Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.0094

58 (2017) 1–11
January

Preparation and characterization of PVC/PAN blend ultrafiltration membranes: Effect of PAN concentration and PEG with different molecular weight

Hesamoddin Rabiee[a,*], S. Mojtaba Seyedi[b], Hossein Rabiei[a], Negar Alvandifar[a], Amir Arya[c]

[a]*Young Researchers and Elites Club, North Tehran Branch, Islamic Azad University, Tehran, Iran, Tel. +98 912 700 1054; email: hesamoddin.rabiee@gmail.com (H. Rabiee); Tel. +98 912 621 7599; email: hossein0782@gmail.com (H. Rabiei); Tel. +98 9112758662; email: negar.alvandifar@gmail.com (N. Alvandifar)*

[b]*Department of Chemical and Petroleum Engineering, Sharif University of Technology, PO Box 11155-9465, Azadi Avenue, Tehran, Iran, Tel. +98 912 748 9866; email: seyedi.mojtaba@gmail.com (S. Mojtaba Seyedi)*

[c]*Australian School of petroleum, the University of Adelaide, Adelaide, Australia, Tel: +61 405 789 450, email: Amir.arya87@gmail.com (Amir Arya)*

Received 23 January 2016; Accepted 29 May 2016

ABSTRACT

The current study investigates the effect of polyacrylonitrile (PAN) addition on morphology and antifouling properties of poly(vinyl chloride) (PVC) asymmetric flat ultrafiltration (UF) membranes. The membranes are prepared via phase inversion method induced by immersion precipitation at different PVC/PAN blending ratio up to 40 wt% PAN. Also, membranes with blending ratio of PVC/PAN:70/30, which showed the highest water flux and flux recovery ratio, were used for membrane preparation with 4 wt% of Polyethylene glycol (PEG) addition in four different molecular weight, 600 Da, 1,000 Da, 6,000 Da and 20,000 Da, which was used as pore former and hydrophilic polymeric additive. The performance of the membranes was studied by using pure water and bovine serum albumin (BSA) as feed at operating pressure of 3 bar. The cross-sections of the fabricated membranes were studied using SEM, and the images showed remarkable changes in morphology and structure of the prepared membranes after PAN and PEG addition. PAN addition led to increment in water flux up to 30 wt% and then decreased. The similar trend was observed in the case of flux recovery ratio. Also, viscosity of polymeric solution, contact angle and porosity of the membranes, antifouling and flux recovery of the membranes were studied.

Keywords: Ultrafiltration blended membranes; Poly(vinyl chloride); Polyacrylonitrile; Desalination; Antifouling

1. Introduction

Using of membrane technology and membrane separation processes has been considerably on the increase within the last decades in various fields from gas separation by different types of membranes [1,2] to protein concentration [3,4]. In particular, varied types of porous and asymmetric membranes that are highly being used for various separation purposes such as water purification [5,6], and waste treatment [7,8]. In this regard, phase separation is the most utilized technique to fabricate membrane and in particular, non-solvent induced phase separation (NIPS) has been widely studied over the years [9,10]. In this method, porous membranes are made of replacement of solvent and non-solvent. Several factors such as solvent, non-solvent, polymer, temperature of non-solvent bath and additives in casting solution, have a role in the structure and morphology of the fabricated membranes [11,12].

The most considered polymers for this process are Poly(vinyli- dene fluoride) (PVDF) [13], polysulfone (PSF) [14, 15], poly(ethersulfone) (PES) [16–19], cellulose acetate (CA) [20], poly(vinyl chloride) (PVC) [21–25] and polyacrylonitrile

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(PAN) [26–29]. Different methods have been applied to modify the morphology and separation factors of the membranes such as incorporation of nano-inorganic particles [22,30–32], addition of Polyethylene glycol (PEG) [33,34] and poly (vinyl pyrrolydone) (PVP) [14], addition of surfactants to polymeric solution [16,35] and blending of two polymers in order to utilize the beneficial properties of both to prepare desired membranes [36–40].

Among the above-mentioned polymers for membrane preparation, PVC is an interesting option due to its low cost, thermal stability and proper chemical and mechanical resistance, and recently, more attentions are paid to this polymer [22,41,42]. However, this polymer is rather hydrophobic, compared with others like PAN, which leads to higher chance of fouling and consequently, high reduction in separation ability with time. Effects of different factors on morphology and separation factor of PVC UF membranes have been studied during the recent years. Effect of frequently used additives of PEG and PVP has been studied in the presence of N, N-dimethylacetamide (DMAc) and water as solvent and non-solvent [21]. They analyzed the morphology and structure of the membranes with and without additive in the isothermal phase diagram and concluded that addition of both PVP and PEG lead to reduction in thermodynamic stability of polymeric solution and result in finer-like pores in membrane structure. Another polymeric additive which has been used to modify ultrafiltration membranes structure is Pluronic F127 which is an amphiphilic copolymer [43–45]. Investigation of the effect of Pluronic F127 on PVC UF membranes indicated increment in water flux, pore size and pore density up to 8 wt% addition, while with 10 wt% addition the flux declined [46].

However, apart from the polymeric additives, inorganic nanoparticles have been also taken into consideration to improve antifouling properties of PVC UF membranes. Recently, effect of titanium oxide (TiO_2) and Zinc oxide (ZnO) addition on PVC UF membranes have been studied by our team [22,47]. The results showed more finger-like pores in membrane structure with addition of nano particles. Besides, higher surface hydrophilicity of the membranes with more water flux was related to the effect of particle addition. The similar results are also reported about TiO_2 addition in PES structure [48]. In this regard also zinc oxide (ZnO) [31,49], alumina (Al_2O_3) [50], ZrO_2 [51,52], silica (SiO_2) [53] and carbon nanotube [54] have been widely taken into consideration to modify UF membranes.

