Polyaniline and Its Derivative Hollow Fiber Membranes for Gas Separation

by

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I, hereby declare that the work presented in this thesis is my own and the works of others cited have been appropriately acknowledged.

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Abstract

This thesis describes research into the utilization of conducting polymer polyaniline (PAni) as a material for the development of asymmetric hollow fiber membranes for gas separations. In order to ensure the consistency of the emeraldine base PAni molecular weight and the quality and purity throughout this research, the fresh batch polymer was synthesized in-house prior to each hollow fiber spinning. The initial gas permeation test revealed that the hollow fiber fabricated with high molecular weight PAni was favourable due to the highly viscous solution prepared with significant polymer chain entanglement that contributed to the formation of a more desirable membrane structure. However, the major turn around of the work was the introduction of volatile tetrahydrofuran (THF) to less volatile N-methyl-2-pyrrolidone (NMP) in the dope solution that promoted a proper formation of integrally skinned membranes. The effective removal of THF at a high spinning air gap further improved the fabricated membrane morphology which consisted of a denser effective skin layer, transition layer and finely porous substructure with smaller macrovoids. In addition, the spine line stress-induced orientation at a high air gap was responsible for further stretching the nascent fiber creating more packed structure that assisted toward improving the gas separation performance of the membranes. The induced molecular orientation also resulted in improvement in mechanical properties of the hollow fibers. Polyaniline derivative was synthesized to overcome the PAni solubility issue and to suppress the formation of PAni micro-agglomerates in the highly viscous dope solution. Integrally-skinned hollow fiber membranes were successfully prepared by dry-jet wet spinning from poly(ortho-anisidine) (POAn) dissolved in NMP and THF system. The bulky methoxy group introduced to the polymer backbone increased both the polymer chain rigidity and specific free volume of POAn as compared to PAni, producing membranes with significantly enhanced gas pair separation factors and small gases (hydrogen and carbon dioxide) permeation rates. The final focus of this study was investigating the potential effect of the aging process on PAni and its derivative membranes gas separation and mechanical properties. Poly(o-anisidine) membrane properties were found to be more stable than polyaniline membranes throughout the aging period, providing a strong foundation for further investigation of poly(o-anisidine) as a membrane material for gas separation towards commercial application.
Acknowledgements

I would like express my deepest gratitude to my supervisor for his endless guidance and ideas when I started this PhD journey with no knowledge of polyaniline. My sincerest appreciation for his optimism and understanding when I was at the junction of feeling really hopeless that the work was not going anywhere near as plan while facing the losses of 2 closest people in my life. Professor Kang Li’s patience upon me towards the finishing line of this bumpy ride and his continuous supports made me forever indebt. Thank you so much Sir for this priceless experience and knowledge.

Someone used to say, ‘nobody can do research on a deserted island’. With the input and assistance of ever-so-energetic Dr. Santosh Kumbharkar, the work was progressing exceeding any national speed limit and making it possible to achieve what it is now. Although, there is so much more can be done in the area, I am thankful that he joined our group even though it was almost towards the final year of my study. My gratitude to Dr. Xun Xing Loh, Dr. Fu Liu, Dr. Yutie Liu and Dr. Sairam Malladi for their contributions at some point throughout the course especially relating to understanding the chemistry side of polyaniline. Thanks to the group members (Zhentao, Ben, Edjiro, Basia, Chris, Francisco, Reza, Awanis, Irfan, Mukhlis and Hafiz) who have helped me grow in one way or another, both academically and personal level. Special thanks to 118-family that made this whole journey was a lot more fun than it would have been and I am sincerely going to miss you guys, Shaima, Shu Ian, Hugo and Jerry.

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Table of contents

Abstract ......................................................................................................................... 1

Acknowledgements ...................................................................................................... 2

List of figures ............................................................................................................... 7

List of tables ................................................................................................................. 10

List of abbreviations and symbols .............................................................................. 11

1. Introduction .............................................................................................................. 13
   1.1. Background ....................................................................................................... 13
   1.2. Scope of thesis .................................................................................................. 15

References .................................................................................................................... 17

