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Preparation and characterization of PVDF membranes incorporated with different additives for dyeing solution treatment using membrane distillation

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ABSTRACT

In this work, the properties of pristine polyvinylidene fluoride (PVDF) hollow fiber membranes were altered by incorporating different types of additives, that is, ethylene glycol (EG) and polyvinylpyrrolidone (PVP) into dope solution. Prior to the separation process, the resulting membranes were first characterized with respect to structural morphology, hydrophobicity, overall porosity, gas permeability, wetting pressure, mechanical, and thermal stability. It is found that PVP has major impact on the membrane structural properties due to the PVP residue in the membrane matrix. The PVP has transformed the PVDF membrane into hydrophilic ones, while EG did not negatively affect the hydrophobicity of the PVDF membrane. During direct contact membrane distillation process, it is reported that both membranes were able to achieve at least 99% rejection of reactive black 5 when tested under counter-current flow condition. Compared to the PVDF–PVP membrane, the experimental results showed that the PVDF–EG membrane demonstrated greater stabilities of flux and rejection during 5 h study period, mainly due to its greater hydrophobicity and higher wetting pressure which play a role in preventing the liquids from both sides penetrating through membrane pores and further minimizing membrane fouling.

Keywords: Direct contact membrane distillation; Polyvinylidene fluoride; Ethylene glycol; Polyvinylpyrrolidone; Reactive black 5

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1. Introduction

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer containing a crystalline phase and an amorphous and/or rubbery phase which can be represented by a complex structure with five possible crystalline phases [1–3]. It is one of the most commonly used polymers in membrane distillation (MD) due to its unique advantages such as low melting point, high chemical resistance, good thermal stability, and low surface energy [4–8]. Compared to other hydrophobic materials such as polytetrafluoroethylene (PTFE) and polypropylene (PP) membranes, PVDF membranes can be fabricated without going through stretching and sintering processes and can be easily dissolved in

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many organic solvents, for example, N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, dimethylsulfoxide. In 2011, Liu et al. [9] has comprehensively reviewed the current progress on the production and modification of PVDF membranes for liquid–liquid or liquid–solid separation. This article summarized various PVDF modification methods which are useful for different industrial applications. Typically, PVDF membrane is transformed into hydrophilic membrane for pressure-driven membrane processes by introducing non-solvent additives or inorganic fillers into the membrane matrix [10–14]. However, in MD process, PVDF membrane is modified to enhance its hydrophobicity so that a lower value of surface energy can be obtained to prevent liquid solution penetration at the membrane pores [8,13,15–18].

Conventionally, porous hydrophobic MD membranes are produced mainly in two ways. One is using hydrophobic materials; the other is transforming hydrophilic membrane into a membrane having hydrophobic properties [6]. Various methods, such as polymer nanofibers [19–21], thermally induced phase separation [22], and non-solvent-induced phase separation [4,5,17,23,24] have been reported in the literature for the preparation of hydrophobic MD membranes. Of these, many researchers preferred to prepare membrane using a simple blending process [5,8,16,23–27]. Normally, the degree of hydrophobicity is measured based on water contact angle in which the higher the water contact angle value the greater the hydrophobicity of the membrane and vice versa. However, it is found that hydrophobic MD membranes are always associated with pore-wetting and fouling problems, especially when operated at higher feed temperature. Previous studies show that PTFE and PP membranes experienced structural changes in their microporous structure upon significant temperature changes which futher led to pore-wetting problem [28,29]. Ge et al. [30] on the other hand found that the water contact angle of PVDF membrane decreased with increasing water (feed) temperature and explained that the membrane wetting was caused by the temperature dependence of the membrane properties. With respect to membrane fouling, Gryta [31] stated that feed temperature is the most influential factor for the membrane fouling because high feed temperature tends to cause more volatile compounds to evaporate and diffuse through the membrane as well as increase the solute concentration on the interface between the feed and membrane phase. It is also elucidated that foulants could be attracted to the surface layer of the membrane due to the hydrophobic and electrostatic interaction between organic materials in the feed water and membrane surface.

As simple blending method is the common technique employed by many researchers to improve their MD performances, the effects of different types of additives (mainly for membrane porosity enhancement) have been explored in this field. Over the past several years, ethylene glycol (EG) is reported as the preferable additive for MD membrane preparation, mainly because of its ability to induce pore formation and produce a thin skin layer during phase inversion process [8,16,23,25,32]. Compatibility of EG in the dope solution is not a main concern as EG can be easily miscible with dope solution containing both NMP (solvent) and water (non-solvent) [23]. It has been previously reported that PVDF membrane blended with EG exhibited much better performances than that of neat PVDF membrane in the desalination process, mainly due to its highly porous structure [25]. Compared with EG additive, another well-known pore-forming agent, that is, polyvinylpyrrolidone (PVP) is scarcely reported in the MD process, although this type of additive is widely used in other membrane applications, in particular ultrafiltration to improve membrane properties by increasing porosity and hydrophilicity [33–36]. Since PVP is hydrophilic in nature, it is rarely used in MD process which typically requires the membrane with hydrophobic characteristics. Till now, only several articles have reported on the use of PVP additive in MD process of desalination [37–39].

