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The Influence of PEG Additive on the Morphology of PVDF Ultrafiltration Membranes and Its Antifouling Properties Towards Proteins Separation

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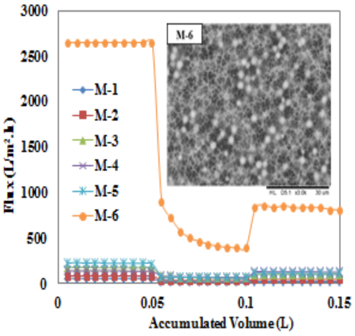
Graphical abstract



Abstract

In the present work, polyvinylidene fluoride (PVDF) ultrafiltration (UF) membranes were prepared by diffusion induced phase separation process (DIPS). N,N'-dimethylformamide (DMF) was used as the solvent and water was used as coagulant. The effect of polyethylene glycol (PEG 2000) concentration in the casting solution on morphology and performance were investigated. The physical properties of PVDF UF membranes were characterized based on pore size distribution, scanning electron microscope (SEM) and contact angle. The permeation performance of the membranes were evaluated in term of pure water flux (PWF), relative flux reduction (RFR), flux recovery ratio (FRR), and bovine serum albumin (BSA) rejection. The pore size distribution increased with the increased in PEG 2000 concentrations, and pure water flux also increased accordingly. The PEG 2000 at concentration of 6 wt.% achieved lowest RFR (50.38%), highest FRR (84.54%) and achieved highest BSA rejection, of 94.55%. This membrane exhibited better antifouling properties as well as improved membrane performance during filtration of BSA due to the optimum pore size, hydrophilic as well as smooth surface.

Keywords: Polyvinylidene fluoride; diffusion induced phase separation; polyethylene glycol; bovine serum albumin; antifouling properties

■1.0 INTRODUCTION

Polyvinylidene fluoride (PVDF) membrane has been widely used in membrane separation due to its outstanding chemical stability, good mechanical properties as well as high thermal stability [1-4]. However, its low surface energy and hydrophobic characteristics impede it with high fouling tendency, which had limited its applications in waste water treatment [5]. There are several ways for preparation of porous polymeric membranes such as solution casting, stretching, track etching and phase inversion. The final membrane morphology varies greatly with the properties of materials and the process condition used [6].

The addition of organic and inorganic components as additive to a casting solution did play an important role in the formation of membrane structure by enlarging or preventing the macrovoid formation, introducing hydrophilicity, enhancing pore formation as well as its pore interconnectivity [7]. The variation of additive concentration or molecular weight can either resulted in pore enlargement or suppression of macrovoid formation [8, 9]. Polymers such as poly(vinyl pyrrolidone) (PVP) and polyethylene glycol (PEG) are widely used as an additive in a casting solution [10]. PEG is less frequently used as additive compared to PVP, however it could plays the similar role as macrovoid suppressor/enlargement and improve membrane hydrophilicity.[9] Han and Nam (2002) had reported the effect of PVP additive on the thermodynamic properties and rheological variation in polysulfone casting solution. The flux increased at low PVP concentration of 5 wt.% but it dropped at higher PVP concentration in the casting solution [11]. Kim and Lee (2004) had also reported an increased in pure water flux and a decreased in rejection by increasing the molecular weight of PEG up to 6 kDa [12]. The addition of PEG 600 in the casting solution increased the exchange rate of solvent and non-solvent during the phase inversion process, resulting in macrovoid formation. At the same time, the pure water flux and equilibrium water content of the membranes were increased while hydraulic permeability was decreased [13].

In this research, different concentration of PEG 2000 was added to the PVDF casting solution. The influences of PEG concentration on membrane morphology and hydrophilicity of the prepared membranes were investigated in detail. The performance of the membranes was investigated by pure water permeation and BSA rejection behavior. Finally, the antifouling properties were evaluated by the percentage of relative flux reduction and flux recovery ratio using ultrafiltration tests.

2.0 EXPERIMENTAL

2.1 Materials

Polyvinylidenefluoride (Solef 6010® PVDF, France) was supplied by Solvay Solexis, was used as the base polymer in the membrane casting solution. Dimethylformamide (DMF), and Polyethylene glycol (PEG) 2000 were purchased from Merck, Germany were used as solvent and the non-solvent pore forming additive in the casting solution, respectively. Bovine Serum Albumin (BSA) was purchased from Sigma Aldrich, used in the solute rejection test. The dipotassium hydrogen phosphate (K_2HPO_4)and potassium dihydrogen phosphate (KH_2PO_4) were purchased from Merck, Germany. Both were used for the preparation of phosphate buffered saline (PBS) pH 7. PVDF was dried in oven at 70ºC before use, while other organic chemicals were obtained in reagent grade and used as received. Distilled water was used for all experiments.

