



Fabrication of hydrophobic flat sheet and hollow fiber membranes from PVDF and PVDF-CTFE for membrane distillation



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ABSTRACT

Hydrophobic polyvinylidene fluoride (PVDF) membranes have been used in membrane distillation, however its performance in terms of permeation flux and salt rejection still needs to be improved. In this study, polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-CTFE), a PVDF based copolymer, was employed to fabricate both flat sheet and hollow fiber membranes. Two pore forming additives (PEG and LiCl) were used in order to examine their effects on the membrane micro-structure and consequently the distillation performance. The crystalline property of the polymers was studied via X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) to reveal its role in the membrane formation. The membrane morphology (SEM), surface property (AFM) and membrane properties (contact angle, pore size, porosity and pore size distribution) were systematically examined and compared among PVDF, PVDF-CTFE membranes as well as their counterparts with pore forming additives. The results revealed that PVDF-CTFE membrane exhibited optimal membrane morphology, pore structure and hydrophobicity, thus delivering better distillation performance (permeation flux up to 62.09 kg/m² h, and distillate conductivity as low as 5 μS/cm) in comparison with their PVDF membrane counterparts.

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1. Introduction

Fluoro-polymers have a wide range of applications in membrane science owing to their excellent mechanical strength, superior chemical and thermal stability and low surface tension [1]. Among the entire fluoro-polymer family, polyvinylidene fluoride (PVDF) is the most commonly used membrane material for a variety of applications including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), membrane distillation (MD), pervaporation (PV) and gas separation (GS) [2,3]. The use of PVDF membrane in MD is particularly common due to its hydrophobicity and its excellent processability in comparison with other typically used polymer materials such as polypropylene (PP) and polytetrafluoroethylene (PTFE).

The research of PVDF hydrophobic membrane has mainly focused on the production of well-structured, super-hydrophobic membranes with good mechanical strength. The membrane with

such ideal properties can be prepared through (i) careful selection of dope solution components and (ii) optimization of the membrane fabrication protocols. In this line of development, through a comprehensive study on dope solution compositions, hydrophobic PVDF flat-sheet membranes with permeation flux of 9.7 kg/m² h was prepared by Tomaszewska et al. for MD process [4]. Bottino et al. [5] further carried out a systematic study on the choice of appropriate organic solvents for PVDF membrane preparation, and more works have been done with the consideration of solvents effect on membrane morphology, hydrophobicity, micro-structure and separation performance [6]. In addition, research efforts had been made to the optimization of the preparation conditions, especially for hollow fiber membrane spinning. The parameters including the type and temperature of the coagulation, air gap distance, dope and bore liquid flow rates, take-up speed and post-treatment conditions had been investigated.

Apart from the aforementioned investigations, improving PVDF membrane performance from material development aspect has become another research focal point [7]. The research efforts on this front have mainly focused on three approaches: (i) the potential use of a variety of additives or mixed-solvent in the dope solution [8–10], (ii) development of smart membrane architecture, for instance, composite and nano-composite membranes [11–14]

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Table 1
Preparation parameters and casting conditions of flat-sheet membrane.

Preparation conditions/parameters	M1	M2	M3	M4
Polymer concentration	PVDF-CTFE, 12 wt%	PVDF, 12 wt%	PVDF-CTFE, 12 wt%	PVDF, 12 wt%
Solvent concentration	DMAc, 88 wt%	DMAc, 88 wt%	DMAc, 80 wt%	DMAc, 80 wt%
Additives (LiCl:PEG)	None	None	8 wt% (1:1)	8 wt% (1:1)
Coagulation	Deionized water	Deionized water	Deionized water	Deionized water
Casting solution temperature (°C)	30	30	30	30
Coagulation temperature (°C)	30	30	30	30
Casting knife gap (μm)	250	250	250	250
Exposure time (s)	15	15	15	15

and (iii) synthesizing novel PVDF-based copolymer with enhanced properties [2]. In terms of the 3rd strategies of PVDF-based copolymer synthesis, one example is the synthesis of PVDF-TFE, which showed better mechanical and hydrophobic properties over PVDF membrane and has better performance in DCMD configuration [15]. More recently, PVDF-TFE novel polymer inclusion membranes (PIMs) were successfully prepared for Cr (VI) transport with high permeability and better selectivity [16]. In addition, another type of PVDF copolymer, PVDF-TrFE was used to prepare membranes for lithium-ion battery [17]. PVDF-HFP, as another commonly used PVDF-based copolymer, has also been widely investigated, not only on the optimization of the membrane preparation protocols [18–20], but also on its potential applications from ethyl acetate separation [21] to lithium-ion batteries [22,23].

