# A Morphological Study of Poly (Vinylidene Fluoride) Pvdf Membranes: In Perspective of Membrane Pervaporation Process

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Membrane separation plays an important role in chemical industry (Prabhat *et al*. 2011). Pervaporation is one of the most promising membrane separation processes which is used in a wide range of applications such as separation of organic mixtures and dehydration of solvents.

This study investigated the effect of polymer concentration on the morphology of pervaporation membrane, where polyvinylidene fluoride (PVDF) was chosen as the base polymeric material while phase inversion method was employed as a technique to prepare an asymmetric PVDF membrane. The polymer concentration in dope solution was varied from 16 to 20wt% and the prepared membranes were characterized in terms of its structure, porosity, contact angle, and pore size. Five PVDF membrane samples were prepared (without any post-treatment) with polymer concentration of 16, 17, 18, 19, and 20wt% respectively. Depending on permeating component, two main areas of pervaporation processes can be identified: hydrophobic and hydrophilic and consequently two types of membranes could be observed: hydrophobic and hydrophilic membranes.

From the results, it was found that the increase in polymer concentration has produced membranes with low pore size and porosity and as a result, high contact angle (low hydrophilicity).The highest contact angle of 83° was found for membrane with highest polymer concentration of 20wt% with the lowest pore size and porosity of (0.4156µm and 65%) respectively. The lowest contact angle of 76° was found for membrane with the lowest polymer concentration of 16wt% with the highest pore size and porosity (0.8671µm and78%) respectively.

## INTRODUCTION

Due to its significant advantages over the other separation processes, membrane separation plays an important role in chemical industry. In comparison to other separation technologies, membranes offer lower energy consumption, cheaper construction cost and higher selectivity (Prabhat *et al*. 2011). There are various types of membrane processes one of which is pervaporation, which is used in a wide range of applications such as separation of organic mixtures and dehydration of solvents (Jinhui *et al.* 2013)..

Pervaporation is a separation process in which a liquid mixture contacts the membrane, which preferentially permeates one of the liquid components as a vapor. The vapor, which is enriched in the more permeable component, is cooled and condensed, spontaneously generating a vacuum that drives the process (Johanna *et al.* 2013). Membrane materials and fabrication method are among the key factors that determine the performance of pervaporation membrane. Compared to other separation processes, such as distillation and evaporation, it offers lower energy and often is refered to as (clean technology); especially for the treatment of volatile organic compound. Thus it is considered a promising alternative to these processes. Different from thermal processes, the separation in PV process is not based on relative, but rather on the relative rates of permeation through a membrane (Enu *et al.* 2011).

Poly(vinylidene fluoride) (PVDF) has been considered as a very attractive polymer as well as membrane material, exhibiting superior mechanical, thermal, and chemical properties, and is widely used to synthesize a lot of membrane separations (Mônica *et al.* 2012). For different types of applications such as pervaporation, membrane distillation, and others. Thus, it is the best option of membrane material (Masuelli *et al.* 2012). First fluorinated polymeric PVDF membrane was fabricated early 1980s (Fu Liu *et al.* 2011). Phase inversion, stretching, electrospining, track-etching, and interfacial polymerization are the most commercially employed techniques for membranes fabrication.

Due to its simplicity and flexible production scale, phase inversion method is used to produce the most of the commercial membranes (Boor *et al.* 2013). Phase inversion is a process where a polymer is transferred from a liquid to solid phase (Yee *et al.* 2011). Preparation of phase inversion membranes often follows five different techniques which are precipitation by solvent evaporation, precipitation from vapor phase, precipitation by controlled evaporation, thermal precipitation, and immersion precipitation (Agnieszka *et al.* 2013). The most commercial polymeric membranes are produced by immersion precipitation. In immersion precipitation process the polymer solution (polymer + solvent) is cast on a suitable support followed by immersion in a coagulation bath (nonsolvent) and as a result of the exchange of solvent and nonsolvent the precipitation occurs (Iwona *et al.* 2011).

