

Morphology control in PVDF membranes using PEG/PVP additives and mixed solvents

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Abstract. The effects of the mixed two solvents, Dimethylacetamide (DMAc) and Dimethylformamide (DMF), and Polyethylene glycol (PEG) and Polyvinylpyrrolidone (PVP) as additives on performance of Polyvinylidene fluoride (PVDF) membranes were studied. Initially, PEG200 was used as a primary additive at fixed percentage of 5% wt. PVP was then blended with PEG200 in different concentrations. PVDF and DMAc were used as polymer and solvent in the casting solutions, respectively. To control the diffusion rate of PVP in the presence of PEG200 and PVP blend, mixtures of DMAc and DMF were used as the mixed solvent in the casting solutions. Asymmetric PVDF membranes were prepared via phase inversion process in a water bath and the effects of two additives and two solvents on the membrane morphology, pure water flux (PWF), hydrophilicity and rejection (R) were investigated. Attenuated Total Reflection Fourier Transform Infrared Spectra (ATR-FTIR) analysis was used to show the residual PVP on the surface of the membranes. Atomic Force Microscopy (AFM) was utilized to determine roughness of membrane surface. The use of mixed solvents in the casting solution resulted in reduction of PVP diffusion rate and increment of PEG diffusion rate. Eventually, PWF and R values reduced, while porosity and hydrophilicity increased.

Keywords: PVDF membranes; blending; PEG/PVP; mixed solvents; DMAc/DMF

1. Introduction

Due to its prominent properties such as high mechanical solidity, acceptable thermal resistance, high chemical resistance in comparison with other polymers, PVDF has grabbed special attention. Different methods have been introduced for fabricating PVDF membranes. They include sintering, track etching, and phase inversion. The latter is the most common method in fabricating polymer membranes (Ulbricht 2006, van de Witte *et al.* 1996). Two phenomena, thermodynamic and kinetic, play role in phase inversion process. The former affects skin layer of the membrane, while the latter affects sublayer. The additive type, the additive concentration and the solvent type control these two parameters (Mohsenpour *et al.* 2016)(Shockravi *et al.* 2017) (Wang, Wang and Wu 2012). There are two types of exchange in phase inversion; solvent-nonsolvent exchange and additive-nonsolvent exchange which are mutually dependent. Dimethyl sulfoxide (DMSO), DMF, and DMAc are solvents with high solubility capability. Higher solubility capability of the solvents helps phase inversion process occur more quickly and results in formation of the finger-like structure followed by complete expansion of the pores. In this circumstances, the solubility

capability of solvent controls thermodynamics. In fact, the skin layer of the membranes can be controlled by changing the solubility capability of solvents. Applying suitable solvent makes the solution more unstable from thermodynamics point of view. Likewise, thermodynamic instability results in faster phase inversion and more surface porosity. Actually, it can be claimed that using mixed solvents can control the skin layer of the membranes (Madaeni and Taheri 2011, Hyun *et al.* 2004, Bottino, A, Capannelli G., Munari, S, Torturro 1988, Tavakolmoghadam, Mohammadi and Hemmati 2016).

The type and concentration of additives added into the membrane casting solution are two important factors to be considered. The presence of additives increases viscosity of the membrane casting solution. Any increase in viscosity decreases solvent-nonsolvent diffusion rate. Controlling the diffusion rate can also affect the membrane sublayer (Yeow, Liu, and Li 2003). The presence of hydrophilic additives in the casting solutions prepared using hydrophobic PVDF makes the membrane less hydrophobic (more hydrophilic). In phase inversion process, hydrophobic PVDF chains slow down entrance of water molecules into the membrane casting solution. This problem can be tackled by adding PVP or PEG. Because of their hydrophilic chains, they can increase solvent-nonsolvent exchange rate. On the other hand, increasing the additive concentration results in the higher viscosity of the casting solution. This increased viscosity reduces the exchange rate via controlling the

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kinetic parameter that eventually leads to formation of the sponge-like pores (Geburu and Das 2017)(Ma *et al.* 2011).

In PVP concentration up to 5% by influencing kinetic parameter, the sponge-like pore structure starts to form. In reality, PVP concentration below 5% controls thermodynamics and due to the hydrophilicity of PVP, the solvent-nonsolvent exchange rate increases (Mohsenpour *et al.* 2016)(Shockravi *et al.* 2017).

In this article, two series of PVDF membranes with asymmetric structures produced via phase inversion method were investigated. PWF, R, and volumetric porosity were investigated to study the effects of mixed solvents and mixed additives on performance of the membranes. SEM images were also used to observe the membranes structure. The amount of residual PVP over the surface of two membranes with PVP concentration of 3%, one fabricated with pure solvent and the other with mixed solvents was compared using AT-FTIR analysis. To investigate hydrophilicity of the membranes, CA measurement was performed. Also, EWC of the membranes was measured. The roughness of surface membrane was examined by AFM. Actually, the main novelty of our article is to study the effect of simultaneous application of mixed solvents and mixed additives to benefit their synergic effects in controlling the additive exit rate in the phase inversion process which is an important factor in the membrane preparation and to our best knowledge, there is no information about it.

