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A Morphology Studies On Effect Of A Coagulation Bath Mediums As The Phase Inversion Parameter For Poly (Vinylidene Fluoride) (Pvdf) Membranes

A.R. Nurul Izzati [1]
M.D. Irfan Hatim [*,1]
H. Hasbullah [2]
Adil Hatem Rashid [1,3]
[1] *School of Bioprocess Engineering, Universiti Malaysia Perlis, Malaysia*
[2] *Advanced Membrane Technology Research Centre (AMTEC), Faculty of Petroleum & Renewable Energy Engineering, Universiti Teknologi Malaysia, Malaysia*
[3] *Faculty of Chemical Engineering, Al-Nuthanna University, Al-Samawah, Iraq*
[*]*e-mail:* irfan@unimap.edu.my

In recent years there has been a considerable interest in modifying the PVDF membrane properties to suit with a wide range of applications. However, due to the multivariate nature in membrane fabrication steps, the fabrication techniques remain the key issue. In this article, the uses of different concentration of ethanol in the coagulation bath were investigated as it can improve the hydrophobicity of PVDF membrane and the membrane porous microstructure, i.e. finger-like microstructure. In addition, the coagulation mediums play an important role in determining extended of liquid-liquid demixing/crystallization via an immersion precipitation process. In this study, the effects of coagulation bath mediums on the morphology of PVDF membrane were investigated. Scanning electron microscope (SEM) was used to characterize the membrane microstructure. Octanol was used as a medium to estimate porosity of the membrane by determining the weight of liquid occupied within the membrane pores. The concentration of ethanol in the coagulation bath was varied at 0% until 75% with different evaporation time of 0 and 2 min. The SEM results indicate that the membrane surface porosity changes as ethanol concentration increases. Interestingly, at 0 to 25% ethanol, an asymmetric structure which consists of a dense skin layer accompanied by finger-like structure was formed during membrane casting. The more porous finger-like region which extends towards the skin layer is beneficial for membrane fuctionalization.

Keywords: PVDF membrane, Phase inversion, Ethanol Concentration, Evaporation Time

INTRODUCTION

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer become one of the popular membrane materials which relatively more hydrophobic compared with other materials such as polysulfone (PS), polyethersulfone (PES) and polyimide (PI). The hydrophobic material is well known for being thermally stable, possessing a high mechanical strength and having an excellent resistance to the most corrosive chemical and organic compound (Ahmad et. al, 2011), (Ooi et al., 2012) -4].

In preparing PVDF membranes, several techniques and parameters were considered for different application requires different membrane morphology and properties. Recently, most of the commercial membranes have been produced via phase inversion technique due to its simplicity, flexible production scales and helps to reduce the cost of production (Fiu et al, 2010).

In polymeric membrane formation, the immersion precipitation technique is commonly used. At this point, the skin is formed by gelation, and the porous sub layer is the result of liquid-liquid phase separation by nucleation and growth (Koenhen et. al, 1977). The physico-chemical properties of the polymer casting solution influence the structure of the integrally skinned membranes and membrane morphologies at the end of the phase inversion process. The final membrane morphologies and performances depend on various experimental parameters, including composition of casting solution (polymer concentration, type of solvent and non-solvent), the thickness of casting polymer film, the temperature of casting, the time and temperature of evaporation prior to immersion, relative humidity, the composition and temperature of the coagulation bath and the post-treatment (Fiu et al, 2010).

The objective of this work is to investigate either the composition of the coagulation bath and the time of evaporation prior to immersion will affect the structure of the PVDF membrane by the morphological analysis using SEM. By allowing partial evaporation of the volatile solvent prior to immersion in the coagulation bath, denser skin-layer generally forms (Holda et. al, 2013) & (Soroko et. al, 2011). Reported by Liu et al, in 2010, the evaporation period influenced the structure, the mechanical properties and the performance of the membrane as a result of precipitation phenomena. Using only water, which acts as the strong non-solvent as a coagulation medium in immersion precipitation leads to the formation of the membrane with asymmetric structure consists finger-like void. By the addition of the solvent such as ethanol into the coagulation composition may result the formation of the sponge-like structure due to induce delayed liquid-liquid demixing of a polymer. The finger-like structure is important indeed to impregnate solvent such as ionic liquid to improve the performance of separation using this membrane (Joskowska et. al, 2012).

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (PVDF) powder and anhydrous N-methyl-2-pyrrolidinone (NMP) were purchased from Sigma Aldrich. NMP was used as a solvent without any further purification. The Hmbg ethanol absolute was used as a composition in coagulation bath.

