*Desalination and Water Treatment*
www.deswater.com

doi: 10.1080/19443994.2015.1051123

57 (2016) 12090–12098
June

Taylor & Francis
Taylor & Francis Group

# Enhanced separation performance of PVDF/PAN blend membrane based on PVP tuning

Arezou Anvari[a], Aliakbar Safekordi[a], Mahmood Hemmati[b], Fatemeh Rekabdar[b,*], Maryam Tavakolmoghadam[b], Amir Azimi Yancheshme[a], Ali Gheshlaghi[b]

[a]*Chemical Engineering Department, Sharif University, Tehran, Iran, Tel. +98 2166161; emails: arezu.anvari@gmail.com (A. Anvari), safekordi@sharif.edu (A. Safekordi), amirazimi.y@gmail.com (A. Azimi Yancheshme)*
[b]*Research Institute of Petroleum Industry, Tehran, Iran, Tel. +98 2148253109; emails: hemmatim@ripi.ir (M. Hemmati), rekabdarf@ripi.ir (F. Rekabdar), tavakolm@ripi.ir (M. Tavakolmoghadam), gheshlaghia@ripi.ir (A. Gheshlaghi)*

Received 12 July 2014; Accepted 4 May 2015

---

## ABSTRACT

Ultrafiltration (UF) membranes were prepared from blends of poly(vinylidene fluoride) (PVDF)/polyacrylonitrile (PAN) via phase inversion method induced by immersion precipitation. Polyvinylpyrrolidone (PVP) was used as pore former and hydrophilic polymeric additive. N,N-dimethylacetamide (DMAc) and water were used as solvent and coagulant (non-solvent), respectively. The effect of different concentrations of PVP on the morphology and performance of the prepared membranes was investigated. Performance of the membranes was evaluated based on pure water flux and filtration of buffered bovine serum albumin (BSA) solution. The contact angle measurements indicated that the hydrophilicity of PVDF/PAN membranes improved by increasing the PVP concentration in the casting solution. However, such improvement was limited to PVP concentration of the casting solution up to 4 (wt.%) and then decreased by further addition of PVP. According to the obtained results, the rejection of BSA decreased with increase in the PVP concentration in the casting solution. The morphology of the prepared membranes was studied by scanning electron microscopy.

*Keywords:* Polymeric blend membrane; PVDF/PAN; Phase inversion; PVP; Separation performance

---

## 1. Introduction

The most widely used technique for fabrication of asymmetric polymeric membranes is the phase inversion method, in which the solvent of the cast film is exchanged with the non-solvent and phase separation occurs in the coagulation bath [1,2]. In order to obtain a membrane with the desired morphology and performance, phase inversion process should be properly controlled [3,4]. One of the important key factors affecting the morphology and performance of the prepared membranes is the composition (weight percent of the component such as additives) of the casting solution [5].

Among various polymeric materials, poly(vinylidene fluoride) (PVDF) has become one of the most widely employed membrane materials for wastewater treatment due to its good thermal and mechanical

---

*Corresponding author.

stability, great antioxidation, superior resistance to solvent, and strong chemical resistance to acids, alkalis, and bacteria. Since PVDF easily dissolves in conventional organic solvents, the phase inversion method is known as the most common method for producing PVDF membranes [6].

PVDF membranes go through fouling, permeability decline, substantial energy consumption, and high operational costs because of hydrophobicity as a main disadvantage which has limited their widespread application [7–9]. As revealed by many researchers, the membrane fouling can be remarkably reduced by increasing the hydrophilicity as well as the pore walls of the membranes [6,10]. Therefore, various methods including blending, coating, adsorption, chemical grafting, and radiation-induced grafting have been employed to modify the membrane surface using hydrophilic additives [6,11,12]. Among these methods, polymer blending is more interested due to its facility and high efficiency to obtain new types of materials with properties intermediate between those of the pure components [8]. Many researchers have investigated the blending of PVDF with polyethersulfone [8], poly(vinyl butyral) [9], sulfonated polycarbonate [13], poly(styrene sulfonic acid) [14], poly(methyl methacrylate) [15], perfluorosulfonic acid [16], cellulose acetate [17], cellulose acetate propionate [18], and polyvinyl alcohol (PVA) [19]. Polyacrylonitrile (PAN) is a hydrophilic polymer which has relatively low price and good aging-resisting property [5,20,21]. A few studies have also been done on preparing membranes by blending poly(vinylidene fluoride) with polyacrylonitrile [20,22,23].

In most of the researches about PVDF membranes, the aim was first to investigate the effect of the preparation parameters, including dope compositions, additives, coagulation medium, bath temperature, and evaporation time on the membrane morphology and second to find a correlation between the membrane morphology and its performance [6]. The most common additives that have been used in the fabrication of PVDF membranes are polymeric additives such as poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG), weak non-solvents such as glycerol, weak cosolvents such as ethanol and acetone, and low-molecular-weight inorganic salts such as lithium chloride (LiCl) and lithium perchlorate (LiClO). The effects of these additives on the resulting PVDF membrane morphology have been reported in various publications [6,24].

