

Synthesis and Preparation of Asymmetric PVDF-co-PTFE/DES Supported Membrane for CO₂/N₂ Separation

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Abstract. Incorporation liquid into membrane polymer pores structure would overcome challenges in developing a membrane with increasing gas permeability while maintaining the excellent selectivity. Asymmetric Polyvinylidene fluoride-co-polytetrafluoroethylene (PVDF-co-PTFE) and PVDF-co-PTFE/Deep Eutectic Solvent (PVDF-co-PTFE/DES) supported membrane was prepared using phase inversion method. Membranes prepared were coated with 3 wt. % of polydimethylsiloxane (PDMS) in n-hexane and were dried in a room temperature. While, deep eutectic solvent (DES) was prepared by mixing choline chloride and ethylene glycol with a ratio of 1:3. The membranes was characterized using scanning electron microscopy (SEM), fourier transform infrared (FTIR) and gravimetric methodology to determine the membrane porosity. The membrane performance was carried out using gas permeation test at 3.5 psi. FTIR spectra revealed that existence of DES in the membrane pore structures. Empty PVDF-co-PTFE membrane coated with PDMS shows CO₂ permeance at 12×10^3 GPU with CO₂/N₂ selectivity at 0.72. Interestingly, incorporation of DES showing an improvement for both CO₂ permeance and CO₂/N₂ selectivity up to 49% and 36% respectively. Thus, employing DES as a liquid filler into PVDF-co-PTFE matrix shows a promising membrane for CO₂/N₂ separation.

1. Introduction

Carbon dioxide (CO₂) separation via polymeric membrane shows as one of the good potential technologies to replace conventional techniques such as chemical absorption, physical adsorption and cryogenic distillation. Gas separation involving membrane technology has certain advantages which are compactness and light in weight, low labor intensity, modular design allows easy expansion or operation at partial capacity, low maintenance due to no moving parts, low energy requirements and also low in cost [1]. However, polymeric membranes performance is limit by Robeson's trade-off limit between selectivity and permeability [2]. Thus combination of liquid with membranes for CO₂ separation is a one of the approach to surpass Robeson's trade-off limit, called supported (or immobilized) liquid membrane (SLM). SLM is a non-dispersive-type liquid membrane, where the liquid-phase selective material is immobilized in the membrane pores by capillary forces. Traditional SLMs have been develop by using amine-based aqueous solution such as diethylenetriamine (DETA), diaminoethane (DAE), diglycolamine (DGA) and triethylene glycol (TEG) [5].



First SILM was reported by Scovazzo et al. in a year of 2002, where ionic liquid (IL) was impregnated into the membrane pores for CO₂/N₂ separation. They found that supported ionic liquid membrane shows high in selectivity with high in flux in comparison to polymer membranes itself [3]. Even though ILs have been reported widely as a green solvent for the past two decades due to their tuneable physiochemical properties, there are still some challenged need to be encounter such as poor biodegradability, biocompatibility and sustainability. Thus, deep eutectic solvents (DES) has become a new substitute to ILs, where DES also possess an ionic character where it is a mixture of organic compounds having a melting point significantly lower than that of either individual component. DES have similar characteristics to ILs but are cheaper to produce due to lower cost of raw materials, less toxic and biodegradable [4].

The application of SLM is still not widely been used in industrial level due to the mechanical stability of liquid to retain in the membrane pore support. Changes of the operating conditions especially on pressure variations is considered as the most challenging issue. Yet, having high viscosity of DES would help to prevent the liquid loss. However, this makes filling up the pores is quite challenging, hence a vacuum method impregnation needs to be applied. Apart from that, having a very narrow pore size distribution of membrane pores support also could possibly reduce the chances of liquid loss [5].

