



A STUDY OF THE EFFECTS OF ADDING PEG ON THE PROPERTIES AND MORPHOLOGY OF ASYMMETRIC MEMBRANES COMPRISING PVDF-HFP CO-POLYMER FABRICATED BY PHASE INVERSION METHOD

Hameed R. Dawood Alamery^{1,2}, M. D. Irfan Hatim¹ and Muhammad Syarhabil Ahmad¹

¹School of Bioprocess Engineering, Universiti Malaysia Perlis Malaysia Kompleks Pusat Pengajian, Jejawi, Arau, Perlis, Malaysia

²Department of Chemical Engineering, Faculty of Engineering, University of Al-Muthanna, Iraq

E-Mail: hrd_alamery@yahoo.com

ABSTRACT

PVDF-HFP flat sheet asymmetric membranes were prepared via phase inversion technique with N, N dimethyl acetamide (DMAc) as solvent. In this study polyethylene glycol (PEG Molecular weight 10,000) was utilized as additive at different compositions (0.0 - 10 wt. %) and deionized water was used as a coagulant bath. The structure and morphology of the resulting membranes were characterized by scanning electron microscope (SEM), FTIR, XRD, as well as measurements of contact angle, porosity, pore size and viscosity. The SEM images very clearly indicate that all membranes are of asymmetric structure and the porosity is increased with increased PEG additive. Additionally, the membranes' crystallinity was found to be less than its pure state of PVDF-HFP. It was also found to decrease with increased PEG as additive. Finally, the results gave the best interpretation of the influence of PEG as additive on the properties and structure of the relevant membrane.

Keywords: PVDF-HFP, poly (ethylene glycol), phase inversion technique, asymmetric membrane.

1. INTRODUCTION

The commercial membrane was first invented in 1960 by phase inversion methods. Significant progress has been achieved since then in the development of membranes both scientifically and commercially. Nowadays, membranes are so widely used with many applications in the most industrial sectors including environmental, electronic, energy and chemical. In particular, many major processes including reverse osmosis, ultrafiltration, microfiltration and gas separation have been established in large-scale membrane production [1]. Currently, Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is a copolymer which attracted great attention as membranes materials in this field compared with poly (vinylidene fluoride) (PVDF) homopolymer. The inclusion of HFP (namely hexafluoropropylene) constituent as an amorphous phase within the main blocks of VDF (or vinylidene fluoride) blocks contributed to give lower crystallinity and higher free volume to the PVDF-HFP. Also, introducing any HFP group contributes to enhancing the content of fluorine and helps make the PVDF-HFP more a hydrophobic polymer than the PVDF. More than one type of polymeric membranes used phase inversion method during preparation. Loeb and Souriajian were the first who introduced this method [2, 3], the phase inversion is the commonly-used method for the preparation of asymmetric polymeric membrane. Many researchers had made progress in understanding the formation mechanism of asymmetric membranes [4]. There are several methods to achieve phase inversion, some of which are: solvent evaporation, non-solvent precipitation and thermal precipitation. The most widely used method is the dry-wet phase inversion technique which is used in membrane manufacturing. All of these processes produce one of two

types of structures: the first, symmetrical micro-porous structures; the second is asymmetric membrane structures. In asymmetric membranes, consisting of two layers, the top is a very thin dense layer (skin layer) and its role is to allow permeation of the membrane (permeation properties) while the bottom layer is a porous sub-layer whose role is to offer mechanical built and strength for the structure of the membrane. It is possible too to control the tailored characteristics of membranes morphologies for various applications using the phase inversion technique; they range from microfiltration membrane to gas separation. The performance of asymmetric membranes produced for gas separation is mainly governed by membrane morphology [5, 6].

In order to get membrane with skin layer that is responsible for the selectivity of membrane while the membrane permeability depends on the resistance of the skin and structure. This means the overall morphological structure of membrane is critical for the desired final use [7]. It is necessary for the substructure to have a good mechanical support for the skin layer and should not give any additional transport resistance [8].

There are two typical sub-structures; one is a sponge-type structure and the other is a finger-like substructure. The membranes suitable for gas separation purposes; a sponge-like structure with good interconnecting pores has been shown to give good support to the separating skin and gives very little resistance to gas transportation, while the membranes that contain finger-like structures can run into problems if used at high gas pressures.

At for membranes with skin layers, there are some basic factors that contribute to affecting the permeation ability and the membrane morphology include: non-solvent and solvent systems, concentration of



polymer, polymer solution temperature, casting solution temperature, while another factor is the additives' role in both of the precipitation bath and the casting solution. In order to obtain a membrane suitable pore size and porosity, should be used the additional additive like PVP and PEG can be dissolved within the casting solution [9]. Quite a few researchers cared to study and investigate the influence of additives within a casting solution. Eventually affecting the formation of the membrane [10]. PEG had been widely used as a common additive in the process of membranes preparation. The PEG unique features and properties is the reason behind that, properties like good solubility, fine compatibility and non-irritating nature [11, 12].

In present work, PEG with different concentrations was added to the PVDF-HFP casting solutions. The influences of PEG concentration polymer on structure and properties of the resultant membranes were investigated by SEM, XRD, FTIR, pore size, porosity and viscosity. Additionally, in order to a better understanding of the role played by these additives, the membrane formation mechanism was discussed extensively based on PEG concentration as additive and the affinity between PEG and casting solutions.

2. EXPERIMENTAL

2.1. Materials

PVDF-HFP co-polymer was used as polymer for preparation of the membrane casting solutions (PVDF-HFP with average M wt. ~ 400,000 by GPC) in pellet form was Sigma-Aldrich (USA). Poly (ethylene glycol) (PEG) (reagent grade, with average M wt. ~ 10,000 obtained from Sigma-Aldrich (Germany) were used as organic additives in PVDF-HFP/ DMAc solution. N, N Dimethyl acetamide (DMAc) (Anhydrous 99.5% (Sigma- Aldrich) had been employed here as a solvent, in the current research because it is virtually a very good solvent with many polymer, finally; pure deionized water was used as the coagulation bath [13, 14].

