Effect of dope solution temperature on the membrane structure and membrane distillation performance

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Abstract. Membrane distillation (MD) is a non-isothermal process applicable to purify water using hydrophobic membrane. Membrane in MD is hydrophobic, permeable to water vapor but repels liquid water. MD membrane is expected to pose high flux, high fouling and scaling resistances and most importantly high wetting resistance. This study develops flat-sheet polyvinylidene fluoride (PVDF) membrane by exploring both liquid-liquid and liquid-solid phase inversion technique largely to improve its wetting resistance and flux performance. We hypothesize that temperature of dope solution play roles in solid-liquid separation during membrane formation and an optimum balance between liquid-liquid and liquid-solid (crystallization) separation leads to highly performance PVDF membrane. Findings obtained from differential scanning calorimeter test show that increasing dope solution temperature reduces degree of PVDF crystallinity and suppresses formation of crystalline structure. The morphological images of the resulting membranes show that at elevated dope solution temperature (40, 60, 80 and 100°C), the spherulite-like structures are formed across the thickness of membranes ascribed from due to different type of crystals. The performance of direct-contact MD shows that the obtained flux of the optimum dope temperature (60°C) of 10.8 L/m²h is comparable to commercial PTFE-based MD membrane.

1. Introduction

Membrane distillation (MD) is a promising technology that claimed suitable technology in response to the water scarcity issue. MD utilizes the difference in vapor pressure between the feed and permeate sides of the membrane to drive mass-transport. In MD, porous hydrophobic membrane acts as a barrier that only allows vapors to pass through the membrane pores, but thanks to hydrophobic properties, repels liquid water and other non-volatile solutes. The vapor passes through the membrane pores, then condenses at the cold side as permeate.

The ideal structural requirements of membrane for MD are; high flux and high salt rejection, high wetting resistance, low scaling and fouling properties and low thermal heat conductivity [1]. MD flux can be improved by having membrane with large pore size, high bulk and surface porosity, small tortuosity factor and thin film layer. As for wetting resistance, it is dictated by hydrophobic properties and the size of the largest pore (bubble point). Pores size distribution (PSD) of membrane must be narrow and small to obtain high wetting resistance (i.e., average pore size close to the bubble point).

Hydrophobicity of the membrane can be increased by using materials of low surface energy (i.e., fluorinated) than can lead to high water liquid entry pressure (LEP). The indicator for determining hydrophobicity of membrane surface includes water contact angle (CA) and maximum-pore size (or bubble point, BP) [2]. Meanwhile, membrane with high hydrophobicity can also increase scaling and
fouling resistance. Fouling occurs when particles or minerals deposited on the membrane surface or blocking pore mouth causing it to plug which might cause severe flux decline and diminish permeate quality [3].

Most of researchers employ polyvinylidene fluoride (PVDF) as polymer for fabrication of porous membrane because of its excellent properties such as high thermal stability, good chemical resistance and excellent membrane forming properties [4]. It also has outstanding morphological properties which enhance formation of highly porous film other than offering low surface energy (that helps to improve membrane hydrophobicity). Currently, PVDF membranes have been extensively used as material for MD, membrane bioreactor (MBR), oil/water separation and others.

Although PVDF offers a low surface energy, phase–inverted PVDF membranes fabricated using a strong non-solvent (i.e. water) usually have surface CA of less than 90°, and sometimes even below 70° [5]. The low CA is caused by the lack of surface structural features that enhance hydrophobicity. As reported by Peng et. al [6], surface hydrophobicity can be increased by introducing roughness (both micro- and nano-scales) to the membrane surface. Therefore, many attempts have been done to enhance PVDF membranes’ hydrophobicity, mostly by manipulating phase inversion parameters [7]. Application of strong non-solvent often results in “flattening effect.” A term to describe the movement of polymer on the top of the cast film due to distinct difference between surface (cast-film and air) and interfacial (cast-film and water) tensions, which forces the polymers molecules to move from the top of cast-film downwards into the bulk of film. The long-chain nature of polymer leads to formation of flat and smooth surface that lowers the surface CA [8].

Since PVDF is a semi-crystalline polymer, some degree of crystallization occurs during formation of membrane via phase inversion. Yet, it occurs at a very slow rate relative to the fast nature of liquid-liquid demixing. Earlier study identifies that degree of crystallization, PVDF crystalline structure and separation properties can be improved by manipulating both casting and coagulation conditions, in particular non-solvent type and its temperature [9]. The total of crystallinity and type of crystal structure are affected by temperature of coagulation bath [10], or by applying a weak non-solvent that slows down liquid-liquid demixing to facilitate crystallization.

This study focuses on utilizing crystallization behavior of PVDF film to develop PVDF membrane by manipulating the temperature of dope solution. We hypothesize that the crystalline structures help to improve hydrophobicity, too high crystallinity leads to pack/dense nature of the crystals arrangement in membrane matrix can depress the porosity. Therefore, an optimum degree of crystallinity and suitable crystalline phase are required. All prepared PVDF membranes were thoroughly characterized before their performances were tested using direct-contact MD (DCMD) by treating simulated seawater.

