Enhanced both water flux and salt rejection of reverse osmosis membrane through combining isophthaloyl dichloride with biphenyl tetraacyl chloride as organic phase monomer for seawater desalination

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Abstract

The mixed organic monomers of isophthaloyl dichloride (IPC) and 3,3',5,5'-biphenyl tetraacyl chloride (BTEC) were used to prepare polyamide thin film composite (PA TFC) membranes for seawater desalination. IPC and BTEC act as a linear monomer and a cross-linking agent, respectively. As a result, the ratio of linear portion to cross-linking portion of polyamide film can be controlled by adjusting the fraction of monomer. It was found that the chemical composition, chain segment relaxation property, and the surface morphology of polyamide films changed significantly with the ratio of IPC to BTEC increasing. The rougher surface is formed while less pendant carboxylic acid groups present at higher IPC concentrations or lower BTEC concentrations. As the fraction of IPC increases, the length of linear segment between two cross linking point is increased, hence the enlarged polyamide network pore is formed. When IPC weight percentage increases from 0% to 70%, the water flux of the TFC membrane increases from 30 to 43.7 L/m²h and the salt rejection increases from 99.3 to 99.7% at 5.5MPa, 32800 ppm NaCl , 25±3°C testing condition. We demonstrated that both water flux and salt rejection of the polyamide membrane can be improved by the control of ratio of IPC to BTEC.

Keyword: Isophthaloyl dichloride; Water flux; Salt rejection; Seawater desalination

1. Introduction

Reverse osmosis (RO) process, removing salts and most of organics, has been used extensively in many fields such as for the desalination of seawater, ultrapure water production, and wastewater treatment [1, 2]. In RO process, a high operating pressure is applied in the saline water feed on one side of the membrane in order to overcome osmotic pressure and achieve desirable water flux. This takes up 65% – 85% of total energy required in typical seawater RO (SWRO) desalination [3]. Obviously RO membrane plays a highly significant role in determining the economics of the RO process. Therefore, it is desirable to develop RO membranes having superior water flux and high salt rejection.

Most commercial RO membranes are composite and have a partially cross-linked aromatic polyamide active layer prepared by interfacial polymerization of *m*-phenylenediamine(MPDA) and trimesoyl chloride(TMC)[4]. The active layer is consisted of the cross-linked portion and the linear portion containing free pendant carboxylic acid from the partial hydrolysis of acyl chloride unit of TMC during the interfacial polymerization. It is widely accepted that the chemical structure of the active layer determines its physicochemical properties such as hydrophilicity, surface charge, polymer chain mobility and in turn influences the separation performance of the membrane[5-7]. The polymerization conditions such as monomer concentration[8, 9], choice of solvents[10], temperature[11], and catalysts and additives[12] can influence the chemical structure of the active layer and further influence water flux and salt rejection [13]. The water flux can be improved by introducing hydrophilic monomers such as including sulfonic acid or carboxylic acid monomers[4, 8] or forming a ultrathin active layer and ridge-and-valley roughness surface structure which increase the contact area between water and membrane [14-16] using additives [15, 17-19]. The high salt rejection was achieved by increasing curing temperature[11] and using multiple functional monomers [20, 21] to enhance the cross linking degree. However, there is a limit to optimize the membrane property by experimenting with a

variety of interfacial polymerization conditions. For this reason, many researchers are seeking to select or design monomers or reactants for optimizing membrane separation performance. Perera et al.[22] introduced 1,3-diamino-2-hydroxypropane(DAHP), a linear hydrophilic amine, into aqueous phase and observed water flux enhanced with a little reduction of salt rejection because of a more flexible backbone and a thinner active layer compared to membrane produced with MPD. Yu et al.[23] demonstrated that blending diacyl chloride such as isophthaloyl chloride with 5-chloroformylisophthaloyl chloride (CFIC) was able to effectively improved polyamide-urethane TFC permeability while maintaining good rejection. Zhao et al.[24] added the hydrophilic additives, o-aminobenzoic acid-triethylamine(o-ABA-TEA) salt, into the aqueous m-phenylenediamine(MPDA) solution. Compared with MPDA, the cross-linked degree of PA TFC membrane reduces led to water flux increase with a slight decrease in salt rejection. But because the “trade-off” phenomenon[25] exists in the transport process, most studies improve the water flux through decreasing the rigidity and chain cross-linked degree with sacrificing salt rejection or improve the salt rejection with water flux decrease. Therefore, how to keep high salt rejection with excellent water flux is a question deserving to study further.

