PVDF-CLOISITE HOLLOW FIBER MEMBRANE FOR CO₂ ABSORPTION VIA MEMBRANE CONTACTOR

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Graphical abstract

Abstract

The effect of cloisite concentrations on CO₂ absorption via polyvinylidene fluoride-cloisite hollow fiber in membrane contactor system was investigated. PVDF polymer was modified by introducing different compositions of cloisite clay (S1: 0%, S2: 1 wt%, S3: 3 wt% and S4: 5 wt%) into the polymer solution. The hollow fiber membranes were examined via liquid entry pressure (LEPw), contact angle and scanning electron microscope (SEM). CO₂ absorption test was conducted at different liquid absorbent flow rates of 1M MEA. S4 gives highest liquid entry pressure value and S3 obtained highest contact angle value at around 87.21º. Different concentrations of cloisite exhibited various finger-like structure with sponge-like morphology on the membrane lumen side. Meanwhile, the highest CO₂ absorption flux of 3.41×10⁻² mol/m².s at flow rate of 200 ml/min was obtained for membrane S4. Long term performance for membrane S4 up to 55 hours of CO₂ absorption showed increasing absorption trend up to 6.78×10⁻² mol/m².s of CO₂ fluxes.

Keywords: PVDF-Cloisite hollow fiber membrane, CO₂ absorption, Hollow fiber membrane contactor, clay

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1.0 INTRODUCTION

Natural, synthesis and refinery of the raw gases contain acid gases such as hydrogen sulphide (H₂S) and carbon dioxide (CO₂). The removal of CO₂ is very important in natural gas processing to prevent corrosion problem in pipeline and plant equipment [1]. To minimise these effects, various conventional methods were used to remove CO₂ such as pressure swing adsorption, cryogenic distillation, membrane technologies [2]. In recent years, there has been an increasing interest in membrane contactor application due to its modularity and high CO₂ absorption efficiency [3]. The membranes were coupled with liquid absorbent; usually aqueous alkanolamine such as monoethanolamine (MEA), diethanolamine (DEA), N-methyl diethanolamine (MDEA), disopropanolamine (DIPA) and diglycolamine (DGA). This liquid selection is probably due to the high selectivity of amine group
towards CO2 [4]. It was reported that the CO2 absorption process by membrane contactor can reduce in volume and weight by more than a factor of 10 compared to other conventional absorption methods [5]. In conventional method for gas-liquid separation process, the liquid and gas streams cannot be controlled independently thus resulting operational problems such as flooding, foaming, and entrainment [6]. In contrast, hollow fiber membrane contactor is claimed to be more practical equipment as an alternative to the conventional equipment. In hollow membrane contactor system, the gas flows in one side of the membrane, meanwhile the liquid absorbent flow in the other side without phase inversion [7]. So, the operating problem faced by conventional equipment can be solved. Hollow fiber membrane contactor (HFMC) indeed are more efficient than conventional absorption method but it also has several disadvantages such as tendency to fouling when used in long term, limited lifetime, pre-treatments needed to reduce fouling, and membrane wetting. The pore of the membrane could be filled with liquid absorbent instead of flow gas thus increases the mass transfer resistance and decrease the membrane contactor performance. The wettability of the membrane depends on the structural characteristic of the porous membrane, the operating condition and the absorbance nature and properties [8]. Therefore, the membrane must be highly hydrophobic to prevent the membrane wetting from aqueous absorbent solution. There are several types of polymer that can be used in HFMC which include polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE). However, these polymer (PE, PP and PTFE) cannot be dissolved in most common solvent at low temperature and need to be prepared by stretching and thermal method which lead to formation of large pore size and symmetric structure [9]. PVDF is the most favourable polymer used for CO2 absorption due to its hydrophobicity and can easily dissolved in organic solvent. The membrane preparation can be prepared by using dry-wet phase inversion which is simple and much easier compared with stretching and thermal method. Therefore, it can be useful for producing asymmetric membrane which suited for membrane contactor application. In contrast, PVDF had a low surface tension resulted in less porous membrane structure because of the coagulant cannot easily penetrate into the membrane and lead to slow solidification [10]. Therefore, the addition of non-solvent additive to enhance the phase-inversion process is a must as for improving the membrane structure.