2. Experimental

2.1 Material

Solef®1015 PVDF (MW= 573000 gr/mole) was purchased from Solvay Advanced Polymers company. It was pre dried at 60 °C. for 24 h before being used. DMAc ($\geq 99.0\%$ purity) and DMF ($\geq 99.0\%$ purity) as solvents and PEG200 as additive were supplied by Merck, Germany. PVP10 kDa and Dextran450 kDa were obtained from Sigma, Germany. Deionized water (DI) was used as nonsolvent in coagulation bath.

2.2 Membrane preparation

The flat PVDF membranes were prepared via the well-known isothermal immersion precipitation method. The PVDF powder (18wt.%) and the additives (PVP and PEG200) were added to the solvents in a triangle baker and the solutions were mechanically stirred for 48 h at 60 °C to obtain a homogeneous solution. Different compositions of the casting solutions were shown in Table 1. The first membrane casting solution of membranes contained pure DMAc and the rest contained mixtures of the two solvents (DMAc/DMF). Considering the published results (Wang, Wang, and Wu 2012), a 20/80 ratio was selected for DMAc/DMF mixture to control the solvent diffusion rate. All the membrane casting solutions contained PVDF and mixtures of the two additives (PEG200 and PVP). Concentration of PEG200 was constant (5 wt.%) and concentration of PVP gradually increased from 0 to 5wt.%.

Table 1 Composition of the prepared membrane in percentage

No.	polymer/PVDF (wt.%)	Solvent	PEG200 (wt.%)	PVP (wt.%)
M1	18	DMAc (77%)	5	0
M2	18	DMAc/DMF (77%)	5	0
M3	18	DMAc (76%)	5	1
M4	18	DMAc/DMF (76%)	5	1
M5	18	DMAc 75%	5	2
M6	18	DMAc/DMF 75%	5	2
M7	18	DMAc 74%	5	3
M8	18	DMAc/DMF 74%	5	3
M9	18	DMAc 73%	5	4
M10	18	DMAc/DMF 73%	5	4
M11	18	DMAc 72%	5	5
M12	18	DMAc/DMF 72%	5	5

Higher concentrations resulted in twisting and aggregation of the chains and influenced pore size distribution (Ngang *et al.* 2014).

The homogeneous casting solutions were cast on the support by a digital casting knife with thickness of 200 μm at room temperature and then immediately immersed into the coagulation bath (deionized water at 25 °C). After complete coagulation, the membranes were kept in deionized water to remove their residual solvents for subsequent analysis.

2.3 Membrane morphology

The surface and cross-sectional membrane morphology were observed using Scanning Electron Microscope (SEM) (model VEGA-TESCAN, Check Republic). Before using images from cross section, membrane samples were fractured in liquid nitrogen. All samples were coated with thin gold layers.

2.4 Porosity and hydrophilicity measurement

To study the membranes' hydrophilicity, two parameters, Equilibrium Water Content (EWC) and Contact Angle (CA), were measured. The CA measurements of the prepared membranes were conducted using a contact angle measuring instrument (VIT6000).

The EWC and porosity (ϵ) measurements were performed using a simple gravimetric method, where each membrane sample ($2 \times 2 \text{ cm}^2$) was immersed in a beaker containing DI water for a specific period (for the ϵ measurements, the membrane sample was immersed in butanol instead). Then, the samples were dabbed with dry filter paper and weighed immediately (Ww). Finally, the membranes were kept inside a vacuum atmosphere for 24 h at 50 °C. The final dry weight of the samples (Wd) were

measured again. The membrane porosity values were calculated via dividing the pores volume by the total membrane volume. Therefore, the results were calculated using the following equation:

$$\varepsilon = \frac{(W_w - W_d) / \rho_w}{(W_w - W_d) / \rho_w + W_d / \rho_p} \times 100 \quad (1)$$

where W_w is the weight of wet membrane (gr); W_d is the weight of dry membrane (gr); ρ_w is butanol density (0.805 gr/cm^3) and ρ_p is the PVDF polymer density (1.78 gr/cm^3). The EWC results were calculated using the following equation:

$$EWC(\%) = \frac{W_w - W_d}{W_w} \times 100 \quad (2)$$

The average values were reported after five different position measurements for each sample with standard deviation of less than 9%.

2.5 FTIR-ATR spectra

FTIR-ATR spectra of the two prepared membranes were recorded using Bruker-ALPHA FTIR spectrometer (Germany) with horizontal ATR device.

2.6 Pure water flux

To determine pure water flux (PWF) of the membranes at the constant pressure of 1.0 bar, the membrane sample was compacted by a dead end set up, first. For compacting the membrane, water passed through the membrane at transmembrane pressure of 1.0 bar for 10 min and 1.5 bar for 15 minutes. Then, the pressure was increased to 2.0 bar for 2 h. After compaction, permeability of the membrane was measured at 1.0 bar under steady state flow. PWF was calculated as follows:

$$PWF = \frac{V}{A \cdot \Delta t} \quad (3)$$

where PWF is pure water flux (LMH), V is permeate volume (L), A is membrane area (m^2) and Δt is permeation time (h).

2.7 Rejection

After compacting the membranes, 1000 ppm aqueous solution of Dextran 450K was filtered by the membrane in the dead end cell at 1.0 bar for 30 min. Concentrations of Dextran 450K in permeate and feed were determined by Total Organic Carbon analyzer (TOC) (Dohrmann DC-190). It was calculated as follows:

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

where C_p and C_f are concentrations of the protein in permeate and feed, respectively. Standard deviation of porosity, EWC and CA were calculated to be less than 9%.