In the previous paper, we reported the preparation of RO membranes from biphenyl acyl chloride such as 3,3',5,5'-biphenyl tetraacyl chloride(BTEC), 2,3',4,5',6-biphenyl pentaacyl chloride(BPAC) and 2,2',4,4',6,6'-biphenyl hexaacyl chloride(BHAC), and found that the functionality of the acid chloride monomer strongly influenced the properties of the RO membrane[20, 21]. As the functionality of the acid chloride monomer increased, the resulting membrane skin layer became more negatively charged, thinner, smoother, and less permeable than the membrane prepared by TMC. The decreased water flux could be contributed to the stiffness of polyamide containing biphenyl moieties and high degree of cross-linking. In this paper, attempting is made to enhance the performance, especially the water flux of biphenyl polyamide RO membrane by blending of 3,3',5,5'-biphenyl tetraacyl chloride(BTEC) and isophthaloyl chloride(IPC). The reaction path way is illustrated

in Fig. 1. The introduction of isophthaloyl chloride is to increase the linear portion and decrease the cross-linked portion of the polyamide active layer. We show that the water flux and the salt rejection simultaneously increase with the content of IPC increasing. The effect of blending on the chemical composition, cross-linking, polymer chain segment relaxation property and the morphology of the polyamide active layer are investigated to explain the mechanism.

Fig.1. Schematic representation of the reaction process between MPDA and BTEC/IPC

2. Experimental

2.1. Materials

The BTEC was synthesized as previously described [21]. *m*-phenylenediamine (MPDA, analytical grade) and isophthaloyl dichloride (IPC) were purchased from Tianjin guangfu fine chemical research institution. The preparation of microporous polysulfone support membrane followed the previous literature procedure [20].

2.2. Preparation of TFC membrane

A rubber frame was firstly manufactured to fix the microporous polysulfone support membrane. The aqueous solution (a) including *m*-phenylenediamine (MPDA) (3.5% w/v) and camphor sulfonic acid was adjusted pH to 10.5 using triethyl amine (TEA). Then solution (a) was poured on the surface of polysulfone support membrane and immersed 2min. Redundant solution was drained from the surface and the membrane was dried in air to no obvious droplets. After that the isopaG solution (b)

(the total concentration was 0.2% w/v) of different BTEC and IPC concentration ratio was poured into the frame. After 1 minute, the excess solution (b) was poured off, and the membrane was kept at 90°C in an air dry oven for 6 minutes so that the reaction could continue to form more crosslinked structure. Finally, the TFC membrane was put into 1% Na₂CO₃ solution for 2.5mins then kept in deionized water 24h. All operations were finished at 30°C thermostatic chamber.

2.3 Preparation of polymer

The recipes were same to the preparation of TFC membrane, but interfacial polymerization was occurred in beaker. Then the polymer were washed by ethanol, methanol and deionized water three times to remove residual monomers and dried in vacuum oven at 40 °C, 24 h.

2. 4.Evaluation of membrane performance

The membrane samples used rhodamine aqueous solution to stain in order to avoid some obvious flaws before test. If there are defects, the membrane surface becomes pink. All tests for RO performance were conducted at 5.5MPa using a 32800ppm NaCl solution at 25±3°C in cross-flow cells. Testing membrane samples were positioned in the test cell with the polyamide skin layer facing the incoming feed. The valid membrane area of each cell was about 15.79cm². The membranes sustained a pure water pressure of 4.0MPa for 4 h before testing.