2. Methods

2.1 Membrane preparation

PVDF (molecular weight of 534 kDa by GPC, Sigma Aldrich), dimethylacetamide (DMAC, Sigma Aldrich) and deionized water was used as polymer solvent and non-solvent respectively to prepare the membrane via phase inversion [9]. Polymer solution was prepared by dissolving 17% w/w of PVDF into DMAC [11]. The mixtures were stirred and heated at different temperatures of 25, 40, 60, 80 and 100°C to form homogeneous dope solution. In order to ensure that the polymer was thoroughly dissolved, the solutions were stirred at least for 24 hours using electrical magnetic stirrer at 150 RPM before degassing for overnight to get rid air bubbles [9]. The dope solutions were maintained at required temperatures (25, 40, 60, 80 and 100°C) before casted on non-woven support (NWS, Novatexx 24413, Freudenberg-filter, Germany) using casting knife with a wet-casting thickness of 240μm. After casting, the cast films were immediately immersed in coagulation bath containing water as the non-solvent at 25°C. After 24 hours of immersion, the membranes were dried at room temperature.
2.2 Membrane characterization

The morphological structures of the developed membrane were observed using scanning electron microscopy (SEM, Quanta-250, FEI) to obtain microstructure images of cross section and surface of the membranes. To avoid effect of cutting on the membranes’ cross section structure, they were frozen in liquid nitrogen before cutting with blade. Samples were coated with gold and palladium at a thickness of 50 Å to avoid over charging. Contact angle goniometer was used to measure the CA of deionized water on the membrane using sessile drop of 7μL. Multiple measurements (at least 5) were taken at different locations of the membrane sample to ensure data accuracy. Degrees of crystallinity of the developed membranes were determined by using differential scanning calorimeter (DSC).

2.3 DCMD set-up

![Figure 1. Basic schematic diagram of DCMD.](image)

The performances of the resulting membranes were evaluated in a lab-scale DCMD set-up as shown in figure 1 [12]. Both feed and permeate were cycled through the membrane cell. Synthetic seawater (3.5 wt% NaCl) and deionized water were used for the feed and permeate respectively. The hot and cold fluids were pumped at equal and constant cross-flow velocity of 2.22 cm/s. The temperature of the feed was maintained at 65°C while the temperature of permeate side was set at 25°C. The flux was measured and calculated based on the permeate overflow using weighing balance.

3. Results and discussion

3.1. Morphological structure of PVDF membrane during phase inversion

The effect of dope solution temperatures on the membrane surface and cross section morphologies can be observed from first and second row of figure 2, respectively. Larger size of mouth pores formed at the top surface when the dope temperature is at 25°C, as shown clearly from the SEM images with 30k magnification in figure 2. When temperatures of the dope solutions are greater than 25°C (40, 60 and 80°C), the pore size shows insignificant difference. However, the surface of membrane fabricated at 100°C shows larger pore size but still smaller than 25°C.

From all top surface SEM images, the surfaces are quite smooth and flat. Since the surface of the cast films during immersion are exposed directly to the strong non-solvent (water), it caused flattening effect which reduces surface hydrophobicity [5]. The easy access of nonsolvent to the surface of the cast film also promotes faster liquid-liquid demixing which will produce highly porous membrane at the surface.
Figure 2. Top surface and cross-sectional morphologies of the resulting membranes with magnification of 30,000x. Images on the same row share the scales.

The morphological structure of the membranes’ cross section changes with an increase of dope solution temperature. In figure 2 (second row), it shows that there are no spherulite-like structures formed at dope temperature of 25°C. Large macrovoids are form just underneath the top layer supported by sponge-like structure. The spherulite-like structures only developed when the temperature of dope solution was increased above 25°C as seen from all cross-section images of all samples. The size of spherulite-like structure seems to increase when dope temperature increased up to 60°C and remains almost same beyond that value (at 80 and 100°C). The presence of spherulite-like structures perhaps is due to the formation of imperfect crystallization which is in line with obtained DSC curves. The cross-sectional images also demonstrate that crystallization may take place across the full thickness of membranes, but less so on the top membrane surface. The membrane wetting propensity for all membranes prepared using dope temperature above 25°C might be then reduced.

3.2. Membrane properties

Table 1 summarizes the properties of the developed membranes including CA of both top and bottom surfaces, thickness, porosity and total crystallinity that have been obtained from DSC testing. For CA, both sides show insignificant changes with the increment of dope solution temperatures. Although the values of CA obtained are quite low compared to previous studies [5], they are in good agreement with the top surface images obtained by SEM. This explains the occurrence of flattening effect which reduces the presence of surface structural features and hydrophobicity properties. Never the less, judging from the cross-section image a highly hydrophobic nature, similar to the bottom surface, is expected across the thickness of the membranes that prepared from high temperature dope solution. Membrane morphologies can also explain the trends in membrane thickness and porosity. As shown in table 1, both membrane thickness and porosity vary according to the temperatures of dope solution, most likely due to the formation of different type of crystalline phase.