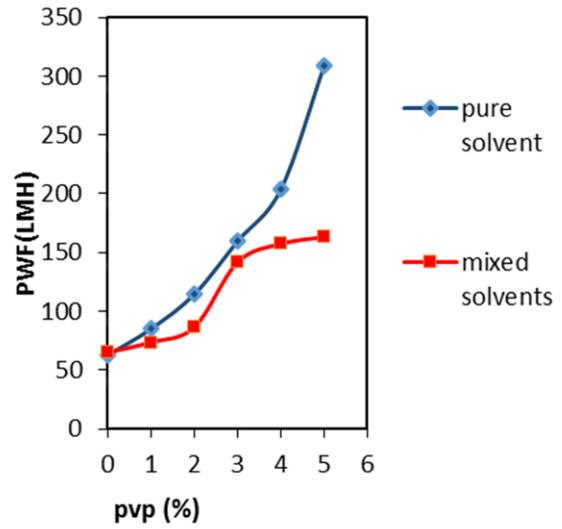


Fig. 1 PWF for the membranes prepared using mixed solvents (DMF/DMAc) and pure solvent (DMAc)

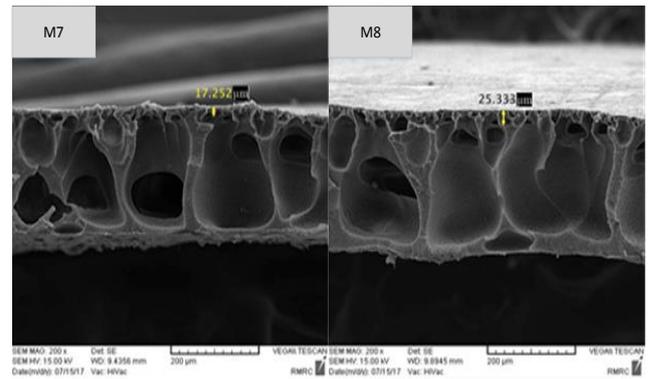


Fig. 2 Cross SEM images of M7 and M8 membranes

2.8 AFM

Samples of prepared membranes (approximately 1 cm^2) were cut and areas of $5 \mu\text{m} \times 5 \mu\text{m}$ each sample were scanned by non-contact mode.

3. Results and discussions

3.1 Flux analysis

Figure 1 illustrates PWF for the membranes prepared using mixed solvents and pure solvent. For all the membranes, PWF increases with increasing the PVP concentration. In equal concentration of PVP, however, PWF of the membranes prepared using mixed solvents is less than that of the membranes prepared using pure solvent. To show accuracy of the experimental measurements, PWF results of membranes and their corresponding standard deviations were also given in Table 2.

Membrane thickness and pore size are two vital parameters in investigating PWF. As the skin layer gets

Table 2 The summary PWF results of membrane and standard deviations

No.	PWF (LMH)	Standard deviation
M1	63	±2
M2	65	±8
M3	85	±7
M4	73	±7
M5	114	±6
M6	86	±9
M7	159	±7
M8	142	±7
M9	204	±8
M10	157	±7
M11	309	±9
M12	163	±9

thicker, PWF of the membrane decreases. When the mixed solvents are used in the membrane casting solutions, the solutions get more unstable thermodynamically due to the reduced solubility. This results in the faster phase inversion process. Quick phase inversion and thus rapid outflow of the membrane solvents makes pores extend thoroughly. Hence, the membrane thickness increases (Wang, Wang, and Wu 2012). M7 and M8 membranes were prepared using pure solvent and mixed solvents respectively, containing 3 wt.% PVP. M7 membrane thickness is 201.2 μm and M8 membrane thickness is 219.3 μm . Figure 2 shows cross SEM view of the two membranes. As it is clear, the skin layer thickness of the membrane prepared using pure solvent is 17.2 μm , while that of the membrane prepared using the mixed solvents is 25.3 μm . This increase in the membrane thickness increases the membrane resistance and reduces PWF. The thickness of skin layer measurement in SEM images is done by software coupled to the SEM device and the maximum error of it is 1 nm. Due to the accuracy of the measurements, the difference between the two 17.25 and 25.3 nm is significant.

In phase inversion process, there are two types of exchange: solvent-nonsolvent exchange and additive-nonsolvent exchange. These two types of exchange are mutually influential (Chakrabarty, Ghoshal, and Purkait 2008). Figure 3 shows the chemical structure of PEG and PVP. PEG molecule has linear structure with molecular mass of 200 Da. PVP with higher molecular mass of 10 kDa, on the other hand, has circular structure which results in more spatial prevention.