Another method to improve separation properties of UF membranes is preparation of membranes out of blending polymers [55]. This can provide this opportunity to use the advantages of two polymers. Addition of PAN into PES matrix led to changes in membrane morphology and contributed to long and wide finer-like structure [36]. Furthermore, as PAN is more hydrophilic in comparison with PES, the contact angle measurements showed enhancement in hydrophilicity of the blended membranes and antifouling properties of the membranes are also improved [29]. A similar conclusion is observed in another study [38]. Ai-lian et al. have investigated PSf/PAN blended membranes, and their results indicate that the fabricated membranes show high water flux in comparison with PAN UF membranes with more finger-like pores in membrane cross-section [56]. Xiuli et al. used PAN and PVDF to fabricate blend hollow-fiber membranes [39]. They reported better membrane structure for blended membrane in comparison with bare PAN membrane, which proved blending is a prospective method for developing a new type membrane material [57]. Blending of PAN and PVC to prepare hollow-fiber membranes has been worked on by Shu et al. [58]. They also reported considerable reduction in contact angle of the prepared membranes after PAN addition, indicating improvement in surface hydrophilicity of the membranes. Enhanced antifouling performance and higher flux recovery were observed as well.

PVC/PAN blending membranes have been considered in some previous studies, however they were related to Hollow-Fiber membranes or the studies did not pay attention to investigate antifouling, flux recovery performance, water flux and structure of the UF flat sheet membranes widely [58–60]. To the best of our knowledge, preparation of blending flat UF membranes with PVC and PAN has not been worked on; thereby the current study concentrates on fabrication of flat UF membranes using PVC and PAN as the polymer materials. The membranes are prepared using phase separation method using water as the non-solvent. Cross-sectional structure of the membranes were precisely studied via SEM images to observe changes in the form of finger like pores and the results indicate remarkable changes, which are due to more viscosity of solution after PAN or PEG addition and changes in the driving force of instantaneous demixing in phase separation. The blended membranes show higher water flux and recovery ratio up to 30 wt% PAN addition. Also, addition of PEG with lower molecular weight (MW) causes improvement in water flux and recovery, whereas for the case of MW of 6,000 Da and 20,000 Da, the reverse results were observed. Other important and effective characterization data such as contact angle, viscosity of polymeric solution and membranes porosity were obtained and performance of the membranes in flux recovery and rejection was studied.

2. Experimental

2.1. Materials

Polyacrylonitrile (T_g = 86°C, MW = 150,000 Da) was obtained from Aldrich. Polyvinyl chloride (PVC) was supplied from Arvand Petrochemical Co., Iran in the form of fine powders. The solvent, 1-methyl 2-pyrrolidone (NMP), and polyethylene glycol (PEG) in different MW of 600, 1,000, 6,000 and 20,000 Da, were purchased from Merck. Bovine serum albumin (BSA) was bought from Sigma.

2.2. Membrane preparation

In order to prepare flat sheet asymmetric membranes, immersion precipitation phase inversion method was used. First, PVC was homogeneously dissolved in NMP as solvent. After obtaining a homogeneous solution, PAN was added to the casting solution, and it was allowed to stir for about 24 hr at room temperature to ensure having homogenous solution. For the case of membranes with PEG additives, PEG was added to the homogenous of solution PVC + PAN and the mixture was stirred for other 2 hr. Then, the homogeneous

Table 1
Composition of the casting solutions

Polymer (wt%)		Additive (wt%)			
PVC	PAN	PEG 600	PEG 1000	PEG 6000	PEG 20000
100	0	0	0	0	0
90	10	0	0	0	0
80	20	0	0	0	0
70	30	0	0	0	0
60	40	0	0	0	0
70	30	4	0	0	0
70	30	0	4	0	0
70	30	0	0	4	0
70	30	0	0	0	4

solution sonicated for 30 min to remove air bubbles which could be formed during mixing. Then, the solution was casted by a 150 µm casting knife on a glass plate substrate. Following that, the casted films were immersed in a deionized water coagulation bath at 30°C and was kept there for 2 hr and then in order to ensure that solvent is completely leached, the samples were immersed in another bath with fresh water at the same temperature. Finally, the membranes were put between two sheets of filter paper to dry before using for performance and charactrization. Table 1 presents the composition of the casting solutions. The total concentration of polymer is 16 wt% for all the bare and blended membranes.

3. Membrane characterization

3.1. SEM

The cross-sectional morphology of the fabricated membranes was investigated via scanning electron microscopy (SEM) images (VEGA\\TESCAN SEM, Czech Republic). The membranes were fractured in liquid nitrogen. For SEM analysis, the samples were coated with gold.

3.2. Contact angle

Static water contact angle measurement was applied to investigate hydrophilicity of the membranes. For this purpose, deionized water droplets were put on the membrane surface and then the contact angle between membrane and water was measured. In order to increase the reliability and repeatability of the results, contact angles of five random points of each sample was observed at room temperature and the average are reported.

3.3. Porosity

The porosity of the porous membranes was calculated using the following equation (gravimetric method):

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times l \times d_w} \tag{1}$$

where, ω_1 is the weight of the wet membrane, ω_2 is the weight of the dry membrane. l is the membrane thickness (m), A is the membrane area (m^2) and d_w is the water density (0.998 g/cm^3).

For investigation of membrane porosity, first a piece of the membrane with measured is immersed in water for 6 hr to make sure that all the pores of membranes are filled. Then, the membrane surface is kindly cleaned and immediately after that the samples are weighted to obtain ω_1. Subsequently, the samples are placed in the oven for 3 hr at 65°C to get fully dried and ready to weight for ω_2.

3.4. Molecular weight cut-off (MWCO)

MWCO of the fabricated membranes were measured by calculation the rejection of PEGs with different molecular weights, 50,000, 70,000 and 100,000 Da. The amount of PEG in permeate was measured via modified Dragendorff reagent method and rejection values were estimated [61,62].

3.5. Tensile strength

Tensile strain of the blend membranes were investigated by using an INSTRON (5566, England) instrument at room temperature and at least three times for each membrane in order to make sure of reproducibility of the results. Tests were performed with speed of 5 mm/min and sample length of 5 cm (grip to grip).

