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A study on the relationship between preparation condition and properties/performance of polyamide TFC membrane by IR, DSC, TGA, and SEM techniques

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ABSTRACT

High-performance thin-film composite polyamide membranes for inorganic solute separation were prepared by the interfacial polymerization of trimesoyl chloride (TMC) with diethylenetriamine, 1,3-cyclohexanebis(methylamine), 2,3-diaminopyridine (DAP), m-phenylenediamine (MPD), piperazine (PIP) or a mixture of MPD and PIP/DAP, on the surface of a reinforced microporous polyethersulfone (PES) membrane support. The polyamide skin layers were isolated by dissolving the PES support in dichloromethane and the characteristics of the free skin layers were studied by infrared spectroscopy (IR), differential scanning calorimetry, thermogravimetric analysis (TGA), and scanning electron microscope (SEM) techniques. It was attempted to correlate the observed flux and rejection properties of the membranes with their preparation conditions such as reactant concentrations, reaction time, curing temperature etc. The glass transition temperatures (T_gs) of PES and polyamide blends are dependent on the concentration of the monomers (TMC/diamine) that are used for polyamide skin formation. An increasing trend in T_g values was observed with an increase in the concentration of TMC/diamine. The TGA thermograms show that the initial decomposition temperatures of the PES and polyamide blends are in the range of 330–400˚C, which is about 20–90˚C lower than that of PES (420˚C). SEM images display that the top polyamide skin surface presents a honeycomb-like structure and the cross-section image of the membranes clearly displays the presence of a nodular structure that arises from the dense polyamide skin. In between the nodules, there are pore channels that traverse up to the polyester support. The stability of a polyamide skin layer strongly depends on the preparation conditions such as concentrations of the reactants and skin layer formation conditions such as the reaction time. A higher concentration of the acid chloride (TMC > 0.5%) results in the formation of a low molecular weight *amide–acid* [HOOC-(Ar-COHN-X-NHOC-Ar)$_n$-COOH] skin layer, whereas a higher concentration of amine (Amine > 4%) produces a low molecular weight *amide–amine* [H$_2$N-(X-NHOC-Ar-COHN-X)$_n$-NH$_2$] skin layer, as observed by the IR spectra, which are unstable for performance evaluation. The performance, i.e. rejection and water flux, of the composite membranes is strongly dependent on the chemical nature of the reactants used for the formation of polyamide skin, and on the skin layer preparation conditions such as concentrations of the reactants, curing time, and curing temperature. The relationship

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between the preparation conditions of polyamide skin and performance of the membranes was measured using 2,500 ppm feed solutions of NaCl and Na_2SO_4 at an operating pressure of 10 kg/cm^2. Membranes having a wide range of performances ranging from reverse osmosis to nanofiltration to ultrafiltration can be obtained due to the synergistic effects by utilization of aromatic and aliphatic amine mixtures for the formation of polyamide skin layer.

Keywords: Thin-film composite membrane; Polyamide skin stability; Reactant concentration; Membrane performance; Thermal analysis

1. Introduction

Thin-film composite (TFC) membranes have received tremendous importance in recent times for a wide range of applications such as desalination, purification of chemical and biological products, waste water treatment, chemical sensors, gas separation, etc. [1–10]. Such membranes are usually covered by an ultra-thin selective barrier layer laminated on a chemically different asymmetric porous support membrane, which is formed by the *in situ* interfacial polymerization of polyfunctional amine and acid chloride. Interfacial polymerization takes place very quickly and many parameters, such as the reaction time, the reaction temperature, types of monomers and curing conditions, could affect the polyamide structure on the membrane surface. The chemical nature and morphological properties (pore structure and pore size distribution) of skin layer are the vital components that control the membrane performance (i.e. solute rejection and permeate flux). The unique advantage in the preparation of composite membranes is the possibility to tailor-make individually both the porous support and the skin layer for their specific function. The porous support can be optimized for maximum strength with minimum resistance for permeate flux, whereas the skin layer can be optimized for any desired combination of the solvent flux and solute separation. It is possible to produce appropriate membranes that are suitable for reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), pervaporation, and gas separation by a careful selection of the skin layer.

Several efforts are still underway to enhance the performance of a TFC membrane by altering the chemistry of the polyamide skin layer [11–14]. We have earlier reported the synthesis of poly(amide–imide)s and poly(amide–imide) composite membranes by the interfacial polymerization technique [15]. Recently, Yu et al. made an interesting attempt to improve the membrane properties of an interfacially synthesized polyamide thin-film composite RO membrane by depositing *N*-isopropylacrylamide-co-acrylic acid copolymers P(NIPAm-co-AAc). The membrane surface layer was shown to increase the fouling resistance of the TFC membrane on account of the enhanced surface hydophilicity caused by the deposition of P(NIPAm-co-AAc) [16]. An innovative approach combining both the biomimetic mineralization process and the polymer network structure manipulation was adopted by Pan et al. to fabricate a polymer-inorganic skin layer of the composite membrane [17]. Antimicrobial surface properties were reported when the surface of the TFC membrane was imparted with single-walled carbon nanotubes [18].

