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Effects of pore-forming additives on structures and properties of PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes

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ABSTRACT

The polyvinylidene fluoride (PVDF)/Fe^{3+}/Cu^{2+} hollow fiber membranes were prepared via dry-jet wet phase-inversion method to investigate the effects of pore-forming additives on structures and properties of the membranes in this study. Using polyethylene glycol (PEG) (molecular weight: 400, 6,000, and 20,000 Da), polyvinyl pyrrolidone (PVP) K30, and glyceryl alcohol as pore-forming additives respectively, the membranes were fabricated with the dope solutions of PVDF/additive/Fe^{3+}/Cu^{2+} when the temperatures of bore liquid/water bath were 60/40˚C. The structures and properties of the membranes were characterized by microscope, measurement of pure water permeability (PWP), bovine serum albumin (BSA) rejection ratios, dry strength test and measurement of porosity. The results suggested that these membranes were single skinned external-pressure membranes. The resultant membranes with different organic additives were born with large and long finger-like macrovoids from inner surface. PVP K30 and glyceryl alcohol made the distribution of Fe^{3+}/Cu^{2+} in PVDF nonuniform. The BSA rejection ratios of the resultant membranes decreased from 91.6 to 87.9 and 80.1% in parallel with the increase in PEG molecular weight from 400 to 6,000 and 20,000 Da, and PWP increased from 35 to 44 and 58 $L\,m^{-2}h^{-1}$ respectively. The optimal organic pore-forming additive is PEG 400. This study will give a reference to fabricate PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes with high PWP, high rejection ratio, and high antifouling properties.

Keywords: Polyvinylidene fluoride; Hollow fiber membranes; Additives; Polyethylene glycol

1. Introduction

The polyvinylidene fluoride (PVDF) is applied in membrane separation technologies, including membrane distillation [1–3], organic/water separation [4], gas absorption and stirring [5], ultrafiltration [6] and so on, as a membrane material with excellent properties of mechanical, weather, chemical, and ultraviolet resistances. But it also has disadvantage such as strong hydrophobicity, low water permeate fluxes, easily polluted by organics when it is applied in water filtrations. So there are many modifications in reports aiming at the disadvantage of PVDF. Liu et al. [7] prepared and characterized a PVDF/nanoγ-Al_2O_3 ultrafiltration membranes by the phase inver-

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sion method. The addition of nano γ-Al_2O_3 increased the viscosity of the complex solution and the surface hydrophilicity of the prepared membranes. Rahimpour et al. [8] prepared and characterized PVDF membranes via immersion precipitation technique and modified by UV photo-grafting of hydrophilic monomers on the top membrane surface. The pure water permeability (PWP) of membranes decreased but the membranes hydrophilicities and the protein rejection ratio were increased by UV photo-grafting of hydrophilic monomers onto the membrane surface. In addition, the antipollution properties and flux recovery of PVDF membrane were all improved. Zhang et al. [9,10] prepared novel heterogeneous catalytic flat-sheet membranes via phase inversion method by adulterating Fenton-like catalysts into casting solution. The prepared PVDF membrane can catalyze H_2O_2 to degrade macromolecular organics to small molecule even harmless matters in water. That is in favor of alleviating fouling and keeping up water permeability of membranes in water treatment. In practice, hollow fiber membranes are popular because of more packing density than flat sheet membranes. Because of more influencing factors on preparations, the casting processes of hollow fiber membranes are different from that of flat sheet membranes, so the preparations of catalytic hollow fiber membranes need more careful investigations.

The Fenton-like catalysts can be loaded on PVDF according to the preceding studies. PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes were prepared via dry-jet wet phase-inversion method in this study, and the effects of different pore-forming additives on membrane morphologies, permeabilities, and mechanical properties were studied. The morphologies of PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes were characterization by microscope. The PWP, bovine serum albumin (BSA) rejection ratios, mechanical properties, and overall porosity also were tested.