An ideal pervaporation membrane should consist of an ultra-thin defect free

dense layer (skin layer) supported by a porous support (asymmetric structure). The skin layer is perm-selective and hence responsible for the selectivity of the membrane. Industrially, asymmetric structure is the most popular and the phase inversion is the common method to fabricate asymmetric membranes (Wang and Lai 2013).

In this method, two phase systems that are produced from a polymer solution transformation, consist of polymer poor-liquid phase which form the voids and the polymer rich-solid phase which forms the rigid membrane structure (Agnieszka *et al.* 2013). Many parameters such as solvent type, evaporation time, coagulation bath medium and temperature, non-solvent additives, and polymer concentration could give significant effects on PVDF membrane morphologies and eventually the membrane performance (Fu Liu *et al.* 2011).

The objective of this study is to verify the effect of the polymer concentration on the membrane morphologies in terms of its structure, contact angle, porosity, and pore size.

## EXPERIMENTAL

## Material and Methods

### *Materials*

The materials used for fabrication included PVDF (average Mwt~534,000 by PC, powder) (Sigma Aldrich) and (1-Methyl-2-Pyrrolidinone (NMP)) (Anhydrous 99.5%) (Sigma Aldrich) as a solvent.

### *Preparation Method*

Poly(vinylidene fluoride) (PVDF) powder was dissolved in (1-Methyl-2-Pyrrolidinone) (NMP) with a determined polymer concentration (16-20wt%) and a dissolution temperature (30-40°C) for 6h. This was followed by cooling at room temperature for 3h to remove all bubbles formed upon dissolution. After 3h the solution was cast on a glass plate with a certain thickness of 250μm followed by immersion of the cast film with the glass plate in the coagulation bath until the membrane formed. The formed membrane then was left immersed in the coagulation bath for 24h followed by drying at room temperature for another 24h before characterization. Five flat sheet PVDF polymeric membranes samples with different polymer concentration in polymer solution (16, 17, 18, 19, and 20wt%) were prepared (without any post-treatment) at dissolution temperature of 40°C. Deionized water (100%) was used as a coagulation medium to remove all the residual solvent as well as to complete the membrane solidity. The composition and preparation conditions of the prepared membranes are shown in Table 1.

## Characterization of Prepared Membranes

### *SEM Microscopy*

The morphology of the prepared PVDF membranes was observed using scanning electron microscope (SEM) (Hitachi TM-3000). The prepared membranes were coated with platinum using Auto line cutter, JEOL: JFC-1600 to reduce sample charging under the electron beam.

**Table 1.** Compostition and preparation conditions of prepared membranes

| Membrane | Polymer Concentration wt % | Solvent Concentration wt % | Dissolution Temp. ($^0$C) | Dissolution Time (h) | Coagulation Medium |
|----------|---------------------------|----------------------------|--------------------------|---------------------|--------------------|
| M1 | 16 | 84 | 40 | 6 | 100%water |
| M2 | 17 | 83 | 40 | 6 | 100%water |
| M3 | 18 | 82 | 40 | 6 | 100%water |
| M4 | 19 | 81 | 40 | 6 | 100%water |
| M5 | 20 | 80 | 40 | 6 | 100%water |

### Contact Angle Measurement

Contact angle measurements on the prepared membranes were conducted using the contact angle goniometer (Model: OCA 15EC, Dataphysics with deionized water as contact liquid. The water droplets of 2 µL were dropped on the membrane surfaces. An average and standard deviation of at least 5 independent measurements was obtained at different points of one sample.

