Study on the effect of air gap on physico-chemical and performance of PVDF hollow fibre membrane

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Abstract. Polyvinylidene fluoride (PVDF) was chosen in this study as the main material in fabricating membrane due to its excellent chemical resistance and good thermal stability. Combination of triethyl phosphate (TEP) with DMAc produce better structure of membrane which safer and provide high mechanical strength for membrane. Surface modified PVDF hollow fibre membrane (HFM) was prepared using dry-wet spinning technique by varying air gap namely 10 cm, 20 cm and 30 cm. The morphology was evaluated using scanning electron microscopy (SEM), atomic force microscopy (AFM), mercury intrusion porosimetry (MIP), contact angle, tensile test and performing water flux testing. From the characterization data, PVDF HFM with 3 wt.% PEG 400, HFM 3-10 and HFM 3-20 referred as microfiltration membrane with pore size range 0.1-0.8 µm. While, HFM 3-30 act as ultrafiltration membrane with pore size ranging 0.01-0.1 µm. Experimental results revealed that by increasing the air gap from 10 cm to 30 cm, the porosity and finger-like length decreased due to the higher elongational stress that shift the pores from broad to narrow. Thus, PVDF HFM at 10 cm air gap, HFM 3-10 achieve the highest water flux due to the higher porosity, longer finger-like length and hydrophilicity achieved. The modified HFM at shorter air gap was found to be a promising membrane structure for excellence water performance and eco-friendly to environment.

1. Introduction

Membrane technology widely used as a separation process to eliminate unwanted contaminants in the water due to its excellent separation system, outstanding capability of high capacity of contaminants removal and low energy consumption [1]. Polymeric membrane especially polyvinylidene fluoride (PVDF) was chosen as one of the attractive organic macromolecule polymers in fabrication of membrane on account of its excellent chemical resistance, high mechanical strength, longer timespan and good thermal stability [2]. Furthermore, PVDF possess high solubility in various organic solvents compared to other materials.

Dimethylacetamide (DMAc) is stated as one of the widely used solvent for dissolving the PVDF due to its high solubility in DMAc. However, the toxic content of DMAc needs to be considered. According to Chang et al [3], triethyl phosphate (TEP) is believed to have much safer solvent due to its low toxic content. In addition, the used of TEP as solvent can help in producing high mechanical strength of membrane [4]. Thus, the membrane produced can withstand high resistance and pressure as well act as green membrane for safety environment.
Although PVDF experiencing excellent characteristics for wastewater treatment, however, it can encounter fouling issue due to its hydrophobic nature which can encounter lower water flux performance. Surface modification was needed to obtain the hydrophilic PVDF membrane. Polyethylene glycol (PEG) found to be one of the most frequently used additives in membrane fabrication. PEG easily dissolves in water and various organic solvents as well as known as non-toxic material and low cost [5]. In addition, it acts as pore former [6] and help in increasing the membrane permeability [5]. Moreover, modification of membrane by varying the air gap during fabrication procedure also affected the properties of produced membrane.

To acquire a good physico-chemical property of membrane in terms of robust and outstanding performance for water treatment, DMAc and TEP were chosen as solvents in dissolving PVDF in order to produce high mechanical strength of membrane. In addition, lower molecular weight of PEG (PEG 400) was used as pore former and different air gap were applied to increase the hydrophilicity of the polymeric membrane. There are various configuration of polymeric membrane including flat sheet, hollow and tubular. Flat sheet is widely used configuration and the easiest to be fabricated. However, it tends to have lower surface area. Hollow fibre configuration was chosen in this study due to its favor condition such as high surface area that can be fabricated using dry-wet spinning technique.

2. Methodology

2.1 Materials
Polyvinylidene fluoride (PVDF, Kynar 760 Series-powder, Solvay Specialty Polymers France) was used as polymer. Polyethylene glycol (PEG 400) as pore former purchased from Evergreen Engineering & Resources. Dimethylacetamide (DMAc, Sigma Aldrich) and triethyl phosphate (TEP, Merck) were used as solvent to dissolve a polymer.