2.2. Preparation of PVDF-HFP support

The PVDF-HFP copolymer was dissolved in N, N Dimethyl acetamide (DMAc) to form about 17 wt. % homogeneous solution and a variety of concentrations PEG-10,000 (0.5-10) wt. % were added into the polymer solution by stirring for 3 hr. at $40 \pm 1^\circ\text{C}$ as shown in Table-1. The stirring had been conducted at 350 rpm. Next to forming a solution that is homogenous, the dope solution had been kept at ambient temperature for duration of 1 hr. (approximately) in order to get rid of the air bubbles. Next to that, the polymeric solution had been cast on a clean glass plate ($150 \pm 10 \mu\text{m}$ thickness) using a casting knife at room temperature. After casting it was horizontally immersed into de-ionized water bath for at least 24 h to remove the solvent and solidify the membrane structure.

Table-1. Composition and preparation condition of prepared membranes.

Membrane	Poly. Con. wt. %	Add. Poly. Con. (PEG) wt. %	Solvent Con. wt. %	Coagulation bath
Z1	17	0.0	83.0	DI water
Z2	17	0.5	82.5	DI water
Z3	17	1	82.0	DI water
Z4	17	3	80.0	DI water
Z5	17	5	78.0	DI water
Z6	17	10	73.0	DI water

3. MEMBRANES CHARACTERIZATION

3.1. Determination of viscosity; Porosity and pore size

Viscosity of the casting solution has the ability to obstruct the rate of exchange of non-solvent and solvent during the process of phase inversion. Thus, viscosity can be regarded as an essential factor affecting the kinetics of precipitation. Eventually affect on the morphology of the prepared membrane. Using Viscometer (Brookfield DV-11+ Pro, USA) at 25°C and the result of all measurements was taken from the mean of at least five single measurements. Meanwhile, the porosity (ϵ) of the membranes was measured using equation (1). Using suitable pieces from the PVDF-HFP/ PEG membranes are immersed in n- octanol (ACS, ISO, Reag pH Eur, Merck)

for exactly 2 hours and then filter paper was used to dry the membrane surface. Also, the weight of the membrane before and after immersion was equally measured.

$$\epsilon \% = \frac{M_o/\rho_o}{M_o/\rho_o + M_p/\rho_p} \times 100 \quad (1)$$

Where M_p , M_o refer to the mass of dry and n-octanol absorbed in the wet membrane, respectively, ρ_p is the density of the polymer and ρ_o is the density of n-octanol. The surface area and pore size distribution of the prepared membranes were measured using BET (Brunauer-Emmett-Teller) gas adsorption, analyses were carried out by nitrogen adsorption-desorption isotherms at



77 K using a surface area and pore size instrument Modal (ASAP 2020 Surface Area and Porosimetry Analyzer). Degassing of samples was carried out at 50 °C Under vacuum conditions for duration of 4 h before the investigation was started.

3.2. Scanning Electron Microscope (SEM)

Cross section view for the flat sheet membrane was obtained via the use of SEM Model (JEOL, JSM-6460 LA). The membranes were frozen and broken under liquid nitrogen in order to get a clean and consistent cut. So as to get images with better resolution, these membranes were coated with thin film of platinum sputter using, these membranes were coated with thin film of platinum sputter using (JEOL, JFC-1600) before being placed on a stainless steel plate using a double sided adhesion tape in a lateral position.

3.3. Hydrophobicity

The water contact angle method was deployed in this research to ascertain the hydrophobicity of the membrane surface. Via this technique, the water contact angle values had been measured using sessile drop methods using Rame-Hart (Model 300 Advanced Goniometer) instrument with deionized water as contact liquid. Moreover, 2 μ L of the water droplets were dropped on the PVDF-HFP membrane surfaces and the corresponding result of all measurement are taken from the mean of at least five single measurements.

3.4. XRD, DSC and FTIR

The wide-angle X-ray diffraction (WAXD) patterns were recorded on a X-ray diffractometer (XD-98,

Philips X light pipe) using Cu K α as source (40 Kv and 30 mA) with 2 θ at 10- 60°. The amorphous and crystalline components diffractions were separated using XRD intensity data so as to estimate the crystallinity of the sample. Alternatively, can be used differential scanning calorimeter (DSC) (Pyris I, Perkin Elmer Instrument Inc., USA). To study crystallinity of PVDF-HFP membranes also, for the purpose of comparison, while experimenting, the samples were heated from 30-180 °C, with a heating rate of 10 C/min. Sample weight in the range was 5-8 mg and nitrogen had been used as a carrier gas, the flow rate was 20 ml/min. All changes in chemical structure while blending had been identified through the use of Fourier Transform IR Spectroscopy. Measurements had been taken for the Infrared absorption spectra, at room temperature from 4000 to 650 cm⁻¹, the spectral resolution of 8 cm⁻¹ averaging over 16 scans. This test is done to ensure the presence of PVDF-HFP and PEG on the membrane.

4. RESULTS AND DISCUSSIONS

4.1. Viscosity, porosity and pore size of the PVDF-HFP/PEG dopes

Viscosity of the polymer dope is a very important parameter to affect the membrane formation kinetics and then the resultant membrane structure. Thus, the viscosity of the polymer dope as a function of PVDF-HFP/PEG concentrations was determined. As illustrated in Figure-1 and Table-2, there is drastic surge in the value of viscosity with a PEG polymer concentration increase observed.

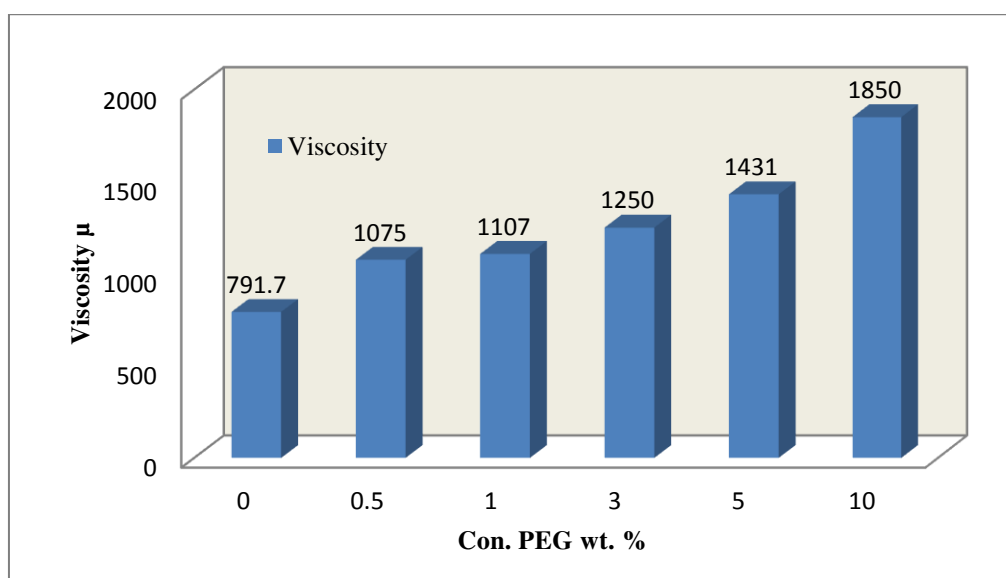


Figure-1. Viscosity vs. PEG polymer concentration (wt. %).