Preparation of PVDF casting solution

The PVDF casting solution was prepared by dissolving 20% PVDF powder in NMP in a sealed glass flask under continuous agitation using an overhead stirrer. During dissolution, the solution temperature was controlled in a range between 30 to 40 °C for 4 h. The speed of agitation was kept constant at 200 rpm. The PVDF solution was then sonicated and left at room temperature for 1 h to reduce the air bubbles prior to casting.

Preparation of PVDF membrane

The flat sheet PVDF membranes were fabricated by casting the solution on a glass plate and exposed to the solution to surrounding air for a period of time (0 min and 2 min). Then, the glass plate covered with casting solution was immersed into the coagulation bath containing distillated water and ethanol. Then, the formed membrane was continuing to immerse for at least 24 h to remove the solvent as well as to allow membrane solidification (Gao et. al, 2009).

Characterization of Fabricated Membrane

The surface and the cross-section of casted membranes were observed using SEM (Hitachi TM 3000). Samples were cryogenically fractured and coated with platinum using Auto line coater, JEOL: JFC-1600 to reduce sample charging under the electron beam.

Determination of percent of porosity

The PVDF membrane was immersed in octanol (ACS, ISO, Reag Ph Eur, Merck) for 15s to improve the hyrophilicity of the membrane. The membrane was later immersed in the deionized water before being dried using a filter paper. The membrane was weighed both as the wet and dry state in order to calculate the porosity using Eq. (1):

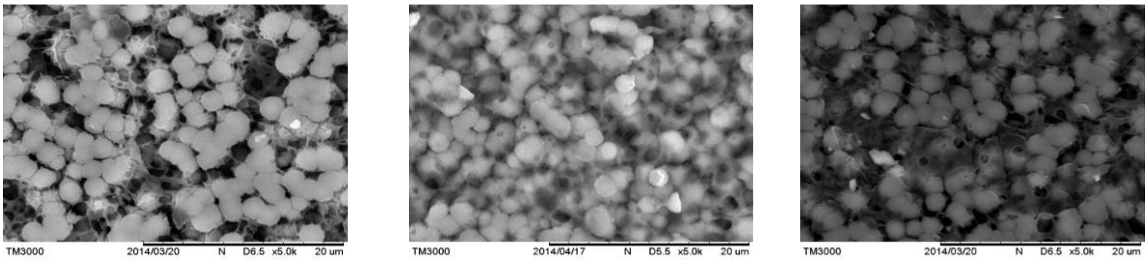
$$\varepsilon = \frac{m_n/\rho_n}{m_n/\rho_n + m_p/\rho_p}\, X\, 100\% \qquad (1)$$

Where ε is the porosity of the membrane, m_p is the mass of the dry membrane, m_n is the mass of the absorbed octanol, ρ_p is the density of the PVDF membrane and ρ_n is the density of octanol. This method used to estimate the porosity by determining the weight of liquid contained in the membrane pores (Ahmad et. al, 2012).

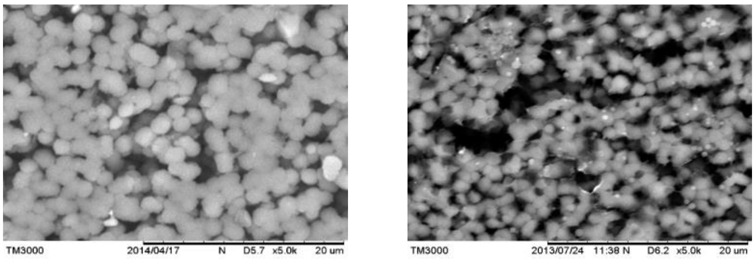
RESULT AND DISCUSSIONS

Surface morphology

The surface morphologies of the fabricated PVDF membrane were shown in Figure 1 and 2. The images show the effect on the ethanol composition in coagulation bath with two different sets of evaporation time. In comparison to the membranes with ethanol concentration of 0%, 25%, 35%, 50%, and 75%, at the evaporation time of 2min., the highest porosities of (65.9, 46.8, 44.3, 51.7, and 69.0), respectively, were obtained for

