

Poly (Vinylidene Fluoride) Membrane Preparation and Characterization: Effects of Mixed Solvents and PEG Molecular Weight

Maryam Tavakolmoghadam^{1,2}, Fatemeh Rekabdar², Mahmood Hemmati^{2*}, and Toraj Mohammadi¹

¹ Research Centre for Membrane Separation Processes, Faculty of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran

² Research Institute of Petroleum Industry, (RIPI) Tehran, Iran

ABSTRACT

In this study, polyvinylidene fluoride (PVDF) ultrafiltration membranes were prepared via immersion precipitation method using a mixture of two solvents triethyl phosphate (TEP) and dimethylacetamide (DMAc), which had different affinities with the nonsolvent (water). Properties of the prepared membranes were characterized using scanning electron microscope (SEM) and contact angle and membrane porosity measurements. The prepared membranes were further investigated in terms of pure water flux and BSA rejection in cross flow filtration experiments. The results showed that by using a mixture of DMAc and TEP as solvent and changing the mixed solvent composition, membranes with different morphologies from sponge-like to macrovoid containing were obtained.

Maximum flux of the prepared membranes with different solvent mixing ratios was obtained for the one with 60%wt TEP in the casting solution of PVDF/TEP-DMAc/ PEG which equals to $76.8 \text{ l m}^{-2} \text{ h}^{-1}$. The effect of addition of polyethylene glycol with different molecular weight on morphology and performance of the membranes has also been discussed.

Keywords: Polyvinylidene Fluoride, Mixed Solvent, Poly (Ethylene) Glycol, Phase Inversion

INTRODUCTION

Membrane processes have been used to reuse wastewater due to increasing demand for clean water and shortage of water resources, in recent years. Recent technical innovation of producing new polymeric membranes with desired filtration properties and reduced cost, make membrane filtration the technology of choice for many wastewater treatment applications in different industries such as oil, gas, pharmaceutical, chemical, paper, semiconductor, and textile [1]. Among various polymeric membrane materials suitable

for wastewater treatment, polyvinylidene fluoride (PVDF) has drawn much attention due to its outstanding mechanical and physicochemical properties besides good thermal and chemical resistance to acid and basis cleaning [2]. Phase inversion via immersion precipitation (IP) is the most commonly employed method in fabrication of the PVDF membranes [2]. In this technique, the polymer solution is cast as a thin film on a proper substrate and then immersed into a coagulation bath containing a nonsolvent. The exchange of solvent and nonsolvent causes unstable

*Corresponding author

Mahmood Hemmati*
Email: hemmatim@ripi.ir
Tel: +98 21 4825 3093
Fax: + 98 21 4473 9517

Article history

Received: June 18, 2014
Received in revised form: November 10, 2014
Accepted: November 11, 2014
Available online: October 20, 2016

thermodynamic condition in the cast film and final precipitation of the polymer occurs [3].

The ultimate structure of the membrane is affected by its formation process parameters, which enable one to set the membrane characteristics through proper selection of these variables. Among many formation process parameters affecting polymer precipitation during phase inversion method, solvent plays a very important role in determining the ultimate membrane properties and performance. Low mutual affinity between solvent and nonsolvent results in a relative dense structure, while high mutual affinity favors the formation of a more porous structure [4]. Therefore, proper selection of solvent leads to maintenance of the high polymer chain mobility and consequently formation of the uniform distribution of polymer configuration.

Many researchers have investigated effect of solvent on PVDF membrane properties and performance. Bottino et al. [5] identified eight organic solvents including N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), hexamethylphosphoramide (HMPA), tetramethylurea (TMU), triethylphosphate (TEP) and trimethylphosphate (TMP) as good solvents for PVDF. They showed that by employing each type of these solvents, various structures of PVDF flat sheet membranes could be obtained [6].

Their experimental results demonstrated that the mechanism of PVDF membrane formation is governed by the kinetic factor, i.e. the mutual diffusivity between solvent and non-solvent, rather than their thermodynamic properties. Yeow et al. illustrated by SEM images that, by using TEP as solvent, a uniform sponge symmetric structure could be observed throughout the membrane cross-section using water as coagulant [7]. Similar observations have been previously reported by Bottino et al. [5] and Shih et al. [8]. It is also possible to prepare membranes with a wide range of porosities by using a mixture of two

solvents with different affinities toward the nonsolvent [4]. In this case, the membrane structure is directly affected by the composition of the solvent mixture.

Maghsoud et al. investigated membrane formation from polyvinylchloride (PVC)/dimethyl formamide (DMF)-THF/water system with changing THF to DMF ratio [4]. They explained that by changing the ratio of the two solvents in the solvent mixture, preparation of membranes with different structures and separation performance from one polymer would be possible. Applying this method, it is possible to obtain the desired morphology and performance in any membrane forming system by appropriate selection of solvent pair.

