. reported a novel salt-responsive TFC reverse osmosis membrane having superior antifouling and easy-cleaning properties. The zwitterionic polymer poly (4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine) was grafted to impart the membrane improved antifouling and foulants release properties regulated by salt concentrations [26]. Yu et al. developed a polyamide RO composite membrane with natural polymer sericin through surface coating technique, for improving fouling resistance [27]. The modified membranes improved surface hydrophilicity, smoothed surface morphology, and enhanced negative charges, which are an important criterion for the purpose of improving fouling. We have also previously reported low-pressure thin-film composite membranes containing poly(amide–imide) skin layer [28] and fouling resistant PTFC membranes for desalination and water recovery [29].

The present paper describes the preparation, characterization, and performance evaluation of composite membranes containing different polyamide skin layer formed by the *in situ* interfacial polymerization of AADs with TMC. This chemical interaction of these monomeric constituents provides good prospects for the development of polyamide membranes with different barrier layers and morphologies. The produced membranes could be utilized for a wide range of separation applications, for example inorganic solute separations, aqueous–organic liquid mixtures, organic–inorganic separations etc. An attempt has been made to understand the relationships between polyamide barrier layer, stability of the skin layer, and performances of the composite membranes for inorganic solutes.

2. Experimental

2.1. Materials

Trimellitic anhydride chloride (TMAc), 1,3,5-Benzenetricarbonyl trichloride (TMC), 1,3-cyclohexanebis (methylamine) (CDA), *m*-Phenylenediamine (MPD), 4,4´-diaminophenylmethane (MDA), 4,4´-oxydianiline (ODA), and 3-Aminophenyl sulfone (3APS) were received from Sigma Aldrich Co. Ltd. All the other reagents and solvents were of analytical grade samples and purified according to standard procedures.

2.2. Preparation of amic acid diamines (AA^{D1-7})

A typical procedure for the synthesis of AADs (Fig. 1) is described as follows (AA^{D1}). In a 100 mL flask, CDA (9.60 g; 0.0675 mol) was dissolved in 25 mL dimethylformamide (DMF), and the solution was cooled to 5–10°C. TMAc (6.31 g; 0.03 mol) in 25 mL DMF was added all at once and the reaction mixture was stirred at 5–10°C for 1 h and at room temperature for 2 h. AA^{D1} was isolated by adding the reaction mixture to ice-cold water and filtered. The sample was further washed with methanol and dried at 65–70°C. It was then recrystallized from ethanol. Similarly, AA^{D2-6} were prepared by reacting MPD, ODA, 3APS, and MDA, respectively, with TMAc. The amic acid diamines did not show any obvious melting points and decompose above 200°C. The structures of the AADs were confirmed by IR technique.

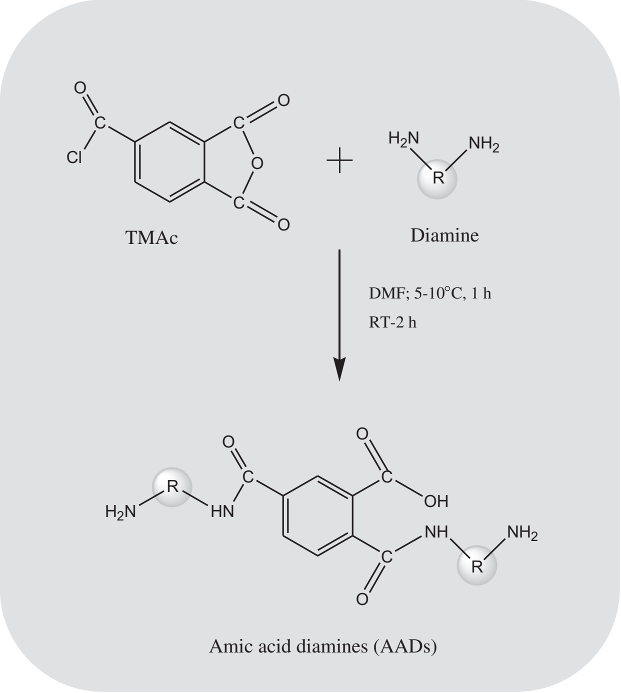


Fig. 1. Synthesis of AADs.

