Poly(Ethylene Oxide)-block-Polysulfone-block-Poly(Ethylene Oxide) / Poly(ether-block-amide) Composite Membrane for Carbon Dioxide Separation

Thesis by
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Polyethylene Oxide-block-Polysulfone-block-Polyethylene Oxide / poly(ether-block-amide) Composite Membrane for Carbon Dioxide Separation.

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This research study describes the gas separation performance of different sets of Polyethyleneoxide-block-Polysulfone-block-Polyethyleneoxide/poly(ether-block-amide) (PEO-b-PSU-b-PEO/Pebax) composite membranes for CO\textsubscript{2} separation from N\textsubscript{2} and CH\textsubscript{4}. Gas permeation properties of the membranes prepared were studied at ambient temperature (21\textdegree C) and 8bar. The dependence of gas flux and selectivity on pressure was explored for different pressures from 2.5 bar up to 19 bar also at ambient temperature.

Pebax/PAN composite membranes have a range of CO\textsubscript{2} permeance of 4467±274 GPU, 365±64 GPU for CH\textsubscript{4} and 152±17 GPU for N\textsubscript{2} with CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities ranges of 30 and 13 respectively. Improved CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities coupled with flux reduction were obtained from the introduction of PEO-b-PSU-b-PEO films on Pebax/PAN composite membranes. The gas flux reduced to about one-tenth of Pebax/PAN membrane’s while the selectivities obtained for all the PEO-b-PSU-b-PEO/Pebax/PAN membrane range from 33 to 60 for CO\textsubscript{2}/N\textsubscript{2} and 17 to 33 for CO\textsubscript{2}/CH\textsubscript{4} as the thickness of PEO-b-PSU-b-PEO top layer increases.
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CHAPTER 1
INTRODUCTION

Global warming and climate change are two important topics being commonly discussed. They are caused by the combustion of fossil fuels (e.g. natural gas) and other human activities which emit carbon dioxide into the atmosphere. Carbon dioxide concentration in the atmosphere has been projected to double by 2050 if measures are not taken to control its release into the atmosphere[1]. Thus, in order to reduce carbon dioxide emission into the atmosphere, it is important to separate carbon dioxide from different sources (especially power plants and chemical industries) as well as from natural gas prior to its combustion. Natural gas may contain up to 4%-50% carbon dioxide (depending on the source) which has to be removed during natural gas pre-processing to reduce its escape into the atmosphere and also to meet the typical natural gas pipeline specification (about 2% or less in the US)[2], raise its heating value, prevent corrosion in pipelines and prevent crystallization during the liquefaction process.[3]

Conventional methods used for carbon dioxide isolation from gas streams include adsorption and absorption, cryogenics and membranes. In adsorption, solid adsorbents such as activated carbons, zeolites, several amine enriched sorbents and other materials are used to preferentially remove carbon dioxide from gas mixture [4] but activated carbons are the most versatile because of their extremely high surface area and micropore volume [5]. Liquid solvents (mostly amines) are used in absorption operations. In
absorption, gaseous components are bubbled through an amine solution and the alkaline amine solution absorbs the acidic carbon dioxide alone. Later, a thermal process is used to release the CO₂. This process is costly and needs a large area [6]. Cryogenics involves liquefaction of carbon dioxide at a temperature-pressure domain which makes it easy to be separated them from other gases. Low temperatures (near -100°C) and high pressures of about 40 bars are needed to operate this separation process.

However, many existing processes for carbon dioxide separation have become less attractive due to increase in the cost of energy, hence some alternative processes with lower energy consumption have to be developed [7]. Such processes should have simple designs, require lower energy to operate, be highly reliable and flexible. These properties are offered by membranes and have therefore drawn more attention for adoption in carbon dioxide and other gas separation processes [7],[8].

A wide range of materials is used for making membranes but most gas separation membranes are being made of polymers because polymeric membranes offer high separation efficiency. More research work is on-going to improve the performance (selectivity and flux) of these membranes through chemical (cross-linking) or physical modification (addition of fillers into polymer matrix) [9].

1.1 Aims and Organisation of the Thesis

Many works have been reported on developing membranes for CO₂ separation from light gases. This study seeks to harness the high affinity of ether oxygen in polyethylene oxide
(PEO) for CO\textsubscript{2} by using two PEO-based block copolymers i.e. di-block poly(amide-b-ether) and tri-block polyethyleneoxide-block-polysulfone-block-polyethyleneoxide (PEO-b-PSU-b-PEO) polymers to fabricate composite membranes for CO\textsubscript{2} separation from nitrogen and from methane as well.

This thesis is made up of five chapters. Introduction is written in the first chapter. Chapter Two elaborates on the theory of gas permeation through polymeric membranes and various factors affecting membrane performance. Later in this chapter, Henis and Tripodi [10] model used for gas transport analysis through composite membranes is applied to predict the resistances of the membranes made in this work to gas permeation. Chapter three presents the materials used for this work, experimental procedures, and membrane characterization. The results obtained from the work are presented and discussed in chapter four while deductions from experimental findings and their discussions are put together as conclusion in chapter Five.

1.2 Research Questions

This thesis will discuss questions and observations such as:

- How does PEO-b-PSU-b-PEO tri-block polymer affect gas permeation performance of Pebax composite membrane for CO\textsubscript{2} separation from nitrogen and methane on the basis of pure gas permeation test?

- Variation of gas permeances of the multilayer PEO-b-PSU-b-PEO/Pebax membrane with pure gas (N\textsubscript{2}, CH\textsubscript{4}, and CO\textsubscript{2}) feed pressure.
• Responses of CO₂/ N₂ and CO₂/CH₄ selectivities to increase in gas feed pressure for the membranes?

• Relationship between film thickness, high sorbing gases and membrane swelling

• Membrane morphology as observed under Scanning Electron Microscope.
CHAPTER 2

THEORY AND APPROACH

2.1 Mechanism of Gas Transport in Membranes

According to Sir Thomas Graham, the solution-diffusion model is often used to describe gas transport through dense, nonporous polymeric films. In this model, high pressure feed gas molecules with upstream pressure $P_2$ are absorbed into the membrane, diffuse through the membrane, and eventually desorb on its other side at low pressure $P_1$. This is understood to be driven by pressure difference across the membrane. The rate controlling step in penetrant permeation is diffusion and it involves gap creation in the matrix of the polymer as a result of random local segmental polymer motions, thermally stimulated, in order to accommodate penetrant molecules [11]. Fig. 2.1 presents a schematic of gas transport across a membrane.