DMAc and phosphates solvents (TEP) are good solvents for PVDF, and DMAc demonstrates a stronger solvent power to PVDF. When DMAc is used as solvent, PVDF membrane exhibits a two part structure composing finger-like and sponge like. However, the flat sheet membranes cast with TEP as solvent exhibits symmetry sponge structure. Therefore, using phosphate–DMAc mixture as solvent, the solvent power to PVDF membrane can be improved, as well as membrane morphology can be controlled.

Pore forming agent is another important factor affecting membrane morphology and performance. Zuo et al. have used different molecular weights of polyethylene glycol (PEG) as pore forming agent to prepare PVDF membranes via phase inversion method [9]. They concluded that using PEG with a relatively low molecular weight as a pore-forming agent will result in enhanced pure water flux and reduced solute rejection of membranes, but PEG can also be used as a pore-reducing agent with a further increment of PEG molecular weight to result in pure water flux decreasing and solute rejection increasing. In another work Liu et al., studied fabrication of polyvinylidene fluoride (PVDF) membranes from non-solvent induced phase separation process (NIPS) and particular focus was given to the effects

of triglycol and Tween 80 as non-solvent additive (NSA) on the polymer solution viscosity and membrane performance. They showed that the addition of triglycol promoted the formation of sponge-like structure and suppressed the formation of finger-like structure. While, Tween80 promoted the formation of macrovoid structure and induced the disappearance of the finger-like pores [10]. Only one single solvent and one single molecular weight of triglycol were investigated while the different molecular weights of PEG were investigated in this study with mixed solvents. Khayet et al. prepared PVDF hollow fiber membranes using the solvent spinning method. DMAc was used as single solvent and ethylene glycol was employed as non-solvent additive. Different membrane characterization method have been performed and compared with each other [11].

To our best knowledge, there is little information about the effect of mixed solvent (TEP/DMAc) and different molecular weight of PEG on morphology and performance of PVDF membranes. In the light of previous research, in this study, mixtures of DMAc and TEP with different mixing ratios were used to prepare PVDF membranes. Different techniques such as SEM, contact angle measurements and filtration experiments of water and BSA were applied to evaluate the morphology and performance of the membranes. The effect of PEG molecular weight less than 1000 gr L^{-1} on the morphology and performance of the PVDF membranes has also been discussed.

EXPERIMENTAL PROCEDURES

Materials

Polyvinylidene fluoride (PVDF) powder ($M_w=573,000 \text{ gr/mol}$, Solvay, France) was used as base polymer. N, N –dimethylacetamide (DMAc) and triethyl-phosphate (TEP) as solvents were obtained from Sigma Aldrich and Merck (Germany), respectively. Polyethylene glycol (PEG, $MW=200,400,600 \text{ Da}$) as pore forming agent was supplied by Merck (Germany). Bovine serum albumin (BSA, $MW=67,000$

gr/mol) was purchased from Sigma Aldrich (Germany). Deionized (DI) water was used throughout the experiments.

Membrane Preparation

Mixed Solvents Ratio

In order to investigate the effect of TEP/DMAc mixing ratio, the flat PVDF membranes were prepared via immersion precipitation process. To prepare the casting solution, the pore forming agent (PEG200) fixed at the amount of 5%wt., was added to a mixture of two solvents TEP and DMAc with different ratios as shown in Table 1 and mechanically stirred to mix completely. Then, PVDF powder (15%wt.) which had been dried at 100°C for 24 h was added and each casting solution was mechanically stirred at 200 rpm for at least 12 hrs at $60\text{--}70^\circ\text{C}$ to guarantee complete dissolution of the polymer. The casting solutions were cast onto a glass plate at 25°C by means of a casting knife with a gap of $250 \mu\text{m}$, and then immersed into a coagulation bath (deionized water at 25°C) immediately.

Table 1: Casting solution specification with different solvent mixing ratio

Rank	Membrane ^{a, b}	Solvent (wt%) ^c	
		DMAc	TEP
1	MTEP0	100	0
2	MTEP20	80	20
3	MTEP40	60	40
4	MTEP60	40	60
5	MTEP80	20	80
6	MTEP100	0	100

a. PVDF = 15%wt.

b. PEG 200 = 5%wt.

c. Solvent = 80%wt. of the total casting solution weight

After complete coagulation during 3 hrs immersion in the bath, the membranes were transferred into a fresh water bath, which was refreshed frequently, to remove traces of the residual solvents, and then the prepared membranes were kept in deionized water until used. The membrane samples were entitled based on the TEP content. As presented in Table 1, "MTEP40" corresponds to the membrane which was prepared from a solvent mixture of TEP/DMAc of 40/60 and so on.

Calculation of Solubility Parameters

Affinity of solvents to polymers can be estimated based on Hansen solubility parameters by introducing the solubility parameter (δ) which is defined as the square root of the cohesive energy density and describes the strength of attractive force between molecules. The solubility parameter (δ) of liquids and polymers can be defined as: [9, 12]

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (1)$$

where, δ_d , δ_p and δ_h denote contributions of dispersive interactions (d), polar bonding (p) and hydrogen bonding (h), respectively.