In order to develop high performance of SLM for CO₂ gas separation, good interaction between liquid medium with the polymer membrane is compulsory. The right choice of the liquid medium is necessary to avoid carrier degradation and the loss of membrane lifetime. Thus, this study aims to develop an asymmetric PVDF-co-PTFE membrane as a support and the pores to be filled up with DES via vacuum method. Polyethylene glycol (PEG) will be added as a pore additive. While, DES is synthesized using choline chloride and ethylene glycol. The influence of DES in the polymer pores is investigated.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride)-co-Poly(tetrafluoroethylene) PVDF-co-PTFE was obtained from Arkema Pte Ltd, Singapore. N,N-dimethylacetamide (DMAc) solvent was purchased from Merck Milipore Corporation with $\geq 99.0\%$ purity. Polyethylene glycol, PEG with a reagent grade and average MW 10,000 was purchased from Sigma Aldrich with $\geq 99.0\%$ purity. In this study, ethylene glycol ($\geq 99.0\%$ purity) was bought from Merck Milipore Corporation. For coating solution, polydimethylsiloxane (PDMS) was purchased from Sigma Aldrich and n-hexane was purchased from Merck.

2.2. Preparations of Polymer Solution

Homogenous polymer solutions were prepared by dissolving 20 wt. % of PVDF-co-PTFE polymer in 77 wt. % of DMAc solvent. Then 3 wt. % of PEG additives was added and continuously stirred at 200 rpm until a clear and homogenous solutions were obtained. Throughout the stirring process, the temperature of the mixture was maintained at 50 °C. A homogenous polymer solution was then degassed in a room temperature for 24 hours.

2.3. Phase Inversion Method

The non-solvent induced phase separation (NIPS) technique was chosen to cast a flat sheet membrane. A polymer solution was casted onto a glass plate using a hand-casting knife with a knife gap set at $400 \pm 10 \mu\text{m}$ and followed by exposed to the surrounding air for 30 seconds. The cast film together with the glass plate was immersed into a coagulation bath for 24 hours. The coagulation bath medium consists of 75 wt. % of distilled water and 25 wt. % of ethanol. The formed membrane was taken out from the coagulation bath and dried at room temperature for 24 hours [6].

2.4. Synthesis of Deep Eutectic Solvent

The deep eutectic solvent (DES) used was a mixture of ChCl and ethylene glycol with a ratio of 1:3. DES was prepared by adding choline chloride in the ethylene glycol at room temperature. The mixture was continuously agitated at 200 rpm until a clear and homogenous solution was obtained.

2.5. Preparation of Supported Deep Eutectic Solvent Membranes

All supported membranes throughout this study were prepared by using vacuum immobilization techniques. The prepared membrane was submerged into the deep eutectic solvent in a petri dish and both were placed in the desiccator. A vacuum pump was applied and the pressure was set at -10 mbar for 3 hours at room temperature. The desiccator was aerated for every hour to ensure that the membrane pores were filled with DES. The excess DES on the membrane surface was wiped off with a filter paper. The weight of membrane before and after impregnation were recorded to determine the amount of DES immobilized in the membrane pores.

2.6. Membrane Coating

The membrane was then brought into contact with 3 wt. % PDMS/n-hexane solution for 10 minutes to seal pinholes before it was cured at room temperature for 24 hours.

2.7. Membrane Characterization

The prepared membrane top surface and the cross section morphological studies was carried out by using a scanning electron microscope (SEM) model JSM 6260 LE JEOL. The pore sizes were observed through the SEM images and measured by using SEMAFOR software.

FTIR analysis was used to study the effect of addition DES into the membrane by observing at their functional group presence before and after functionalized membrane. The FTIR analysis was carried out by using a FTIR spectroscopy, Perkin Elmer, Model L128044. The attenuated total reflectance (ATR) method was used. The 4 scans were recorded per sample in the frequency range 4000 – 650 cm⁻¹, with a resolution of 4 cm⁻¹.