4. Permeation experiment

4.1. Ultrafiltration test apparatus

In this study, the apparatus which is schematically shown in Fig. 1 is used for permeation experiments. This apparatus has a dead-end cell with effective area of about 19.8 cm^2 and the membrane is located in it. A feed tank for pure water or BSA is on the top of the cell and the required driving force for the feed to pass through the membrane is provided by N_2. The feed is magnetically stirred while it is

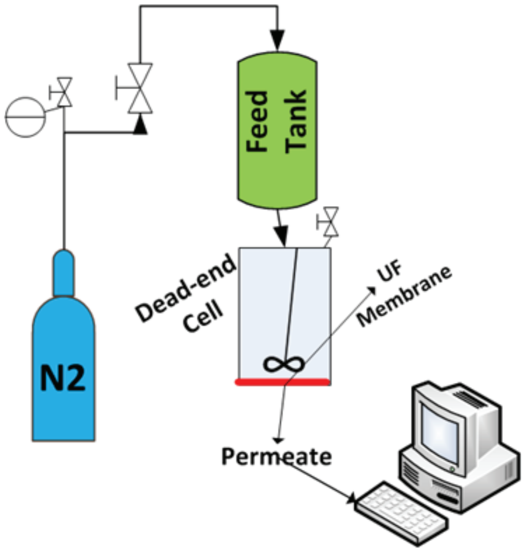

Fig. 1. Schematic of UF setup.

under pressure in the cell and due to this stirring, the composition of the feed can be considered almost constant. The weight of permeation is recorded continuously by a computer in a period of time.

4.2. Ultrafiltration experiments

In order to perform permeation tests, first the membranes are compacted by applying 4 bar pressure for approximately 30 min. After that permeation of pure water and BSA (with concentration of 500 ppm) is measured at operating pressure of 3 bar and flux recovery and rejection can be calculated. Pure water flux is for 90 min and is calculated by the following equation:

$$J = \frac{M}{A\Delta t} \qquad (2)$$

where J, Δt, M and A are flux, permeation time, mass of permeated water, membrane effective area and, respectively.

After 90, min pure water flux and washing the feed tank, the permeation of 500 ppm BSA is measured to study membrane rejection and antifouling properties. This step is also for 90 min and then the membranes are put in distillated water for 1 hr for wasing and finally another 90 min pure water flux is applied to obtain recovery ratio (FRR) of the membranes, using the following equation:

$$FRR(\%) = \left(\frac{J_{\text{water},2}}{J_{\text{water},1}}\right) \times 100 \qquad (3)$$

where $J_{\text{water},2}$ and $J_{\text{water},1}$ are flux of pure water after and before BSA flux, respectively.

Also, BSA rejection can be calculated as follows:

$$R(\%) = (1 - \frac{C_p}{C_f}) \times 100 \qquad (4)$$

where C_p and C_f are BSA concentration in permeate and feed, respectively.

5. Results and discussion

5.1. Contact angle

It is well known that flux and antifouling properties of the UF membranes are quite affected by hydrophilicity of their surface. Contact angle measurement is a useful method to study this parameter [31,63]; therefore, for the blended membranes, contact angle was calculated to investigate the effect of PAN addition of hydrophilicity. The results of this test are presented in Fig. 2(a). As it can be seen, contact angle for the bare PVC is higher than blended membranes, thereby its wettability is lower than the blended ones and as PAN is added to casting solution, contact angle reduces, continuously. Images of contact angle test for PVC and PVC/30 wt% PAN membranes in Fig. 2(b) shows this change evidently. From the images, the angle between the water droplet and surface reduces as PAN is added to the membrane. Thereby, the bare PVC membrane has lowest hydrophilicity and the blended membranes show higher hydrophilicity in comparison with the bare one and this causes higher water flux [64], which will be discussed later.

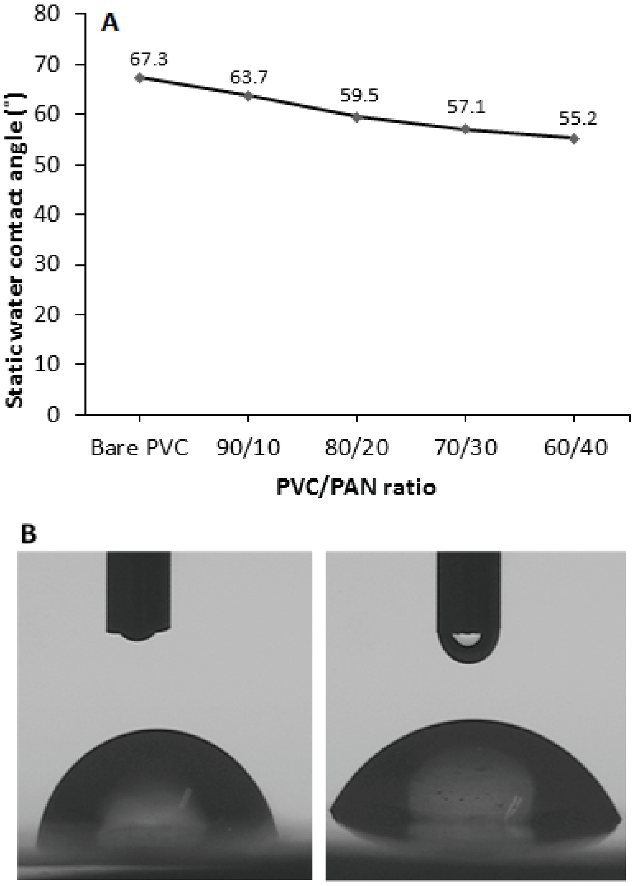

Fig. 2. (a) Static water contact angle of the blended membranes, (b) Images of contact angle test (Left: PVC membrane, Right: PVC/30 wt% PAN membrane.