The addition of PVP and PEG has been reported to favor macrovoid formation in the fabrication of PVDF membrane [24]. The addition of PVP as an additive has been investigated in previous researches such as PVDF/additives (i.e. ethanol, glycerol, lithium chloride, lithium perchlorate, water, and PVP (as pore former)) [24], PVDF/PVP [25–27], and PVDF/PES/PVP [8].

To our best knowledge, the effect of PVP addition to PVDF/PAN blend to prepare ultrafiltration (UF) membranes has not been investigated, while its effect on pure water flux (PWF) is significant according to our results. In this work, the suitable concentration of PVP in the PVDF/PAN casting solution has been determined.

In this study, the effect of poly(vinyl pyrrolidone) (PVP) on the performance of PVDF/PAN blend membrane has been studied. The effects of different weight percentages of PVP in the casting solution of PVDF/PAN blend on morphology, hydrophilicity, and performance of the prepared membranes were investigated by scanning electron microscopy (SEM), contact angle measurements, and UF using a cross-flow setup.

## 2. Experimental

### 2.1. Materials

Polyvinylidene fluoride (PVDF with MW = 573,000 Da) was supplied by Solvay. Polyacrylonitrile (PAN, $T_g$ = 85°C, MW = 150,000 Da) was obtained from Aldrich. N,N-dimethylacetamide (DMAc) was supplied as solvent from Merck (Germany). The polymeric additive polyvinylpyrrolidone (PVP, MW = 25,000 Da) supplied by Merck was used as a pore former in the casting solutions. Deionized water was used as the main non-solvent in the coagulation bath. Bovine serum albumin (BSA, MW = 67,000 g/mol) obtained from Merck was used as a model protein feed solution. PEG (MW = 35,000 Da) and PEO (MW = 100,000 Da) were supplied by Aldrich.

### 2.2. Membrane preparation

PAN was dissolved in DMAc and stirred for 24 h at 50°C to form a homogeneous solution. Then, PVDF was added to the solution. Finally, PVP additive was added to the PVDF/PAN solution and mixed to form a homogeneous solution. The viscosity of the prepared casting solution was measured using a Polyvisc digital rheometer (Model Anton paar, model Physica MCR 5, 1) at constant temperature of 25°C. Then, the prepared solution was cast by a casting knife adjusted at 250°μm thickness. The casted film was moved to a distilled water bath to induce precipitation. Different casting solutions were prepared as presented in Table 1.

Table 1
The composition of casting solution

| Membrane code | PVDF/PAN (wt.%) 90/10 | PVP (wt.%) | DMAC (wt.%) |
|---|---|---|---|
| PA | 18 | 0 | 82 |
| PAP2 | 18 | 2 | 80 |
| PAP4 | 18 | 4 | 78 |
| PAP6 | 18 | 6 | 76 |

## 2.3. Membrane characterization

### 2.3.1. Contact angle measurement

Contact angle between water and the surface of the membranes was directly measured using a contact angle measuring instrument (OCA 15 plus) to evaluate their hydrophilicity. All the measurements were taken at room temperature with de-ionized water as the probe liquid. In order to minimize the experimental error, the contact angle was measured at four random points of each sample and the average values were reported.

### 2.3.2. Scanning electron microscopy (SEM)

A model VEGA3 (TESCAN, Czech republic) SEM was used to observe the cross-sectional area of the dry membranes. Samples were fractured in liquid nitrogen, and then, they were torn using tweezers. Samples were coated with a thin layer (80 Å) of gold in a Hummer VII sputtering system (Anatech, Springfield).

The presence of PAN on the surface of the membrane and its dispersion were detected by energy-dispersive X-ray spectroscopy (EDX).

### 2.3.3. Porosity determination

Membrane porosity ($\varepsilon$, %) was determined by gravimetric method as follows [7]:

$$\varepsilon = \frac{m_1 - m_2}{\rho_w \cdot A \cdot L} \tag{1}$$

where $m_1$ (g) is the weight of the wet membrane, $m_2$ (g) is the weight of the membrane dried at 60℃ for 24 h, $\rho_w$ is the density of pure water (0.998 g/cm$^3$), $A$ is the effective surface (cm$^2$) of the membrane which is 4 cm$^2$ in this work, and $L$ is the thickness (μm) of the wet membrane.

### 2.3.4. Permeation experiment

The prepared membranes were evaluated by UF cross-flow filtration setup. The system components were pump, valves, reservoir, pressure regulator, flowmeter, and a membrane cell.