2.2 Fabrication of PVDF hollow fibre membrane

2.2.1 Polymer dope preparation. PVDF was dried in a 60 °C vacuum oven for 24 h to remove moisture. The compositions of single layer dope solutions are shown in Table 1. TEP and DMAc respectively were mixed and stirred at 240 rpm inside a Scott bottle at 80 °C until homogenous. 15 wt.% of PVDF was added into the solution and stirred at 80 °C for 24 hours until completely dissolved. 3% of PEG 400 was added into the solution as pore former and stirred for another 24 hours as stated in Table 1.

| Table 1. Composition of PVDF hollow fibre membrane. |
| PVDF (wt%) | PEG 400 (wt%) | TEP (wt%) | DMAc (wt%) |
|-----------|--------------|----------|-----------|
| 15        | 3            | 50       | 32        |
2.2.2 Dry/wet Spinning technique. Normal tube and orifice spinneret were used to produce hollow fibre membranes. Dope solution was filled into dope reservoir with spinning conditions as shown in Table 2 to fabricate the hollow fibre membranes [7]. Then, as-spun hollow fibre was immersed in a deionized water tank for 1 day to extract the residual diluent. The post treatment was done by soaking the membrane into 50% of ethanol for 1 hour followed by immersing the membrane into 100% ethanol for another 1 hour. Finally, the membrane was dried at room temperature for 1 day.

### Table 2. Parameters for spinning conditions.

| Sample   | Dope flow rate (ml/min) | Bore fluid flow rate (ml/min) | Bore fluid | Spinneret dimension (mm) | Air gap (cm) |
|----------|-------------------------|-------------------------------|------------|---------------------------|--------------|
| HFM 3-10 | 7.81                    | 8                             | Distilled water | 0.8/1.2          | 10           |
| HFM 3-20 | 7.81                    | 8                             | Distilled water | 0.8/1.2          | 20           |
| HFM 3-30 | 7.81                    | 8                             | Distilled water | 0.8/1.2          | 30           |

2.3. Characterization

2.3.1 Scanning Electron Microscopy (SEM). SEM (Model: TM3000, Hitachi) was used to observe the finest structural morphology of the cross-section and the surface of PVDF HFM. The sample was coated with platinum for 10 s under vacuum to ensure the micrograph produced was clear and reduce charging effect. The micrograph was obtained with magnification of 60x, 600x and 10Kx.

2.3.2 Mercury Intrusion Porosimetry (MIP). The porosity of membrane was analyzed using Automated Mercury Porosimeter (Model: AutoPore IV Series, Micromeritics). The membrane was cut with size 1 cm and weight around 0.25 g. This technique was controlled with pressure and able to measure the diameter of pore [6].

2.3.3 Atomic Force Microscopy (AFM). Atomic force microscopy (Model: SE-100 Park System) was used to investigate the roughness of PVDF HFM surface [6]. A micro cantilever is located at one end while tiny probe is equipped at the other end. Firstly, sample membrane was put on the object stage by keeping the surface in horizontal plane. Then, the studied area with the lop of the optical microscope was selected. Finally, the instrument scan the tested area and the surface information was obtained [8].

2.3.4 Contact angle. The changes in contact angle of PVDF HFM surface with water was measured using contact angle goniometer (Model: OCA15EC, Dataphysics). Deionized water was used as a contact liquid. Multiple points of the sample were measured to obtain the result.