The solubility parameter of mixed solvents can be calculated by Equation 2, based on volumetric average of the δ values of pure compounds: [9,12]

$$\delta_i = \frac{x_1 v_1 \delta_{i,1} + x_2 v_2 \delta_{i,2}}{x_1 v_1 + x_2 v_2}, \quad i = d, p, h \quad (2)$$

where, δ_i is the solubility parameter of the mixed solvents, x is molecular fraction, and v is molecular volume, and 1 and 2 stand for the two solvents, respectively.

The smaller difference between the solubility parameters of polymer and solvent means the stronger dissolving capacity of the solvent and is calculated as:

$$\delta_{ps} = \sqrt{(\delta_{pd} - \delta_{sd})^2 + (\delta_{pp} - \delta_{sp})^2 + (\delta_{ph} - \delta_{sh})^2} \quad (3)$$

where P and S represent polymer and solvent. The solubility parameter values of the polymer and the solvents are presented in Table 2.

Table 2: Solubility parameters of PVDF and solvents

Component	δ_d [9,12]	δ_p [9,12]	δ_h [9,12]	δ	δ_{ps}
	$MPa^{1/2}$	$MPa^{1/2}$	$MPa^{1/2}$	$MPa^{1/2}$	$MPa^{1/2}$
PVDF	17.2	12.5	9.2	23.17	-
DMAc	16.8	11.5	10.2	22.77	1.43
TEP	16.8	11.5	9.2	22.34	1.08
TEP/DMAc=(20/80)	16.8	11.5	10.02	22.69	1.35
TEP/DMAc=(40/60)	16.8	11.5	9.83	22.61	1.25
TEP/DMAc=(60/40)	16.8	11.5	9.63	22.52	1.16
TEP/DMAc=(80/20)	16.8	11.5	9.42	22.43	1.10

PEG Molecular Weight

In the next step, to study the effect of PEG molecular weight on PVDF membrane morphology, among the membranes prepared based on Table 1,

the membrane with the maximum flux and porosity was selected and the casting solution were prepared with different PEG molecular weights according to Table 3.

Table 3: Casting solution specification with different PEG

Rank	Membrane ^{a, b}	PEG type	TEP/DMAc
1	MPEG200	200	40/60
2	MPEG400	400	40/60
3	MPEG600	600	40/60

a. PVDF=15 %wt.

b. PEG 200= 5 %wt.

Membrane Characterization

Scanning Electron Microscope (SEM)

Morphology of the prepared membranes was characterized using a scanning electron microscope (SEM, TESCAN, Czech Republic). The membranes were cryogenically fractured in liquid nitrogen to observe their cross-sections. Both surface and cross-section of the membrane samples were sputter-coated with thin films of gold to make them conductive.

Contact Angle Measurement

The contact angles formed by water droplets (4 μ l) on the membrane surfaces were measured using sessile drop technique (OCA15 Plus, Dataphysics, Germany). The average of at least 5 measurements was reported.

Porosity, Thickness, and Pore Size

The membrane porosity ε (%) is defined as the volume of the pores divided by the total volume of the microporous membrane. It can be usually determined by gravimetric method, measuring the weight of liquid (here, pure water) contained in the membrane pores:

$$\varepsilon = \frac{(m_1 - m_2) / \rho_w}{(m_1 - m_2) / \rho_w + m_2 / \rho_p} \times 100 \quad (4)$$

where m_1 is the weight of the wet membrane (g); m_2 is the weight of the dry membrane (g); ρ_w is the water density (0.998 gr cm^{-3}) and ρ_p is the polymer density (1.778 g cm^{-3})[8].

The membrane thickness was measured by an Electronic outside micrometer (Model 3109-25).

Mean pore radius r_m (μm) was determined by the filtration velocity method. According to Guerout-Elford-Ferry equation, r_m could be calculated [12].

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l q}{\varepsilon \times A \times \Delta P}} \quad (5)$$

Where η is water viscosity (8.9×10^{-4} Pas); l is the membrane thickness (m); q is the volume of permeate of the membrane (m^3), and ΔP is the operation pressure (1 bar).

Filtration Experiments

PVDF UF membranes were characterized by determination of pure water flux (J) and BSA rejection (R). A cross flow filtration setup as shown in Figure 1 was used to measure pure water flux of the PVDF membranes and composed of a feed tank, a water pump (Grundfos, France, model: JP6.BA-CVBP), a flow meter (Azmoon Motamman Co., Iran, model: P2861, a membrane cell with effective surface of 33.3 cm^2 , pressure gauges (Swagelok, U.S.A) and a balance (A&D, Japan) for permeate collection. The rejection measurement test was carried out with aqueous solution of bovine serum albumin (BSA, MW = 67000, 300 mg L⁻¹) in phosphate buffer (0.1M). The membrane samples were initially compacted under pressure of 2 bar and at a cross flow velocity of 2 m/s with deionized water for 1 hr before starting the filtration measurements. Pure water flux of each membrane samples was measured under pressure of 1 bar and at a cross flow velocity of 1.25 m/s for 1.5 hr all experiments were conducted at room temperature (25°C) and at a constant operation pressure of 1 bar. Pure water flux and BSA rejection are defined as Equations (6) and (7), respectively.

$$J_{pw} = \frac{Q}{A \times T} \quad (6)$$

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (7)$$

where J_{pw} is pure water flux ($l\ h^{-1}\ m^{-2}$), Q is volume of the permeated pure water (l), A is effective area of the membrane sample (m^2), and T is permeation time (r). Also, R is BSA rejection (%), C_p and C_f are permeate and feed concentrations (%wt.), respectively. BSA concentration was estimated using UV-visible spectrophotometry (Jasco-V670, Japan) at 280 nm.