![Fig. 2.1: Schematics of gas permeation through a polymer film](image-url)

Membrane

Upstream/High Pressure Side

Downstream/Low Pressure Side

Flux, $N_A$

Lighter gas molecules

Heavier gas molecules
In rubbery polymers, gas sorption often obeys Henry’s law while gas diffusion obeys Fick’s law (provided that polymer does not crystallize in the presence of gas). Thus at low gas concentration, the diffusivity does not typically depend on gas concentration [12]. At high pressures, polymer swells due to high concentration of sorbed gas leading to a situation where gas sorption may deviates from Henry’s law (equation 2.1). Flory-Huggins expression written in equation 2.2 is used to describe the penetrant concentration in the polymer under this condition [13].

\[ C = K_D p \]  \hspace{1cm} 2.1

\[ \ln \frac{p}{p_o} = \ln(1 - v_p) + v_p + \chi v_p^2 \]  \hspace{1cm} 2.2

where \( K_D \) is the Henry’s law constant, \( C \) is the concentration of gas in the polymer, \( p_o \) is the penetrant vapour pressure, \( p \) is penetrant pressure in contact with the polymer, \( v_p \) is the volume fraction of the polymer, and \( \chi \) is the Flory-Huggins parameter.

For glassy polymers, the dual sorption model is popularly used to describe sorption. In this model, sorption is conceptualized to occur in two idealized environments i.e. in the dense polymer matrix and in the polymer’s non-equilibrium excess volume. The first mode of sorption, described by Henry’s law, is assumed to be similar to sorption in rubbery polymers while the second population is viewed to be due to uptake of penetrant molecules into microvoids of the polymer. This is termed hole-filling or Langmuir mode[13], [14] and it is expressed mathematically as;
\[ C = C_D + C_H \]  

\[ C = K_D p + \frac{C'_H b p}{1 + b p} \]

where \( C'_H \) is the Langmuir sorption capacity, \( b \) is the Langmuir affinity parameter. Fig. 2.2 [13] shows a schematic representation of unrelaxed, non-equilibrium, excess volume that is responsible for Langmuir sorption in a glassy polymer.

**Fig. 2.2:** Schematic representation of unrelaxed, non-equilibrium, excess volume, \( V_g - V_l \), in a glassy polymer.
2.2 Permeability, Selectivity and Separation Factor

Consider the gas transport through a thin polymer film of thickness $l$ as shown in figure 2.3 above, $c'$ is the concentration of the gas just at the polymer film-gas interface upstream, $c''$ is the concentration of the gas just at the polymer film-gas interface downstream, $p'$ is the pressure upstream (high) while $p''$ is the downstream pressure (low). According to Henry’s law, the gas concentrations in the polymer at these points are proportional to the pressures and thus can be expressed as:

$$C' \sim p'$$  \hspace{1cm} 2.5

$$c' \sim p'$$  \hspace{1cm} 2.6

Including Henry’s law proportionality constant, $S$, in eq. 2.5 and eq.2.6 gives:

$$c' = Sp'$$  \hspace{1cm} 2.7

$$c'' = Sp''$$  \hspace{1cm} 2.8
Also, Fick’s law is used to describe one-dimensional gas flux through the membrane. With respect to the x direction it is given by [12]:

\[ J = -DA \frac{dc}{dx} \]  

2.9

Since the concentration profile of the penetrant is linear within the polymer film, we can write eq. 2.9 as:

\[ J = DA \frac{c' - c''}{l} \]  

2.10

Substituting eq. 2.7 and 2.8 into 2.10 gives:

\[ J = DA \frac{S(p' - p'')}{l} \]  

2.11

After rearrangement and replacing \((p' - p'')\) with \(\Delta p\), eq.2.11 becomes;

\[ J = DS.A \frac{\Delta p}{l} \]  

2.12

The product \(D.S\) is the permeability coefficient, \(P\), of the polymer film.

The permeability coefficient is the parameter commonly used for characterizing the rate of gas transport through polymeric membranes. For the polymer film of thickness \(l\) (cm) described above, the permeability, \(P_A\) (\(cm^2.cm/cm^2.s.cmHg\)), of a pure gas A, through it is given by [12], [15]:

\[ P_A = \frac{J_A \cdot l}{(p_1 - p_2)} = \frac{J_A}{-\Delta p/l} \]  

2.13
Where $J_A (\text{cm}^3/\text{cm}^2\cdot\text{s})$ is the steady state gas flux through the membrane, $p_1$ and $p_2 (\text{cmHg})$ are the downstream and upstream pressures respectively, and $\Delta p$ is defined as $(p_2 - p_1)$.

$D$ is gas diffusivity, $dC_A/dx$ is the concentration gradient of the gas in the polymer,

For a binary gas mixture with components A and B permeating a membrane, the ratio of the pure gas permeabilities, $P_A$ and $P_B$ gives the ideal selectivity, $\alpha_B^A$, of the membrane for gas A over gas B [15]:

$$\alpha_B^A = \frac{P_A}{P_B} \quad 2.14$$

Substituting eq. 2.12 into 2.13,

$$\alpha_B^A = \frac{D_A S_A}{D_B S_B} \quad 2.15$$

where $D_A/D_B$ is the mobility or diffusivity selectivity and $S_A/S_B$, the solubility selectivity [16].

For the same binary gas system mentioned above, the separation factor, $\alpha_{AB}^*$, for component A relative to component B can be expressed as:

$$\alpha_{AB}^* = \frac{y_A/y_B}{x_A/x_B} \quad 2.16$$

where $x_j$ is the mole fraction in of component $j$ in the upstream gas phase and $y_j$, the mole fractions of component $j$ in the downstream phase.
2.2.1 Factors Affecting Gas Permeability and Permselectivity

Temperature is one of the major factors that influence gas permeability, diffusivity and solubility in polymers. This is due to the fact that gas diffusion and dissolution are thermally activated processes [12]. However, gas diffusivity has a stronger dependence on temperature than solubility coefficient and as a result permeability usually increase as temperature increases [12]. Van’t Hoff equation is used to express the temperature dependence of diffusion coefficients and permeability while Arrhenius equation is employed to describe the dependency of solubility coefficient on temperature as shown in the equations below [17]:

\[ D = D_o \exp\left\{ -\frac{E_d}{RT} \right\} \]  \hspace{1cm} 2.17

\[ P = P_o \exp\left\{ -\frac{E_P}{RT} \right\} \]  \hspace{1cm} 2.18

\[ S = S_o \exp\left\{ -\frac{\Delta H_S}{RT} \right\} \]  \hspace{1cm} 2.19

Where \( D_o, S_o, P_o \) are pre-exponential factors, \( E_d \) is the activation energy of diffusion, \( E_P \) is the activation energy of permeation. \( \Delta H_S \) defines the overall enthalpy difference between penetrants in the pure penetrant phase and penetrant sorbed in the matrix of the polymer. Thus, from the eq. 2.17 - 2.19;

\[ P = D_o S_o \exp\left\{ -\frac{\Delta H_S + E_d}{RT} \right\} \]  \hspace{1cm} 2.20
where \( P_o = D_o S_o \) and \( E_p = \Delta H_s + E_d \).

