Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.795015

51 (2013) 3948–3953
May

Taylor & Francis
Taylor & Francis Group

Preparation and characterization of poly(tetrafluoroethylene–cohexafluoropropylene) (FEP) hollow fiber membranes for desalination

Qing-Lin Huang[a], Changfa Xiao[a,b,*], Zhong-Qing Miao[a], Xianshe Feng[c], Xiao-Yu Hu[a]

[a]*State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin 300160, China*
Tel. +86 022 83955138; email: cfxiao@tjpu.edu.cn
[b]*Department of Materials, Tianjin Polytechnic University, No. 399 West Binshui Road, Xiqing District, Tianjin, China*
[c]*Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

Received 6 August 2012; Accepted 20 March 2013

ABSTRACT

High porosity and strong hydrophobicity of polymeric hollow fiber membranes are of great interest for membrane distillation (MD). Poly(tetrafluoroethylene–cohexafluoropropylene) (FEP) exhibits excellent chemical resistance, thermal stability, strong hydrophobicity owing to the perfluoro-structure. Comparing with polytetrafluoroethylene (PTFE), the meltable property endows FEP good processability for fabricating hollow fiber membrane by melt-spinning method. In our previous articles, FEP hollow fiber membranes have been fabricated successfully by melt spinning method for the first time. In this study, the effect of the dioctyl phthalate (DOP) content on the performance and morphology of FEP hollow fiber membrane was discussed. And the hollow fiber membranes' properties in terms of porosity, liquid entry pressure (LEP), mean pore size and also morphologies were characterized, respectively.

Keywords: Perfluoro-structure; Poly(tetrafluoroethylene–cohexafluoropropylene) (FEP); Hollow fiber membrane; Hydrophobicity

1. Introduction

As the aggravation of water pollution, the emergency of wastewater treatment and water purification becomes more and more evident [1,2]. In comparison with other water purification technologies, reverse osmosis (RO) is a widely used membrane process for water desalination, especially for seawater desalination. However, RO suffers many problems such as high operating pressure, sensitive to membrane fouling, and secondary pollution caused by the concentrated water [3–6]. Nowadays, membrane distillation (MD) receives increasing attention because it provides many advantages [7–9] including (1) a low operating pressure, (2) much larger membrane pore sizes than RO which results in a higher water flux, (3) a high rejection for

*Corresponding author.

Presented at the 2012 Qingdao International Desalination Conference June 26–29, 2012, Qingdao, China

non-volatile components, and (4) much less sensitive to membrane fouling. Furthermore, comparing with the conventional distillation, MD requires less head space for vapor and lower feed temperatures (40–80°C). Thus, this provides a potential opportunity to use such alternative energy sources as geothermal, solar energies or other low grade energies in MD [10–13].

MD is a potential membrane technology based on the use of hydrophobic micro-porous membrane [14]. The principle of MD can be simply described like this [4,15], a porous hydrophobic membrane is used to perform the barrier between feed streams and permeate side. The aqueous liquid feed stream is kept out of the membrane pores because of the hydrophobic nature of membrane, while water vaporizes from the "hot" feed side. Then, water vapor diffuses through the membrane under a vapor pressure gradient across the membrane to reach the permeate side, where water vapor is condense into liquid on the "cold" permeate side. As a result, purified water is obtained on the permeate side, and minerals and other nonvolatile components are left on the feed side [4,11]. Therefore, the membrane plays a significant role during the MD process. The membrane properties, including membrane hydrophobicity, pore size distribution, are crucial to MD process [16,17]. Nevertheless, most of the membrane materials for MD process have not been specifically made. Presently, the three most common polymer materials suit for MD process are polypropylene (PP), PTFE, and polyvinylidenefluoride (PVDF) [18,19]. Comparing with PP and PVDF, PTFE has the lowest surface tension which induces the most strong hydrophobicity [20,21]. In addition, the exceptional combination of outstanding thermal resistance, good chemical stability, and low surface friction makes PTFE be the preferred material for MD [22,23]. However, the main disadvantage of PTFE is the poor processing property which prohibits common phase inversion or melt spinning methods from manufacturing porous membrane [24,25]. As same as PTFE, poly(tetrafluoroethylene–cohexafluoropropylene) (FEP) exhibits excellent chemical resistance, thermal stability, strong hydrophobicity owing to the perfluoro-structure [26,27]. Comparing with PTFE, the introduction of $-CF_3$ into the tetrafluoroethylene endows FEP good meltable processability [28,29]. Therefore, FEP can be fabricated into hollow fiber membrane by melt spinning method. Thus, not only the membrane pore size distribution but also the efficiency of membrane manufacturer can be improved effectively [30]. Fortunately, FEP hollow fiber membranes were fabricated successfully for the first time with dioctyl phthalate (DOP) as diluent and composite powder (composed of dissolvable and indissolvable particles) as pore-creating agent.