### Porosity

To measure the prepared membranes porosity, PVDF membranes were immersed in octanol (ACS, ISO, Reag Ph Eur, Merck) for 2 hours and then the membrane surface was dried by filter paper. The wet and dry membranes were weighed then the porosity was calculated using Eq (1) [5]:

$$\varepsilon = \frac{\left(\frac{m_b}{\rho_b}\right)}{\left(\frac{m_b}{\rho_b} + \frac{m_p}{\rho_p}\right)} x100 \qquad (1)$$

where $\varepsilon$ is the porosity of membrane (%), $m_b$ is the mass of the observed octanol (gm) , $m_p$ is the mass of dry membrane (gm) $\rho b$ is the density of octanol (gm/cm$^3$)

$\rho_b$ is the density of octanol (gm/cm$^3$) and $\rho_p$ is the density of membrane (gm/cm$^3$).

### Pore Size Measurement

Pore size distribution of the prepared membranes was measured by using a Porolux 1000 Porometer (IB-FT GmbH, Germany).

### RESULTS AND DISCUSSION

In order to investigate the role of polymer concentration on membrane morphologies and performances, different polymer concentration (16-20wt%) were used. The membrane composition and preparation conditions are shown in Table 1. The effect of polymer concentration on the membrane morphology is discussed in this study:

### Surface and Cross Section Morphology

Fig.1. shows the surface morphology of the prepared membranes (M1, M2, M3, M4, and M5).The images clearly show the effect of the increase in the polymer concentration on membrane surface. It was shown that for the membranes with higher polymer concentration a dense skin layer with very small pores was observed while a dense skin layer exhibited larger
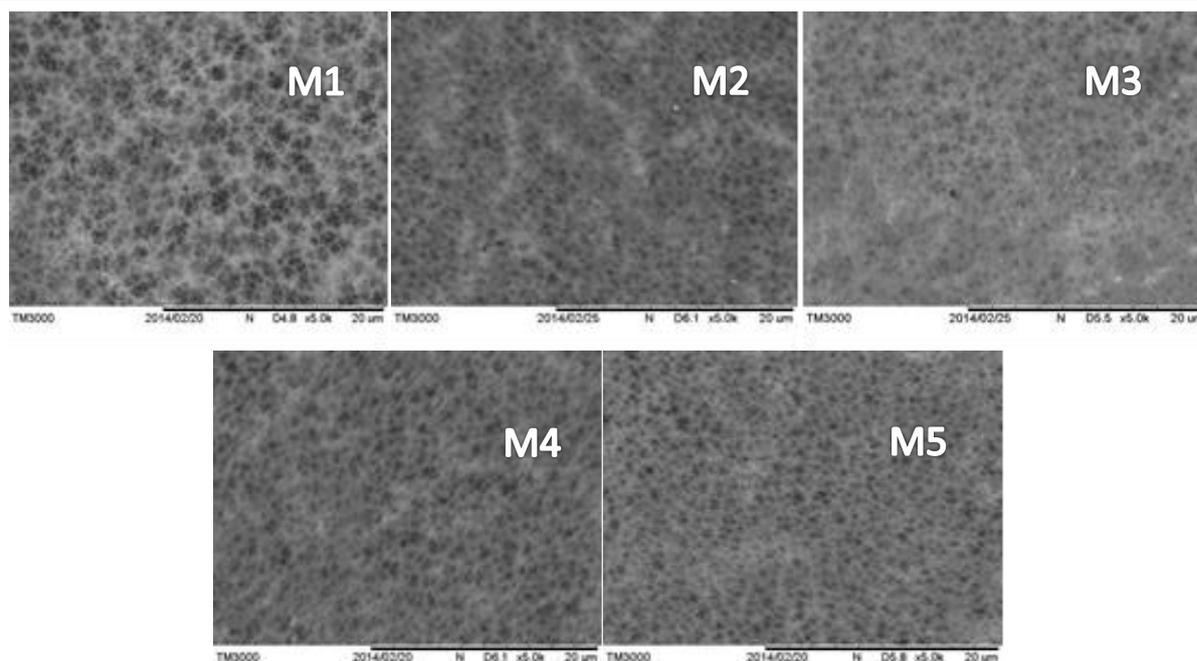
**Fig. 1:** SEM images for membranes surface (M1, M2, M3, M4,and M5), (Top surface).

pores for membranes with lower concentration in the order of M1>M2>M3>M4>M5 with values of (0.8671, 0.7155, 0.6454, 0.5991, and 0.4156) respectively.

