

Development of novel surface modified poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) membrane contactor for CO₂ absorption

Fosi-Kofal Mohamoud^{1,2,*}, Azeman Mustafa^{1,2}, Ahmad Fauzi Ismail^{1,2}

¹Advanced Membrane Technology Research Centre (AMTEC), University Technology Malaysia, 81310, Skudai, Johor, Malaysia

²Faculty of Chemical and Energy Engineering, University Technology Malaysia, 81310, Skudai, Johor, Malaysia

Abstract: The ever increasing industrial activities worldwide are the main culprits for the greenhouse gases like carbon dioxide (CO₂) that cause global warming. Various methods were suggested to curb the production of CO₂, and the latest technology is the utilization of the flexibility of membranes in gas-liquid contactors. The principal aim of this study is to fabricate a surface modified poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) by blending surface modifying macromolecules (SMM) in the polymer dope. Lithium chloride (LiCl) was employed as pore-forming agent. The surface modified PVDF-HFP showed large pore size, higher effective surface porosity and overall porosity, critical water entry pressure and contact angle than plain PVDF-HFP. Moreover, the surface modified PVDF-HFP showed a maximum CO₂ flux of 6.74×10^{-4} mol/m².s, which was nearly 38% higher than that of the control plain PVDF-HFP.

Key words: Carbon dioxide absorption; PVDF-HFP; Hydrophobic SMM; Hydrophobicity; Porosity

1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) warns about damaging effects of climate change unless the carbon dioxide (CO₂) emissions to the atmosphere are reduced by 50-80% until 2050. Since renewable energies are not capable of replacing fossil fuels entirely in the growing energy demand, real-time implementable concepts to minimize CO₂ output are needed (Vogt et al., 2011). Therefore, to curb CO₂ emissions, there is the need for low energy-consumption, available efficient technologies for the capture and removal of CO₂ from gas mixtures produced by industrial sources (Lu et al., 2009).

Traditionally, conventional techniques such as packed towers were utilized for CO₂ capture. However, these techniques are not easy to operate because of the frequent problems including foaming, flooding, channeling and entrainment (Li and Chen, 2005). Moreover, those conventional methods usually involve substantially complicated equipment, higher energy consumption and capital cost (Zhang et al., 2013).

Hollow fiber membrane contactor is a promising alternative for CO₂ capture. Unlike conventional techniques, the absorption of CO₂ in a membrane contactor occurs in non-dispersion mechanism of the gas and liquid phases. The CO₂ and a liquid absorbent are flown counter-currently in the lumen and shell sides of a hollow fiber, which enables independent control of gas and liquid flow rates (Atchariyawut et al., 2008). Moreover, the modularity of the

membrane modules makes membrane contactors highly flexible in operations. The performance of a membrane contactor can be easily predicted from the known interfacial surface area (Li et al., 2005). Yeon et al. (2005), who used a polyvinylidene fluoride (PVDF) hollow fiber membrane contactor for absorption and a stripper column as desorber for the removal of CO₂ from nitrogen, showed that this configuration has a higher CO₂ removal efficiency than the conventional absorption column. The CO₂ absorption rate per unit volume of the membrane contactor was 2.7 times higher than that of the packed column, presumably caused by the increased interfacial area.

On the other hand, there are also certain drawbacks associated to membrane contactors. The flow of gas and liquid are normally laminar due to the small diameter of fibers and the small channels around the fibers. Therefore, it is inferior to the conventional devices in terms of mass-transfer coefficient. However, large interfacial area of the membrane contactor makes it a more efficient absorber (Li and Chen, 2005). Hence, since gas-liquid membrane contactors combine both absorption (high selectivity) and membrane separation (modularity and compact structure), this technology presents significant advantages over the conventional absorption techniques.

In hollow fiber membrane contactors, wetting of the porous membrane by the liquid absorbents is a serious problem as it significantly increases the resistance to mass transfer. This is due to the introduction of a stagnant liquid layer in the pores of the membrane (Kreulen et al., 1993; Kumar et al., 2002). Depending on the membrane material, the

* Corresponding Author.

liquid absorbent nature and the pressure of the two phases, the membrane pores may be filled with gas or liquid which corresponds to the non-wetted mode and the wetted mode respectively (Rongwang et al., 2009). The reduction of the overall mass transfer coefficient may reach up to 20% even if the membrane pores were 5% wetted (Wang et al., 2005).