The porosity of the prepared membrane was analysed by using an octanol. The sample was immersed in octanol for 15s to improve the hydrophilicity. The sample was later immersed in distilled water for 2 minutes before dried using a filter paper. Mass of samples before and after soaked in both octanol and distilled water were recorded. Equation (1) was used to calculate the membrane porosity.

$$\omega = \frac{m_n/\rho_n}{m_n/\rho_n + m_p/\rho_p} \quad (1)$$

Where ω is the porosity of the membrane, m_p is the mass of dry membrane, m_n is the mass of absorbed octanol, ρ_p is the density of the membrane, and ρ_n is the density of octanol. This method is used to estimate the porosity by determined the weight of liquid contained in the membrane pores.

The membrane was characterized using pure gas permeation tests. The pure gas permeance was determined by a constant volume. The membranes were placed into the permeation cell with an effective area of 11.34 cm² and exposed to pure CO₂ or N₂ respectively. The transmembrane pressure was constant at 3.5 psi and the temperature was 27 °C. The permeance (pressure-normalized flux) of gas i was calculated as follows;

$$\left(\frac{P_i}{l}\right) = \frac{1}{A\Delta p} \times \frac{dV_i}{dt} \quad (2)$$

Where i represents the gas penetrant, V_i is the volume of the gas permeated through the membrane (cm³, STP), A is the effective membrane area (cm²), t is the permeation time (s) and Δp is the transmembrane pressure drop (cmHg). The permeance is expressed in gas permeation unit, GPU, as

$$GPU = 1 \times 10^{-6} \frac{cm^3(STP)}{cm^2.S.cmHg}$$

Meanwhile, the selectivity was obtained by

$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \quad (3)$$

Where $\alpha_{i/j}$ is the selectivity of gas i over gas j. Both $(P/l)_i$ and $(P/l)_j$ are the permeance of gas i and j, respectively.

3. Results and Discussion

3.1. Characterization

The SEM images of empty PVDF-co-PTFE membrane cross sectional area and top surface are presented in Figure 1. Existence of pores on top of membrane surface is believe due to addition PEG as a pore additives. PEG as a polymer additives will increase the polymer solution viscosity, improve pore formation and suppress macro-void formation. This is the reason existence of combination both micro voids and sponge like structure as can be seen in the cross sectional area of the membrane [7]. The formation of sponge like structure also can be said due to the formulation of bath medium. The coagulation bath medium plays an important role in the formation of membranes via the phase inversion method. This phenomenon is related to the coagulation ability of the non-solvent. The presence of 25 wt. % of ethanol in the bath medium was believe to reduce the polymer precipitation rate in phase inversion process. Similar phenomena can be seen from a research conducted by Deshmukh and Li in a year 1998 [8]. Table 1 listed the empty PVDF-co-PTFE membrane configuration used for both DES impregnation and gas permeation test. Both membrane pore size and thickness were measured by using SEMAFORE software while the membrane porosity was obtained via gravimetric method.