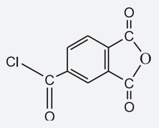
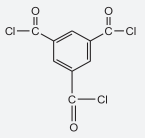
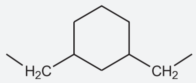
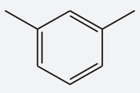
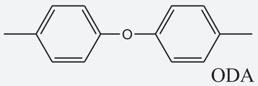
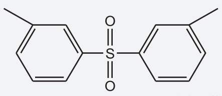
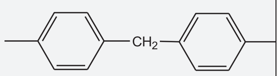
2.3. Preparation of PTFC membranes

Reinforced porous PES support membrane was prepared on a motor-driven mechanical membrane casting device using 15 wt.% DMF solution of the polymer. Poly(amide–amic acid) skin layer on the top of PES support was formed by *in situ* interfacial polymerization of AADs (0.5–3 wt.%) in aqueous NaOH solution (0.01wt.%) with TMC (0.05–0.4 wt.%) in hexane. PES support (15 × 20 cm size) was fixed in a glass trough at the edges and filled with diamine solution. After 3 min, the solution was decanted and the PES support was allowed in air at ambient temperature for about 4 min to drain out the excess solution from the top of the support. It was then contacted with TMC solution for 90 s, which results in the formation of poly(amide–amic acid) thin film on the top of PES support by the interfacial polycondensation of AAD at the pore surface of the support with TMC. Thus, the nascent PTFC membrane was cured at 70–75˚C for 5 min in air-circulating oven. Table 1 gives the general characteristics of reactants used in the preparation of polyamide skin layer.

2.4. Measurements

Structural confirmation of the AADs was done using NICOLET 380-FTIR spectrometer, in a spectral range of 400–4,000 cm^{-1}. ^{1}H NMR spectra were obtained with a Bruker Avance DPX 200 MHz FT-NMR spectrometer. Spectra were recorded in DMSO-d6 using tetramethylsilane as the external standard. DSC Q200 was used to investigate the change in endothermic transitions of the membranes. The entire membrane was heated from 50 to 350˚C following the same heating rate as for TGA analysis. The performances of the membranes were tested for 2,500 ppm aqueous feed solutions of NaCl and Na_2SO_4 in a reverse osmosis test kit at the operating pressure of 10 bar using cross-flow filtration method. After fixing the membranes in the test cells, pure water was passed initially for about 1 h and their pure water flux was measured at 10 bar. Salt solution was passed at 20 bar and the permeate flux was measured after 20/40 min. Salt concentration in the feed and permeate solutions were determined by measuring the electrical conductivity of the salt solution. An average

Table 1
Diamines and acid chlorides used in the preparation of PTFC

Acid chloride R	 TMAc	 TMC	T_g^{a}
 CDA	**AA**^{D1} (TMAc-CDA)	**PA**^{1} Poly(AA^{D1}–TMC)	192
 MPD	**AA**^{D2} (TMAc-MPD)	**PA**^{2} Poly(AA^{D2}–TMC)	240
 ODA	**AA**^{D3} (TMAc-ODA)	**PA**^{3} Poly(AA^{D3}–TMC)	237
 3APS	**AA**^{D4} (TMAc-3APS)	**PA**^{4} Poly(AA^{D4}–TMC)	232
 MDA	**AA**^{D5} (TMAc-MDA)	**PA**^{5} Poly(AA^{D5}–TMC)	230

[a] T_g—glass transition temperature (obtained by DSC).
[b] IDT—initial decomposition temperature (obtained by TGA).

of four tested membranes was taken to check the reproducibility of each sample. The solute separation was calculated using the following expression:

$$\text{Solute rejection } (R\%) = \{(1 - C_p/C_f) \times 100\} \qquad (1)$$

where C_f and C_p are solute concentrations in the feed and permeate, respectively. The values reported in the paper are the average of four tests of each membrane samples.

3. Results and discussion

The performance of the composite membranes is mainly governed by (a) structural chemistry of monomeric constituents and (b) preparation conditions of the ultrathin barrier layer [30,31]. The former is an inherent property of the reactants taken to form the barrier layer; whereas, preparation conditions that are decisive in determining the properties (stability and performance) of the composite membranes depends on many parameters such as nature and concentrations of reactants, and skin layer formation conditions like reaction time, curing time, curing temperature etc. For any chosen pair of reactants, a systematic optimization of the preparation conditions of polyamide skin layer is essential to obtain membrane having stable polyamide selective layer with optimum performance characteristics. Hence, polyamide composite membranes were prepared under different conditions such as variation in monomer structures and concentrations (AADs: TMC), to optimize the conditions to obtain membranes having stable polyamide skin layer with ideal performances.