In this work, an attempt was made to prepare PVDF membranes incorporated with two different hydrophilic additives, that is, EG and PVP for the MD process of dyeing wastewater application. To the best of our knowledge, no study has been conducted by using PVDF membrane in treating dyeing solution in MD field. A literature search revealed that only commercial membranes made of PP polymer were ever studied for the separation and purification of solution containing dye compounds using MD process [40–43]. Therefore, this paper will study the effect of the hydrophilic additives on the PVDF membrane properties with respect to structural morphology, hydrophobicity, gas permeability, wetting pressure, mechanical, and thermal stability. Performance of membranes during direct contact membrane distillation (DCMD) process will be evaluated using dyeing solution containing 0.5 g/L reactive black 5 (RB5).

2. Experimental

2.1. Materials

Commercial PVDF polymer (Kynar® 760, MW = 440,000 g/mol) was purchased from Arkema

Inc., Philadelphia, USA, in the form of pellets. N-methyl-2-pyrrolidone (NMP, 99.5%) was used as solvent without further purification. Ethylene glycol (EG, MW = 62.07 g/mol) (Merck) and polyvinylpyrrolidone (PVP, MW = 40,000 g/mol) (Sigma-Aldrich) were used as additives in the polymer solution. Reactive black 5 (RB5, MW = 991 g/mol) from Sigma-Aldrich was used to prepare dyeing solution by dissolving it in DI water.

2.2. Fabrication of PVDF hollow fiber membranes with different additives

Prior to dope preparation, PVDF pellets and PVP powder were first dried in vacuum oven at 60˚C overnight to remove moisture. Afterward, 18 wt% PVDF pellets were dissolved in NMP solvent under stirring rate of 350 rpm and at temperature of 40˚C. After 30 min of stirring, the stirring rate and temperature were increased to 550 rpm and 60˚C, respectively. Six wt% additive (EG or PVP) was started to add slowly into the dope solution once PVDF was completely dissolved in the solvent. The solution was left to cool down to room temperature after a permanent homogeneous dope solution was obtained. The resultant membranes prepared were then denoted as PVDF–EG and PVDF–PVP membrane, respectively. A pristine PVDF membrane (control) was also prepared in this work from the dope solution containing no additive and was referred as PVDF-*p*. The viscosity of the dope solutions was measured at the constant temperature of 25˚C using a basic viscometer (Model: EW-98965–40, Cole Parmer). The viscosity measurements were carried out by driving a spindle (which is immersed in the test fluid) through a calibrated spring. The viscous drag of the fluid against the spindle was measured by the spring deflection, which was measured by a rotary transducer. All dope solutions were measured using same spindle, that is, L4 which was suitable for high viscosity samples. Using the solutions prepared, the modified and unmodified PVDF membranes were fabricated using dry-jet wet spinning method as described elsewhere [44]. After completing the spinning process, the as-spun fibers were soaked in a water bath for at least 24 h to remove residual solvent and additive from the membrane matrix. At last, the membranes were post-treated with pure ethanol before drying at room temperature. The detailed spinning conditions are given in Table 1.

2.3. Liquid entry pressure and contact angle measurement

To perform liquid entry pressure (LEP) analysis, a test module (0.22 m long) filled with DI water was required in which one unit of hollow fiber membrane was attached at the bottom of the test module, while the other end was connected to a diaphragm pump. The water was then pressurized slowly into the lumen side of the fiber at 0.5 bar interval. At each pressure interval, the membrane module was kept at the constant pressure for 10 min to check if any water has permeated through the outer layer of dry membrane. At least three measurements were performed to yield the membrane LEP. To evaluate the degree of membrane hydrophobicity, a contact angle goniometer (OCA15plus, DataPhysics), equipped with image-processing software, was used. A technique called sessile drop was used to measure the contact angle of the outer surface of the fibers. Fifteen contact angle measurements were performed at various positions on the same sample to yield average result.

2.4. Gas permeation measurement

The membrane with known effective length was first potted into a fitter before putting the membrane

Table 1
The detailed spinning conditions for preparing PVDF hollow fiber membranes

Spinning conditions	PVDF-*p*	PVDF-EG	PVDF-PVP
Dope solution composition (wt%)	PVDF/NMP (18/82)	PVDF/NMP/EG (18/76/6)	PVDF/NMP/PVP (18/76/6)
Dope viscosity (mPa s)	9588	14457	19517
Bore fluid composition	Tap water		
Bore fluid flow rate (mL/min)	1.8		
Dope extrusion rate (mL/min)	3.6		
External coagulant	Tap water		
Air gap distance (cm)	10		
Spinneret O.D./I.D. (mm/mm)	1.30/0.55		
Spinning dope temperature (˚C)	25		
External coagulation temperature (˚C)	25		

sample into module. Nitrogen gas was used during gas permeation test to measure gas permeance, mean pore size, and membrane effective porosity. The gas pressure was varied starting from small magnitude until certain pressure. Usually, the upstream pressure is in the range of 0.5–4 bar for a porous membrane. The measurement is based on the volume displacement method by using a burette to measure the collected air bubble volume in predetermined time. Based on the common gas permeation method by Wang et al. [45] gas permeance, J_G, for porous membrane can be expressed as:

$$J_G = \frac{2r_p\varepsilon}{3RTL_p}\left(\frac{8RT}{\pi m}\right)^{0.5} + \frac{r_p^2\varepsilon}{8\mu RTL_p}\overline{P} = K_0 + P_0\overline{P} \tag{1}$$

where J_G is the gas permeance (mol/m^2 s Pa), r_p and L_p are pore radius and effective pore length, respectively (m), ε is surface porosity, R is gas constant (8.314 J/mol K), μ is gas viscosity (kg/m s), M is gas molecular weight (0.028 kg/mol N_2), T is gas temperature (K), and $\overline{P}$ is mean pressure (Pa). By plotting J_G with mean pressures according to Eq. (1), mean pore size and effective porosity over pore length, ε/L_p can be calculated from the intercept (K_0) and slope (P_0) as follows:

$$r_p = 5.333\left(\frac{P_0}{K_0}\right)\left(\frac{8RT}{\pi M}\right)^{0.5}\mu \tag{2}$$

$$\frac{\varepsilon}{L_p} = \frac{8\mu RTP_0}{r_p^2} \tag{3}$$

2.5. Membrane overall porosity

According to Chabot et al. [46], the overall porosity of the hollow fiber membrane, ε(%) which is defined as the volume of the pores per the total volume of the porous membrane can be determined by the following equation:

$$\varepsilon = \frac{\frac{(w_{\text{wet}} - w_{\text{dry}})}{\rho_w}}{\frac{(w_{\text{wet}} - w_{\text{dry}})}{\rho_w} + \frac{w_{\text{dry}}}{\rho_p}} \times 100 \tag{4}$$

where w_{wet} is the weight of wet membrane (g), w_{dry} is the weight of dry membrane (g), ρ_p is the density of the polymer (g/cm^3), and ρ_w is the density of water (g/cm^3).

2.6. Field-emission scanning electron microscopy (FESEM) analysis

The dry hollow fiber samples were immersed in liquid nitrogen and fractured, followed by sputter-coating with platinum using a sputtering device (JFC-1100E, JEOL). The membrane cross sections of the membrane samples were examined using FESEM (JSM-6700, JEOL).

2.7. Tensile test

To study the mechanical strength of the fibers, tensile test was performed according to ASTM D3039 standard using an LRX 2.5 SKN Llyod Instrument. The gauge length and width of dumbbell tensile specimens were 50 and 4 mm, respectively. The fiber sample was clamped at both ends and pulled in tension at elongation rate of 10 mm/min. At least five measurements of the tensile strength were recorded to yield the average result.

2.8. Thermogravimetric analysis

Thermogravimetric analysis was performed on a thermogravimetric analyzer (TGA, Mettler Toledo TGA/SDTA851e) under nitrogen flow at a heating rate of 10℃/min. The weight loss of membranes was monitored over temperature ranging from 30 to 800℃.

2.9. DCMD experiments

DCMD experiments were conducted using a stainless steel membrane module consisted of twenty hollow fiber membranes with an effective length of 0.19 m. The module which coated with fiber glass (to minimize heat loss) had an effective membrane area of approximately 0.0137 m^2. As illustrated in Fig. 1, the DCMD system was designed to have two circulating streams, that is, hot stream was fed through the lumen side of hollow fiber membrane, while cold stream was circulated through membrane shell-side in counter-current flow. Both streams were controlled at 60 and 20℃ using coiled heater (830, PROTECH) and chiller (F26-ED, JULABO), respectively.

Prior to the dyeing solution treatment process, the permeate flux, J, of membrane (kg/m^2 h) was determined using Eq. (5).

$$J = \frac{\Delta W}{A\Delta t} \tag{5}$$

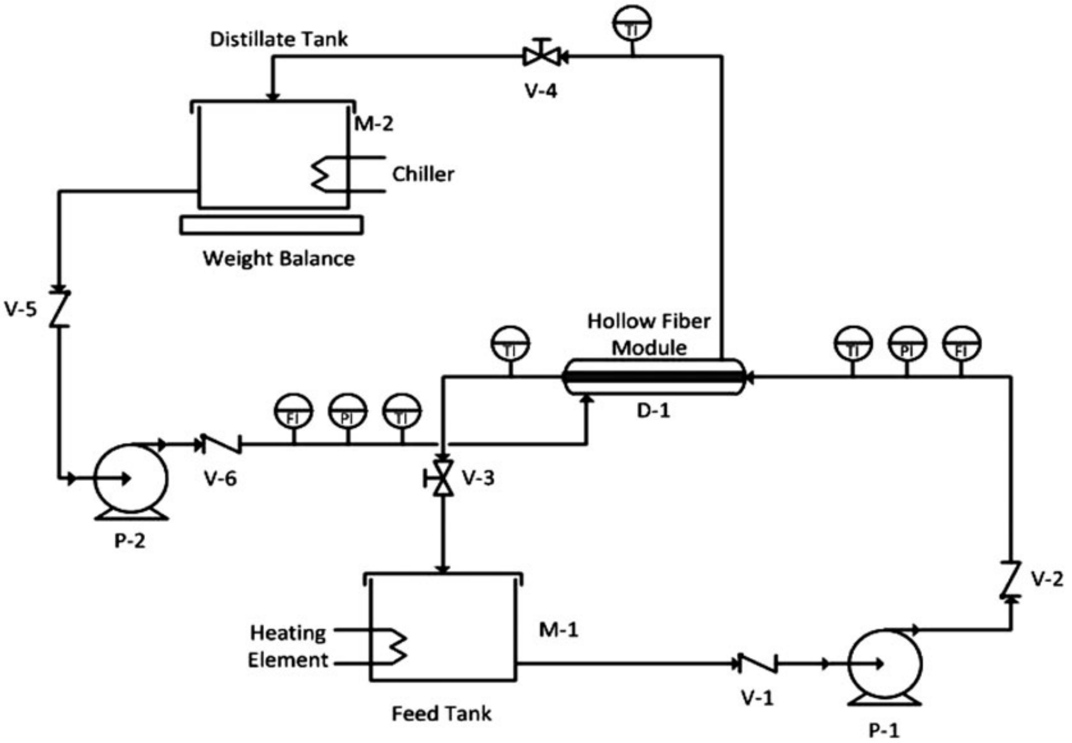

Fig. 1. Schematic diagram of lab-scale DCMD system.

where ΔW (kg) is the weight of permeate collected over a predetermined time Δt (h) of process and A (m^2) is the effective membrane area. Same equation was used to calculate the water flux of dyeing solution which contained 0.5 g/L RB5. To determine dye rejection, R, of the membrane, Eq. (6) was employed.