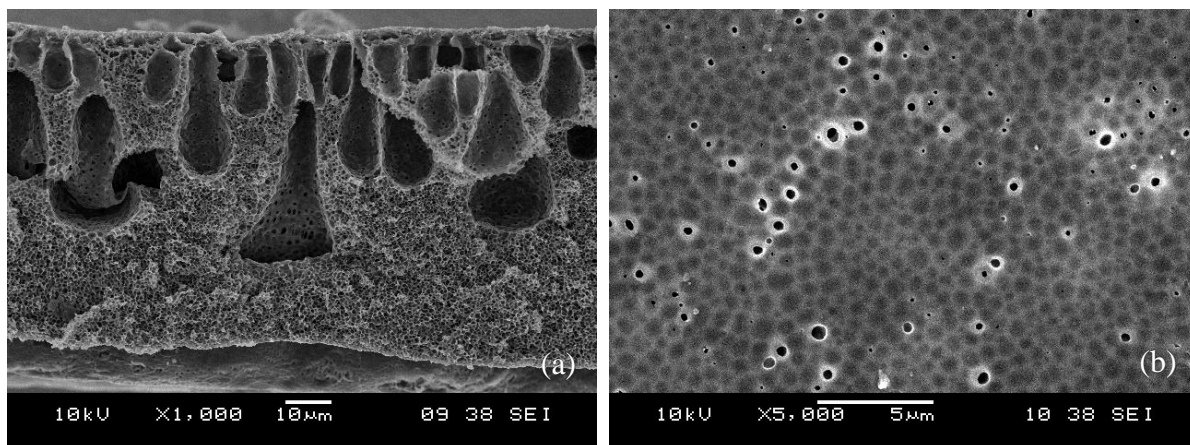
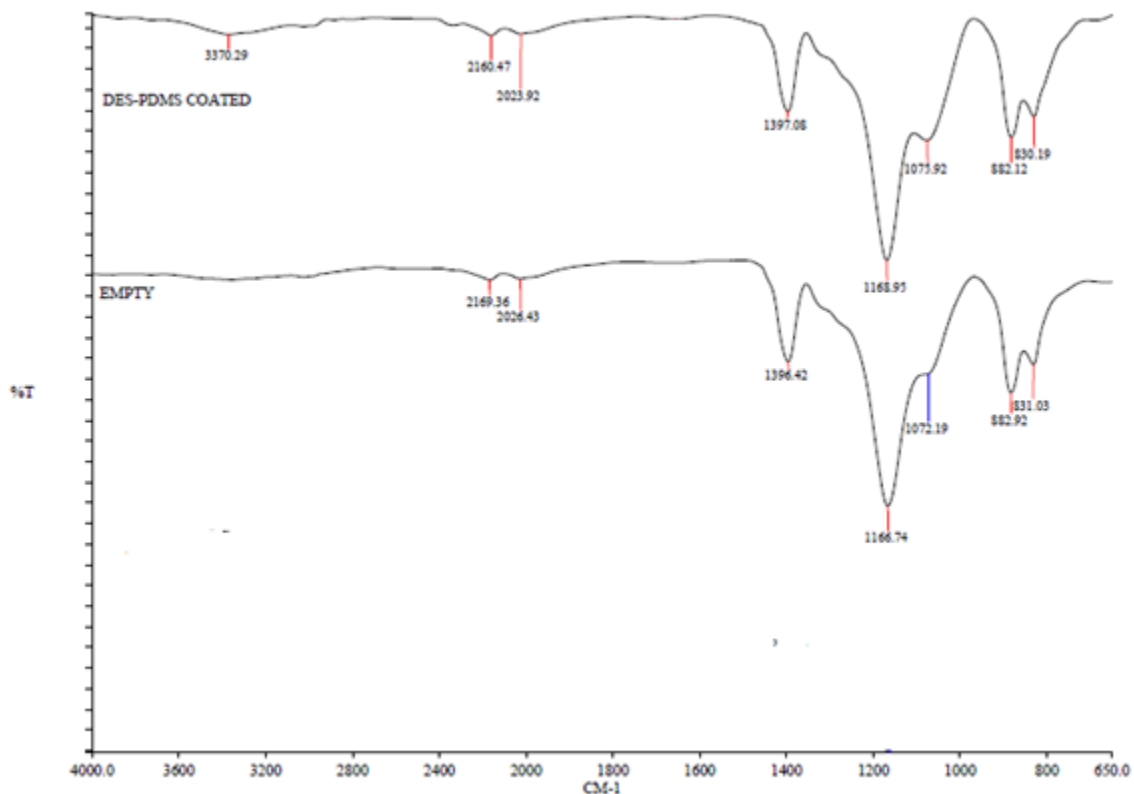


Figure 1. Micrographs of empty PVDF-co-PTFE membrane: (a) cross sectional view and (b) the membrane top surface.