Since both PVP and PEG are present in the solvents (except for M1 and M2 membrane), the contest of these two additives for outflowing the membrane casting solution influences the membrane structure. Smaller PEG molecules generate smaller pores and bigger PVP molecules generate bigger pores (Ma *et al.* 2011)(Vilakati, Hoek, and Mamba 2014). Additionally, using mixed solvents increases the solvent-nonsolvent exchange rate. This increase also affects the additive-nonsolvent exchange rate. At the moment of fast nonsolvent outflow, the chains of circular-structured

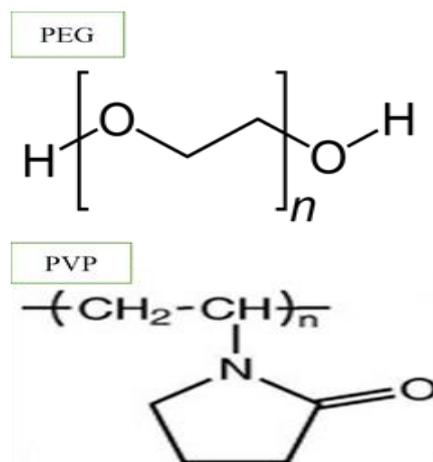


Fig. 3 Chemical structure of PEG and PVP

PVP have little mobility and thus cannot quickly leave the solution. But, due to its hydrophilic properties, it tends to accumulate on the membrane surface without outflowing the solution. On the other hand, due to its linear structure, PEG molecules can be exchanged with the nonsolvent well. Eventually, the quick outflow of PEG from the solution generates smaller pores in comparison with PVP over the membrane surface. It should be noted that at low PVP concentration, PWF difference between the membranes prepared using pure solvent and the ones prepared using mixed solvents is low but at high PVP concentration, PWF difference is higher. As seen, for 0 wt.% of PVP concentration, PWF amounts are almost equal. The reason is that mixed solvents have no effect on PEG performance at low PVP concentration; PVP outflow from the solution is low but, at high PVP concentration, PVP outflow increases resulting in higher PWF differences. Figure 4 shows a surface SEM image for the both M7 and M8 membranes. Smaller pores on the M8 membrane surface prepared using mixed solvents and bigger pores on the M7 membrane surface prepared using pure solvent can be observed. This result shows that in the presence of pure solvent, PVP molecules have the opportunity to leave the membrane matrix (in section 3.4, the FTIR-ATR shows this issue too) and generate bigger pores on the membrane surface. Consequently, by increasing the PVP concentration, PWF increases more significantly when pure solvent is used.

In the membranes prepared with pure solvent (M1, M3, M5, M7, M11), more PVP concentration results in immediate solvent- nonsolvent exchange. In fact, higher PVP concentration can generate more finger-like pores and increases the PWF through affecting thermodynamic parameters (Fontananova *et al.* 2006).

3.2 SEM analysis

Cross SEM and surface SEM of the prepared membranes are presented in Figure 5 and 6. Figure 5 shows cross SEM images of the membranes prepared using DMAc/DMF mixed solvents with PVP concentrations of 0, 1, 3 and 5 wt.%. As observed, all the membranes have