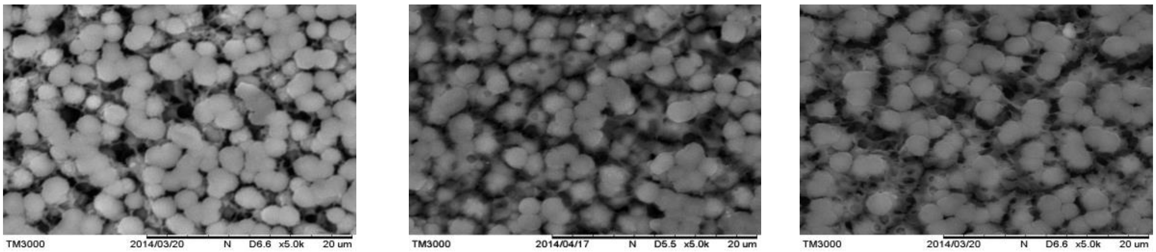


a) 75 % ethanol b) 50 % ethanol c) 35% ethanol

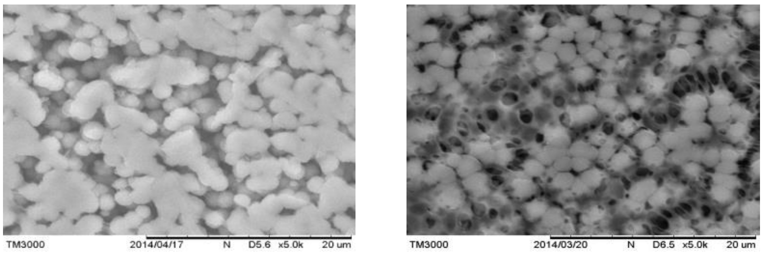


d) 25 % ethanol e) 0 % ethanol

Fig. 1: Surface morphology at different ethanol/water composition in the coagulation bath without evaporation time (t = 0 minutes).



a) 75 % ethanol b) 50 % ethanol c) 35% ethanol



d) 25 % ethanol e) 0 % ethanol

Fig. 2: Surface morphology at different ethanol/water composition in the coagulation bath with a 2.0 minutes evaporation time.

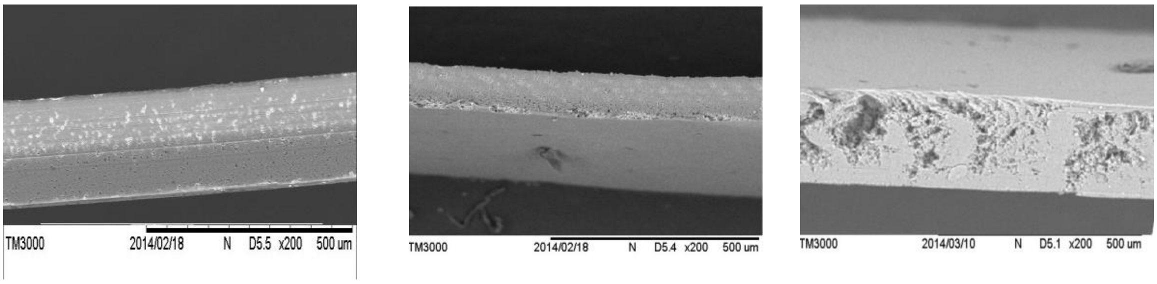
membranes with the same ethanol concentration and the evaporation time of 0 min., which proved the reverse relationship between porosity and evaporation time. Membranes prepared at the evaporation time of 0 min. and 2 min. with the same ethanol concentration of 0% and 75% show the largest pore sizes and as a result of higher porosities and these results supported by those in Figure

5.

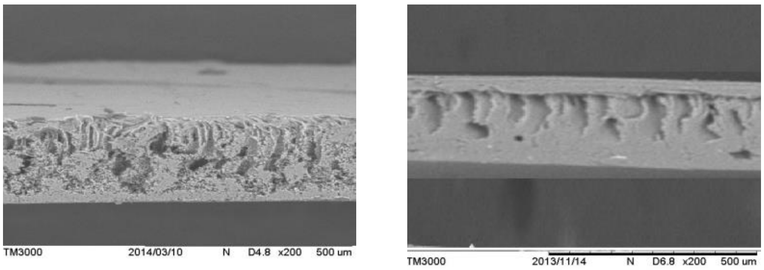
This could be attributed to the changes of polymer concentration that effect by the evaporation time. This happened when the evaporation solvent increased, the polymer concentration in the surface layer increases, leading to a dense surface layer (Ooi et. al, 2012).. This layer inhibits the exchange rate of solvent and non-solvent through the membrane surface during the immersion process and resulting in smaller pores and as a result lower porosity (Liu et. al, 2010).

