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Study on CO₂/ N₂ separation: the effect of rubbery polymer coating on PVDF membrane

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Abstract. The emission of harmful gases such as carbon dioxide (CO₂) via gas processing plant and daily human activities gave negative impacts to the environment and global inhabitant. Flat sheet asymmetric membranes were produced from homogenous solution of Poly(vinylidene fluoride) (PVDF) via phase inversion method using N-methyl-2-pyrrolidone (NMP) as the solvent. While the poly ether b-amide (PEBAX) was dissolved by using of (70% ethanol and 30% water) as a solvent and lithium chloride as additives. The morphology and cross section of the produced membranes were observed by Scanning Electron Microscope (SEM). Then, the membranes were tested for chemical analysis to define the presence of PEBAX in the membrane by using Fourier Transform Infrared (FTIR) spectroscopy. The permeation performances of the membranes were evaluated in terms of permeability and selectivity of the membranes by using gas permeation test. Increasing the PEBAX content significantly increased the selectivity of the PVDF membrane to separate the CO₂/N₂ gases but decreased the amount of the gases that passed through the membrane.

1. Introduction

One of the top problems the world is facing nowadays is how to reduce greenhouse gas. Carbon dioxide (CO₂) is one of the main greenhouse gases. More than six and a half billion people burn fuel to keep warm, to provide electricity to light their homes and to run industry, and to move about using cars, buses, boats, trains, and airplanes. The burning of fuel produces carbon dioxide, which is released to the atmosphere. The burning of fuels adds about 6 gigatons of carbon to the atmosphere each year [1].

There are three primary methods for reducing the amount of CO₂ in the atmosphere: employing energy efficiency and conservation practices; using carbon-free or reduced-carbon energy resources; and capturing and storing carbon either from fossil fuels or from the atmosphere. CO₂ capture and sequestration (CCS) could play an important role in reducing greenhouse gas emissions, while enabling low-carbon electricity generation from power plants. CCS technologies are currently available and can dramatically reduce (by 80-90%) CO₂ emissions from power plants that burn fossil fuels. The amount of GHG emissions avoided (with a 90% reduction efficiency) would be equivalent to [2]:

- Planting more than 62 million trees, and waiting at least 10 years for them to grow



- Avoiding annual electricity-related emissions from more than 300,000 homes

Being one of the main greenhouse gases, CO₂ still can be treated by removing it from the atmosphere and storing it deep in the oceans and the soil surrounding the roots of many plants. In industries, the emission of CO₂ is through the combustion of fossil fuel such as coal, oil and natural gas. CO₂ is captured from the flue gas or syngas and will be passed through a series of membranes in order to separate it from nitrogen gas (N₂), sulfur oxide (SO₂) and nitrogen oxide. The separation occurs based on the different molecular size of the gas compositions that are passed through the membrane pores. Therefore, in order to remove the CO₂ in the flue gas or syngas, the thin film composite membranes were developed consisting of PVDF and PEBAX in this research. From literature, the PEBAX membranes are very competitive in performance and economic. It also suitable membranes for separation in terms of its chain rigidity, chain interactions, stereoregularity and polarity of its functional group and offer the ability to separate CO₂ from syngas and in particular hydrogen with reasonable selectivity [3]. Meanwhile, PVDF polymer has excellent, almost universal chemical resistance. It can be used both at high and very low temperatures (-260 to +260°C). It also possesses outstanding resistance to weathering (UV-stability).

The hydrophobicity of the PVDF membranes can be improved through various methods such as physical blending, chemical grafting, and surface modification. However, physical blending with inorganic materials like lithium chloride, glycerol, polyvinyl pyrrolidone or polyethylene glycol provides a great interest due to the ease of handling the materials and good performances. The production of composite membranes of PEBAX and PVDF membranes were observed with SEM for the morphology and tested with FTIR for the chemical analysis while the performances of the membranes were investigated using gas permeation test.

2. Methodologies

2.1 Chemicals

Chemicals used in this study are Poly (vinylidene fluoride) (PVDF) polymer pellets, poly ether amide (PEBAX), N-methyl-2-pyrrolidone (NMP) with 99.5% purity, ethanol and Lithium Chloride (LiCl). The pure CO₂ and N₂ gases were ready in Chemical Engineering Laboratory, Universiti Malaysia Pahang.

