Synthesis of polyamide-based RO membranes for saline water treatment

Nguyen Thi Anh Huy[1, 2], Duong Minh Triet[2], Tran Thanh Viet[2],
Tran Van Cuong[2], Pham Quoc Nghiep[2], Le Anh Kien[2*]

[1]Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), VNU-HCM, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Vietnam;
[2]Institute for Tropical Technology and Environmental Protection, Academy of Military Science and Technology, 57A Truong Quoc Dung, Phu Nhuan, Ho Chi Minh City, Vietnam.
[*]Corresponding author: anhkien.le@gmail.com
Received 9 Sep. 2024; Revised 8 Nov. 2024; Accepted 15 Nov. 2024; Published 6 Dec. 2024.
DOI: https://doi.org/10.54939/1859-1043.j.mst.FEE.2024.226-230

ABSTRACT

Reverse osmosis (RO) technology is a widely used method for converting seawater into fresh water, known for its high efficiency and broad applications. This study focuses on optimizing the synthesis conditions for polyamide (PA) membranes, including the concentrations of m-phenylenediamine (MPD) and trimesoyl chloride (TMC), the choice of solvent, soaking time, and reaction time. FTIR and SEM analysis confirmed the successful synthesis of the PA layer and revealed that the surface morphology of the membrane was significantly influenced by synthesis conditions. Mechanical testing demonstrated that the optimized membranes exhibited high tensile strength (41.18 MPa) and low elongation at break (11.69%), indicating a robust but relatively brittle material. The study determined that the optimal conditions were 1.0 wt.% MPD and 0.1 wt.% TMC, hexane as a solvent, a soaking time of 2 min, and a reaction time of 60 sec, achieving a maximum salt rejection of 86.45%. These findings are critical for enhancing RO membrane efficiency and addressing the global demand for clean water.

Keywords: Reverse osmosis; Polyamide membranes; Synthesis conditions; Surface morphology; Salt rejection.

1. INTRODUCTION

The global water scarcity crisis, exacerbated by population growth, industrialization, urbanization, and climate change, has intensified the demand for freshwater and advanced purification technologies. Current methods include filtration, sedimentation, distillation, and membrane-based separation processes like reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) [1]. Among these, RO is a leading solution for purifying water by passing it through a semipermeable membrane to remove salts, particles, and bacteria [1]. However, PA-TFC RO membranes face challenges such as fouling and a trade-off between permeability and salt rejection [2]. Optimizing membrane chemistry and structure is crucial to improve performance, including water flux, salt selectivity, and resistance to fouling. Most RO membranes are thin-film composite (TFC) structures, with layers of polyester support, polysulfone (PSF) intermediate, and a PA top layer [2]. The PA layer is formed through interfacial polymerization (IP) of MPD and TMC in a water–hexane system [3]. The membrane performance depends on factors like reaction time, temperature, curing conditions, and monomer concentration [4]. Despite the widespread use of polyamide chemistry, there is still room for improvement in water permeance and salt rejection for RO membranes [5]. Improving these characteristics is not just a technical challenge but a vital part of ensuring access to clean water for people around the world, especially in areas where water scarcity is a daily struggle.

This article focuses on the synthesis of aromatic PA polymer via interfacial polycondensation of MPD and TMC, examining factors influencing polymerization, such as precursor concentration, solute-solvent system and several conditions in synthesizing. The successful synthesis was confirmed using SEM, FTIR, and mechanical properties analysis, and the RO performance of the membranes was evaluated by measuring salt rejection.

2. EXPERIMENTAL

2.1. Materials

PSF polymer was generously provided by RisingSun Membrane Technology (Beijing, China). TMC (purity 98%) and MPD (purity 99%) monomers were obtained from Sigma-Aldrich. Sodium chloride (NaCl, purity 99.5%), n-Hexane (C_6H_{14}, purity >97%), and n-Heptane (C_7H_{16}, ≥99%) were purchased from Xilong Scientific Co., Ltd., Guangdong, China. Deionized water was used in all experiments.