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100 \tag{6}$$

where C_p and C_f are the RB5 concentration (g/L) in the bulk permeate and feed solution, respectively. The concentration of the RB5 in the sample solutions was detected by a UV–vis spectrophotometer (DR5000, Hach) with absorbance measured at 597 nm which the maximum absorption occurs. For the fouling study, the DCMD experiments were carried out continuously for up to 5 h under same operating conditions. The permeate fluxes and dye rejection were recorded to observe change in the membrane performance as a function of time. Additional fouling characterization was also performed using Educational Stereo Microscope (EZ4HD, Leica Microsystems) to physically examine the change on membrane inner and outer surface after treatment process.

3. Results and discussion

3.1. Morphology of the PVDF hollow fiber membranes

Porous PVDF hollow fiber membranes were prepared via a dry-jet wet spinning process. Two types of hydrophilic additives were introduced into the PVDF spinning dope to alter the properties of the PVDF membranes for MD application. Fig. 2 shows the FE-SEM micrographs of the cross-sectional morphology of the prepared PVDF-*p*, PVDF-EG, and PVDF–PVP membranes. As can be seen, finger-like structure was developed at the outer skin layer and inner layer of each membrane. For PVDF–EG membrane, the finger-like structure is quite similar with the pristine PVDF membrane. Both membranes showed thinner and longer finger-like structure than that of PVDF–PVP membrane at the cross section of outer layer. Although these three membranes have a combination of sponge-like substructure and macrovoids at the middle of the membranes, the PVDF–EG membrane is found to have the thickest sponge layer followed by PVDF-*p* and PVDF–PVP membrane. The significant reduction on the intermediate sponge layer thickness on the PVDF–PVP membrane is mainly due to the expansion of macrovoids from the inner layer of that membrane. This phenomenon can be related to the

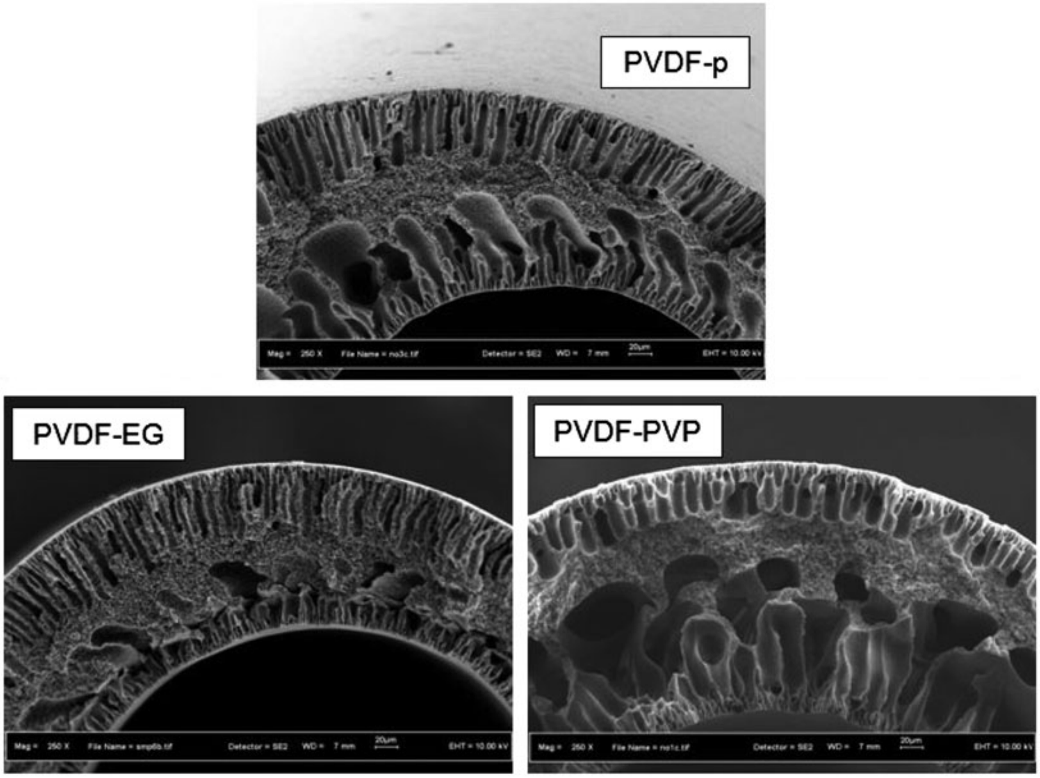

Fig. 2. FESEM images of PVDF hollow fiber membranes with and without additive incorporation.

characteristics of the additives added into the PVDF dope solution. As reported in the previous study [37], the addition of PVP in dope solution could induce big-cavities formation as well as development of finger-like structures in PVDF membrane. Compared with EG additive, it is observed that the pore-forming effect of PVP was more pronounced, mainly caused by the easier immigration of PVP towards the membrane surface, leading to faster solvent and non-solvent diffusion into the internal of the membrane. Besides, the enlargement of macrovoids in the PVDF–PVP membrane can be initiated by non-homogeneous demixing on the lumen side of the hollow fiber membrane, which is favored by dynamic fluctuation caused by the rapid exchange between the solvent and non-solvent [33,35,37], although the viscosity of the PVDF/PVP dope was the highest among the three dopes prepared (see Table 1). Han and Nam [35] stated that there are two factors contributing to the macropore formation by the addition of PVP, first is a thermodynamic instability and the second one is a rheological barrier. In our case, because of the thermodynamic immiscibility is more significant than the kinetic effect of the high viscosity, it is preferable that PVP would act as a demixing enhancer to increase the phase separation rate and induce bigger macrovoids. Furthermore, it is also experienced that the PVDF–PVP membrane possessed the thickest membrane overall thickness in comparison with the PVDF-*p* and PVDF–EG membranes which might give it the advantage of minimizing heat losses due to conduction during MD process [6].

