Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.932707

55 (2015) 1771–1785
August

Taylor & Francis
Taylor & Francis Group

Improved permeation properties of polyacrylonitrile-based ultrafiltration membranes incorporated with poly(vinyl alcohol)

N.A.M. Nazri[a], W.J. Lau[a], A.F. Ismail[a,*], D. Veerasamy[b]

[a]*Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, Skudai 81310, Johor, Malaysia, Tel. +60 7 5535592; Fax: +60 7 5535625; email: afauzi@utm.my*
[b]*Technology and Engineering Division, Rubber Research Institute of Malaysia, Malaysian Rubber Board (MRB), Sungai Buloh 47000, Selangor, Malaysia*

Received 20 October 2013; Accepted 21 May 2014

ABSTRACT

Polyacrylonitrile (PAN)-based hollow fiber membranes were fabricated via a dry/wet phase inversion process with the addition of poly(vinyl alcohol) (PVA). The hollow fiber ultrafiltration (UF) membranes were prepared by varying the weight ratio of PVA:PAN in dope solution followed by investigation on the effect of PVA composition on the UF membrane properties and performance. Protein filtration experiments using bovine serum albumin (BSA) were conducted to study the permeation and anti-fouling properties of the PAN/PVA blend membranes as a function of time. It is found that PAN/PVA blend membranes showed better hydrophilicity than that of pristine PAN membrane. It is also found that the best ratio of PAN:PVA in dope solution is 85:15 in which the membrane exhibited good morphology and was able to achieve excellent pure water flux of 251.37 L/m^2 h bar and BSA rejection of 97%. Nevertheless, it must be pointed out that the presence of excessive PVA composition in dope solution could negatively affect membrane morphology and its performance. For anti-fouling performance, blend membrane prepared from PAN:PVA ratio of 95:5 demonstrated the best fouling resistant among all the membranes studied. Results showed that further increase in the composition of PVA in the PAN membrane did not necessarily enhance anti-fouling properties of UF membrane.

Keywords: Ultrafiltration; Polyacrylonitrile; Poly(vinyl alcohol); Anti-fouling; BSA rejection

1. Introduction

Irreplaceable role of ultrafiltration (UF) membrane has driven its widespread adoption in different applications such as water and wastewater treatment, protein purification, and biomedical applications. The unique advantages of UF membrane such as ambient temperature operation, low pressure, and energy consumption have facilitated the employment of this type of low pressure-driven membrane in many industrial processes. Research interest in UF membrane area has prompted the seeking of efficient modification methods to improve performance of UF membrane in terms of permeation properties and excellent anti-fouling properties. Still, it remains challenging to achieve both ideal dope formulation and preparation conditions that would be cost effective, easy, and also efficient in producing desired membrane properties. In this regard, several modification techniques such as

---

*Corresponding author.

surface grafting hydrophilic species onto membrane surface [1,2], coating [3], and blending with hydrophilic nanoparticles/polymers [4,5] have been introduced in UF membrane technology. Of these techniques available, blending the dope solution with hydrophilic components is the simplest way to enhance simultaneously membrane morphological properties as well as its filtration performance. For instance, Alsalhy [6] studied the effect of polystyrene as a second polymer on poly(vinyl chloride) (PVC) hollow fiber membrane. The resulted blend membrane showed a significant change on morphological properties, which led to the enhancement in membrane mechanical properties and rejection performance as compared with PVC-based membrane. Li et al. [7], on the other hand, have shown the evidences on the improvement of the hydrophilicity and permeability of modified poly(vinylidene fluoride) (PVDF) UF membrane after blending the membrane with hydrophilic poly(vinyl alcohol) (PVA). Instead of hydrophilic PVA, Amirilargani et al. [8] made an attempt to modify polyethersulfone (PES) UF membrane using hydrophilic polyacrylonitrile (PAN) and they found that the performance of the modified PES membrane is exceptionally increased when optimum loading of PAN is present in the dope solution.

PAN is appeared to be one of the important materials in UF membrane area, owing to its good chemical stability, hydrophilicity, and good solubility to common solvents used in fabricating membrane. It has higher degree of hydrophilicity compared with other polymeric materials such as PES, polysulfone (PSF), and polyethylene thus, demonstrating better fouling resistant [9]. Although PAN is hydrophilic in nature, several modification methods have been proposed to further improve its performance in terms of anti-fouling resistance and permeation properties. Commonly, hydrophilic additives such as polyvinylpyrolidone (PVP) and polyethylene glycol (PEG) are introduced into membrane matrix to alter properties of UF membranes. Jung [9] has pointed out that the addition of PVP into PAN-based membranes can change the kinetic behavior of the phase separation which consequently affects morphological properties of the UF membrane and thus its degree of hydrophilicity. With respect to performance, the researcher reported that the permeation properties of the membranes are particularly influenced by the quantity and molecular weight of PVP added. Other published reports have also manifested the properties of PAN membranes blended with other types of additives such as organic acid [10], calcium chloride ($CaCl_2$) [11], and phenolphthalein polyethersulfone (PES-c) [12]. Recent research works on the development of PAN-based UF membrane have interestingly demonstrated the viability of direct blending with amphiphilic copolymer in improving membrane surface properties as well as anti-fouling performance [13–15]. However, synthesis of amphiphilic copolymer may require complicated preparation steps and harsh chemical usage. In this regard, simple blending method with hydrophilic polymer might be the easiest alternative and hold great potential to enhance membrane performance.

PVA which is known as a hydrophilic material and possess excellent film forming ability combining with its physical and chemical stability have made it as a good choice for membrane fabrication [16–18]. However, the solubility of PVA with water resulted from the large amount of hydroxyl groups in PVA infers the disadvantages of easier degradation and elimination after use [19–21] Also, pure PVA has poor stability in the aqueous solutions, which makes it difficult to be used directly without modification [22,23]. Because of this, many modification strategies have been attempted to improve the stability of PVA in membrane matrix which include chemical cross-linking, blending, hybridization, heat treatment, grafting, and interfacial polymerization [24–28]. A burgeoning literature exists on this aspect. For example, cross-linking methods have been studied extensively using various cross-linking agents such as glutaraldehyde (GA) [29,30], formaldehyde [31], sulfur–succinic acid [32], and UV irradiation [33,34].

Mostly found research studies are on utilization of PVA for the preparation of pervaporation, reverse osmosis, and thin-film composite nanofiltration membrane [22,35–38]. It is believed that PVA has immense potential as UF membrane material because of the presence of hydroxyl groups which is favorable for the creation of hydrophilic surfaces, leading to improvement in water permeability, and anti-fouling properties [21,27]. It should be noted that despite the excellent properties of PVA, only a few research groups have studied the incorporation of PVA polymer for UF membrane fabrication. The difficulties in controlling PVA swelling, relatively poor stability of PVA in membrane matrix, and reduced mechanical strength of the resulted membrane upon PVA addition might be the main reasons hindering the application of PVA in UF membrane. Available reports on PVA for UF membrane fabrication have manifested the use of various preparation methods which include cross-linking with various cross-linking agents, coating, hybridization via sol–gel technique, and blending, as summarized in Table 1. It should be noted that quite limited researches have concerned the modification using simple blending method. Yet, this method is facile with minimal preparation steps and can instantaneously modify membrane properties during phase

Table 1
The use of PVA in UF membrane preparation via different preparation method