This indicated significant chain entanglement occurring in the dope solution Zuo, D.-y., *et al.* suggested that a dope exhibiting significant chain entanglement might produce flat sheet with ultra-thin skin layer and

increased porosity [15]. The major objective of this study was to explore suitable conditions for asymmetric micro-porous flat sheet preparation.



Another consideration was that the viscosity of dope solution should be also reasonably high to ensure consecutive and smooth casting of the dope solution out of precipitation. As such, the dope solution 17 wt.% PVDF-HFP has been selected in order to prepare flat sheet being an initial attempt, the addition of 0.5, 1, 3, 5 and 10 wt. %

PEG into the dope solution caused a significant increase in its viscosity ($Z6 > Z5 > Z4 > Z3 > Z2 > Z1$), as shown in Table-2 and Figure-1. Upon using 10 wt. % PEG as additive for preparing the solution, it became almost solid at 25°C in several days.

Table-2. Effects of polymer concentration on membrane maximum pore size; Porosity; Viscosity and contact angle. Membranes

Membranes	Viscosity Mpa. sec	Porosity %	Pore size Å	Contact angle	Crystallinity (%)	
					XRD	DSC
Z1	791.7	72.45	32.28	70.4	21.9	19.27
Z2	1075	69.22	30.65	73.2	21.51	18.44
Z3	1107	71.15	21.82	66.5	18.60	17.41
Z4	1250	75.72	24.6	54.3	18.40	16.29
Z5	1431	78.65	43.77	47.4	17.83	16.22
Z6	1850	83.16	170.85	46.2	16.89	18.30

Note: 1 c.p = 1 Mpa.sec = 0.001Pa.sec; 1nm = 10 angstroms = 10^{-9} m, 1 angstrom = 10^{-10} m.

In addition, the porosity is one of the main factors which affect the performance of polymer membrane in gas separation processes [16]. In this study, porosity and pore size membrane of Z1 to Z6 had been measured and the results are shown in Figure-2, Figure-3 and Table-2. It was observed in Fig. 2 and Table 2 increase of the porosity values with the increase of PEG polymer concentration additive ($Z6 > Z5 > Z4 > Z3 > Z2$) of ($83.16 > 78.65 > 75.72 > 71.15 > 69.22$) respectively.

When comparing (Z2, Z3) (0.5, 1 Wt. %) with Z1 (0.0 Wt. %) the values of porosity Z2, Z3 were found to be less than the value of Z1, as shown ($Z1 > Z3 > Z2$)

($72.45 > 71.15 > 69.22$) respectively. Due to both increased total polymer content and degraded effect of PEG additive due to its insufficiency, the result was a decreased porosity at Z2 and Z3. In general, the increase in porosity is directly proportional to the increase of PEG polymer concentration additive. While the highest value for porosity (83.16%) and high viscosity (> 1850 cp) of the membrane were found to be with highest polymer concentration additive of (10wt. %), and the low porosity (69.22 %) and lower viscosity (1075 cp) were found in membrane with the low polymer concentration additive of (0.5 wt. %).

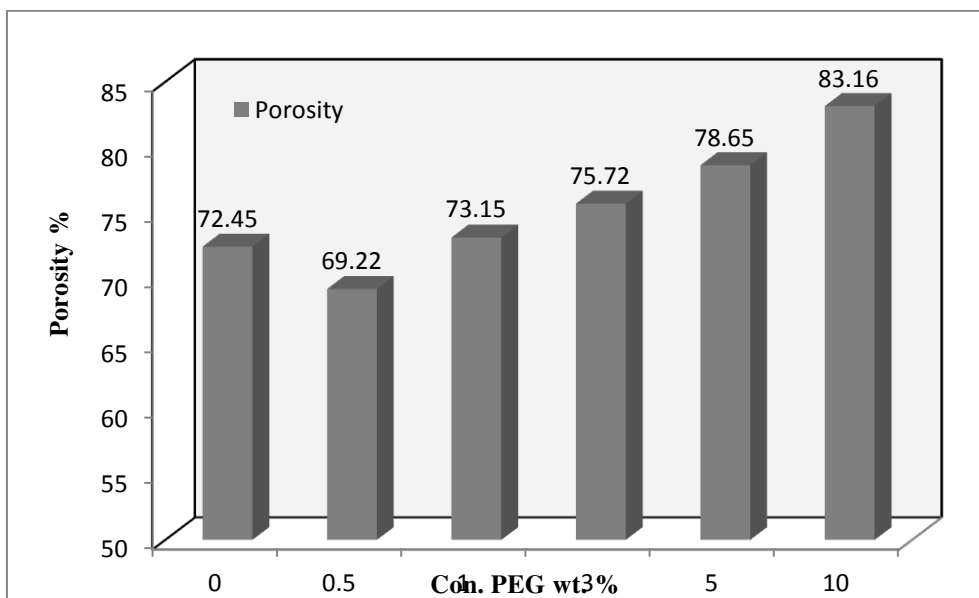


Figure-2. Porosity % vs. PEG polymer concentration (wt. %).



Pore size is one of the crucial important factors to evaluate the performance of polymer membrane in a gas separation process [8, 16] As show in Figure-3 the pore size decreases when the PEG polymer concentration additive is less than 1 Wt. % ($Z3 < Z2 < Z1$) ($21.82 < 30.65 < 32.28$ Å) while the pore size increases when the PEG polymer concentration additive is more than 1Wt. % ($Z6 > Z5 > Z4 > Z3$) ($170.85 > 43.77 > 24.60 > 21.82$ Å). Because the quantity of PEG additive was very little and the effect of the PEG was not clear enough at less than 1 Wt. %, while the effect of the PEG was very clear and sharply increased at more than 1 Wt. % because PEG is considered as one of these additives that act as pore-forming agents. Generally, there is a directly proportional relationship between the PEG polymer concentration additive (when more than 1Wt. % PEG) and all of: pore

size, porosity and viscosity. Also, it was closely observed in the aforementioned Table-2 that the 1 Wt. % PEG polymer concentration additive gives small pore size (21.82 Å) and the 10 Wt. % PEG polymer concentration additive gives large pore size (170.85 Å). The proposed pore size is due to lower diffusion rate of non-solvent at a high solution viscosity. While an increase in the polymer concentration results in significant increase in solution viscosity of PVDF-HFP polymer solution. This phenomenon will lead to a higher mass transfer resistance between the solvent (DMAC) and non-solvent (precipitation bath) in the system during solidification of the casting solution. Thus, at high polymer concentration, the precipitation process stops after a longer period of time, this phenomena leads to the formation of denser membrane, with smaller pore sized distribution.