Mansourizadeh and Ismail [11] investigated different additives for CO2 absorption in gas-liquid membrane contactor such as polyethylene glycol of average molecular weight 200 Daltons (PEG200), glycerol, acetic acid and ethanol on the polysulfone (PSf) membrane. The results showed that glycerol additive was the best additive which possessed a thin finger-like and thick sponge-like layer for the membrane. The enhanced membrane structure improves the membrane contactor performance thus increasing the CO2 absorption rate and produced higher critical entry pressure (CEPw) compared to other PSf hollow fiber membrane. Meanwhile, Fosi-Kofal et al. [12] used calcium carbonate (CaCO3) as additive into PVDF dope solution. The used of CaCO3 as additive enhances the surface roughness, porosity, permeation rate and wettability resistance. Hou et al. [13] prepared PVDF composite hollow fiber membrane by introducing modified calcium carbonate into the polymer dope solution resulting in narrow pore size distribution while enhancing the surface roughness and contact angle properties. Mixed matrix membrane (MMMs) is one the attractive method that widely acknowledged for their ability to combine the advantages of both organic and inorganic fillers [14]. Rezaei et al. [15] study the performance of PVDF hollow fiber MMMs by introducing MMT and cloisite as organic fillers for CO2 absorption. Their fabricated MMMs result in increase wetting resistance, surface hydrophobicity and liquid entry pressure (LEPw) with loading.

Other researchers may have been working on PVDF/cloisite membranes, but very scarce reported on the study of CO2 absorption at long hour operation. Therefore, the objective of this research is to investigate the effect of cloisite concentrations on membrane properties and to evaluate the performance of CO2 absorption flux at long hour operation. Several tests have been conducted to examine the PVDF-cloisite hollow fiber membranes in term of morphology analysis, liquid entry pressure (LEPw) and contact angle measurement. CO2 absorption test was performed at different liquid absorbent flowrates. The long term operation of CO2 absorption via membrane contactor was performed at constant liquid absorbent flowrates.

2.0 METHODOLOGY

2.1 Chemicals

Polyvinylidene fluoride (PVDF) purchased from Solvay was used as the base polymer. Monoethanolamine (MEA) (99.9%) purchased from MERCK as the liquid absorbent in the membrane contactor. Cloisite clay (MERCK) was used as a non-solvent additive in the polymer solution. Methanol (99.9%) (MERCK) and n-hexane (99%) (MERCK) were used as post-treatment for the membrane. Tab water was used as the coagulation bath medium in the spinning process.

2.2 Fabrication Process

The PVDF polymer pellets were dried in a vacuum oven for 24 hours to remove any moisture content. The spinning dope of PVDF/cloisite solution was prepared by stirring homogenously at 60-70°C for
several hours. This is followed by an ultrasonic degassing process to remove suspended gas-bubbles. Then, the solution was kept at room temperature for 24 hours prior to spinning process. The hollow fiber spinning process by the wet phase inversion was described elsewhere [16]. The spun fibers were immersed in water overnight to remove excess solvent. The fibers were post-treated with methanol and n-hexane, done at room temperature. This is to reduce fiber shrinkage and pore damage. The spinning process condition and dope composition are presented in Table 1 and Table 2.