3.1. Characterization

The FT-IR spectra of the AADs show strong bands around 1,720 and 1,665 cm^{-1} due to the carbonyl stretchings of carboxylic acid and amide units, respectively. Broad absorption bands were seen around 3,350 cm^{-1} which corresponds to carboxylic acid (O–H) and amide (N–H) stretchings. The band at 1,500 cm^{-1} may be assigned to aromatic >C=C< stretchings. ^{1}H NMR spectra (Fig. 2) of AADs show signals at 10.5–11.0 ppm (in DMSO-d6) due to the protons of amic acid functionality, i.e. carboxylic acid O–H and amide N–H groups, because of the ring opening of anhydride unit in TMAc. Two characteristic multiplets corresponding to aromatic protons are also witnessed. The multiplet at 8.6–7.8 ppm may be attributed to Ar–H of TMAc unit, while the other one at 6.4–7.4 ppm corresponds to the aromatic protons of amine unit. The signals due to amide (N–H) protons are overlapped with those of TMAc unit around 8.0 ppm.

3.2. Membrane performance

Membranes are usually characterized by their performance i.e. solute separation and permeate flux for any selected application. The performance of composite membranes strongly depends on the chemical nature of the skin layer (i.e. nature and type of reactants such as aliphatic, aromatic, functionality), concentration of reactants, and skin layer formation conditions. The variation in membrane performances with modification in skin layer are discussed below.

3.2.1. Nature of the reactants on polyamide skin stability

The nature of reactant and the concentration of reactants play a key role in shaping the performance and stability of the polyamide skin layer. Table 2 shows the performances of composite membranes having different polyamide skin layer when tested using 2,500 ppm aqueous feed solutions of NaCl and Na_2SO_4 at 20 bar. Membranes exhibited very broad range of separations, viz. 35–83% for NaCl, and 40–89% for Na_2SO_4, with water fluxes of 38–172 L m^{-2} h. The

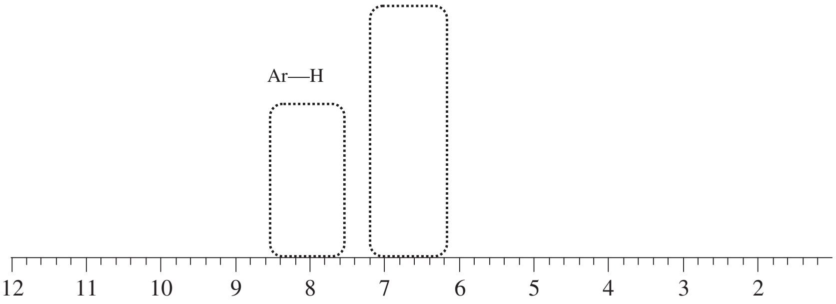


Fig. 2. ^{1}H NMR spectra of AA^{D3} (TMAc-ODA).

difference in the performance of the composite membranes may be due to the variation in the reactivity of the AADs with the acid chloride which results in the formation of polyamide skin layer of different morphology. The chemical reaction of AAD and TMC at the polyamide skin layers is shown in Fig. 3.

It was clearly evident that PA^2 membrane with poly(TMAc–MPD–TMC) skin layer exhibited very high salt separations (NaCl 85%, Na_2SO_4 89%) with water flux of 82 $L\,m^{-2}\,h$. In case of these membranes, the rate of formation of polyamide structure is much faster, which reduces other side reactions like hydrolysis of acid chloride and thus resulting in the formation of a cross-linked polyamide skin layer. PA^1 membranes with poly(TMAc–CDA–TMC) skin layer have shown lower salt separations (35% for NaCl, 40% for Na_2SO_4) with high water permeation rates (172 $L\,m^{-2}\,h$). This inferior performance of these membranes can be credited to the aliphatic CDA unit which forms more open structures that result in lower separations. It has been reported that stability of polymers having aliphatic linkages is lower than those of a polymer having fully aromatic structures [32]. The salt rejections of PA^3, PA^4, and PA^5 composite membranes are in between (45/68/70% for NaCl and 80/75/72% for Na_2SO_4,) those of membranes having PA^1 and PA^2 skin layer. Nevertheless, the water fluxes of these membranes are lower than that of PA^2 membrane.