Water flux and salt rejection are two most important factors to RO membrane. The water flux was computed by utilizing the equation 2-1, and the ratio of desalinization was calculated by using the equation 2-2.

$$F = \frac{V}{At} \quad 2-1$$

Where V(L) is volume of permeate water, A(m²) is the effective membrane area, t(h) is the test time.

$$R_j(\%) = (1 - \frac{C_p}{C_f}) \times 100 \quad 2-2$$

Where C_p (mg/l) is the permeate concentration, C_f (mg/l) is the feed concentration. These two concentrations were measured by a conductance meter (DDS-11A, China).

The RO performance of all membrane samples was tested in at least duplicate with a total of 6 membranes, result of which has been averaged.

2.5. Characterization

The membranes were washed used deionized water and methanol three times and freeze-dried utilized freeze dryer for 10h.

The membrane surface constitutions were characterized by attenuated total reflectance infrared (ATR-IR) using a Bio-Rad Digilab Division FTS-80 spectrometer and an Irtran crystal at an incidence angle of 45°.

Surface elements distribution was measured by X-ray photoelectron spectroscopy (XPS) with a Thermo ESCALAB 280 system using Mg/K α as the radiation source.

The morphology of membrane surface was estimated using a scanning electron microscope (SEM, XL 30 ESEMFEI, FEI Company). All membranes were sprayed gold before SEM characterized.

Atomic force microscopy (AFM) images illuminate surface roughness measured by SPI 3800/SPA 300HV (Seiko Instruments Inc., Japan) with idiot mode. All samples were fixed on a 1cm² silicon slice and scanned 10 μ m $\times$ 10 μ m of the membranes by a SiN₄-cantilever with 2 N/m spring constant.

Water contact angles (CA) were evaluated by Dataphysics OCA 20(POWEEACH, China) at room temperature. Water droplets were dropped about 4 mg every time. In order to sure the accuracy, at least 6 test points were performed on different places of each membrane.

The solid-state NMR experiments were performed on BRUKER AVANCE III 400 spectrometer equipped with a 4mm MAS probe. Larmor frequencies of ¹H and ¹³C respectively are 400 and 100MHz. The 90° pulse width for ¹H is 4.5us. ¹³C CP-detected method was used to measure the ¹H spin-lattice relaxation time T_{1ρ} in rotation frame.

3. Results and discussion

3.1 Permeation properties of TFC RO membranes

In our previous study, the preparation parameters of the interfacial polymerizations of the tetra-functional biphenyl acyl chloride (BTEC) with MPDA had been optimized. In present study, TFC membranes were prepared using the same conditions. As shown in Fig.1, IPC as an acyl chloride can react with MPDA producing a linear portion and is introduced into the PA active layer. PAI-X is used to represent the sample of prepared PA TFC membranes. The X represents the weight percent of IPC in total organic phase monomers. The water flux and salt rejection of PA TFC membranes are shown in Table 1 and Fig.2. The water flux of those samples increased with IPC content. The salt rejection gradually increased, then, slightly decreased when IPC content exceeds 70%. The water flux of 43.7 L/m²h and the salt rejection of 99.7% was achieved for PAI-70 at 5.5MPa, 32800 ppm NaCl, 25±3°C testing condition. The result demonstrated that both water flux and salt rejection could be improved simultaneously by adjusting the ratio of comonomers. The effect of the active layer structure on the performance of the copolymer membranes are discussed at the following sections by analyzing their chemical constitution, chain structure and surface morphologies of polyamide film.

Fig.2. Permeation properties of PAI-X samples. All the membranes were tested at

5.5MPa and with 32800 ppm NaCl as the feed.

Table1. Permeation properties of PAI-X membranes

Sample	IPC(w/v%)	BTEC(w/v%)	Rejection(%)	Flux(L/m ² h)
PAI-0	0.00	0.20	99.3	30.2
PAI-30	0.06	0.14	99.5	35.3
PAI-50	0.10	0.10	99.5	38.6
PAI-60	0.12	0.08	99.7	40.5
PAI-70	0.14	0.06	99.7	43.7
PAI-80	0.16	0.04	99.4	48.3

