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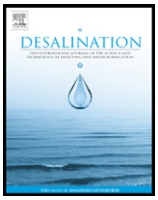

Preparation and characterization of poly (vinylidene fluoride) ultrafiltration membrane with organic and inorganic porogens

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HIGHLIGHTS

- Effect of different additives on PVDF membrane properties was studied.
- Contact angle decreased as PEO-PPO-PEO was added in the casting solution.
- Membrane with PEO-PPO-PEO/oxalic acid combined addition showed the best properties.

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ABSTRACT

In this paper, the effects of high molecular weight additive (PEO-PPO-PEO), low molecular weight additive (oxalic acid) and inorganic additive (nano-TiO_2) on PVDF membranes were studied by phase inversion method. The experimental results showed that the contact angle decreased as PEO-PPO-PEO was added in the casting solution. With the increasing concentration of PEO-PPO-PEO from 0.5 to 3.0 wt.%, the water flux increased from 0 to 1136 L/m^{2}h and the rejection decreased from 99.0% to 64.0%, meanwhile, the static contact angle stabilized basically around 66°. When the oxalic acid concentration increased from 0 to 3.0 wt.% and the concentration of PEO-PPO-PEO maintained at 0.5 wt.%, the water flux increased from 0 to 192 L/m^{2}h, while the rejection firstly decreased and then stabilized around 88.0%. Compared with PEO-PPO-PEO, PEO-PPO-PEO/nano-TiO_2 and PEO-PPO-PEO/oxalic acid/nano-TiO_2, the PVDF membrane with PEO-PPO-PEO/oxalic acid combined addition showed the best properties. As the concentrations of PEO-PPO-PEO and oxalic acid were 2.0 and 3.0 wt.% respectively, the water flux of PVDF membrane reached 2271 L/m^{2}h.

1. Introduction

The excellent properties of PVDF, such as thermal, chemical stability and oxidation resistance against corrosive chemicals have made it interesting as a membrane material [1]. PVDF membranes have been extensively applied in ultrafiltration and microfiltration for general separation purposes. Due to its hydrophobic property, PVDF membrane is susceptible to contamination by proteins and some other organic pollutants in water and wastewater treatment, which often leads to a sharp decrease in the water flux of the membrane and shortens its service life. Consequently, hydrophilic PVDF membranes have attracted much attention.

For phase inversion method, adding inorganic and organic additives in the membrane casting solution is one of the methods to improve the membrane performances and structure. The type of additives used in the fabrication of PVDF membranes could be divided into three categories [2]: (a) high molecular weight additives or known as polymer additives (such as, polyvinyl pyrrolidone, polyethylene glycol); (b) low molecular weight additives (such as, LiCl, $LiClO_4$); (c) other types of additives (such as, H_2O, TiO_2).

As a high molecular weight additive, polyethylene oxide-poly propylene oxide-polyethylene oxide (PEO-PPO-PEO) is an amphiphilic triblock copolymer, displayed in Fig. 1 [3]. It was found that PEO-PPO-PEO could migrate onto the surface of the PVDF membranes during the inversion precipitation process. The hydrophilic PEO segments spontaneously gather on the membrane surface, while hydrophobic PPO segments play a role of anchoring in the membrane. Researches show that contact angle decreases and water flux increases with increasing the concentration of PEO-PPO-PEO in casting solution because of the segregation of PEO segments on the membrane surfaces [4–6].

As a low molecular weight additive, oxalic acid can form hydrophilic coordination complexes with the solvent; as a result, it changes the interaction between the solvent and nonsolvent, which affects the nature of the gelation kinetics of the casting solution and the performance of membrane. In Zhao's study [7], pore size in the skin layer becomes larger as well as the porosity, and finger-like pores turn into sponge-like pores in the cross-sectional morphologies with the increase of oxalic

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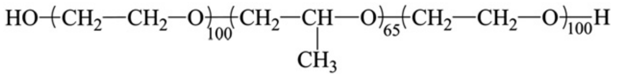

$$HO\left(CH_2-CH_2-O\right)_{100}\left(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O\right)_{65}\left(CH_2-CH_2-O\right)_{100}H$$

Fig. 1. Molecular structure of PEO-PPO-PEO.

acid concentration. Thus, the water flux increases and rejection decreases.

As an inorganic additive, nanoparticles can enhance the mechanical and thermal properties of the macromolecule materials due to their small size, large surface to volume ratio and strong activities [8,9]. Among various nanoparticle additives, nano-TiO_2 has been the most popular one because of its innocuity, resistivity and superhydrophilicity to improve the permeability and anti-fouling properties of membranes. Cao [10] found that the TiO_2/PVDF membrane with smaller nano-TiO_2 particles had smaller mean pore size and less roughness on its surface and more apertures inside the membrane. Oh [11] reported that with the addition of nano-TiO_2 in the PVDF solution, the membrane surface changed from hydrophobic to hydrophilic and typical large finger-like structure appeared.

Many researchers studied the separate influences of PEO-PPO-PEO, oxalic acid and nano-TiO_2 on the PVDF membrane performances. In the present work, a systematic research was carried out to investigate the effects of different porogens combinations, such as alone PEO-PPO-PEO, PEO-PPO-PEO/oxalic acid, PEO-PPO-PEO/nano-TiO2, PEO-PPO-PEO/oxalic acid/nano-TiO_2 on the properties and structure of the PVDF membranes.