Membrane	Modification methods for PVA	Ref.
Main polymer: PVDF Additive: PVA[a]	*Direct blending*: Dope solution was prepared by dissolving PVDF/PVA/PEG in DMSO. The solution was then underwent dry-jet wet spinning process to fabricate hollow fiber membranes via phase inversion process	[7]
Main polymer: Acetalized PVA Additive: PEG600[a]	*Acetalization process*: Acetalized PVA was conducted by reaction of PVA with acetaldehyde under an acidic condition (2% acid hydrochloric, HCl); PVA was firstly dissolved in water (90˚C) and cooled down to 15˚C before addition of 2% HCl and 40% acetaldehyde. The acetalized PVA (in powder form) and PEG as additive were then dissolved in DMAc to prepare casting solution	[17]
Main polymer: PSF Coating layer: PVA[b]	*Crosslinking reaction with diidocyanate (TDI)*: PVA solution was pumped into the lumen of PSF hollow fiber membrane by using dead-end filtration process. The membrane was taken out to remove residual solution and incubated in oven (45˚C). Crosslinking step was then took place by allowing TDI solution to flow slowly inside the membrane lumen for a few minutes	[19]
Main polymer: PVA/tetraethoxysilane (TEOS) Additive: PEG[a]	*Hybridization* via *sol–gel technique*: TEOS solution containing 6.9 mL DI water, 0.1 mL HCl, 20 mL TEOS were mixed and stirred for 3 h. Desired amount of PVA and PEG were dissolved in water (95˚C, 6 h) before addition of the TEOS solution. The homogeneous solution was then cast on a glass plate	[20]
Main polymer: PVDF Additive: PVA[a]	*Crosslinking reaction with ferric trichloride*: Desired amount of PVDF, PVA and crosslinking agent (ferric trichloride) was dissolved in DMAc (70˚C, 24 h). The homogeneous solution was then cast on a glass plate	[21]
Main polymer: PES Coating layer: PVA[a]	*Adsorption-crosslinking process*: PVA solution was prepared by dissolving PVA in water at 90˚C. PES membrane was then immersed in the PVA solution for10 min before air-drying. At last, the membrane was immersed in borax solution containing 0.5 wt.% borax and 0.001 N NaOH	[24]
Main polymer: PVA/poly(4-vinylpyridine) P_4VP Additive: silica[a]	*Semi-interpenetrating polymers for preparation of porous PVA/P_4VP membrane*: Homogeneous solution of PVA in aqueous solution and P_4VP in acidic medium were mixed together to achieve ratio of 60/40. This solution was then underwent solvent evaporation to fabricate thin film and the prepared film was later contacted with 1,2-dibromoethane for crosslinking reaction. Silica impregnation was further carried out to modify the membrane	[26]
Main polymer: PES Coating layer: PVA[a]	*Interfacial polymerization with toluene diisocyanate*: Aqueous solution was prepared by mixing solutions of PVA, sodium dodecyl sulphate and NaOH in DI water and toluene diisocyanate in cyclohexane. PES support membrane was then immersed in the homogeneous aqueous solution for interfacial polymerization	[27]
Substrate: electrospun PAN Thin barrier layer: crosslinked PVA[c]	*Crosslinking reaction of PVA onto composite scaffold*: Composite scaffold containing electrospun PAN nanofibrous (supported by PET non-woven) was soaked in 0.8 M boric acid. The scaffold was then fixed and sealed on a glass plate. Crosslinking of PVA onto the composite scaffold was conducted using solution containing PVA/GA	[28]
Main polymer: cellulose ester Coating layer: PVA[a]	*Dynamical coating*: PVA was firstly dissolved in water before it was transferred to a mixture of poly(acrylic acid) (PAA) and GA. The solution was then poured on a filtration cell which was loaded with cellulose ester membrane. Then, the membrane was sandwiched between two glass plates, crosslinked in an oven (50˚C) and was further immersed in DI water to remove PAA	[39]

(*Continued*)

Table 1 (*Continued*)

Membrane	Modification methods for PVA	Ref.
Main polymer: PVDF Coating layer: PVA[a]	*Solid-vapor interfacial crosslinking*: PVA solution was introduced on PVDF membrane surface and was allowed to contact with membrane surface for a given time before being air-dried. GA was sealed in a chamber in which crosslinking reaction on the membrane surface was conducted	[40]
Substrate: electrospun PAN Thin barrier layer: crosslinked PVA-multi-walled carbon nanotubes (MWCNT)[c]	*Crosslinking reaction of PVA onto composite scaffold*: Composite scaffold containing electrospun PAN nanofibrous (supported by PET non-woven) was soaked in 0.8 M boric acid. The scaffold was then fixed and sealed on a glass plate. 2 wt.% coating solution (PVA: 4.0 wt.%, MWCNT: 0.4 wt.%, GA: 0.1 mol/L, HCl: 0.03 mol/L, allowed to react 16–18 min before coating) was cast on the scaffold surface, incubated in oven (16 h) before testing	[41]

[a] Membrane prepared in flat sheet format.

[b] Membrane prepared in hollow fiber format.

[c] Membrane prepared using nanofiber as substrate.

inversion process [6]. A major issue related to blending approach when PVA is used as additive is the lack of stability in which the additive tends to leach out during phase inversion and/or filtration process. It is also difficult to form membrane with desired properties when only PVA is used as main membrane forming material owing to its water solubility characteristic [22,23]. However, it must be pointed out that the behavior of PVA and its impact to UF membrane formation might still depend on various factors such as composition of PVA in dope solution and the type of main membrane material chosen. Since, blending approach might offer the easiest preparation procedure and also cost effectiveness, it is necessary to fully understand the impact of blending with PVA in UF membrane properties and performance.

While major emphasis has been given to more complicated preparation procedure such as cross-linking and coating method, this present study addresses direct blending approach for preparation of PAN-based membrane incorporated with PVA. To the best of our knowledge, none of research study has been conducted to evaluate the performance of blend membrane made of PAN/PVA. Additionally, present work meant to impart greater understanding and to highlight underlying problems associated with preparation of PAN/PVA blend membranes. Thus, the aims of this study were to fabricate hollow fiber UF PAN-based UF membranes incorporated with PVA via simplified blend method and to determine optimum composition of PVA in dope solution in order to produce high-performance UF membranes with excellent anti-fouling properties. A series of analyses using field-emission scanning electron microscope (FESEM), contact angle goniometer, thermo gravimetric analyzer (TGA), differential scanning calorimeter (DSC), and atomic force microsope (AFM) were performed to characterize the hollow fiber membranes. The effect of PVA addition on the membrane permeation and anti-fouling properties was also discussed in detail. These membranes might be useful for the development of UF membrane for application in purification/separation associated with proteinaceous component such as wastewater treatment, biomedical, and food and manufacturing.

2. Experimental

2.1. Materials

PAN-based UF hollow fiber membranes were prepared using PAN (Mw: 150,000 g/mol) purchased from Sigma Aldrich. Dimethyl sulfoxide (DMSO) (ACS grade, assay 99.9%) that was purchased from Sigma Aldrich was used as solvent without purification. PVA with degree of polymerization 1,400 was purchased from Fluka (Mw: 61,000 g/mol). Bovine serum albumin (BSA) (69 kDa) was purchased from Sigma Aldrich.

2.2. Membrane preparation

For dope solution preparation, certain amount of PAN and PVA was added into DMSO solvent that was weighted previously to achieve desired weight ratio of PAN:PVA in dope solution. The composition of dope solution is presented in Table 2. The mixture was continuously stirred using IKA RW20 digital mechanical stirrer at 60°C until it was completely dissolved. The homogeneous solution was then underwent dry-jet wet spinning process to fabricate hollow fiber membranes via phase inversion process. The detailed spinning parameters are listed in Table 3. Spinneret with the outer diameter of 1.10 mm and the inner diameter of 0.55 mm was used in this study to fabricate hollow fiber UF membrane. The extrusion rate of the dope solution was controlled at 4–5 mL/min, while the injection rate of internal coagulant was kept constant at 2.0 mL/min. The nascent hollow fiber emerging from the tip of spinneret and passing through an air gap of 5 cm was guided through two water coagulation baths at take-up velocity of 10.32 cm/s. The take-up velocity was nearly the same as the free falling velocity of the nascent hollow fibers. The resulted membranes were then immersed in water for 3 d, with daily change of water in order to remove residual DMSO solvent and polymeric additives. The as-spun hollow fibers were then post-treated with 10% glycerol in water for 3 d, to reduce shrinkage and pore collapse during drying. After drying, the fibers were ready to undergo characterization.