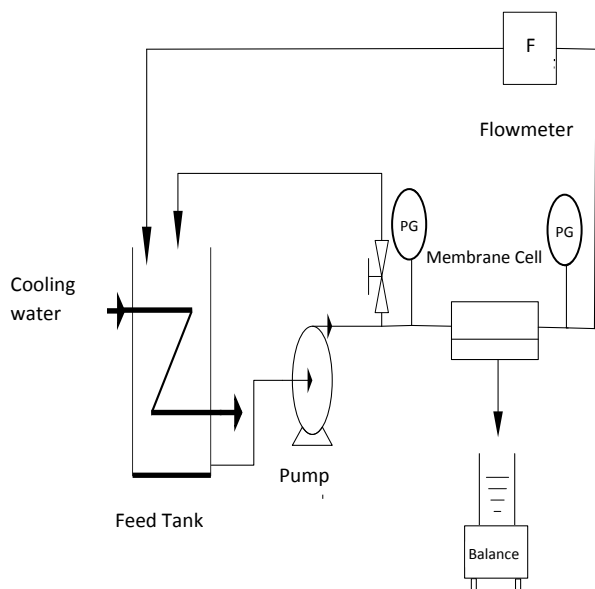


Figure 1: Cross flow filtration setup

RESULTS AND DISCUSSION

Effect of TEP/Dmac Ratio

Solvent plays a very important role in determining the ultimate membrane properties and performance. By mixing TEP and DMAc as solvent, PEG200 used as additive fixed at 5 %wt., the effects of TEP content of the solvent mixture on the membrane morphologies and performances were investigated.

Cross-section and top surface of the membranes which were prepared from different mixing ratios of TEP and DMAc are shown in Figure 2. As illustrated, most of the membranes present a typical asymmetric structure consisting of a thin dense top-layer and a thick porous sub-layer. The porous sub-layer itself, consists of two separate parts of a finger-like and a sponge-like structure similar to the reported structures in previous researches [12]. According to Figure 2, the fingerlike pores became wider with the increase of TEP content from 0 to 60 %wt (MTEP0 to MTEP60) but then were shortened as the content of TEP further increased from 60 to 100 %wt (MTEP60 to MTEP100).

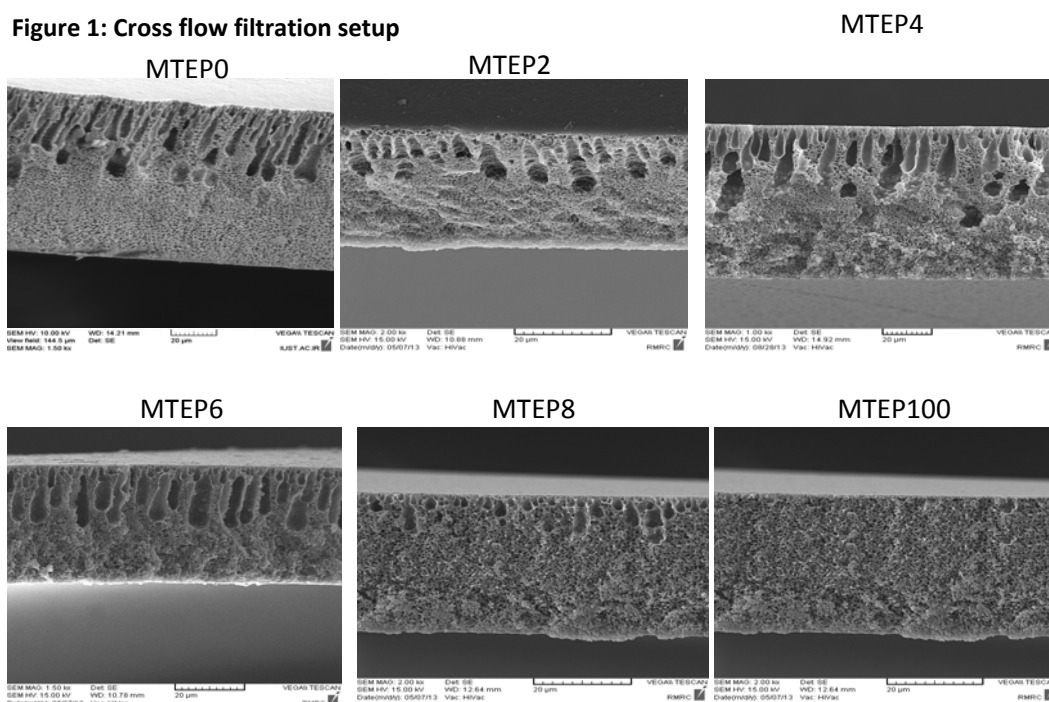


Figure 2: SEM image of the prepared membrane using different mixed solvent

It can be concluded that due to the faster precipitation rate of the casting solution systems in which Kinetic is dominant such as PVDF/DMAc-TEP, by adding 60%wt of TEP to the solvent mixture, the macrovoids, became wider and extended to bottom surface of the membrane. Among the solubility parameter values in Table 2, there is an optimum value which corresponds to the best performance of the membrane.