### Table 1 PVDF hollow fiber spinning conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bore flow rate (ml/min)</td>
<td>2.0</td>
</tr>
<tr>
<td>Dope extrusion rate (ml/min)</td>
<td>4.0</td>
</tr>
<tr>
<td>Bore fluid composition (wt%)</td>
<td>NMP/H₂O : 80/20</td>
</tr>
<tr>
<td>Coagulation medium</td>
<td>Tap water</td>
</tr>
<tr>
<td>Spinneret OD/ID (mm/mm)</td>
<td>1.0/0.5</td>
</tr>
<tr>
<td>Air gap distance (cm)</td>
<td>0</td>
</tr>
<tr>
<td>Spinning dope temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>External coagulation</td>
<td>25</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2 PVDF-Cloisite dope composition

<table>
<thead>
<tr>
<th>Spinning dope</th>
<th>HF₁</th>
<th>HF₂</th>
<th>HF₃</th>
<th>HF₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF (wt%)</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Cloisite (wt%)</td>
<td>0</td>
<td>1</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>NMP (wt%)</td>
<td>82</td>
<td>82</td>
<td>82</td>
<td>82</td>
</tr>
</tbody>
</table>

2.3 LEP and Contact Angle

Membrane LEPw described as the pressures applied onto distillate before it penetrate into dried membrane pores [17] which is the minimum pressure required to drive water through the membrane pores. The lumen side of the hollow fiber were filled with deionized water and 1 bar of pressure was applied from the gas cylinder. The gas pressure was increased gradually at 0.5 x 10⁵ Pa and kept constant at each pressure interval for 20 minutes to check for the appearance of water droplet at the outer surface of the hollow fiber. For the water contact angle, the hollow fiber was dried in a vacuum oven at 60°C for 12 hour prior to testing. Sessile drop method using goniometer was used to measure the contact angle of the outer surface of the hollow fiber [14]. An average of 15 contact angle value was measured at various positions at the membrane outer surface.

2.4 SEM Analysis

Scanning electron microscopy (SEM) (Philips XL40) was used as a standard method to analyze the morphology of the hollow fiber membrane. The sample is softly fractured in liquid nitrogen prior to gold coating. The cross sectional structures, as well as the outer and inner skin layer of the spun fiber micrographs were taken at various magnifications.

2.5 Absorption Test

Pure CO₂ was employed as the feed gas stream through the lumen side of the membrane at pressure of 1.5 bars. MEA as the liquid absorbent were supplied through the lumen side of the membrane. The pressure of liquid absorbent was controlled at 0.2 bar higher than the gas pressure to prevent bubble formation in the liquid phase. Inlet and outlet liquid absorbent from the membrane contactor system was collected to check the concentrations by using double titration method. The system was left for 30 min to achieve steady state before inlet and outlet liquid collection was carried out (Figure 1).

The outlet liquid of MEA was collected to measure the CO₂ absorption flux by double titration method. To perform the double titration method, 10ml of outlet liquid of MEA sample was taken and diluted with distilled water. Six drops of 0.5M NaOH was added followed by 2 drops of BaCl₂ and a drop of phenolphthalein. The sample was titrated with 1M of HCl until liquid colour changes from pink/purple to colourless. Then, a drop of methyl orange was added and titrated again until the liquid colour changed from light yellow to orange. The amount of HCl used to change the colour of the liquid from light yellow to orange was recorded to determine the CO₂ absorption flux and efficiency. The process was repeated for five times for each sample and average reading was taken. The CO₂ concentration in the solution was calculated using equation (Eq. 1) and the CO₂ absorption flux was calculated using equation (Eq. 2):

$$M_{CO_2} = \frac{(M \times V)_{NaOH}/2}{V_{sample}}$$  \hspace{1cm} (Eq 1)

where $M_{CO_2}$ is CO₂ concentration (mol/L), M is NaOH concentration (mol/L), V is NaOH volume (m³) and $V_{sample}$ is solution sample volume (m³).
\[
J_{CO_2} = \frac{(C_{in} - C_{out}) \times Q_l}{A_l}
\]  
(Eq 2)

where \(J_{CO_2}\) is CO₂ absorption flux (mol/m².s), \(C_{in}\) is CO₂ concentration inlet of the membrane module (mol/L), \(C_{out}\) is CO₂ concentration outlet of the membrane module (mol/L), \(Q_l\) is liquid flowrate (m³/s), and \(A_l\) is liquid flowrate (m³/s). Long term performance of CO₂ absorption test was performed for 50 hours for selected membranes at constant liquid flow rates of 50 ml/min.