5.2. Mechanical properties of the PVC/PAN membranes

The mechanical properties of the membranes are presented in Fig. 3 and show that tensile strength of the PVC/PAN blend membranes do not change remarkably and a slight reduction is seen which can be attributed to intrinsic properties of added PAN or compatibility of the blended polymers [40,41]. The result achieved for pure PVC membrane is consistent with other studies [41]. However, for the membrane containing 40 wt% PAN, tensile reduces considerably. This is mainly due to formation of macro-voids in the structure of the PVC/40 wt% PAN membrane [60]. Fragility of PVC/40 wt% PAN membrane was visually observable by handling. All the membranes had enough mechanical stability for UF performance testing.

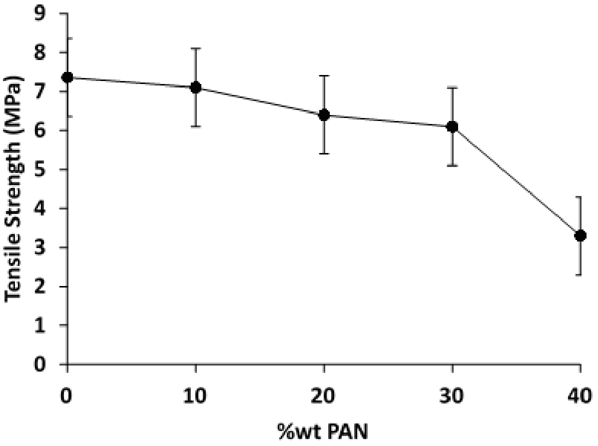

Fig. 3. Tensile strength of the PVC/PAN blend membranes.

5.3. *Morphological properties and casting solution viscosity*

The viscosity of the polymeric solutions was measured to inspect the effect of PAN addition on casting solution and membrane structure, as it is shown in Fig. 4. Also, SEM images were used to investigate the cross-sectional morphology of the fabricated membranes. SEM images of the bare PVC membranes show typical asymmetric structure as shown in Figs. 5 and 6. However, as PAN is added to polymeric solution obvious changes in morphology can be observed and the finger-like form is developed in membrane cross-sectoin.

Addition of PAN to casting solution leads to changes in both thermodynaic and kinetic of phase inversion. In fact, phase separation is mostly affected by these two factors. As the thermodynamic of the polymeric solution gets more unstable, phase separation occurs faster, and it leads to more porous structure. This can happen by addition of hydrophilic additives to polymeric solution. However, the other factor that affects this process and instantaneous demixing, is the kinetic of membrane formation, which can be influenced the viscosity of casting solution [65,66]. Thereby, addition of hydrophilic compounds like PEG and PAN (hydrophilic in comparison with PVC) may lead to more instable solution which leads to fabrication of membranes with more finger-like pores, however, as the percentage of PAN increases in the solution or PEG with higher MW is used, the viscosity increases considerably (Fig. 4). In this case, kinetic parameter is against instantaneous demixing and delays it. Thereby, formation and the structure of membrane pores are the trade-off between these two very effective factors that have been widely and numerically explained in the work of Sadrzadeh et al. [12].

PAN is more hydrophilic in comparison with the main polymer (PVC), thereby its addition causes more thermodynamical instability and as a consequence, percipitation occurs faster. It means that replacement of solvent and non-solvent easier and the prepared membranes are more porous [65,67]. But, it was observed that viscosity of casting solution increases as more PAN is added, as it can be seen from Fig. 4. This increment in viscosity acts as a hindrance for faster simultaneous diffusion of solvent-nonsolvent and instantaneous demixing because it hinders water diffusion to downer layers of the casting solution, then rate of solvent-nonsolvent exchange decreases, thereby precipitation occurs slower (delayed demixing) and the morphology changes to dense structure with macrovoids in the substructure of the membranes.

SEM images were also used to observe changes in morphology with addition of 4 wt% PEG with different MWs. Four various PEG with MWs from 600 Da to 20,000 Da were added to casting solution with PVC/PAN ratio of 70/30. As the MW of PEG increases, the viscosity of the solution goes up and it slows demixing of solvent and non-solvent [68]. Hence, as it is obvious from Figs. 5(e) and 6(e),

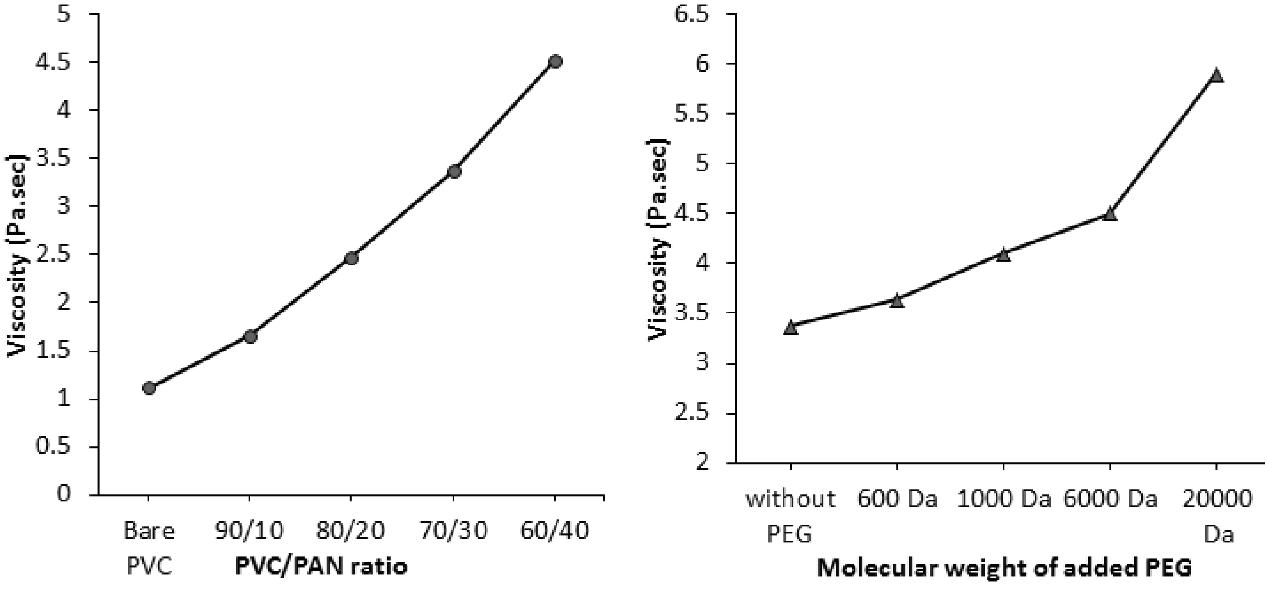

Fig. 4. Viscosity of casting solution.