On the basis of our previous researches [31], the main objective of this article was the investigation of the effects of DOP contents on the performance and morphology of FEP hollow fiber membrane.

2. Experimental

2.1. Materials

FEP resin (6100, DuPont Co., Ltd.), and dilute dioctyl phthalate (DOP, >99.5%, Tianjin Kermel Chemical Reagent Co., Ltd). The composite powder (mixture of nanoscale KCl and SiO_2 particles) was provided by Tianjin Motian Membrane Engineering & Technology Co., Ltd. (Tianjin, China).

2.2. Preparation of FEP hollow fiber membrane

FEP resin, composite powder (dried for 12 h at 100 ± 2 °C in a vacuum oven to remove the moisture content, respectively) and DOP mixture with different DOP contents were homogeneous mixed under high speed agitation. Then, the mixture melt was extruded into the hollow fiber spinneret by a twin-screw spinning machine, the resulting hollow fiber were spun into external coagulation bath (water) after passing through an air gap of 3 cm. Subsequently, the FEP hollow fiber membranes were obtained after immersing in pure water for approximately two days. The scheme of melt-spinning apparatus was shown in our previous article [31]. The spinning conditions were tabulated in Table 1 for a quick reference.

2.3. Characterization of FEP hollow fiber membrane

2.3.1. Membrane porosity and mean pore size

The porosity of the membrane was determined by the gravimetric method [32], which is based on the weight of liquid contained in the membrane pores. Owing to the hydrophobicity of FEP, isopentane was used as the wetting liquid, and the porosity (ε) of the membrane was determined from

$$\varepsilon = \frac{(w_1 - w_2)/D_1}{(w_1 - w_2)/D_1 + w_2/D_p} \quad (1)$$

where w_1 is the weight of the membrane wetted by isopentane, w_2 is the weight of the dry membrane, D_1 is the density of isopentane ($D_1 = 0.62\ g/cm^3$) and D_p is the density of the FEP polymer ($D_{FEP} = 2.15\ g/cm^3$). The mean pore size was determined by the gas permeation method using a capillary flow porometer (CFP-1100-A, Porous Materials Inc., Ithaca, NY).

Table 1
Spinning parameters of FEP hollow fiber membranes

	FEP hollow fiber membrane ID			
	F-0	F-3	F-5	F-10
Dope composition	FEP/composite powders: 60/10			
DOP loading in polymer mixture (%)	0	3	5	10
Bore fluid	N_2			
External coagulation bath	Water (temperature was 0, 25, 50, 90 °C, respectively)			
Air gap (cm)	3			
Take up speed	Free flow			
Post treatment	Three days store in tap water			
Spinneret dimension (mm)	OD/ID/L: 2.6/2.0/6			

2.3.2. Liquid entry pressure (LEP)

Liquid entry pressure (LEP) is the pressure that must be applied onto liquid before it penetrates into dried membrane pores. In this study, the LEP of FEP hollow fiber membranes were measured at 25 °C. The outside of hollow fiber (feed side) was filled with 3.5% NaCl aqueous solution while the inside (permeate side) was in contact with the pure water. Then, pressure was applied to the NaCl aqueous solution using regulated nitrogen. The pressure increased until the NaCl solution penetrated through the membrane and was mixed with the pure water in the beaker. The penetration of NaCl was detected via a change in conductivity in the pure water by using a conductivity meter. The pressure at which the NaCl aqueous solution penetrated the membrane was recorded, and the average of three measurements was recorded the LEP of FEP hollow fiber membrane.