Most of the literature on composite membranes focus on the solute rejection and permeate flux for specific application under various test conditions such as feed concentration, feed velocity, feed temperature, applied pressure, etc., and/or mathematical modeling of their performance. Relatively less information is available on the relationship between skin layer formation conditions (i.e. reactants' concentrations, reaction time, etc.) and the properties (stability and performance) of the composite membrane. Understanding the relationship between the preparative conditions and the properties of composite membranes is a key factor for the successful development of membranes for various separation applications. The present paper describes the preparation and characterization of composite membranes containing polyamide skin layer of the reaction product of diethylenetriamine (DETA), 1,3-cyclohexanebis(methylamine) (CBMA), 2,3-diaminopyridine (DAP), piperazine (PIP), m-phenylenediamine (MPD), or a mixture of MPD and PIP/2,3-DAP with trimesoyl chloride (TMC). Effort was also bestowed to understand the relationship between polyamide skin layer formation conditions and stability of the polyamide skin layer as well as the performance of the composite membranes.

2. Experimental section

2.1. Materials

TMC, 1,3-CBMA, DETA, 2,3-DAP, m-MPD, and PIP were obtained from Aldrich. Co., USA. All the other chemicals were of analytical grade and were used without further purification.

2.2. Preparation of TFC membranes

A porous polyethersulfone (PES) membrane was used as a support material. It was prepared by the traditional-phase inversion method using 15 wt% of polymer in a dimethylformamide solution on a non-woven fabric. The polyamide skin layer was formed on the PES support by *in situ* interfacial polymerization of different diamines (CBMA, DETA, DAP, PIP, MPD) with TMC under different experimental conditions using a coating machine as shown in Fig. 1.

The solutions of amines (0.25–4%) in water, and TMC (0.01–1.0%) in hexane, were used for the formation of polyamide skin layer. The residence time of water-wet PES membrane in aqueous diamine solution was kept at 1–4 min and then the mixture was allowed to drain at room temperature for 1–5 min. It was then made to come into contact with a solution of TMC in hexane for 30–180 s, to form polyamide skin layer on the top of the PES support. The nascent polyamide composite membrane thus obtained was cured at a predetermined temperature (45–75˚C) and time (1–10 min) in a hot-air circulating woven.

2.3. Membranes' performance

The performance of the membranes was tested using 2,500 ppm aqueous NaCl and Na_2SO_4 solutions at an operating pressure of 10 kg/cm^2 using a cross-flow RO test kit. Initially, pure water was passed for about 1 h at 12 kg/cm^2 and then the salt solution was passed at 10 kg/cm^2 and the permeate flux measured after 30, 60, 90, and 120 min. The water flux was measured by flowing the permeate at the rate of liter per square meter per hour (l/m^{2}h). The salt concentration in the feed and permeate solutions was determined by measuring the electrical conductivity of the salt solution. Salt separation was then calculated using the following expression:

$$\text{Solute rejection} : R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

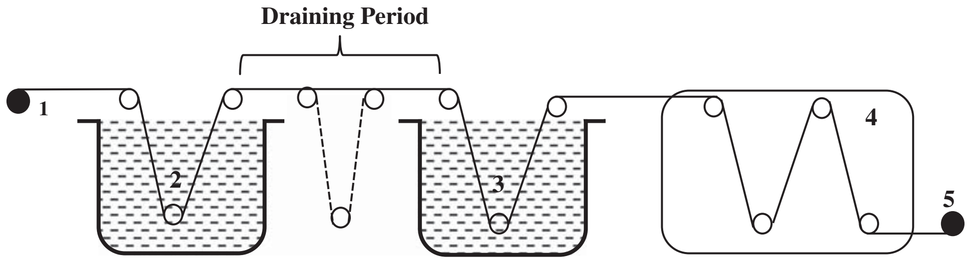
where C_f and C_p are the salt concentrations in the feed and permeate, respectively.

2.4. Techniques

The IR spectra were recorded on a Perkin Elmer fourier transform infrared spectrophotometer. A Mettler Toledo 831^e thermal analyzer was used for differential scanning calorimetry (DSC) and TGA techniques. The samples (5 mg) used for DSC were heated at the rate of 10˚C/min to 300˚C under a nitrogen atmosphere, cooled to 50˚C, and heated again to 400˚C. The TGA thermograms were recorded under nitrogen at a heating rate of 10˚C/min. The scanning electron microscope (SEM) analyses were performed with a Leo 1,400 variable pressure microscope using dried membrane samples.

3. Results and discussion

Several TFC membranes having polyamide skin layer on a reinforced PES support membrane were prepared by the procedure mentioned in Section 2.2. The performance of composite membranes is usually



1) PES support membrane 2) Amine solution 3) Acid chloride solution 4) Curing chamber

5) TFC membrane rolling

Fig. 1. Schematic diagram for the preparation of polyamide skin layer on the PES support membrane.

determined by the chemistry and the preparation conditions of the ultrathin barrier layer. The stability of the membrane is definitely affected even by a slight change in the preparation conditions of the skin layer. The nature and concentration of the reactant and the skin layer formation conditions (such as the reaction time, curing time, and curing temperature) play a crucial role in shaping the membrane's properties. For any chosen pair of reactants, a systematic optimization of the preparation conditions of polyamide skin layer is essential to obtain a membrane having stable polyamide skin layer with optimum performance characteristics. Hence, polyamide composite membranes were prepared under different conditions such as variation in amine and TMC concentrations, reaction time, curing time, curing temperature, etc., to optimize the conditions to obtain membranes having stable polyamide skin layer with optimum performances. The structures of reactants used in the preparation of polyamide skin layer are shown in Fig. 2.