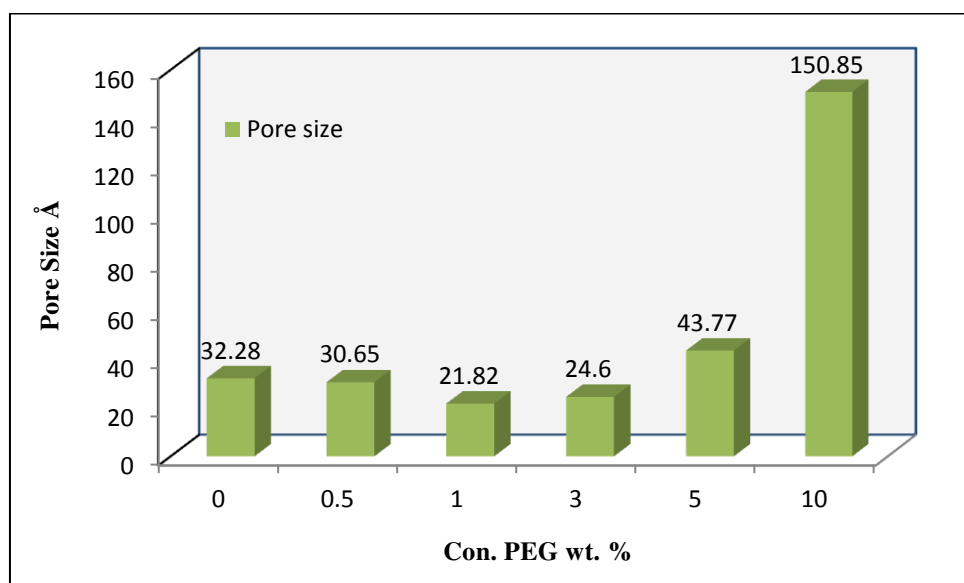


Figure-3. Pore size Å vs. PEG polymer concentration (wt. %).

4.2. SEM analysis

For the sake of understand the results, the cross-sections and the upper surface of membrane, was studied very carefully using SEM. Figure-4 (A and B) shows the SEM images of membranes cast from 17 wt.% PVDF-HFP solutions using PEG additive with different concentrations between 0.5- 10 wt.%. All membranes showed the characteristics of an asymmetric membrane consisting of a skin layer near the top surface and sub layer solid matrix (porous supporting layer). PEG with different concentrations gave an obvious impact on membrane surface and cross-section. In general the size and number of pores on the membrane upper surface increased with increase of concentration of PEG additive from (0.5 wt. % to 10 wt. %) except for sample Z3 because the quantity of PEG additive was very little and the effect of the PEG was

not clear enough with increased total polymer content, which led to a decreased pore size. This was clearly noticed in the image B-Z3. The trend of macro void growth variation in the cross section had been found to have similarity with that trend of the membrane upper surface pores. The sponge-like cavities grew gradually and became more porous and interconnected at the PEG concentration 0.5, 1 wt. % (Z2 and Z3) while the concentration that was higher than the 3 wt. % revealed the structure is finger-like and these pores expanded in breadth and length towards the membrane bottom when PEG concentration increased to 10 wt.%. At the same time, the wall of fingerlike macro-voids also become sponge-like and of porous morphology as shown in Figure-4 (A-Z4, A-Z5 and A-Z6).