Permeate stream through membrane was gathered and weighted. Retentate stream was circulated to the reservoir. The effective area of the membrane in the experimental cell was 33.3 cm$^2$. A schematic of the system is shown in Fig. 1.

Compaction and conditioning of the prepared membranes were carried out by performing filtration test for 1 h at a transmembrane pressure (TMP) of 200 kPa. Then, the membrane permeability was measured.

The PWF of the membrane in steady state condition, and at a pressure of 100 kPa and a feed flow rate of 6 L/min, was calculated by the following equation [5]:

$$J_{w_1} = \frac{V}{A \cdot \Delta t} \tag{2}$$

where $J_{w_1}$ $\left(\frac{\mathrm{L}}{\mathrm{m^2h}}\right)$ is the pure water flux, $V$ (L) is the volume of permeate stream through membrane, $A$ (m$^2$) is the area of the membrane, and $\Delta t$ (h) is the permeability measurement time.

In order to reduce the experimental errors, calculation of each flux was repeated three times.

### 2.3.5. Solution rejection and analysis of membrane fouling

To investigate the membrane fouling, filtration experiments were performed using protein solution. This solution was prepared from buffered BSA dissolved in de-ionized water to obtain the concentration of 1 g/L. The concentration of the protein in all experiments was fixed at 1 g/L. Phosphate-buffer saline (PBS) was used to keep the pH of solution at 7.2. The flux of the protein solution ($J_p$) was calculated by

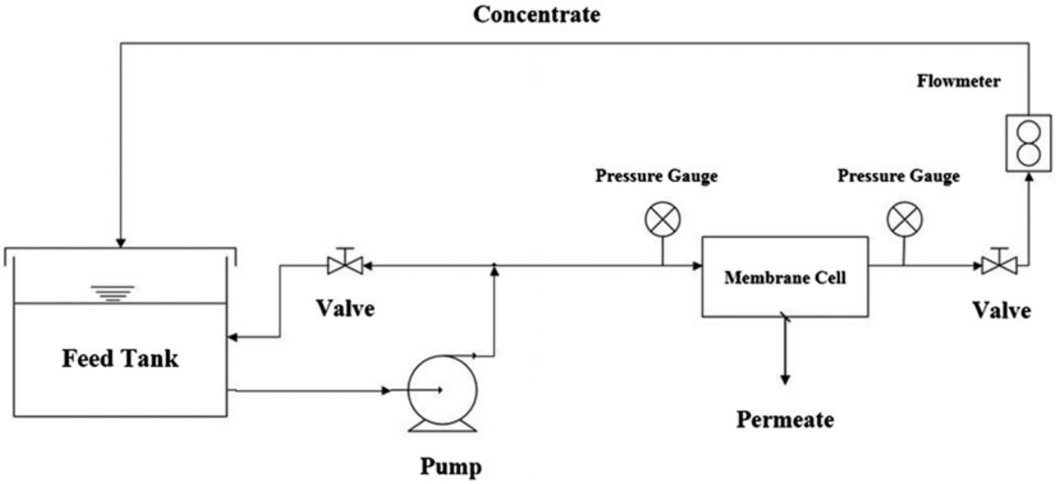


Fig. 1. Cross-flow filtration setup.

Eq. (2). BSA rejections of the membranes were obtained from the following equation [5]:

$$R(\%) = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100 \tag{3}$$

where $C_p$ and $C_f$ are protein concentrations in permeate and feed solution, respectively. In order to determine the BSA concentration, UV spectrophotometer (Shimadzu UVmini-1240) in 280 nm was employed.

After filtration of protein solution, membranes were washed by de-ionized water for two times. Then, PWF of the washed membranes was measured and calculated using Eq. (2).

For fouling analysis of the membranes, flux recovery ratio (FRR) was determined by the following relation [5]:

$$\text{FRR}\ (\%) = \left(\frac{J_{w_2}}{J_{w_1}}\right) \times 100 \tag{4}$$

Fouling resistant potential of blend membranes was estimated using resistance ratios. The first ratio was $R_t$ which was defined as follows [5]:

$$R_t = 1 - \frac{J_p}{J_{w_1}} \tag{5}$$

$R_t$ represents the total decrease in flux due to the total fouling. $R_r$ and $R_{ir}$ were defined as following to determine the flux reduction due to the reversible and irreversible fouling, respectively [5]:

$$R_r = \frac{J_{w_2} - J_p}{J_{w_1}} \tag{6}$$

$$R_{ir} = \frac{J_{w_1} - J_{w_2}}{J_{w_1}} \tag{7}$$

where $R_t$ is the sum of $R_r$ and $R_{ir}$:

$$R_t = R_r + R_{ir} = \frac{J_{w_1} - J_p}{J_{w_1}} \times 100 \tag{8}$$

### 2.3.6. Molecular weight cutoff (MWCO) measurement

The MWCO is defined as the lowest molecular weight which has a solute rejection of 80–100%. MWCO of all membranes was measured using 1 wt.% polyethylene glycols (PEG) with molecular weights 35, 68, and 100 kDa in water by UF cross-flow system. The PEG concentration in feed and permeate samples was determined using a UV–visible spectrophotometer at a wavelength of 535 nm [18].