3.2 Effect of IPC on membrane chemical composition

3.2.1 ATR-IR characterizes the functional groups in membrane surface.

For analyzing the membrane surface functional groups and further illustrating the reaction extent of monomers, ATR-IR spectra is utilized to do comparative evaluation of TFC membranes. The 1500-1800cm⁻¹ region of the ATR-IR spectra of the PA active layer is shown in Fig.3. The vibrational bands characteristic of amide functionalities are present at 1668 cm⁻¹ (amide I, C=O stretching vibrations of amide) and 1543cm⁻¹ (amide II, N-H in-plane bending). The band at 1602 cm⁻¹ belongs to the polyamide aromatic ring breathing. The band at 1735cm⁻¹ is assigned to the C=O stretching of carboxylic acids. There is no acyl chloride group characteristic peak at 1770 cm⁻¹ to be observed, indicating that all monomers have reacted entirely. In the figure, A_C and A_{NH} respectively represent C= O stretch of carboxylic acid and amide II band bending characteristic peaks area integration. Table 2 shows the area integration value of carboxylic acid stretch (A_C) and amide II band bending (A_{NH}). As shown in Table 2, the value of A_C and A_C/ A_{NH} decreases with the increase of IPC content. This suggests that the content of free carboxylic acid decreases with the increase of IPC concentration. The carboxylic acids in the active layer come from the hydrolysis of acyl groups. Because the IPC reacts with MPDA forming a linear structure which makes a little contribution to the carboxylic acid content, the carboxylic acid content in active layer is mainly from the unreacted -CO-Cl groups in BTEC monomer. Therefore, the value of A_C gradually decreases with the content of BTEC decrease.

Table2. TFC membrane characteristic peak area integration

Sample	Total (-CO-Cl) mmol/100ml	A _C	A _{NH}	A _C /A _{NH}
PAI-0	1.99	0.26	3.5	0.074
PAI-30	1.99	0.17	4.2	0.041
PAI-50	1.99	0.17	4.3	0.039
PAI-70	1.98	0.13	4.4	0.03
PAI-80	1.98	0.10	4.7	0.021

Fig.3. The 1500-1800 cm^{-1} region of the infrared spectra of active layer. (a-e represent PAI-0 to PAI-80, respectively.)

3.2.2 XPS characterizes the surface element constitution

The chemical composition of the polyamide active layer was analyzed by X-ray

photoelectron spectroscopy (XPS). The atomic composition (%) of the membranes measured by XPS was shown in Table 3. It can be seen from the table that the atomic ratio of N/O of PAI-X membrane increases with the increase of IPC content. Since oxygen atoms exist theoretically in the -COOH (hydrolyzed from the unreacted acyl chloride groups during IP) and the -NHCO- bond functionality whereas nitrogen atoms are present in -NHCO- bond and the -NH_2 end groups, the increased ratio of N/O implies the decreased content of the -COOH group. The result is consistent with that of ATR-IR characterization. The polymerization between the mixture of BTEC and IPC with MPDA generated three possible chemical structure of the active layer as shown in Fig. 4. The structure A represents a linear structure having two free -COOH groups on the BTEC unit, and the structure C is corresponded to a fully cross-linked structure, whereas the structure B is a partially cross-linked structure with one free -COOH group on the BTEC unit. The theoretical N/O values of three chemical structures were calculated using the equation 3-1, 3-2 and 3-3, and the results along with the experimental N/O values of active layer of PAI are listed in the Table 3. According to Table 3, the measured N/O atomic ratio of the active layer of PAI-X membranes is much closed to the theoretical N/O ratio of the structure B when the weight percent of IPC in total organic monomers is less than 50%, indicating about three -COCl groups on BTEC react with MPDA. However, the measured N/O values of the active layer of PAI-70 and PAI-80 membranes are higher than the theoretical N/O value of the structure B and lower than the theoretical N/O value of the structure C suggesting more than three -COCl groups on BTEC react with MPDA. Taking BTEC as a core of cross linking, adding IPC in organic phase will decrease the concentration of BTEC, in other words, concentration of cross linking cores decreases. The number of cross linking core is decreased, but the cross linking degree of each core increased with the increase of IPC content. The increase of the cross linking degree about each core is benefit for the improvement of membrane salt rejection. The water flux and salt rejection of PAI-70 membrane is better than that of other PAI-X membranes. This indicates that an appropriate ratio of the linear portion and the cross-linking portion is needed to improve the performance of PAI-X membranes.