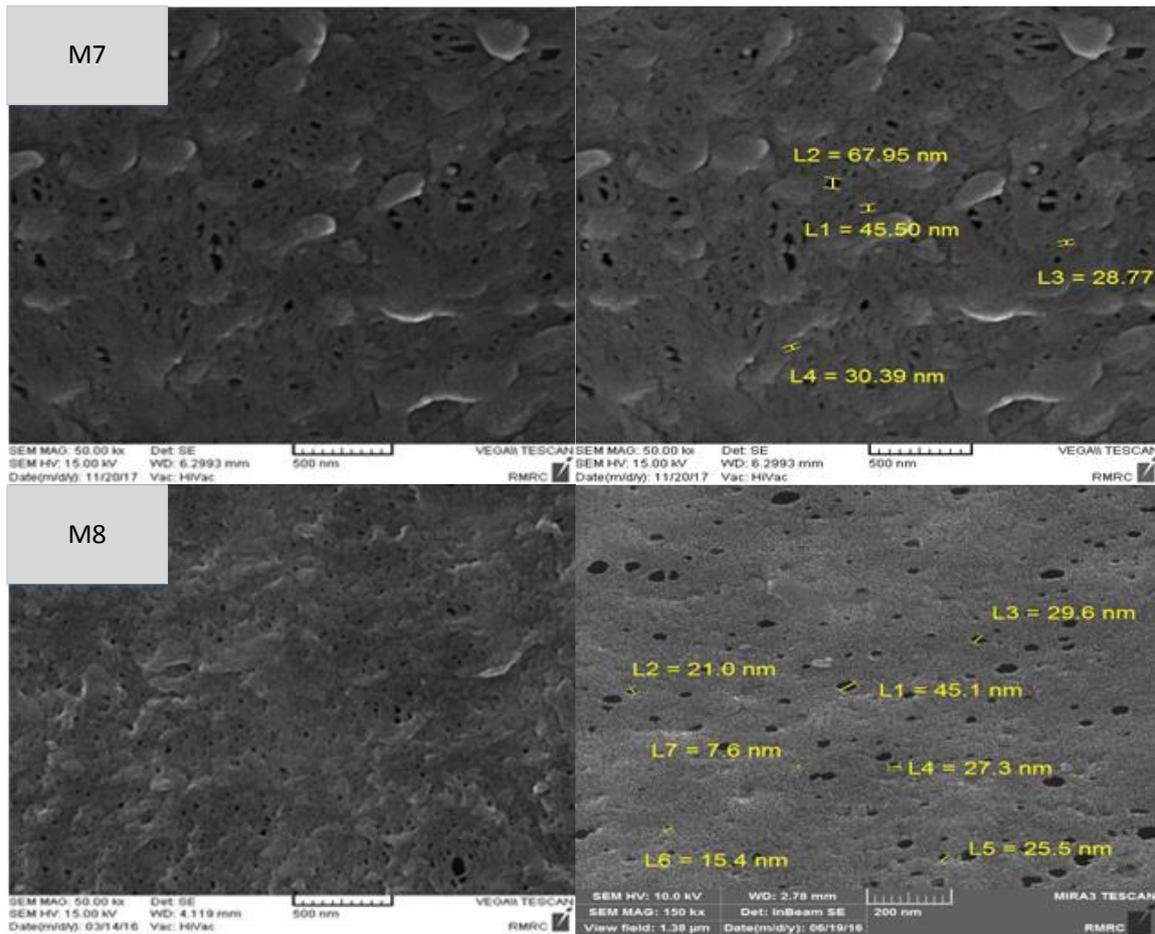


Fig. 4 Surface SEM images of M7 and M8 membranes

asymmetric porous structure of skin layer and finger-like structure on sublayer. The membrane without PVP (M2) has thicker skin layer. Higher PVP concentration results in thinner and denser skin layer. On the other hand, higher PVP concentration can widen finger-like pores in sublayer. As mentioned previously, PEG molecules can leave the structure faster due to their higher mobility and generate finger-like pores. To sum up, increasing PVP concentration and forcing it to leave the structure together with PEG leads to generation of wider and bigger pores in the membrane.

Figure 6 shows surface SEM images of the membranes prepared using mixed solvents with PVP concentration of 0 to 5 wt.% (M2, M4, M8 and M12). As observed, higher PVP concentration results in more number of pores on the membrane surface.

As can be seen in the cross SEM images, not all the pores that formed on skin layer are extended in sublayer and some of these pores are dead end. Consequently, all surface pores are not active in permeation and only pores that are extended in sublayer can increase PWF which is one of the reasons for low PWF. Indeed, PVP creates large pores on the membrane surface due to its high outflow rate. However, as can be seen in the surface SEM images, limited number of such large pores resulting in less surface porosity of the membrane is another reason for low PWF and simultaneously low rejection of Dextran. Such phenomenon

is not desirable but it is worth studying that in various membrane casting solutions.

3.3 Rejection analysis

Figure 7 shows Dextran 450 K rejection through the membranes prepared using DMAc/DMF mixed solvents and pure DMAc solvent. It can be seen that the membranes prepared using mixed solvents show lower rejection compared to the membranes prepared using pure solvent when equal concentration of PVP is used. By increasing the PVP concentration, rejection reduces for the both types of membranes.

Rejection behavior of the membranes depends on both top layer and sublayer structure (Geburu and Das 2017). As stated before, using mixed solvents can affect the exchange rate of PVP and PEG. By increasing the influx rate of nonsolvent into the solution, the outflow rate of PEG increases because of higher mobility of the polymer chains and this eventually generates finger-like pores with higher porosity. Generation of finger-like pores and reduction of sublayer wall thickness reduces rejection of the membranes in comparison with the membranes prepared using pure solvent. With pure solvent, outflow rate of PEG is slower and this results in narrower pores in sublayer. As mentioned, presence of pure solvent can generate bigger pores in skin