2.3.3. Membrane morphologies

The morphologies of FEP hollow fiber membranes were examined using a field emission scanning electron microscope (FESEM X4800, Hitachi, Japan). Samples were frozen in liquid nitrogen followed by fracturing to expose the cross-sectional areas. Where after, they were gold sputtering using an ion beam sputtering device (JFC-1100E, JEOL, Japan) and viewed by FESEM.

3. Results and discussion

3.1. Liquid entry pressure (LEP)

LEP determines the maximum operating pressure at which the hot feed water does not wet and penetrate the membrane pore. It depends on the integration of hydrophobic character of the membrane material, the liquid surface pressure, and the pore diameter. The relation is described by the Laplace-Young equation.

$$\Delta P = P_F - P_D = \frac{-4B\sigma\cos\theta}{d_p} \quad (2)$$

where B is the pore geometry coefficient ($B = 1$ for cylindrical pores), σ is the surface tension of the liquid (Nm^{-1}), θ is the contact angle (°), d_p is the pore size (m), P_F and P_D are the hydraulic pressure on the feed and distillation side (MPa), respectively.

As it is well known, the larger LEP would lead to higher water permeate flux. However, according to the Eq. (3), a higher LEP requires membrane stronger hydrophobicity and smaller pore size. The porosity, mean pore size and also LEP of FEP hollow fiber membranes were characterized, as listed in Table 2.

Table 2
Summary of the characterization results for FEP hollow fiber membranes

Hollow fiber ID	Wall thickness (mm)	Porosity (%)	Mean pore size (μm)	LEP (MPa) calculated	LEP (MPa)
F0	0.61 ± 0.01	52.4	0.432 ± 0.002	0.339	0.32 ± 0.02
F3	0.52 ± 0. 01	65.8	0.526 ± 0.002	0.278	0.25 ± 0.02
F5	0.52 ± 0.01	75.4	0.554 ± 0.002	0.264	0.24 ± 0.02
F10	0.53 ± 0.01	79.3	0.658 ± 0.002	0.225	0.18 ± 0.02

The characterization results indicated that the porosity and mean pore size increased with the increase in DOP content. The porosity enhancement resulted from the increase of DOP volume in the ternary mixture. This brought about more dissolved pore when membrane suffered extracting with alcohol. It was easy to understand the decrease LEP as the DOP content increasing. As the DOP content increasing, the bigger membrane pore size induced the lower LEP. The results agreed the Laplace-Young equation well.

3.2. Morphologies of FEP hollow fiber membrane

The micrographs in Fig. 1 showed the cross-section morphologies of FEP hollow fiber membranes with different DOP contents. It can be clearly seen that there were two parts in the cross-section which were the dense layer and microvoid structure in the cross-section. The formation of the dense layer was owing to the dissolve of DOP while the microvoid structure was owing to the composite powder. The dissolved DOP was aided to form dense pore structure, and the dissolved composite powder was aided to form microvoid structure. The dense layer was in the surface of membrane which was because the increase of DOP content brought about the decrease of melt viscosity, and the DOP migrated to the membrane surface during the spinning process. When DOP was extracted, the small pore structure of dense layer was formed.

Microvoids formation was owing to the dissolve of the composite powder which was micron size. Furthermore, the quantity and size of the microvoids increased with the increase of the DOP contents which induced the promotion of the membrane porosity. It was because that the liquid DOP made the connection of composite powder which made the dissolved pore formation easier.

The micrographs in Fig. 2 showed the inner and outer surface morphologies of FEP hollow fiber membranes. The inner surface image exhibited a relatively highly porosity. This result was mainly due to the different temperatures in the inner and outer surface of hollow fiber membrane during the spinning process. When the DOP content was 3% (F3), there were amounts of pores in the inner surface, and the pore size was relative small. When the DOP content rose to 10% (F10), the pore size increased obviously in the fiber axis direction. It was owing to the promotion