Table 2
Performances of composite membranes for inorganic solutes

Reactant	PWP ($L\,m^{-2}\,h$)	Permeate Flux ($L\,m^{-2}\,h$)	Rejection (%) NaCl	Rejection (%) Na_2SO_4
PA^1	164	172	35	40
PA^2	88	82	83	89
PA^3	45	38	45	80
PA^4	46	40	68	75
PA^5	47	41	70	72

Notes: Membrane preparation conditions:
AAD concentration: 2 wt.%; TMC concentration: 0.1 wt.%.
Curing time: 4 min, Curing temperature: 70˚C.
Feed concentration: 2,500 ppm; Applied pressure: 20 bar.
PWP: Pure water permeation rate.

All the composite membranes have shown higher separations for divalent anionic Na_2SO_4 salt when compared to monovalent anionic NaCl salt. This difference may be attributed to the Donnan's ion exclusion effect which arises due to the presence of negatively charged carboxylic acid functional group on the polyamic acid skin layer [33,34]. The occurrence of negative charge on the membrane surface is assumed to affect the mobility of solute ions in the feed solution. When the concentration of feed becomes equivalent to the fixed charge on the membrane, a Donnan equilibrium exists between the solution and the membrane phase which eliminates co-ions from the membrane resulting in high solute rejection.

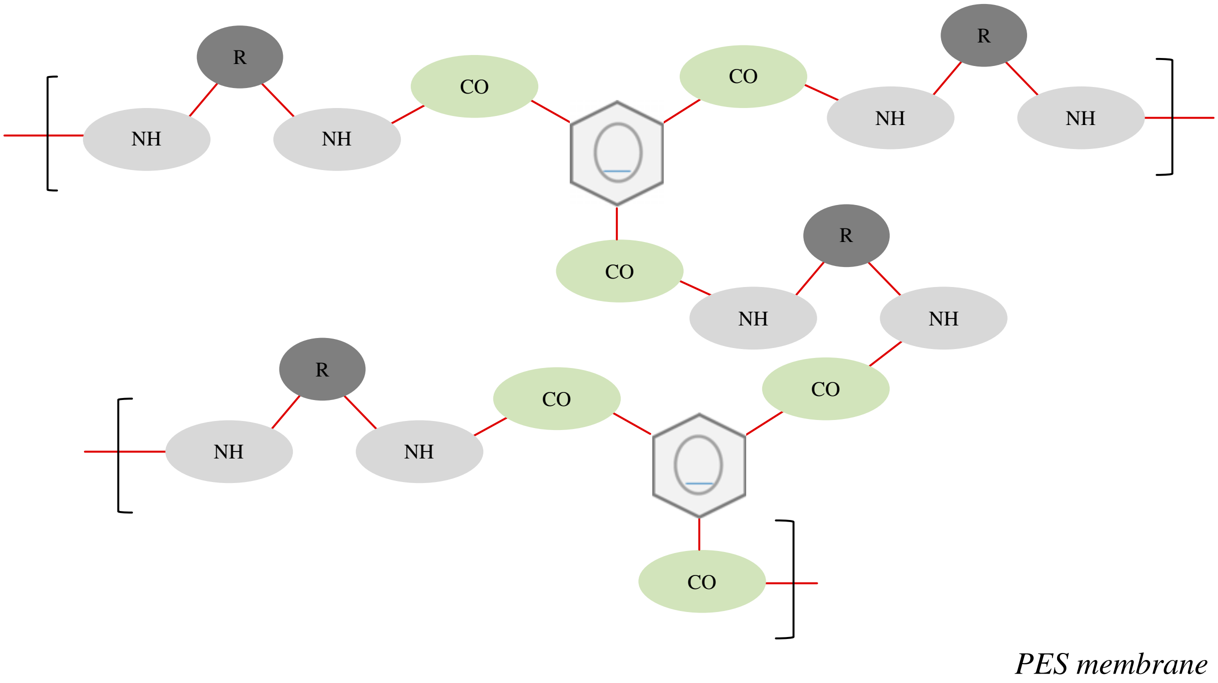


Fig. 3. Interfacial polymerization reaction of AADs and TMC on the surface of PES support.