PSD of the selected membranes synthesized from 25, 60 and 100°C dope solutions are illustrated in figure 3 with mean pore size (MPS) of 0.238, 0.138 and 0.099 μm and BP of 0.989, 0.139 and 0.153 μm respectively. Increasing dope solution temperature decreases the MPS and BP. This trend is most likely because of high temperature that accelerates exchange of solvent and nonsolvent by lowering cast solution viscosity. Quick liquid-liquid demixing then suppresses formation of large macrovoids resulting in thinner membrane (table 1). In addition, formation of different crystalline phases may also contribute to the variations of membrane pore size. It is worth noting that the narrow PSD, close value
between MPS and BP showed by membrane developed from 60°C dope solution promotes wetting resistibility, a property desirable for MD.

Membrane total crystallinity, $X_c$ have been calculated by integrating the DSC curves (figure 4) to determine the heat of fusion before comparing to melting enthalpy of 100% PVDF crystalline which is 104.7 J.g$^{-1}$. [13]. Based on table 1, total crystallinity of each membranes prepared from dope solution temperature above 25°C are almost the same (45.85-46.77%), and significantly lower than the one prepared from dope solution temperature of 25°C (51.93%). Above 25°C, increment of dope solution temperature does not give significant effect to total crystallinity of PVDF.

The DSC curves in figure 4 show that there are three obvious peaks at temperatures of 128, 159 and 165°C. The first peak indicates the melting of NWS while others correspond to melting of crystalline structures at different perfection. Membrane casted from 60°C dope solution consists more imperfect crystalline structures as compared to other samples, judging from more intense peak at 159°C, which may affect other membrane properties such as porosity, thickness and pores size [14, 15], and (as discuss later) mass transport resistance of the membrane.

### Table 1. Membrane properties.

| Dope solution temperature (°C) | Thickness (µm) | Porosity (%) | Total crystallinity, $X_c$ (%) | Contact Angles (°) | 
|-------------------------------|----------------|--------------|-----------------|------------------|
| 25                            | 333.00         | 45.85        | 51.93           | Top Surface 77.40, Bottom Surface 104.60 |
| 40                            | 280.40         | 45.37        | 46.77           | Top Surface 77.20, Bottom Surface 113.80 |
| 60                            | 250.20         | 40.68        | 44.77           | Top Surface 80.40, Bottom Surface 121.80 |
| 80                            | 265.80         | 47.87        | 45.85           | Top Surface 82.80, Bottom Surface 120.20 |
| 100                           | 276.00         | 50.71        | 46.77           | Top Surface 75.60, Bottom Surface 114.20 |

**Figure 3.** Pore size distribution (PSD) of membranes from dope solution temperature of 25, 60 and 100°C.

**Figure 4.** Differential scanning calorimeter (DSC) curves of samples casted at different temperature dope solution.

### 3.3. MD performance

The presence of more imperfect crystalline structures in membrane matrix improves MD performance when top facing feed membrane orientation is applied. From DCMD results in figure 5, it seems that transportation of water vapor from feed to the permeate sides improved due to the decrease of membrane pore’s tortuosity factor, as results of low crystallinity coupled with imperfect crystalline
shape. The decrement of tortuosity factor perhaps is due to formation of different crystalline phase. As shown in figure 5a, the flux is at its maximum (10.8 L/m²h) for membrane prepared from dope solution of 60°C. The flux obtained is considerably high with the operating temperatures between 65°C and 25°C for the feed and permeate sides, respectively. The low flux obtained by 25°C dope solution membrane may be attributed to the partial pore wetting. The wetted pores block the transport of water vapor from feed side hence reduces the obtained flux due to less available pores. After certain times, when the pores are totally wet, salt bridging will take place which then will reduce salt rejection. The percentage of salt rejection has been summarized in figure 5b and it shows that the membrane casted from 25°C dope solution has the lowest rejection while others are almost the same. Pore wetting also promotes low gradient of temperature that lowers the MD driving forces because the liquid penetrating the pore is static without mixing from the cross-flow velocity.

![Figure 5. a) Flux performance b) Percentage of salt rejection of the resulting membrane when top facing feed configuration was used.](image)

4. Conclusion
Manipulating temperature of dope solution was found effective to increase flux but not the hydrophobicity of membrane top surface. Higher temperature of dope solution (> 25°C) defects crystalline structure which contributes to different crystal structures. Formation of crystalline structures in the membrane matrix (to certain extent) affect the tortuosity factor and improves the mass transfer across the membrane from feed to permeate sides which results to higher flux performance. It is recommended to use a weaker non-solvent instead of water (strong non-solvent) to improve the surface hydrophobicity without reducing the flux performance.

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