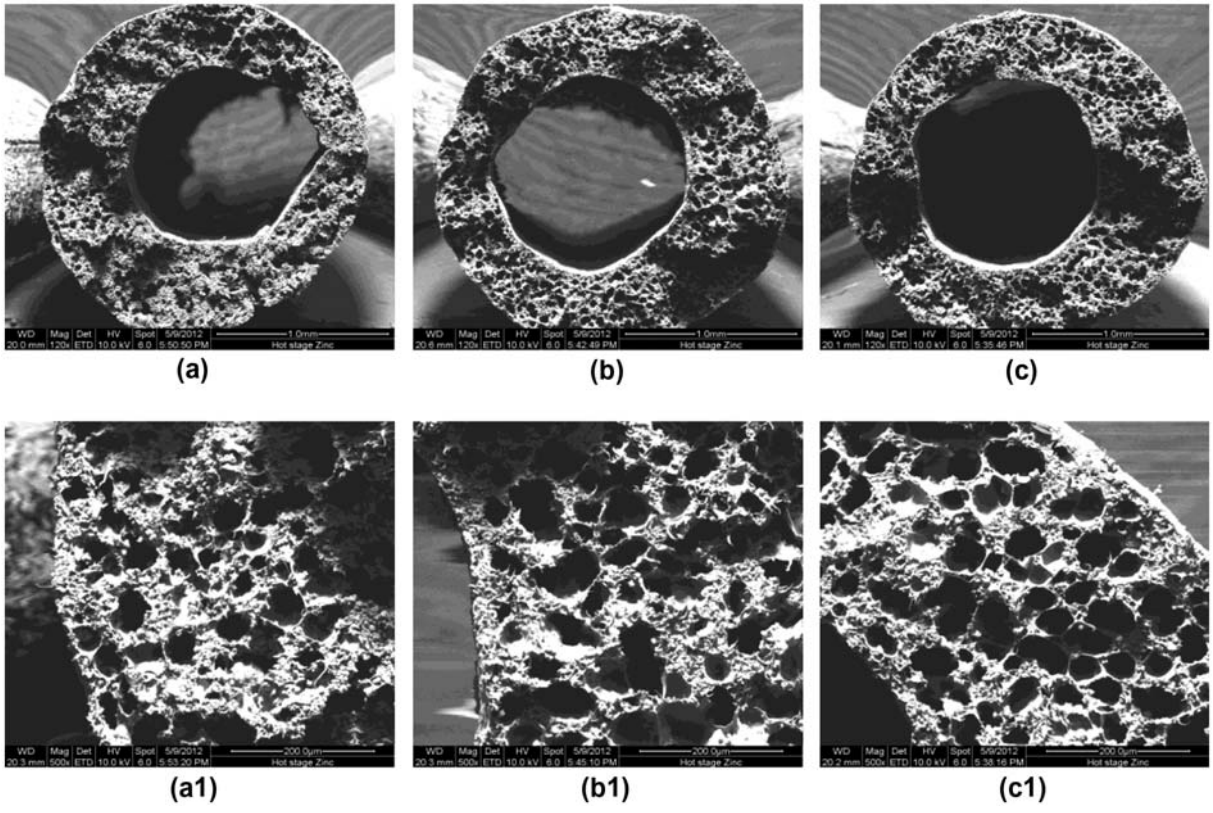

Fig. 1. SEM micrographs show the cross-section morphologies of the FEP hollow fiber membrane. (a) F3; (b) F5; (c) F10. (a1) (b1) (c1) represent the enlarge cross-section.