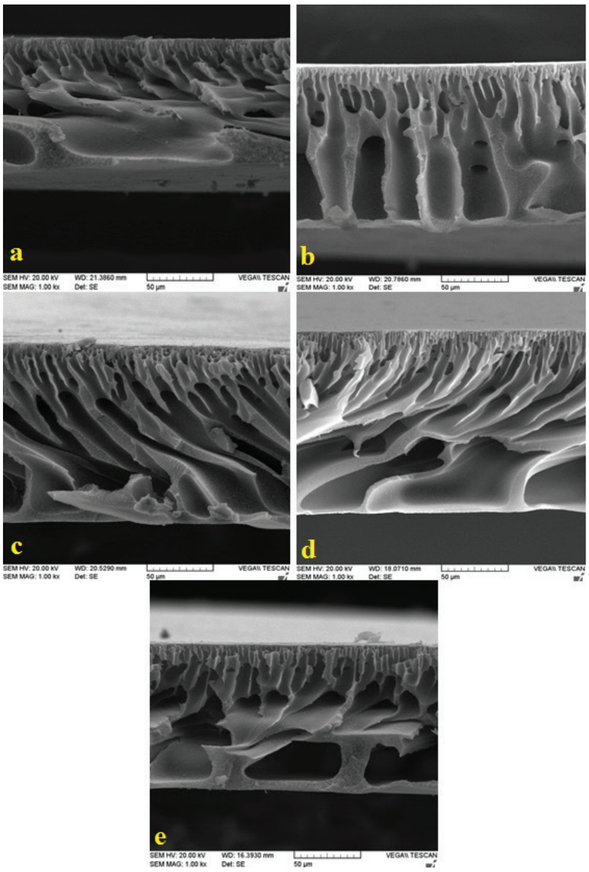

Fig. 5. SEM images of membranes cross section, Effect of PAN addition on membrane morphology: (a) Bare PVC and PVC:PAN ratio of (b) 90:10 (c) 80:20 (d) 70:30 (e) 60:40.

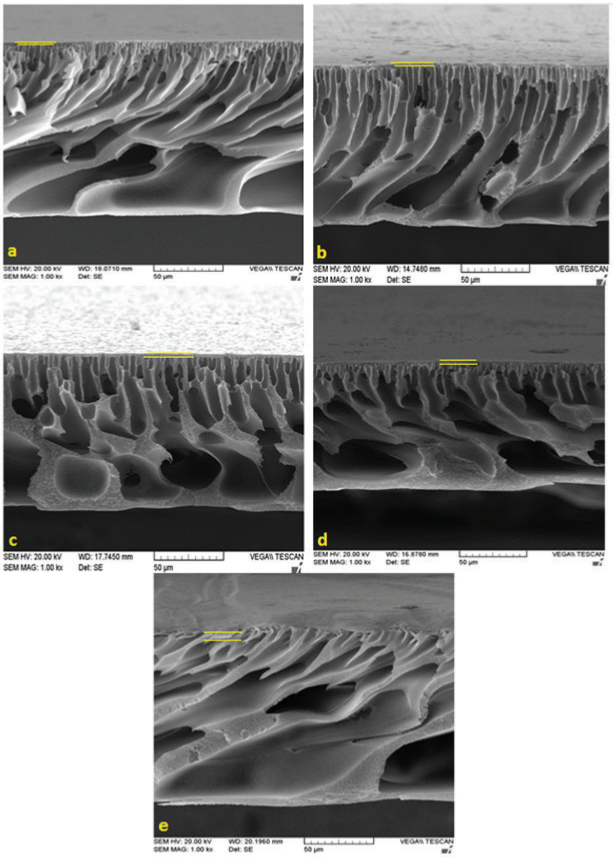

Fig. 6. SEM images of membranes cross section: Effect of 4 wt% PEG addition on membrane morphology with PVC/PAN ratio of 70/30: (a) without PEG (b) PEG 600Da (c) PEG 1000Da (d) PEG 6000Da (e) PEG 20000Da.

the membranes have two different sections: top section is fingerlike pores whereas from the halfway of the cross section these pores are attached to macro voids in the other section of the membranes. It should be also pointed out that the morphology of surface was observed via SEM images as well, but as no significant change was detected, as mentioned in a similar work [36], they are not included here.

The observations from the SEM images show that as the viscosity goes up (with addition of more PAN or increment in molecular weight of PEG), macro-voids are forming in the structure. However, for the case of PAN addition, no obvious increment in skin layer thickness can be obseved, while for thhe case of PEG, increment in skin layer thickness with increasing of MW is more evident [36]. Our assumption is that it is because of leakage of PEGs from the casting film, whereas PAN stay at the structure and do not leak. Thereby, leaskage of PEG with higher molecular weight from the casting film is slower which delays the demixing of solvent and non-solvent, thus membranes with thicker skin layer are formed [12].

6. Permeation and rejection properties of the prepared membranes

The effect of PAN addition on water flux of the prepared membranes were investigated at 3 bar for 90 min. As it can be seen from Fig. 7, addition of PAN leads to higher permeation from 213 Kg/m^{2}h for the bare PVC membrane to 343 Kg/m^{2}h for 70/30: PVC/PAN membrane. This phenomenon can be illustrated by looking at two points: (a) Addition of PAN with higher hydrophilicity leads to higher hydrophilic membrane surface, thereby water permeation increases. (b) Changing in morphology of the blended membranes after PAN addition, which was observed in SEM images [23,69]. Permeation properties of these membranes should be examined by considering these two effects. Increment in surface hydrophilicity was observed from the results of contact angle; therefore water flux is expected to go up [18]. However, as PAN addition reaches 40 wt%, obvious reduction in membrane water flux is observed. This reduction can be explained via observing considerable changes in membrane morphology at this PAN composition. Increasing PAN addition to 40 wt% causes disappearing fingerlike pores in membrane structure. In this PAN composition cross-section of membranes is almost divided into two separated parts with different morphologies as mentioned earlier that lead to reduction of water flux through membranes.