3.2. Characteristics of the PVDF hollow fiber membranes

Table 2 summarizes the important properties of the PVDF membranes prepared in this work. As can be seen, PVDF–PVP membrane has the highest overall porosity among the membranes studied, and this can be attributed to the large macrovoids formed in the membrane structure as observed from FESEM image. Wang et al. [23] also reported that larger macrovoids and sponge-like pore network could significantly improve membrane porosity, leading to better molecular diffusion and higher flux. According to Adnan et al. [47], membrane porosity is the main influencing factor in MD process compared to membrane pore size and membrane thickness. Therefore, highly porous membrane is preferable to decrease resistance of vapor molecules diffusing to the permeate side during MD process.

Table 2
Characteristics of PVDF hollow fiber membranes

Membrane	PVDF-*p*	PVDF-EG	PVDF-PVP
Membrane overall porosity (%)	70.77	73.18	83.31
Contact angle (°)	92	87	68
LEP (bar)	5.5	2.5	2.0
N_2 permeance at 1 bar (10^{-3} cm^3/cm^2 s cm Hg)	7.87	44.28	0.12
Mean pore radius (μm)	0.09	0.15	0.17
Effective surface porosity, ε/L_p (m^{-1})	192.05	567.18	1.22
Tensile strength (MPa)	1.15	1.54	1.12
Hollow fiber I.D. (μm)	581 ± 52	467 ± 16	445 ± 6
Hollow fiber O.D. (μm)	903 ± 12	751 ± 17	889 ± 12
Fiber wall thickness (μm)	165 ± 50	140 ± 12	221 ± 3

With respect to contact angle, it is reported that PVDF–PVP membrane displayed the lowest contact angle value (68°) followed by PVDF–EG (87°) and PVDF-*p* membrane (92°). The results indicated that PVP has stronger influence than EG in reducing the hydrophobicity of the PVDF membrane, possibly caused by the covalent hydrogen bonding between the PVDF and PVP component as explained in previous works [48–50]. Similar to PVP additive, EG is also hydrophilic in nature, but its low molecular weight has made it relatively easier to leach out from membrane matrix during fabrication process, thus has minimal impact on membrane hydrophobicity. Because of this, EG is one of the widely used pore formers in preparing membrane for MD process [8,16,23,25,32,51].

Even though the PVDF–PVP membrane is hydrophilic, its wetting pressure is still comparable with the PVDF–EG membrane. Both membranes displayed LEP value of at least 2 bar which is considered good enough for MD process which generally requires 1 bar or less to operate, although PVDF-*p* membrane gave the highest LEP value among three studied membranes. In general, the narrow and fine finger-like structure at the inner layer of membranes are able to prevent water molecules from penetrating through membrane pores and permeate at the outer side. The sponge-like structure formed at the middle of the membrane structure on the other hand could play a role retaining water from entering the membrane pores (outer layer) as elucidated by Naim et al. [52]. It is worth to note that each membrane has mean pore size less than 0.5 μm which is the suitable pore size to avoid severe pore-wetting problem [53].

3.3. Thermal and mechanical stability study

Fig. 3 shows the TGA profiles for the fabricated membranes. It is shown that PVDF–PVP membrane demonstrated two significant weight loss regimes in comparison with single weight loss regime found in PVDF-*p* and PVDF–EG membranes. For PVDF–PVP membrane, the first weight loss was observed in the temperature range of 100–200˚C with 21.7% weight reduction recorded, and this result could be attributed to the loss of water due to the extremely hygroscopic nature of PVP polymer coupled with low polymer glass transition temperature [54,55]. The second weight loss of the PVDF–PVP membrane which happened at 420–440˚C was similar to the first weight loss of the PVDF-*p* and PVDF–EG membrane. The relatively low thermal stability of the PVDF–PVP membrane at temperature between 100 and 200˚C indicated that this membrane type might not be suitable for non-isothermal membrane process in long run.

With respect to mechanical properties, it can be seen from Table 2 that PVDF–EG membrane exhibited

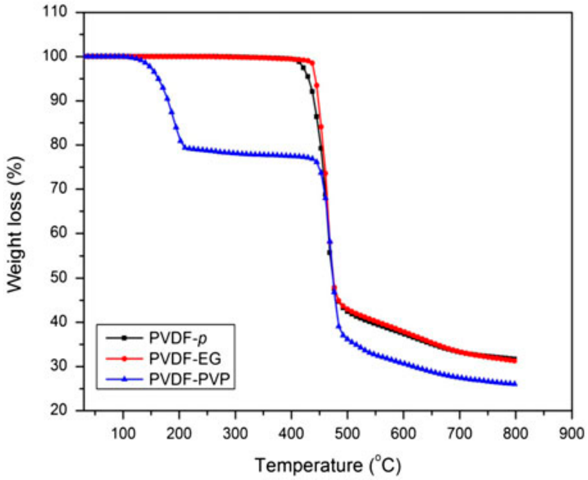

Fig. 3. TGA curves for PVDF-EG and PVDF-PVP membranes.

the highest mechanical strength among the membranes studied. The order of the tensile strength showed clear connection to the membrane morphology (i.e. size and quantity of macrovoids). Table 2 also shows that even though both PVDF-*p* and PVDF–PVP membranes possessed thicker fiber wall in comparison with PVDF–EG membrane, their mechanical strengths were not improved accordingly. This is mainly due to the formation of significant amount of macrovoids in PVDF-*p* and PVDF–PVP membranes which negatively affected the membrane mechanical properties [33,37].