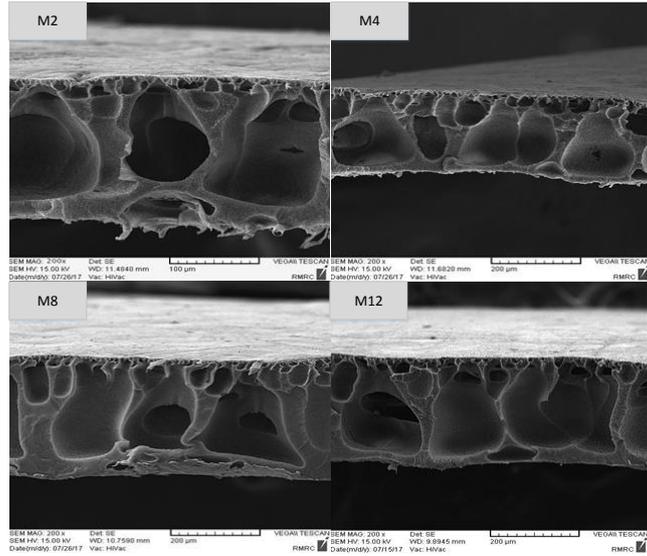


Fig. 5 Cross SEM images of M2, M4, M8 and, M12 membranes

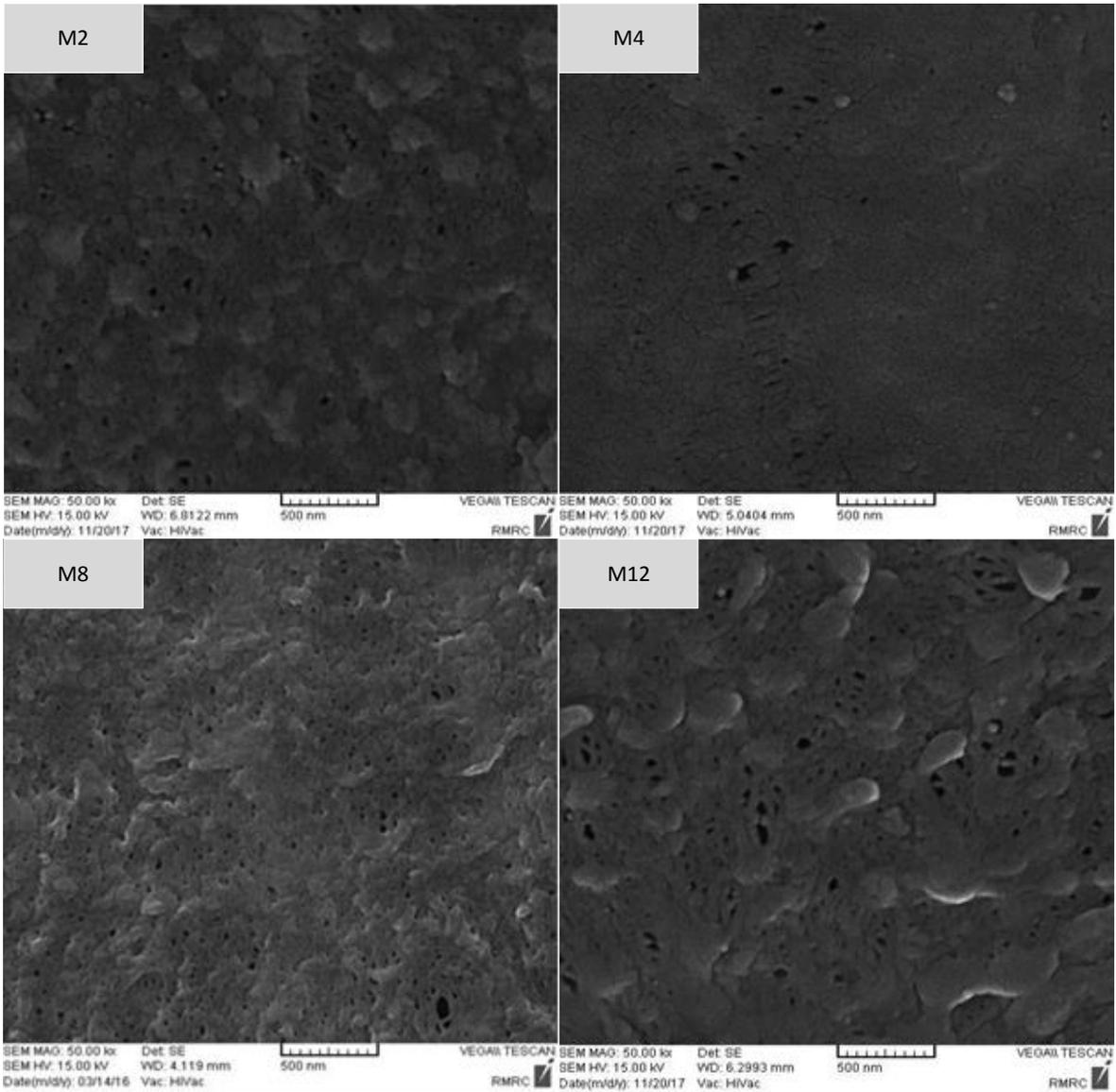


Fig. 6 Surface SEM images of M2, M4, M8 and, M12 membranes

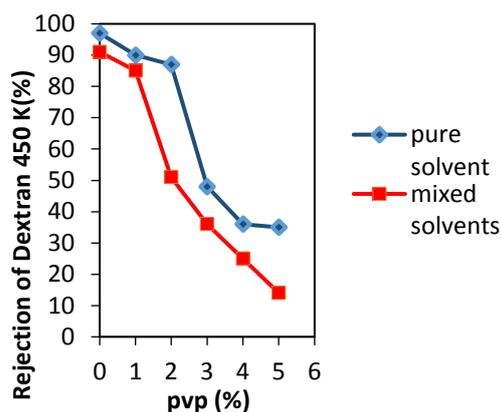


Fig. 7 Rejection of Dextran 450 K from membranes prepared using mixed solvents (DMAc/DMF) and pure solvent (DMAc)

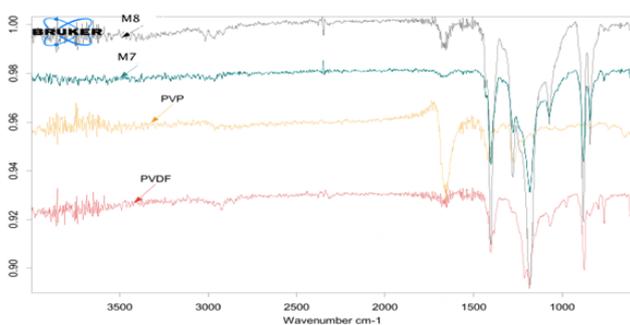


Fig. 8 FTIR-ATR of the M7 and M8 membranes

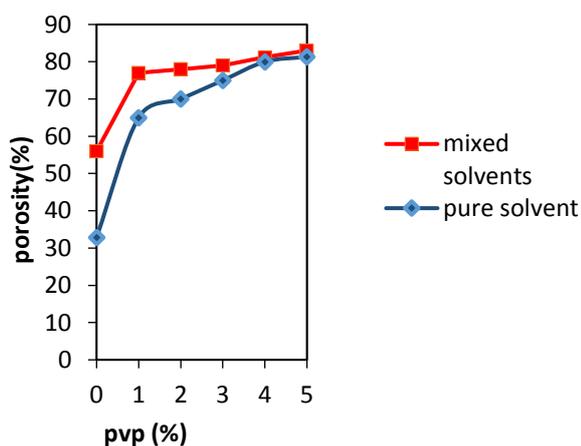


Fig. 9 Porosity of membranes prepared using mixed solvents (DMAc/DMF) and pure solvent (DMAc)

layer. However, formation of narrow finger-like pores in sublayer reduces PWF. Consequently, rejection of the membrane increases in comparison with the membrane prepared using mixed solvents. With Presence of these bigger pores in skin layer, it is expected that rejection declines but because of narrow finger-like pores in sublayer, rejection increases in comparison with the membrane

