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Preparation of PVDF/PTFE hollow fiber membranes for direct contact membrane distillation via thermally induced phase separation method

Jie Zhao[a,b], Lei Shi[a], Chun Heng Loh[a], Rong Wang[a,b,*]

[a] Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141, Singapore

[b] School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

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ABSTRACT

Polyvinylidene fluoride (PVDF)/polytetrafluoroethylene (PTFE) hollow fiber membranes were developed via thermally induced phase separation (TIPS) method for direct contact membrane distillation (DCMD). The effects of PTFE addition on the thermal behavior of the dope mixtures and membrane formation were investigated. It was found that the crystallization of PVDF was significantly enhanced with increased nucleation sites provided by PTFE particles, leading to promoted formation of smaller spherulites in a greater density. Furthermore, the improved uniformity and increased amount of cavity between the spherical crystallites coherently facilitated the formation of smaller pores ranging from 0.08 to 0.12 μm. With certain PTFE loading, the membranes exhibited improved porosity, water permeability and hydrophobicity as well as enhanced tensile strength of 9.4 ± 0.3 MPa. To examine the DCMD performance, the membranes were tested under various conditions using 3.5 wt% NaCl solution. A stable permeation flux of 28.3 kg m^{-2} h^{-1} at the feed temperature of 60 °C with 99.99% NaCl rejection for over 50 h of operation was achieved, which is comparable with similar type of PVDF membranes while the newly developed membrane exhibited better mechanical strength. This study suggests that the as-spun PVDF/PTFE hollow fiber membranes have potential for DCMD applications.

1. Introduction

Membrane distillation (MD) is a non-isothermal membrane-based separation process involving vapor transport through non-wetted microporous membranes thermally driven by vapor pressure difference between two sides of the membranes [1]. It provides attractive features such as theoretically 100% rejection of salts and less fouling as compared with pressure driven membrane processes, insensitivity to salt concentration and lower requirements on membrane mechanical properties in comparison with other separation techniques [2]. As a promising alternative to reverse osmosis (RO), MD could be applied in seawater desalination [3], industrial wastewater treatment [4] and many other applications if waste or low-grade heat resources are accessible [5].

To maintain the effectiveness and stability of the MD process over a long-term operation, the membrane should possess reasonably high water vapor transfer with minimized tendency of wetting and fouling [6]. With regard to the materials utilized for MD membrane development, fluoropolymers, such as polyvinylidene fluoride (PVDF), have been well-investigated owing to their notable chemical and thermal stabilities, hydrophobicity and good mechanical properties [7]. Various fabrication methods have been employed in hollow fiber membrane development for MD applications [8], among which, two techniques of phase inversion are commonly applied: nonsolvent induced phase separation (NIPS) and thermally induced phase separation (TIPS) [9]. Compared with the NIPS, the TIPS method offers many advantages for porous membrane preparation: (1) fewer influence parameters; (2) ease of operation and scale-up; (3) narrow pore size distribution and large porosity; (3) outstanding mechanical strength [10,11]. In addition, the TIPS method has been demonstrated to have a high commercial maturity for PVDF membrane development in the industry [12–14].

In a typical TIPS process, a homogeneous solution is formed by dissolving a polymer in a low-molecular-weight diluent with a high boiling point at high temperature. The diluent could be a single solvent or a combination of different solvents and non-solvents [12]. By cooling down or quenching (cooling down at a rapid rate) the homogeneous solution, the phase inversion occurs. After the nucleation and solidification of the polymer-rich phase, a membrane with porous structure can be obtained by extracting the solvent [13]. To achieve an optimum structure, numerous attempts on membrane surface modification or

* Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, 639798, Singapore.
E-mail address: rwang@ntu.edu.sg (R. Wang).

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Table 1
Effects of additives on PVDF membranes through TIPS method.

Type of additive	Additive	Solvent	Structure	Spherulite formation	Polymorphism	Tensile strength	Hydrophilicity	Porosity	Water permeability	Geometry	Ref.
Nucleating agent	$CaCO_3$	DBP, GBL/DOP	Cellular	Decrease size, improve uniformity	/	Increase	Decrease	Increase	Increase	HF/FS	[14,15]
	TiO_2	DMP	Spherulitic	Decrease size, increase amount	α	Increase	Decrease	Increase	Increase	FS	[16]
	MMT	DPK	Spherulitic	Decrease size, increase amount	α, β	Increase	/	/	/	FS	[17]
	PTFE	DPK	Spherulitic	Decrease size, increase amount	α	Increase	/	/	/	FS	[17]
	O-MWCNTs	DBP	Cellular	Decrease size, increase amount	/	Increase	Increase	Decrease	Decrease	FS	[18]
Crystallization inhibitor	PVP	GBL, DEP	Spherulitic	Decrease size, improve uniformity	α, β to γ	Increase	Increase	/	Decrease	HF	[19,20]
	PMMA	Sulfolane, DEP	Cellular (sulfolane), spherulitic (DEP)	Decrease size, improve uniformity	/	Decrease	Increase	/	Decrease	HF/FS	[19,21]
	SiO_2	DBP	Spherulitic	Decrease size, improve uniformity	/	Increase	Increase	Increase	Increase	FS	[22]
	Glycerol	Triacetin	Spherulitic	Improve connectivity	/	Decrease	/	Increase	Increase	HF	[11,23]