3.4. Pure water vapor flux of membranes

Fig. 4 shows the pure water vapor flux of the PVDF membrane blended with different additives during DCMD process. Membrane pure water vapor flux was increased in the following order: PVDF-*p* > PVDF–EG > PVDF–PVP. The average pure water vapor flux achieved by PVDF–PVP and PVDF–EG membrane is about 4.45 and 3.92 kg/m^2 h, respectively. Compared to the PVDF-*p* membrane, the enhancement in the pure water vapor flux of the modified PVDF membranes are attributed to the increase in overall porosity and mean pore size. As rapid flux increment of the PVDF–PVP membrane was observed after 1 h of the operation, it is expected that this experimental result could be related to the partial pore-wetting problem since the water contact angle of this membrane is the lowest among the membranes prepared. Usually, partial pore wetting is likely to reduce flux, but in this case, the permeate flux of the PVDF–PVP membrane is reported to increase with operation time. This can be possibly caused by the water leakage in the permeate side. As PVDF–PVP membrane has the lowest wetting pressure, the tendency for this membrane to have leaking problem is relatively higher.

3.5. Separation performance of PVDF membranes in the treatment of dyeing solution

The performances of the PVDF hollow fiber membranes blended with different types of additives were further evaluated in the DCMD system for the treatment of dyeing solution containing 0.5 g/L RB5. Fig. 5 shows that the permeate fluxes of PVDF–EG membrane were always higher than PVDF–PVP membrane, except for the first hour of MD operation. At the end of the experiments, the water flux of PVDF–EG membrane was recorded at 9.88 kg/m^{2}h in comparison with 7.84 kg/m^{2}h achieved by PVDF–PVP membrane. The steady fluxes achieved by PVDF–EG membrane can be attributed to the hydrophobic property of that membrane that acts as a physical barrier preventing liquid penetration from both feed and permeate solutions into the membrane pores. Furthermore, the higher wetting pressure coupled with smaller pore size as shown by PVDF–EG membrane are also found to be important criteria to ensure the consistent water permeability of the membrane.

By comparing the results shown in Figs. 4 and 5, it is found that membrane flux data of dyeing solution was much higher than that of pure water, even

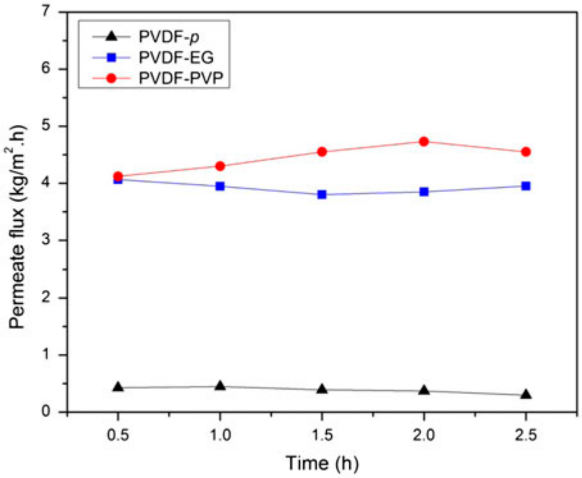

Fig. 4. Permeate fluxes of pure water vapor flux as a function of time. (Operating conditions: temperature of hot stream/cold stream: 60°C/20°C and cross-flow velocity of hot stream/cold stream: 0.016 m/s/0.01 m/s).

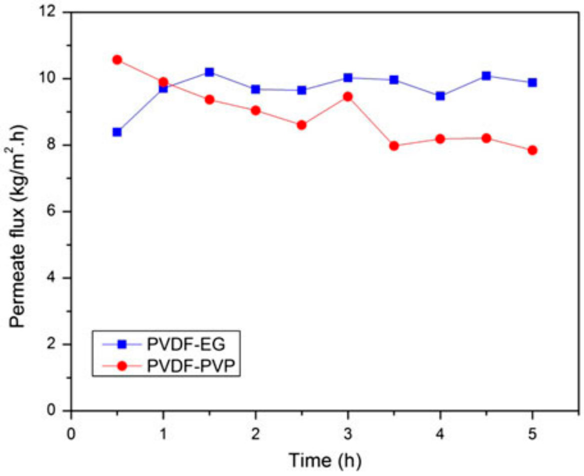

Fig. 5. Permeate fluxes of PVDF hollow fiber membranes as a function of operation time. (Operating conditions: temperature of hot stream/cold stream: 60°C/20°C and cross-flow velocity of hot stream/cold stream: 0.016 m/s/0.01 m/s).

though both were operated under similar conditions. In view of this, it is suspected that the higher flux obtained for the dyeing solution is most likely due to the complex reaction between the polymer and dyeing solution at hot condition. Criscuoli et al. [42] in their research work also experienced similar flux enhancement and explained that it is due to the interaction between membrane (made of PP polymer) and dyeing solution as well as membrane swelling effect. However, it is less likely that the PVDF membrane prepared in this work tended to swell easily with hot dyeing solution as PVDF membrane is well-recognized as a highly chemical resistant polymer to a hazardous feed solution and has a good thermal resistance.