Nevertheless, when the concentration of feed solution is in excess of the concentration of fixed charge on the membrane, the sorption of co-ions into the membrane phase is less hindered, which results in lower solute separation.

3.2.2. Concentration of the reactants on polyamide skin stability

Since the membrane having poly(TMAc–MPD–TMC) skin layer has shown higher salt rejection for inorganic solutes, they were selected to investigate the membrane performance by varying the concentration of reactants. Membranes were prepared with wide range of concentrations of TMC (0.025–0.4%) and AAD (0.1–3%) while keeping the other reaction conditions such as reaction time, curing time, and curing temperature as constant. It was noticed that the polyamide skin layers which were formed using either of higher TMC (>0.4%) or higher AAD (>3%) concentrations were very brittle and collapsed during performance evaluation. Fig. 4 shows the effect of TMC concentration on the performance of PA^2 membrane. As the acid chloride concentration was increased, the salt rejection of the membrane was increased up to a certain extent and then almost leveled off. For example, at 0.02% of TMC, the rejection in the membranes was ~32%, which increased to about 83% (at 0.15%) with the increase in acid chloride concentration and reached a saturation point. Further increase in TMC concentration had no effect on the rejection of solute particles. However, water flux rate was decreased with the increase in acid chloride concentration. Similar observations were witnessed when AAD concentration was varied at a constant TMC concentration (Fig. 5). At lower concentration (0.1%) of AAD, the rejection for NaCl and Na_2SO_4 was around 20 and 58% with a permeate flux of 138 L m^{-2} h. At higher concentration (2%), the rejection improved to 83 and 89% for NaCl and Na_2SO_4 with a decrease in permeate flux. The concentration range (acid chloride/amine) where maximum salt separation was observed depends on the nature as well as concentration of the reactants which were used to form the polyamide skin layer. The results indicate that both lower and higher concentrations of the reactants result in the formation of more open and less compact polyamide barrier layer which may be due to the presence of non-equivalent concentrations of monomers at the reaction site. Liu et al. [35], reported this kind of performance for nanofiltration membranes based on polyvinylamine (PVAm) and TMAc on a porous polysulfone support membrane. The concentration range (acid chloride/amine) where maximum salt separation was noticed was governed by the nature as well as concentration of the reactants which were used to form the polyamide skin layer. Two types of possible structures can be obtained when lower/higher concentration of amine/acid chloride was reacted to form the barrier layer. Lower concentration of acid chloride results in the formation of unstable amide–amine network, due to the existence of higher number of diamine molecules at the interface. Lower amine concentration leads to the formation of brittle low molecular weight amide–acid structure, owing to

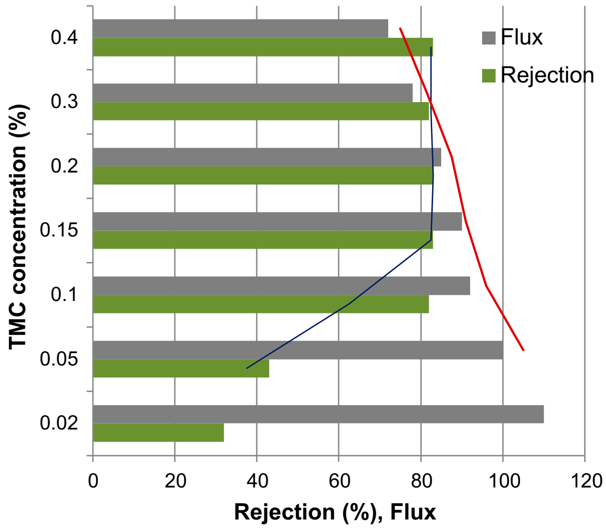


Fig. 4. Membrane performance of PA^2 (Poly(AA^{D2}-TMC) with variation in TMC concentration. AAD concentration = 2%, pressure = 10 bar.