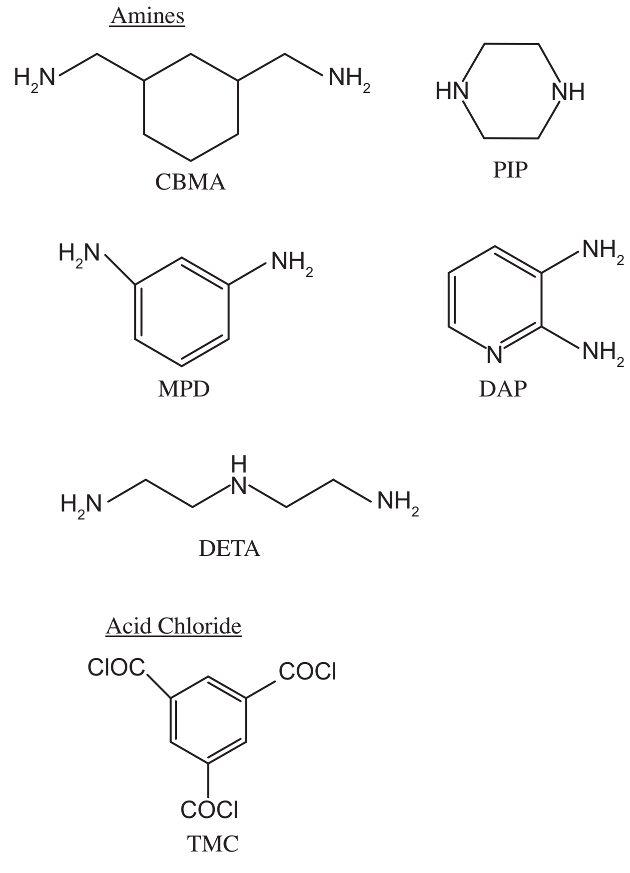
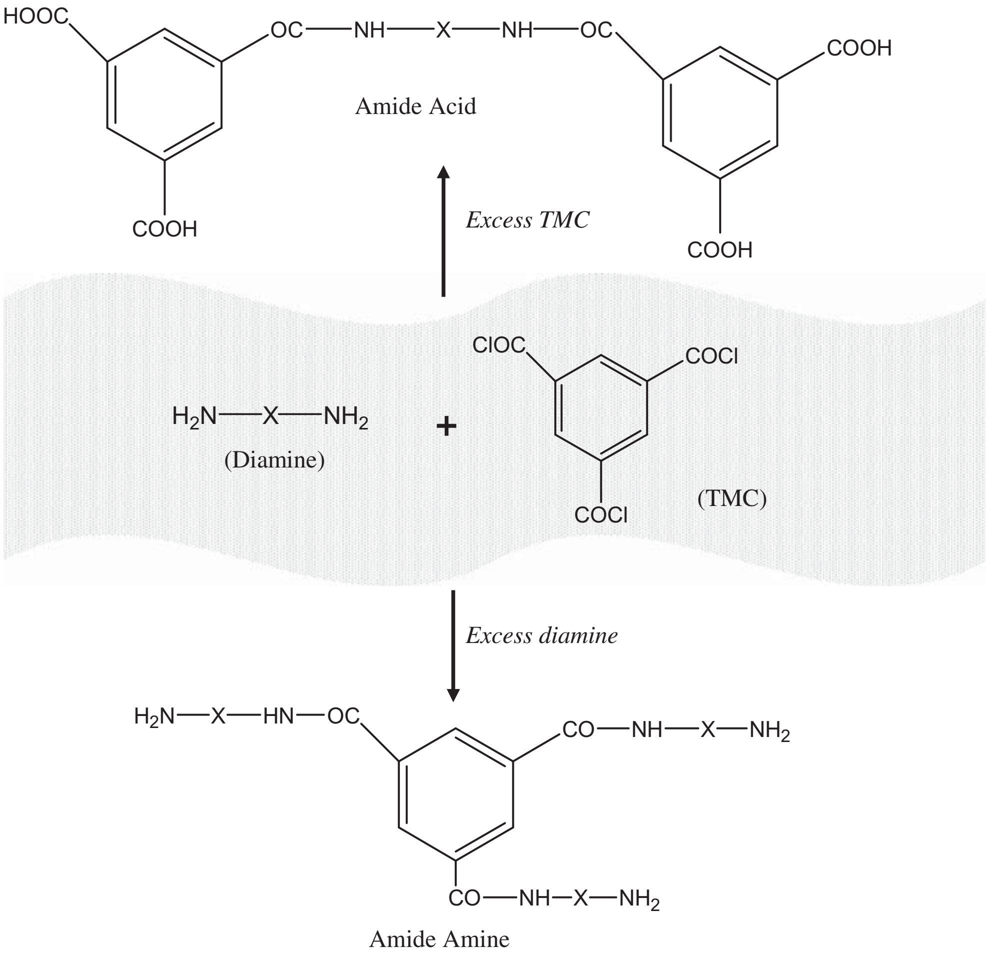


Fig. 2. Chemical structures of monomers.