2.2. Synthesis process of RO membrane

A 1 wt% MPD solution was prepared by dissolving MPD in deionized water and sonicating for 15 min, while a 0.1 wt% TMC solution was prepared similarly in hexane. A PSF support membrane (0.15-0.16 mm thick) was soaked in the MPD solution for 2 min, excess removed with a rubber roller, air-dried for 2 min, and coated with TMC for 1 min to form a polyamide film. The resulting TFC membrane was washed with hexane, dried at 80 °C for 5 min, and stored at 4 °C.

2.3. Characterization

The structural morphology of materials was analyzed using SEM (TESCAN MIRA LMU). FTIR (Alpha II, Bruker, Germany) identified functional groups in the sample. Tensile strength, measured per ASTM D882-18 using a Zwick/Roell Z010, was tested on three standard-shaped samples under ambient conditions, with average values reported. Salt rejection of the TFC membranes was evaluated with a 2000 ppm NaCl solution at 8 bar and a flow rate of 2.5 L/min at room temperature. The salt concentration in the permeate was measured using a GroLine Monitor (HANNA HI981420-02), and salt rejection was calculated using the formula:

$$Salt\ Rejection\% = \frac{Feed\ Water\ Salt\ content - Permeate\ Salt\ content}{Feed\ Water\ Salt\ content} \times 100 \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1. Chemical structure and mechanical properties of RO membrane

The interaction between MPD and TMC was confirmed using FTIR analysis. Figure 1a displays the infrared spectra of the support layer and the PA membrane.

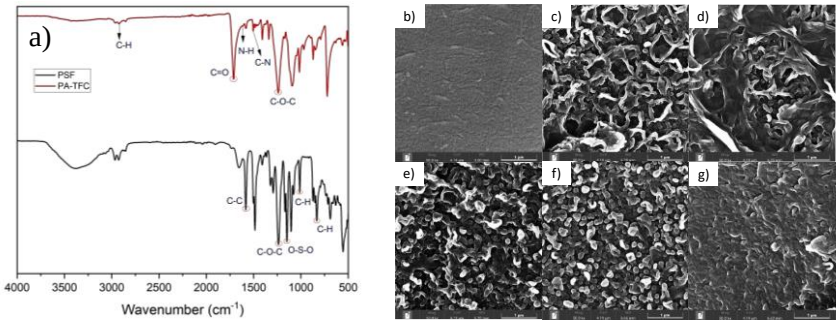

Figure 1. *FTIR spectra of the support layer and polyamide membrane (a), along with SEM images of the PSF layer (b) and RO membrane at various MPD concentrations: 1-5% (c-g).*

The support layer shows characteristic peaks of PSF: a C-O-C bond at 1237 cm^{-1}, a C-C bond at 1583 cm^{-1}, and C-H bonds at 1013 cm^{-1} and 831 cm^{-1} [6]. In the polyamide spectra, key features include the amide-I and amide-II bands, with a carbonyl peak at 1710 cm^{-1} and amide II bands at 1630 cm^{-1} and 1504 cm^{-1}, corresponding to N-H bending and C-N stretching. The leftward shift of PSF peaks indicates the formation and expansion of C-O-C, C-C, and C-H bonds in the PA membrane due to the interaction between the two layers [6]. The ultimate strength of the membranes reached 41.18 MPa, which is notably higher than the typical values reported for some

membranes such as flat sheet poly(vinylidene fluoride) (PVDF)/nanoclay membranes [7], PSF and PA-TFC membranes [8], or RO membrane [9], which are generally under 40 MPa. High tensile strength typically indicates a material that is strong and resistant to breaking. However, this doesn't always mean the material is ductile. The material in this study has high tensile strength but low elongation at break (11.69%), it is considered brittle.

3.2. Impact of monomer concentrations and solvents on morphology and salt rejection

SEM images (figure 1b-g) demonstrate that lower MPD concentrations (1 - 2%) produce smoother, less developed PA layers with fewer modular structures and reduced roughness. In contrast, higher concentrations (3 - 5%) lead to well-developed, wavy PA layers with dense, cross-linked networks, providing a better balance of porosity and thickness.