2.2 Membranes Preparation

To prepare the microporous support membrane, a casting solution of 10 wt % PVDF in 80 wt % NMP and 10 wt % lithium chloride was prepared. This membrane was cast at a casting speed of 3.5 m/min and casting thickness of 178 µm. The membranes were precipitated in water, washed for 24 hours, and dried in an oven at 80°-100° C. After that, the casting membranes of PVDF membranes were coated with the PEBAX solution which is 90 wt % of (70% ethanol and 30% water), 4 wt % of PEBAX and 6 wt % of lithium chloride which is (90:4:6) for first ratio and followed by (90:6:4), and (90:2:8) for the second and third ratio as shown in the Table 1.

Table 1. The PEBAX and LiCl compositions in the membranes

Composite Membrane	PEBAX content (wt%)	LiCl content (wt%)
A(90:2:8)	2	8
B(90:4:6)	4	6
C(90:6:4)	6	4

2.3 Chemical and Physical Characterization

The thin film composite (TFC) membrane will be analyzed physical and chemically by using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) devices. The SEM device was used to examine the membrane morphology. The FTIR is use for chemical characterization of the membrane.

2.4 CO₂/N₂ Separation Test

The TFC membrane was then tested with CO₂/N₂ separation test. The pressure-normalized fluxes were measured for the desired gases at certain temperature and pressure. According to researchers, (1) was used to determine the permeance through membranes [4,5]. The calculation for the gas permeability, P is shown in (2). Meanwhile, selectivity was calculated using (3).

$$\left(\frac{P}{l}\right) = \frac{V}{(At\Delta P)} \quad (1)$$

where P is permeability, l is the thickness of membrane, A is the effective membrane area, V is the volume displaced in time(s) and ΔP is the pressure differences across the membrane.

$$P = \frac{Vl}{At\Delta P} \quad (2)$$

The membrane selectivity is the membrane ability to separate 2 gases which is A and B. It is the ratio of the permeabilities of A and B as shown in (3).

$$\alpha_{AB} = \frac{P_A}{P_B} \quad (3)$$

To study the effect of feed pressure to the performance of the membrane, the feed pressure was varied from 0.5 to 1 bar. Similar type of method was applied to get the permeability and selectivity of the produced membrane.

3. Results and Discussion

3.1 Effect of different PEBAX ratio on the PVDF Membrane Morphology

The top layer of a membrane usually consist of a finger-like macro void structure that can be observed in most types of membrane that is fabricated through phase inversion method as the exchange rates of solvent and non-solvent occur rapidly. Figure 1 (a-c) shows the cross-sectional morphology of the prepared PVDF membrane with 90:2:8 ratio of PEBAX. The structure is more like a macro porous structure in the membrane cross-section with addition of additive on PEBAX ratio to the membrane casting solution.

According to [6], only small amount of LiCl added to the casting solution can significantly increase the viscosity of the solution. The viscosity of the polymer casting solution is the main parameter which affects the kinetics of the phase inversion that affects the structure and performance of the produced membrane. The cross-section morphology of the PVDF membranes indicated that with more additives on PEBAX ratio to the casting solution have improved the structure of the membrane to be more sponge-like structure as illustrated in Figure 1 (b-c). This phenomenon could be caused by the strong interaction between LiCl and NMP. As reported by [7], a great increase in viscosity was observed when NMP was used as solvent instead of DMAc although same amount of LiCl added to the solutions and this indicates that LiCl exhibit a stronger interaction with NMP than DMAc.

Increasing the additive on PEBAX ratio concentration demonstrated a better morphology and the finger-like macro voids are suppressed. The above observations were believed to be associated with the change of the thermodynamic and kinetic properties of the casting solution after the addition of additive on PEBAX ratio. The strong interactions between LiCl, polymer and solvent have increased the viscosity of casting solution that caused the delayed in liquid-liquid demixing process and lower the phase separation rate. This will result in the suppression of the macro voids and provided less porous sponge-like structure [8,9].