Effect of PEG addition with different MW into the blended membranes structure was also investigated at the same condition, and the results are shown in Fig. 8. Addition of PEG as a well-known pore former which has been used

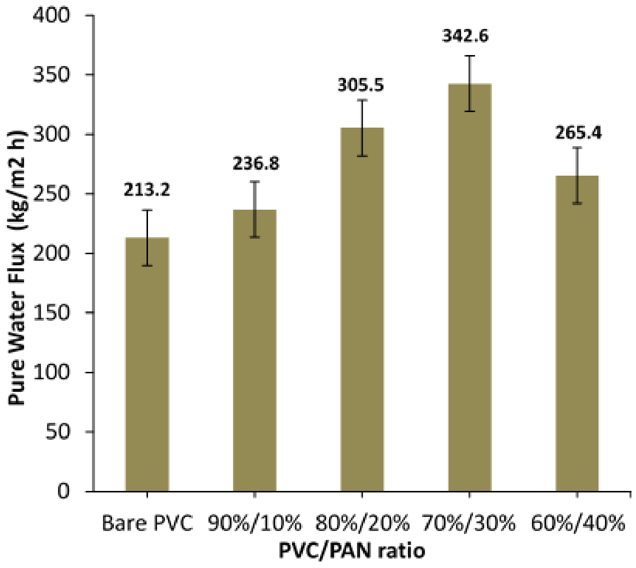

Fig. 7. Pure water flux through the bare PVC and PVC/PAN blended membranes.

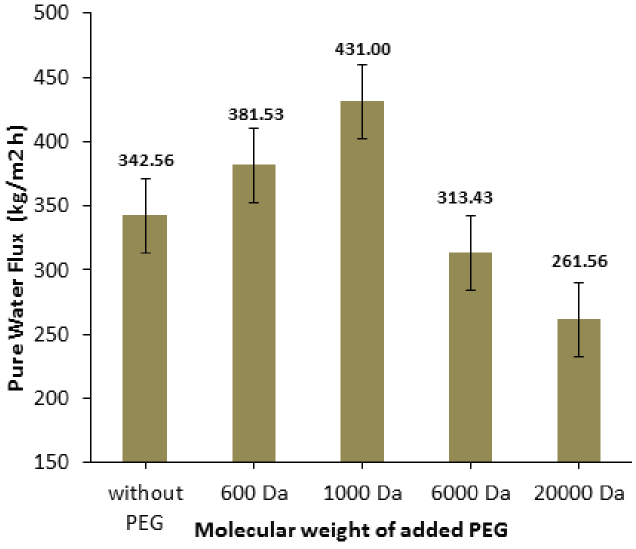

Fig. 8. Effect of PEG MW on pure water flux through the membranes fabricated from PVC:PAN ratio of 70:30.

widely in other filtration membranes, leads to increment in water flux, however, as the MW increases to 6,000 Da and 20,000 Da, this trend changes. For the membranes prepared at almost this polymer content, reduction in water flux has been observed [23,36]. The main reason for this observation is indeed the collapse of fingerlike morphology (as seen and described in the SEM images) and consequently, water permeation reduces [70].

The effect of PAN and PEG addition of BSA rejection properties of the membranes was also studied. As it can be seen in Figs. 9 and 10, addition of PAN and PEG leads to reduction in BSA rejection of the membranes. Two main cases in this respect should be taken into consideration. First, as the membranes surface hydrophilicity increases after PAN and PEG addition to casting solution, thereby BSA adsorption on the pore walls decreases, which means increment in concentration of BSA in permeation flow and consequently, lower BSA rejection [71,72]. The important factor is indeed increasing in membrane porosity after PAN and PEG addition, as it can be seen from the porosity data presented in Table 2 and also from porosity of skin layer of the membranes, observed in the SEM images, the porosity increases and membranes become more permeable for protein and accordingly, rejection decreases. Hence, structure of membrane pores and hydrophilicity are the effective parameters in changes of rejection.

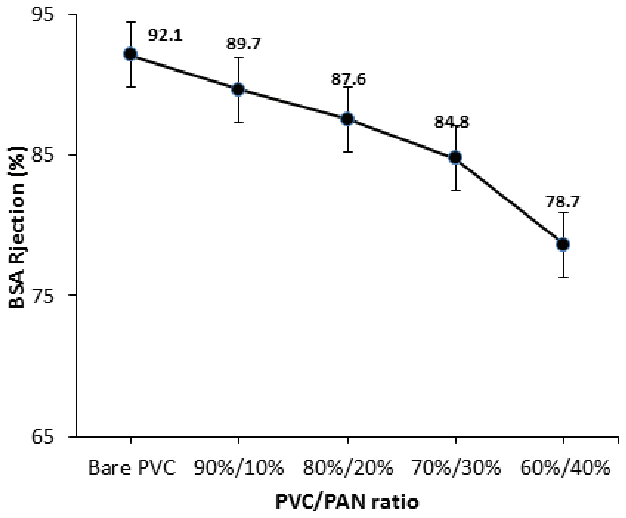

Fig. 9. BSA rejection for the bare and PVC/PAN blended membranes.