Likewise, the diffusivity of penetrant is a strong function of polymer fractional free volume (FFV), which is the fraction of the total polymer specific volume unoccupied by polymer molecules and is available for penetrant transport. The relationship between diffusivity and FFV is summarized in Doolittle equation [18]:

\[
D = A \exp \left( \frac{-b}{FFV} \right)
\]

where \( b \) and \( A \) are constants peculiar to polymer-penetrant system.

### 2.3 Conventional Membrane Materials

The selectivity of a membrane is dependent on the nature of the polymer because flexibility or rigidity of polymer chains affects gas permeation. Rubbery polymers have flexible chains which can far more easily be rotated than the more rigid chains in glassy polymers. Thus, rubbery polymers have much shorter relaxation time, larger free volume, exhibit higher flux and lower permselectivity compared to glassy polymers.

The overall permselectivity of polymeric membranes usually comes from contributions of solubility selectivity and diffusivity selectivity [16]. For rubbery polymeric membrane materials, the rate controlling mechanism in the permeation process is dissolution hence the contribution of solubility selectivity is much higher than diffusivity selectivity. In contrast, diffusion is the dominant mechanism for gas sorption in glassy polymeric
membranes. Thus, rubber polymers are more appropriate for separating gases that can be easily condensed while glassy polymers are well suited for separation of light gases [19]. For polymeric membranes, it is a common experience that polymers with high permeability often have low selectivities and vice versa [11]. To illustrate this, table 2.1 shows CO₂ permeabilities and CO₂/N₂ selectivities for some rubbery and glassy polymers.

**Table 2.1: Gas permeability and selectivity of some conventional rubbery and glassy polymers [19]**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T°C</th>
<th>P₇CO₂ (Barrer²)</th>
<th>α₇CO₂/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methylacrylate), PMA</td>
<td>35</td>
<td>0.62</td>
<td>31</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>35</td>
<td>4.6</td>
<td>25.6</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>35</td>
<td>5.5</td>
<td>23.9</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>35</td>
<td>6.5</td>
<td>25</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>35</td>
<td>12.4</td>
<td>23.8</td>
</tr>
<tr>
<td>6FDA-TAPA Polyimide</td>
<td>35</td>
<td>65</td>
<td>30</td>
</tr>
<tr>
<td>Poly(1-trimethylsilyl-1-propyne)</td>
<td>35</td>
<td>2800</td>
<td>5.6</td>
</tr>
<tr>
<td>Natural rubber</td>
<td>25</td>
<td>134</td>
<td>15.4</td>
</tr>
<tr>
<td>Poly(cis-isoprene)</td>
<td>35</td>
<td>191</td>
<td>13.2</td>
</tr>
<tr>
<td>Silicone-nitrile copolymer</td>
<td>25</td>
<td>670</td>
<td>20.3</td>
</tr>
<tr>
<td>Polydimethylsiloxane (PDMS)</td>
<td>35</td>
<td>4553</td>
<td>3.37</td>
</tr>
</tbody>
</table>

Table 2.1 shows that of all the polymers listed, PDMS has the highest selectivity and the lowest CO₂/N₂ selectivity while PMA has the lowest CO₂ permeability but the highest CO₂/N₂ selectivity. Comparison among the polymers in the list shows that high permeability is often accompanied by low selectivity and vice versa. It is therefore not easy to obtain a combination of high permeability and high selectivity for a particular

---

² Barrer = 10⁻¹⁰ cm³(STP).cm/(cm².s.cm.Hg)
polymer [19]. Permeability and selectivity were recognized as trade-off parameters and the trade-off was shown to be related to an upper bound relationship which is expressed as $P_i = k \alpha^{n_{ij}}$, where $P_i$ is the permeability of the more permeable gas, $\alpha$ is the selectivity $(P_i/P_j)$, $k$ is a constant which depends on $n$, $n$ is the slope of the log-log limit and it is dependent on gas molecular kinetic diameter obtainable from the Lennard-Jones potential [13][20]. Fig. 2.4 and Fig. 2.5 show the Robeson upper bound correlation for separation of CO$_2$/CH$_4$ and CO$_2$/N$_2$ which are the gas pairs of interest in this work [20].

![Fig. 2.4: Upper bound correlation for CO$_2$/N$_2$](image)

![Fig. 2.5: Upper bound correlation for CO$_2$/CH$_4$](image)
2.4 PEO-based Polymers for Carbon dioxide Separation

Polar ether oxygen molecules have high affinity for CO$_2$ and this has drawn much attention to designing polymers containing PEO for CO$_2$ separation. This high affinity for CO$_2$ is as a result of high oxygen content in PEO. However, it is not easy to make a defect-free film with PEO because of its high crystallinity [21]. Thus, several ways have been devised to reduce the crystallinity of PEO so that it would be more useful in CO$_2$ separation. These methods include: designing highly branched, cross-linked networks with high PEO concentration; fabricating a phase separated block with ethylene oxide chains; using poly(ethylene glycol), PEG, or low molecular weight liquid PEO as an additive to other polymers [22–24].

Since PEO-based copolymers have been identified as good candidates for carbon dioxide separation membranes [25–27], many works have been reported on developing PEO-based membranes for carbon dioxide separation from mixture of light gases such as H$_2$, CH$_4$ and N$_2$. PEO-containing block copolymers such as Pebax, poly(ethylene oxide-b-polysulfone) (PEO-b-PSU), poly(ethylene oxide–b-butylene terephthalate) (PEO-PBT) etc. have been synthesized to fabricate membranes which for carbon dioxide separation analysis and permeation studies[24] [28].

Car et al [22] reported PEG modified Pebax membranes for CO$_2$ separation. Pebax® 1657 was blended with low molecular weight PEG, with PEG content ranging from 10%-50%. Dense films membranes were prepared and their gas transport properties for H$_2$, N$_2$, CH$_4$ and CO$_2$ were studied at 30°C. They found out that the PEG modified Pebax
have higher CO₂ permeability and diffusivity coefficient than pristine Pebax. Both CO₂ has higher CO₂ permeability and the diffusivity coefficient than pristine Pebax. Both CO₂ permeability and diffusion coefficients increase with PEG content. However, changes in CO₂/N₂ and CO₂/CH₄ selectivities and the solubility coefficient with increasing PEG were slight as shown in Table 2.2.