This phenomenon has been also observed in similar study for the mixture of DMAc and TMP [12]. This is in consistence with the results illustrated in Figure 3 related to the pure water flux and porosity of the membranes with different ratios of DMAc/TEP.

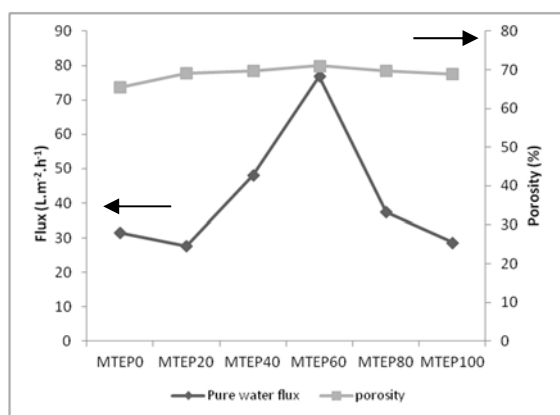


Figure 3: Pure water flux of the membranes prepared using different solvent mixing ratios.

It has been generally accepted that the morphology of microporous membrane affected by the precipitation rate influences the performances of the membrane.

As shown in Figure 3, the flux and the porosity of the membrane cast with TEP (60%wt)–DMAc (40%wt) (MTEP60) are the maximum amount, which are $76.8 \text{ Lm}^{-2}\text{h}^{-1}$ and 71.05%, respectively. According to the aforementioned experiment results, the growing of macrovoids decreases permeation resistance and leads to the higher flux and porosity. However, as shown in Figure 4, the rejection of MTEP60 is not significantly different from that of others (MTEP0, MTEP20, MTEP40, MTEP80, and MTEP100), and equals to 82.46%; this result can be explained by the

existence of macrovoids beneath the skin layer in all of the cross-section morphologies.

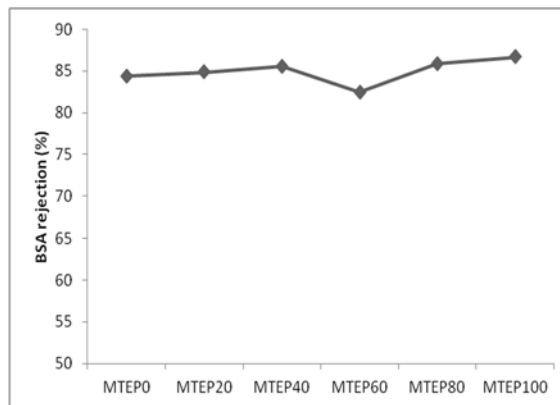


Figure 4: BSA rejection of the membranes prepared using different solvent mixing ratios

The above discussion has been confirmed by determination of pore size of the membranes as illustrated in Table 4. It can be observed that the pore sizes of all the prepared membranes are in UF region [3] and MTEP60 has the largest surface pore size. Consequently, the corresponding highest pure water flux of that membrane is due to increased surface pore size while volume porosity (Figure 3) increased less than 10%. As we know, porosity is one of the parameters affecting the membrane flux, but there are also some other factors influencing the membrane flux. Among them are the number and size of the pores on the surface of active layer and the morphology and structure of the membrane pores. Similar trend has been reported by Li et al [12].

Table 4: Determination of pore size of the prepared membranes

Rank	Membrane	$r_m(\text{nm})$
1	MTEP0	10.44
2	MTEP20	9.69
3	MTEP40	13.24
4	MTEP60	17.35
5	MTEP80	11.55
6	MTEP100	9.30

Therefore, the addition of 60%wt of phosphate in the mixed solvent is used in our further

investigation on the effects of different mixed solvent on the membrane morphology and performances, as discussed in the following investigations relating to the effect of PEG molecular weight on membrane morphology and performance.