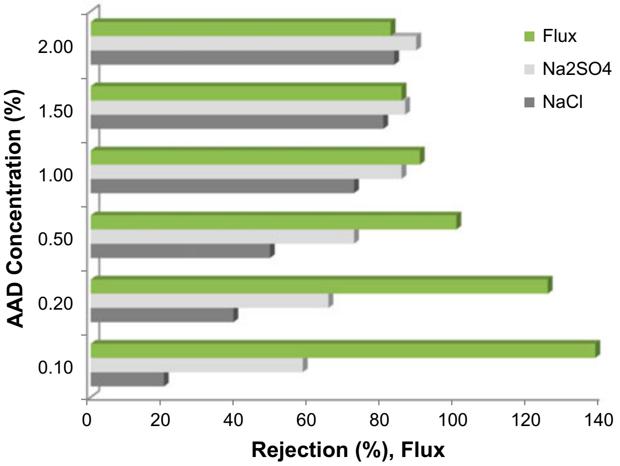


Fig. 5. Membrane performance of PA^2 with variation in AAD concentration. TMC concentration = 0.1%, pressure = 10 bar.

higher availability of acid chloride molecules at the interface. The formation of amide–amine and amide–acid at the skin layer was confirmed by IR analysis. The skin layer was isolated by dipping the virgin composite membrane in dichloromethane to dissolve the porous PES support, washed and dried at 80°C. The skin layer formed from higher concentration of TMC showed a strong peak at 1,719 cm^{-1} and a weak peak at 1,664 cm^{-1} which are assignable to >C=O (carbonyl) group, stretching of –COOH (carboxylic acid) and $-\mathrm{NH}_2$ (amide) group, respectively. Strong absorption peak at 1,719 cm^{-1} arises due to the hydrolysis of –COCl (carbonyl chloride) group of TMC. The intensity of the peak at 1,719 cm^{-1} decreases with the decrease of the concentration of TMC in the reaction solution. The skin layer formed from higher concentration of AADs does not contain a peak corresponding to carboxylic acid group. It exhibits peaks around 1,643 and 1,550 cm^{-1} which correspond to carbonyl stretchings of amide group and amine N–H bending vibrations, respectively.

The salt separation and water flux behavior of the membranes may be interpreted in terms of both the chemical and structural changes that occur during the formation of polyamide skin layer. The change in monomer concentration causes a variation in thickness as well as the chemical properties of the interfacial film. According to the "solution-diffusion" mechanism proposed by Lonsdale et al. [36], both the solvent and the solute molecules are dissolved in the nonporous active layer of the membrane and are subsequently transported by diffusion in a coupled manner. Accordingly, the water flux depends on the thickness and material properties of the active layer, as shown in Eq. (2):

$$\text{Water flux } (J_\mathrm{w}) = \frac{D_\mathrm{w} C_\mathrm{w} V_\mathrm{w}}{R_\mathrm{g} T t}(\Delta p - \Delta \pi) \qquad (2)$$

where D_w is the diffusion coefficient of water in the membrane, C_w is the concentration of dissolved water in membrane, V_w is the partial molar volume of water in the external phase, Δp is the applied pressure difference across the membrane, $\Delta\pi$ is the osmotic pressure difference across the membrane, R_g is the gas constant, T is the absolute temperature, and t is the active layer thickness. When the reactant concentration was reduced, the process of interfacial polymerization slows down due to the lack of reactant at the interfacial reaction site, which leads to the formation of thin, unstable skin layer, resulting in poor rejection of solutes and high permeation of water. But, with the increase in reactant concentration in the organic phase, the rate of polymerization accelerates and forms compact skin layer with higher salt rejections and lower water flux. Literature reported that there is an optimum range of TMC concentration to obtain membranes with good performances. In the preparation of FT-30 composite membrane, the optimum concentrations of *m*-phenylenediamine and trimesoyl chloride have been reported as 2 and 0.1 wt.%, respectively. Optimum concentrations in the range of 0.1–0.2% have been testified for cyclohexane–1,3,5-tricarboxylic acid chloride [37].

3.3. Thermal stability

The variation in the chemical/structural composition of the interfacial polyamide films formed using different concentrations of diamine and TMC was investigated using DSC. PES support along with polyamide skin layer was isolated from non-woven support by keeping the dry membrane in dichloromethane. The resultant blend of PES and polyamide was washed thoroughly with water and methanol and dried in vacuum oven. The glass transition temperature (T_g) (Table 1) of membranes PA^2–PA^5 are in the range of 230–240°C, thus indicating the higher stiffness nature of the polymer chain due to the presence of fully aromatic structural units. The T_g of PA^1 was somewhat lower i.e. 192°C, which may be attributed to the presence of flexible aliphatic units in the polymer chain. The matrix PES has shown a glass transition temperature of about 215°C. Fig. 6 indicates that the membrane formed from PES—PA^1 shows T_gs which are lower than the T_g recorded for pure PES. A minimum T_g of about 192°C, which is about 23°C lower than for PES, was observed for systems prepared using 0.01% TMC and 2% PA^1 for film formation. The T_gs of the membranes increased with the increase of TMC concentration used for polyamide film formation. Similar trend in the glass transition