It was also shown that the number of pores is higher for membranes with lower concentration in comparison to those with higher concentration (M1>M2>M3>M4>M5). With the increase in polymer concentration of the solution, coagulation value was reduced. That could be attributed to stronger polymer/solvent interaction and slower interaction between nonsolvent and polymer, which lowered down the solvent power for polymer. Slower precipitation rate could have resulted in the formation of a skin layer and, then, the diffusional exchange between solvent (NMP) and nonsolvent (water) in the sublayer would be hindered (Andy *et al.* 2013). Depending on the rate of polymer precipitation, fast phase

separation at surface layer and slower phase separation at sublayer resulted in asymmetric membrane formation with dense and thick skin layer by a higher polymer concentration solution (as shown in Fig.2) (Rinku *et al.* 2014). Also, as shown in Fig.2 all prepared membranes have an asymmetric structure consisting a dense top layer and a porous sublayer. The number of  macrovoids was decreased with the increase of polymer concentration and the finger like structure was clearly shown in the cross section of membranes with lower polymer concentration (M1 and M2) of (16 and 17wt%) respectively. It was noted that hydrophilic pervaporation processes require a hydrophilic pervaporation membranes with higher pore size and porosity and as a result lower contact angle (< 90º). At the same time hydrophobic pervaporation membranes with lower pore size and porosity, and as a result higher contact
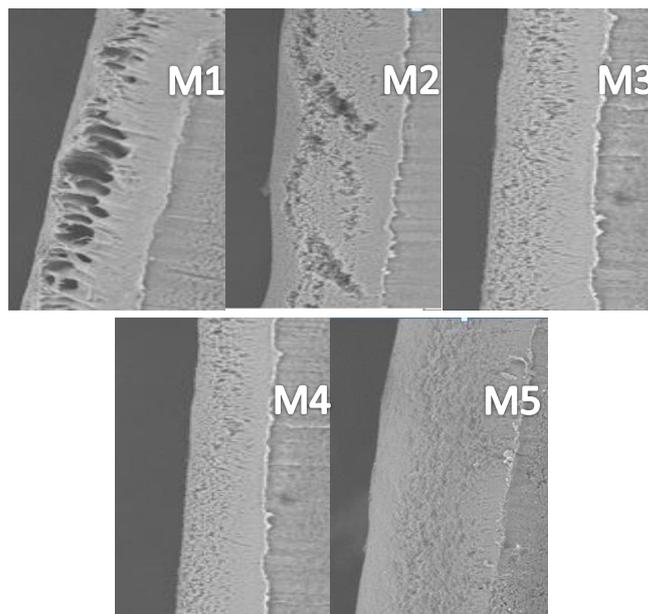
**Fig. 2:** SEM cross-sectional images of PVDF membranes (M1, M2, M3, M4, and M5)

angle (≥90º), are required to hydrophobic pervaporation processes.

**Porosity and Pore Size**

Porosity or void fraction is a measure of the void spaces in a material, and is a fraction of the volume of voids over the total volume, between 0 and 1, or as a percentage between 0 and 100%.

The prepared membranes in our work were also characterized in terms of porosity and pore size measurement. Based on the results shown in Figs.3(a) and (b), pore size and porosity values (`0.8671, 0.7155, 0.6454, 0.5991, and 0.4156μm) and (78%, 75.5%, 72%, 69%, and 65%) respectively exhibited a declining trend with increasing polymer concentration in dope solution (M5<M4<M3<M2<M1) of (20, 19, 18, 17, and 16wt%) respectively.That which proved the proportional relationship between the pore size and porosity while the reverse relationship of the polymer concentration with both of pore size and porosity was clear. From the results, the highest values of pore size (0.8671μm) and porosity (78%) were found for membrane with the lowest polymer concentration of (16 wt% ) while the lowest values of pore size (0.4156μm) and porosity (65%) were found for membrane with the highest polymer concentration of (20wt%).