3.1. Concentration of the reactants on polyamide skin stability

During interfacial polymerization of diamine with acid chloride under unstirred conditions, growth of the polymer chain takes place in the organic side of the interface, and there are optimum concentrations of reactants to obtain a polymer with good mechanical properties [19]. When the diamine was present in a higher ratio, inherent viscosity of the polymers became reduced and the resultant films were weak and poorly coherent. Similar results were observed when higher ratios of the acid chloride were used for polymer synthesis. Hence, the effect of concentration of the reactants on the stability of the polyamide skin layer has been investigated by preparing composite membranes using a wide range of concentrations of the acid chloride (0.01–1.0%) and amines (0.25–4%), without altering any other parameters such as the reaction time, curing time, and curing temperature. It was observed that the polyamide skin layers that were produced using either of higher acid chloride (TMC > 0.5%) or of higher amine (Amine > 4%) concentrations were very brittle and collapsed during the performance evaluation. However, the polyamide skin layers, which were formed using intermediate concentrations (TMC = 0.05–0.5%; Amine = 1–3%), were stable during the performance evaluation. These observations could be explained in terms of chemical changes that take place during the formation of polyamide skin layer. During polycondensation, the first diamine meets a high concentration of acid chloride and gets presumably acylated, i.e. the formation of an amide linkage at both ends. The subsequent diamine finds a layer of acid chloride-terminated oligomer plus diacid chloride, and the reaction proceeds by an irreversible coupling of the oligomers by the diamine. The concentration and size of the oligomers depend on the availability of monomers at the polymerization zone at that point of time. The reaction between amine and acid chloride is a quick process and insufficient amounts of either amine or acid chloride, or both can lead to the formation of a brittle or a defective PA layer. The skin layer, which was formed using solutions of lower acid chloride or higher amine concentrations, may not show a stable network polyamide structure but turns out to be a brittle low molecular weight *amide–amine,* owing to the presence of excess concentration of an diamine at the interface. Accordingly, a low molecular weight *amide–acid* was formed when the solutions of higher acid chloride or lower amine concentrations were



Scheme 1. Reaction products of TMC and diamine.

used, due to the presence of a higher concentration of acid chloride at the interface (Scheme 1).

The formation of amide–amine and amide–acid structures has been confirmed by the IR analysis. The skin layers were isolated by dipping the virgin composite membrane in dichloromethane to dissolve the porous PES support. It is clearly evident that the skin layer, which was formed by higher concentration of TMC (Fig. 3(a)), shows a strong peak at 1,719 cm^{-1} and a weak peak at 1,664 cm^{-1} which are attributable to the carbonyl (>C=O) stretchings of carboxylic acid and amide groups, respectively. The strong peak at 1,719 cm^{-1} arises due to hydrolysis of the carbonyl chloride group of TMC. The intensity of the peak at 1,719 cm^{-1} decreases with a decrease in the concentration of TMC in the reaction solution. The spectrum (Fig. 3(b)) of the skin layer, which was formed using a higher diamine concentration does not display a peak corresponding to the carboxylic acid group. It exhibits peaks at around 1,643 and 1,550 cm^{-1}, which correspond to the carbonyl stretchings of amide group and amine N–H bending vibrations, respectively. The spectral data clearly indicate the formation of amide–acid and amide–amine structures depending on the reactants' concentrations.

3.2. Membrane performance

3.2.1. Chemical nature of reactant

The performance of composite membranes having different polyamide skin layers is shown in Fig. 4. The membranes were tested using 2,500 ppm aqueous feed solutions of NaCl and Na_2SO_4 at an operating pressure of 10 kg/cm^2. It was seen that the membrane with a poly(MPD-TMC) skin layer exhibited very high salt separations (NaCl-95%, and Na_2SO_4-97%) with a water flux of 61 l/m^2h. On the other hand, membranes with a poly(PIP-TMC) skin layer have shown lower salt separations (16% for NaCl and 39% for Na_2SO_4) with high water permeation rates (196 l/m^2h). Poly (DAP-TMC) composite membrane displayed lower

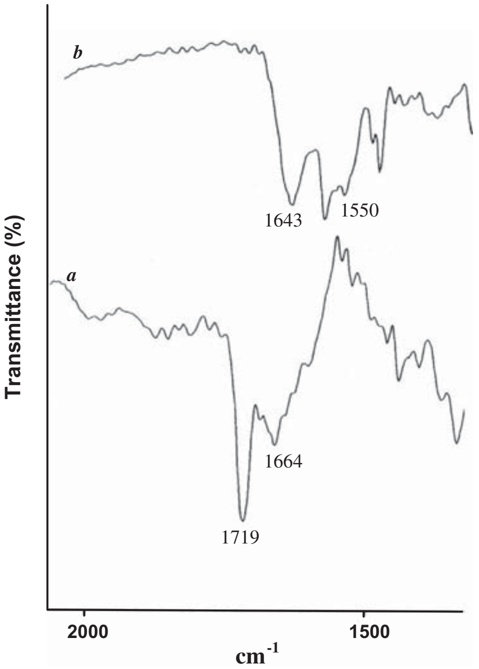


Fig. 3. IR spectra of the skin layers prepared under different conditions.

