Effect of extrusion temperature on PP hollow fiber membrane properties and its CO2 degassing performance

Su-Ying Yan1, Yu-Jie Wang1,2, Wen-Zhi Wang1, and Zhi-Ping Zhao1*

1 School of Chemistry and Chemical Engineering, Beijing Institute of technology, Beijing 102488, China
2 Environmental Protection Research Institute, Beijing Research Institute of Chemical Industry, SINOPEC, Beijing 100013, China
*Corresponding author’s e-mail: zhaozp@bit.edu.cn

Abstract. It is challenging to remove low concentration CO2 from water. Membrane degassing has potential advantages in degassing from water. In this paper, PP hollow fiber membrane (HFM) was prepared via TIPS method using carnauba wax (Cwax) and soybean oil (SO) as binary green diluents. The effects of extrusion temperature on the membrane properties were studied. The results showed that when the extrusion temperature increased from 155 °C to 170 °C, the membrane pore size first increased and then decreased, and the maximum value was obtained at 165 °C. The extrusion temperature had little effect on morphology and liquid entry pressure (LEP) of the membrane. Considering the pore size and LEP synthetically, the optimized PP HFM was prepared at the extrusion temperature of 170 °C, and fabricated into the membrane module. The CO2 degassing performance from the water in RO system was studied. The results showed that the degassing efficiency (η) decreased as the water flow rate increased, which was mainly due to the decreasing water residence time in the membrane module. When the effective membrane length increased to 4.41 m, the η was almost stable at 80%.

1. Introduction
CO2 removal from water is an essential water purification process in many fields such as petrochemical production, thermal power generation and electronic device production[1]. It is challenging to remove low concentration CO2 from RO effluent water. Compared with traditional degassing technology, membrane degassing has potential advantages, including large specific surface area, flexible control of the flow rate, small size, and ease to modular[2]. High performance hydrophobic membrane is the core component of the membrane degassing technology, and the polypropylene (PP) membrane has wide application potential.

PP hydrophobic microporous membrane can be prepared by thermally induced phase separation (TIPS) method. Compared with single diluent, the binary diluents can modulate the interaction between the polymer and the diluents more effectively, and then affect the final membrane properties[3]. With the increasingly strict environmental requirements, the environment-friendly binary diluents for PP membrane preparation have become the focus topic in TIPS research.

In our previous research[4], PP hydrophobic porous flat-sheet membrane was successfully prepared via TIPS method with environment-friendly binary diluents, which was composed of carnauba wax (Cwax) as a poor solvent and soybean oil (SO) as a good solvent. By investigating the effects of PP content and Cwax/SO mass ratio on phase diagram and membrane properties, the optimized
membrane performance was achieved when the composition of casting solution was PP (30 wt%) and Cwax/SO (70 wt%), and the mass ratio of Cwax and SO was 35/65.

Based on that, the PP hollow fiber membrane (HFM) was prepared through TIPS spinning process. The extrusion temperature can affect the structure and performance of the final membrane. In the TIPS spinning process, the extrusion temperature is generally about 30 °C higher than the polymer crystallization temperature ($T_c$), and the casting solution needs to have a certain viscosity for spinning. For the PP in this research, the $T_c$ was 127 °C, so the studied extrusion temperature ranged from 155 °C to 170 °C. The morphology, pore size and liquid permeation pressure (LEP) of PP HFMs prepared at different extrusion temperatures were characterized to optimize the extrusion temperature. Finally, the optimized PP HFM was fabricated into membrane module and used for CO$_2$ degassing from the water in RO system. The effects of the water flow rate and effective membrane length on the CO$_2$ degassing performance were studied.

2. Experimental section

2.1. Materials
The PP was provided by Sinopec Maoming Branch, China. Cwax was supplied by Alfa Aesar, China. SO and castor oil (CO) were purchased from COFCO Group, China. Ethanol of analytical grade was purchased from China Sinopharm Chemical Reagent, China.

2.2. Preparation of PP HFM
At first, the PP and the binary diluents were added to the stirred tank, heated to 180 °C under 0.2 MPa pressure and nitrogen phenomenon. After stirred for about 2 h, the casting solution was defoamed for 1.5 h. At the same time, SO and CO with mass ratio of 90/10 were added to the bore liquid tank and heated to 142 °C. After the casting solution passed through the filter, it was sent to the spinneret by a diaphragm metering pump. The spinneret is double-tube type, and the bore liquid was introduced into the inner tube of the spinneret to make a lumen of the fiber. At the same time, the spinneret’s extrusion temperature changed from 155 °C to 170 °C. The casting solution passed through the air gap of a certain distance, and entered the normal temperature water coagulation bath. Finally, the PP HFMs with different extrusion temperatures were taken out by a godet wheel, wound up by a winder, extracted by hot ethanol for 8 h to remove the binary diluents, and lastly air-dried.