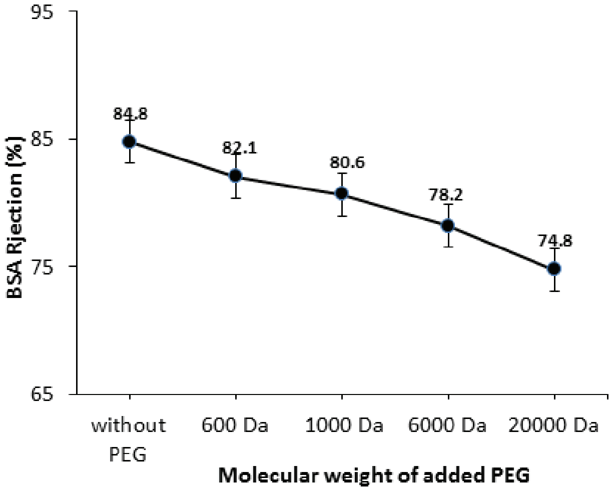

Fig. 10. BSA rejection for the membranes fabricated from PVC:PAN ratio of 70:30 with addition of different PEG.

Table 2 also presents information about MWCO of the fabricated membranes from PEG rejection. As it can be

Table 2
Porosity and MWCO of the PVC/PAN blended and blended membranes with PEG addition

PVC/PAN ratio	Bare PVC	90%/10%	80%/20%	70%/30%	60%/40%
Porosity (%)	67.5	70.2	74.9	79.4	73.6
MWCO (KDa)	63	66	69	72	74
Molecular weight of PEG	Without PEG	600 Da	1000 Da	6000 Da	20000 Da
Porosity (%)	79.4	82.3	86.4	87.1	83.2
MWCO (KDa)	72	75	77	78	80

seen from this Table, all the membranes have MWCO in the range of 63 to 80 KDa which are usual for UF membranes. MWCO increases along with reduction in BSA rejection of the membranes. This means that the membranes are becoming permeable to PEGs with higher molecular weights, as expected.

7. Antifouling properties of the membranes

Fouling during the filtration processes is a very usual disadvantage and in particular, membranes fabricated from hydrophobic materials like PES and PVC suffer from it very much. Thereby, this feature should be taken into consideration in membrane modification, and membranes should be as reversible as possible to gain their permeation after washing in existence of BSA, whey or other micro-organisms [41]. In order to investigate the fouling-resistant ability of the fabricated membranes, pure water flux was measured and compared before and after BSA permeation. As PAN addition has led to lower hydrophobicity in membrane surface, improvement in antifouling ability is expected. These three periods permeation for the blended and PEG-modified membranes can be seen in Figs. 11 and 12. According to these figures, all the permeations follow the same trend [22]. They start with higher flux and then decline as time goes on and reaches almost a constant value.

As it is known, BSA like the other foulants has interaction with the surface of membrane pores and makes a gel layer on them, therefore, water permeation after that is affected. But, existence of PAN in membrane structure and surface lead to lower interaction in between BSA and membrane walls and surface and prevent BSA adsorption as a result.

Flux recovery ratio (FRR) was taken into consideration to assess antifouling ability of the fabricated membranes. Fig. 13 shows that the FRR of the blended membranes increased with PAN addition from 69% for the bare PVC membrane to 87% for the membranes with 30 wt% PAN. After 90 min BSA permeation, the membranes with 20 wt% and 30 wt% PAN have FRR more than 82%, which confirms the blended membranes are much less susceptible to be fouled. This clearly shows higher antifouling ability of the membranes after PAN addition. This observation is in good accordance with similar work [36]. Plus, FRR also increases with addition of PEG to the membranes with 30 wt% PAN and reaches to the maximum of 93% for the membrane fabricated with PEG 1,000 Da, as it can be seen in Fig. 14. However, increment of PEG with higher MW leads to reduction in FRR, thereby, the blended membranes containing PEG 6,000 Da have more desired antifouling ability.

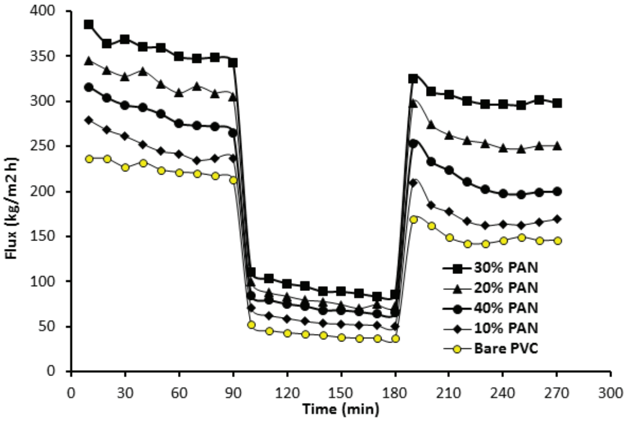

Fig. 11. Pure water and BSA flux for Bare PVC and PVC/PAN blended membranes in three 90 min sections: first pure water flux, then BSA flux and third water flux again after washing the membranes for 30 min with pure water.

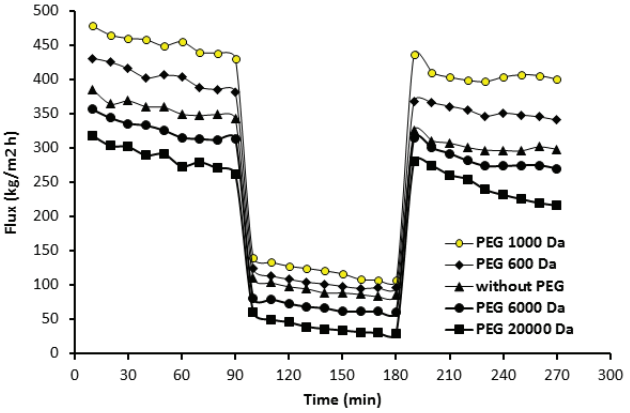

Fig. 12. Pure water and BSA flux 70/30: PVC/PAN blended membranes with and without PEG in three 90 min sections: first pure water flux, then BSA flux and third water flux again after washing the membranes for 30 min with pure water.