2.3. Characterization of blend membranes

ATR/FTIR analysis was conducted using PerkinElmer Spectrum 400 (PerkinElmer, Inc, USA). The spectra were measured in the wave number range of 4,000–650 cm^{-1} with an accumulation of 16 scans at a resolution of 2.0 cm^{-1}.

FESEM (JEOL JSM-6700F) was used to examine the spun membrane morphology. Prior to FESEM analysis, hollow fiber membranes were immersed and fractured in liquid nitrogen before sputter coated with gold element. The cross-sectional and surface morphologies of membrane samples were taken at different magnifications during FESEM analysis.

Table 2
Hollow fiber PAN/PVA blend membranes with different PAN:PVA ratio

Sample code	PAN:PVA ratio[a]
PAN	100:0
P95	95:5
P90	90:10
P85	85:15
P80	80:20

[a] Total polymer weight in dope solution is 12 wt.%.

Table 3
Spinning condition of PAN-based UF hollow fiber membrane

Dope extrusion rate (mL/min)	4–5
Bore fluid	Pure water
Bore fluid flow rate (mL/min)	2.0
External coagulant	Pure water
Air gap distance (cm)	5
Spinneret o.d/i.d (mm)	1.10/0.55
Coagulation temperature (°C)	25
Take up velocity (cm/s)	10.32

Degree of hydrophilicity of UF membranes was evaluated by tangent method using contact angle system OCA 15pro (DataPhysics Instruments GmbH, Filderstadt). The hollow fibers were cut and DI water was doped on the surface of the hollow fiber at 15–20 different points using automated microsyringe. Contact angle values were then calculated from mean value of the different measurements to yield reliable value.

Surface topography and roughness of the membranes were characterized by AFM using tapping mode nanoscope III equipped with a 1553D scanner (SPA-300 HV, USA). Small squares of the prepared membranes (1 cm^2) were cut and glued on paper card. The root mean square (RMS) was used to determine the surface roughness of the hollow fiber membrane based on $5.0 \times 5.0\ \mu m$ scan area.

The thermal behavior of the blend membranes was evaluated using DSC (DSC 822e Mettler Toledo) and TGA (SDTA851e Mettler Toledo). The measurement was carried out under nitrogen flow at a heating rate of 10°C/min from 30 to 300°C for DSC and 30 to 800°C for TGA.

2.4. UF experiments

To evaluate the separation, permeation, and antifouling properties, filtration experiments were conducted using lab-scale cross-flow UF membrane system. Hollow fiber bundle consisted of 10 fibers with 20 cm long was placed within a stainless steel housing. Feed solution was transferred from solution tank to membrane housing using a low pressure booster pump. Before any measurement, the hollow fiber membranes were compacted at 1.5 bar using DI water until it reached steady state condition. Filtration experiment was conducted at ambient temperature and 1 bar. Initial pure water flux (J_{W1}) was then calculated using Eq. (1):

$$J_{W1}\ (\%) = \frac{v}{t \times A} \tag{1}$$

where v (L) is the volume of permeate, A (m^2) is the effective area of the hollow fiber membrane, and t (h) is the UF time. For protein (BSA) rejection and anti-fouling analysis, the feed liquid was displaced with 1.0 g/L of BSA solution and the real-time fluxes were also recorded under 1 bar. Protein flux was measured until it reached constant flux (J_p). Then, protein rejection (R) was calculated using the following equation:

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p is the permeate concentration (mg/L) and C_f is the feed concentration (mg/L). The concentration of protein in feed and permeate sample was determined using UV–Vis spectrophotometer (DR5000, Hach). To investigate fouling analysis, the solution tank was refilled with DI water and the membranes were cleaned with DI water for 30 min. Pure water flux (J_{W2}) was measured again after the cleaning process. In order to evaluate anti-fouling performance of the UF membranes, the flux recovery ratio (R_{FR}) and the flux decline rate (R_{FD}) were calculated as follows:

$$R_{FR}\ (\%) = \frac{J_{W2}}{J_{W1}} \times 100 \tag{3}$$

$$R_{FD}\ (\%) = \left(1 - \frac{J_p}{J_{W1}}\right) \times 100 \tag{4}$$

3. Results and discussion

3.1. FTIR analysis

Fig. 1(a) and (b) show the spectrum of PAN control membrane and the blend PAN/PVA membranes of different PVA concentration, respectively. For control PAN membrane, three characteristic peaks can be observed at 1,452 cm^{-1} (stretching band of CH), 2,283 cm^{-1} (stretching band of CH_2), and 2,928 cm^{-1} (CN), which represent the typical characteristics of PAN polymeric material. Compared with the control PAN, the PAN/PVA blend membranes also showed the three characteristic bands of PAN. However, the peaks were slightly shifted and appeared at 1,308, 2,070, and 2,748 cm^{-1}, respectively. This might be due to the polymer blending process. Unlike the control membrane, all the blend membranes showed a broad peak at 3,543 cm^{-1} which can be attributed to the stretching vibration of –OH band resulted from PVA in the membrane matrix.

3.2. Morphological properties of the blend membranes

The cross-section and surface morphologies of the hollow fiber UF blend membranes prepared with different ratio of PAN/PVA (95:5, 90:10, 85:15, and 80:20) were observed by FESEM, as depicted in Fig. 2. Theoretically, the morphological change of UF membranes is governed by thermodynamic factor such as polymer/solvent/nonsolvent composition and kinetic factor such as precipitation rate during phase inversion process [9]. As can be seen from the images, all the membranes exhibited typical asymmetric UF membrane morphology which was prepared via phase inversion technique. The cross-section of the membrane can be generally divided into three major regions: (a) top layer for finger-like porous sublayer that extends from outside wall, (b) middle layer which

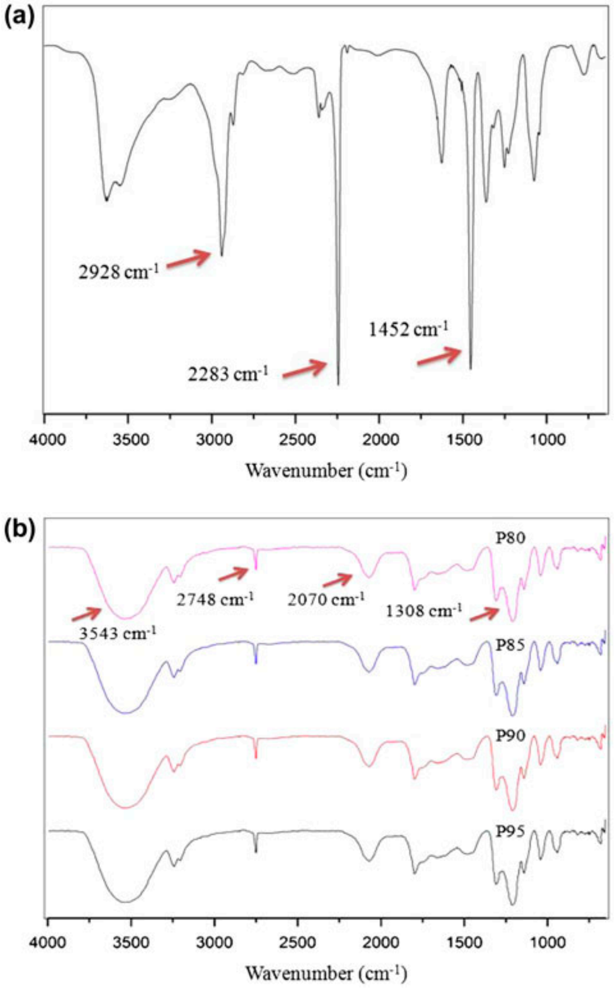

Fig. 1. FTIR spectra of (a) control PAN membrane and (b) PAN/PVA blend membranes with different PVA concentrations.

reflects to the formation of sponge-like structure at the membrane center, and (c) bottom layer for finger-like structure that extends from inner wall. This morphological property might be due to the phase inversion process which occurs simultaneously at both inside and outer lumen.