## 3. Results and discussion

### 3.1. Preparation and characterization of PVDF/PAN membranes

Different PVDF/PAN blend membranes were made via phase inversion method. Fig. 2 shows the effect of PAN content on the pure water flux and rejection of the blend membranes. PWF of the membranes increases

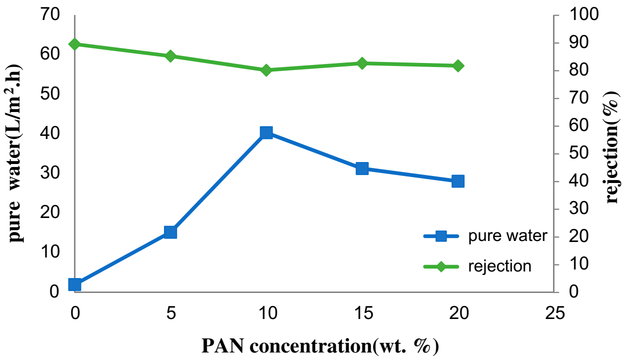


Fig. 2. Effect of PAN content on membrane performance.

gradually with increasing PAN content, while rejection decreases. When the PAN content reaches 10 wt.%, the membrane shows the best separation performance. Therefore, the PVDF/PAN content is fixed at 90/10 wt.% for further investigations.

Actually, PVP plays a key role in controlling the pore size and miscibility of PVDF/PAN blends as it can increase the compatibility of the two-blend polymers [28]. The compatibility of blend polymers is controlled either by the disentanglement of the polymer chains or by the diffusion of the chains through a boundary layer adjacent to the polymer–solvent interface. Since polymer chains are long and mutually entangled, they are inhibited from entering the liquid phase due to the dynamic friction between the chains. In this regard, one of the factors which can control the dissolution rate in polymeric systems is the rate at which the polymer chains disengage themselves from the gel–liquid interface [29]. Hence, an increase in the PVP concentration of the casting solution favors membranes with a more open network structure than that occurring in the absence of PVP [28]. In other words, PVP addition to the casting solution improves disentanglement of the two-blend polymer chains (PVDF/PAN) and consequently increases their compatibility. In casting solutions which contain PVP, the formation of a homogenous solution is accelerated due to better compatibility of polymers. This implies that PVP has a positive effect on the miscibility of PVDF/PAN in the solvent.

### 3.2. *Effect of PVP as an additive on hydrophilicity, morphology, and permeability of the prepared membranes*

As shown in Table 2, increasing the PVP concentration of the casting solution reduces the contact angle of the prepared membranes. It can be concluded that the blend membranes with PVP exhibit more hydrophilic properties than the membrane without PVP. During phase inversion process, PVP dissolves in water and forms macrovoids. However, it should be noted that the molecular weight of PVP used in this study was not relatively low, and therefore, it was not completely removed from the polymer matrix during the solvent and non-solvent exchange. As a result, some PVP was trapped in the membrane structure. This is the reason for improved hydrophilicity of the membrane prepared using PVP as an additive; consequently, the remaining PVP in the membrane matrix is directly correlated with the increased hydrophilicity. This phenomenon has been observed in previous researches too [30,31].