2.2 Membrane Preparation

Table 1 represents the composition of different membranes. Membranes with different composition were designated as M-1, M-2, M-3, M-4, M-5 and M-6. The predetermined amount of PVDF powder and PEG 2000 were dissolved in DMF solvent and stirred at 60-70ºC for 4 hours to ensure a complete dissolution of the polymers. The solution was left to stir overnight at 40ºC to form a homogenous solution. Solvent loss by evaporation was negligible due to the high boiling points of DMF (152-154ºC). The solution was then cast on the tightly woven polyester sheet using Automatic film applicator (Elcometer 4340, E.U.). It was then immediately immersed into the water bath of distilled water and let the phase inversion occur for 24 hours in order to remove the residual solvent. PVDF membrane was kept in distilled water prior to use.

Table 1 Composition of the casting solution

Membranes	Component Compositions		
	PVDF (wt.%)	PEG 2000 (wt.%)	DMF (wt.%)
M-1	18	0	82
M-2	18	2	80
M-3	18	4	78
M-4	18	6	76
M-5	18	8	74
M-6	18	10	72

2.3 Membrane Characterization

2.3.1 Membrane Morphologies

The top surface and cross-sectional morphologies of the PVDF membranes were observed using Hitachi Tabletop Microscope (TM-3000, Tokyo, Japan). The membranes were immersed in liquid nitrogen and fractured carefully to have a clean brittle fracture for cross-sectional images. Membrane samples were mounted on sample stages, using double-sided adhesive tape and were sputter-coated with a thin layer of gold under vacuum using SC 7620 sputter coater (Quorum Technologies, United Kingdom) for 90s to provide electrical conductivity. The samples were examined by using analy mode observation condition.

2.3.2 Pore Size Distribution

The pore size distributions of the membranes were determined by using the Capillary Flow Porometer, Porolux 1000 (Benelux Scientific, Belgium). Perfluoroethers (the pore wetting liquid) was used as a wetting agent. The membrane samples (diameter of 20 mm) were characterized by using a liquid extrusion technique in which the differential gas pressure and flow rates through wet and dry samples were measured and analyzed using the LabView software.

2.3.3 Contact Angle

The membranes surface wettability were performed using water contact angle instrument (Rame-Hart Model 300 Advanced Goniometer) based on sessile drop methods. All membranes film were cut into square coupons and mounted onto glass slides. Water drops were controlled at constant volume using the motor-driven syringe. The acquired images were analyzed using DROPimage software to obtain the measurement of contact angles. Five spots were performed for each membrane and then averaged to minimize experimental errors.

2.4 Dead-end Ultrafiltration Experiments

The UF experiments were performed in a dead-end stirred cell (Amicon 8200, Millipore Co., USA) with a capacity of 200 ml, where the disc membrane has a diameter of 60 mm with a geometric area of 28.27 cm^2 (excluding the area cover by the O-ring). The applied pressure of the filtration system was controlled at 1 bar by N_2 gas and operating temperature was 27±2ºC. The stirring speed was maintained at 300 rpm using the controllable magnetic stirrer (Heidoph MR3000D, Germany). Each membrane was initially compacted for 30 min at 1.5 bars to obtain a stable flux, then the operating pressure was lowered to 1 bar. The pure water flux were measured for every 5 ml of permeate collected.

The pure water flux (J_1) was calculated by Equation (1):

$$J_1 = \frac{V}{A\Delta t} \tag{1}$$

where V is the volume of permeated water, A (m^2) is the membrane area, and Δt (h) is ultrafiltration operation time.

Subsequently, the stirred cell and solution reservoir were emptied and refilled rapidly with model foulant feed solution. The desired concentration of BSA (1 g/L) in the feed solution was achieved by dissolving 1 g of BSA into 1 L of PBS solution at pH 7. The feed solution was stirred at 300rpm using magnetic stirrer (Heidoph MR3000D, Germany) for 30 minutes to ensure a complete dissolution of the BSA and introduced to the solution reservoir of the UF Test Rig. The concentration of BSA in feed and permeate were measured with a UV spectrophotometer, model UV mini-1240 (Shimadzu) at the maximum absorbance of 278 nm. A calibration curve using different solutions containing different concentration of BSA was determined. The flux for the feed solution was recorded as J_p ($L/m^2.h$) based on the water quantity permeating the membranes. The filtration efficiency in removing the BSA from the feed solution was calculated using Equation (2):