Generally, two approaches can be adapted to fabricate membranes that are highly resistant to pore wetting. The first approach is to utilize hydrophobic materials with good chemical resistance for membrane fabrication. The second approach is to apply a more hydrophobic surface coating/modification layer on the existing hydrophobic/hydrophilic membranes to protect the surface pores from wetting. A number of surface modification techniques have been proposed, with the intention to increase the membrane hydrophobicity in mind (Zhang et al., 2013). One of the promising surface modification methods is to blend surface modifying macromolecules (SMMs) into the polymer dope. SMMs are hydrophobic in nature and will concentrate at the polymer-air interface to reduce the system's interfacial tension and as consequence increase its hydrophobicity.

Moreover, in membrane contactor applications, the hydrophobic property of the polymeric material is important for the prevention of the bulk liquid transport across the membrane (membrane wetting). Polyvinylidene fluoride (PVDF) material has been widely used in making asymmetric microporous membranes via nonsolvent-induced phase inversion method. However, a copolymer of PVDF called poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) offers even better hydrophobicity than the PVDF homopolymer due to the increase of fluorine content brought by the HFP group (Wongchitphimon et al., 2011). The addition of an amorphous phase of hexafluoropropylene (HFP) into the main constituent vinylidene fluoride (VDF) blocks increased the fluorine content, thus making PVDF-HFP more hydrophobic than polyvinylidene fluoride (PVDF) (Shi et al., 2007) (Fig. 1).

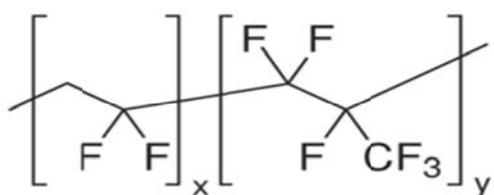


Fig. 1: Chemical structure of PVDF-HFP

One challenge of using PVDF-HFP is the poor overall porosity it exhibits. For the membrane performances, the pure water flux of reported PVDF-HFP hollow fiber membranes was quite low (Shi et al., 2007). Along with high hydrophobicity, high overall porosity is essential for membranes used in gas-liquid contactors in order to achieve competitive CO₂ absorption fluxes. One way to enhance the pore-

forming process is to reduce polymer concentration. Another favourable method is the usage of pore-forming additives to balance or improve the permeation performance of the final membrane through adjusting the membrane structure in the phase inversion process.

Therefore, the main aim of this work is to fabricate a polymeric hollow fiber membranes with high performance to be used in the separation of CO₂ in gas-liquid contactor applications. To achieve this, PVDF-HFP asymmetric hollow fibers will be fabricated with and without the addition of SMM into the spinning dope and employing lithium chloride (LiCl) as a pore-forming agent. The prepared membranes will be characterized by conducting gas permeation test, critical entry pressure of water (CEPw), water contact angle and CO₂ absorption performance in gas-liquid contacting process.

2. Experimental

2.1. Materials

Commercially available polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) (Kynar powder flex® 2801, 12 wt. % HFP), was used as the base membrane material. *N*-Methyl-2-pyrrolidone (NMP, 99.5%) was employed as the solvent without further purification. Hydrophobically modified SMM were supplied by University of Ottawa, Ontario, K1N 6N5, Canada. Lithium chloride (LiCl, Sigma-Aldrich®, > 99%) was used as a pore-forming agent. During spinning, distilled water and tap water were employed as internal and external coagulants respectively. Methanol (GR grade, 99.9%) from Merck was used for the post-treatment of the spun membranes.

2.2. Hollow fiber fabrication

Non-solvent induced phase separation was the preferred method of membrane fabrication in order to produce membranes of asymmetric structure. The dope formulation of the prepared membranes is shown in Table 1.

Table 1: Dope formulation for hollow fiber membrane spinning

	M0	M1
PVDF-HFP (wt.%)	14.0	14.0
SMM (wt.%)	0.0	1.0
LiCl (wt.%)	3.0	3.0
NMP (wt.%)	83.0	82.0

The prepared solutions were loaded into a reservoir and force fed into a spinneret by pressurized nitrogen. The dope extruded from the spinneret at constant rate with no air-gap. As the external coagulant, tap water was used to induce the phase inversion of nascent fibers. The take-up speed of was adjusted according the dope extrusion rate from the spinneret. The hollow fibers were spun at room temperature of 25°C. Distilled water was

selected as the bore fluid and delivered to the spinneret at a constant rate by a syringe pump. The details of the spinning conditions are given in Table 2.