salt separations (9% for NaCl and 55% for Na_2SO_4) with water permeation rates of 134 l/m^{2}h. The salt rejections of poly(CBMA-TMC) and poly(DETA-TMC) composite membranes were in between (55/63% for NaCl and 83/88% for Na_2SO_4) those of membranes having poly(PIP-TMC) and poly(MPD-TMC) skin layer. The water flux (27/53 l/m^{2}h) of these membranes was lower than that of poly(MPD-TMC) membrane. The large variation in the performance of the composite membranes may be attributed to the aromatic/aliphatic nature and the difference in the reactivity of the diamine with the acid chloride which results in the formation of a polyamide skin layer of different morphology. MPD being a primary aromatic amine, the rate of formation of the polyamide structure may be much more rapid which minimizes other side reactions such as hydrolysis of acid chloride thus resulting in the formation of a network polyamide skin layer and hence exhibits higher salt separations. However, the utilization of aliphatic amines results in the formation of a skin layer with more open structures which results in lower salt separations. These observations have also been reported by several other authors [20,21].

Since the membrane with poly(MPD-TMC) skin layer has shown a higher salt rejection and a lower water flux, while membranes with poly(PIP-TMC) or poly(DAP-TMC) skin layer exhibited lower salt rejection and high water fluxes, composite membranes containing poly(MPD-PIP-TMC) and poly(MPD-DAP-TMC) skin layer were prepared to observe the synergistic effect of different amine structures on the membrane performance. Fig. 5 evidently indicates that salt separation increases, whereas water flux decreases, with the increase of MPD content in the MPD-DAP amine mixture for interfacial polymerization. NaCl rejection was increased from 19 to 43% and

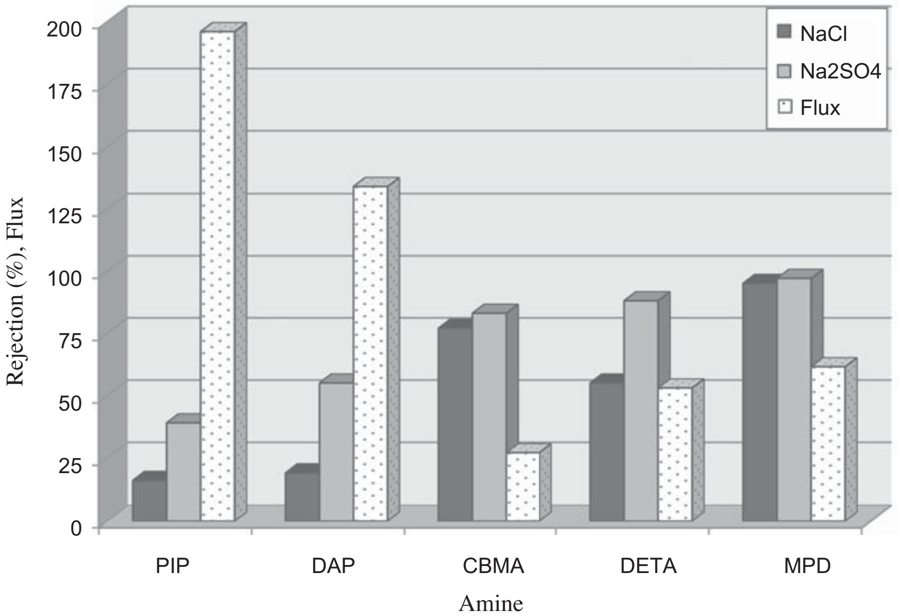


Fig. 4. Dependence of the membrane performance on the chemical nature of polyamide skin TMC concentration = 0.1%, feed concentration = 2,500 ppm, pressure = 10 kg/cm^2.

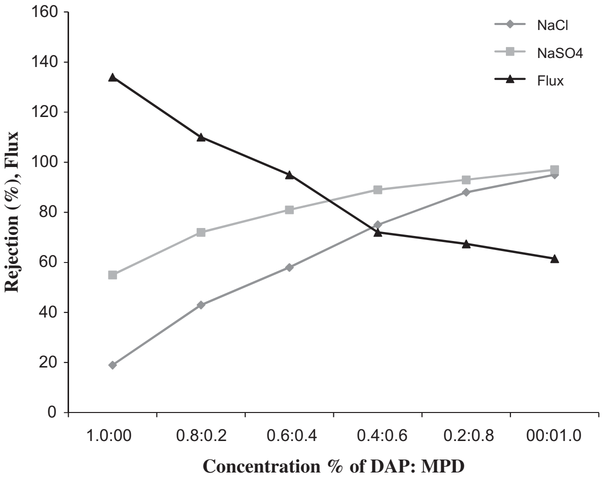


Fig. 5. Variation of the membrane performance with DAP-MPD composition in polyamide skin. TMC concentration = 0.1%, feed concentration = 2,500 ppm, pressure = 10 kg/cm^2.