$$R\,(\%) = \left[1 - \frac{C_p}{C_0}\right] \times 100 \tag{2}$$

where C_p is the BSA concentration in the permeate and C_0 is the initial concentration of the BSA in the feed.After filtration of the BSA solution, the membrane were washed with distilled water for 10 min and then the water flux of cleaned membrane, J_2 (L/m^2.h) was measured again. Several ratios, including the relative flux reduction (RFR), and flux recovery ratio (*FRR*) were applied to examine the antifouling properties using Equation (3)-(4):

$$RFR = 1 - \frac{J_p}{J_1} \times 100\% \quad (3)$$

$$FRR = \frac{J_2}{J_1} \times 100\% \quad (4)$$

Membranes with lower value of *RFR* and higher value of *FRR* indicated better antifouling properties.

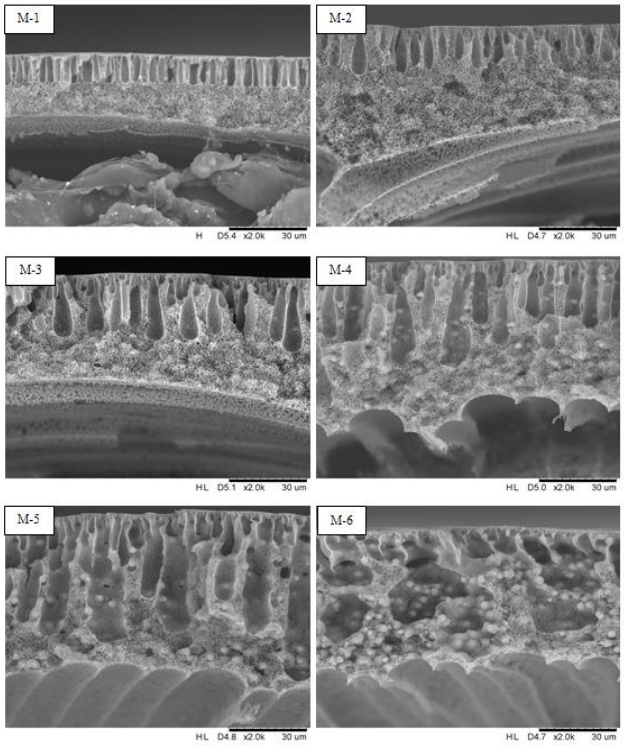


Figure 1 SEM images of the cross-section of PVDF membrane at different PEG 2000 concentration

3.0 RESULTS AND DISCUSSION

3.1 Effect of PEG Concentration on Membrane Structure and Morphology

SEM analysis is an important microscopic technique to provide quantitative information for surface and cross-section of the prepared membranes. Figure 1 shows the SEM cross-section images of different membranes prepared with different PEG 2000 concentration. It can be seen that prepared membranes had asymmetric structure consisting of a dense top skin layer and porous sub layer. The porous sub layer had a top finger-like structure as well as sponge-like structure at the bottom. Generally, with the increasing of PEG 2000 concentration, non-solvent (water) inflow and solvent outflow (DMF) of the top layer is greatly changed. Figure 1 illustrates that at higher PEG 2000 concentration, the length and diameter of the fingerlike structure became larger, which indicating the instantaneous demixing of polymer solution was actually occurred. It could be due to hydrophilic nature of PEG 2000 (high affinity of PEG with water) which increased the inflow rate of water diffusion during phase inversion process, resulting in the enhancement of macrovoid formation [13]. Ma *et al*. (2011) also found the similar phenomenon that larger size of finger-like structures and large voids near to the bottom surface were observed with the increased of PEG concentration [9]. Also it was interesting to note that for PEG content more than 6 wt.%, obvious agglomeration of PEG was noticed. It shows that poor distribution of PEG was actually occurred.

Figure 2 shows the SEM images for the top surface of membranes prepared at different PEG 2000 concentration. From Figure 2, it was observed that membrane surface pores size as well as porosity increased with the increased of PEG 2000 concentration. Membranes M-2 and M-3 exhibited smaller pores distributed evenly at lower PEG concentration. However, the pore size increased significantly with the further increased of PEG 2000 concentration which can be further proven from the pore size distribution as shown in Figure 3. The pore size shows wider distribution at higher PEG 2000 concentration due to agglomerations of PEG 2000 start to occur from 6wt.% onwards. The agglomeration of PEG 2000 entrapped on the membrane surface as well as cross-section which can be seen obviously from the SEM images, resulting in higher surface roughness.