Table 3 The CA results for the M5, M6, M7 and M8 membranes

No	Average CA
M5	66.5256 ⁰
M6	54.1723 ⁰
M7	53.6579 ⁰
M8	48.4405 ⁰

prepared using mixed solvents. In both conditions (using pure solvent or mixed solvents), any increasing in PVP concentration leads to faster and more outflow of PVP. As a result, more and bigger pores are formed in skin layer and as a result rejection of the membrane declines.

3.4 Porosity and hydrophilicity

As mentioned in the flux analysis section, using mixed solvent boosts phase inversion process. This increase in process speed can increase the additive-nonsolvent exchange rate. Linear structure and low molecular weight of PEG help it abandon the solution quickly. But in case of PVP, its bulky structure and entanglement of polymer chains prevents it from rapid outflow from the solution. Thus, it tends to reside on the surface of the membrane and remain over there, especially because of its high hydrophilic property. Actually, the mixed solvents make the membrane more hydrophilic. To investigate this issue, the M7 and M8 membranes surfaces were evaluated by ATR-FTIR analysis. The M7 and M8 membranes were prepared using pure solvent and mixed solvents, respectively, and both of them contain 3wt.% PVP. Through such analysis, the amount of remaining PVP on the membrane surface was measured using C=O bound wavelength available in PVP structure that is equal to 1679 cm⁻¹. ATR-FTIR spectra for the M7 and M8 membranes are represented in Figure 8. The spectrum normalizing based on a unique PVDF peak area was done for comparing PVP content of samples M7 and M8. The amount of normalization M7 and M8 was 1.2827 and 4.847, respectively. The normalized peak area for M8 is bigger than M7 and this Difference shows that M8 has higher content of PVP than M7. The accuracy of the comparison is ±5%. This accuracy shows that some PVP is remained on the M8 membrane surface, which prepared using mixed solvents, while almost all PVP is washed away from the M7 membrane surface that prepared using pure solvent. In other words, it seems that the advantage of mixed solvents can be utilized to maintain PVP on the membrane surface and control PVP concentration up to 5 wt.%.

CA test was applied in order to conduct a deeper investigation on the claim that the mixed solvents along with PVP has made the membrane surface more hydrophilic. CA results for four membranes are presented in Table 3. The M5 and M6 membranes, both contained 2 wt.% of PVP and prepared using pure solvent and the mixed solvents, respectively. CA for the M6 membrane is almost degrees smaller than that of the M5 membrane. The M7 and M8 membranes, both contained 3wt.% of PVP and prepared

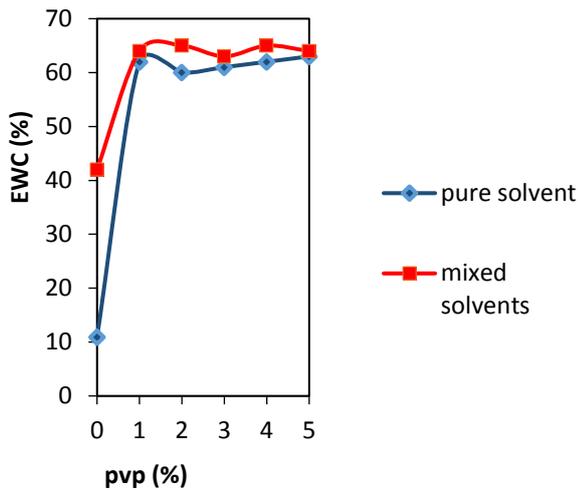


Fig. 10 EWC for membranes prepared using mixed solvents (DMAc/DMF) and pure solvent (DMAc)

using pure solvent and the mixed solvents, respectively. Here again, CA of the M8 membrane is about 5 degrees smaller than that of the M7 membrane. This reduction of CA is an evidence for increased hydrophilicity in the presence of the mixed solvents. Another noticeable point is that the improved hydrophilicity with increased PVP concentration is declined in comparison with the pure solvent. As it can be seen, hydrophilicity difference between the M5 and M6 membranes is 11 degrees while hydrophilicity difference between the M7 and M8 membranes is 5 degrees. In other words, when the PVP concentration increases with the presence of the mixed solvents, the number of PVP molecules that can remain on the surface reduces. Actually, the bulky and huge structure of PVP occupies most of the space and limits the number of PVP molecules on the surface.

Figures 9 and 10 illustrate porosity and EWC for the membranes prepared using mixed solvents and pure solvent, respectively. EWC has a direct relationship with membrane hydrophilicity. The level of EWC and porosity in constant concentrations of PVP for the membranes prepared using mixed solvents is higher than that of the membranes prepared using pure solvent. For the membranes prepared using pure solvent, the level of EWC and porosity rises with increasing PVP concentration. However, in the membranes prepared using mixed solvents, for PVP concentration above 2 wt.%, EWC remains constant and porosity increases very slightly. As verified and stated before, the presence of mixed solvents controls outflow rate of PVP from the solution. In lower PVP concentration, hydrophilicity of the surface increases, but for higher PVP concentration, the membrane surface gets saturated, which results in stable hydrophilicity values, as strongly confirmed by the CA results.