PVDF-CTFE is another common PVDF-based copolymer, similar to PVDF-HFP, it has high mechanical strength and good chemical and thermal stability [24]. Furthermore, owing to its CTFE segment, PVDF-CTFE can be easily grafted via atom transfer radical polymerization (ATRP) without compromising the mechanical, thermal and chemical stability. For instance, Kim et al. [25] synthesized graft copolymer PVDF-CTFE-g-PSSA by ATRP and applied it as electrolyte membranes. Later they prepared PVDF-CTFE-g-PSSA composite NF membrane [26]. In addition, poly(hydroxyl ethyl acrylate) [27], 4-vinylpyridine [28], and poly(oxyethylene methacrylate) [29] have been grafted onto the PVDF-CTFE main chains to obtain the corresponding amphiphilic copolymer membranes for either proton conducting properties or silver nanoparticle templates. In 2011, Liu et al. [30] prepared PVDF-CTFE hydrophobic membranes followed by the hydrophilic modification with immobilization of hydrophilic poly(ethylene glycol) methyl ether methacrylate (PEGMA) by ATRP.

However despite the great research efforts paid on the PVDF-based copolymer development, especially the PVDF-CTFE-based grafted polymers, all the attentions have been dedicated to enhancing the hydrophilicity of the membranes, whilst their potential in hydrophobic membrane preparation has been largely overlooked. Although the investigations on the use of PVDF membrane for MD process has been carried out in the past as aforementioned, the use of PVDF-based copolymer, PVDF-CTFE in particular, in the same MD application has never been explored, and the performance comparison between the conventional PVDF and PVDF-CTFE membranes was also not evaluated in the past, to the best knowledge of the authors. In this regard, the research in this line is certainly necessary and warranted.

Here, we report on the preparation of PVDF-CTFE and PVDF hydrophobic flat-sheet and hollow fiber membranes through the non-solvent induced phase separation technique (NIPS). The effect of the pore forming additives (PEG and LiCl) was also assessed. The membrane morphology (SEM), surface property (AFM) and membrane properties (contact angle, pore size, porosity and pore size distribution) were systematically examined and compared among PVDF, PVDF-CTFE membranes as well as their counterparts with pore forming additives. The performance of these

membranes in membrane distillation process was also studied to demonstrate its potential in industrial implementation.

2. Experimental

2.1 Materials

Commercial PVDF-CTFE copolymer (Solef[®] PVDF 32008) and PVDF homopolymer (Solef[®] PVDF 1015) were purchased from Solvay (Belgium) and was dried at 50 °C for 24 h before use. DMAc (> 99%) was employed as the solvent, which was obtained from Shanghai Jingwei Chemical Co., Ltd. (Shanghai, China). LiCl and polyethylene glycol (PEG) were used as the additives, both LiCl (AR, > 95%) and PEG-400 (AR, > 99.5%) were supplied by Tianjin Guangfu Research Institute of Fine Chemical Engineering (Tianjin, China). Ethanol (GR grade, 99.9%), NaCl (GR grade, 99.5%), glycerol (AR, 99%), and diiodomethane (CP) were purchased from Beijing Chemical works (Beijing, China). In terms of the flat sheet membrane casting, deionized water was used as coagulant. Whilst for the hollow fiber fabrication, deionized water was used as bore solution, and tap water as external coagulant. All reagents and materials were used as received.

2.2 Membrane preparation

The PVDF-CTFE and PVDF polymers were dried at 50 °C for 24 h prior to polymer solution preparation. Different amounts of polymers, solvents and non-solvent additives were mixed in a sealed flask and stirred at 30 °C for 24 h to obtain a homogeneous polymer solution (detailed polymer solution compositions can be found in Tables 1 and 2). The polymer solution was then allowed for degassing in an oven at 30 °C for 24 h.

Dry-wet phase inversion process was adopted to prepare the flat sheet membrane. A piece of hydrophilic PET nonwoven fabric (18 cm × 20 cm) was firstly attached on a glass plate, followed by the casting of the polymer solution on the nonwoven fabric with a 0.25 mm casting knife. After exposing in the air for 15 s, the film was immersed in a deionized water bath at 25 °C to allow for the phase inversion. The nascent flat sheet membrane was then collected from the water bath and rinsed with deionized water to remove the residual solvent and non-solvent additives. Finally, the wet flat sheet membrane was dried in air at room temperature. The polymer solution compositions along with the casting conditions are compiled in Table 1.

In this study, asymmetric PVDF and PVDF-CTFE hollow fiber membranes were also fabricated utilizing the dry-jet wet spinning technique. The dope solution was extruded through a spinneret with a gear pump to control the dope flow rate. The nascent hollow fiber membrane went through an air gap before immersing into the coagulation bath, before being collected by a roller with a fixed take-up speed. The hollow fibers were then stored in a tap water bath for at least 2 days to remove the residual solvent and

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