water flux was decreased from 134 to 110 l/m^{2}h when the amine solution contained 0.3% MPD, instead of pure DAP. Further, NaCl rejection was raised to 88% and water flux decreased to 67.4 l/m^{2}h when the amine solution containing 0.2:0.8% of DAP:MPD was used for polyamide skin formation. A similar trend was noticed when the MPD was used along with the PIP in the preparation of composite membranes. This phenomenon may be attributed to the increasing aromatic nature of the polyamide skin layer with the increase of MPD component in the amine mixture. These results clearly indicate that membranes having a wide range of performances ranging from RO to NF to UF can be obtained by the synergistic effects due to the utilization of aromatic and aliphatic amine mixtures for the formation of polyamide skin layer.

3.2.2. Concentration of acid chloride

The effect of TMC concentration on the performance of poly(MPD-PIP-TMC) composite membrane is shown in Fig. 6. When the concentration of acid chloride was increased, the salt rejection was increased to a certain level and then almost leveled off. Initially, the solute rejection increased up to 0.1% TMC and was maintained at the same level up to 0.3% TMC concentration. However, the water flux rate decreased with the increase in TMC concentration. An almost analogous behavior was observed when the amine concentration was varied at a fixed concentration of acid chloride. Two types of reactions occur depending upon the concentration of the reactants: (a) the formation of a network polyamide structure due to the reaction between amine and acid chloride groups and (b) the formation of a carboxylic acid group due to the hydrolysis of acid chloride group. The formation of a network structure by the crosslinking reaction increases salt rejection, whereas the formation of a carboxylic acid functionality increases the water flux of the membrane. As the concentration of acid chloride increases, initially, there is a possibility for the formation of a network compact polyamide structure, which results in decreased flux and increased salt separation. Any further increase in acid chloride concentration could result in the formation of loose polyamide skin having a more hydrophilic carboxylic acid functional group which could being about an increase in water permeation rates and a decrease in salt rejection. It has been reported that there is an optimum level for acid chloride concentration to obtain composite membrane with good performance [22].

3.2.3. Curing temperature and time

The curing temperature and time of the nascent polyamide composite membrane have a profound influence on the membrane performance. Fig. 7 shows the effect of curing temperature on the rejection and water flux of the composite membranes for 2,500 ppm aqueous solutions of NaCl and Na_2SO_4. Increase of the curing temperature increases the salt separation; however, water flux decreases continuously. This condition is attributed to the fact that as the curing temperature is increased from 45 to 65°C, the nascent polyamide gel structure becomes more and more compact. Consequently, this causes pore shrinkage in the support membrane, which results in an increase in salt rejection and a decrease in water permeability [23]. The evaporation of inbound water after the solvent evaporation leads to the compactness in the polyamide structure. An almost a similar trend in the performance of the composite membranes was perceived when the curing time had been increased while keeping the other parameters unchanged. The results evidently suggest that curing of the nascent polyamide composite membrane at higher temperatures for longer time makes the membrane less selective with reduced overall permeability. Hence, a proper combination of the curing time and temperature enhances the performance of the composite membranes.

3.2.4. Membrane morphology

The cross-sectional morphology of composite membranes has been investigated by the SEM. The micrograph of polyamide skin layer shows the presence of a nodular structure which arises from the

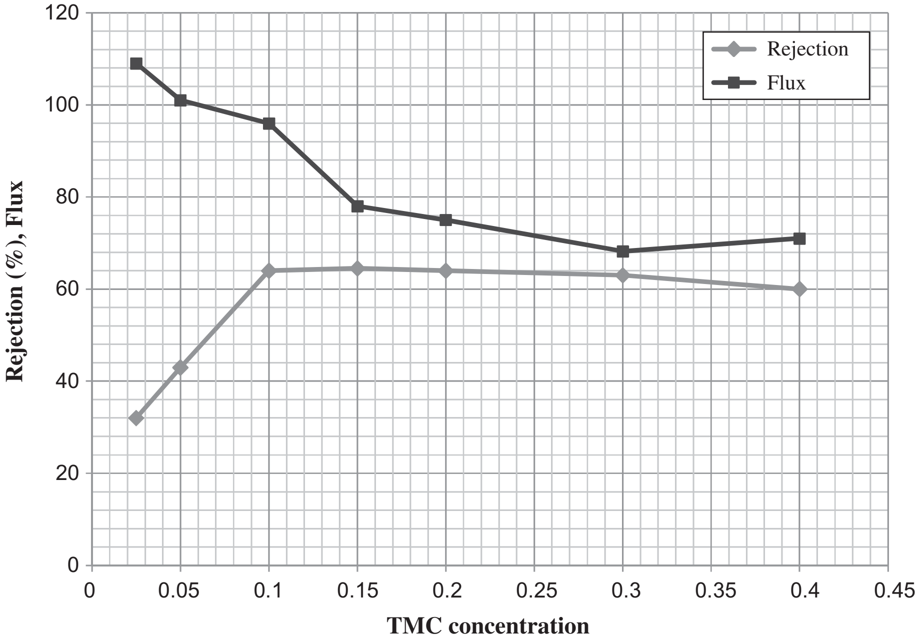


Fig. 6. Variation of membrane performance with acid chloride (TMC) concentration, amine (MPD:PIP = 0.5:0.5%), feed = NaCl (2,500 ppm), pressure = 10 kg/cm^2.