Table 2.2: CO₂ permeability, diffusivity, solubility coefficients measured at 30°C and CO₂/light gas selectivity for Pebax® 1657 and its blend with PEG [22].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_{CO_2}$ b</th>
<th>$D_{CO_2}$ c</th>
<th>$S_{CO_2}$ d</th>
<th>$\alpha_{CO_2/H_2}$</th>
<th>$\alpha_{CO_2/N_2}$</th>
<th>$\alpha_{CO_2/CH_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pebax®</td>
<td>24.8(73)</td>
<td>4.6</td>
<td>5.3</td>
<td>9.1</td>
<td>45</td>
<td>15.6</td>
</tr>
<tr>
<td>Pebax®/PEG10</td>
<td>25.6(75)</td>
<td>4.9</td>
<td>5.2</td>
<td>9.2</td>
<td>47</td>
<td>15.8</td>
</tr>
<tr>
<td>Pebax®/PEG20</td>
<td>27.2(80)</td>
<td>5.1</td>
<td>5.4</td>
<td>9.3</td>
<td>45</td>
<td>15.9</td>
</tr>
<tr>
<td>Pebax®/PEG30</td>
<td>35.8(105)</td>
<td>6.2</td>
<td>5.8</td>
<td>9.6</td>
<td>43</td>
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<tr>
<td>Pebax®/PEG40</td>
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<td>8.0</td>
<td>5.6</td>
<td>10.0</td>
<td>44</td>
<td>15.1</td>
</tr>
<tr>
<td>Pebax®/PEG50</td>
<td>51.3(151)</td>
<td>9.6</td>
<td>5.3</td>
<td>10.8</td>
<td>47</td>
<td>15.5</td>
</tr>
</tbody>
</table>

In another work by Car et al [24], gas permeation properties of polymeric dense membranes made from segmented block PEO-PBT, commercially referred to as Polyactive®, was reported for carbon dioxide separation from H₂, CH₄ and N₂. They found that CO₂ permeability increases with increasing molecular weight of the PEO content of the block copolymer as shown in Fig. 2.6 [24].

b Permeability coefficient $[\text{mol/m}^2\cdot\text{s.Pa}] \times 10^{15}$ (Barrer)
b Diffusivity coefficient $[\text{m}^2/\text{s}] \times 10^{11}$

Solubility coefficient $[\text{mol(STP)/m}^3\text{Pa}] \times 10^{4}$. 
In earlier reports by Matteucci et al [29] and Hirayama et al [21], an increase in PEO crystalline phase in the PEO-based block copolymers they synthesized caused a sharp reduction in diffusivity and solubility leading to decrease in permeability. Based on this,

![Permeability of PEO as a function of Mw of PEO in Polyactive® measured at 30°C](image)

**Fig. 2.6:** Permeability of PEO as a function of Mw of PEO in Polyactive® measured at 30°C

Car et al aimed at improving the performance of the PEO-PBT block copolymers by adding 50wt% low molecular weight PEG (200 gmol⁻¹) which helped to reduce/destroy the crystallinity of the PEO phase as well as increasing the content of the EO units. This resulted in membranes with slightly higher permeability, higher selectivity for CO₂/N₂ and moderate selectivity for CO₂/CH₄ as shown in Table 2.3 [24]. The CO₂/N₂ and CO₂/CH₄ selectivities decreased with increasing PEG content except at 30wt% PEG
content when CO₂/N₂ selectivity hits a peak. The effects of PEG in different polymer chains on CO₂ transport have been reported in other studies which also proved ether oxygen positive influence on CO₂ transport in rubbery and glassy polymers [30–32].

Table 2.3: Permeability and permselectivity of PEG blend membranes with polymer 1500PEO77PBT23

<table>
<thead>
<tr>
<th>PEG [wt %]</th>
<th>Permeability (Barrer)</th>
<th>Permselectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂ N₂ CH₄ CO₂ α₁₂</td>
<td>α₂₁</td>
</tr>
<tr>
<td>0</td>
<td>113 2.52 6.76 115 10.2</td>
<td>45.6 17</td>
</tr>
<tr>
<td>10</td>
<td>11.8 3.1 7.63 130 11 42.1</td>
<td>17</td>
</tr>
<tr>
<td>20</td>
<td>11.5 3.2 8.3 126 11 40 15.2</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>12.1 2.8 8.9 134 11.1 48.7 15.1</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>10.8 3.8 7.6 114 10.6 30.1 15</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>10.1 3.0 7.5 110 10.9 36.9 14.7</td>
<td></td>
</tr>
</tbody>
</table>

Bondar et al [33] also studied gas permeation properties of dense isotropic films of different grades of Pebax segmented block copolymers containing hard polyamide phase of nylon 6 [PA6] or nylon 12 [PA12] and PEO or poly(tetramethylene oxide) as the rubbery polyether phase [34]. They found out that the Pebax copolymers studied exhibit high selectivity for polar/nonpolar gas. The selectivities obtained for CO₂/N₂ and for H₂ /CO₂ were 56 and 9.8 respectively. In both cases, the high selectivities was as a result of high solubility selectivity attributed to high carbon dioxide solubility in the copolymers due to the strong affinity of the polar ether linkages for carbon dioxide. Furthermore, they
noted that the Pebax copolymers grade containing higher concentrations of polar ether repeating units have higher CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/H\textsubscript{2} solubility selectivity.

Other studies which have been reported about understanding the relationship between structural features and transport properties of PEBAX were reported by Sheth et al. and Alberola et al. [35], [36]. The results reported in all the studies confirm the affinity of polyether oxygen for carbon dioxide, hence PEO containing block copolymers as good candidate materials for fabricating membranes for CO\textsubscript{2} separation. Thus, for this work, PEO-based PEO-b-PSU-b-PEO and Pebax have been used to make composite membranes for CO\textsubscript{2} separation due to the high content of PEO in their chains.

### 2.5 Composite Membranes for Gas Separation

From the expression for estimating permeability through a dense membrane, the permeability of a membrane varies inversely with its thickness. Typically, high permeability and selectivity are desired of a good membrane for gas separation and these are usually targeted by designing dense membranes of very low thickness. However, such dense film of low thickness might not have the required mechanical strength especially when the membrane is used for high pressure gas applications. Addressing this limitation has led to the development of composite membranes.

A composite membrane consists of one or more thin films applied onto suitable support of inorganic or organic materials. The support material must be highly permeable, and stable with respect to their shape. The permselective separating layer is coated onto the
surface of the porous support which provides mechanical strength to the film of the permselective membrane material. In order to allow for great gas flow during gas separation, it is desirable to make the permselective film as thin as possible, e.g. 0.5-3\(\mu\)m [37].

2.5.1 Methods of Making Composite Membranes

Generally, a composite membrane can be prepared using various techniques like interfacial polymerization and dip coating. Interfacial polymerization is a well-established method of preparing dense and thin active layer for composite membranes [38]. It is based on a polycondensation reaction between two monomers dissolved in immiscible solvents. Usually, one of the immiscible phases impregnates the substrate and an ultra-thin film which remains attached to the substrate is instantaneously formed when the two immiscible phases interact following the reaction of the monomers at the interfacial boundary [38]. Interfacial polymerization technique has potential implication in fabricating nanocomposites for microencapsulation in drug delivery, chemical and biological sensors etc. [38]

In dip coating, an ultrafiltration or a microfiltration membrane as a support layer and a solution of a material is coated on it as the active layer. The support layer comprises pores of regularly size and the support layer has dense structure with very few pores. Thus the mechanical strength of the composite membrane is derived from the support while the thin film coating gives the permselective function. Dip coating is the most widely used technique.
Different configurations are possible as it is possible to coat more than one layer of polymer film on a microporous support. Thus a composite membrane may be a single-layer composite membrane or a multi-layer composite membrane. Fig. 2.7 and Fig. 2.8 [39] show schematics of two different configurations of composite membranes.