Effect of PEG Molecular Weight

Permeability of PVDF membranes with different PEG additives with fixed ratio of mixed solvents (DMAc/TEP=40/60) are shown in Figure 5. As shown, with increasing PEG molecular weight, water flux decreased, although for all molecular weights of PEG, the pure water fluxes for the membranes prepared from mixed solvents are higher than single solvent. As can be observed the flux enhancement for the membrane prepared from mixed solvent and PEG200 is much more than two others. The reason relates to trade-off between thermodynamic enhancement and kinetic hindrance effect of additives on the phase inversion process and also viscosity of the casting solution [14]. From the obtained results it can be concluded that the kinetic hindrance of PEG400 and 600 as additive were dominant in the phase inversion process and had less effect on flux enhancement in comparison with PEG200. Zuo et al. which have also studied the effect of different molecular weight of PEG on PVDF membranes concluded that Low MW PEG, less than 6 kDa, enhanced the PWF and reduced solute rejection of membranes, but higher MW PEG acted as pore-reducing agent [13]. However it is not in consistence with our measured results for PEG 400 and 600. Considering the results, it can be concluded that in a system of mixed solvents (TEP/DMAc)/PVDF/water using PEG with higher molecular weight of 200 can reduce the pure water flux while it is expected to act as a pore forming agent.

In order to explain this phenomenon we should consider the trade-off between thermodynamic enhancement and kinetic hindrance affected by addition of different additives to the casting solution as have also been reported by Sadzadeh et al. [14].

Journal of Petroleum Science and Technology 2016, 6(2), 11-21
© 2016 Research Institute of Petroleum Industry (RIPI)

When a polymer additive is included in the initial casting solution, its influence manifests in two ways, namely, enhanced polymer volume fraction in the system, and an additional interaction between the new type of functional groups in the additive and the solvent. In the presence of a polymeric additive, the binodal curve moves toward the polymer/solvent axis and the single phase region decreases [14]. Hence, whatever the precipitation path, it will be shortened and the coagulation process is accelerated. This results in formation of more porous membranes [14]. On the other hand, kinetics only affects the precipitation path line while the position of binodal points changes owing to thermodynamics. Viscosity of casting solution is an important factor controlling phase inversion kinetics and as can be observed due to viscosity increment by using mixed solvent the effect of PEG molecular weight on phase inversion is more obvious.

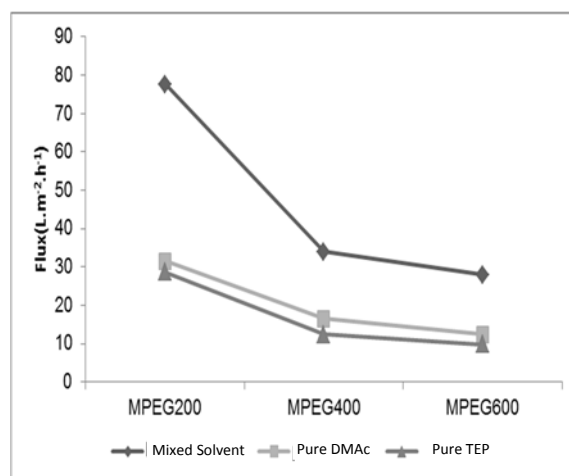


Figure 5: Pure water flux of the membranes prepared using different molecular weight of PEG.

In order to understand these results, the cross-sections and the upper surface of membranes were carefully studied with SEM. Figure 6 shows the SEM micrographs of membranes cast from solutions with fixed ratio of mixed solvents and PVDF using PEG additives with different molecular weight. Although membranes all showed the characteristics of an asymmetric membrane composing of a skin layer near the top surface and a porous supporting solid

<http://jpst.ripi.ir>

matrix, PEG with different molecular weights exerted an obvious effect on membrane surface and cross-section. The size and number of pores on the membrane upper surface decreased when the molecular weight of PEG additive increased from 200 to 600. The finger-like cavities shape

changed gradually with PEG molecular weight increasing from 200 to 600. The finger-like pores shortened in width and length towards the membrane bottom when PEG molecular weight increased to 600, as seen from Figure 6.