2.3.5 Tensile strength. The tensile strength of the PVDF HFM was tested by loading the 500 N (Zwick/Roell) load cell with the test standard of ASTM D 2256/D 2256 M at room temperature. The tensile strength was calculated using equation 1 [6]:

\[
\text{Tensile strength (Pa)} = \frac{\text{Load at break (N)}}{\text{Cross sectional area (m²)}}
\] (1)
2.3.6 Water permeation analysis. The changes in water flux of PVDF HFM was conducted using dead-end cross-flow permeation cell of the membrane by pumping the feed across the membrane and allow the permeate to flow out through lumen side of membrane. All the analysis was carried out with pressure 1 bar at 25°C with the length of membrane of 10 cm. The flux, \( F \) (L/m\(^2\).h) was calculated using the following equation 2.

\[
F = \frac{V}{At}
\]

(2)

Where \( V \) (L) is the permeate volume collected. While \( t \) (h) is time and \( A \) (m\(^2\)) is the exposed membrane area.

3. Results and discussion

3.1 Physical properties

The morphology structure of the fabricated PVDF hollow fibre membrane (HFM) were investigated using SEM as shown in Figure 1. Average outer diameter of HFM 3-10, HFM 3-20 and HFM 3-30 were 1.53 mm, 1.50 mm and 1.41 mm respectively. The reduction of the diameter was due to the higher air gap that possess higher elongational stress which make the membrane’s wall stretched. The decrease of membrane’s wall diameter also effected from the presence of PEG 400 that increase the thermodynamic instability of dope with water because of its non-solvent effect as a phase separation enhancer [9]. However, HFM 3-20 and HFM 3-30 exhibit shorter average finger-like length of 52.37 \( \mu \)m and 31.30 \( \mu \)m respectively at outer and inner layer membrane with sponge-like structure at intermediate space. The spongy structure developed at intermediate space was called as sandwich-like structure on account of pension-coagulant interface instability happened during phase inversion procedure [10;6]. The formation of shorter finger-like may be due to the higher percentage of PEG 400 that lead in low viscosity of dope solution not suitable to be interacted with higher air gap. Macrovoids can be seen near inner finger-like structure and the size increased when air gap increased due to the stretching process where dope solution experienced longer exposure to air before it reaches water to form membrane. The length of finger-like structure was crucial for determination of higher permeability that highly required for water treatment process [11].
Figure 1. SEM images of PVDF HFM with 3% PEG 400 at different air gap.

Figure 2 and Figure 3 depicts the porosity and pore size distribution respectively decreased when air gap increased. As can be seen in Figure 3, the broad peak of each membrane indicates that the membrane composed of sponge-like structure, represented by uniform pore formation throughout the membrane [11]. The intense pore size distribution from average sponge-like structure at the first peak of HFM 3-10 and HFM 3-20 lies in the range between 0.1-0.8µm referring to microfiltration membrane [12]. While, pore size distribution of HFM 3-30 reduced and numerous below 0.1 µm that nominated them as ultrafiltration membrane. Additionally, the mercury intrusion intensity decreased upon the reduction of air gap. This indicate that pore size became smaller when increasing the air gap during spinning procedure. This was due to the greater molecular orientation and a tighter molecular packing. Moreover, the elongation-induced pore deformation occurred when increasing the air gap. A round pore might be elongated as an elliptical pore with narrow fluid channel and the pore size diameter may shift from broad to narrow [13]. Besides, no significantly differences observed at the pore size distribution between 100-1000 µm which corresponded to the formation of finger-like structure.
Surface roughness of the membrane was observed by AFM analysis. From observation in Figure 4 and Figure 5, the surface roughness was decreased from 8.78 nm to 4.18 nm when air gap increased from 10 cm to 30 cm. This may be due to the polymer aggregates are merging with each other when increasing the air gap [14]. Moreover, it could be due to the longer contact time of dope suspension exposed to air at higher air gap before it touches the water to form membrane. Thus, stretching the membrane and produce smooth surface. Surface roughness of membrane was crucial for selecting a suitable one for coating process. Higher surface roughness of membrane possessed higher selectivity as support for coating procedure as it provides higher available surface area for particle attachment and expected to
minimize the leaching problem during water treatment process [15]. This is because, the higher the roughness, the stronger the attachment of material onto the membrane surface [16].