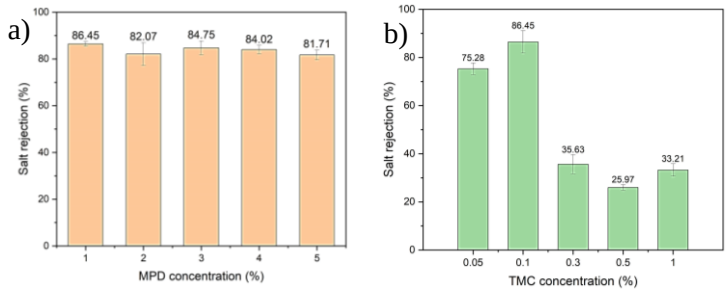

Figure 2. *Salt rejection of RO membrane at different MPD (a) and TMC (b) concentrations.*

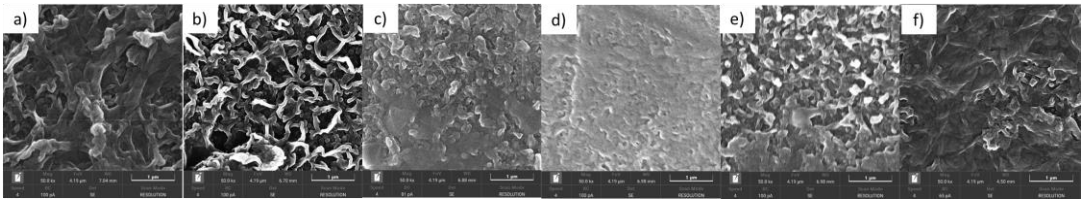

Figure 3. *SEM images of RO membranes at different TMC concentrations: 0.05% (a), 0.1% (b), 0.3% (c), 0.5% (d), 1% (e) and synthesized in heptane solvent (f).*

Figure 2a shows that as MPD concentration increased from 1.0 wt% to 5.0 wt%, salt rejection initially decreased before slightly rising. The highest salt rejection of 86.45% occurred at 1.0 wt% MPD. Although higher MPD concentrations generally improve cross-linking and selectivity, further increases result in a denser polyamide layer with reduced permeance. At 5.0 wt%, membrane defects may occur due to insufficient acyl chloride monomer, reducing filtration efficiency [10]. The TMC concentration during surface polymerization significantly influences RO membrane morphology and performance (figure 3a-e). Low TMC levels (0.05 wt%) result in a smooth, undeveloped PA layer with minimal cross-linking. Optimal TMC concentration (1 wt%) forms a dense, uniform PA layer with a corrugated structure, while excessive TMC causes a rough, nodular surface and an overly thick PA layer, reducing water permeability but enhancing initial salt rejection. As shown in figure 2b, 0.05 wt%, desalination efficiency was low (75.28%) due to insufficient cross-linking. Salt rejection peaked at 86.45% with 0.1 wt% TMC but dropped to 35.63% at 0.3 wt% due to residual acyl chloride groups, which reduced cross-linking and perm-selectivity [11]. Membranes fabricated with hexane exhibit a uniform, smooth polyamide layer with fine, evenly distributed pores due to rapid evaporation and a lower boiling point, enhancing salt rejection and minimizing residue (figure 3f**)**. In contrast, heptane membranes have a rougher, less uniform surface from slower evaporation and a higher boiling point, which can increase water flow but reduce salt rejection and raise fouling rates. Hexane achieves 86.45% desalination efficiency, outperforming heptane at 68.41% due to the smaller molecular size of hexane that enhance penetration, whereas the bulkiness of heptane can lead to swelling and larger pores.

3.3. Impact of and synthesis conditions on morphology and salt rejection

Soaking in 1 min shows the surface is heterogeneous with weak, thin bonds and small pores (figure 4**)**. At 2 min, the surface becomes more uniform with distinct nano- and microstructures, indicating improved stability. Beyond 3 min, the surface smooths, and the polymer layer becomes denser, reducing filtering ability and performance. Desalination performance (figure 5a) peaked at 86.45% efficiency with a 2-minute soak, attributed to optimal MPD absorption, improved wettability, and fewer defects in the PA selective layer. Soaking for 1, 3, 4, and 5 min showed fluctuations and reduced stability, highlighting 2 min as the ideal soaking time. At 30 sec of reaction, the membrane surface is smooth with minimal roughness, limiting filtration efficiency (figure 4). By 60 sec, nodules and wavy structures form, indicating improved cross-linking. At 90 and 120 sec, increased surface complexity optimizes filtration and desalination. However, at 180 sec, excessive growth produces a thick polyamide layer, reducing water permeability. A 60-second reaction time yields the highest salt rejection (86.45%, figure 5b). While salt rejection slightly improves beyond 30 sec due to a thicker dense layer, it remains stable at longer times, likely due to the rapid MPD-TMC reaction limiting additional MPD transfer [12].