2.3. Characterization of PP HFM
The morphology of PP HFM was observed by a scanning electron microscope (SEM, Hitachi S-4800, Japan) working at 1.0 kV.

Table 1. Specifications of the PP HFM module

| Properties          | Length of module / cm | Effective length / cm | Module I.D/O.D / cm | Fiber I.D/O.D / μm | Internal surface area / m$^2$ |
|---------------------|-----------------------|-----------------------|---------------------|-------------------|-----------------------------|
| Values              | 70                    | 63                    | 4.3/5.0             | 921.4/1272.2      | 0.0156                      |
The water flowed through the tube side of the membrane module, and the vacuum was applied in the shell side. The water was collected from RO system effluent in Luoyang Petrochemical Engineering Corporation, and its CO$_2$ concentration was about 16.41 mg·L$^{-1}$. The water temperature was controlled by the thermostatic water bath and the water flow rate was regulated by the peristaltic pump. The experimental setup is shown in figure 1.

![Experimental setup of CO$_2$ degassing using PP HFM module.](image)

1, thermostatic water bath; 2, inlet water tank; 3, peristaltic pump; 4, PP HFM module; 5, outlet water tank; 6, buffer tank; 7, circulating water vacuum pump

The CO$_2$ concentrations of water were measured by the chemical titration method[5]. The CO$_2$ degassing efficiency ($\eta$) was calculated by the equation (1):

$$\eta(\%) = 100\% \times \left(1 - \frac{C_{o,l}}{C_{i,l}}\right)$$

where $C_{o,l}$ and $C_{i,l}$ are the CO$_2$ concentrations (mg·L$^{-1}$) in outlet and inlet water of the PP HFM module, respectively.

3. Results and discussion

3.1. Effects of extrusion temperature on membrane properties

3.1.1. Morphology. The SEM images of PP HFM prepared at 170 $^\circ$C are shown in figure 2.

![SEM images of PP HFM prepared at extrusion temperature of 170 $^\circ$C.](image)

(a) Cross-section, (b) Outer surface and (c) Inner surface. The insert is the corresponding enlarged view.

All the PP HFMs prepared at different extrusion temperatures showed similar morphologies. The extrusion temperature showed little effect on the membrane morphology. As seen in figure 2, the PP HFM showed sponge-like cross-section structure, indicating the occurrence of liquid-liquid phase separation[6]. And the discernible spherulites could be observed in the cross-section area near inner surface, which was mainly due to the relatively slow cooling rate in the lumen[7].

Figure 2 also showed the loose porous morphology on the inner surface, while the outer surface was much denser. The diluents-like solvent in bore liquid had good compatibility with the casting solution, and could exchange with the casting solution on the inner surface, resulting in the porous structure[8].
3.1.2. Pore size and its distribution. As shown in figure 3(a), the PP HFM prepared at different extrusion temperatures from 155 °C to 170 °C showed narrow pore size distribution and no macrospore defect. From the details of figure 3(b), when the extrusion temperature increased, the membrane pore size including maximum pore size, average pore size, and minimum pore size first increased and then decreased, and the maximum value was obtained at 165 °C.

![Figure 3. (a) Pore size distribution and (b) Pore size of PP HFM prepared at various extrusion temperatures.](image)

These results showed that when the extrusion temperature increased from 155 °C to 165 °C, the pore size increased, which was resulted from the increasing droplet growth time during phase separation and the decreasing viscosity of the casting solution. While continuously increased to 170 °C, the pore size decreased, which was caused by the increasing volatile amount of the diluents in casting solution.

3.1.3. LEP. The LEP is an important parameter for characterizing and judging whether membrane wetting occurs. As shown in figure 4, the LEP of PP HFM prepared at different extrusion temperatures were high and almost stable at 0.52 MPa. Thus, the extrusion temperature had little effect on the LEP.

![Figure 4. Effect of the extrusion temperature on the LEP.](image)

3.2. CO₂ degassing performance
The membrane pore size and LEP have great influence on the degassing performance. In this paper, the largest pore size of the PP HFM was obtained at the extrusion temperature of 165 °C. However, the membrane was prone to wetting in this case. Considering the pore size and LEP synthetically, the optimized PP HFM was prepared at extrusion temperature of 170 °C, and fabricated into membrane module used for CO₂ degassing from RO effluent water.