In addition, different positions of flux curves of PVDF–PVP and PVDF–EG membrane could be observed by comparing the results shown in Figs. 4 and 5. For Fig. 4, the higher flux of PVDF–PVP membrane than PVDF–EG membrane can be attributed to the serious pore-wetting problem in PVDF–PVP membrane which leads to leaking problem and higher permeate flux obtained. On the contrary, the permeate fluxes of PVDF–PVP membrane was reported to be lower in comparison with the PVDF–EG membrane during MD process of dyeing solution and tended to decrease gradually with time (see Fig. 5). This phenomenon can be due to the more severe fouling problem occurred in the PVDF–PVP membrane, resulting in the formation of deposit layer in the inner surface of that membrane and blocking the water vapor from entering membrane pores [56,57]. This, as a consequence, leads to a lower permeate flux as evidenced in this work.

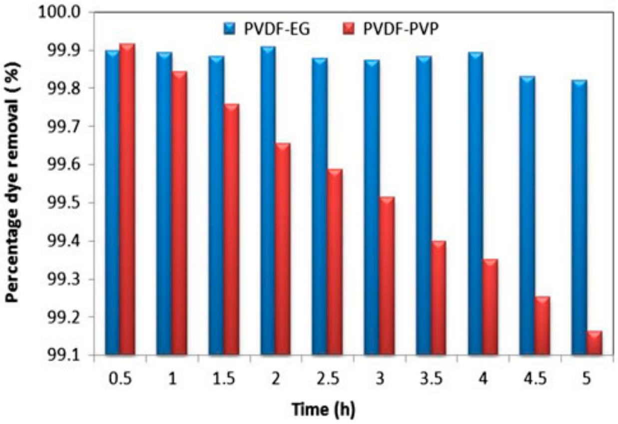

Fig. 6. Separation efficiency of PVDF hollow fiber membranes vs. operation time.

It must be pointed out that membrane fouling used to be a main concern to MD process when high concentration of dye component is used in the feed and the membrane is tested under prolonged period. As shown in Fig. 6, PVDF–EG membrane demonstrated consistent separation efficiency with average dye rejection of 99.88%. Meanwhile, the rejection of PVDF–PVP

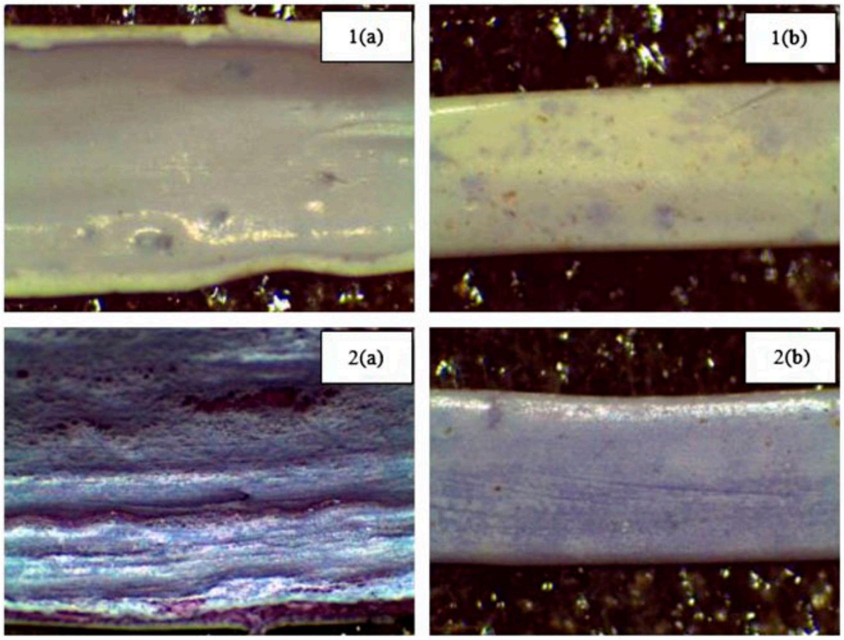

Fig. 7. Stereoscopic images of (1) PVDF-EG and (2) PVDF-PVP membrane after MD tests, (a) at the inner layer and (b) at the outer layer.

Table 3
Comparison of the average permeate flux obtained in this study with the literature for PVDF hollow fiber membranes blended with different types of additives

PVDF concentration (wt%)	Additives	MD configuration	Feed	Permeate flux (kg/m^{2}h)	Feed inlet temperature (°C)	Permeate inlet temperature (°C)	Solute rejection (%)	Reference
20	PVP, H_2O	VMD	Seawater	10.3	50	–	99.98	[37]
18	PVP, H_2O	DCMD	Distilled water	7	50	25	–	[38]
18	PVP, H_2O	VMD	Distilled water	22	50	–	–	[38]
15	PVP, AMAL	DCMD	Distilled water	8	50	25	–	[38]
15	PVP, AMAL	VMD	Distilled water	42	50	–	–	[38]
18	PVP, H_2O	VMD	Seawater	16	50	–	99.99	[39]
15	PVP, H_2O	VMD	Seawater	20	50	–	99.98	[39]
18	LiCl, H_2O	VMD	1,1,1-Trichloroethane	0.006	50	–	85	[58]
12	LiCl, PEG	DCMD	Desalination	20	60	20	99.99	[17]
17	PEG, LiCl	DCMD	Salt solution	10	65	20.3	99.99	[26]
17	PEG, LiCl	VMD	Salt solution	13	65	–	99.99	[26]
12	EG	DCMD	Desalination	20	60	17.5	99.99	[25]
15	EG	DCMD	Desalination	19	60	17.5	99.8	[32]
18	EG	DCMD	Dye solution	9.71 ± 0.49	60	20	99.88 ± 0.03	This study
18	PVP	DCMD	Dye solution	8.92 ± 0.86	60	20	99.54 ± 0.24	This study