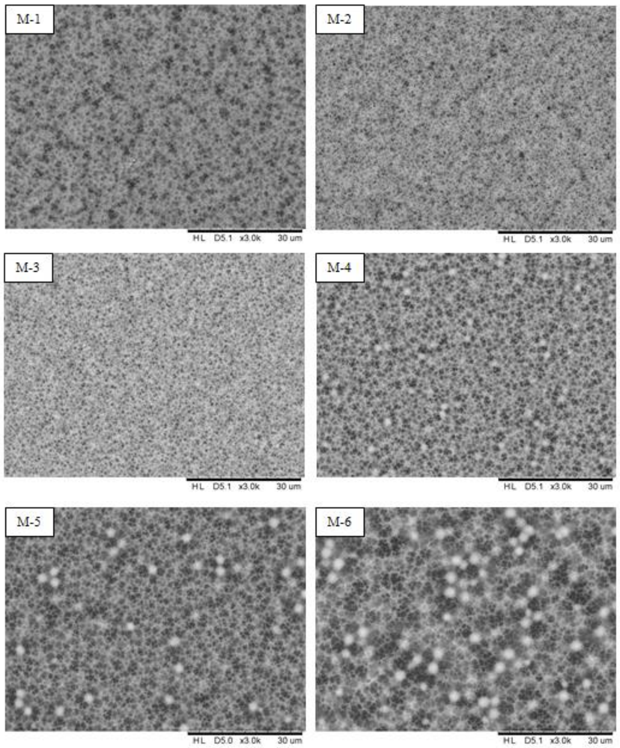


Figure 2 SEM images of the top surface of PVDF membrane at different PEG 2000 concentration

3.2 Effect of PEG Concentration on Membrane Hydrophilicity

Hydrophilicity of the membrane is an important parameter in membrane separation process as it has a close relationship to the membrane permeability and fouling tendency. Figure 4 shows the contact angle of membranes with different PEG 2000 concentration. It can be seen that contact angle had reduce significantly when PEG 2000 was added. The contact angle is 72˚ for pure PVDF membrane and obviously decreased to 64˚ once 2 wt.% of PEG is added. The trace amount of PEG that entrap in the membrane matrix had change the hydrophobic nature of PVDF membrane became more hydrophilic. However, subsequent increased of contact angles at higher PEG concentrations were observed. This might be due to the increased of surface roughness as discussed earlier in Section 3.1. It is an unwanted phenomenon as rougher surface could easily trap foulant which reduce the membrane performance and its antifouling properties [14. Similar phenomenon was found and had been explained in detail in our previous work [15].

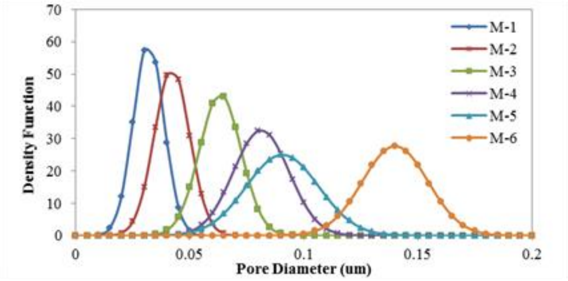


Figure 3 Pore size distribution of PVDF membrane at different PEG 2000 concentration