By increasing PVP concentration with pure solvent, outflow rate of solvent and both additives increase and this results in higher porosity. However with mixed solvents, PVP outflow rate is controlled by increasing PVP

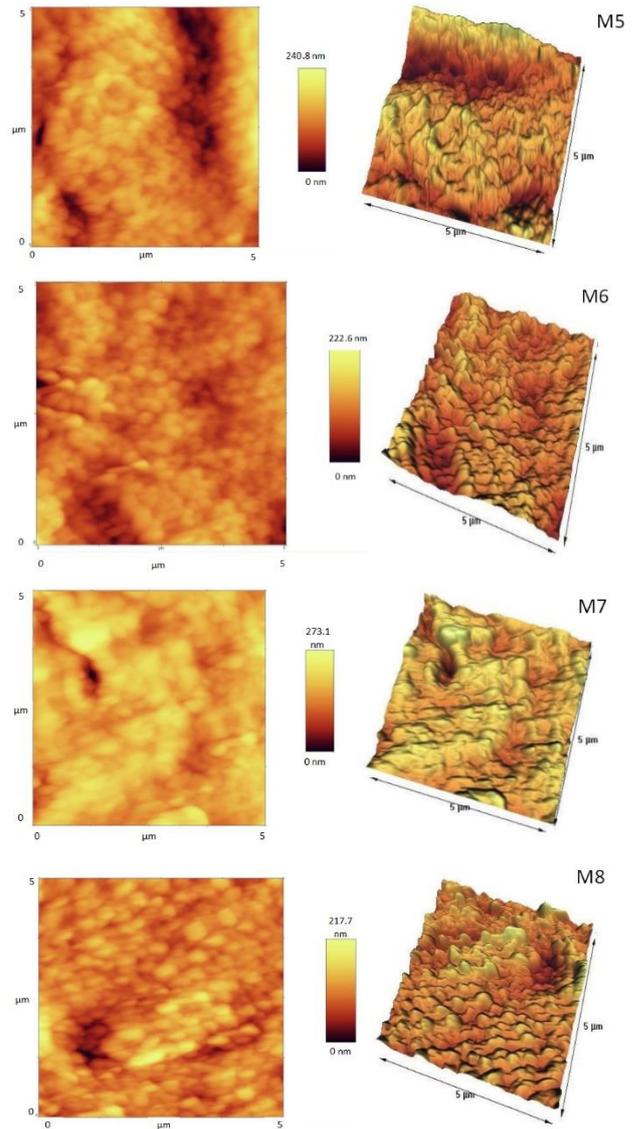


Fig. 11 The two and three dimensional AFM surface images for the M5, M6, M7 and M8 membranes

Table 1 The surface roughness parameters of the membranes

No.	R_a (nm)	R_q (nm)	R_v (nm)	R_p (nm)
M5	31.09	38.82	128.31	112.50
M6	18.60	23.76	124.19	98.36
M7	24.08	30.70	105.37	167.76
M8	18.97	25.41	111.75	105.97

concentration and any increasing porosity that depends on outflow rate of PVP molecules occurs with gentle slope and slower. Also, PEG outflow with mixed solvents results in higher porosity in comparison with pure solvent according to the above explanation. Other researchers also illustrated that using mixed solvents and high PVP concentration increase porosity (Wang, Wang, and Wu 2012, Simone *et al.* 2010).

AFM analysis was used to determine roughness of membrane surface. Figure 11 shows the two and three

dimensional AFM surface images of prepared membranes. The surface roughness parameters of the membranes are presented in Table 4. Average roughness (Ra), Root Mean Square roughness (Rq), Maximum profile valley depth (Rv) and Maximum profile peak height (Rp) were calculated using the AFM analysis software. The accuracy of these measurements are about 1 \AA . As it can be seen, the membrane roughness parameters decline with using mixed solvents in the casting solution. The surface roughness of M6 membrane is lower than M5 membrane and the surface roughness of M8 membrane is lower than M7 membrane. The surface roughness decreasing can result in the increasing hydrophilicity of membranes and these results are consistent with the CA results.

4. Conclusion

Using mixed solvents (DMAc/DMF) in casting solution changes exchange rate of the two additives PVP and PEG. Due to the larger size of PVP molecules and consequently more involvement of its chains with solvent and polymer, the slower additive exchange rate occurs and less amount of additive may exit from the casting solution. Also more agglomeration of PVP molecules on membrane surface results in the membrane hydrophilicity. Since PVP is very hydrophilic and tend to exit the casting solution faster, the mixed solvents can be used to keep PVP on the membrane surface and increase the membrane hydrophilicity.

However, the smaller size of PEG molecules and more mobility of its polymeric chains result in the faster exit of this additive and formation of finger-like pores in the membrane structure. Hence, increasing PVP results in higher flux and lower rejection in both types of the membranes (using single and mixed solvents). Indeed, in PVP of about 5 wt. %, porosity and hydrophilicity become almost stable.

It must be finally mentioned that using mixed solvents and combinations of PEG / PVP as additives can improve hydrophilicity and increase porosity of membranes, although flux and rejection do not improve. Considering the pros and cons of the idea, the research can be continued in future to find better selections of mixed solvents and additives.

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