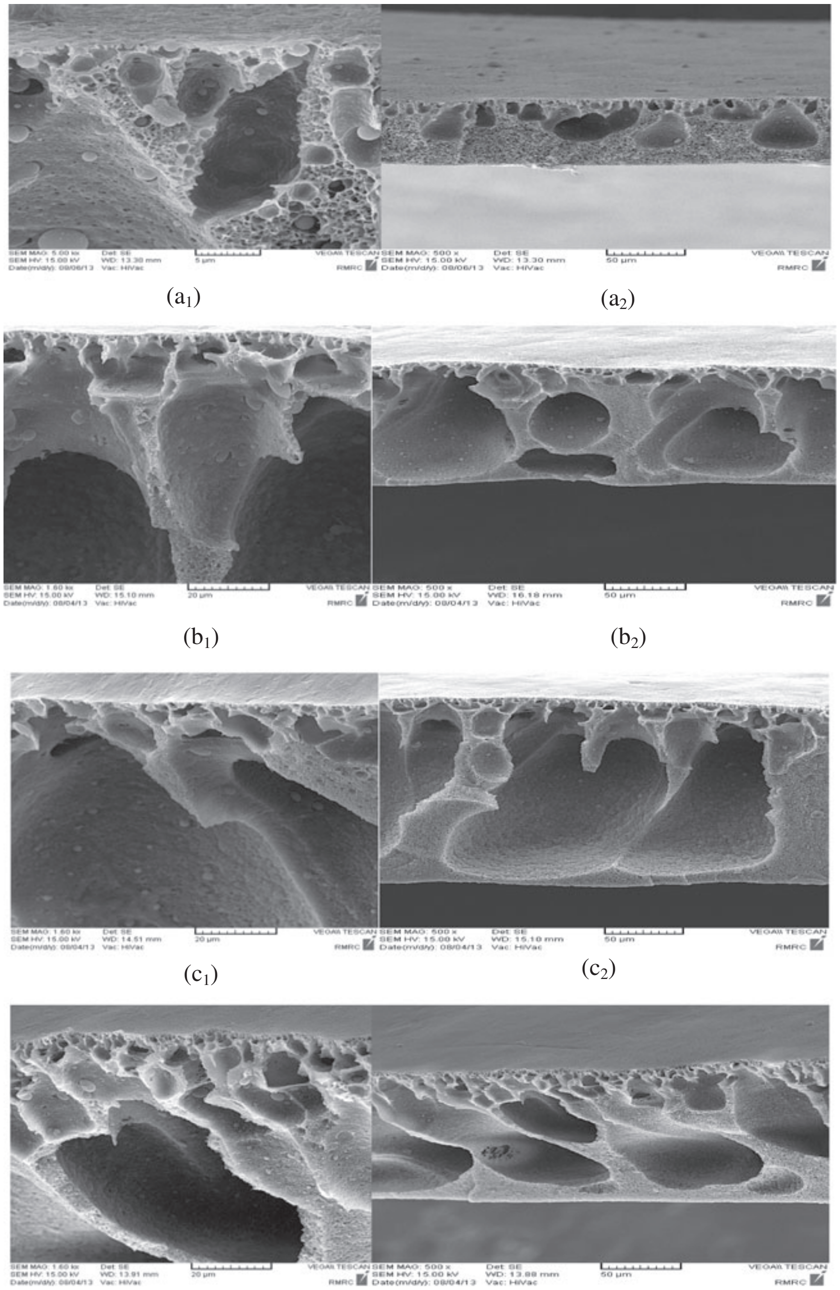
The results of SEM images of the membranes prepared from PVDF/PAN/PVP are shown in Fig. 3. According to these images, the membrane prepared without PVP (Fig. 1(a)) has a finger-like structure with a sponge-like structure in its sub layer. As seen in Fig. 3(b)–(d), PVP addition up to 4 wt.% causes macrovoid formation and thinner skin layer of the membrane. It is obvious from Fig. 3 that the porosity of the membrane first increases by PVP addition up to 4 wt.%, but then decreases by further addition of PVP. It is consistent with the calculated values of porosity in Table 2. The decrease in porosity for PVP percentages greater than 4 wt.% is due to a significant increase in the viscosity of the casting solution (Table 2). The viscosity increment causes a decrease in the solvent and non-solvent exchange rate during the phase inversion process. PVP addition increases the viscosity of the casting solution. Higher viscosity of the cast film results in slower exchange rate of the solvent and non-solvent during the membrane formation process in the coagulation bath, and this consequently hinders instantaneous de-mixing [30]. This can lead to delayed de-mixing and subsequently suppression of macrovoids and formation of a denser structure.

According to Fig. 4, by increasing PVP up to 4 wt.%, PWF increases and BSA rejection decreases. It should be noted that PWF depends on both membrane porosity and also membrane hydrophilicity [30]. As mentioned above and according to Table 2, increasing PVP up to 6 wt.% always increases the membrane hydrophilicity. Hence, the mentioned reduction in PWF by adding more than 4 wt.% PVP cannot be related to the membrane hydrophilicity and can only be related to the membrane porosity.

When PVP concentration is 4 wt.%, the pure water flux and BSA rejection reach the maximum and minimum level, respectively. It can be observed from image c in Fig. 3 that pores have the maximum length and are stretched to the bottom of the membrane which is due to the structure of higher porosity.

Table 2
Contact angle, viscosity, and porosity of membranes

| Membrane | Contact angle ($\theta$) | Porosity | Viscosity of casting solution (Pa s) |
|---|---|---|---|
| PA | 64.4 ± 0.15 | 61.57 | 34 |
| PAP2 | 63.1 ± 0.34 | 88.4 | 41.2 |
| PAP4 | 61.2 ± 0.66 | 93.97 | 58.2 |
| PAP6 | 60.0 ± 0.36 | 86.31 | 79.4 |


(a$_1$) (a$_2$)

(b$_1$) (b$_2$)

(c$_1$) (c$_2$)

(d$_1$) (d$_2$)

Fig. 3. SEM photographs of PVDF/PAN/PVP membranes prepared from the casting solutions with four different composition of PVP (concentration of PVP (a)–(d) are 0, 2, 4, and 6, respectively).