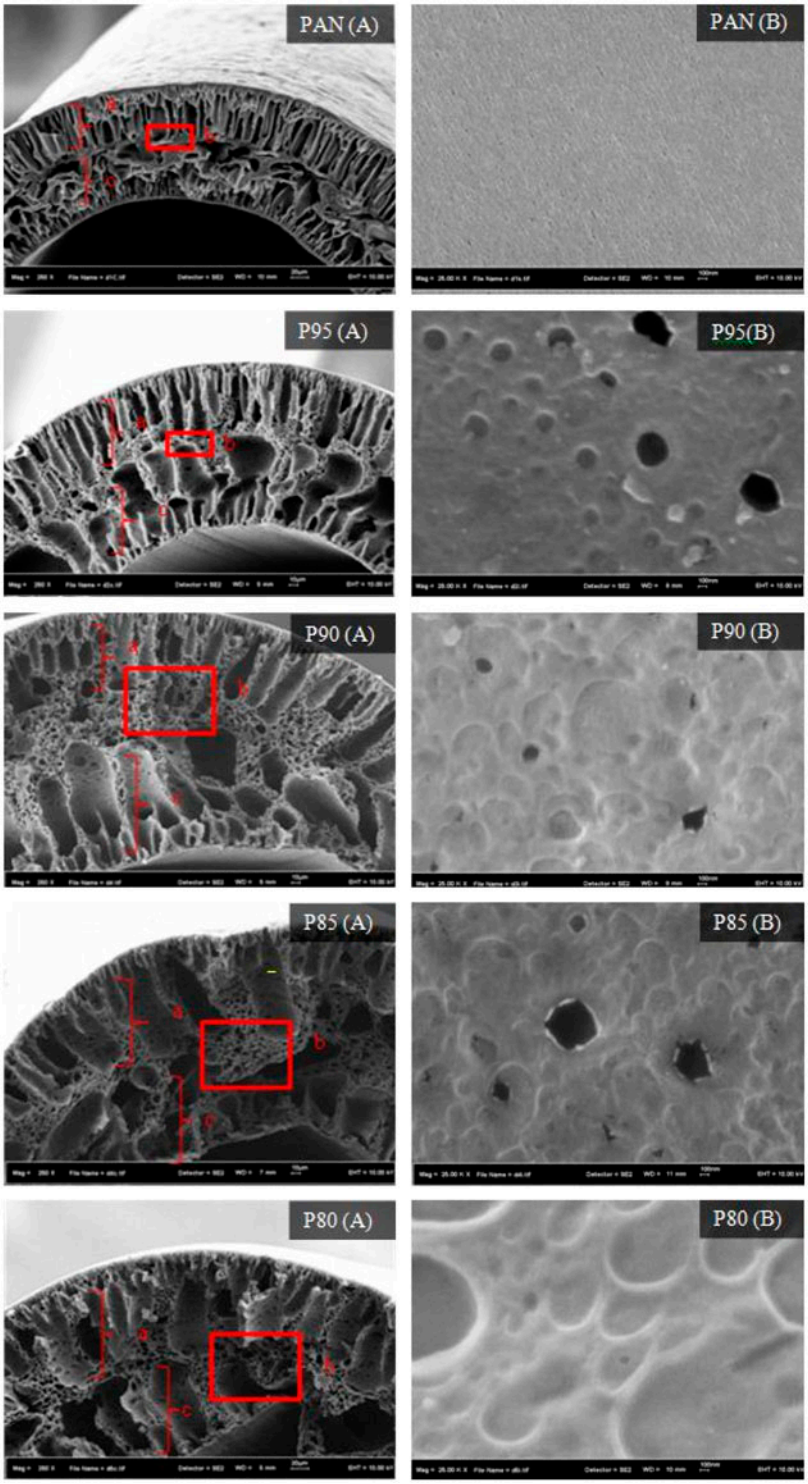

Fig. 2. FESEM images of (A) cross-section morphology and (B) surface morphology of the control PAN membrane and the PAN/PVA blend membranes.

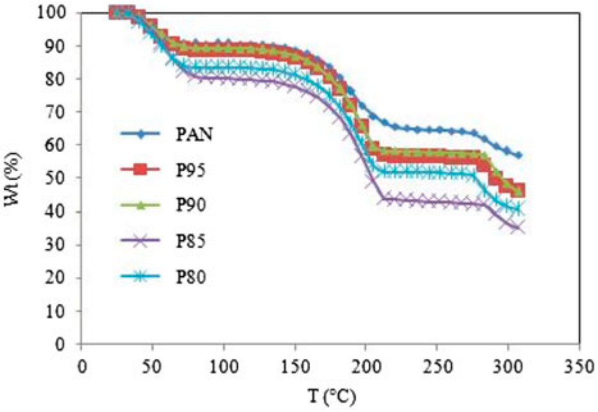

Fig. 3. TGA thermograms of PAN/PVA blend membranes.

It is found that morphology of the PAN/PVA blend membrane is influenced by the ratio of PAN/PVA in the dope solution. Compared with the morphology of control PAN membrane which was prepared without PVA addition, the finger-like macrovoids (region a and c) and surface for the blend membranes were larger and rougher. Such morphologies were arisen from instantaneous demixing process, which was promoted by the presence of hydrophilic PVA. The influence of hydrophilic additive to the UF membrane morphology is well reported in many previous publications [10,42,43]. It is believed that the introduction of hydrophilic additive in the dope solution has contributed to the thermodynamic and kinetic changes which induced rapid inflow and outflow precipitation rate, hence, facilitating the formation of bigger finger-like structure and rougher membrane surface. This result is also consistent with the previous studies in which increasing hydrophilic additive content could impart bigger void size and higher porosity [7,44,45]. It should be noted that the largest macrovoid size and roughest surface were able to happen when blending ratio of PAN/PVA in dope solution was increased up to 80:20, as observed from FESEM micrograph of P80.

On the other hand, despite the formation of larger finger-like structure at both inner and outer lumen and rougher membrane surface, it is obvious that sponge-like structure at the middle of the membrane cross-section (region b) became larger with increasing PVA composition. Enhancing PVA content in membrane could suppress formation of finger-like structure at the middle layer of membrane due to delayed phase inversion process at the intermediate layer. Therefore, it is reasonable to say that the presence of PVA hydrophilic additive tends to have more influence in facilitating rapid demixing process at the layer exposes to the water coagulant (near the inner and outer wall) as compared with intermediate layer. It is also important to note that further increase of PVA to 80:20 ratio of PAN:PVA in dope solution (i.e. P80 membrane) could result in bad phase separation due to the presence of significant amount of highly hydrophilic PVA in dope solution, which drastically changed the thermodynamic and kinetic behavior of the dope system. Our findings showed that membrane was not able to be produced with the use of dope solution containing PAN:PVA ratio of 75:25 as the dope solution tended to dissolve in water due to the high affinity of the hydrophilic PVA with water.

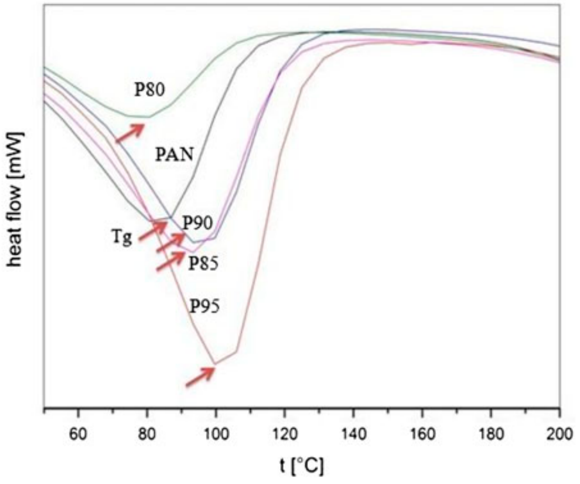

Fig. 4. DSC thermograms of PAN/PVA blend membranes.