![Surface micrograph of PVDF HFM at different air gap.](image)

**Figure 4.** Surface micrograph of PVDF HFM at different air gap.

![Surface roughness of PVDF HFM at different air gap.](image)

**Figure 5.** Surface roughness of PVDF HFM at different air gap.

Figure 6 depicts the contact angle value of hollow fibre membrane with different pore former loading and air gap. The contact angle tends to increase from 77.01° to 84.20° when increasing the air gap. This was due to the reducing of surface roughness which reduce the surface area causing the membrane tend to exhibit hydrophobic nature. Moreover, this could be on account of the longer period for dope suspension exposed to the air before reaching the water resulting smooth surface of membrane. The hydrophobicity was crucial for determination of fouling issue. The higher the contact angle, the higher the hydrophobicity nature that lead to fouling issue. The particles may clog into the pores of membrane and reduce the water flux performance [17].
Figure 6. Contact angle of PVDF HFM at different air gap.

Figure 7 summarizes the results of tensile strength of PVDF HFM 3 at different air gap. The tensile strength increased when increasing the air gap to 30 cm. This could be due to the role of TEP that help in increasing the tensile strength of membrane. The spongy structure at intermediate space of membrane with interconnected porosity produced by TEP as well as shorter finger-like structure at higher air gap help in developing the stronger structure of membrane [4]. Furthermore, all the membrane in this study shows outstanding tensile strength which indicate higher than 2 MPa compared with previous study by Dzinun et al [7]. The tensile strength of single layer PVDF hollow fibre membrane fabricated by using DMAc only as solvent shown only 1.82 MPa [7], lower compared to this study when using combination of DMAc and TEP. It can be proved that the interconnected bicontinuous pores developed with dense skin layer formed by using TEP help to increase the tensile strength of membrane.

Figure 7. Tensile strength of PVDF HFM at different air gap.
3.2 Water flux performance

Water permeation analysis was conducted to indicate the water flux performance of PVDF HFM. The water flux trend shown in Figure 8 correlated with the morphology of membrane. As the porosity and finger-like length decreased at higher air gap, the water flux performance also decreased on account of shorter finger-like that lead a difficulty for the water to pass through the pores. HFM 3-10 exhibit the highest water flux performance at 2338.88 L/m$^2$.h compared to the membrane from previous literature by Abed et al [4] which only possessed at 114.59 L/m$^2$.h. Although water flux at 30 cm air gap reduced to 1334.18 L/m$^2$.h, it revealed as an outstanding performance compared to PVDF hollow fibre membrane produced from previous literature written by Shi et al [18] that exhibit only 350 L/m$^2$.h under similar air gap.

![Figure 8. Water flux of PVDF HFM at different air gap.](image)

4. Conclusions

PVDF hollow fibre membranes with three different air gap, 10 cm, 20 cm and 30 cm have successfully prepared via a dry wet spinning technique. The PVDF HFM 3 membranes have finger-like structure at the outer and inner layer with a sponge-like structure at the intermediate space. Different air gap during spinning procedure significantly affected the finger-like structure, porosity, pore size distribution, membrane surface roughness and increases of tensile strength as well as contact angle which give rise to hydrophobicity. PEG 400 at 3 wt.% loading affected the finger-like structure which form a longer finger-like that help to enhance in water flux performance. The characterization study revealed the HFM 3-10 exhibit the highest porosity of 61.23% and longest finger-like structure which resulting the highest water flux performance at 2338.88 L/m$^2$.h. Furthermore, HFM 3-10 also possessed highest surface roughness which lead the membrane nominated as a good support for coating. Thus, reduce the leaching issue during the water treatment. Besides, HFM 3-10 also experiencing hydrophilicity nature which can minimize the fouling problem. The used of low toxicity of TEP as a solvent also assist in producing a green membrane with outstanding mechanical strength to withstand high pressure. For overall, HFM 3-10 can be nominated as suitable microfiltration membrane for separation process in water treatment.
5. Conflict of interest

The authors declare that they have no conflict of interest

6. Acknowledgement

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