2. Experimental

2.1. Materials

PVDF (FR-904) powder ($M_w \approx 1.02 \times 10^6$ g mol^{-1}) was obtained from Shanghai 3F new materials Co. Ltd. (China). *N*,*N*-dimethylacetamide (DMAc, AR grade, >99%) was used as the solvent, purchased from SAMSUNG fine chemicals Co. Ltd. (Korea). Polyethylene glycol (PEG) 400 (AR grade, >99%), PEG 6,000 (AR grade, >99%), PEG 20,000 (AR grade, >99%), Fe$(NO_3)_3$·$9H_2O$ (AR grade, >99%), Cu$(NO_3)_2$·$3H_2O$ (AR grade, >99%), glyceryl alcohol (AR grade, >99%)were all supplied by Tianjin Guangfu research institute of fine chemical engineering (China). Polyvinyl pyrrolidone (PVP) K30 and (BSA, M_w = 67,000, >98%) were from BASF fine chemical Co. Ltd. (Germany) and Shanghai Yuanye biotechnology Co. Ltd. (China) respectively. Tap water and deionized water were used as external coagulant and the bore liquid, respectively.

2.2. Preparation of spinning dope

The PVDF powder was dried at 70℃ in electric air oven for over 24 h before used. A desired amount of Fe$(NO_3)_3$·$9H_2O$, Cu$(NO_3)_2$·$3H_2O$ and pore-forming additives were weighed and poured into DMAc solvent to dissolved using conical beaker. Then, the predried PVDF powder was added into the solution to prepare spinning dope at 70℃ with stirring for 5 h to make sure the solution was homogeneous. The dope solution was put into electric air oven at 70℃ overnight for curing. Before spinning, the dope solution was degassed under vacuum in the device of hollow fiber spinning to remove gas bubbles at 70℃ for 4 h.

2.3. Spinning of PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes and post-treatment

PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes were fabricated via dry-jet wet phase-inversion method, which has been described elsewhere [11], and the process parameters and spinning conditions are listed in Table 1. The spinning process involved is as same as reported by other researchers. The deionized water

Table 1
Spinning conditions for the PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes

Process parameters/spinning conditions	Value
Pore-forming additives	PEG 400, PEG 6,000, PEG 20,000, PVP K30 and glyceryl alcohol, respectively
Spinneret outer diameter/inner diameter (mm mm^{-1})	1.5/0.65
Dope solution temperature (℃)	70
External coagulant composition	Tap water
Bore liquid composition	Deionized water
Air gap (cm)	12 ± 1
Take-up speed	Free falling velocity
Ambient temperature (℃)	21 ± 2
Room humidity (%)	81 ± 3

was used as bore liquid to form lumen of the hollow fiber. The spinning dope and bore liquid were fed into the spinneret under the nitrogen pressure of 0.4 MPa. The outer tube diameter and inner tube diameter of the spinneret were 1.5 and 0.65 mm, respectively. After extruded from spinneret, the dope including bore liquid passed a 12 cm air gas and immersed into the external coagulant uprightly to induce the phase separation and solidify the membranes.

The nascent membranes were wound by a winder and washed for 2–3 h in tap water to remove residual DMAc and additives in membranes. Then, the membranes were soaked in 35% wt glyceryl alcohol solution for more than 48 h to replace water in membrane pore for preventing pore collapse and shrinkage. At last, the soaked membranes were dried in air at room temperature before putting away.

2.4. Observation of membrane morphology and porosity measurement

An ordinary optical microscope was used to watch for if the Fe^{3+}/Cu^{2+} in membranes were uniform and membrane morphology. The nascent membranes were sliced to very thin pieces with a sharp razor-blade and examined tangent plane under the ordinary optical microscope quickly before being dried in air.

The overall membrane porosity, $\varepsilon(\%)$, is usually determined by gravimetric method, determining the weight of liquid contained in the membrane pores:

$$\varepsilon = \frac{(w_1 - w_2)/\rho_1}{(w_1 - w_2)/\rho_1 + w_2/\rho_2} \quad (1)$$

where w_1 is the weight of the wetting membrane (g), w_2 is the weight of the dried membrane (g), ρ_1 is the water density when measurements were performed ($g\,cm^{-3}$) and ρ_2 is PVDF density ($g\,cm^{-3}$).