3.0 RESULTS AND DISCUSSION

3.1 LEP and Contact Angle

Liquid entry pressure (LEPw) test was conducted to investigate the wetting resistance of the membrane. LEPw represent the pressure at which the liquid absorbent, MEA penetrate into the membrane pores and wet the membrane. LEPw is closely related to the Laplace-Young equation which the membrane pore size, contact angle, pressure difference and liquid surface tension will affect the membrane wetting. The membrane pores must be small enough to prevent liquid absorbent from penetrate into the pore and goes to the gas side. When the pore radius is smaller, the liquid entry pressure is higher. In the stable long operation time during the CO₂ absorption process in membrane contactor system, the membrane pores should be only completely filled with gas. Therefore, membrane with high wetting resistance is necessity to reduce or eliminate wetting problem. Based on the Table 3 below, the average reading of LEPw for PVDF/cloisite membrane for S2, S3 and S4 had showed an increasing in LEPw. Sample membrane S4 which contain 5% of cloisite additive had showed higher LEPw of 6.5 bar compared to 5.5 bar of plain PVDF membrane, S1 which can be correspond to more sponge-like formation in the inner surface of the membrane.

<table>
<thead>
<tr>
<th>Membrane samples</th>
<th>Cloisite clay (wt%)</th>
<th>LEPw (Bar)</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0</td>
<td>5.5</td>
<td>76.09 ±7.0</td>
</tr>
<tr>
<td>S2</td>
<td>1</td>
<td>3.6</td>
<td>87.20 ±2.2</td>
</tr>
<tr>
<td>S3</td>
<td>3</td>
<td>4.2</td>
<td>78.18 ±5.4</td>
</tr>
<tr>
<td>S4</td>
<td>5</td>
<td>6.5</td>
<td>77.22 ±5.5</td>
</tr>
</tbody>
</table>

Further addition of cloisite in a hollow fiber membrane show increased of surface roughness, hence increased the surface hydrophobicity [18]. Hydrophobicity of the membrane is the most important parameter to increase surface wettability and it can be measured by determining the contact angle of the surface layer. Table 3 shows the contact angle of S2 membrane with 1 wt% cloisite concentration had higher contact angle 87.21 ± 2.26° compared to the plain PVDF membrane with a contact angle of 76.09 ± 7.04°. This result indicates that the addition of cloisite to the PVDF membrane had increased the hydrophobicity of the surface membrane.

3.2 SEM Analysis

The morphology of prepared PVDF membrane was characterized using scanning electron microscopy. The cross-sectional of inner and outlet membrane structured for the prepared membranes were showed in Figure 2. Generally, typical asymmetric structure of hollow fibre was observed, which finger-like structures were formed underneath the outer while sponge-like structures were formed in inner skin layers of the hollow fiber towards the middle of the cross-section. To develop membrane structure with improvement, cloisite clay was added into dope polymer as additive. As can be seen in the Figure 2, those 4 prepared membranes showed finger-like structure from outer surface until middle part and from middle to inner surface, the macrovoids form. Meanwhile, the addition of 1 wt% cloisite in the spinning polymer dope solution provided a thick sponge-like structure with thin finger-like structure below the outer surface.

The rapid phase inversion caused the inner membrane to form the large finger-like from outer layer of the membrane, while slow phase inversion formed thick sponge-like structure [19]. A small and narrow finger-like like structure was needed to reduce the mass resistance during gas transport. The narrow finger-like structure at outer surface of the membrane make the mass transfer resistance decreased and the small pore inside the surface make the membrane decreased in wettability [20]. For Figure 2(c) and Figure 2(d), the structure formed almost the same with thick finger-like structure form beneath of the outer surface and a thin sponge-like structure. The addition of 2 wt% and 5 wt% of cloisite caused the formation of long finger-like structure to the inner membrane because of the weak interaction of solvent-polymer and additive polymer. Therefore, it can be stated that high concentration of cloisite tends to form longer and thicker finger-like structure.
3.3 Effect of MEA on CO2 Absorption Test