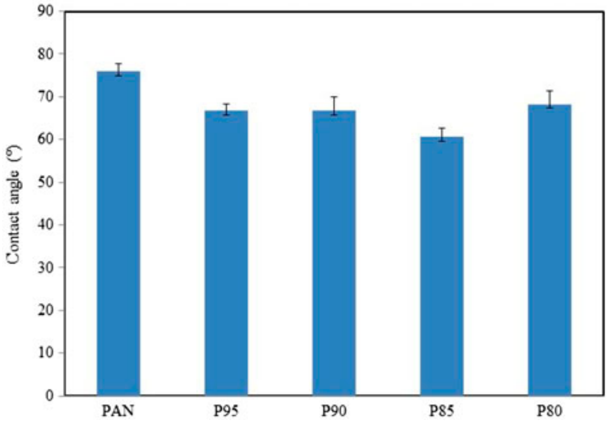

Fig. 5. Contact angles of membranes with different PVA composition.

3.3. Glass transition temperature and thermal stability of blend membranes

Fig. 3 shows the thermal behavior of the hollow fiber membranes. It can be seen that the weight loss process of the membranes can be decomposed into three discrete thermal degradation steps. The weight of PAN control membrane remained at around 90.55%, while P95, P90, P85, and P80 membrane at 88.45, 89.22, 80.02, and 83.40%, respectively, at temperature of 100℃. This first weight loss might be caused by the loss of moisture content in the membranes. At temperature around 150–200℃, which is the occurrence of second decomposition step, remaining weight of PAN, P95, P90, P85, and P80 was further reduced and recorded at 64.37, 56.22, 57.63, 42.69, and 51.48%, respectively. The reduction in membrane weight can be explained by decomposition of the side chain of both polymers. Third degradation step occurred at temperature of around 250–300℃ can be correlated to the backbone decomposition of both polymers. At this stage, complete degradation of the samples was observed in which the mass of both control and blend membranes remained constant after this. The thermal stability of the membranes was observed to follow the order of PAN > P90 > P95 > P80 > P85. All of the blended membranes exhibited lower thermal stability than that of PAN control membrane. From these results, it can be deduced that incorporation of PVA into PAN-based hollow fiber membranes could reduce thermal stability of PAN membrane. However, it must be pointed out the PAN/PVA blend membranes still demonstrated acceptable thermal stability for most of the industrial applications which normally operate at temperature less than 40℃.

Glass transition temperatures (T_g) of the membranes are depicted in Fig. 4. The reported value of T_g for PAN and PVA polymer was 94 and 108.26℃, respectively [45,46]. In comparison, the T_g of PAN membrane prepared in this study was slightly lower i.e. 85.05℃, and is mainly influenced by the presence of moisture content in the fiber. T_g for blend membranes of P95, P90, P85, and P80 were observed at 100.91, 91.18, 85.75, and 82.48℃, respectively, in which P95 membrane exhibited the highest T_g value. It was observed that T_g for the blend membrane increased first with addition of PVA at PAN:PVA ratio of 95:5 which is for membrane P95, whereas the T_g decreased with further increase in PVA content in the PAN membranes as evidenced in P90, P85, and P80. This trend might be influenced by the composition of PVA in the membrane. It is believed that PVA is easy to diffuse out from membrane matrix at high composition due to their good interaction with water. It is also noticed that the existence of single T_g for all PAN/PVA blend membranes indicated the fully miscible polymer blend [6,47]. Zhu et al. [48] pointed out that hydrogen bonding interaction between PVA and PAN is the main reason promoting the miscibility of the two polymers.

3.4. Surface properties evaluation of the blend membranes

Water contact angle analysis was carried out to evaluate surface hydrophilicity of membranes. As shown in Fig. 5, PAN control membrane possessed the highest contact angle value of 75.88˚. Upon comparison, the blend membranes showed lower contact angle than the PAN control membrane, indicating the improved hydrophilicity of the modified PAN membrane upon addition of PVA. Similar improvement in membrane hydrophilicity was also reported by Li et al. [7] when PVDF-based membrane was modified using PVA. It can be observed that the hydrophilicity of the blend membranes was firstly enhanced with increasing composition of PVA, however, further addition of PVA in the dope solution beyond optimum ratio (ratio of PAN/PVA 85:15) led to the decline in the membrane hydrophilicity. Therefore, it can be said that the decline in membrane hydrophilicity is likely due to excessive leaching out of PVA into coagulation water, resulting in increase in membrane contact angle as evidenced in membrane P80.

Another factor that might have contributed to the decline in membrane hydrophilicity could be due to the changes in membrane surface roughness upon addition of PVA. Previous research studies have correlated the changes in membrane hydrophilicity with the membrane top surface roughness in which the higher the surface roughness value, the higher the water contact angle (i.e. less hydrophilic) [13,49]. It can be seen from Fig. 6 that the surface roughness of the blend membranes was increased significantly as compared with the control membrane. It is found that the plain PAN membrane displayed the lowest RMS surface roughness value of 6.50 nm in comparison with 52–54 nm reported for P95, P90, and P85 membranes. Of all the membranes studied, P80 membrane which was prepared from the highest composition of PVA showed the highest RMS value i.e. 77.07 nm. Because of this, it is believed that the remarkable increase in surface roughness of P80 membrane is one of the possible factors influencing the decline in membrane surface hydrophilicity due to Cassie–Wenzel effect [49].

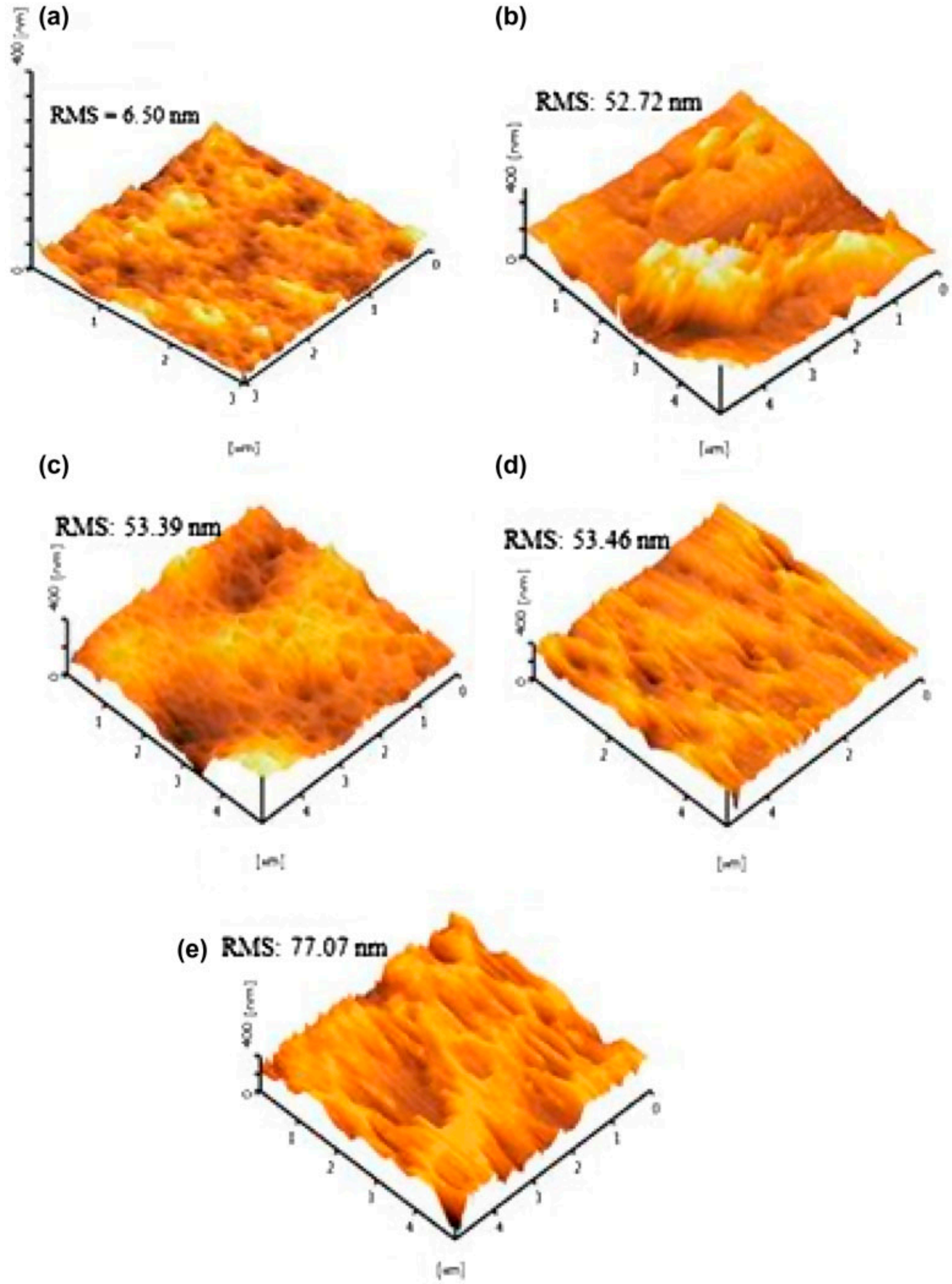

Fig. 6. 3D AFM images for the (a) control PAN membrane, (b) P95, (c) P90, (d) P85, and (e) P80 membrane.