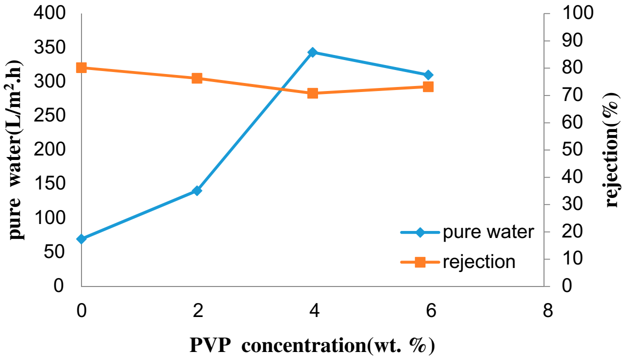


Fig. 4. Pure water flux and retention to BSA of PVDF/PAN/PVP prepared from the casting solutions with different PVP concentration.

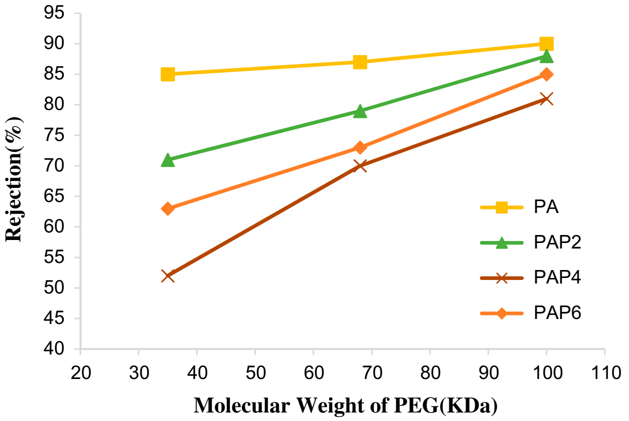


Fig. 5. MWCO analysis of PVDF/PAN/PVP membranes.

According to the calculated values of porosity in Table 2, with increasing PVP concentration up to 6 wt.%, the porosity reduces (Fig. 3), the walls of finger-like pores have a spongy structure and their length and volume are less than pores of membrane with 4 wt.% PVP. As a result, less PWF and more rejection were obtained.

Generally, by adding PVP into casting solution, three cases may happen: First, PVP is immiscible with PVDF and PAN that makes three regions in the casting solution, so the number of microcells is increased by washing out PVP in the skin layer. Second, PVP is a hydrophilic additive with non-solvent properties and by dissolving in water hastens the phase inversion intensity and makes macrovoids [8]. The third situation is related to higher viscosity of the casting solution due to the presence of PVP which slows down phase inversion rate and finally prevents the formation of macrovoids.

So, the final structure of the prepared membrane depends on the priority of instantaneous or delayed de-mixing that may occur in each of the above cases [30]. It can be concluded that for PVP concentrations up to 4 wt.%, the first two cases have dominant roles in the membrane formation. But, when PVP concentration is more than 4 wt.%, the third case has a dominant role. In other words, in this situation (third case), increasing the PVP concentration causes a remarkable increase in the viscosity (Table 2). Similar trends have been observed at concentrations up to 3 wt.% [30] and up to 5 wt.% [8].

### 3.3. Effect of PVP on membrane fouling

To further investigate the membranes fouling behavior, cross-flow protein filtration under constant TMP was performed. Pure water and BSA solution filtration experiments were carried out, and the results are shown in Table 3. The $J_{w_1}$ was obtained by pure water filtrated through the membranes until a steady flux. $J_p$ and $J_{w_2}$ are BSA solution flux and PWF after cleaning, respectively. As observed in Table 3, PWF of all the membranes decrease after BSA filtration. This reduction is higher for the membranes prepared with more PVP in the casting solution. For example, PWF decreases from 40.36 ($J_{w_1}$) to 30.1 ($J_{w_2}$) L/m$^2$ h (25.42% decrease) for the membrane without PVP, while decreases from 343.27 to 250.1 L/m$^2$ h (27.14% decrease) for the membrane with 4 wt.% PVP. It demonstrates that membranes with PVP have larger pores which cause more decrease of PWF. It should be considered that by adding PVP up to 6 wt.%, due to

Table 3
Antifouling properties of PVDF/PAN/PVP membranes

| Membrane | $J_{w_1}\left(\frac{L}{m^2\,h}\right)$ | $J_p\left(\frac{L}{m^2\,h}\right)$ | $J_{w_2}\left(\frac{L}{m^2\,h}\right)$ | $R_r$ | $R_{ir}$ | $R_t$ | FRR (%) |
|---|---|---|---|---|---|---|---|
| PA | 40.36 | 21.5 | 30.10 | 0.213 | 0.254 | 0.467 | 74.58 |
| PAP2 | 140.32 | 79.5 | 102.50 | 0.164 | 0.270 | 0.434 | 73.04 |
| PAP4 | 343.27 | 198.87 | 250.1 | 0.149 | 0.271 | 0.42 | 72.85 |
| PAP6 | 310.10 | 176.30 | 231.2 | 0.177 | 0.254 | 0.431 | 74.56 |

formation of a denser structure, the decrease in PWF is lower than other percentages of increase in PVP.