![Fig. 2.7: Single layer composite membrane](image1)

![Fig. 2.8: Double layer composite membrane](image2)

### 2.5.2 Resistance Model for the Composite Membranes

In this section, the resistance model for predicting gas permeation behavior of a composite membrane will be applied to both the single layer and the double layer composite membranes prepared in this work. Henis and Tripodi [10] used ohm’s law of electricity as an analogy to model gas permeation through a composite membrane. In the analogy, gas flux, $J$, through the membrane is analogous to electric current, $I$, while the concentration difference/pressure gradient which is the driving force for gas permeation can be equated to electrical potential difference, $V$. To define the resistance to permeate
flow, eq. 2.13 is can be re-written for a gas $k$ flowing through membrane area $A \text{ cm}^2$ at $J \text{ cm}^3/s$ as:

$$A \Delta p_k = j_k \frac{l}{P_k}$$  \hspace{1cm} 2.22

So that,

$$R_k = \frac{l}{P_k A}$$  \hspace{1cm} 2.23

where $R_k$ is the resistance of the composite membrane to the flow of gas $k$.

### 2.5.3 Resistance Model for the Single Layer Composite Membranes

Consider a thin defect-free selective Pebax coating on PAN porous support (fig. 2.9). Blume et al [39] explained that dilute Pebax coating solutions ( about 2 wt %) form good coating when applied on a microporous support without the need to prevent penetration by filling the support pores temporarily or without the use an intermediate top sealing layer. They discussed further that the polymer film formed on the microporous support does not break or plug the pores of the porous support because the polymer solution turns viscous instantaneously as the solvent evaporates. Based on the discovery of Blume et al, it would be considered that the selective layer did not plug the pores of the porous support so that the resistances to gas flow through the membrane are the sum of the resistance of the Pebax layer and the resistance of the PAN support. Thus, the resistance in series model could be used to describe the system.
Fig. 2.9: Single layer Pebax composite membrane and the electrical circuit analogue.

where $R_A = \text{resistance of the permselective Pebax layer A; } R_S = \text{resistance of the PAN porous support; } J_i = \text{flux of gas } i \text{ through the membrane.}$

Thus the total resistance of the membrane to gas permeation can be written as:

$$R_T = R_A + R_S \quad 2.24$$

For both the active layer and the support, the resistance, $R_T$, can be written in the form shown in equation 2.23 so that the flux through the membrane can be expressed as:

$$J_i = \Delta p \left( \frac{l_A}{P_A A} + \frac{l_S}{P_S A} \right)^{-1} \quad 2.25$$

### 2.5.4 Resistance Model for the Double Layer Composite Membranes

The double layer membrane comprises of a layer of PEO-b-PSU-PEO applied on single Pebax layer on PAN. According to Blume et al, if a polymer coating solution do not gel
as the solvent evaporates, the pores of the support are usually plugged leading to defects in the selective layer [39]. The coating solution of PEO-PSU-PEO is different from that of Pebax because it does not gel as the solvent used in this work evaporates. Thus, we can apply Henis and Tripodi electrical analogy to the PEO-PSU-PEO/Pebax/PAN composite membrane coupled with the following assumptions made by He et al [40] in their work:

- the diffusive flow in the membrane is one dimensional
- the membrane has a homogeneous, non-porous coating layers
- No Knudsen flow in the membrane

Fig. 2.10: Double layer PEO-PSU-PEO/Pebax/PAN composite membrane and the electrical circuit analogue.
For the composite membrane shown in fig. 2.10, the total resistance, $R_T$, of the membrane to gas flow can be written as [41]:

$$R_T = \left( \frac{1}{R_A + R_B} + \frac{1}{R_2} \right)^{-1} + R_S = \frac{(R_A + R_B)R_2}{R_A + R_B + R_2} + R_S \tag{2.26}$$

where $R_A$ is the resistance of layer Pebax layer A, $R_B$, the resistance of layer B, $R_s$, the resistance of the porous support and $R_2$, the resistance of layer A exposed by the defects in the top layer. Thus we can express the resistances in terms of permeability and thickness for each of the layers as:

$$R_A = \frac{l_A}{P_A A_1} ; R_B = \frac{l_B}{P_B A_1} ; R_S = \frac{l_s}{P_S A} ; R_2 = \frac{l_2}{P_2 A_2} \tag{2.27}$$

where the $P$'s are permeability coefficient of the layers. Then,

$$R_T = \frac{(R_A + R_B)R_2}{R_A + R_B + R_2} + R_S = \frac{\left( l_A P_A A_1 + l_B P_B A_1 \right) \left( l_2 P_2 A_2 \right)}{l_A P_A A_1 + l_B P_B A_1 + l_2 P_2 A_2} + \frac{l_s}{P_S A} \tag{2.28}$$

If we define the defect ratio as $\lambda = A_2/A$, then eq. 2.28 becomes:

$$R_T = \frac{\left( l_A P_A (1 - \lambda) + l_B P_B (1 - \lambda) \right) \left( l_2 P_2 \lambda \right)}{1 \left( l_A P_A + l_B P_B \right) + l_2 P_2 \lambda} + \frac{l_s}{P_S A} \tag{2.29}$$

Thus, eq. 2.29 can be used to predict the gas permeation properties of the membrane shown in fig. 2.10. The gas flux through the membrane can be written as:
\[ J = \Delta p \left( \frac{l_A}{P_A(1 - \lambda)} + \frac{l_B}{P_B(1 - \lambda)} \left( \frac{l_2}{P_B \lambda} \right) + \frac{l_s}{P_s A} \right)^{-1} \]  

However, if the top layer is defect-free, the expression for the flux will be;

\[ J = \Delta p \left( \frac{l_A}{P_A A_1} + \frac{l_B}{P_B A_1} + \frac{l_s}{P_s A} \right)^{-1} \]
CHAPTER 3

EXPERIMENTAL

3.1 Materials

Ethanol absolute (EtOH) of 99% purity, N-Methyl-2-pyrrolidone (NMP), N,N-Dimethylacetamide (DMAc), and Tetrahydrofuran (THF) were purchased from Aldrich Chemical Company (Milwaukee, WI). 99.9% pure carbon dioxide, nitrogen and methane gas cylinders were used as received. A polyacrylonitrile (PAN) microporous support was generously supplied by GMT Membrantechnik (Rheinfelden, Germany). Pebax® MH 1657 block copolymer containing 40 wt% polyamide-6 and 60 wt% polyethylene oxide was purchased from Arkema and used as received. 98g of PEO-b-PSU-b-PEO polymer with 27.4 wt% PEO content was received from polyMATERIALS (synthesis described by Ting et al [42]). The structures of PEO-b-PSU-b-PEO[42] and Pebax [43] are as shown in Fig. 3.1 and 3.2 respectively.