3.5. Filtration performance of the blend membranes

The effect of PVA compositions on PAN-based hollow fiber membranes performance was investigated by pure water permeation and anti-fouling analysis. As depicted in Fig. 7, pure water flux of the UF membranes was increased with increasing PVA content in the PAN dope solution. The addition of PVA at PAN:PVA ratio of 85:15 for P85 membrane has led the pure water flux to increase by six times as compared with the control PAN membrane. However, further increase of PVA to PAN:PVA ratio of 80:20 caused the pure water flux to decline, recording 199.3 L/m^2 h as compared with the highest value of 251.37 L/m^2 h achieved by P85 membrane. This trend is consistent with the previous study conducted by Jung [9], where

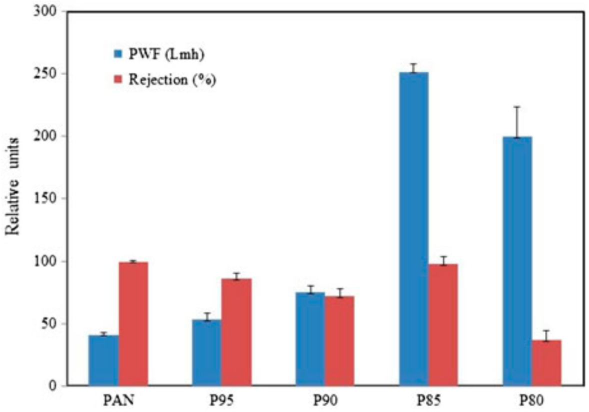

Fig. 7. Pure water flux and BSA rejection data of the membranes.

the addition of polymeric additive to PAN-based membrane has increased pure water flux at a certain concentration of PVA, and decline after the optimum concentration. On the contrary, study conducted by Li et al. [7] showed a linear relationship between pure water flux and PVA content in PVDF-based membrane. However, our results from filtration experiments are consistent with the morphologies of membranes shown in FESEM images. Formation of sponge-like structure at the intermediate layer might have hindered the transport properties across the membrane, resulting in lower water permeation flux at high amount of PVA in dope solution. Jung et al. [50], on the other hand, attributed the decline of membrane pure water flux with increasing hydrophilic additive content to the swelling of the additive entrapped in the membrane matrix. Therefore, it is also believed that high concentration of PVA may also contribute to the entrappment and swelling of PVA inside the membrane pores which consequently lead to decline in pure water flux. In addition, instead of showing higher pure water flux, P85 also exhibited the highest rejection of 97.46% for BSA protein, as evidenced from Fig. 7. The excellent performance of both pure water flux and BSA rejection might be due to the good morphological structure of this membrane which was prepared from optimum PVA content.

Based on the literature search, we found that it is lack of research works reporting the performance of PAN UF membrane incorporated with PVA via direct blending approach. Thus, side-by-side comparison between the performance of our modified PAN membranes with others is rather difficult. Because of this, comparison was made by comparing our PAN/PVA membranes with PVDF/PVA membranes reported in the work of Li et al. [7]. Table 4 shows the percentage flux enhancement for the optimized membrane fabricated in this study and the membrane reported by Li et al. [7]. It can be seen that the flux of our in-house optimized blend membrane was not only higher than that of PVDF/PVA membrane reported earlier but also showed remarkable improvement compared with the control PAN membrane.

3.6. Anti-fouling performance

Filtration performance using protein solution was carried out to evaluate anti-fouling properties of the PAN/PVA blend membranes where BSA was used as a model foulant. As can be seen from Fig. 8, the trend of protein flux of the prepared membranes was similar with the trend of water permeation flux (P85 > P80 > P90 > P95 > PAN). However, the protein flux of membrane was significantly lower than that of the membrane pure water flux as shown in Fig. 7. The decline in water flux during UF of BSA experiment could be due to the deposition of protein on the surface of membrane and/or adsorption of protein in the internal pores of membrane. Previous studies revealed that fouling is more severe in hydrophobic membrane surface than the hydrophilic surface. It is because of the unfavorable hydrophobic interaction between protein and hydrophobic membrane surface that could promote the deposition and adsorption of protein which consequently increase hydraulic membrane resistance and decrease the water flux [51,52].

To quantitatively evaluate the membrane flux decline behavior due to fouling phenomenon, the flux

Table 4
Comparison of the membrane flux of this work with other research work upon addition of PVA

	Flux[a]		
	Control membrane (L/m^2 h)	Optimized blend membrane (L/m^2 h)	Flux enhancement (%)
In this work	PAN (41.1)	PAN/PVA (251.4)	511.6
Work of Li et al. [7]	PVDF (30)	PVDF/PVA (140)	366.7

[a] All the permeation experiments were conducted at 1 bar.

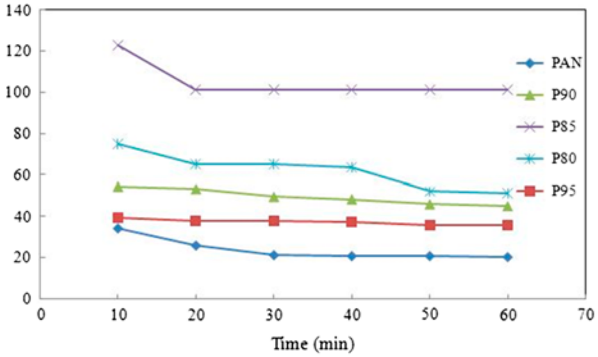

Fig. 8. Time-dependent fluxes of UF membrane of BSA solution. BSA concentration is 1.0 g/L.

Table 5
Recycling and fouling properties of UF membrane

Membrane	R_t	R_r	R_{ir}	R_{FD} (%)	R_{FR} (%)
PAN	0.52	0.25	0.27	51.79	73.12
P95	0.15	0.09	0.06	14.95	93.65
P90	0.36	0.07	0.29	36.10	71.01
P85	0.61	0.33	0.28	60.88	72.47
P80	0.75	0.67	0.09	75.40	91.43

decline rate (R_{FD}) was measured. Smaller value of R_{FD} indicates good anti-fouling properties of the membrane which describes less protein deposition and adsorption. From Table 3, it is reported that P95 exhibited the lowest R_{FD} value, which can be due to presence of hydrophilic PVA on membrane surface. It is also possible to assume that leaching out of hydrophilic PVA into aqueous medium was not significant for the membrane prepared from the lowest composition of PVA. In addition, the low flux decline observed for membrane P95 might also be associated to its lowest surface roughness as compared with other blend membrane. This is because the higher the value of membrane surface roughness, the greater the deposition of foulants on membrane surface thus, higher flux decline is occurred. It is found that P85 and P80 blend membranes demonstrated relatively higher R_{FD} values compared with the control membrane. This trend might be due to the diffuse out of the PVA hydrophilic during phase inversion process at higher composition of PVA and also due to the increase in membrane surface roughness for both membranes [49,53,54].