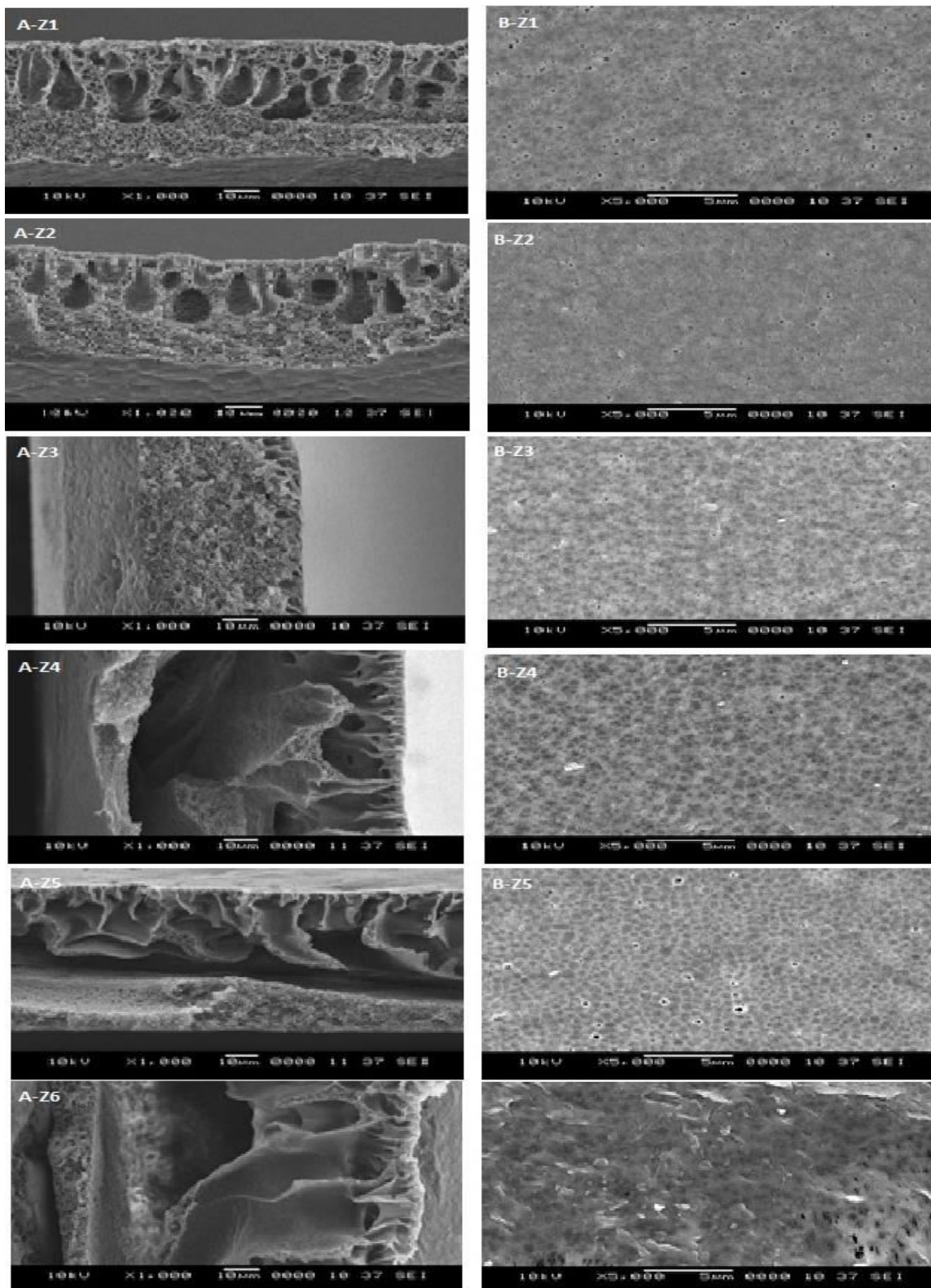


Figure-4. SEM images of PVDF-HFP membranes prepared with different concentrations of PEG between (0 - 10)wt. % (A) Cross-section and (B) Upper surface.

4.3. Contact angle

The contact angle between the water and the surface of the membrane; chemically represents hydrophobicity of membranes. This angle that is between

the liquid and the solid surfaces is called “Contact Angle”. In the case of water, when the contact angle is more than 90° the membranes are called “hydrophobic”, whereas when the contact angle is less than 90° the membranes are called



“hydrophilic”. When water is applied to the membranes surface, the external surface layers interact with the water. If the hydrophobic surface has a low free energy it would produce a high contact of angle with the water unlike the surface that has a high energy where such a surface permits the water drop to spread out resulting in a reduced

angle of contact. The PVDF-HFP membranes are greatly affected when the concentration of PEG additive is increased. In general the pore size and porosity increased with PEG concentration due to PEG being a recognized pore forming agent, whereas as shown in Figure-5 and Table-2, the contact angle decreases with PEG additive.

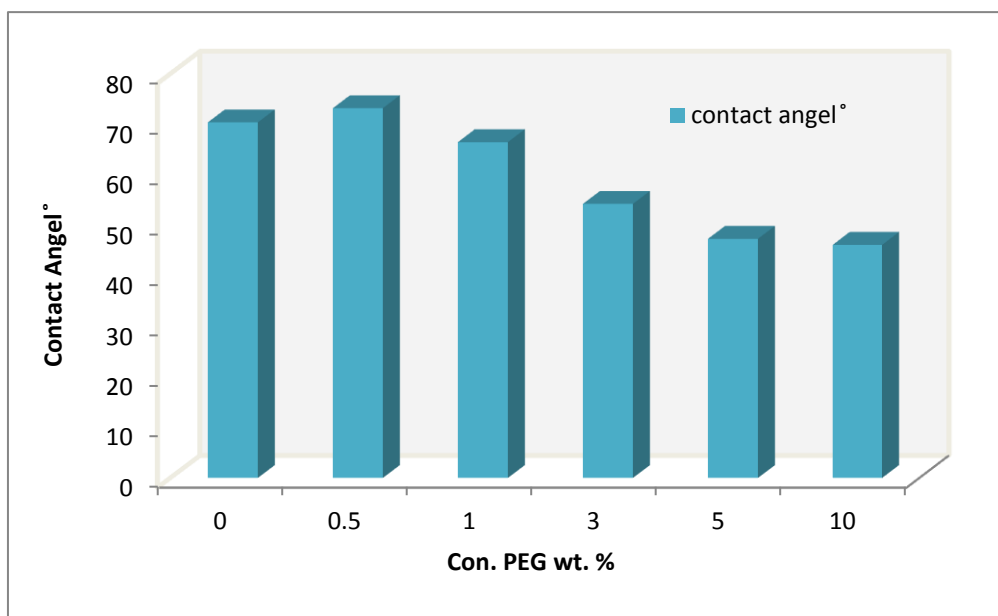


Figure-5. Contact angle vs. PEG polymer concentration (wt. %).

This is mainly due to the big pore size and increased porosity that both led to decreased contact angles. Membranes with higher PEG polymer concentration have less resistance for the water to flow. The highest contact angle (73.2°) was found for the membrane with the lowest PEG polymer concentration of (0.5 wt.%); while the highest value of (46.2°) was rather found in the membrane with the highest PEG polymer concentration of (10 wt.%). This is to prove that the relationship between the Contact Angle and PEG polymer concentration is an inverse one, since Contact Angle decreased with increased PEG polymer concentration as additive, as well the reverse relationship of the contact angle with both of pore size and porosity.

4.4. XRD; DSC and FTIR analysis

The XRD diffraction patterns of PVDF-HFP and PVDF-HFP/PEG with different PEG concentration (0 -10 Wt. %) can be clearly observed by wide-angle X-ray diffraction patterns, as shown in Figure-6, XRD patterns used for calculating a crystallinity index following the empirical methods of segal *et al.* [17]. The patterns of the XRD revealed quite clearly that the PEG poly. Con. additives reduced the crystallinity considerably, as shown by the broad diffraction peak centered at $2\theta = 20^\circ$. By

computing the crystallinity of membranes and pure PVDF-HFP membrane the crystallinity of pure PVDF-HFP was 21.9 % and this value corresponds to the Cao, J. H *et al.* [18] while the crystallinity was 21.9 %; 21.5 %; 18.6 %; 18.4%;17.83% and16.9% (Z1, Z2, Z3, Z4, Z5and Z6) respectively. From the diffraction patterns, peaks were observed at $2\theta = 18.2^\circ$, 20° for PVDF-HFP membranes with all additives percentages used. The membrane's crystallinity is less than it for pure PVDF-HFP and the amorphous domain of membrane increased. When comparing the XRD characteristics with those of PVDF, the same diffraction peaks were noticed, the crystalline in these PVDF-HFP membranes was prepared from vinylidene fluoride (VDF) segments and showed phase crystalline. Additionally, the relative intensity of those peaks were found to decrease in the order of pure PVDF-HFP membrane with PEG 10, 000 as additives. When blending polymer with additives it seemed that the polymer underwent significant structural reorganization. The results indicated that the process of membrane formation decreased the crystallinity of PVDF-HFP while the crystalline did not change. This confirms the partial crystallization of PVDF units in the copolymer and gives a semi-crystalline structure of PVDF-HFP.