Note: this summary is based on the effects of additives before the occurrence of aggregation above the optimum loading.
Abbreviations: HF, hollow fiber; FS, flat sheet; DBP, dibutyl phthalate; DEP, diethyl phthalate; DMP, dimethyl phthalate; DOP, dioctyl phthalate; DPK, diphenyl ketone; GBL, γ-butyrolactone; MMT, montmorillonite; O-MWCNTs, oxidized multi-wall carbon nanotubes; PMMA, poly(methyl methacrylate); PTFE, polytetrafluoroethylene; PVP, polyvinylpyrrolidone.

blending have been made to enhance the properties of PVDF membranes [8]. Compared with surface modification, blending of polymers or inorganic particles is more practical in industrial manufacturing as the membranes can be fabricated in a single step.

Due to its semi-crystalline property, the nucleation and crystallization of PVDF could play a significant role in the formation of membrane microstructures during thermal processes such as the TIPS. Therefore, in recent studies of the TIPS method, a number of additives have been used in PVDF/diluent systems to adjust these two processes during membrane formation, as summarized in Table 1. Based on the effects of the additives on membrane formation, they can be generally classified into two major types: nucleating agents and crystallization inhibitors. In the first category, the nucleating agents represent those additives that can enhance the nucleation and growth (NG) of the polymer-rich phase, as they are able to act as crystal nuclei during the nucleation process. The additives with such functions include $CaCO_3$ [14,15], TiO_2 [16], montmorillonite (MMT) [17], polytetrafluoroethylene (PTFE) [17], oxidized multi-wall carbon nanotubes (O-MWCNTs) [18], etc. The additives in the second category normally act as crystallization inhibitors due to their ability on suppressing the crystallization process of PVDF crystalline phase. Examples from previous study include blending PVDF with poly(vinylpyrrolidone) PVP [19,20], poly(methyl methacrylate) PMMA [19,21], SiO_2 [22], glycerol [11,23], etc.

Among those additives, PTFE was found to be an effective enhancer for the heterogeneous nucleation of PVDF [17,24]. In the study reported by Schneider et al., it was observed that the PVDF matrix could epitaxially crystallized on PTFE chains, resulting in increased nucleation density [24]. This phenomenon also suggested good compatibility between PVDF and PTFE. Ma et al. examined the effect of PTFE on the crystallization and melting characteristics of PVDF/diphenyl ketone (DPK) flat sheet membranes [17,25]. The results showed that the addition of PTFE could enhance the nucleation of PVDF during TIPS process. On the other hand, PTFE was demonstrated to be an effective additive to enhance the anti-wetting property of membranes for MD applications given its outstanding hydrophobicity [26]. By using the conventional NIPS method, Teoh et al. obtained single-layer and dual-layer PVDF/PTFE hollow fiber membranes with increased hydrophobicity and improved long-term MD performance [27]. Despite these reports involving PVDF and PTFE blending, there are few studies on how the nucleation enhancing capability of PTFE particles in TIPS affects the properties of PVDF membranes such as pore structure, mechanical strength and water permeability.

In this work, PVDF/PTFE hollow fiber membranes were fabricated via the TIPS method with various PTFE loadings to thoroughly investigate the impact of PTFE addition on membrane properties and possible mechanisms behind. The addition of PTFE is expected to exert dual effects on PVDF membranes including controlling the microstructures during the TIPS process and enhancing the wetting resistance in MD applications. The characteristics of prepared membranes were examined and the pure water permeability and performance of direct contact membrane distillation (DCMD) were also evaluated. To our best knowledge, there is no report on the development of PVDF/PTFE hollow fiber membranes via TIPS method for MD application. It is anticipated that this work is able to provide a better understanding on the PVDF membrane formation mechanism involving PTFE particles in the TIPS process, and to demonstrate the potential of PVDF/PTFE hollow fiber membranes in MD applications.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF Solef® 6020, M_w = 670–700 kDa, Solvay) were used to make porous hollow fiber membranes. Polytetrafluoroethylene (PTFE microparticles, Microdispers-200, MW