Fouling potential of the membranes is further analyzed in terms of its reversible fouling, irreversible fouling, and total fouling. Generally, reversible fouling can be removed by water flushing, back-washing, or using strong shear force such as gas sparging, but irreversible fouling requires more complicated cleaning method such as chemical cleaning [42,53]. The degree of flux loss due to total (R_t), reversible (R_r), and irreversible (R_{ir}) fouling was defined as follows:

$$R_t = 1 - \frac{J_p}{J_{W1}} \tag{5}$$

$$R_r = \frac{J_{W2} - J_P}{J_{W1}} \tag{6}$$

$$R_{\text{ir}} = \frac{J_{W1} - J_{W2}}{J_{W1}} \tag{7}$$

A summary of the R_t, R_r, R_t and R_{FR} is presented in Table 5. Flux recovery ratio of the membrane was also calculated to determine whether the membrane can be reused after water cleaning. It can be seen that P95 and P80 membrane showed the lowest fouling potential in which up to 93.65 and 91.43% of their initial pure water fluxes could be recovered. The high R_{FR} value also described the low potential of irreversible fouling, which was confirmed by the smaller R_{ir} value of the membranes i.e. 0.06 for P95 and 0.09 for P80. It is interesting to note that P80 membrane with highest surface roughness also possessed good flux recovery which is likely due to the entrapment of PVA inside the membrane pores, reducing irreversible fouling phenomenon. On the other hand, P90 and P85 blend membranes exhibited almost the same R_{FR} value compared with the control PAN membrane, indicating the addition of PVA did not significantly enhance the anti-fouling performance of the blend membranes. This is due to the increase in membrane surface roughness upon addition of the PVA which consequently increased deposition of BSA protein on membrane surface and suppress the efficiency of cleaning process in retrieving water flux. Even though the flux recovery of the control membrane is considerably high, its low initial flux (41.06 $\text{L/m}^2\,\text{h}$) is the main barrier making it unsuitable for commercial use. In general, P95 blend membrane showed the best anti-fouling performance compared with other membranes by which it demonstrated low R_t (0.15), R_r (0.09), and R_{ir} (0.06). Low values of R_t, R_r, and R_{ir} are a sign of low flux loss due to deposition and adsorption of protein. This result suggested that PVA could facilitate good anti-fouling properties of membrane at its optimum composition in dope solution.

4. Conclusions

In this study, simple blending method was utilized to fabricate PAN/PVA blend UF membranes. FESEM results indicated that the addition of PVA could enlarge macrovoids size of finger-like structure in the top and bottom layer as well as sponge-like structure at the middle of the PAN membrane. The blend membranes also possessed better hydrophilicity compared with the control PAN membrane and of the blend membranes prepared, P85 membrane displayed the lowest contact angle i.e. 60.7°. From DSC analysis, it is found that the polymer blend was fully miscible as only single T_g value was displayed. However, the thermal stability of the blend membrane tended to decrease upon addition of the PVA in the membrane matrix. Roughness parameter from AFM evaluation demonstrated a remarkable increase in the surface roughness of blend membrane after PVA was introduced. Filtration performance results suggested that the blend membranes exhibited better permeability as compared with the control membrane. Highest flux of $251.4\,\mathrm{L/m^2\,h}$ was achieved by P85, which also showed highest BSA rejection of 97.5%. With respect to antifouling property, it is noticed that protein fouling could be effectively minimized, provided an appropriate amount of PVA was used for PAN/PVA membrane preparation.

Acknowledgment

We gratefully acknowledge the financial support from the Ministry of Education under Long-term Research Grant Scheme (LRGS, grant number R.J130000.7837.4L803) for the research work conducted.

References

[1] P.S. Yune, J.E. Kilduff, G. Belfort, Using co-solvents and high throughput to maximize protein resistance for poly(ethylene glycol)-grafted poly(ether sulfone) UF membranes, J. Membr. Sci. 370 (2011) 166–174.

[2] A. Rahimpour, Preparation and modification of nanoporous polyimide (PI) membranes by UV photo-grafting process: Ultrafiltration and nanofiltration performance, Korean J. Chem. Eng. 28(1) (2011) 261–266.

[3] D.G. Kim, H. Kang, S. Han, J.C. Lee, The increase of antifouling properties of ultrafiltration membrane coated by star-shaped polymers, J. Mater. Chem. 22 (2012) 8654–8661.

[4] X. Zhang, C. Xiao, X. Hu, Preparation and properties of polysulfone/polyacrylonitrile blend membrane and its modification with hydrolysis, Desalin. Water Treat. 51 (2013) 3979–3987.

[5] Y. Chen, Y. Zhang, H. Zhang, J. Liu, C. Song, Biofouling control of halloysite nanotubes-decorated polyethersulfone ultrafiltration membrane modified with chitosan-silver nanoparticles, Chem. Eng. J. 228 (2013) 12–20.

[6] Q.F. Alsalhy, Hollow fiber ultrafiltration membranes prepared from blends of poly(vinyl chloride) and polystyrene, Desalination 294 (2012) 44–52.

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

[8] 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.

[9] B. Jung, Preparation of hydrophilic polyacrylonitrile blend membranes for ultrafiltration, J. Membr. Sci. 229 (2004) 129–136.

[10] H. Lohokare, Y. Bhole, S. Taralkar, U. Kharul, Poly (acrylonitrile) based ultrafiltration membranes: Optimization of preparation parameters, Desalination 282 (2011) 46–53.

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

[12] M. Wang, L.G. Wu, J.X. Mo, C.J. Gao, The preparation and characterization of novel charged polyacrylonitrile/PES-C blend membranes used for ultrafiltration, J. Membr. Sci. 274 (2006) 200–208.

[13] B. Liu, C. Chen, T. Li, J. Crittenden, Y. Chen, High performance ultrafiltration membrane composed of PVDF blended with its derivative copolymer PVDF-*g*-PEGMA, J. Membr. Sci. 445 (2013) 66–75.

[14] C.H. Loh, R. Wang, L. Shi, A.G. Fane, Fabrication of high performance polyethersulfone UF hollow fiber membranes using amphiphilic pluronic block copolymers as pore-forming additives, J. Membr. Sci. 380 (2011) 114–123.

[15] Y.H. Cho, H.W. Kim, S.Y. Nam, H.B. Park, Fouling-tolerant polysulfone–poly(ethylene oxide) random copolymer ultrafiltration membranes, J. Membr. Sci. 379 (2011) 296–306.

[16] L. Na, L. Zhongzhou, X. Shuguang, Dynamically formed poly(vinyl alcohol) ultrafiltration membranes with good anti-fouling characteristics, J. Membr. Sci. 169 (2000) 17–28.

[17] Y. Zhang, H. Li, H. Li, R. Li, C. Xiao, Preparation and characterization of modified polyvinyl alcohol ultrafiltration membranes, Desalination 192 (2006) 214–223.

[18] A.L. Ahmad, N.M. Yusuf, B.S. Ooi, Preparation and modification of poly(vinyl) alcohol membrane: Effect of crosslinking time towards its morphology, Desalination 287 (2012) 35–40.

[19] Y. Peng, H. Han, H.W. Fan, Characterization and performance of PVA/Psf composite hollow fiber UF membrane prepared with interfacial polymerization, Polym. Eng. Sci. 52(3) (2012) 557–565.

[20] H. Yuan, J. Ren, L. Cheng, L. Shen, Preparation and characterization of a poly(vinyl alcohol)/tetraethoxysilane ultrafiltration membrane by a sol–gel method, J. Appl. Polym. Sci. 130(6) (2013) 4066–4074.

[21] H. Danxi, W. Lei, M. Xiaorong, W. Xudong, B. Juanli, Study on the effect of modified PVDF ultrafiltration membrane for secondary effluent of urban sewage, Desalin. Water Treat. (2014) 1–8. doi: 10.1080/19443994.2014.883058.