2. Literature review ..................................................................................................... 19
   2.1. Introduction ....................................................................................................... 19
   2.2. Progress in membrane separation .................................................................... 19
       2.2.1. Basic concept of membrane separation ..................................................... 21
       2.2.2. Classifications of membrane structure ...................................................... 23
       2.2.3. Asymmetric membrane ............................................................................. 26
       2.2.4. Mechanisms of membrane separation ..................................................... 28
   2.3. Membrane fabrication by phase inversion process .......................................... 35
       2.3.1 Asymmetric membrane formation by dry-wet phase inversion ............... 38
       2.3.2 Effects of dope solution formulation on asymmetric membrane formation .......................................................... 39
       2.3.3 Spinning parameters in asymmetric membrane production .................. 41
   2.4. Defects on asymmetric membrane skin layer ................................................. 43
       2.4.1. Sealing the defects on the outer surface of asymmetric membrane ...... 44
   2.5. Polyaniline: Synthesis and applications ......................................................... 47
       2.5.1. Synthesis of polyaniline ............................................................................ 47
       2.5.2. Progress in polyaniline derivatives ........................................................... 52
       2.5.3. Polyaniline based gas separation membrane ............................................. 54
       2.5.4. Preparation of highly viscous PAni emeraldine base solution ............... 59
2.6. Summary of literature review

References

3. Polyaniline synthesis and hollow fiber membrane fabrication

3.1. Introduction

3.2. Experimental

3.2.1. Materials

3.2.2. PANi synthesis

3.2.3. Infrared spectroscopy analysis of the produced polymer

3.2.4. Molecular weight measurement of polyaniline powder

3.2.5. Preparation of high concentration polyaniline dope solution

3.2.6. Measurement of dope solution viscosity

3.2.7. Polyaniline hollow fiber spinning process

3.2.8. Scanning electron microscopy (SEM)

3.2.9. Gas permeation measurement by soap-bubble method

3.2.10. Silicone rubber coating

3.3. Results and discussions

3.3.1. Synthesis of polyaniline emeraldine base

3.3.2. FTIR spectroscopy analysis on PANi

3.3.3. Effect of reaction temperature on the molecular weight

3.3.4. Effect of molecular weight on PANi dope solution viscosity

3.3.5. Fabrication and morphological analysis of PANi hollow fiber membrane

3.3.6. PANi membrane gas separation performance

3.4. Conclusions

References

4. Polyaniline hollow fiber membrane for gas separation

4.1. Introduction

4.2. Experimental

4.2.1. Materials

4.2.2. PANi synthesis

4.2.3. Preparation of dope solution and viscosity measurement

4.2.4. Polyaniline hollow fiber spinning process

4.2.5. Gas permeation measurement
4.2.6. Silicone rubber coating ................................................................. 126
4.2.7. Scanning electron microscopy (SEM) ........................................... 126
4.2.8. Mechanical properties measurement ........................................... 126
4.3. Results and discussions ................................................................. 127
  4.3.1. PANi membrane gas separation performance .............................. 127
  4.3.2. Morphological analysis of the hollow fibers ............................... 133
  4.3.3. Mechanical properties of PANi hollow fiber membranes ............. 138
4.4. Conclusions .................................................................................. 140
References .......................................................................................... 141

5. Gas transport properties investigation on ring substituted polyaniline
   hollow fiber membranes ................................................................. 144
5.1. Introduction .................................................................................. 145
5.2. Experimental ................................................................................ 147
  5.2.1. Materials .................................................................................. 147
  5.2.2. Poly(ortho-anisidine) synthesis and characterization ................. 147
  5.2.3. Preparation of POAn dope solution ........................................... 148
  5.2.4. Measurement of dope viscosity ............................................... 149
  5.2.5. Fabrication of poly(o-anisidine) hollow fiber membrane .......... 149
  5.2.6. Preparation of testing modules and gas permeation measurement .. 151
  5.2.7. Silicone rubber coating ............................................................ 152
  5.2.8. Scanning electron microscopy (SEM) ......................................... 152
  5.2.9. Mechanical properties measurement ........................................ 152
5.3. Results and discussions ................................................................. 152
  5.3.1. POAn synthesis and characterisation ........................................ 152
  5.3.2. Determining the critical polymer concentration of POAn dope solution ................................................................. 154
  5.3.3. Effect of length of air gap on POAn hollow fiber membrane geometry .... 155
  5.3.4. Morphological and structural analysis of POAn hollow fiber membrane ... 157
  5.3.5. Poly(o-anisidine) hollow fiber membrane gas separation performance .... 162
  5.3.6. Mechanical properties analysis of POAn hollow fiber membranes .... 171
6. Stability analysis of polyaniline and its derivative base hollow fiber membranes