Cross-section morphology

The SEM images of the cross-section membrane of five prepared PVDF membranes with two different evaporation times are illustrated in Figure 3 and. 4. As observed from the SEM cross-sectional image, all membranes have an asymmetric structure consisting of a dense top layer and a porous sub layer with finger-like cavities as well as a macrovoid (sponge-like) structure (Gao et. al, 2009). The formation of a dense skin layer served to hinder the exchange of solvent and insolvent, resulting the phase separation proceed for a longer time as going away from the interface (Kingsbury et. al, 2010). Its clearly observed that the trend of morphological change in the increase as the ethanol concentration in coagulation bath and evaporation time. The structure becomes longer at an ethanol concentration (25% and 0%) with evaporation time 2 min., (as shown in Figure 4. (d) and (e)). Asymmetric morphology generally resulted from the step of concentration and activity gradients of non-solvent, solvent and polymer across the polymer solution (Strathmann, 2003). As the ethanol concentration in the coagulation bath are increasing, the membrane effective porosity and the rate of precipitation

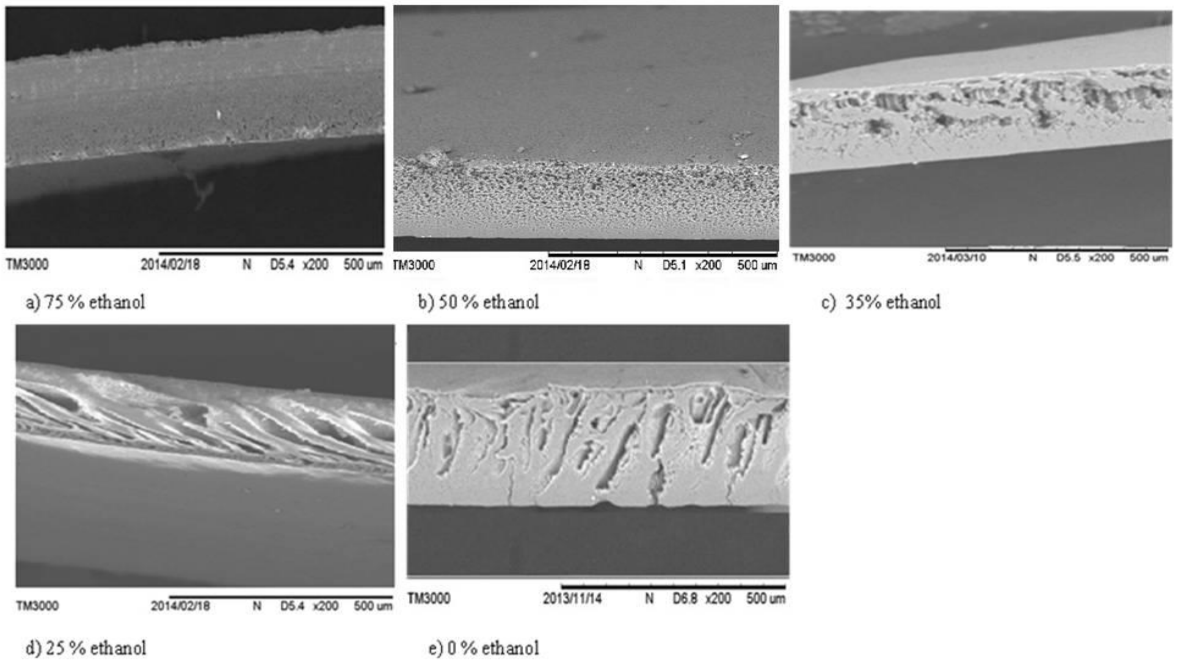


a) 75 % ethanol b) 50 % ethanol c) 35% ethanol



d) 25 % ethanol e) 0 % ethanol

Fig. 3: Cross Sectional morphology at different ethanol/water composition in the coagulation bath without evaporation time (t = 0 minutes).



a) 75 % ethanol

b) 50 % ethanol

c) 35% ethanol

d) 25 % ethanol

e) 0 % ethanol

Fig. 4: Cross sectional morphology at different ethanol/water composition in the coagulation bath with a 2.0 minutes evaporation time.