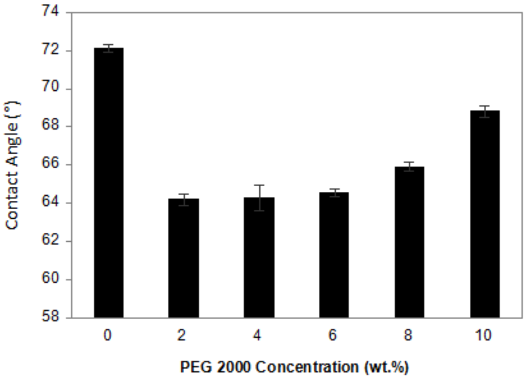


Figure 4 Contact angle of PVDF membrane at different PEG 2000 concentration

3.3 Effect of PEG Concentration on Membrane Permeability, Solute Rejection and Antifouling Behaviour

Permeation test is one of the key specification factors to investigate the structure, morphology and performance of the prepared membranes. The prepared membranes were evaluated in terms of PWF, BSA rejection as well as its antifouling properties. Hydrophilic additive concentrations of pore former, PEG 2000 were varied from 2 wt.% to 10 wt.% for this study. BSA was used as a model protein to investigate the fouling behavior of the prepared membranes. Figure 5 shows that the permeate flux of BSA solution (J_p) was significantly dropped compared with PWF for all prepared membranes which is due to the protein fouling and concentration polarization on membrane surface. Steady flux was observed when the protein adsorption was saturated. The concentration polarization effect can be reduced by rigorous stirring during the filtration of BSA solution [16, 17]. The membranes were washed thoroughly by distilled water flushing, and the water flux of the cleaned membranes was measured again. The PWF, BSA rejection, RFR, and FRR for all membranes with various PEG 2000 concentrations are reported in Table 2. Table 2 shows that when the PEG 2000 concentration increases from 2 wt.% to 10 wt.%, the pure water fluxes increases from 59.26 L/m^2.h to 2923.86 L/m^2.h. The increase in flux with the increase of PEG concentration was due to the increase in pore size and porosity which reduces the permeation resistance of water through membrane. These results also agree well with the SEM and pore size distribution results as discussed in previous section. The widest pore size distribution and largest pore size were observed at PEG concentration of 10 wt.%, which had led to dramatically increased of PWF from 205.84L/m^2.h (M-5) to 2923.86 L/m^2.h (M-6), respectively. PEG in this case could be regarded as pore forming agent rather than a pore reducing agent. It also agrees well with the previous studies on the role of hydrophilic PEG additive as the pore forming agents for enhancing the permeation properties [8, 9]. Although larger pore size will favor high PWF, the solute rejection was drastically decrease from 93.28% (M-5) to 26.9% (M-6), accordingly due to the wider pore size formed.

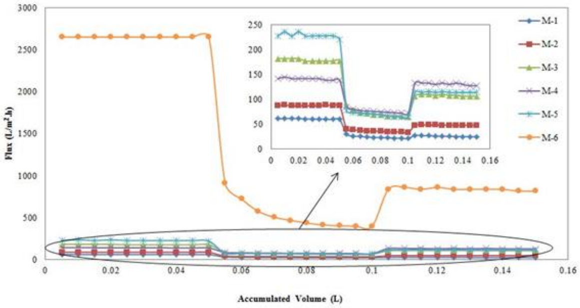


Figure 5 The variations of the fluxes with the accumulated volume for PVDF membrane at different PEG 2000 concentration. The ultrafiltration process includes three steps: pure water permeation, BSA solution filtration, and pure water permeation of the cleaned membranes

■4.0 CONCLUSION

PVDF UF membranes were prepared from casting solution containing 18 wt.% of PVDF and 82 wt.% of DMF using diffusion induced phase separation process (DIPS). Different concentration of PEG at average molecular weight of 2000 Da was used as additive. The effects of PEG 2000 concentration on the membrane morphology and properties such as pore size distribution and contact angle were studied. The permeation tests of prepared membranes were evaluated in term of PWF, BSA rejection as well as its antifouling properties. It was found out that all the prepared membranes have asymmetric structure as shown in SEM figures. The addition of PEG 2000 increased the inflow rate of water diffusion during phase inversion process, resulting the formation of fingerlike structure and subsequently macrovoid formation. The surface hydrophilicity was greatly enhanced once the PEG 2000 was added. The PWF was remarkably elevated with the increasing of PEG 2000 concentration due to higher pore size and porosity of the prepared membranes. The PEG 2000 additives at concentration of 6 wt.% achieved lowest RFR (50.38%), highest FRR (84.54%) and achieved highest BSA rejection, of 94.55% among all the prepared membranes, which exhibited significantly improved antifouling.

Table 2 Permeation test and antifouling properties of PVDF membrane at different PEG 2000 concentrations

Membranes	PWF (L/m^2.h)	BSA Rejection (%)	RFR (%)	FRR (%)
M-1	59.26 ± 1.90	85.41 ± 0.90	66.03 ± 1.65	45.20 ± 2.19
M-2	85.36 ± 1.86	80.32 ± 2.26	61.78 ± 0.45	55.30 ± 0.71
M-3	178.74 ± 4.48	78.16 ± 0.45	63.84 ± 1.12	59.76 ± 0.60
M-4	146.70 ± 8.28	94.55 ± 0.77	50.38 ± 2.68	84.54 ± 4.07
M-5	205.84 ± 38.90	93.28 ± 0.65	72.83 ± 2.42	49.42 ± 2.36
M-6	2923.86 ± 153.27	26.90 ± 2.04	86.40 ± 1.40	30.09 ± 0.68

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