6.1. Introduction

6.2. Experimental

6.2.1. Materials

6.2.2. Synthesis of polyaniline and its derivative

6.2.3. Preparation of dope solution preparation

6.2.4. Fabrication of hollow fiber membranes

6.2.5. Preparation of testing modules and gas permeation measurement

6.2.6. Infrared spectroscopy analysis of hollow fiber membranes

6.2.7. Mechanical properties measurement

6.3. Results and discussions

6.3.1. Degradation study of polyaniline hollow fiber membrane

6.3.2. Degradation study of poly(ortho-anisidine) hollow fiber membrane

6.4. Conclusions

References

7. Conclusions and future work recommendations

7.1. Conclusions

7.2. Future work recommendations
List of figures

Fig. 1.1 Schematic diagram of the fundamental principle of spinning process. .......... 14

Fig. 2.1 Typical membrane process for gas separation............................................. 22
Fig. 2.2 Membrane structure classifications and their typical applications. .............. 24
Fig. 2.3 Schematic illustration of the structure of integrally-skinned asymmetric
membranes of various configurations; (A) flat sheet and (B) hollow fiber..... 26
Fig. 2.4 Schematic of basic membrane gas separation process................................. 29
Fig. 2.5 Various mechanisms for gas separation membrane process on; (A-C) porous
membranes, and (D) dense membranes.............................................................. 30
Fig. 2.6 A quasi-crystalline lattice exhibiting vacancies of holes. ........................... 31
Fig. 2.7 Various transport mechanisms involved in an asymmetric membrane....... 35
Fig. 2.8 Schematic of defective anisotropic gas separation membrane as proposed by
Loeb-Sourirajan. ............................................................................................................ 44
Fig. 2.9 Sealing the defects of asymmetric membrane outer surface by silicone coating
as proposed by Henis and Tripodi............................................................................. 45
Fig. 2.10 Basic polyaniline molecular structure in base form..................................... 48
Fig. 2.11 The three most common oxidation states of polyaniline............................ 48
Fig. 2.12 Milestones in the development of polyaniline polymerization [111-116]. ..... 49
Fig. 2.13 The oxidation of aniline with ammonium peroxysulfate in aqueous medium
yields polyaniline (emeraldine form). ................................................................. 50

Fig. 3.1 (A) Schematic diagram and (B) photo of polyaniline synthesis reaction system.
........................................................................................................................................ 82
Fig. 3.2 Schematic diagram of hollow fiber spinning system................................. 86
Fig. 3.3 Pictures of spinneret used during spinning process; (A) spinneret, (a) inner
diameter (bore fluid), (b) outer diameter (dope solution), and (c) overall lumen
geometry. ......................................................................................................................... 86
Fig. 3.4 Schematic diagram of the gas permeation apparatus by soap-bubble method.. 88
Fig. 3.5 Infrared spectrum of polyaniline emeraldine base produced at -15 °C............. 92
Fig. 3.6 A typical GPC curve of polyaniline powder produced at 0 °C (batch P0_1,
Mw=96600, polydispersity=5.4).................................................................................... 94
Fig. 3.7 Effect of oxidative polymerisation temperature on average Mw of polyaniline. ................................................................. 95
Fig. 3.8 Effect of PANi Mw on the dope solution viscosity. ..................... 96
Fig. 3.9 PANi hollow fiber membranes outer layer cross section of PT2 with LAG of;
(A) 2 cm, (B) 25 cm and (C) 50 cm. ...................................................... 99
Fig. 3.10 PANi hollow fiber membranes outer layer cross section spun at LAG=50 cm
for; (A) Sample PT1, (B) Sample PT2 and (C) Sample PT3.................... 101

Fig. 4.1 Effect of concentration on the PANi dope solution viscosity. ............ 122
Fig. 4.2 Schematic diagram of hollow fiber spinning system using syringe pumps. 123
Fig. 4.3 Schematic diagram of the gas permeation apparatus by feed pressure drop
method. ................................................................................................. 125
Fig. 4.4 Gas separation performance of as-spun membranes at different length of air
gaps......................................................................................................... 128
Fig. 4.5 PANi hollow fiber membranes overall cross section; (A) Sample L2.5, (B)
Sample L30 and (C) Sample L50.............................................................. 134
Fig. 4.6 PANi hollow fiber membranes cross section; (A) Sample L2.5, (B) Sample L30
and (C) Sample L50. ............................................................................. 135
Fig. 4.7 PANi hollow fiber membranes top layer; (A) Sample L2.5, (B) Sample L30 and
(C) Sample L50.................................................................................... 137
Fig. 4.8 Stress versus strain curve for Sample L50...................................... 138