2.5. Measurement of PWP and BSA rejection ratios

Four pieces of dried hollow fiber membranes with 250 mm effective length were assembled into a glass tube to make laboratory-scale modules. The two ends of the bundle of hollow fiber membranes were sealed using solidified epoxy resin. The PWP at and BSA rejection ratios were tested through cross-flow filtration under 0.1 MPa and feed solution was on the shell side. The ultrapure water was prefiltered for 20 min in the module then began to evaluate the volume of water in certain time. After the measurement of PWP, the feed solution was changed to BSA solution of certain concentration to measure BSA rejection ratios. A UV-7504 single-beam ultraviolet-visible spectrophotometer (Shanghai Xinmao instrument Co. Ltd.) was used to measure the concentration of BSA solution at 280 nm. Each sample was measured three times and obtained the average value. The PWP, J ($L\,m^{-2}h^{-1}$), and BSA rejection ratios, $R(\%)$ were calculated according to the following equations:

$$J = \frac{\Delta V}{A\Delta t} \quad (2)$$

where ΔV is the volume of filtered (L), A is the total effective outer surface area of the hollow fiber membranes (m^2), Δt is the sampling time (h).

$$R = \frac{C_f - C_p}{C_f} \quad (3)$$

where C_f is the concentration of the feed ($mg\,L^{-1}$) and C_p is the concentration of the permeate ($mg\,L^{-1}$).

2.6. Membrane mechanical property tests

The tensile strength and elongation at break are used to evaluate the mechanical properties of the synthesized PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes. Every dried sample with 100 mm length was hung and bottom-end was nipped by clip. A very light container was connected with the clip. Then put fine sand into the container slowly until the membranes broke. The ratio of the sum of gravity of the system and fine sand to crossectional area of hollow fiber membrane was the tensile strength. The ratio of the outstretched length when membrane broke to original length was the elongation at break. Each sample was measured three times and obtained the average value.

3. Results and discussion

3.1. Effect of pore-forming additives on membrane morphologies

The codes of membranes using PEG 400, PEG 6,000, PEG 20,000, PVP K30 and glyceryl alcohol as pore-forming additives are M1, M2, M3, M4, and M5, respectively. The colors of M1, M2, and M3 are all brown and M4 and M5 are pale yellow under microscope. Especially, Fe^{3+}/Cu^{2+} distributions in M4 and M5 were extremely heterogeneous, as shown in Fig. 1. The initial concentrations of Fe^{3+}/Cu^{2+} in dope solutions and spinning conditions were same, but that became running off during phase separation and that finally made the colors of M4 and M5. PVP K30 and glyceryl alcohol do not favor to the loading of

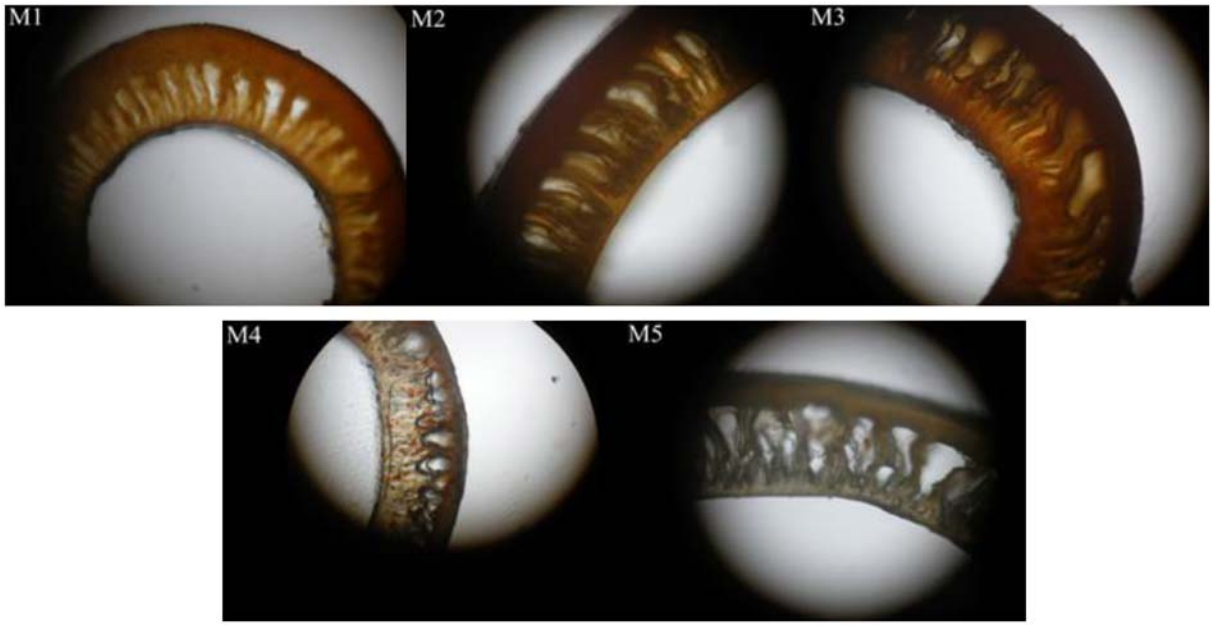

Fig. 1. PVDF/Fe^{3+}/Cu^{2+} hollow fiber membrane morphologies and Fe^{3+}/Cu^{2+} distributions in membranes under ordinary optical microscope.