Lower porosity for higher polymer concentration could be attributed to the slower exchanging process between the solvent and non-solvent which resulted in a dense and compact membrane structure (Ahmad, and Ramli 2013).

As stated before, the increase of the polymer concentration in polymer solution leads to a lower diffusion rate of non-solvent and as a result leads to a higher mass transfer resistance between the non-solvent and solvent in the system during solidification of the casting solution. Thus, denser membrane with smaller pore size distribution will be formed after a long
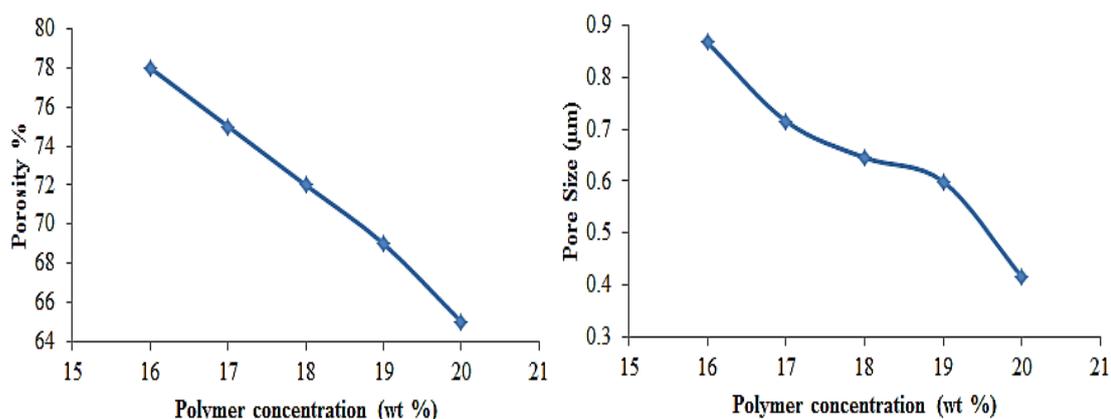
**Fig. 3:** Porosity and pore size as a function of polymer concentration.(a) Porosity; (b) Pore size.

period of precipitation process (Ahmed *et al.* 2013).

Hydrophilic pervaporation processes require a hydrophilic pervaporation membranes with higher pore size and porosity. At the same time, hydrophobic pervaporation membranes with lower pore size and porosity are required to hydrophobic pervaporation processes The results were also supported with SEM images of membranes presented in Figs. 1and 2.

**Contact Angle**

In chemistry, the repelled molecules from a mass of water refer to its hydrophobicity. It is represented in terms of the contact angle between the water and the surface of the membrane The contact angle is the angle between the solid and liquid surface. When water is applied to the surface, the outermost surface layers interact with the water and the membrane is said to be hydrophobic if the contact angle exceeds 90º. A high contact angle could be achieved on a hydrophobic surface with low free energy whereas a wet high energy allows the drop

to spread resulting in a low contact angle (Ahmad *et al.* 2012).

Porous surfaces of the membranes have a significant effect on the hydrophobic property of PVDF membranes. In order to eliminate the wetting problems, the membranes must have high hydrophobicity at the same time low hydrophobicity combined with bigger pore size. A membrane with a higher polymer concentration has higher resistance for the water to flow mainly due to the smaller pore size as well as an increased higher contact angles (Ooi *et al.* 2012).