3.2.1. Water flow rate. In this part, the water temperature was 30 °C and vacuum degree was 0.095 MPa. As shown in figure 5(a), when the water flow rate increased from 10 mL·min⁻¹ to
50 mL·min⁻¹, the $\eta$ decreased from 56% to 30%. Although the liquid phase boundary thickness reduced and the mass transfer was enhanced with the increasing water flow rate, the water residence time in membrane module sharply decreased. The results indicated that the water residence time played an important role in the CO₂ degassing[9]. Therefore, a higher $\eta$ could be achieved at longer residence time.

**3.2.2. Effective membrane length.** Increasing the membrane length is an effective method to prolong the water retention time in membrane. In this paper, as the limit of membrane module, the longer effective membrane length was achieved by increasing the operation times. Herein, 0.63 m of the effective membrane length could be achieved by one operation; 1.26 m of effective membrane length could be achieved by two operation times, and so on. The same initial water with CO₂ concentration of 16.41 mg·L⁻¹ was employed for the experiments at the vacuum degree of 0.095 MPa and the flow rate of 10 mL·min⁻¹.

From figure 5(b), when the effective membrane length increased from 0.63 m to 6.3 m, the CO₂ removal efficiency first increased and then almost unchanged. The $\eta$ of the first circle was small, but increased in the next circle, and then the value was almost stable in the subsequent circles. The final degassing efficiency reached about 80% at 4.41 m.

![Figure 5. Effects of (a) water flow rate and (b) effective membrane length on the $\eta$.](image)

**4. Conclusions**

In this study, the PP HFM was prepared via TIPS method with binary green diluents of Cwax/SO. The effects of extrusion temperature on the morphology, pore size and LEP of PP HFM were studied. The results showed that when extrusion temperature increased from 155 °C to 170 °C, the pore size first increased and then decreased, the LEP and membrane morphology had few changes. The optimized PP HFM was prepared at 170 °C, and fabricated into membrane module. The CO₂ degassing performance of PP HFM module was investigated, the results showed that the $\eta$ decreased when increasing water flow rate. The $\eta$ could be enhanced by increasing effective membrane length, when the length increased to 4.41 m, the $\eta$ was almost stable at 80%, which had certain significance in the industrial applications.

**Acknowledgements**

This study was financially supported by the National Natural Science Foundation of China (No.21576024) and the project fund (no.15-16ZS0522) from BRICI, SINOPEC.

**References**

[1] Peng, Z. G., Lee, S. H., Zhou, T., Shieh, J. J., and Chung, T. S. (2008). A study on pilot-scale degassing by polypropylene (PP) hollow fiber membrane contactors. Desalination, 234, 316-322.

[2] Mansourizadeh, A., and Ismail, A. F. (2011). CO₂ stripping from water through porous PVDF hollow fiber membrane contactor. Desalination, 386, 386-390.
[3] Yang, Z., Li, P., Chang, H., and Wang, S. (2006). Effect of diluent on the morphology and performance of iPP hollow fiber microporous membrane via thermally induced phase separation. *Chin. J. Chem. Eng.*, 14(3), 394-397.

[4] Wang, Y. J., Zhao, Z. P., Xi, Z. Y., and Yan, S. Y. (2018). Microporous polypropylene membrane prepared via TIPS using environment-friendly binary diluents and its VMD performance. *J. Membr. Sci.*, 548, 332-344.

[5] Rahbari-Sisakht, M., Ismail, A. F., Rana, D., Matsuura, T., and Emadzadeh, D. (2013). Carbon dioxide stripping from water through porous polysulfone hollow fiber membrane contactor. *Sep. Purif. Technol.*, 108, 119-123.

[6] Zhou, B., Tang, Y., Li, Q., Lin, Y., Yu, M., Xiong, Y., and Wang, X. (2015). Preparation of polypropylene microfiltration membranes via thermally induced (solid–liquid or liquid–liquid) phase separation method. *J. Appl. Polym. Sci.*, 132(35), 42490.

[7] Matsuyama, H., Yuasa, M., Kitamura, Y., Teramoto, M., and Lloyd, D. R. (2000). Structure control of anisotropic and asymmetric polypropylene membrane prepared by thermally induced phase separation. *J. Membr. Sci.*, 179(1-2), 91-100.

[8] Ji, G. L., Zhu, L. P., Zhu, B. K., Zhang, C. F., and Xu, Y. Y. (2008). Structure formation and characterization of PVDF hollow fiber membrane prepared via TIPS with diluent mixture. *J. Membr. Sci.*, 319(1+2), 264-270.

[9] Fang, M. X., Wang, Z., Yan, S. P., Cen, Q. G., and Luo, Z. Y. (2012). CO₂ desorption from rich alkanolamine solution by using membrane vacuum regeneration technology. *Int. J. Greenh. Gas Con.*, 9, 507-521.