8. Effect of PAN addition on PVC/PEG membranes with comparison

Comparison between the blending membranes in this study with the membranes without PAN and in the presence of PEG as a pore former shows that PAN addition has led to better water flux and fouling resistance. For

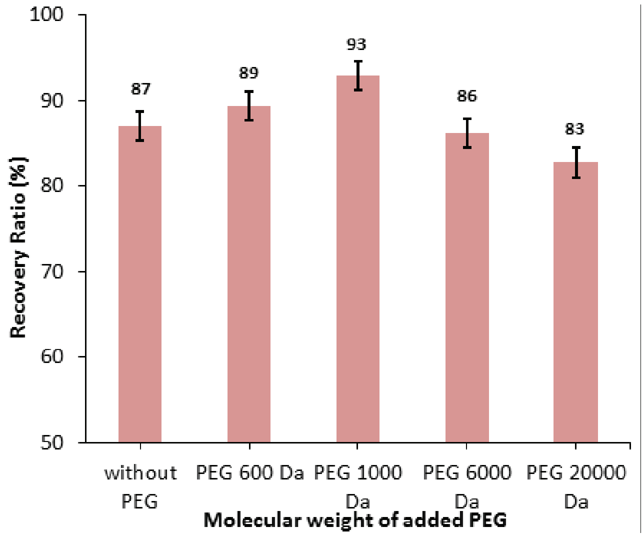

Fig. 13. Flux Recovery Ration of the blended membranes.

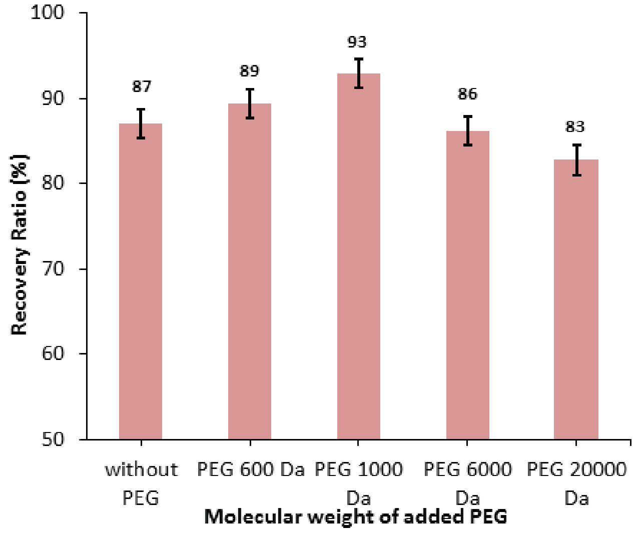

Fig. 14. Flux Recovery Ration of the membranes containing PVC:PAN ration of 70:30 with addition of PEG with different MW.

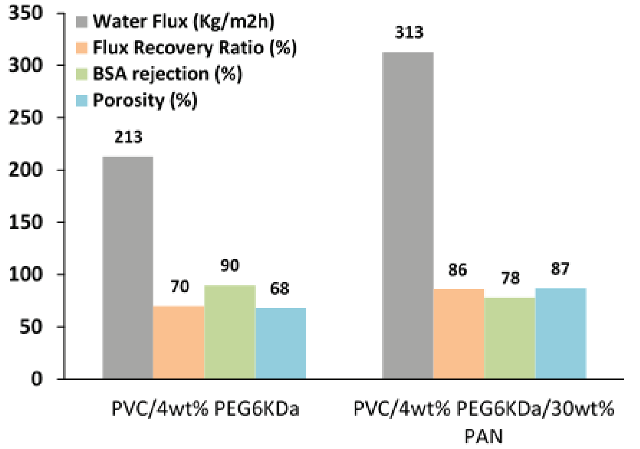

Fig. 15. Comparison between the membranes containing similar amount of PEG 6KDa with and without 30 wt% PAN.

example for the case of PVC/PAN membranes with PEG 6KDa here, the water flux is around 313; however, this number for the PVC membranes with the same percentage of similar PEG is around 213, in our previous study [22,47]. Also flux recovery ratio increases from nearly 70% to 86%, then PAN addition improves antifouling performance of the PVC membranes with PEG. This is obviously because of higher surface hydrophilicity of the membranes after addition of hydrophilic PAN and the fact that PAN maintains in the membranes' structure after membrane formation [36]. Plus, addition blending membrane with 4 wt% PEG KDa has higher porosity in comparison with PVC UF membrane with the same amount of similar PEG [47]. This can be another reason for higher water flux for the membranes fabricated here, containing PVC.

However, PVC/PEG membranes without PAN possess better BSA rejection compared with the one in the presence of PAN. BSA rejection is 90% for PVC with 4 wt% PEG 6KDa, while it reduces to almost 78% in this study for the one with 30 wt% PAN addition. This trend is compatible with the reduction of BSA rejection trend with PAN addition, as we observed here. This mainly due to two reverse effects from more hydrophilic and more porous structure, as discussed earlier [56,57] and in accordance with increment in MWCO of the membranes containing PAN. The comparison between PVC/PEG with and without PAN can be seen in Fig. 15.

9. Conclusion

In the present study, the effect of PAN addition to structure of PVC membranes was investigated. Also, PEG was added to the blended membranes as a pore former and the changes in structure and performance were studied. Water and BSA flux, flux recovery, BSA rejection and antifouling properties were the performance parameters that were inspected. Also, static water contact angle, SEM images and viscosity of the polymeric solutions were taken into consideration to observe changes after PAN and PEG addition. The membrane morphology changes to long fingerlike pores with addition of PAN but this structure falls apart when PAN reaches to 40 wt% which is due to high increment in polymeric solution viscosity that affects instantaneous demixing. The performance results showed higher water flux for the PVC/PAN blended membranes in comparison with the bare PVC membrane and to be more precise for the membranes containing 30 wt% PAN, water flux reached the highest amount which is due to hydrophilic nature of PAN and changes in membrane pore structure. However, for 40 wt% PAN, the water flux started to decrease and collapse in the structure of the fingerlike pores is supposed as the main reason for this. Flux recovery also increased considerably for all the membrane compared with the bare membrane which proves that the fabricated membranes are more reversible to obtain their water flux after protein flux, thereby fouling is improved. BSA rejection declined with PAN and PEG addition, which can be due to higher hydrophilicity in membrane surface and lower BSA adsorption.

Acknowledgment

The authors are grateful for the support of Young Researchers and Elites Club, North Tehran Branch.

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