Table 2: Hollow fiber spinning conditions

Dope Extrusion rate (ml/min)	4.0
Bore fluid flow rate (ml/min)	1.7
Bore fluid composition (wt.%)	Distilled water
External coagulant	Tap water
Air gap distance (cm)	10
Spinneret o.d./i.d. (mm)	1.2/0.55
Temperature (°C)	25

The fibers were kept immersed in water for 72 h to remove the residual solvent and non-solvent. Due to the potential defects present if the fibers are dried when the pores are filled with water, the fibers were subjected to post-treatment and immersed in methanol in over 30 min. Then, they were hung to dry at room temperature.

2.3. Gas permeation test

The hollow fibers were subjected to nitrogen (N₂) gas permeation test in order to obtain the membrane mean pore size and effective surface porosity. One hollow fiber about 10 cm in length was potted to steel fitting at one side and the other side was closed by epoxy resin. For each type of membrane fabricated, at least three testing modules were prepared to obtain accurate results. The feed gas (N₂) was delivered to the shell side and the pressure was increased from 0.5 to 5 bar (gauge) with 0.5 increment each time. Soap-bubble flow meter was then employed to measure the gas permeance at each pressure.

The background theory of the gas permeation test is based on few assumptions. First, the shape of the membrane pores is simplified as straight and cylindrical. Second, Knudsen and Poiseuille flow regimes are assumed to control the gas flow via the pores to obtain the overall gas permeance.

2.4. Overall porosity

The membrane overall porosity, ϵ_m , defined as the volume of the pores divided by the total volume of the membrane, was quantified by gravimetric method formula (Eq. 1):

$$\epsilon_m = \frac{(w_1 - w_2)/\rho_w}{(w_1 - w_2)/\rho_w + w_2/\rho_p} \quad (1)$$

Where w_1 is the weight of the wet membrane, w_2 the weight of the dry membrane, ρ_w is water density and ρ_p is the polymer density. Three spun hollow fibers were randomly chosen after the solvent exchange. Prior to measuring the wet weight, an air stream was used to blow the lumen side of the membrane. The dry was later measured when the membranes were adequately dried in an oven for 2 h at 120 °C.

2.4. Critical Entry Pressure of Water and Contact Angle

Critical entry pressure of water (CEPw) is the lowest pressure necessary for water penetration into membrane pores and is a measure of the wetting resistance of the membranes. CEPw experiments were conducted using hollow fiber modules similar to those employed in the permeation test. Pressurized nitrogen was used to force-feed distilled water into the lumen side of the hollow fiber membranes. After 30 minutes of keeping the pressure constant, an increment of 0.5 bar intervals was added to the original pressure. The pressure at which the first water droplet appeared on the membrane shell side was recorded as the CEPw.

To measure contact angle, the fibers were kept in an oven at 60 °C for 12 h. The sessile drop method using a goniometer (model G1, Krüss GmbH) was employed to determine the contact angles at ten different points on the outer surface of the hollow fibers and then the arithmetic mean value was calculated.

2.5. CO₂ absorption performance experiment

The CO₂ absorption experiment was carried out to evaluate the performance of the spun hollow fibers in membrane contactor application. Five hollow fibers of 175 mm in length were packed in a contactor module with both ends open. The desired configuration used during the absorption experiment was to flow pure CO₂ in the shell side and distilled water in the lumen side in a counter current mode. While the gas side pressure was maintained at to 1×10^5 Pa (1 bar), the liquid side pressure was set at 0.2×10^5 Pa (0.2 bar) to avoid the formation of bubbles in the liquid stream. Before taking any samples, the experiment was left to run in a steady state condition for 30 min. Titration was used to quantify the concentration of CO₂ absorbed in the distilled at the lumen side exit using. The characteristics of membrane contactor module employed in the experiments are presented in Table 3.

Table 3: Membrane contactor module specifications

Module I.D. (mm)	14.0
Module length (mm)	270.0
Effective fiber length (mm)	175.0
Number of fibers	5.0
Gas side pressure (bar)	1.0
Liquid side pressure (bar)	1.2

3. Results and discussions

3.1. Gas permeation, overall porosity, critical water entry pressure and contact angle results

In order to prepare hydrophobic porous asymmetric membranes with well-tailored structure for CO₂ absorption, a certain amount of SMM was dispersed in the spinning dope solution to enhance the performance of the membrane. In this study, PVDF-HFP was used as the base polymeric material. PVDF-HFP is highly hydrophobic membrane material

such as PVDF-HFP. However, there are a limited number of studies about the fabrication of PVDF-HFP hollow fibers (Garcia-Payo et al., 2010). Therefore, when compared to conventional hydrophobic membranes, the understanding of the fabrication and limitations of PVDF-HFP is limited.