Fe^{3+}/Cu^{2+} on PVDF. The five membranes were all single-layers and large and long finger-like macrovoids born from inner surface, except different thicknesses and sizes. That proved the membranes were external-pressure membranes.

The additions of additives and higher temperature of bore liquid made a delayed demixing of precipitation [12]. The scanty phase of polymer can enrich and dissolve in bore liquid to form large and long finger-like macrovoids. But the scanty phase of polymer near outer membrane surface had no enough time to enrich and dissolve plenty because of the lower temperature of external coagulant, and the polymer solution solidified fast to form the massive ectosome with spongy-like.

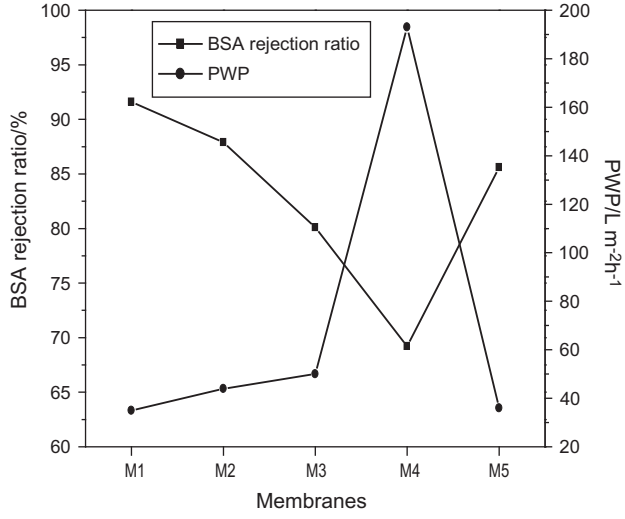

Fig. 2. Effect of PEG (400, 6,000, 20,000), PVP K30 and glyceryl alcohol on PWP and BSA rejection ratios of PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes.

3.2. *Effect of pore-forming additives on porosity, PWP and BSA rejection ratios*

The PWP and BSA rejection ratios under 0.1 MPa with different additives at same spinning conditions can be seen in Fig. 2 and overall membrane porosity in Fig. 3. M4 had the maximum overall membrane porosity and PWP but minimum BSA rejection ratio. This is because PVP K30 had more effect on delaying demixing of precipitation than the other four additives, the porosity and efficient size of membrane pore of M5 was the maximum. The PWP of M5 got close to M1 but BSA rejection ratio was close to M3. The PWP of M1, M2, and M3 were 35, 44, and 58 L $m^{-2}h^{-1}$ by the molecular weight of PEG increasing from 200 to 6,000, 20,000 Da, respectively, and BSA rejection ratios were the opposed order, decreased from 91 to 87.9 and 80.1%. That is because the effect of PEG on delaying demixing of precipitation increased with the increasing of molecular weight of PEG.

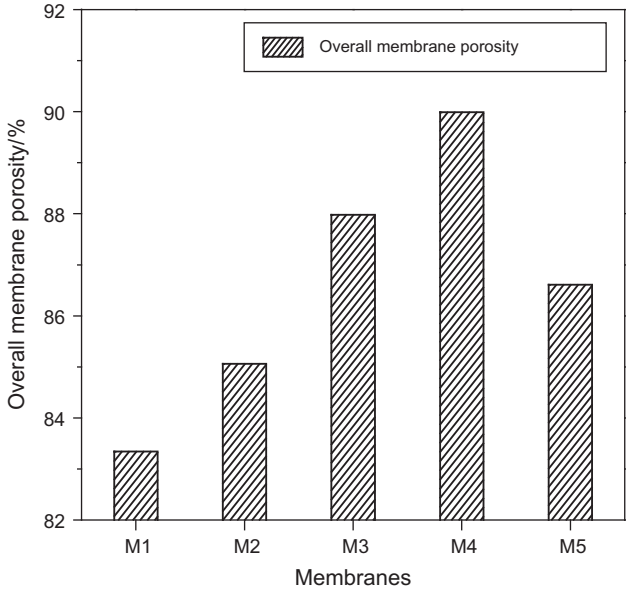

Fig. 3. Effect of PEG (400, 6,000, 20,000), PVP K30 and glyceryl alcohol on porosity of PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes.