$$N/O_{Atheory} = N/O_A * (1-X/100) + N/O_{PAI-100} * X/100 \quad 3-1$$

$$N/O_{Btheory} = N/O_B * (1-X/100) + N/O_{PAI-100} * X/100 \quad 3-2$$

$$N/O_{Ctheory} = N/O_C * (1-X/100) + N/O_{PAI-100} * X/100 \quad 3-3$$

Fig.4. Chemical units of aromatic polyamides

Table3. The element constitution of samples PAI-X

Sample	C	O	N	N/O	N/O _{Atheory}	N/O _{Btheory}	N/O _{Ctheory}
PAI-0	77.66	14.30	8.04	0.562	0.333	0.600	1.00
PAI-30	81.80	11.20	7.00	0.625	0.461	0.650	0.929
PAI-50	76.72	13.98	9.30	0.665	0.549	0.682	0.882
PAI-70	80.08	11.50	8.41	0.731	0.635	0.715	0.836
PAI-80	78.91	11.89	9.20	0.774	0.679	0.732	0.812
PAI-100	77.27	12.88	9.85	0.765	-	-	-

3.3 Effect of IPC on chain segment relaxation property

The ^1H spin-lattice relaxation time in rotation frame ($^1\text{H } T_{1\rho}$) is sensitive to the slow motion of the polymer chain and is served for the study of slowly cooperative motion about the polymer segments [28]. When the measured temperature is lower than the polymer segments motion temperature, the $T_{1\rho} \propto \omega_1^{-2} \tau$ [29]. τ is relaxation time of polymer segments. The measured temperature is 295K which is much lower than the PA segments motion temperature, so $T_{1\rho} \propto \omega_1^{-2} \tau$. To network polymer, relaxation time of polymer segments τ is proportional to the segment length between two cross linking points [30]. The $T_{1\rho}$ values of samples PAI-0 to PAI-80 are shown in Table.4. It can be seen the values increase with the IPC content. The increased $T_{1\rho}$ indicates the increased polymer segment length between two cross linking points. As depicted in Fig.5, the longer length of the linear segment may leads to bigger network hole [28]. The results indicate that the polymer chain flexibility and the network pore of the active layer of PAI-X membranes is increased with the increase of the content of IPC. This explains the water flux of PAI-X membranes increases with the increase of the content of IPC. On the other hand, improving the molecular weight between two cross linking points also makes for the salt rejection enhancing.

Fig.5. The possible chain structure of TFC active skins (The figure is not intended as an exact representation of the molecular structure of polyamide network, but as a visual aid to explain the larger and smaller pores adding IPC). Figure (a) represented the structure not adding IPC and Figure (b) represented the structure adding IPC.

Table 4. Relaxation property of TFC membrane samples.

Relaxation property	PAI-0	PAI-30	PAI-50	PAI-70	PAI-80
$T_{1\rho}$ (ms)	7.58	7.87	8.99	9.5	9.88
Checked position	C=O	C=O	C=O	C=O	C=O

3.4 Effect of IPC on surface morphology and contact angle

Fig.6. SEM images of PA TFC membranes (a represents PAI-0, b represents PAI-30, c represents PAI-50, d represents PAI-70, and e represents PAI-80.)