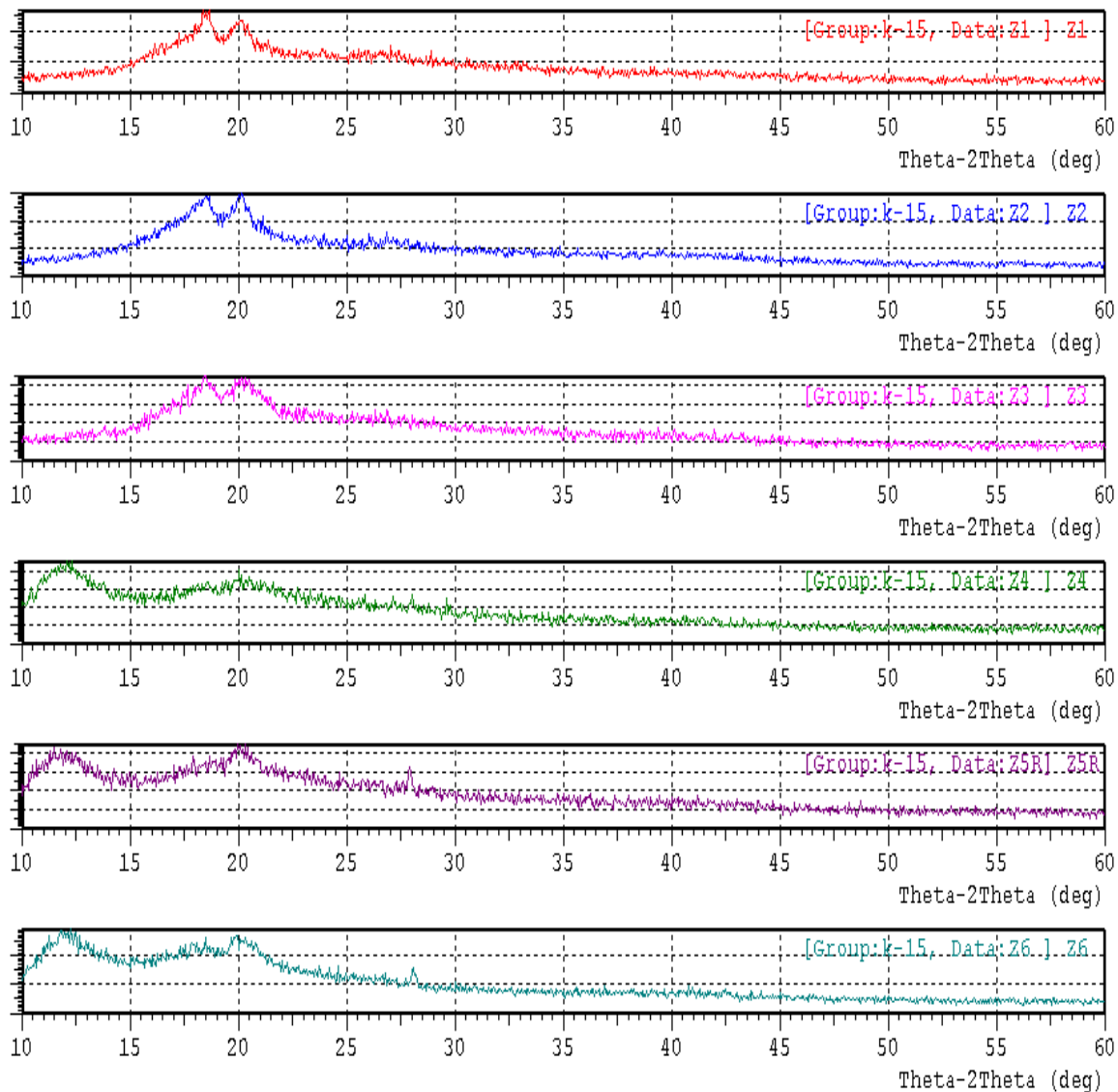


Figure-6. XRD patterns of pure PVDF-HFP and PVDF-HFP membranes prepared with various additives of PEG from above to down (Z1-Z6) (0.0 - 10 Wt. %) respectively.

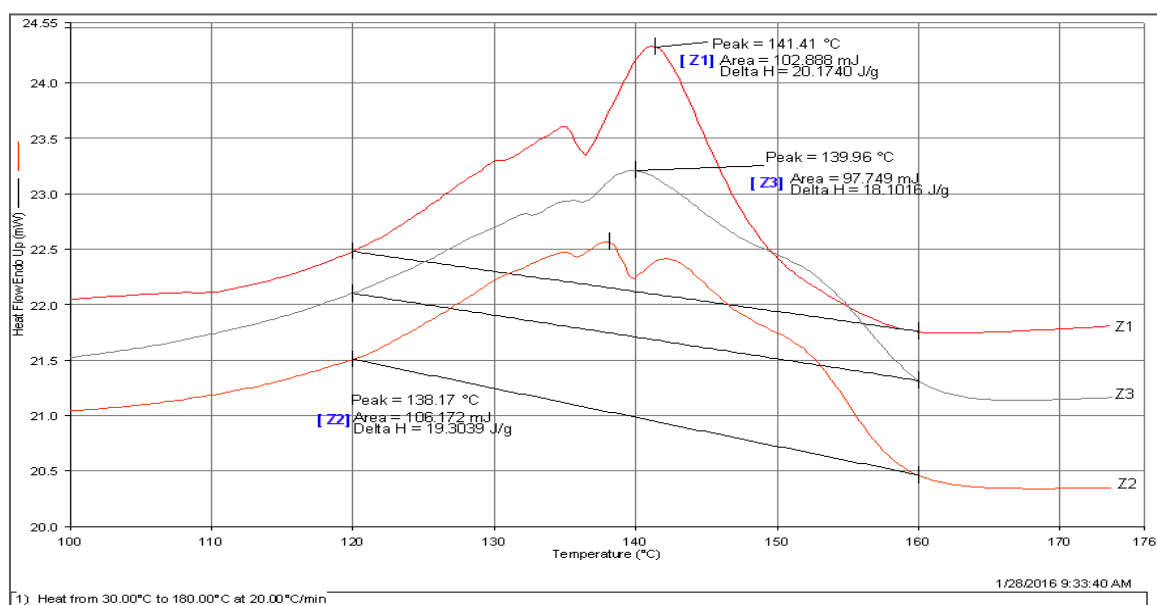
Additionally, the percentage of crystallinity can be calculated using equation (2); also, it can be obtained from the enthalpy of fusion from DSC measurements