[22] J.M. Gohil, P. Ray, Polyvinyl alcohol as the barrier layer in thin film composite nanofiltration membranes: Preparation, characterization, and performance evaluation, J. Colloid Interface Sci. 338 (2009) 121–127.

[23] R. Guo, C. Hu, B. Li, Z. Jiang, Pervaporation separation of ethylene glycol/water mixtures through surface crosslinked PVA membranes: Coupling effect and separation performance analysis, J. Membr. Sci. 289 (2007) 191–198.

[24] X. Ma, Y. Su, Q. Sun, Y. Wang, Z. Jiang, Enhancing the antifouling property of polyethersulfone ultrafiltration membranes through surface adsorption-crosslinking of poly(vinyl alcohol), J. Membr. Sci. 300 (2007) 71–78.

[25] R.K. Nagarale, V.K. Shahi, R. Rangarajan, Preparation of polyvinyl alcohol–silica hybrid heterogeneous anion-exchange membranes by sol–gel method and their characterization, J. Membr. Sci. 248 (2005) 37–44.

[26] H. Bessbousse, J.-F. Verchère, L. Lebrun, Increase in permeate flux by porosity enhancement of a sorptive UF membrane designed for the removal of mercury (II), J. Membr. Sci. 364 (2010) 167–176.

[27] Y. Shang, Y. Peng, UF membrane of PVA modified with TDI, Desalination 221 (2008) 324–330.

[28] K. Yoon, B.S. Hsiao, B. Chu, High flux ultrafiltration nanofibrous membranes based on polyacrylonitrile electrospun scaffolds and crosslinked polyvinyl alcohol coating, J. Membr. Sci. 338 (2009) 145–152.

[29] G.S. Mukherjee, Modification of poly(vinyl alcohol) for improvement of mechanical strength and moisture resistance, J. Mater. Sci. 40 (2005) 3017–3019.

[30] G. Li, W. Zhang, J. Yang, X. Wang, Time-dependence of pervaporation performance for the separation of ethanol/water mixtures through poly(vinyl alcohol) membrane, J. Colloid Interface Sci. 306 (2007) 337–344.

[31] B. Han, J. Li, C. Chen, C. Xu, S.R. Wickramasinghe, Effects of degree of formaldehyde acetal treatment and maleic acid crosslinking on solubility and diffusivity of water in PVA membranes, Chem. Eng. Res. Des. 81, Part A (2003) 1385–1392.

[32] J.-W. Rhim, C.-K. Yeom, S.-W. Kim, Modification of poly(vinyl alcohol) membranes using sulfur-succinic acid and its application to pervaporation separation of water–alcohol mixtures, J. Appl. Polym. Sci. 68 (1998) 1717–1723.

[33] J.M. Yang, H.Z. Wang, C.C. Yang, Modification and characterization of semi-crystalline poly(vinyl alcohol) with interpenetrating poly(acrylic acid) by UV radiation method for alkaline solid polymer electrolytes membrane, J. Membr. Sci. 322 (2008) 74–80.

[34] J.M. Yang, C.Y. Chiang, H.Z. Wang, C.C. Yang, Two step modification of poly(vinyl alcohol) by UV radiation with 2-hydroxyethyl methacrylate and sol–gel process for the application of polymer electrolyte membrane, J. Membr. Sci. 341 (2009) 186–194.

[35] Y.Q. Dong, L. Zhang, J.N. Shen, M.Y. Song, H.L. Chen, Preparation of poly(vinyl alcohol)-sodium alginate hollow-fiber composite membranes and pervaporation dehydration characterization of aqueous alcohol mixtures, Desalination 193 (2006) 202–210.

[36] M.N. Hyder, R.Y.M. Huang, P. Chen, Correlation of physicochemical characteristics with pervaporation performance of poly(vinyl alcohol) membranes, J. Membr. Sci. 283 (2006) 281–290.

[37] N.R. Singha, T.K. Parya, S.K. Ray, Dehydration of 1,4-dioxane by pervaporation using filled and crosslinked polyvinyl alcohol membrane, J. Membr. Sci. 340 (2009) 35–44.

[38] Q. An, F. Li, Y. Ji, H. Chen, Influence of polyvinyl alcohol on the surface morphology, separation and anti-fouling performance of the composite polyamide nanofiltration membranes, J. Membr. Sci. 367 (2011) 158–165.

[39] C. Wu, A. Li, L. Li, L. Zhang, H. Wang, X. Qi, Q. Zhang, Treatment of oily water by a poly(vinyl alcohol) ultrafiltration membrane, Desalination 225 (2008) 312–321.

[40] J.R. Du, S. Peldszus, P.M. Huck, X. Feng, Modification of poly(vinylidene fluoride) ultrafiltration membranes with poly(vinyl alcohol) for fouling control in drinking water treatment, Water Res. 43 (2009) 4559–4568.

[41] H. Ma, K. Yoon, L. Rong, M. Shokralla, A. Kopot, X. Wang, D. Fang, B.S. Hsiao, B. Chu, Thin-film nanofibrous composite ultrafiltration membranes based on polyvinyl alcohol barrier layer containing directional water channels, Ind. Eng. Chem. Res. 49 (2010) 11978–11984.

[42] A. Asatekin, S. Kang, M. Elimelech, A.M. Mayes, Anti-fouling ultrafiltration membranes containing polyacrylonitrile-*graft*-poly(ethylene oxide) comb copolymer additives, J. Membr. Sci. 298 (2007) 136–146.

[43] H. Susanto, M. Ulbricht, Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives, J. Membr. Sci. 327 (2009) 125–135.

[44] J.H. Li, M.Z. Li, J. Miao, J.B. Wang, X.S. Shao, Q.Q. Zhang, Improved surface property of PVDF membrane with amphiphilic zwitterionic copolymer as membrane additive, Appl. Surf. Sci. 258 (2012) 6398–6405.

[45] T. Barroso, M. Temtem, T. Casimiro, A. Aguiar-Ricardo, Antifouling performance of poly(acrylonitrile)-based membranes: From green synthesis to application, J. Supercrit. Fluids 56 (2011) 312–321.

[46] A.K. Sahu, G. Selvarani, S. Pitchumani, P. Sridhar, A.K. Shukla, N. Narayanan, A. Banerjee, N. Chandrakumar, PVA-PSSA membrane with interpenetrating networks and its methanol crossover mitigating effect in DMFCs, J. Electrochem. Soc. 155(7) (2008) B686–B695.

[47] H.W. Kim, H.B. Park, Gas diffusivity, solubility and permeability in polysulfone–poly(ethylene oxide) random copolymer membranes, J. Membr. Sci. 372 (2011) 116–124.

[48] G. Zhu, F. Wang, K. Xu, Q. Gao, Y. Liu, Study on properties of poly(vinyl alcohol)/polyacrylonitrile blend film, Polimeros 23 (2013) 146–151.

[49] R. Jamshidi-Gohari, W.J. Lau, T. Matsuura, A.F. Ismail, Effect of surface pattern formation on membrane

fouling and its control in phase inversion process, J. Membr. Sci. 446 (2013) 326–331.

[50] 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.

[51] P.D. Peeva, T. Knoche, T. Pieper, M. Ulbricht, Cross-flow ultrafiltration of protein solutions through unmodified and surface functionalized polyethersulfone membranes—Effect of process conditions on separation performance, Sep. Purif. Technol. 92 (2012) 83–92.

[52] E. Celik, L. Liu, H. Choi, Protein fouling behavior of carbon nanotube/polyethersulfone composite membranes during water filtration, Water Res. 45 (2011) 5287–5294.

[53] X. Chen, Y. Su, F. Shen, Y. Wan, Antifouling ultrafiltration membranes made from PAN-b-PEG copolymers: Effect of copolymer composition and PEG chain length, J. Membr. Sci. 384 (2011) 44–51.

[54] A.W. Mohammad, N. Hilal, L.Y. Pei, I.N.H. Mohd-Amin, R. Raslan, Atomic force microscopy as a tool for asymmetric polymeric membrane characterization, Sains Malays. 40(3) (2011) 237–244.