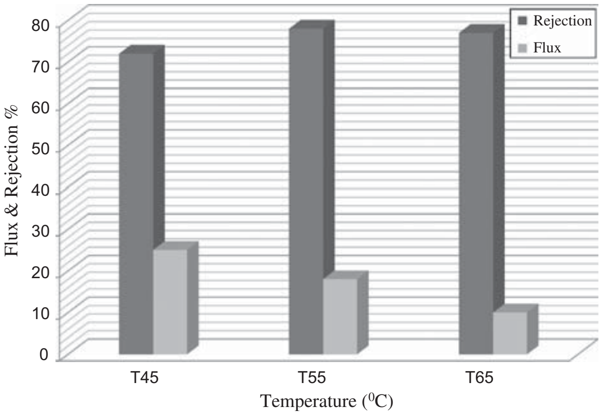


Fig. 7. Variation of membrane performance with the curing temperature of a polyamide skin. CBMA = 2%, TMC = 0.2%; feed = NaCl (2,500 ppm), pressure = 10 kg/cm^2.

dense skin and travels up to the support, as shown in Fig. 8. In between the nodules, there are pore channels and they traverse up to the support. These results are qualitatively consistent with those reported in the literature for different membranes [24,25].

3.2.5. Thin-film composition

The variation in the chemical/structural composition of the interfacial polyamide films formed using different concentrations of diamine and TMC was investigated by IR, DSC, and TGA. The PES supports along with polyamide skin layer were 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, dried, and used for characterization. The DSC and TGA data of PES and polyamide skin are reported in Table 1.

The T_g values of the polymer blends increase with the increase of TMC concentration used for the polyamide film formation. The T_g of the polymer blend has been increased to about 210°C when 0.2% TMC and 2% CBMA solutions were used for polyamide film formation. The same type of trend in glass transition was noticed for films that were formed by varying the diamine concentration at a fixed TMC concentration of 0.1% (Table 1). An important observation is that the T_g values of blends of PES and poly (MPD-TMC) are somewhat greater than those of the PES and poly(CBMA-TMC) blends. These results strongly indicate a difference in 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 a low molecular weight polyamide chain at a lower acid chloride concentration. Further evidence on the difference in the structural composition of

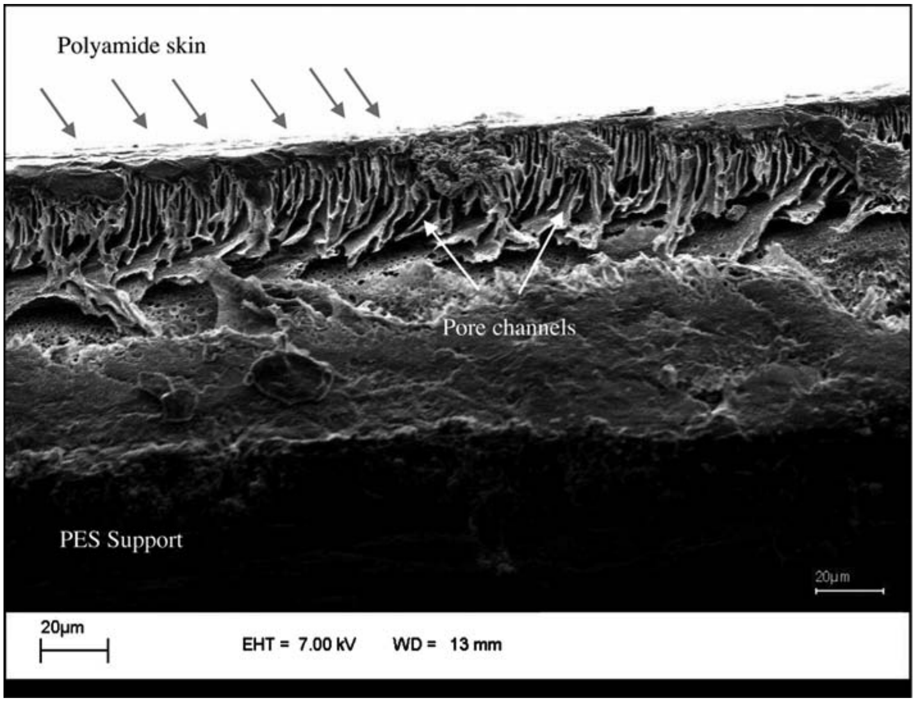


Fig. 8. SEM cross-section microphotograph of a poly(CBMA-TMC) composite membrane.

polyamide skin layers was obtained by thermogravimetric analyses. Fig. 9 shows the TGA thermograms of blends of PES and polyamide that were prepared using different concentrations of acid chloride.