Reversible ($R_r$) and irreversible ($R_{ir}$) resistances and flux recoveries (FRR) of the prepared membranes are also shown in Table 3. $R_r$ decreases by increasing the percentage of PVP due to the improvement in hydrophilicity. As mentioned before, membranes with PVP (up to 4 wt.%) have larger pores and consequently higher decrease in PWF, so it results in higher $R_{ir}$ and lower FRR. In contrast, membranes with 6 wt.% PVP which are spongy have lower $R_{ir}$ and higher FRR compared to other membranes with less PVP. Finally, the total resistance is almost constant as the improvement in hydrophilicity and larger pores neutralize each other, and no net difference is observed in the total resistance.

### 3.4. MWCO measurement

The effect of adding PVP on the pore size of the top surface of all membranes was further investigated by determining the MWCOs using PEG as test solutes. As shown in Fig. 5, addition of PVP causes less rejection rate than PVDF/PAN membrane without PVP. Particularly, PAP4 has even lower rejection rate than all of the membranes. The rejection rate is more dependent on the denseness of the skin layer rather than the porosity of the membrane [18]. Thus, the reason for PAP4 minimum rejection is the thinner skin layers of PAP4 compared to other blend membranes, which is in agreement with PWF values. These results confirm that the addition of PVP causes size enlargement of surface pores of the membrane.

## 4. Conclusions

Various blend membranes with different PVP concentrations were prepared, and their morphology and separation performance were evaluated. It was found out that addition of PVP to the cast film solution up to 4 wt.% results in an increase in the macrovoids formation and PWF. But, further addition of PVP (from 4 to 6 wt.%) restrains macrovoids formation and subsequently reduces the flux. The results showed that addition of PVP can reduce the contact angle of the blend membrane. Increment of the porosity value of 93.97% was observed by PVP addition up to 4 wt.%. However, further addition of PVP will result in an increase in viscosity (79.4 Pa s), and consequently, a reduction in porosity and PWF occurs.

It can be concluded that larger finger-like pores and a thinner skin layer formed in the membrane prepared from the casting solution with 4 wt.% PVP result in maximum pure water flux.

## References

[1] K. Scott, Handbook of Industrial Membranes, second ed., Elsevier Advanced Technology, Oxford, 1998.

[2] A. Bottino, G. Camera-Roda, G. Capannelli, S. Munari, The formation of microporous polyvinylidene difluoride membranes by phase separation, J. Membr. Sci. 57 (1991) 1–20.

[3] M. Mulder, Basic Principles of Membrane Technology, second ed., Kluwer Academic Publishers, London, 1996.

[4] S. Judd, B. Jefferson, Membranes for Industrial Wastewater Recovery and Re-use, Elsevier Advanced Technology, Oxford, UK, 2003.

[5] M. Amirilargani, A. Sabetghadam, T. Mohammadi, Polyethersulfone/polyacrylonitrile blend ultrafiltration membranes with different molecular weight of polyethylene glycol: Preparation, morphology and antifouling properties, Polym. Adv. Technol. 23 (2012) 398–407.

[6] F. Liu, N.A. Hashim, Y. Liu, M.R.M. Abed, K. Li, Progress in the production and modification of PVDF membranes: Review, J. Membr. Sci. 375 (2011) 1–27.

[7] Y. Wei, H.Q. Chu, B.Z. Dong, X. Li, S.J. Xia, Z.M. Qiang, Effect of $TiO_2$ nanowire addition on PVDF ultrafiltration membrane performance, Desalination 272 (2011) 90–97.

[8] L. Wu, J. Sun, Q. Wang, Poly(vinylidene fluoride)/polyethersulfone blend membranes: Effects of solvent sort, polyethersulfone and polyvinylpyrrolidone concentration on their properties and morphology, J. Membr. Sci. 285 (2006) 290–298.

[9] L. Yan, J. Wang, Development of a new polymer membrane—PVB/PVDF blended membrane, Desalination 281 (2011) 455–461.

[10] Y. Wang, Y. Su, Q. Sun, X. Ma, X. Ma, Z. Jiang, Improved permeation performance of Pluronic F127–polyethersulfone blend ultrafiltration membranes, J. Membr. Sci. 282 (2006) 44–51.