2. Experimental

2.1. Materials

PVDF (Mw. 444,000 Dalton) from BASF Co., Germany, was used as membrane polymer. N,N-dimethylacetamide (DMAc) (analytical reagent, purity > 99.0%) used as solvent was obtained from Guangdong Jinhua Co., Ltd., Guangdong, China. PEO-PPO-PEO, oxalic acid and nano-TiO_2 were selected as additives. PEO-PPO-PEO with molecular formula of PEO_{100}-PPO_{65}-PEO_{100} (Mw. 12,600 Dalton) was purchased from Sigma, Germany. Nano-TiO_2 particles (diameter, 5 nm) were supplied by Xuancheng Jingrui new material Co., Ltd., Anhui, China. Oxalic acid (analytical reagent, purity > 99.5%) and bull serum albumin (BSA, Mw. 67,000 Dalton, analytical reagent, purity > 98%) were purchased from Beijing Chemistry Co. Ltd., Beijing, China. All the chemicals were used as received.

2.2. Membrane preparation

PVDF membranes were prepared by the phase inversion method, which included the following steps. PVDF and the additives were dissolved in DMAc solvent, and vigorously stirred at 40 °C for 24 h until a homogenous casting solution (14.0 wt.% of PVDF concentration) was formed. After being degassed for 12 h, the polymer solution would be casted on glass plates with a glass blade at room temperature. The thickness between the glass blade and the glass plate was controlled constant with 0.25 mm. 5–6 sheets of membrane were prepared for every casting solution and precipitated by being immersed into gelation bath tap-water until membrane formed. To remove the residual solvent, the membrane was moved into fresh tap-water bath at room temperature for 24 h.

2.3. Characterization of the casting solutions and PVDF membranes

The viscosity of the casting solution was measured by a rotary viscosimeter (NDJ-1, Shanghai Changji Co., Ltd., Shanghai, China). The membrane sample for contact angle tests was firstly air-dried, and a water droplet was deposited on the dry membrane surface using a microsyringe (Shanghai Gaoge Co., Ltd., Shanghai, China). The contact angle was measured with a contact angle meter (Shanghai Zhongchen Digital Technology Apparatus Co., Ltd., Shanghai, China).

The membrane sample for scanning electron microscopy (SEM) (Quanta200, FEI Co., Ltd.) was firstly immersed in liquid nitrogen, then fractured, and finally sputtered with metallic gold. Cross-section morphology was then observed.

2.4. Ultrafiltration experiments

Under operation pressure of 0.10 MPa and feed temperature of 25 °C, the water permeation and the solute rejection of membranes were performed in a cross-flow manner (with a cross-flow velocity of 1.2 L/min) by the permeation test instrument which was designed in our laboratory [5]. De-ionized water and 0.05 wt.% BSA were used to measure the water permeation and rejection for each sample membrane, respectively.

The water flux was first measured with distilled water under the pressure of 0.1 MPa at 25 °C, and was expressed by $\text{Flux} = V/(A \times t)$, where V is the total permeate volume (L); A represents the effective membrane area (m^2); t is the filtration time (h).

After the distilled water permeation, the solute rejection of membranes was tested with a 0.05 wt.% BSA solution under the pressure of 0.1 MPa at 25 °C, and the solute rejection was calculated with $\text{Rejection} = (1 - C_p/C_f) \times 100\%$, where C_p and C_f are the protein concentration of permeates and feeds, respectively. The BSA concentration was determined by a UV-spectrophotometer (UNICO-UV2102, China) at the wavelength of 280 nm. The rejection test lasted less than 5 min, and did not involve membrane fouling.

For each casting solution, three sheets of prepared membranes were picked to determine their ultrafiltration properties. The pure water flux and rejection of each sheet of membrane sample was tested under the same conditions. The data reported were the average of three tests.

3. Results and discussions

3.1. Effects of PEO-PPO-PEO on membrane properties

Fig. 2 shows that with the PEO-PPO-PEO concentration increasing from 0.5 to 3.0 wt.%, the water flux of PVDF membrane increased dramatically from 0 to 1136 L/m^2h, while the rejection decreased from 99.0% to 64.0%. When the water flux was 0, the membrane may be considered as a "film" because there was no mass (water and solute)

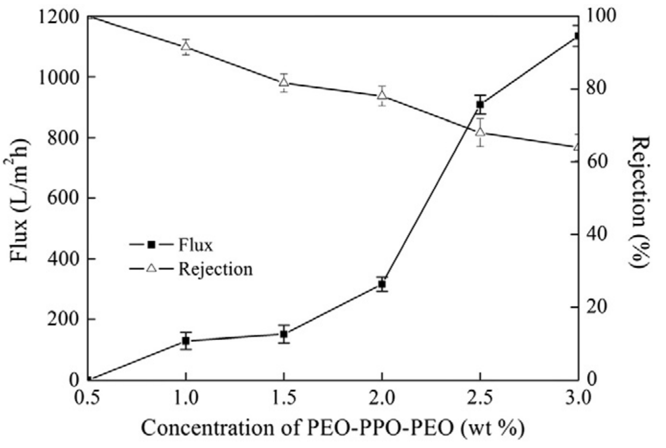

Fig. 2. Effect of PEO-PPO-PEO concentration on the PVDF membrane performances.