$$\Delta X_c = \frac{\Delta H}{\Delta H_m} \times 100 \% \quad (2)$$

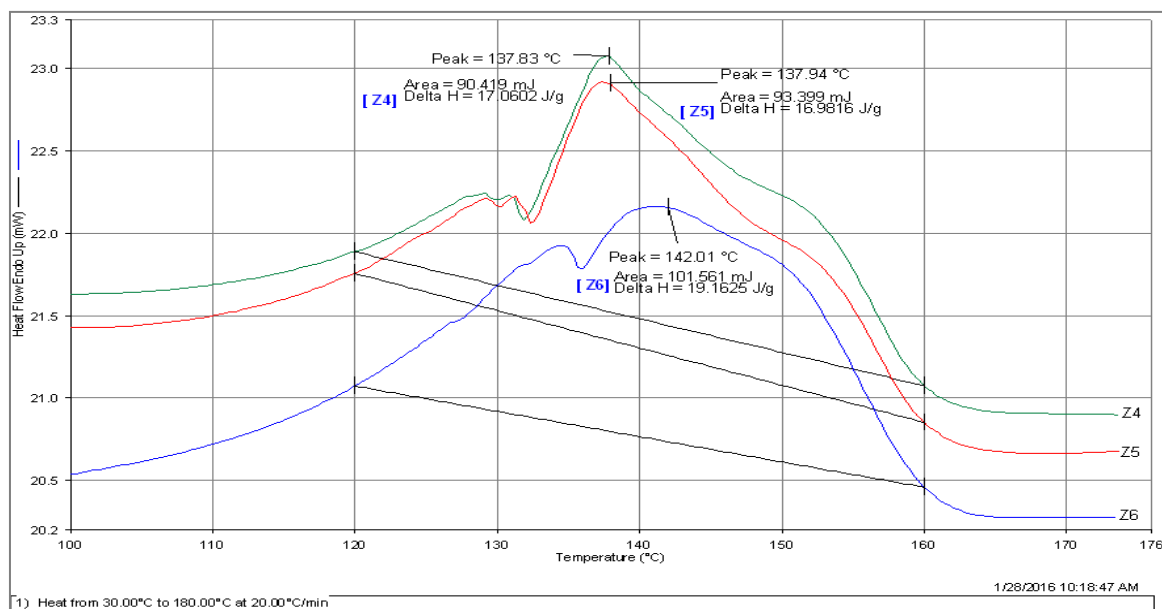
Where: ΔH is the enthalpy of fusion of membrane (J/g),
 ΔH_m is standard enthalpy of fusion of 100% crystalline PVDF (104.7 J/g) [19].

The results revealed that the crystallinity was 19.27, 18.44, 17.41, 16.29, 16.22 and 18.30 in all samples of PVDF-HFP membranes formed using PEG as additive Z1, Z2, Z3, Z4, Z5 and Z6 respectively. It is further

noticed in Figure-7(A, B), that the PVDF-HFP membranes show an endothermic peak between 130°C and 150°C, which was attributed to its melting process. The crystallinity of PVDF-HFP membranes was listed in Table-2. Comparing the crystallinity calculated from XRD and DSC, the results of XRD were higher than results of DSC. It is due to the used empirical methods and the standard enthalpy ΔH_m of PVDF-HFP copolymer was replaced by that of PVDF, it should result in some uncertainty in results. In general, the crystallinity of membranes was calculated by using two methods and the results of formed membranes had varied values with similar tendency. Finally, the crystallinity of PVDF-HFP membranes decreased with increased PEG polymer concentration as additive.



(a)



(b)

Figure-7. (a, b): DSC patterns of pure PVDF-HFP and PVDF-HFP for membranes prepared with various additives of PEG (Z1-Z6) (0.0 - 10 Wt. %) respectively.

The chemical composition of pure PVDF-HFP and PVDF-HFP/PEG with various PEG concentrations (0 - 10 Wt.%) (Z1- Z6) can be clearly observed by the FTIR spectra, as shown in Figure-8. The FT-IR results was revealed that two characteristic absorption peaks of PEG one of them (O-H: 2885 cm^{-1}) were non-existent and the other very small at (C-O: 1110 cm^{-1}). While for the Z5 and Z6 membranes, the presence of the PEG polymer

chain can be ascertained from the band of O-C=O stretching at 1728 cm^{-1} for the ester carbonyl groups.

All characteristic absorption peaks corresponded to those of PVDF. It can be seen that the appearance of the spectrum at 1728 cm^{-1} is becoming increasingly apparent with increasing the concentration of PEG in the PVDF-HFP membranes (Z5, Z6) and this result corresponds to the [20].