The surface morphology of PAI-X membranes are shown in Fig. 6. Most of PAI-X membranes display a characteristic ridge-and-valley surface morphology, in which the white parts represent ridges and the black areas correspond to valleys. Instead, tightly packed globules are distinctly observed for PAI-0 membrane. As a complement tool to SEM, atomic force microscopy (AFM) was also used to characterize the surface morphology of the polyamide skin layer. The root mean square roughness value of membranes is shown in Fig.7. The roughness tends to increase with the increase of the content of IPC, and this result is consistent with the surface morphology from SEM measurements. There was an obvious correlation of the water permeability with the surface roughness. The rougher and larger surface area of the membranes made it possible to contact with more water molecules in the given projected area, which attributed the higher flux. The different morphologies of these TFC membranes may be related to the diffusion rates of the diamine monomer. In the early stage, MPDA molecules diffuse to the organic side of the interface to react with acyl chloride to produce the initial polyamide film. Then for the film to grow, the growing thin polyamide film behaves as a barrier for the diffusion of the amines. For PAI-0 membrane, the highly cross-linked nascent polyamide film blocked the diffusion of the MPDA into the organic phase, hence leading to the smoother surface of the membrane. Since IPC contribute little to the cross-linking, the cross-linking degree and resistance to the diffusion of the MPDA should be decreased with the increase of the content of IPC. Therefore, the roughness of PAI-X membrane is increased with the increase of the content of IPC. On the other hand, the roughness of membrane surface arises from the overlap-add of polymer chain because the aromatic polyamide chain is rigid. Introduction of IPC promoted to the linear chain of polyamide film growing. This may explain the higher salt rejection of PAI-70 membrane due to its higher molecular weight.

Fig.7. AFM surface morphology of PAI-X samples

The surface hydrophilicity of the TFC membranes was assessed by water contact angle analysis. The lower contact angle suggests the greater tendency for water to wet the membrane surface. As shown in Fig.8, the water contact angle decreased from 75° of PAI-0 membrane to 40° of PAI-80 membrane. The surface hydrophilicity of the membrane is determined by the chemical composition and the geometrical structure of the surface. The water contact angle of PAI-X membranes displayed the same trend as the roughness of PAI-X membranes did, indicating that the geometrical structure of the surface of PAI-X membranes play a predominated role in determining the surface hydrophilicity.

Fig.8. Static contact angle of membranes

4. Conclusions

In this work, we prepared a novel class of polyamide thin composite film membranes for sea water desalination using isophthaloyl dichloride (IPC) and 3,3',5,5'-biphenyl tetraacyl chloride (BTEC) as mixed organic monomer. The result shows that both water flux and salt rejection through the PA TFC membrane can be improved by adjusting the ratio of IPC to BTEC. The water flux increased from 30 to 43.7L/m²h along with the increased salt rejection from 99.3 to 99.7%.

The active layer chemical composition and the surface morphology of polyamide film varied with the ratio of IPC to BTEC. As a result, the surface morphologies of polyamide films change significantly with introduction of IPC, from enlarged nodular structure to large ridge-and-valley structures. The water contact angles decreased from 75° of PAI-0 membrane to 40°. Introduction of IPC increased polyamide segment length between two cross linking points, which resulted in the enlarged polyamide network pore. This work provides an improved basis for understanding the relationship between the chemical structure and properties of the resulting PA films, which may help the design and synthesis of novel TFC RO membranes with better performances.

Acknowledgements

The authors gratefully acknowledge the National Basic Research Program of China (no. 2015CB655302) and the National Science Foundation of China (no. 51133008, 51473163 and 51323062).

Abbreviations

A	effective membrane area (m^2)
Ac	C=O stretch of carboxylic acid characteristic peaks area integration
A_{NH}	amide II band bending characteristic peaks area integration
AFM	atomic force microscopy
ATR-IR	attenuated total reflectance infrared
BTEC	3,3',5,5'-biphenyl tetraacyl chloride
C_p	concentration of the permeation (mg mL^{-1})
C_f	concentration of the feed (mg mL^{-1})
CA	contact angle
F	water flux ($\text{L /m}^2 \text{ h}$)
IPC	isophthaloyl dichloride
L	liter
MPDA	<i>m</i> -phenyleneamine
PA	polyamide
$R_{(j)}$	salt rejection (%)
RO	reverse osmosis
SWRO	seawater RO
SEM	scanning electron microscope
T	time(h)

$T_{1\rho}$	spin-lattice relaxation time in rotation frame
TEA	triethyl amine
TMC	trimesoyl chloride
TFC	thin film composite
V	volume of permeate water (L)
XPS	X-ray photoelectron spectroscopy

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Graphical Abstract