[11] S. Kang, A. Asatekin, A.M. Mayes, M. Elimelech, Protein antifouling mechanisms of PAN UF membranes incorporating PAN-g-PEO, J. Membr. Sci. 296 (2007) 42–50.

[12] Q. Sun, Y. Su, X. Ma, Y. Wang, Z. Jiang, Improved antifouling property of zwitterionic ultrafiltration membrane composed of acrylonitrile and sulfobetaine copolymer, J. Membr. Sci. 285 (2006) 299–305.

[13] M. Masuelli, J. Marchese, N.A. Ochoa, SPC/PVDF membranes for emulsified oily wastewater treatment, J. Membr. Sci. 326 (2009) 688–693.

[14] T. Uragami, M. Fujimoto, M. Sugihara, Studies on syntheses and permeabilities of special polymer membranes. 28. Permeation characteristics and structure of interpolymer membranes from poly (vinylidene fluoride) and poly (styrene sulfonic acid), Desalination 34 (1980) 311–323.

[15] S.P. Nunes, K.V. Peinemann, Ultrafiltration membranes from PVDF/PMMA blends, J. Membr. Sci. 73 (1992) 25–35.

[16] W.Z. Lang, Z.L. Xu, H. Yang, W. Tong, Preparation and characterization of PVDF-PFSA blend hollow fiber UF membrane, J. Membr. Sci. 288 (2007) 123–131.

[17] C. Mu, Y. Su, M. Sun, W. Chen, Z. Jiang, Remarkable improvement of the performance of poly(vinylidene fluoride) microfiltration membranes by the additive of cellulose acetate, J. Membr. Sci. 350 (2010) 293–300.

[18] H.H. Tseng, G.L. Zhuang, Y.C. Su, The effect of blending ratio on the compatibility, morphology, thermal behavior and pure water permeation of asymmetric CAP/PVDF membranes, Desalination 284 (2012) 269–278.

[19] N. Li, C. Xiao, S. An, X. Hu, Preparation and properties of PVDF/PVA hollow fiber membranes, Desalination 250 (2010) 530–537.

[20] Y. Xiuli, C. Hongbin, W. Xiu, Y. Yongxin, Morphology and properties of hollow-fiber membrane made by PAN mixing with small amount of PVDF, J. Membr. Sci. 146 (1998) 179–184.

[21] A. Gu, Study of ultrafiltration membrane made from polyvinyl chloride/polyacrylonitrile blend, Polym. Plast. Technol. Eng. 40 (2001) 615–625.

[22] T.Y. Liu, W.C. Lin, L.Y. Huang, S.Y. Chen, M.C. Yang, Surface characteristics and hemocompatibility of PAN/PVDF blend membranes, J. Polym. Adv. Technol. 16 (2005) 413–419.

[23] M.C. Yang, T.Y. Liu, The permeation performance of polyacrylonitrile/polyvinylidine fluoride blend membranes, J. Membr. Sci. 226 (2003) 119–130.

[24] M.L. Yeow, Y.T. Liu, K. Li, Morphological study of poly(vinylidene fluoride) asymmetric membranes: Effects of the solvent, additive, and dope temperature, J. Polym. Adv. Technol. 92 (2004) 1782–1789.

[25] E. Fontananova, J.C. Jansen, A. Cristiano, E. Curcio, E. Drioli, Effect of additives in the casting solution on the formation of PVDF membranes, Desalination 192 (2006) 190–197.

[26] Q. Bi, Q. Li, Y. Tian, Y. Lin, X. Wang, Hydrophilic modification of poly(vinylidene fluoride) membrane with poly(vinyl pyrrolidone) via a crosslinking reaction, J. Appl. Polym. Sci. 127 (2013) 394–401.

[27] B.J. Cha, J.M. Yang, Effect of high-temperature spinning and PVP additive on the properties of PVDF hollow fiber membranes for microfiltration, Macromol. Res. 14 (2006) 596–602.

[28] M. Sivakumar, R. Malaisamy, C.J. Sajitha, D. Mohan, V. Mohan, R. Rangarajan, Preparation and performance of cellulose acetate–polyurethane blend membranes and their applications—II, J. Membr. Sci. 169 (2000) 215–228.

[29] B.A. Miller-Chou, J.L. Koenig, A review of polymer dissolution, Prog. Polym. Sci. 28 (2003) 1223–1270.

[30] E. Saljoughi, T. Mohammadi, Cellulose acetate (CA)/polyvinylpyrrolidone (PVP) blend asymmetric membranes: Preparation, morphology and performance, Desalination 249 (2009) 850–854.

[31] B. Jung, J.K. Yoon, B. Kim, H.W. Rhee, Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes, J. Membr. Sci. 243 (2004) 45–57.