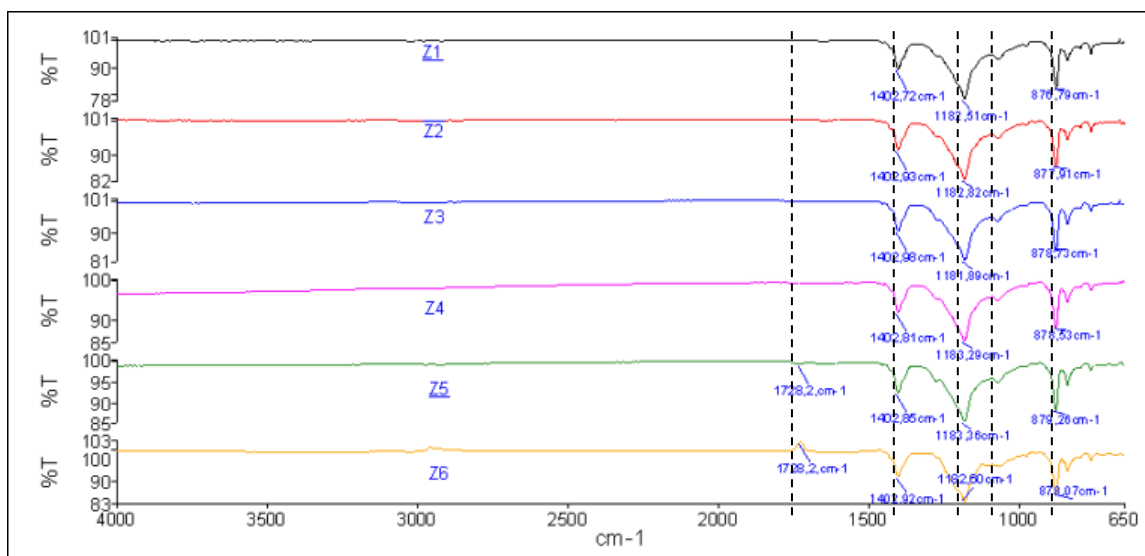


Figure-8. FTIR spectra of pure PVDF-HFP and PVDF-HFP membranes formed with different PEG additives from above to down (Z1-Z6) (0.0 - 10 Wt. %) respectively.

5. CONCLUSIONS

In this study, flat sheet PVDF-HFP membranes were successfully prepared using phase inversion method containing 0.5, 1, 3, 5 and 10 wt. % PEG as additives with DMAC as a solvent. The SEM results showed that all membranes had the characteristics of a membrane that is of asymmetric type comprising of two layers; one skin layer near the top surface while the second sub layer of a solid matrix acting as a (porous layer supporting).

The results showed an increase in porosity and a sharp increase in viscosity with increased concentration of PEG additive from (0.5 wt. % to 10 wt. %). Also and in general, the number and the size of pores on the upper face of the membrane had increased with the increase in concentration of PEG additive from (0.5 wt. % to 10 wt. %). As for the contact angle, it decreases with increase in concentration of PEG additive. The highest contact angle (73.2°) was found for the membrane with the lowest PEG polymer concentration of (0.5 wt. %); whereas the highest value of (46.2°) was rather found in the membrane with the highest PEG polymer concentration of (10 wt. %). In addition, crystallinity of membranes was found to be less than the crystallinity of pure PVDF-HFP. It was found also to be decreasing with increased PEG10000 concentration as additives.

The impact of PEG becomes very clear when the polymer concentration is more than 3%. Finally, the results gave the best explanation of the influence of PEG as additive upon the properties and structure of the membrane.

REFERENCES

- [1] Liu F., *et al.* 2011. Progress in the production and modification of PVDF membranes. *Journal of Membrane Science*. 375(1): 1-27.
- [2] Tian X., B. Zhu and Y. Xu. 2005. P (VDF-co-HFP) membrane for recovery of aroma compounds from aqueous solutions by pervaporation: I. Ethyl acetate/water system. *Journal of membrane science*. 248(1): 109-117.
- [3] Loh C.H. and R. Wang. 2012. Effects of additives and coagulant temperature on fabrication of high performance PVDF/pluronic F127 blend hollow fiber membranes via nonsolvent induced phase separation. *Chinese Journal of Chemical Engineering*. 20(1): 71-79.
- [4] Rezakazemi M., *et al.* 2014. State-of-the-art membrane based CO₂ separation using mixed matrix membranes (MMMs): an overview on current status and future directions. *Progress in Polymer Science*. 39(5): 817-861.
- [5] Zhang Z., *et al.* 2011. Fabrication of polysulfone ultrafiltration membranes of a density gradient cross section with good anti-pressure stability and relatively high water flux. *Desalination*. 269(1): 239-248.
- [6] Liu M., C. Xiao and X. Hu. 2011. Effects of non-solvent additives on PVDF solution viscosity and membrane performance. *Iran Polym J*. 20(12): 979-88.
- [7] Baker R.W. 2002. Future directions of membrane gas separation technology. *Industrial and Engineering Chemistry Research*. 41(6): 1393-1411.



- [8] Abedini R. and A. Nezhadmoghadam. 2010. Application of membrane in gas separation processes: its suitability and mechanisms. *Petroleum and Coal*. 52(2): 69-80.
- [9] Shi L., et al. 2008. Effect of additives on the fabrication of poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) asymmetric microporous hollow fiber membranes. *Journal of Membrane Science*. 315(1): 195-204.
- [10] Tan S., *et al.* 2010. The influence of support layer structure on mass transfer in pervaporation of composite PDMS-PSF membranes. *Chemical Engineering Journal*. 157(2): 304-310.
- [11] Zhang Q., *et al.* 2015. Preparation and Preliminary Dialysis Performance Research of Polyvinylidene Fluoride Hollow Fiber Membranes. *Membranes*. 5(1): 120-135.
- [12] Ren C., et al. 2015. Effect of PEG additive on anode microstructure and cell performance of anode-supported MT-SOFCs fabricated by phase inversion method. *Journal of Power Sources*. 279: 774-780.
- [13] Liu M., *et al.* 2013. Preparation and characterization of polyethersulfone microporous membrane via thermally induced phase separation with low critical solution temperature system. *Journal of Membrane Science*. 437: 169-178.
- [14] Daraei P., et al. 2013. Fouling resistant mixed matrix polyethersulfone membranes blended with magnetic nanoparticles: study of magnetic field induced casting. *Separation and Purification Technology*. 109: 111-121.
- [15] Zuo D.-y., *et al.* 2008. The influence of PEG molecular weight on morphologies and properties of PVDF asymmetric membranes. *Chinese Journal of Polymer Science*. 26(04): 405-414.
- [16] Salleh W. and A. Ismail. 2015. Carbon membranes for gas separation processes: Recent progress and future perspective. *Carbon*. 40: 43.
- [17] Segal L., et al. 1959. An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Textile Research Journal*. 29(10): 786-794.
- [18] Cao, J.-H., B.-K. Zhu, and Y.-Y. Xu, Structure and ionic conductivity of porous polymer electrolytes based on PVDF-HFP copolymer membranes. *Journal of membrane science*, 2006. 281(1): p. 446-453.
- [19] García-Fernández L., M. García-Payo and M. Khayet. 2014. Effects of mixed solvents on the structural morphology and membrane distillation performance of PVDF-HFP hollow fiber membranes. *Journal of Membrane Science*. 468: 324-338.
- [20] Sun F.-q., J.-k. Xu and P.-t. Cao. 2010. Improving hydrophilicity and protein antifouling of electrospun poly (vinylidene fluoride-hexafluoropropylene) nanofiber membranes. *Chinese Journal of Polymer Science*. 28(5): 705-713.