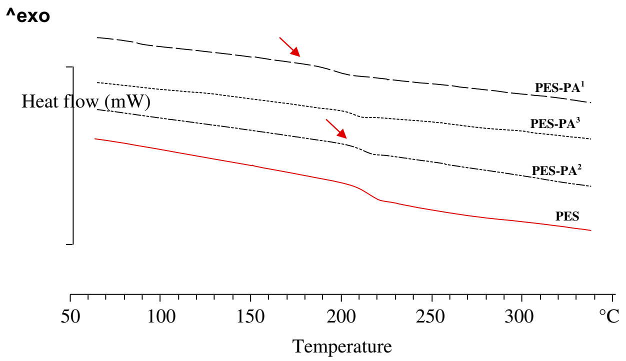


Fig. 6. DSC thermograms of PES, PES-PA^1, PA^2, and PA^3.

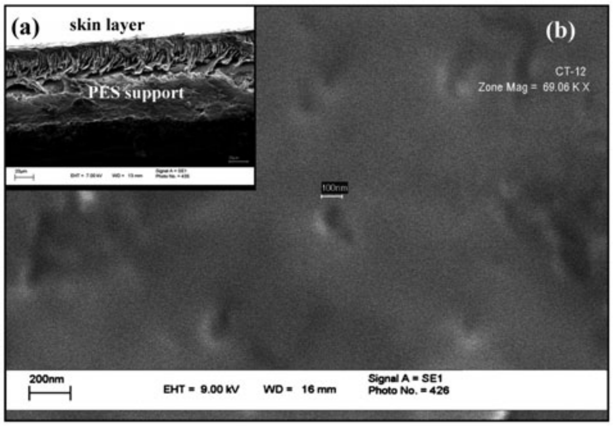


Fig. 7. SEM image of PTFC membrane: (a) cross-section view and (b) top layer.

was observed for the membranes formed by varying the concentration of diamine at a fixed TMC concentration. The T_g value of PA^2 membrane was slightly higher than other membranes under different experimental conditions. These results strongly indicate a difference in the chemical composition and structure of the polyamide films formed using different concentrations of the reactants. The difference in the T_gs may be explained by assuming the formation of low molecular weight polyamide chain at lower acid chloride concentration.

3.4. Morphology

Fig. 7 shows the SEM image of top layer and cross-sectional of PTFC membrane. The top polyamide skin surface appears like a honeycomb-like structure. The cross-sectional view of the composite membranes clearly shows the occurrence of nodular structure which starts from the dense skin layer and follows up to the support. In between the nodules, there are pore channels linked in a symmetrical fashion. With different types of polyamide skin layers, the pattern of the pore channels and the top skin layer display different morphologies, which in turn affects the performance of membranes. Many research groups have previously reported these kinds of nodular structures for several modified TFC membranes [38–40].

4. Conclusions

PTFC membranes having different polyamide skin layers were prepared by *in-situ* interfacial polymerization of AADs with trimesoyl chloride under different experimental conditions. The structure and performance of the membrane were evaluated based on the nature of reactant, concentration of reactant, and morphology. The chemical nature of the AADs and optimum concentration of the TMC played a key role in the formation of stable polyamide skin layer. PA^2 membranes prepared from MPD-based AAD exhibited better performance for divalent Na_2SO_4 salt and monovalent anionic NaCl salt, as compared to other composite membranes. The results indicated that both lower and higher concentration of reactants form more open and less compact polyamide barrier layers due to the non-equivalent monomer concentration at the reacting site. The glass transition of membranes PA^2–PA^5 with aromatic structures was in the range of 230–240˚C, indicating the higher stiffness nature of the polymer chain in the network. These PTFC membranes have shown high separation for inorganics with reasonably good flux and can be used in other separation industries like organic–organic, pervaporation, etc.

Acknowledgments

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