![Chemical Structure of PEO-b-PSU-b-PEO](image_url)

**Fig. 3.1:** Chemical Structure of PEO-b-PSU-b-PEO
3.2 Membrane Preparation

PEO-b-PSU-b-PEO was dried for 24 hours prior to use. Separate solutions were prepared by dissolving PEO-b-PSU-b-PEO in NMP, THF and DMAc respectively. The compositions of all the casting solutions made are shown in Table 3.1. The polymer is soluble in all the solvents at room temperature with gentle stirring.

A 2 wt% Pebax coating solution was prepared by adding Pebax® MH 1657 grade pellets to ethanol/water mixture (70%/30%). The polymer was dissolved under reflux at 75°C with vigorous stirring for 3 hours. The solution was cooled down to room temperature and filtered through a steel filter with pore size 32μm.

Three separate solutions of PEO-b-PSU-b-PEO of different compositions (1 wt%, 1.5 wt% and 2 wt%) were prepared by dissolving PEO-b-PSU-b-PEO in THF and stirring the mixtures for 1 hour.

![Fig.3.2: Chemical Structure of Pebax](image-url)
Table 3.1: Compositions of casting solutions for asymmetric membrane preparation

<table>
<thead>
<tr>
<th>Casting Solutions</th>
<th>Solvents</th>
<th>Solvent wt%</th>
<th>PEO-b-PSU-b-PEO wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>80.0</td>
<td>20.0</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>75.0</td>
<td>25.0</td>
</tr>
<tr>
<td>3</td>
<td>NMP</td>
<td>80.0</td>
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<tr>
<td>4</td>
<td>NMP</td>
<td>77.5</td>
<td>22.5</td>
</tr>
<tr>
<td>5</td>
<td>DMAc</td>
<td>77.5</td>
<td>22.5</td>
</tr>
<tr>
<td>6</td>
<td>DMAc</td>
<td>75.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>

3.2.1 Asymmetric Membranes Preparation

To prepare the asymmetric membranes, the PEO-bPSU-bPEO solutions in Table 3.1 were kept unperturbed for 24 hours to eliminate air bubbles. Each of them was separately cast on a flat glass plate by using a casting blade with an opening gap of about 0.25mm at ambient temperature (21 °C). The solvent in the cast solution was left to evaporate under ambient air for a specified time (typically 10 - 40 seconds) before immersion in water coagulation bath at ambient conditions. The coagulated membrane was left in the coagulation bath for 30minutes after which it was brought out and air dried for 24 hours. The above procedure was carried out again but with coagulation bath consisting of ethanol/water mixture (80/20).

3.2.2 Single layer Composite Membrane Preparation

Rectangular sheets of PAN porous support were cut and laminated using an impulse sealer so that the thin polymer film is deposited only on the side coated with PAN during
dip coating. This is necessary because the thin film, if deposited on the other side of the porous support, would reduce the gas flux through the membrane. Ultrathin layer of Pebax was deposited on the PAN rectangular sheets by dipping them into the filtered Pebax solution (prepared as described above) in a beaker for a residence time of about 20 seconds. The sheets were brought out of the solution and dried overnight in ambient air. After drying, the membranes were cut into circular coupons with diameter 4.13cm for gas permeation tests.

### 3.2.3 Multi-layer Composite Membrane Preparation

The PEBAX/PEO-b-PSU-b-PEO composite membranes were made in a manner similar to the single layer Pebax composite membrane. Some of the dried laminated rectangular sheets already coated with Pebax films from above were dip-coated a second time with 1 wt% solution of PEO-b-PSU-b-PEO in THF (prepared as described above) to deposit ultrathin films of PEO-b-PSU-b-PEO on them. The coated sheets were removed from solution and dried in the ambient air overnight. Other Pebax coated laminated sheets of PAN support were coated with 1.5 wt% and 2wt% coating solutions of PEO-b-PSU-b-PEO in THF to produce other membranes with thicker PEO-b-PSU-b-PEO top layer. After drying overnight, they were also cut into coupons of diameter 4.13cm for use in gas permeation tests.
3.3 Membrane Characterization

3.3.1 Gas Permeation Tests

Permeances of three pure gases (nitrogen, methane and carbon dioxide) were measured by a constant-pressure variable-volume method at 21°C, where the feed pressure was maintained at 8bars for all the gases. Gas permeances were calculated using the formula:

\[ J_i = \frac{V}{A \cdot t \cdot p} \] 

where \( J_i \) is the gas permeance of gas \( i \) in GPU, \( A \)=membrane area in cm\(^2\), \( V \)=gas volume in cm\(^3\), \( t \)=time in seconds required for \( V \)cm\(^3\) of gas \( i \) to travel up the bore of the bubble flow meter and \( p \) is the pressure in cmHg. Necessary conversions were done to convert the units of experimental data to the units of the parameters defined in equation 3.1. Fig. shows a schematic of the gas permeation test set-up. Fig.3.3 shows a schematic of the gas permeation test set-up.

Fig. 3.3: Schematic of the experimental setup used for gas permeation test: (1) Feed gas; (2) Valve; (3) Pressure guage; (4) Membrane module; (5) Cell; (6) Bubble flow meter.
3.3.2 Membrane Morphology

To study the morphologies of the composite membranes, the membranes samples were prepared by fracturing them in liquid nitrogen. The prepared samples were placed in Magellan™ SEM instrument to observe the cross-section of the sample. The structures as observed will be discussed in the next chapter.
CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 PEO-b-PSU-b-PEO Asymmetric Membrane

Dry – wet phase inversion method (described in 3.2.1 above) was used to make PEO-b-PSU-b-PEO membrane with asymmetric structure. It was found out that the membranes prepared using different combinations of solution/coagulation bath mentioned earlier did not come out well when dried. The membranes broke into tiny pieces during drying probably because the percentage of PEO segments in PEO-b-PSU-b-PEO is too high. The PEO segments, due to their high crystallinity, might have crystallized during dry-wet phase inversion process and resulted in inherently brittle membranes. Thus, it was very difficult to make membranes with asymmetric structure using PEO-b-PSU-b-PEO tri-block copolymer.