From Figure 3 and 4, it was demonstrated the addition of cloisite in the spinning dope has improved the CO2 absorption flux and CO2 efficiency in 1M MEA. CO2 absorption flux of PVDF/cloisite membrane increased with an increase in liquid velocity. By increasing the liquid velocity, the liquid mass transfer resistance can be decreased and the liquid boundary layer thickness around the fibers also decreased. This resulted in increasing of CO2 absorption flux and its efficiency. Form Figure 3, the absorption flux increased by increasing the absorbent flowrate and the PVDF/cloisite membrane with 5% cloisite content showed promising result where it produced the highest CO2 absorption flux at the highest flowrate which is 3.41 x 10^-2 mol/m²s compared to the plain PVDF. In comparison with plain PVDF membrane at the highest velocities, the improvement of 56% can be achieved by the addition 5% cloisite. The high CO2 absorption flux of the PVDF/cloisite membrane can be related to the high liquid entry pressure and contact angle of the membrane surface.

Figure 3 illustrates the CO2 absorption efficiency versus liquid velocity, which CO2 absorption efficiency increased by increasing the liquid velocity. PVDF/cloisite membrane with 5 wt% cloisite content have the highest efficiency to remove CO2 gas which is 42%, followed by membrane 3 wt% cloisite content with 30% and the lowest is plain PVDF membrane at 25% efficiency at the same operation conditions.

Membrane with 5% cloisite content had bigger finger-like structure compared to the other membrane. Based on the CO2 absorption flux result, finger-like structure produced an easy pathway for gas diffusion through the membrane to the lumen side and the sponge-like structure prevents the liquid absorbent diffuses to the gas side.

3.4 Long Term Performance of CO2 Absorption

Long term performance of CO2 absorption for hollow fiber membrane (S4) was conducted for 50 hours at constant liquid flow rates of 50 ml/min (Figure 5). It was found that the absorption flux increases with the increasing operation time. For the 1st 10 hours of
operation, the CO₂ flux increases drastically from 2.0 till 3.5 x 10⁻² mol/m²s. Then, for the rest of 10 hours interval of 20, 30 and 40, the absorption fluxes showed exponential increase which indicate that the CO₂ mass transfer between gas and liquid phase has achieved a stable state. It can be observed that there is no flux declining occurs during that 50 hours operation indicating that there is no wetting experience occurs during that period. Therefore, it can be concluded that the employment of cloisite into the PVDF membrane has improved and enhanced the long term CO₂ absorption performance up to 50 hours of operation.

Figure 5 Long term CO₂ absorption performance for hollow fiber membrane [4] for 50 hours

4.0 CONCLUSION

PVDF/cloisite hollow fiber membranes were successfully prepared using wet phase-inversion process. Cloisite clay was introduced into dope solution as a non-solvent additive to improve the membrane structure for CO₂ absorption. The LEPw showed that membrane sample with the 5% cloisite content produced the highest value of CO₂ absorption flux which was 6.5 bars compared to other membranes. Moreover, the PVDF/cloisite membranes showed higher hydrophobicity in term of contact angle and liquid entry pressure compared to plain PVDF membrane, which the prepared membrane can withstand wetting problem during CO₂ absorption. Meanwhile, for contact angle measurement, membrane sample with 3 wt% of cloisite showed the highest value around 87.21°. As shown in the result, the efficiency and the CO₂ absorption flux keep increasing as cloisite composition increased and the liquid velocities increased. The PVDVF/cloisite membrane [4] showed the highest CO₂ absorption flux of 3.41 x 10⁻² mol/m²s at flowrate of 200ml/min. S4 membranes were further evaluated for long term CO₂ absorption and increasing absorption fluxes was demonstrated up to 50 hours of operation (6.8 x 10⁻² mol/m²s). With further research and studies, PVDF/cloisite hollow fiber membrane can be a potential membrane to be applied in membrane contactor system for removal of CO₂ gas in the industry.

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