Table 1. Characteristics of empty PVDF-co-PTFE membrane

| | | |
|-----------------------------|----------------|----------------|
| Pore size (μm) | Minimum | 0.6 ± 0.2 |
| | Maximum | 10.5 ± 6.0 |
| Thickness (μm) | 73.8 | |
| Porosity, ε (%) | 73.5 ± 2.0 | |

The FTIR characterization of empty PVDF-co-PTFE and PVDF-co-PTFE/DES supported membranes are shown in Figure 2. The characteristic peaks of PVDF are at 830 cm^{-1} and 882 cm^{-1} . The first peak is assigned to CH_2 rocking vibration and the peak at 882 cm^{-1} is the CH out-of plane deformations [9]. While, three peaks at 1396 cm^{-1} , 1166 cm^{-1} and 1072 cm^{-1} correspond to PTFE structure. The first two bands are assigned to the C-F stretching vibrations of PTFE [10]. Compared with empty PVDF-co-PTFE membrane, the additional spectra of PVDF-co-PTFE/DES supported membrane at 3370 cm^{-1} , which corresponds to N-H stretching, indicates the successful impregnation of DES in PVDF-co-PTFE membrane pores [11].

**Figure 2.** FTIR spectra of membrane samples.

3.2. Gas Permeation

The gas permeation was conducted to evaluate ideal separation properties of both membranes presented in Table 2. The gas permeation of PVDF-co-PTFE/DES supported membrane shows better in both CO_2 permeance and CO_2/N_2 selectivity. In SLM, the main transport mechanism is solution diffusion. A gas molecule dissolves into the membrane, diffuses through the membrane and finally release to the permeate side of the membrane. The carbon dioxide permeability is greatly dependent on its solubility coefficient within the membrane [12]. According to Leron and Li (2013), solubility of CO_2 in the DES was comparable with those in the ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium dicyanamide. Their findings also indicates the CO_2

solubility in the DES are better than CO₂ solubility in those found in 1-ethyl-3-methylimidazolium based ionic liquids [13]. Table 3 shows relative comparison between this works to literature data using different polymer-liquid membrane combination. Although DES is a new green solvent incorporated into the polymer pores, significant improvement of both CO₂ permeance and CO₂/N₂ selectivity somehow is comparable with literature data.

Table 2. CO₂ and N₂ for empty PVDF-co-PTFE and PVDF-co-PTFE/DES supported membrane.

| Membrane | Permeability of N ₂ (GPU) | Permeability of CO ₂ (GPU) | Selectivity, α (CO ₂ /N ₂) |
|-------------------------------------|---|--|---|
| Empty PVDF-co-PTFE membrane | 17 x 10 ³ | 12 x 10 ³ | 0.72 |
| PVDF-co-PTFE/DES supported membrane | 12.7 x 10 ³ | 25.5 x 10 ³ | 2.00 |

*The gas permeation was conducted at 3.5 psi, 27 °C

Table 3. Comparison between literatures

| Membrane support | Liquid | Permeability of CO ₂ (GPU) | Selectivity, α (CO ₂ /N ₂) | Reference |
|------------------|--|---------------------------------------|---|--------------|
| Porous alumina | Ionic liquid 1-(2-(2-(2-Methoxyethoxy)ethoxy)ethy)- 1-methylpyrrolidinium p-toluenesulfonate | 1.12 | 15.42 | [14] |
| Polyethersulfone | 1-n-butyl-3-methylimidazolium tetrafluoroborate | 13.8 | 60 | [15] |
| PVDF-co-PTFE | Deep eutectic solvent | 25.5 x 10 ³ | 2.0 | In this work |

4. Conclusion

Deep eutectic solvent from choline chloride and ethylene glycol has been successfully synthesized and incorporated into PVDF-co-PTFE membrane pores. The membrane was characterized via SEM and FTIR have shown the existence of DES in the membrane. As expected, PVDF-co-PTFE/DES supported membrane show an improvement in both CO₂ permeance and CO₂/N₂ selectivity as compared to empty PVDF-co-PTFE membrane.

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