The gas permeation through porous membranes generally involves Knudsen diffusion and Poiseuille flow and also in high pressure, surface flow transport. The values of N₂ permeances, effective surface porosity and also mean pore size of the prepared hollow fiber membranes, M0 and M1, were obtained by gas permeation test (Table 4). As shown from this table that was expected, permeability increased by incorporating SMM to the membrane structure due to a significant increase in porosity and a relative increase in the mean size of pores. As can be seen, the addition of SMM increases the contact angle from 86.9° in pure PVDF-HFP membrane to 94.5° in surface modified PVDF-HFP containing 1% SMM. During membrane fabrication process and because of incompatibility of SMM with the base polymer, SMM migrates to the membrane-air interface, accumulates on the surface and makes nanoscale aggregates and changes the surface properties of membrane (Pham et al., 1999). The mechanism of SMM migration to membrane surface was reported elsewhere (Suk et al., 2002). During migration, it is possible that the fluorine-based chains at both ends of SMM orient themselves vertically to the membrane-air interface (Bolong et al., 2009) and make more increase in surface hydrophobicity. The addition of SMM to PES flat sheet membrane can increase the contact angle from 76° to 116°, which is very close to the contact angle of PTFE, an inherently hydrophobic polymer (Nystrom et al., 1987).

Apart from that in measuring the wetting resistance of prepared membranes, CEPw was conducted. Based on the Laplace-Young equation, water cannot easily pass through the surface modified PVDF-HFP compared to plain PVDF-HFP membrane. Zhange et al. (2003) reported that the accumulation of SMM polymer chains containing fluorine on the surface of membrane enhances the surface properties of membrane such as surface lubrication and chemical resistance (Zhang et al., 2003). In addition, it was reported that SMM surface modified PES membrane has higher mechanical strength compared to unmodified membrane (Khayeta et al., 2006).

Finally, the porosities of the prepared membranes, calculated according to Eq. 1, are in the range of 75.40 to 81.91%. The addition of SMM had positive impact on the overall porosity of composite membranes.

The usage of LiCl as a pore-former should be noteworthy as well. At the post-treatment stage, LiCl is washed away from the membrane structure and leaves pores behind. In 2011, Wongchitphimon et al. (2011) investigated the effects of PEG with different molecular weights and different loadings as an additive on the fabrication of PVDF-HFP asymmetric

microporous hollow fiber membranes. They found that the dimension of finger-like macrovoids in the sub-layer of the resultant membrane increased in parallel with the increase of PEG molecular weight from 200 to 600 and 6000 kDa.

Table 4: Membrane structural characteristics

	M0	M1
N ₂ Gas Permeance (x 10 ⁻⁴)	3.76	6.31
Mean pore size (nm)	125.20	258.50
Effective Surface Porosity (m ⁻¹)	27.90	43.60
CEPw (Bar)	5.30	7.40
Contact angle (°)	86.90	94.50
Overall Porosity (%)	75.40	81.20

3.2. CO₂ absorption performance results

To assess the performance of the fabricated membranes in gas-liquid contactors, modules containing 5 hollow fibers each were prepared and distilled water was used as the liquid absorbent. In physical CO₂ absorption, the mass transfer resistance of the gas side is neglected since pure CO₂ was used as feed gas. Therefore, the rate of mass transfer depends primarily on the liquid phase boundary and the membrane (Atcharyawut et al., 2007). The CO₂ absorption flux was obtained at different absorbent flow rates in the shell side and the results are shown in Fig. 2.

As can be deduced from Fig. 2, the CO₂ flux of the surface modified PVDF-HFP, M1, were significantly higher than those of the membrane, M0, prepared without SMM as an additive. The pore size and effective surface porosity of M0 are smaller than those of M1. Hence, the membrane of larger pore size and higher porosity (M1) has higher flux. The membrane prepared with SMM in the spinning dope has a maximum CO₂ flux of 6.74 x 10⁻⁴ mol/m².s at 300 ml/min absorbent flow rate. In a similar fashion, Rahbari-Sisakht et al. (2012) fabricated novel surface modified PVDF hollow fiber membrane for CO₂ absorption in hollow fiber membrane contactor system. The performance of the surface modified membrane in contactor application for CO₂ absorption via distilled water as absorbent was studied. The results showed that the surface modified PVDF membrane has higher performance compared to control PVDF membranes. With the membrane prepared from SMM in the spinning dope a maximum CO₂ flux of 7.7x10⁻⁴ mol/m²s was achieved at 300ml/min of absorbent flow rate, which was almost 93% more than the plain membrane.