3.2 Chemical Analysis using FTIR

FTIR is an important analysis as it provides the support data for the results obtain in this research. FTIR will demonstrate the bands that show the functional group of the membranes and provide information about the molecular interaction between the components contain inside the polymer solution. The significant peaks formed indicated the molecular orientation of the molecules. The distribution of the functional groups present in the membrane and the allocation of the peaks of interest are tabulated in Table 2.

The same bands of PVDF functional group will appear at all the membrane as the same type of membrane was used. The C-H stretches vibration in vinylidene groups of the PVDF chain have wavelength of $3000 - 3020\text{ cm}^{-1}$ were detected in all the PVDF membranes together with C-F stretch alkyl halides that appeared at 1400 cm^{-1} . A sharp and strong peak detected around 837 cm^{-1} which belong to the C-Cl group indicated the presence of LiCl in the membranes while pure PVDF membrane without additive shows a rough and weak peak at the same wavelength [10,11,12].

3.3 The Performance of Membrane using Gas Permeation Test

Figure 2 illustrate the CO_2/N_2 gas permeance and CO_2/N_2 selectivity. The test was carried out at room temperature with the feed pressure of 1.0 bar. As can be seen, higher amount of additive

results in increase of CO₂/N₂ selectivity. This could be caused by the compactness of the membrane at high addition of LiCl that leads to a decrease in the fractional free volume of the membrane and this will consequently higher CO₂/N₂ selectivity [13].

Polymeric membrane exhibit the performance of quite high CO₂/N₂ selectivity but quite low CO₂ permeability and most of the polymeric membrane for gas separation in post-combustion will worked at below 200°C due to low permeability.

Table 2. Characteristic IR absorption for the functional groups present in the membrane

Sample	Allocation	Functional Group	Wavenumber (cm ⁻¹)
a	C-H stretch	Alkanes (vinylidene group) (ether b-amide)	3000
	C-F stretch	Alkyl Halide	1400
	C-Cl stretch	Alkyl Halide (presence of LiCl)	838
b	C-H stretch	Alkanes (vinylidene group) (ether b-amide)	3020
	C-F stretch	Alkyl Halide	1400
	C-Cl stretch	Alkyl Halide (presence of LiCl)	837
c	C-H stretch	Alkanes (vinylidene group) (ether b-amide)	3019
	C-F stretch	Alkyl Halide	1400
	C-Cl stretch	Alkyl Halide (presence of LiCl)	837