As shown in Figs. 3(a) and (b) the high polymer concentration in polymer solution produced membranes with low pore sizes (0.4156, 0.5991, 0.6454, 0.7155, and 0.8671µm ) and low porosities of (65%, 69%, 72%, 75.5%, and 78%) in the order (M5<M4<M3<M2<M1) respectively. As a result, an increase in the polymer concentration increased the contact angle values (as shown in Fig.4) (M5>M4>M3>M2>M1) of (83° > 81° > 79° > 77° > 76°) respectively (intrinsic

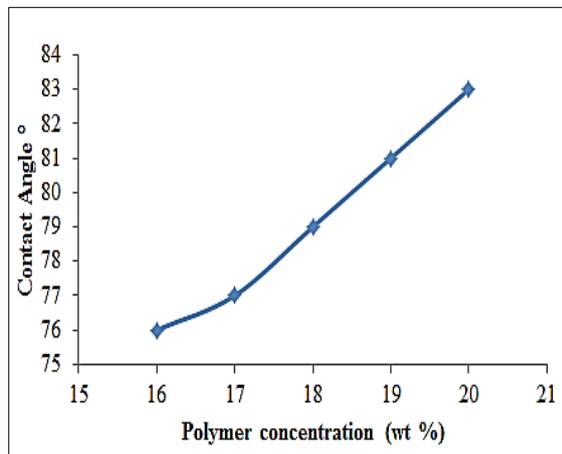contact angle of dense PVDF membrane is less than 90º) (Kang and Cao 2014).



**Fig. 4:** Contact Angle as a function of polymer concentration

It is noted that the hydrophobicity of PVDF membranes is affected by porous surfaces of the membranes.The highest contact angle (83°) was found for membrane with the highest polymer concentration of (20wt%) while the lowest one (76°) was found for membrane with the lowest polymer concentration of (16wt%). This has proved the proportional relationship between the contact angle and polymer concentration and as a result the reverse relationship of the contact angle with both of pore size and porosity was observed (high polymer concentration produced a low free energy surface membrane).

As stated before, membranes with higher contact angle (≥90º) are required for hydrophobic pervaporation processes. On the other hand, hydrophilic pervaporation processes require hydrophilic membranes with lower contact angle (<90º).

## CONCLUSIONS

Pervaporation is one of the most promising membrane separation processes which is used in a wide range of applications such as separation of organic mixtures and dehydration of solvents.

- The type of permeating component plays a very important role in pervaporation processes classification. Two main areas of PV can be identified: hydrophobic and hydrophilic PV and consequently two types of PV membranes could be observed: hydrophilic (contact angle <90º) and hydrophobic membranes (contact angle ≥90º). For dehydration of solvents, hydrophilic membranes are always used while hydrophobic (or hydrophilic) membranes are used for separation of organic mixtures.

- Hydrophobicity/hydrophilicity of membranes is always affected by all of the above mentioned factors (membrane structure, pore size, and porosity). Thus, they have a significant effect on the determination of the appropriate type of membrane used in PV process.

- In this study, it was found that polymer concentration in polymer solution has a significant effect on membrane morphology in terms of its structure, pore size, porosity, and contact angle.The results showed that the polymer concentration has a reverse relationship with both of pore size (0.8671, 0.7155, 0.6454, 0.5991, and 0.4156μm) and porosity (78, 75.5,

72, 69, and 65%) for membranes (M1, M2, M3, M4, and M5) respectively and , as a result, the contact angle increased proportionally (76º, 77º, 79º, 81º, and 83º) with the increased polymer concentration for membranes (M1, M2, M3, M4, and M5) respectively.

- The highest value of contact angle (83º) was found for membrane with the highest polymer concentration of (M5) with lowest pore size of (0.4156μm) and lowest porosity of (65%). In contrast, the membrane with the lowest polymer concentration (M1) produced the lowest contact angle of (76º), highest pore size of (0.8671μm), and highest porosity of (78%).

- Experimentally, there are several approaches to improve any of the mentioned factors (membrane structure, porosity, pore size, and contact angle) depending strongly on the PV separation process type and conditions.

## NOMENCLATURE

$\varepsilon$     :    Porosity of the membrane (%)

$m_b$   :    Mass of the observed octanol (gm)

$\rho_b$   :    Density of octanol (gm/cm$^3$)

$m_p$   :    Mass of the dry membrane (gm)

$\rho_p$   :    Density of PVDF membrane (gm/cm$^3$)

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