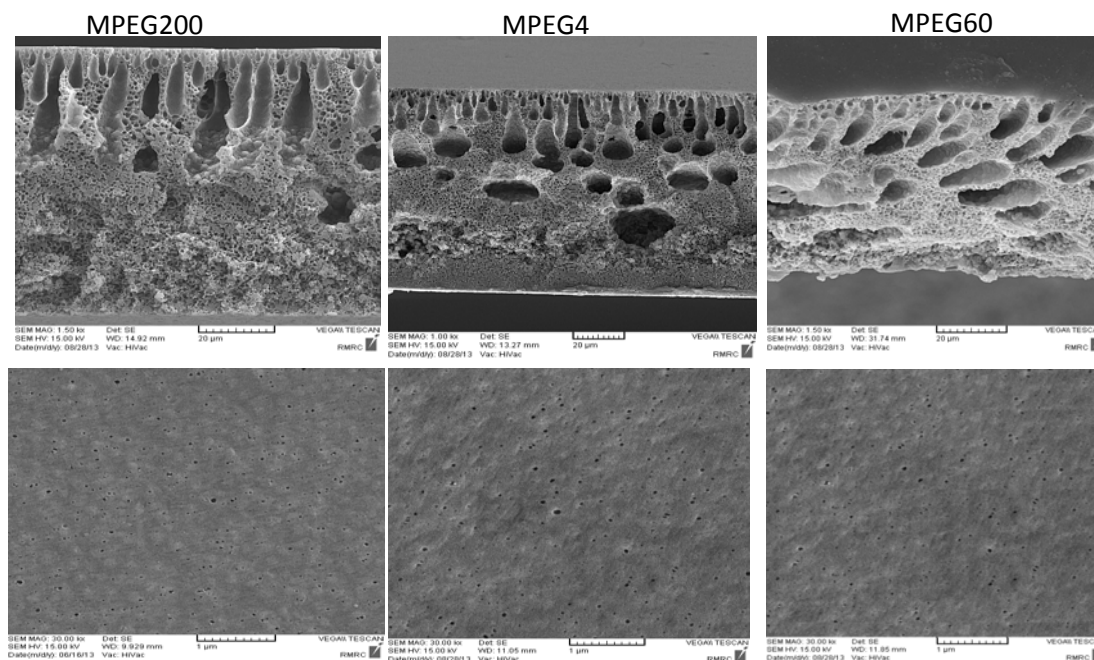


Figure 6: SEM images of prepared membrane using different mixed solvent.

It could be concluded from SEM observations of membranes that the membrane morphologies and structures agreed well with permeation results which presented in Figure 5 and depend on not only the overall membrane morphologies but also especially, on the upper surface of membranes. Generally, more pores on membrane surface and the better interconnectivity inside membrane would contribute to enhancing pure water flux and reducing solute rejection [15]. When PEG molecular weight increased from 200 to 600, the pore size and pore number on membrane upper surface decreased. Correspondingly, pure water fluxes reduced. The sufficient development of macrovoids and interconnectivity leads to the increase of the membrane porosity. As PEG molecular weight increased from 200 to 600, more dense structure for membrane appeared, as a result of delayed demixing.

It could be deduced from the above analysis that PEG acted as a pore-forming agent whereas it could suppress the growth of finger-like macrovoids with the further molecular weight increasing [13].

Contact angle provide an indication of membrane hydrophilicity. Lower contact angle indicates greater hydrophilicity of the membrane. The hydrophilicity of the membrane have been investigated using contact angle measurement which is presented in Table 5.

Contact angle of membrane M0 shows that the additive free PVDF membrane using only DMAc as solvent is hydrophobic. PEG is a hydrophilic material, and is expected to increase hydrophilicity of the membranes. The extent of this induced hydrophilicity is related to the amount of additives that remains in the polymer matrix during demixing process. As shown in Table 5, the molecular weight of PEG has not have significant effect on hydrophilicity of the membranes since relatively

similar values (with less than 2 degrees difference) obtained for the membranes prepared from PEG200 and 400. However as observed in Table 5, increasing molecular weight of PEG decreased the contact angle of the PVDF membranes to some extent. Generally, the extent of this induced hydrophilicity is related to the amount of additives that remain in the polymer matrix during demixing process which depends on molecular weight of additives and in our case PEG [12].

Table 5: Contact angle of the prepared membrane using different molecular weight of PEG

Rank	Membrane	Contact angle (°)
1	M0	80.3
2	MPEG200	60.15
3	MPEG400	58.03
4	MPEG600	57.5

BSA rejection of the membranes prepared using different PEGs are illustrated in Figure 7. Since thermodynamic enhancement effect of PEG200 resulted in more porous membrane with larger surface pore size, its BSA rejection was minimum among other molecular weights of PEG used as additives, however it is still small enough for obtaining a reasonable BSA rejection.

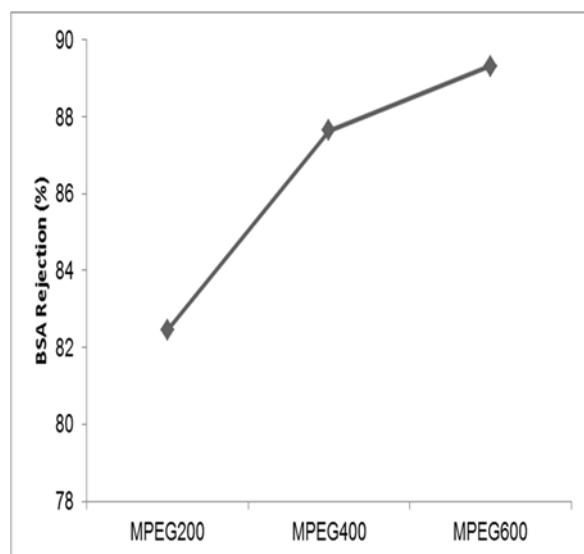


Figure 7: BSA rejection of the membranes prepared using different molecular weight of PEG

CONCLUSIONS

PVDF membranes with different mixing ratios of (TEP/DMAc) as solvent and PEG as pore forming agent have been prepared via phase inversion method.