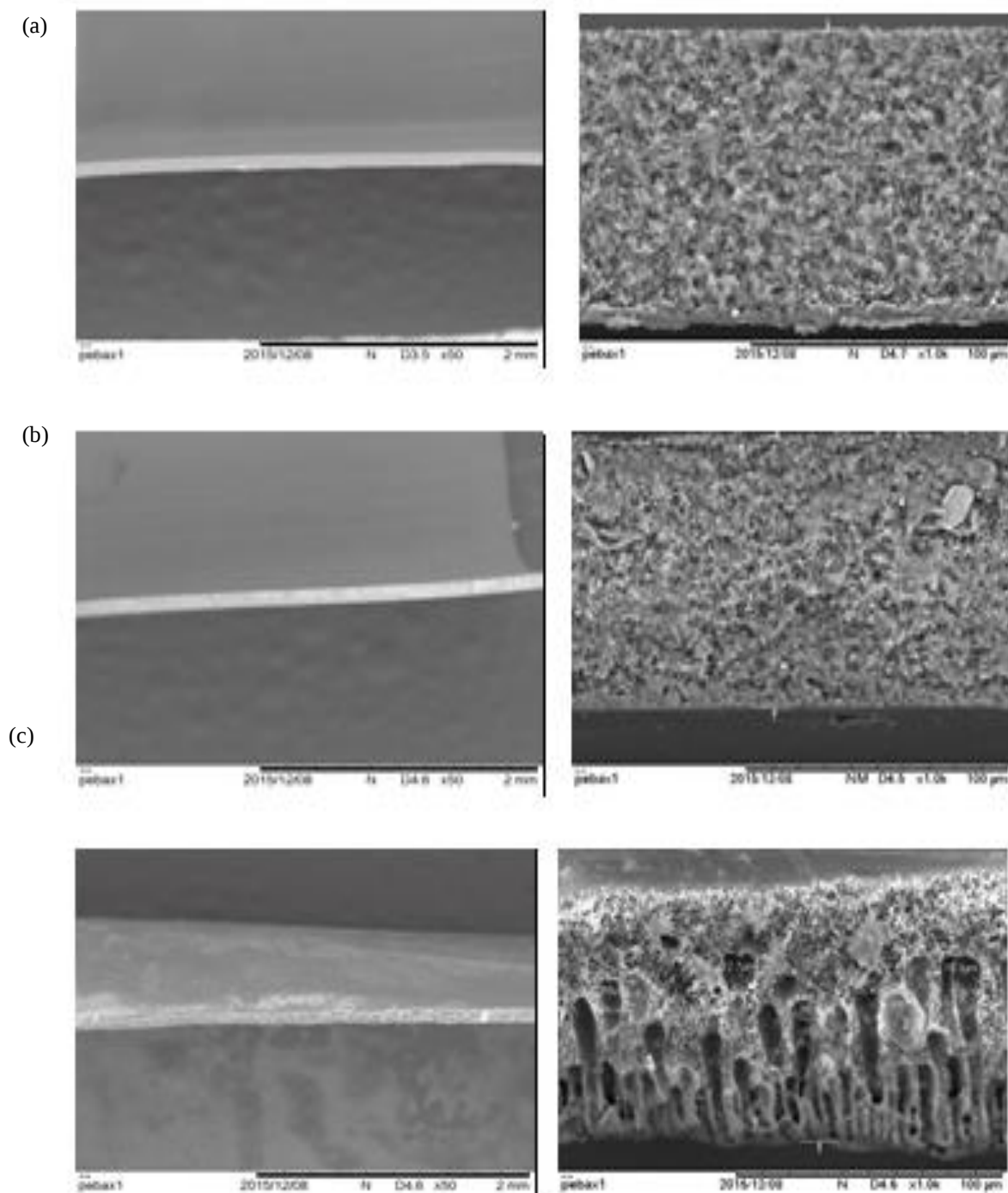


Figure1. Cross-section of flat sheet membranes in different PEBAX ratios (a) 90:2:8, (b) 90:4:6, (c) 90:6:4.

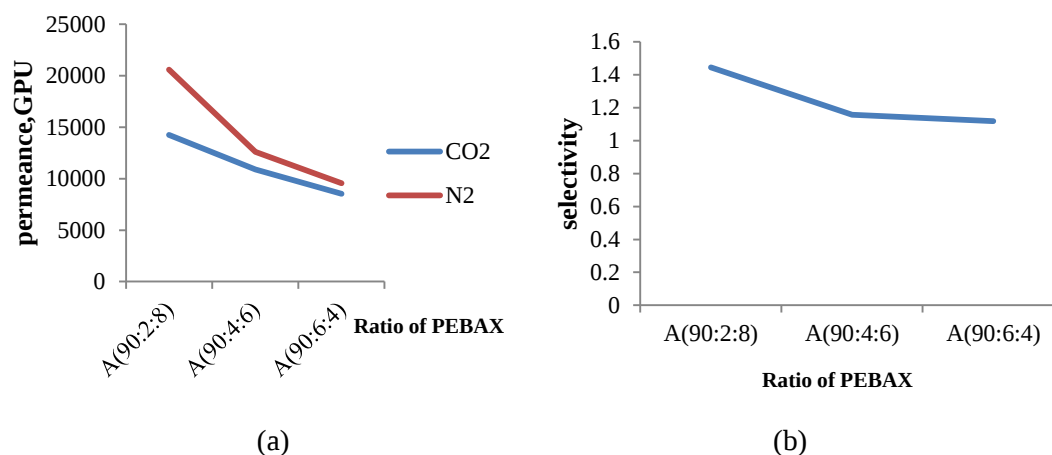


Figure 2. (a) Graph of permeance of CO₂/N₂ vs Ratio of PEBAX, (b) Graph of selectivity CO₂/N₂ vs Ratio of PEBAX.

4. Conclusion

This study successfully developed the TFC PVDF/ PEBAX membrane. More sponge-like asymmetric structures were formed across the membrane wall and the macro void formation is suppressed. This is due to the higher viscosity of the casting solution that delayed the phase inversion rate (kinetic effect) which results in a sponge-like structure.

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