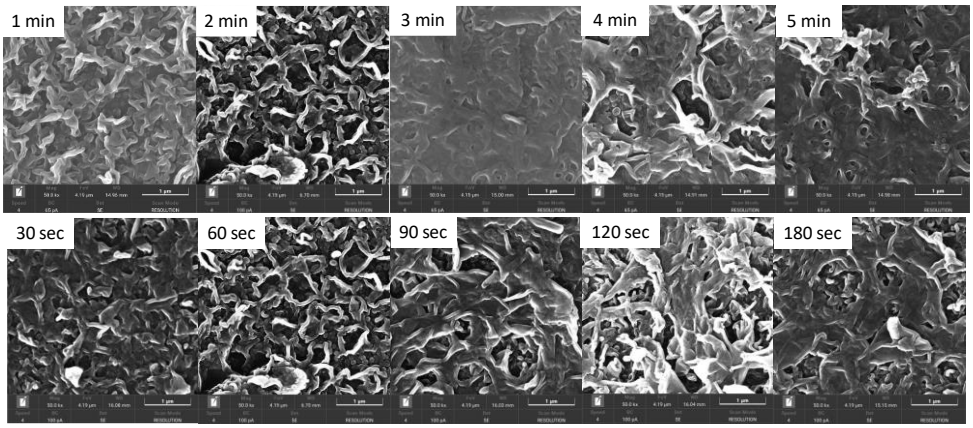

Figure 4. *SEM images of the RO membrane at various soaking times and reaction times.*

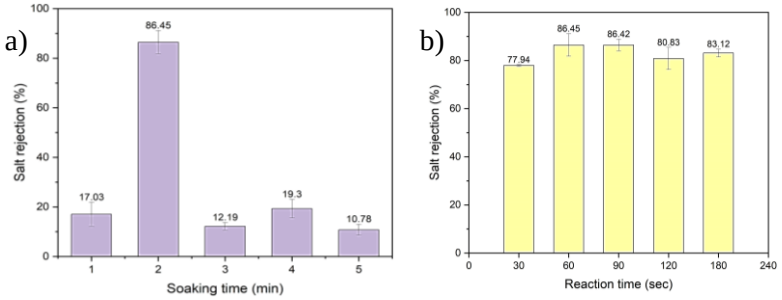

Figure 5. *Salt rejection of RO membrane at different soaking times (a) and reaction times (b).*

4. CONCLUSIONS

In conclusion, this study explored the impact of synthesis parameters on the structure, mechanical properties, and desalination performance of polyamide (PA) reverse osmosis membranes. FTIR confirmed successful polymerization between MPD and TMC, producing robust membranes with structural integrity. The membranes achieved a tensile strength of 41.18 MPa, exceeding many previous designs, though their 11.69% elongation at break indicated brittleness. The study showed that MPD and TMC concentrations significantly affect membrane morphology, structure, and desalination efficiency. Optimal conditions - 1.0 wt% MPD, 0.1 wt% TMC, hexane as the solvent, 2-minute soaking, and 60-second reaction - yielded membranes with

86.45% salt rejection. These optimized membranes demonstrated enhanced mechanical strength and reliable performance, making them suitable for demanding desalination applications. These findings highlight the potential of tailored synthesis to improve PA RO membranes for water treatment and desalination, offering durability and efficiency for broader use.