The PES and polyamide blends undergo thermal decomposition in two stages with initial decomposition temperatures (IDTs) lower than for PES. The first stage corresponds to the decomposition of polyamide and the second stage to the degradation of PES. The IDTs of the blends depend on the polyamide composition and increases with an increase in the TMC concentration at a fixed concentration of the diamine. A similar trend in TGA thermograms was witnessed when the diamine concentration was varied at a fixed TMC concentration. The difference in the thermal properties of the skin layers clearly suggests a difference in their chemical compositions.

The IR spectra of PES and polyamide blends clearly support the above-mentioned observations based on the DSC and TGA. The IR spectra show that the intensities of the peak at 1,649–1,655 cm^{-1} due to C=O stretching (amide I band), and at 1,540–1,545 cm^{-1} due to N–H stretching (amide II band), increased with the increase of TMC concentration in the reaction mixture.

Table 1
The TGA and DSC data of PES and polyamide blends: effect of the TMC and amine concentration

Reactant	T_g (°C)		TGA			
	CBMA	MPD	IDT (°C)		T_{d10} (°C)	
			CBMA	MPD	CBMA	MPD
TMC[a] (%)						
0.01	195	198	330	375	410	418
0.10	204	208	365	388	432	440
0.20	210	212	380	400	448	485
Amine[b] (%)						
1.0	199	204	352	375	405	407
2.0	204	208	370	388	430	440
3.0	213	213	390	395	447	470

[a] Concentration of CBMA/MPD: 2%.
[b] Concentration of TMC: 0.1%.

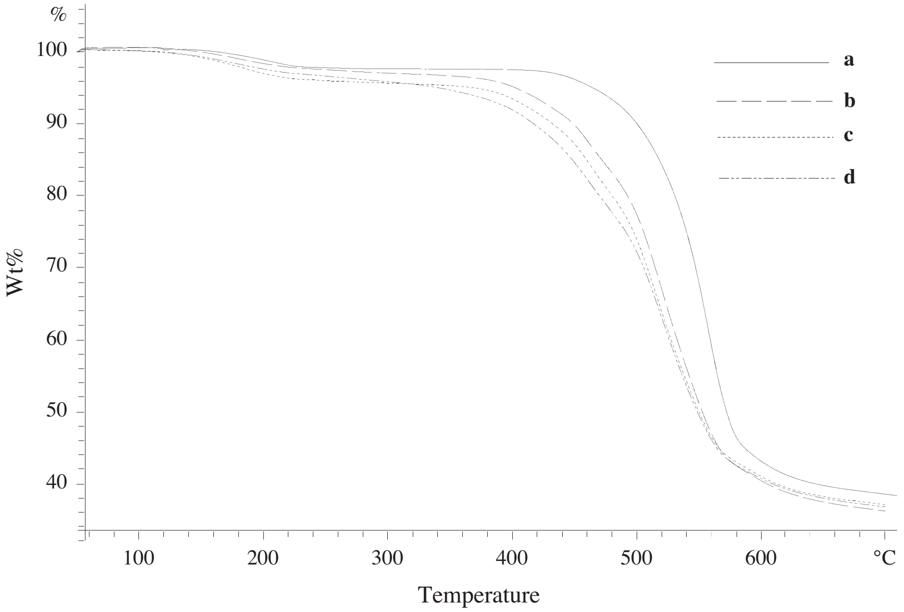


Fig. 9. TGA thermograms of: (a) PES and (b)–(d) PES + poly(CBMA-TMC) blends; CBMA = 2%, TMC = 0.01, 0.1 and 0.2% in b, c, and d, respectively.

It was also seen that the intensity of peaks at 1,649–1,655 and 1,540–1,545 cm^{-1} decreases with the increase of amine concentration at a fixed TMC concentration. This strongly suggests the formation of a higher amount of polyamide skin layer at higher TMC concentrations. In other words, the presence of a higher concentration of TMC molecules at the interface facilitates the reaction between TMC and amine, which results in the formation of compact polyamide skin. The data obtained on water flux and NaCl rejection strongly favor the above-mentioned observations.

4. Conclusions

TFC membranes having a polyamide barrier layer were prepared by the *in situ* interfacial polymerization of a diamine with TMC under various conditions. The stability and the performance of the composite membranes were related to: (a) the chemical nature and (b) the physical structure of the active skin layer. The chemical nature and concentrations of the reactants usually influence the performance of the membrane, whereas the reaction timings relating to preparative conditions affect the stability of the barrier layer and thereby the membrane performance. For a pair of reactants taken to form the polyamide skin layer, there are optimum concentrations of reactants to obtain a strong barrier layer with maximum performance. Higher concentrations of acid chloride (TMC > 0.5%) produce an oligomeric amide–acid [HOOC-(Ar-COHN-X-NHOC-Ar)$_n$-COOH] skin layer, whereas a higher amine concentration (Amine > 4 %) results in an oligomeric amide–amine [H_2N-(X-NHOC-Ar-COHN-X)$_n$-NH_2] skin layer, which becomes unstable for performance evaluation. The membrane performance was affected by various factor such as the chemical nature of a polyamide skin layer, reactant concentration, curing temperature, and curing time.

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