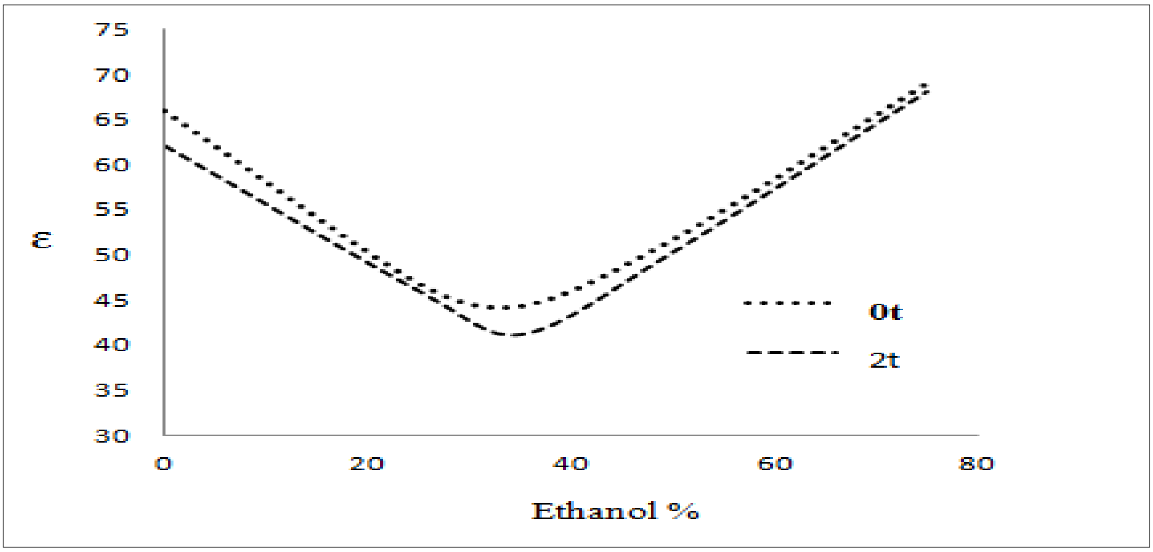


Fig. 5: Porosity analysis on PVDF membrane with different ethanol/water composition and evaporation time.

decrease, leading to a gradual change in the morphology of the membrane outer wall from finger-like structure to sponge-like structure (Fiu et al, 2010).

Porosity Analysis

The porosity value is influenced by the pore size of the membrane. Porosity analysis of the PVDF membrane with different ethanol/water composition inside the coagulation bath and different evaporation time are shown in Figure 5.

It was found that the increase of ethanol concentration in the coagulation bath from 0% to 35% was combined to decrease in porosity values (65.9, 46.8, and

44.3) for membranes without evaporation step. Meanwhile, the increase of ethanol concentration of 35% to 75% increased the porosity values (44.3, 51.7, and 69.0. For the same evaporation time, it was found that the highest value of porosity was 69.0 for the membrane with ethanol concentration of 75%, and the lowest value was 44.3 for membrane with ethanol concentration of 35%.

The same morphology was observed for the membranes prepared for the evaporation time of 2 min. as shown in Figure 2. It was also found that the increase of ethanol concentration of 0% to 35% decreased the porosity values (62, 46.0, and 41.2). Meanwhile, the proportional increase was shown in porosity values (41.2, 50.3, and 68.0) for membranes with ethanol concentration of 35%, 50%, and 75%, respectively. For the same evaporation time, the highest value of porosity (68.0) was found in membrane with ethanol concentration of 75%, while the lowest one (41.2) was for the membrane with ethanol concentration of 35%.

Comparing both evaporation time, membranes with the same ethanol; concentrations have the highest porosity values of (65.9, 46.8, 44.3, 51.7, and 69.0) at the evaporation time of 0 min. Further, the highest porosity value (69.0) was found in membrane with ethanol concentration of 75% and evaporation time of 0 min., while the lowest value (41.2) was at the evaporation time of 2 min. and ethanol concentration of 25%.

In elucidating this effect, the PVDF membranes made with NMP and water as an internal coagulant has been very close to binodal on the solvent /non-solvent axis of a ternary phase diagram for PVDF and hence gelation is not favored phase separation mechanism, the microvoids are open ended on inside.

CONCLUSIONS

This study reports the effect of parameters involved during the phase inversion process during the PVDF membrane preparation. The compositions of the coagulation bath and evaporation time before coagulation were the parameter selected to control the morphology of the membrane. At the same evaporation time, the porosity of all prepared membranes started to decrease with increasing ethanol concentration from 0% to 35%, then started to increase after ethanol concentration inside the coagulation bath was 35% to 75%. It was also found that increase the evaporation time decreased the porosity values for membranes with the same ethanol concentration. The high porosity value was at an ethanol concentration of 75% and 0 min. evaporation time, which is 69.0%. Meanwhile the lowest value (41.2) was at evaporation time 2 min. and ethanol concentration of 25%. All the membranes had an asymmetrical structure, and the finger-like structures are formed for that of the lower amount of ethanol in coagulation bath. With the increase of ethanol concentration, this finger-like structure start disappears and as a result formed the sponge-like one. The structure becomes longer for membranes with ethanol concentration of 25% and 0% at evaporation time 2 min.

NOMENCLATURE

ε : membrane porosity (-)
ρ_p : density of the PVDF membrane (g/cm^3)
m_n : mass of the absorbed octanol (g)
ρ_n : density of octanol (g/cm^3)
m_p : mass of the dry membrane (g)

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