Note: AMAL = maleic anhydride, PEG = polyethylene glycol, LiCl = lithium chloride.

membrane decreased gradually from initial 99.91% to 99.16% at the end of the experiment. The slight reduction of dye rejection in PVDF–PVP membrane could be related to the pore wetting and fouling occurred in this membrane. Fig. 7 compares the inner and outer layer of both PVDF–PVP and PVDF–EG membranes after being used for dyeing treatment process. Obviously, the inner and outer layer of the PVDF–PVP membrane was severely stained with dye components in comparison with the marginal change on the whitish color of the PVDF–EG membrane. The direct observation on the physical color of the membranes has confirmed the penetration of dye molecules from the lumen side of the PVDF–PVP membrane toward to outer layer.

Table 3 compares the performances of the MD reported in this work with other MD processes documented in the literature. It can be observed that the flux of the MD obtained in this study is comparable with the findings of some previous reports. Usually, most of the MD technical papers focused on the water desalination process with little attention paid on the wastewater treatment application. To the best of our knowledge, the use of PVDF membranes modified by PVP and EG was first reported for the dye separation in MD process. Although some researchers reported much higher membrane water flux than our reported data, one must realize that there are several important factors contributing to the variation in water flux during MD process. These include (a) lower PVDF concentration used in membrane preparation, (b) different MD configuration in which vacuum membrane distillation (VMD) in general shows higher flux than that in DCMD mainly due to the higher mass transfer coefficient in VMD configuration, and (c) different properties of feed solution.

Table 4 compares the performance of the DCMD process studied in this work with the previously published works for the treatment of dyeing solutions. As can be seen, the water flux of the PVDF membrane prepared in this work is much higher than those of the previous studies, except for the study conducted by Criscuoli et al. [42]. Although other factors such as MD configuration, operating temperatures, and feed properties might also affect the MD performance, in addition to the membrane property itself, the results shown in this work have revealed that the performance of the self-made PVDF membrane is comparable or better than the commercial PP membranes for textile wastewater treatment process. The attempt of

Table 4
Comparison of the maximum flux obtained in this study with the literature in the MD process for textile wastewater treatment

Membrane material	Membrane configuration	[a]MD configuration	[b]Dye (concentration)	Permeate flux (kg/m^2/h)	[c]T_f (in) (℃)	[d]T_c (in) (℃)	Rejection (%)	References
PP (commercial membrane module)	Hollow fiber	DCMD	Blue E-G (5 g/L)	1.62	50	35	100	[40]
PP (Enka Microdyn, USA)	Capillary	VMD	MB (0.0185 g/L)	6.3	70	N/A	100	[41]
PP (Membrana GmbH, Germany)	Capillary	VMD	Blue R (0.05 g/L)	57	60	N/A	> 90	[42]
PP (Membrana GmbH, Germany)	Capillary	Hybrid photocatalysis-DCMD	AR18 (0.03 g/L)	3.5×10^{-3}	65	20	100	[43]
PVDF/EG (fabricated)	Hollow fiber	DCMD	RB5 (0.5 g/L)	9.71 ± 0.49	60	20	99.88 ± 0.03	This study
PVDF/PVP (fabricated)	Hollow fiber	DCMD	RB5 (0.5 g/L)	8.92 ± 0.86	60	20	99.54 ± 0.24	This study

[a] DCMD = direct contact membrane distillation and VMD = Vacuum membrane distillation.

[b] Blue E-G = 1,200 g/mol, MB (methylene blue) = 373.9 g/mol, Blue R (Remazol brilliant blue R) = 626.54 g/mol and AR18 (Acid red 18) = 375.4 g/mol.

[c] $T_{f(\mathrm{in})}$ = Feed inlet temperature.

[d] $T_{c(\mathrm{in})}$ = Permeate inlet temperature.

using MD for treating dyeing solution is to take the advantage of the hot effluent discharged from the textile industry (80–90˚C), minimizing the energy required for MD operation and further offering a novel strategy to treat textile effluent economically.

4. Conclusions

This work demonstrated the ability of PVDF–EG and PVDF–PVP hollow fiber membranes in treating RB5 via DCMD process. It is found that the membrane blended with additive has a greater overall porosity and mean pore size than a pristine PVDF membrane. However, in comparison with EG, the PVP effect on the properties of the PVDF membrane is more pronounced, leading to the decrease in membrane hydrophobicity, big-cavities formation, low thermal stability, and mechanical strength which contribute to the variation in MD performance.

During DCMD experiments, high and consistent permeate flux (9.71 ± 0.49 kg/m^2 h) could be produced by PVDF–EG membrane with a very excellent selectivity against dye compound, that is, 99.88% rejection. These promising results are mainly due to the greater wetting pressure of PVDF–EG membrane coupled with its higher hydrophobicity degree. The permeate flux obtained in this study is comparable to or even better than those reported in the literature, confirming that PVDF–EG membrane has a great potential to be utilized for textile wastewater treatment.

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