4.2 Pebax/PAN Composite Membrane

Pebax® MH 1657 is soluble in few solvents. Their dissolution depends on the ability of the solvent to interact strongly with the polymer to break down their hydrogen bonds [39]. Such solvent include n-butanol, or a mixture of n-butanol/1-propanol and the low concentration polymer solution is usually prepared at high temperature under reflux [22]. Solutions prepared with these solvents tend to form gel when cooled to room temperature thus making it difficult to prepare composite membrane. To prevent gelation, formic acid,
concentrated sulphuric acid, m-cresol, liquid sulphur dioxide and hydrogen chloride/methanol can be used as solvents but they are inconvenient for use in large-scale membrane preparation because they are difficult to handle [39]. Muller et al found out that a binary mixture of ethanol and water (7:3) could be used as a solvent for the polymer without any form of gelation as the solution cools to room temperature. A 2 wt% Pebax solution in ethanol/water mix was used to prepare the membranes studied in this work.

4.2.1 Gas Transport Properties of Pebax/PAN Composite Membranes

The gas transport properties of seven representative samples of Pebax/PAN composite membranes were determined by measuring pure gas flux through them. The flux measurement through the membranes was carried out for pure CH\textsubscript{4}, N\textsubscript{2} and CO\textsubscript{2} in the listed order. The permeances for all the gases as well as the pure gas selectivities for CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} are as shown in Table 4.1. Table 4.1 shows that the first six membranes have comparable gas permeances and pure gas selectivities while the property of the last membrane deviates from others. The seventh membrane has higher CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities but lower flux compared to the other membranes in the group but this result could not be reproduced. CH\textsubscript{4} permeance is slightly higher than that of N\textsubscript{2} even though N\textsubscript{2} has a smaller kinetic diameter and the CO\textsubscript{2} permeance is far greater than CH\textsubscript{4} and N\textsubscript{2} as expected considering the fact that CO\textsubscript{2} has great interactions with EO units in the polymers.
4.2.2 SEM scan of Pebax/PAN Composite Membrane

Images of the cross-sectional morphology of Pebax/PAN membranes as observed by scanning electron microscopy (SEM) are displayed in Fig. 4.1. Two distinct layers and an obvious interface were observed. These SEM images demonstrate that a defect free Pebax film has been coated on PAN substrate and the pebax film did not plug the pores of the PAN substrate.

4.3 PEO-b-PSU-b-PEO/Pebax/PAN Composite Membrane

It is easier to find solvents that dissolve PEO-PSU-PEO polymer than Pebax. Solvents like dimethylformamide (DMF), NMP, DMAc, and THF. A key point to note here is that

<table>
<thead>
<tr>
<th>s/n</th>
<th>J_{N_2}*10^2</th>
<th>J_{N_2}(GPU)</th>
<th>J_{CH_4} * 10^2</th>
<th>J_{CH_4}(GPU)</th>
<th>J_{CO_2} * 10^2</th>
<th>J_{CO_2}(GPU)</th>
<th>\alpha_{N_2}^{CO_2}</th>
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<td>7</td>
<td>0.25</td>
<td>33</td>
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<td>95.1</td>
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<td>2567</td>
<td>78</td>
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Range^b 1.16 ±0.13 152 ±17 2.8 ±0.5 365 ±63 34.0 ±2.1 4467 ±274

<table>
<thead>
<tr>
<th>s/n</th>
<th>J_{N_2}*10^2</th>
<th>J_{N_2}(GPU)</th>
<th>J_{CH_4} * 10^2</th>
<th>J_{CH_4}(GPU)</th>
<th>J_{CO_2} * 10^2</th>
<th>J_{CO_2}(GPU)</th>
<th>\alpha_{N_2}^{CO_2}</th>
<th>\alpha_{CH_4}^{CO_2}</th>
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<td>2567</td>
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<td>27</td>
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</tbody>
</table>

Range^b 1.16 ±0.13 152 ±17 2.8 ±0.5 365 ±63 34.0 ±2.1 4467 ±274

a: Gas permeance in m^3(STP)/m^2-hr-bar
b: Range within which properties of membrane samples 1-6 are expected to lie
the solvent to be used for making PEO-PSU-PEO coating solution must not interact with the porous support material as well as Pebax layer. From different test conducted to search for the best of the solvents, THF emerged as the best solvent because it does not alter the morphology of the porous support, neither does it interact with Pebax film. Its low boiling point and high volatility are also of advantage as the thin PEO-PSU-PEO film is formed almost instantaneously as the solvent evaporates.

**Fig.4.1:** Cross-sectional SEM scan of Pebax/PAN composite membrane

### 4.3.1 Gas Transport Properties of PEO-b-PSU-b-PEO/Pebax/PAN Composite Membranes

Gas permeation experiment was done with these sets of membrane starting with the set having Pebax/PAN coated with 1.0 wt% PEO-b-PSU-b-PEO solution in THF. From this point onward, the sets of PEO-b-PSU-b-PEO/Pebax/PAN membranes made will be
referred to as M1, M1.5 and M2 membranes with M1 being PEO-b-PSU-b-PEO/Pebax/PAN made with 1 wt% PEO-b-PSU-b-PEO solution, M1.5 with 1.5 wt% PEO-b-PSU-b-PEO solution and M2 with 2 wt% PEO-b-PSU-b-PEO solution. Membranes M1.5 and M2 were also tested.

Tables 4.2–4.4 display the gas permeation results for the membranes. The tables show properties variation within same set of membrane. This is because thickness change is experienced along the membranes and this causes differences in the resistances offered by the membrane to gas flow through them. M1, M1.5 and M2 PEO-b-PSU-b-PEO/Pebax/PAN membranes exhibit similar behaviors to gas permeation. It can be seen from Tables 4.2–4.4 that their gas permeances decrease while the selectivity increase as the thickness of the PEO-b-PSU-b-PEO top layer increases.

**Table 4.2:** Permeances of N\(_2\), CH\(_4\), and CO\(_2\) with CO\(_2\)/N\(_2\) and CO\(_2\)/CH\(_4\) selectivities for M1 composite membranes made measured at 8bar, 21\(^\circ\)C.

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<tr>
<th>S/No</th>
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<th>(J_{N_2}(GPU))</th>
<th>(J_{CH_4} \times 10^4)</th>
<th>(J_{CH_4}(GPU))</th>
<th>(J_{CO_2} \times 10^2)</th>
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<td>19</td>
</tr>
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<td>30.5 ±3.3</td>
<td>4.3 ±0.3</td>
<td>576 ±32</td>
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Table 4.3: Permeances of N\textsubscript{2}, CH\textsubscript{4}, and CO\textsubscript{2} with CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities for M1.5 composite membranes measured at 8bar, 21°C.

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<th>J\textsubscript{CH4} *10\textsuperscript{4}a</th>
<th>J\textsubscript{CH4}(GPU)</th>
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<th>J\textsubscript{CO2}(GPU)</th>
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<th>(\alpha)\textsubscript{CH4}</th>
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Table 4.4: Permeances of N\textsubscript{2}, CH\textsubscript{4}, CO\textsubscript{2} with CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities for M2 composite membrane measured at 8bar, 21°C.