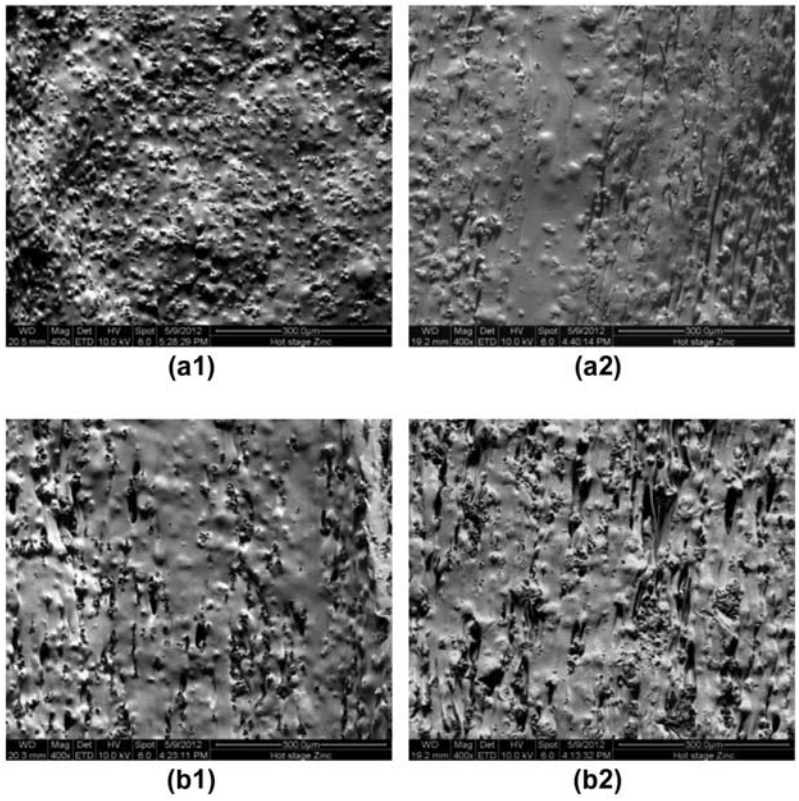

Fig. 2. SEM micrographs show the inner and outer surface morphologies of FEP hollow fiber membrane. (a1) F3 inner surface; (a2) F10 outer surface; (b1) F5 inner surface; (a2) F10 outer surface.

of melt flowability which induced the stretching of the nascent hollow fiber F10, the unsolidified inner surface was easily to deform. And the deformation of the inner surface was the main reasons of the pore formation.

4. Conclusions

A series of FEP hollow fiber membranes with different DOP contents have been fabricated via melt spinning method. Effects of DOP content on the membrane properties and morphology were discussed. Results showed that the formation of dense layer was owing to the DOP while the formation of big microvoid was owing to the composite powder. The membrane porosity and mean pore size increased with the increase in DOP content. And there founded stretching pore structure in the inner surface when the DOP content rose to 10% which induce the promotion of membrane porosity.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 51073120) and Tianjin Scientific and Technology Program (10SYSYJC27900). Research support via the Applied Fundamental Research project of the National Textile and Apparel Council of China is also gratefully acknowledged.

References

[1] S. Simone, A. Figoli, A. Criscuoli, Preparation of hollow fiber membranes from PVDF/PVP blends and their application in VMD, J. Membr. Sci. 364 (2010) 219–232.
[2] K.W. Lawson, D.R. Lloyd, Membrane distillation, J. Membr. Sci. 124 (1997) 1–25.
[3] E. Curcio, E. Drioli, Membrane distillation and related operations – a review, Sep. Purif. Rev. 34 (2005) 35.
[4] M.S. El-Bourawi, Z. Ding, R. Ma, M. Khayet, A framework for better understanding membrane distillation separation process, J. Membr. Sci. 285 (2006) 4.
[5] C. Cabassud, D. Wirth, Membrane distillation for water desalination: how to choose an appropriate membrane, Desalination 157 (2003) 307–314.
[6] Y. Xu, B.K. Zhu, Y.Y. Xu, Pilot test of vacuum membrane distillation for seawater desalination on a ship, Desalination 189 (2006) 165–169.
[7] S. Bonyadi, T.S. Chung, Flux enhancement in membrane distillation by fabrication of dual layer hydrophilic–hydrophobic hollow fiber membranes, J. Membr. Sci. 306 (2007) 134–146.
[8] J.Z. Zhang, N. Dow, M. Duke, E. Ostarcevic, J.D. Li, S. Gray, Identification of material and physical features of membrane distillation membranes for high performance desalination, J. Membr. Sci. 349 (2010) 295–303.

