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Effect of polyethylene glycol (PEG) as an additive on the fabrication of polyvinylidene fluoride-*co*-hexafluropropylene (PVDF-HFP) asymmetric microporous hollow fiber membranes

Sunee Wongchitphimon[a], Rong Wang[b,c,*], Ratana Jiraratananon[a], Lei Shi[b], Chun Heng Loh[b,c]

[a] *Department of Chemical Engineering, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand*
[b] *Singapore Membrane Technology Centre, Nanyang Technological University, 639798 Singapore, Singapore*
[c] *School of Civil and Environmental Engineering, Nanyang Technological University, 639798 Singapore, Singapore*

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ABSTRACT

Polyvinylidene fluoride-*co*-hexafluropropylene (PVDF-HFP) has received much attention recently as a promising membrane material for membrane contactor application. A systematic study has been carried out to investigate the effects of polyethylene glycol (PEG) with different molecular weights and different loadings as an additive on the fabrication of PVDF-HFP asymmetric microporous hollow fiber membranes. Moreover, the synergetic effects of coagulation temperature and the second additive (lithium chloride: LiCl) with PEG are also evaluated.

Experiments revealed that the addition of PEG into the PVDF-HFP/NMP solution resulted in the system thermodynamically less stable in reaction with water, promoting rapid phase demixing in the phase inversion process. When the same 3 wt% PEG was added into the dope solution, the dimension of finger-like macrovoids of the resultant membrane increased in parallel with the increase of PEG molecular weight from 200 to 600 and 6000 kDa, and pure water permeability (PWP) also increased accordingly. An increase in PWP was also observed when PEG-200 loading in the dope solution was increased from 3 to 5 and 10 wt%, corresponding to the morphology change of resultant membranes.

As a synergetic effect of coagulation temperature with PEG, the finger-like pores occurred in the membrane at room temperature expanded to much larger macrovoids using 10 °C water as the coagulant, and the big finger-like pores almost disappeared when the coagulation bath temperature was increased to 40 °C because of delayed phase demixing. The big macrovoid size can also be suppressed by adding the second small molecule additive, LiCl, due to its strong interactions with NMP and PVDF-HFP to delay the dope precipitation. The irregular inner contour of the membrane can be eliminated by the increase of coagulation bath temperature to 40 °C. The hollow fiber membrane made by a dope of PVDF-HFP/PEG-6000/LiCl/NMP (15/3/3/79 in weight) using 40 °C water as the coagulant exhibited a high PWP of 117 L/m^2 h atm and reasonably good MWCO of 150 kDa. An improvement has been made in the current work as compared to previous PVDF-HFP hollow fiber membranes reported in literatures.

1. Introduction

Polyvinylidene fluoride-*co*-hexafluropropylene (PVDF-HFP) has received much attention recently as a promising membrane material because of its desirable properties such as high hydrophobicity, excellent chemical and thermal resistances, and processing ability in making membranes using nonsolvent-induced phase inversion separation (NIPS) [1–8]. Addition of an amorphous phase of hexafluropropylene (HFP) group into the main constituent VDF blocks increases the fluorine content, making PVDF-HFP more hydrophobic than PVDF material. This property is extremely important for the application of membrane contactor, where hydrophobic microporous membranes are used as an interfacial media for liquid and gas phases to interact. The hydrophobicity and surface pore structure of the membrane are critical factors associated with membrane wetting, which was often encountered in the long-term operation of membrane contactors to hinder the practical applications of membrane distillation for seawater desalination, gas–liquid absorption process for CO_2 capture [1–6], etc.

However, there were a handful of literatures available regarding the fabrication of PVDF-HFP hollow fibers [1–4,9,10]. The understanding of the formation of PVDF-HFP asymmetric mircoporous

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* Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, 639798 Singapore, Singapore.
Tel.: +65 6790 5327; fax: +65 6791 0676..
E-mail address: rwang@ntu.edu.sg (R. Wang).

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hollow fiber membranes was limited as compared with conventional polymeric membranes. Fontananova et al. [9] found that both membranes prepared from PVDF and PVDF-HFP without any additive showed finger-like pores but the membrane made of PVDF had a bigger and longer finger-like pores compared to the membrane prepared from PVDF-HFP. For the membrane performances, the pure water flux of reported PVDF-HFP hollow fiber membrane was quite low [4]. In order to prepare high performance membranes used as contactors, high porosity and suitable surface pore sizes and pore size distribution are essential in addition to membrane's hydrophobicity. Reducing polymer concentration is one of the options to promote pore formation, but membrane mechanical strength might be sacrificed [5]. Therefore, as a commonly adopted approach, additives or pore formers are often used to balance or improve the permeation performance of the final membrane through adjusting the membrane structure in the phase inversion process. Shi et al. [3,4] used polyvinylpyrrolidone (PVP, Mw 15 kDa), LiCl and glycerol as additives for the PVDF-HFP hollow fiber fabrication. It was found that the prepared fibers presented different structures with different additives. LiCl or glycerol addition made the resultant membranes exhibit a narrow pore size distribution compared to the addition of PVP. The hydrophobic property of the membranes was affected by three additives in the sequence of PVP > LiCl > glycerol. Moreover, the use of mixed additives, LiCl with Tween 80, and PVP with glycerol, resulted in the development of finger-like macrovoids across the cross-section of the membranes [10]. Therefore, different additives play different roles on the thermodynamic and kinetic effects resulting in different membrane structures and performances.