Acknowledgement: *We acknowledge the support of time and facilities from the Institute for Tropical Technology and Environmental Protection for this study.*

REFERENCES

[1]. S. K. Patel et al., *"The relative insignificance of advanced materials in enhancing the energy efficiency of desalination technologies,"* Energy & Environmental Science, vol. 13, no. 6, pp. 1694-1710, (2020).
[2]. W. Xie *et. al., "Polyamide interfacial composite membranes prepared from m-phenylene diamine, trimesoyl chloride and a new disulfonated diamine,"* J. of Membrane Science, vol. 403, pp. 152-161, (2012).
[3]. R. J. Petersen, *"Composite reverse osmosis and nanofiltration membranes,"* Journal of membrane science, vol. 83, no. 1, pp. 81-150, (1993).
[4]. M. Namvar-Mahboub and M. Pakizeh, *"Optimization of preparation conditions of polyamide thin film composite membrane for organic solvent nanofiltration,"* Korean Journal of Chemical Engineering, vol. 31, pp. 327-337, (2014).
[5]. K. P. Lee, T. C. Arnot, and D. Mattia, *"A review of reverse osmosis membrane materials for desalination—Development to date and future potential,"* Journal of Membrane Science, vol. 370, no. 1-2, pp. 1-22, (2011).
[6]. H. Guo, X. Tang, G. Ganschow, and G. V. Korshin, *"Differential ATR FTIR spectroscopy of membrane fouling: Contributions of the substrate/fouling films and correlations with transmembrane pressure,"* Water Research, vol. 161, pp. 27-34, (2019).
[7]. C. Y. Lai *et al., "Investigation of the dispersion of nanoclays into PVDF for enhancement of physical membrane properties,"* Desalination and Water Treatment, vol. 34, no. 1-3, pp. 251-256, (2011).
[8]. F. G. Alabtah, A. Alkhouzaam, and M. Khraisheh, *"New insights into the mechanical behavior of thin-film composite polymeric membranes,"* Polymers, vol. 14, no. 21, p. 4657, (2022).
[9]. M. Ashraf *et al., "Synthetic polymer composite membrane for the desalination of saline water,"* Desalination and Water Treatment, vol. 51, no. 16-18, pp. 3650-3661, (2013).
[10]. H. Zhu, B. Yuan, and Y. Li, *"Preparation and Desalination of Semi-Aromatic Polyamide Reverse Osmosis Membranes (ROMs),"* Polymers, vol. 15, no. 7, p. 1683, (2023).
[11]. W. Choi et al., *"Thin film composite reverse osmosis membranes prepared via layered interfacial polymerization,"* Journal of Membrane Science, vol. 527, pp. 121-128, (2017).
[12]. H. Meng, B. Gong, T. Geng, and C. Li, *"Thinning of reverse osmosis membranes by ionic liquids,"* Applied surface science, vol. 292, pp. 638-644, (2014).

TÓM TẮT

Tổng hợp màng thẩm thấu ngược gốc polyamide để xử lý nước mặn

Công nghệ thẩm thấu ngược (RO) là một phương pháp được sử dụng rộng rãi để chuyển đổi nước biển thành nước ngọt, nổi bật với hiệu suất cao và nhiều ứng dụng khác nhau. Nghiên cứu này tập trung vào việc tối ưu hóa các điều kiện tổng hợp màng polyamide (PA), bao gồm nồng độ của m-phenylenediamine (MPD) và trimesoyl chloride (TMC), lựa chọn dung môi, thời gian ngâm và thời gian phản ứng. Phân tích FTIR và SEM đã xác nhận thành công trong việc tổng hợp lớp PA và cho thấy hình thái bề mặt của màng bị ảnh hưởng đáng kể bởi các điều kiện tổng hợp. Các thử nghiệm cơ học cho thấy màng được tối ưu hóa đạt được độ bền kéo cao (41,18 MPa) và độ giãn dài khi đứt thấp (11,69%), cho thấy một vật liệu vừa chắc chắn vừa có độ giòn nhất định. Nghiên cứu xác định các điều kiện tối ưu bao gồm nồng độ phần trăm khối lượng của MPD là 1% và TMC là 0,1%, sử dụng hexane làm dung môi, thời gian ngâm là 2 phút và thời gian phản ứng là 60 giây, đạt được khả năng loại bỏ muối tối đa là 86,45%. Những phát hiện này rất quan trọng trong việc nâng cao hiệu quả của màng RO và đáp ứng nhu cầu toàn cầu về nước sạch.

Từ khoá: Thẩm thấu ngược; Màng polyamide; Điều kiện tổng hợp; Hình thái bề mặt; Loại bỏ muối.