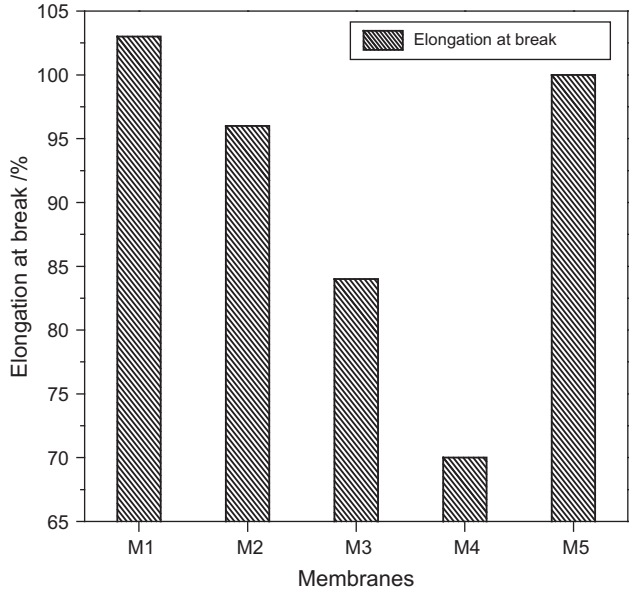

Fig. 5. Effect of PEG (400, 6,000, 20,000), PVP K30 and glyceryl alcohol on elongation at break of PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes.

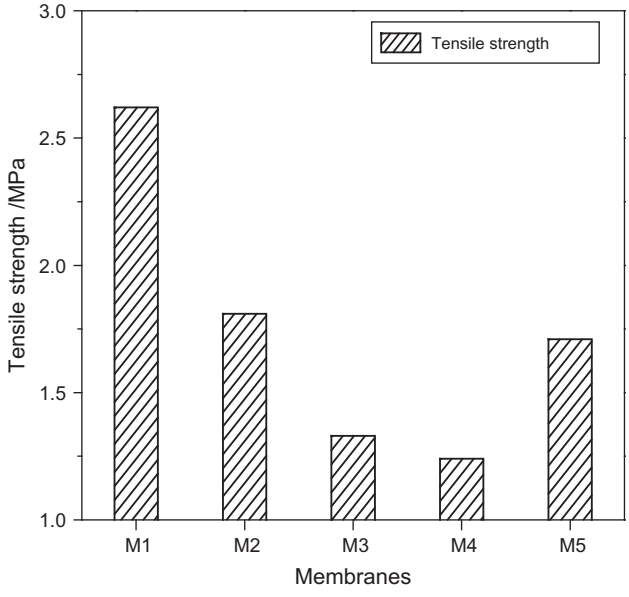

Fig. 4. Effect of PEG (400, 6,000, 20,000), PVP K30 and glyceryl alcohol on tensile strength of PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes.

3.3. Effect of pore-forming additives on mechanical property

Figs. 4 and 5 show the overall membrane tensile strength and elongation at break of membranes spun with different pore-forming additives. The mechanical properties declined with the increasing of molecule weight of PEG and PVP K30 made the worst. This is because different porosity caused a different of aggregation density of polymer chains. The density of prepared membranes decreased with the increasing of overall membrane porosity. The polymer chains were broke easily with less density. So the mechanical properties declined with the increasing porosity.

4. Conclusions

Single-skinned external pressure PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes with different pore-forming additives were prepared via dry-jet wet phase-inversion method. The effects of additives on membrane morphologies, overall porosity, PWP, BSA rejection ratios and mechanical properties were investigated. The additions of PEG, PVP K30, and glyceryl alcohol all formed large and long finger-like macrovoids from inner surface. PVP K30 made a maximum PWP but the worst BSA rejection and mechanical properties. PVP K30 and glyceryl alcohol made distributions of Fe^{3+}/Cu^{2+} in membranes were extremely heterogeneous that would impair the impact of Fenton-like catalyst. The PWP and overall porosity increased with the increase in the molecular weight of PEG, but BSA rejection ratios and mechanical properties were reverse. So PEG 400 was picked as the optimal organic pore-forming additive in future study of PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes with high PWP, high rejection ratio and high anti-fouling properties.

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