Polyethylene glycol (PEG) is one of the additives used to promote pore formation in the polymeric membranes. PEG is a linear polyether compound available in a variety of molecular weight, which is indicated by a numeric suffix followed the abbreviation (PEG). Its general formula is expressed as $H(OCH_2CH_2)_nOH$, where n is the average number of repeating oxyethylene groups [11]. PEG is water-soluble. It is also soluble in many organic solvents including aromatic hydrocarbons. Thus PEG has been reported as a pore former to enhance the permeation properties for not only hydrophilic membranes but also hydrophobic membrane preparation [6,12–14]. For instance, Arthanareeswaran et al. [12] observed that the ultrafiltration membrane made from cellulose acetate (CA) and silica (SiO_2) blended solution containing PEG-600 (i.e., the molecular weight of PEG is 600 Da) possessed a high average pore size and porosity; the membrane made of polysulfone (PSf) blended with sulfonated poly(ether ether ketone) (SPEEK) showed improved pure water flux with the addition of PEG-600 in the dope solution [13]; PVDF-HFP flat-sheet membranes presented higher pure water permeation flux and higher permeate flux in the direct contact membrane distillation when the PEG concentration in the polymer solution was increased [6]; the addition of PEG-600 in the PVDF dope solution resulted in increases of the inner and surface porosities of final hollow fiber membranes [14].

PEG-600 is a commonly used additive. Other types of PEG with different molecular weights are also used for membrane formation. Examples include PEG-6000 as an additive for preparing PVDF-HFP hollow fibers used in membrane distillation by García-Payo et al. [1,2]. Xu and Xu [15] prepared polyvinyl chloride (PVC) hollow fiber ultrafiltration membranes using PEG with different molecular weights of PEG-600, PEG-800 and PEG-1000 as additives. Their results showed that membrane porosity and permeation flux increased with increasing PEG molecular weight, but protein rejections and mechanical strength decreased. Similar results were reported by Kim and Lee [16]. When the molecular weight of PEG additive increased from 600 to 2000 and 6000 Da, pure water flux of resultant polysulfone (PSf) membranes increased and solute rejection decreased. Moreover, with an increase in the ratio of PEG-600 additive to NMP, water flux increased and solute rejection decreased. Chakrabarty et al. [17] also studied the effect of PEG molecular weight on PSf flat-sheet membrane. They used PEG-400, PEG-6000 and PEG-20000 as additives. It was found that the porosity remained almost unchanged when the PEG molecular weight increased from 400 to 6000 Da while it increased significantly with increasing PEG molecular weight from 6000 to 20,000 Da. The poor miscibility of the casting solution with water due to the addition of PEG-20000 was attributed to this result.

From the above, it can be seen that there are many works involving PEG as an additive for various membrane preparation via nonsolvent-induced phase separation (NIPS), and PEG with different molecular weights might present different impacts on membrane structure. However, no systematic report was found with respect to the behavior of PEG additives during the formation of PVDF-HFP hollow fibers. From the polymer chemistry point of view, the interaction of PEG additive with a polymer solution depends on not only the polymer and solvent, but also PEG molecular weight and concentration, which may couple with the condition of phase inversion to affect the thermodynamics and kinetics of membrane formation process, resulting in different structures and performances of final membranes. In the present work, the effects of PEG with different molecular weights and different loadings as an additive on the fabrication of PVDF-HFP asymmetric microporous hollow fiber membranes are investigated systematically. Moreover, the synergetic impacts of coagulation temperature and the second additive with PEG additive are also included in this study.

2. Experimental

2.1. Membrane material and chemicals

Commercially available polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP) pellets Kynar® 2800 (12 wt% HFP, $M_n = 380{,}000$ g/mol) were used as membrane material. This polymer was purchased from ARKEMA, Singapore. The polymer was dried at 50 °C under vacuum. *N*-Methyl-2-pyrrolidone (NMP, 99%, CAS#872-50-4, Panreac, Spain) was used as a solvent. Polyethylene glycol with three molecular weights (PEG-200 and PEG-600, Samchun Pure Chemical and PEG-6000, Panreac Synthesis) and lithium chloride (LiCl, 99%, CAS#7447-41-8, UNILAB, Australia) were added in the dope solution as an additive. All the reagents were used as received.

2.2. Isothermal phase diagram of PVDF-HFP/NMP/water system

The cloud point of PVDF-HFP/NMP/H_2O ternary system was determined by the titrimetric method at the room temperature. The PVDF-HFP pellets were first dried at 50 °C under vacuum. A desired amount was dissolved into a pre-weighed NMP solvent with or without certain amount of PEG to make a dope solution. Milli-Q water acting as a nonsolvent was added into the PVDF-HFP/NMP dope solutions with the polymer concentration ranging from 1 to 10 wt% by a buret. The quantity of Milli-Q water that made the solution turbid was recorded and regarded as the cloud point.

2.3. Spinning dope preparation and dope viscosity measurement

To prepare spinning solutions, 15 wt% of pre-dried PVDF-HFP polymer pellets and one type of selected PEG with a pre-designed amount was dissolved into NMP using a jacket flask, then the dope solution was subjected to continuous stirring for 3 days. Dope temperature was maintained at about 60 °C until all polymer pellets and PEG were dissolved. The homogeneous PVDF-HFP dope solution was then transferred into a stainless tank. The prepared dope was