[9] M. Tomaszewska, Membrane distillation-examples of applications in technology and environmental protection, Environ. Stud. 9 (2000) 27.
[10] C. Cabassud, D. Wirth, Membrane distillation for water desalination: How to choose an appropriate membrane, Desalination 157 (2003) 307–314.
[11] Y. Xu, B.K. Zhu, Y.Y. Xu, Pilot test of vacuum membrane distillation for seawater desalination on a ship, Desalination 189 (2006) 165–169.
[12] J. Koschikowski, M. Wieghaus, M. Rommel, Solar thermal-driven desalination plants based on membrane distillation, Desalination 156 (2003) 295–304.
[13] M. Teoh, T.S. Chung, Membrane distillation with hydrophobic macrovoid-free PVDF–PTFE hollow fiber membranes, Sep. Purif. Technol. 66 (2009) 229–236.
[14] K.W. Lawson, D.R. Looyd, Membrane distillation. II. Direct contact membrane distillation, J. Membr. Sci. 120 (1996) 123–133.
[15] S. Bonyadi, T.S. Chung, Highly porous and microvoid-free PVDF hollow fiber membranes for membrane distillation by a solvent-dope solution co-extrusion approach, J. Membr. Sci. 331 (2009) 66–74.
[16] R.W. Schofield, A.G. Fae, C.J.D. Fell, R. Macoun, Factors affecting flux in membrane distillation, Desalination 77 (1990) 279–294.
[17] L. Song, B. Li, K.K. Sirkar, J.L. Gilron, Direct contact membrane distillation-based desalination: Novel membranes, devices, large-scale studies, and a model, Ind. Eng. Chem. Res. 46 (2007) 2307.
[18] K.W. Lawson, M.S. Hall, D.R. Lloyd, Compaction of microporous membranes used in membrane distillation. I. Effect on gas permeability, J. Membr. Sci. 101 (1995) 99–108.
[19] R.W. Schofield, A.G. Fane, C.J.D. Fell, Gas and vapour transport through microporous membranes. II. Membrane distillation, J. Membr. Sci. 53 (1990) 173–185.
[20] H.Y. Lin, C.R. Wu, X.L. Lu, Modification of the super-hydrophobic polyvinylidene fluoride membrane, Membr. Sci. Technol. 30 (2010) 39–43.
[21] Q.L. Huang, C.F. Xiao, X.Y. Hu, A novel method to prepare hydrophobic poly(tetrafluoroethylene) membrane, and its properties, J. Mater. Sci. 45 (2010) 6569–6573.
[22] A.M. Alklaibi, N. Lior, Membrane-distillation: Status and potential, Desalination 171 (2005) 111–118.
[23] D. Newman, F. Morizio, S. Kidd, Porous Polytetrafluoroethyelne Membrane, US Patent 6,274,043, 2001.
[24] R.C. George, A.M. Richard, W.S. Charles, Low Melting Tetrafluoroethylene Copolymer and its Uses, US Patent 5547761, 1996.
[25] K. Ralph, T. Helmut. Perfluoro Copolymer of Tetrafluoroethylene And Perflouro Alkyl Vinyl Ethers, US Patent 6686426 B2, 2004.
[26] U. Lappan, U. Geissler, U. Scheler, Macromol. Mater. Eng. 291 (2006) 937–943.
[27] T. Uno, S. Miyata, H. Shirai, Melt-spinning process of a tetrafluoroethylene–hexafluoropropyllene copolymer, J. Appl. Polym. Sci. 84 (2002) 2366–2371.
[28] N. David, F. Morizio, Porous Polytetrefluoroethylene Membrane, US Patent 6274043, 2001.
[29] Q.L. Huang, C.F. Xiao, X.Y. Hu, Fabrication and properties of poly(tetrafluoroethylene–cohexafluoropropylene) hollow fiber membranes, J. Mater. Chem. 21 (2011) 16510–16516.
[30] H. Matsuyama, M. Teramoto, S. Kundari, Y. Kitamura, Effect of diluents on membrane formation via thermally induced phase separation, J. Appl. Polym. Sci. 82 (2001) 169–177.
[31] J. Zhang, N. Dow, M. Duke, E. Ostarcevic, J.D. Li, S. Gray, Identification of material and physical features of membrane distillation membranes for high performance desalination, J. Membr. Sci. 349 (2010) 295–303.
[32] J. Zhao, D.L. Yang, S.H. Zhang, X.G. Jian, Hydrophobic modification of poly(phthalazinone ether sulfone ketone) hollow fiber membrane for vacuum membrane distillation, J. Membr. Sci. 310 (2008) 20–27.