Since the absorption performance of the M1 membrane proved to be the highest among the prepared membranes in this study, its performance in gas-liquid contactors was compared to other membranes covered in the literature as shown in Table 5.

As the results in Table 5 show, at absorbent liquid flow rate of 300 ml/min the surface modified PVDF-HFP and PEI with SMM showed the highest CO₂ absorption performance of 6.74 x 10⁻⁴ mol/m².s and 8.90 x 10⁻⁴ mol/m².s among the membranes listed.

These can be attributed to the effects of SMM on the different properties of the membranes and the surface modified membrane has superior performance in contactor applications due to its characteristics such as bigger pores, higher membrane porosity and higher surface hydrophobicity.

Specifically when comparing the two membranes surface modified by SMM, i.e. PEI and PVDF-HFP, both membranes seem to exhibit similar structural characteristics. Bakeri et al. (2012) investigated the application of SMM to surface modify PEI hollow fiber membrane and used the surface modified membranes in membrane gas absorption process. They used Response Surface Methodology (RSM) to investigate the effect of SMM on the properties of surface modified PEI hollow fiber membrane in terms of mean pore size, helium gas permeance, contact angle of inner and outer surfaces of membrane, membrane porosity, liquid entry pressure of water and CO₂ absorption flux in case of

distilled water in lumen side and pure CO₂ in shell side of contactor.

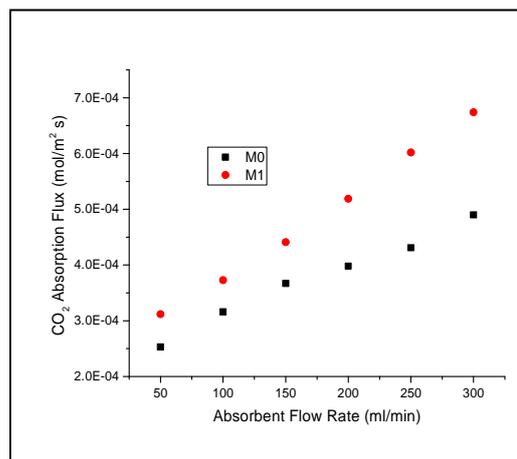


Fig. 2: CO₂ Absorption Performance of M0 and M1

Table 5: Comparison of surface modified PVDF-HFP with in-house and commercial membranes

Membrane Type	Absorption flux (x10 ⁻⁴ mol/m ² .s)	Reference
PVDF + phosphorous acid	5.60	Atchariyawut et al., 2006
PVDF + phosphoric acid	4.80	Mansourizadeh et al., 2010
Poly(tetrafluoro ethylene) (PTFE)	4.30	Khaisri et al., 2009
Poly (etherimide) (PEI)+ SMM	8.90	Bakeri et al., 2012
M1 (PVDF-HFP + SMM)	6.74	This study

The test results that surface modified PEI, like surface modified PVDF-HFP, has bigger pore size, gas permeance, contact angle and overall porosity and CEPw than plain PEI membrane.

Nevertheless, PEI+SMM have the edge in the short-term contactor applications where it showed higher CO₂ absorption than surface modified PVDF-HFP. However, since PEI is inherently hydrophilic polymer, its hydrophobicity is not high enough for long-term stability when prolonged contactor applications are to be conducted. Therefore, the superior wetting resistance of PVDF-HFP with SMM over PEI with SMM gives it potential to be applied in gas-liquid contactor processes.

4. Conclusions

The test results of prepared PVDF-HFP membranes revealed that the addition of a certain amount of SMM in spinning dope solution has significant effect on permeation and hydrophobicity and therefore the CO₂ absorption performance of spun membranes. The gas permeation test obtained revealed that permeance, mean pore size, effective surface porosity and overall porosity of surface modified PVDF-HFP membrane were higher than those of plain of PVDF-HFP membrane. Also the addition of SMM into the polymer dope affected on CEPw and contact angle of prepared MMMs and increased these two parameters significantly. The high hydrophobicity together with sufficient permeability are the desirable parameters for membranes intended for cotactor processes.

Therefore, as surface modified PVDF-HFP showed those favourable characteristics, it could be suggested to have dormant potential to be applied in industrial high pressure gas-liquid contactors.

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