Properties of the prepared membranes were characterized using scanning electron microscope (SEM) and contact angle and membrane porosity measurements. The prepared membranes were further investigated in terms of pure water flux and BSA rejection in cross flow filtration experiments. The results showed that by using a mixture of DMAc and TEP as solvent and changing the mixed solvent composition, membranes with different morphologies from sponge-like to macrovoid containing were obtained. The membrane had the maximum flux of $76.8 \text{ Lm}^{-2}\text{h}^{-1}$ when the content of TEP in the TEP–DMAc mixed solvent reached 60 %wt. The effect of addition of polyethylene glycol with different molecular weights has been discussed on morphology and performance of the membranes. However according to the obtained results changing PEG molecular weight below 600 Da. has not significant effect on membrane hydrophilicity.

REFERENCES

- [1] Loahardjo N., Xie X., Yin P., and Morrow N. R., "Low Salinity Water flooding of A Reservoir Rock," Paper SCA2007-29-Presentated at *the International Symposium of the Society of Core Analysts*, Calgary, Canada September 10-12, **2007**.
- [2] Austad T., Rezaei Doust A., and Puntervold T., "Chemical Mechanism of Low Salinity Water Flooding in Sandstone Reservoirs," Paper SPE 129767-PP. Presented at *the SPE Improved Oil Recovery Symposium*, Tulsa, Oklahoma, USA, **2010**.
- [3] Salathiel R. A., "Oil Recovery by Surface Film Drainage in Mixed Wettability Rocks," *Journal of Petroleum Technology*, **1973**, 25, 1216-1224.
- [4] Jadhunandan P. and Morrow N. R., "Effect of Wettability on Water flooding Recovery

- for Crude Oil/Brine/Rock Systems," *SPE Reservoir Engineering*, **1995**, *10*, 40-46.
- [5] Tong Z. X., Morrow N. R., and Xie X., "Spontaneous Imbibition for Mixed-wettability States in Sandstones Induced by Adsorption from Crude Oil," *Journal of Petroleum Science and Engineering*, **2003**, *39*, 351-361.
- [6] Ligthelm D. J., Gronsveld J., Hofman J. P., Brussee N. J., et al., "Novel Water Flooding Strategy by Manipulation of Injection Brine Composition," Paper SPE 119835. Presented at the **2009 SPE EUROPEC/ EAGE Annual Conference and Exhibition**, Amsterdam, The Netherlands, **2009**.
- [7] Rezaei Doust A., Puntervold T., and Austad T., "A Discussion of the Low Salinity EOR Potential for a North Sea Sandstone Field," Paper SPE 134459. Presented at the *SPE Annual Technical Conference and Exhibition*, Florence, Italy, **2010**.
- [8] Alotaibi M. B., Azmy R. M., and Nasr-El-Din H. A., "A Comprehensive EOR Study Using Low Salinity Water in Sandstone Reservoirs," Paper SPE 129976. Presented at the *SPE Improved Oil Recovery Symposium*, Tulsa, Oklahoma, USA, **2010**.
- [9] Lager A., Webb K. J., Black C. J. J., Singleton M., et al., "Low Salinity Oil Recovery: An Experimental Investigation," Paper SCA2006-36. Presented at the *International Symposium of the Society of Core Analysts* Trondheim, Norway, **2006**.
- [10] Boston W. G., Brandner C. F., and Foster W. R., "Recovery of Oil by Water flooding from an Argil-laceous, Oil-containing Subterranean Formation," US Patent 3740956, October **1969**.
- [11] Tie H. and Morrow N., "Low-Flood-Rate Residual Saturation in Carbonate Rocks," Paper SPE 10470 Presented at the *SPE International Petroleum Technology Conference*, Doha, **2005**.
- [12] Morrow N. R., "Wettability and its Effect on Oil Recovery," *Journal of Petroleum Technology*, **1990**, *42*, 1476-1484.
- [13] Anderson W. G., "Wettability Literature Survey-Part 2: Wettability Measurement," *Journal of Petroleum Technology*, **1986**, *18*, 1246-1262.
- [14] Madsen L., Grahl-Madsen L., Grøn C., Lind Ida., "Adsorption of Polar Aromatic Hydrocarbons on Synthetic Calcite," *Organic Geochemistry*, **1996**, *24*, 1151-1155.
- [15] Thomas M. M., Clouse J. A., and Longo J. M., "Adsorption of Organic Compounds on Carbonate Minerals: 1. Model Com-pounds and Their Influence on Mineral Wettability," *Chemical Geology*, **1993**, *109*, 201-213.
- [16] Zou L., Han B., Yan H., Kasperski K. L., et al., "Enthalpy of Adsorption and Isotherms for Adsorption of Naphthenic Acid onto Clays," *Journal of Colloid & Interface Science*, **1997**, *190*, 472-475.
- [17] Legens C., Toulhoat H., Cuiec L., Villieras F., et al., "Wettability Change Related to the Adsorption of Organic Acids on Calcite: Experimental and Ab Initio Computational Studies," Paper SPE 49319 Presented at the *SPE Annual Technical Conference and Exhibition*, New Orleans, USA, **1998**.
- [18] Zhang P. and Austad T., "The Relative Effects of Acid Number and Temperature on Chalk Wettability," Paper SPE 92999 Presented at the *SPE International Symposium on Oilfield Chemistry*, Houston, USA, **2005**.