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Thus the composite membranes exhibit the behavior typical of polymeric membranes because the membrane set having the highest gas permeance have the lowest selectivity and vice versa. Generally, for nonpolar gases (like N\textsubscript{2} and CH\textsubscript{4}), the permeance increases with increasing molecular size because the membrane has a reverse selective property typical of rubbery polymers. The higher CO\textsubscript{2} permeance and selectivity are attributable to the difference in sorption between polarizable gases and nonpolarizable gases in PEO blocks of PEO-b-PSU-b-PEO and Pebax.

**4.3.1.1 Effects of Pure Gas Feed Pressure on Gas Permeances of PEO-b-PSU-b-PEO/Pebax/PAN Composite Membrane.**

The effect of pressure on gas permeance of PEO-b-PSU-b-PEO/Pebax/PAN membrane was studied by varying the feed gas pressure for each of the gases from 2.5bar to 19bar. Fig. 4.2 – 4.4 show the behaviors of M1, M1.5 and M2 membranes. For all the membranes, CO\textsubscript{2} permeance showed a significant variation with increasing pressure while N\textsubscript{2} and CH\textsubscript{4} permeance slightly increase with pressure. Higher increase in CO\textsubscript{2} permeance was experienced because CO\textsubscript{2} has high sorption in the membrane because of its interaction with polar ether oxygen in Pebax and PEO-b-PSU-b-PEO. Thus as the pressure increases more CO\textsubscript{2} is absorbed in the membrane which may cause swelling/plasticization of the membrane thereby resulting in higher CO\textsubscript{2} permeance [23]. The plasticization effect, if any, would be more pronounced in the composite membrane set M1 because of its lower film thickness compared to M1.5 and M2 membranes.
Fig. 4.2: Variation of gas permeances with pressure for M1 composite membrane measured at 21°C.

Fig. 4.3: Variation of gas permeances with pressure for M1.5 composite membranes measured at 21°C.
M1 has the film with the lower thickness, so it tends to have lower resistance to gas permeation and thus swells up more quickly than films in M1.5 and M2 membranes with higher film thicknesses. Also, this is confirmed by estimating the mean slope of the CO\textsubscript{2} permeance versus pressure plots for the membranes. The average slopes of the plots for the membranes are 13.62 GPU/bar (0.00104m\textsuperscript{3}/m\textsuperscript{2}-hr-bar-bar) for M1 membranes, 10.20 GPU/bar (0.00080m\textsuperscript{3}/m\textsuperscript{2}-hr-bar-bar) for M1.5 membranes and 5.67 GPU/bar (0.0005m\textsuperscript{3}/m\textsuperscript{2}-hr-bar-bar) for M2 membranes. The slope of the permeance versus pressure may be related to how fast membranes swell.

4.3.1.2 Effects of Pure Gas Feed Pressure on CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities of PEO-b-PSU-b-PEO/Pebax/PAN Composite Membrane.

The variation of CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities with pressure was studied and the relationship between pressure and the selectivities are shown in Fig. 4.5-4.7 for all
membrane sets. All the membranes showed increased CO₂/N₂ and CO₂/CH₄ selectivities as the pressure was increased from 2.5 to 19 bar. This may be due to increased CO₂ solubility relative to N₂ and CH₄ solubility in the membranes as pressure rises which occurs as a result of strong interaction between CO₂ and ethylene oxide units in the membranes material. For high sorbing gases, solubility selectivity contributes more to the overall selectivity than diffusivity selectivity. Thus, increase in CO₂ sorption in the membrane increased CO₂/N₂ and CO₂/CH₄ solubility selectivities as pressure rises. This consequently led to increase in overall CO₂/N₂ and CO₂/CH₄ selectivities.

For rubbery polymers, the permeability, and hence the permeance of condensable gases (e.g. CO₂) increases with pressure whereas it decreases slightly with pressure increase for glassy polymer. Thus, PEO-b-PSU-b-PEO/Pebax/PAN composite membranes display the permeation behavior of a typical rubbery polymeric membrane.

![Fig. 4.5: Variation of CO₂/N₂ and CO₂/CH₄ Selectivities with Gas Feed Pressure for M1 composite membrane measured at 21°C.](image-url)
Fig. 4.6: Variation of CO2/N2 and CO2/CH4 Selectivities with gas feed pressure for M1.5 composite membrane measured at 21°C.

Fig. 4.7: Variation of CO2/N2 and CO2/CH4 selectivities with gas feed pressure for M2 composite membrane measured at 21°C.
4.3.2 SEM Scan of PEO-b-PSU-b-PEO/Pebax/PAN Composite Membrane

Fig 4.8 below shows the SEM images obtained. It shows a more complex morphology than the one observed for Pebax/PAN. Three layers are observed and the interface between the PAN substrate and the Pebax layer on top of it is crystal clear. However, the interface between the top PEO-b-PSU-b-PEO film and the Pebax film is not as visible as that of Pebax/PAN probably because both PEO-b-PSU-b-PEO and Pebax films are dense and thus have pores of similar sizes that are not easily distinguishable at the resolutions at which the images were taken. These images also confirmed that PEO-b-PSU-b-PEO/Pebax/PAN membranes have been successfully prepared.

![Cross-sectional SEM Scan of PEO-b-PSU-b-PEO/Pebax/PAN double layer composite membrane](image)

**Fig. 4.8:** Cross-sectional SEM Scan of PEO-b-PSU-b-PEO/Pebax/PAN double layer composite membrane
CHAPTER 5

CONCLUSION

Pebax and PEO-b-PSU-b-PEO/Pebax with PAN support were used to prepare composite membranes in this study. The thicknesses of the PEO-b-PSU-b-PEO top layers were varied by changing the composition of the PEO-b-PSU-b-PEO coating solution from 1.0 to 2.0 wt%. The abilities of these membranes to separate carbon dioxide from nitrogen and methane was studied at a temperature of 21°C and pressure up to 19 bar using pure gases. The Pebax/PAN composited membrane shows CO\textsubscript{2} permeances which compares reasonably with some literature values for CO\textsubscript{2} permeance through Pebax dense films and composite membranes. Introduction of PEO-b-PSU-b-PEO films on Pebax film on PAN support led to a decrease in CO\textsubscript{2} permeance by approximately a factor of 7.8 for the first set of PEO-b-PSU-b-PEO/ Pebax/PAN composited membrane made with 1 wt% PEO-b-PSU-b-PEO solution, 9.1 for the second set made with 1.5 wt % solution and 10.4 for the third set made with 2 wt% solution. However, CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities increase as PEO-b-PSU-b-PEO film thickness increase.

The SEM images of the membranes showed that the composite membranes were successfully prepared as the polymer film layers can be seen clearly as distinct layers on the PAN support.
Finally, future studies may be done to explore the possibilities of improving the gas permeances of PEO-b-PSU-b-PEO/Pebax/PAN membranes in order to improve gas separation property of these membranes.
BIBLIOGRAPHY