Fig. 5.1 Chemical structure of poly(o-anisidine)........................................ 148
Fig. 5.2 $^1$H-NMR spectra of POAn.......................................................... 153
Fig. 5.3 FT-IR spectra of poly(o-anisidine) hollow fiber membrane............ 154
Fig. 5.4 The trend of changes in poly(o-anisidine) dope viscosity as a function of
polymer concentration........................................................................... 155
Fig. 5.5 POAn hollow fiber membranes overall cross section; (A) Sample A0, (B)
Sample A2, (C) Sample A30 and (D) Sample A50. .................................. 158
Fig. 5.6 POAn hollow fiber membranes cross section of; (A) Sample A0, (B) Sample
A2, (C) Sample A30 and (D) Sample A50................................................ 159
Fig. 5.7 POAn hollow fiber membranes top layer of; (A) Sample A0, (B) Sample A2,
(C) Sample A30 and (D) Sample A50...................................................... 160
Fig. 5.8 POAn as-spun hollow fiber membrane gases permeabilities prepared at various air gap distances................................................................. 163
Fig. 5.9 POAn as-spun hollow fiber membrane ideal gas pairs selectivities prepared at various air gap distances................................................................. 164
Fig. 5.10 Average pressure-normalized fluxes of N\textsubscript{2}, O\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2} of coated POAn hollow fiber Sample A0 as a function of pressure........................................ 165
Fig. 5.11 Average pressure-normalized flux of carbon dioxide for coated POAn hollow fiber spun at various air gaps as a function of pressure.................................. 171
Fig. 5.12 Stress versus strain curve for Sample A50................................................................. 172

Fig. 6.1 Gases (N\textsubscript{2}, O\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}) fluxes of PANi hollow fiber membranes aged upto 28 weeks in air at room conditions. ................................................................. 188
Fig. 6.2 Gas pair selectivity of polyaniline hollow fiber membranes (LAG = 50 cm) aged upto 28 weeks in air at room temperature......................................................... 189
Fig. 6.3 FTIR analysis of PANi hollow fiber membranes aging in air at room conditions upto 196 days (A) overall spectra and (B) spectra of wavenumber 1000-2000 cm\textsuperscript{-1} ........................................................................................................... 190
Fig. 6.4 Mechanical properties profiles of PANi hollow fiber membranes aging upto 196 days: (A) tensile at break and Young's Modulus, and (B) elongation at break. ........................................................................................................ 193
Fig. 6.5 Gases (N\textsubscript{2}, O\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}) fluxes of POAn hollow fiber membranes aged upto 28 weeks in air at room conditions. ................................................................. 195
Fig. 6.6 Gas pair selectivity of polyaniline hollow fiber membranes (LAG = 50 cm) aged upto 28 weeks in air at room temperature......................................................... 196
Fig. 6.7 FTIR analysis of POAn hollow fiber membranes aging in air at room conditions upto 196 days (A) overall spectra and (B) spectra of wavenumber 1000-2000 cm\textsuperscript{-1} ........................................................................................................... 198
Fig. 6.8 Mechanical properties profiles of POAn hollow fiber membranes aging upto 196 days: (A) tensile at break and Young's Modulus, and (B) elongation at break. ........................................................................................................ 200
List of tables
Table 2.1 General relative hierarchy of common gases permeabilities........................................... 34
Table 2.2 Estimated kinetic diameter of common gases molecules............................................... 34

Table 3.1 Polyaniline hollow fiber spinning conditions............................................................... 87
Table 3.2 Yield of polyaniline powder synthesised at various reaction temperatures .................. 90
Table 3.3 Infrared spectral peak assignments of polyaniline emeraldine base............................ 93
Table 3.4 Gas separation performance of uncoated and coated PANi hollow fiber membranes spun at various air gaps (3, 25, 50 cm) and dope solution viscosities.............................................................. 105

Table 4.1 Polyaniline hollow fiber spinning conditions............................................................... 123
Table 4.2 Pressure-normalized fluxes of H₂, CO₂, O₂ and N₂ and ideal selectivities measured for silicone-coated PANi hollow fiber membranes...................................................... 130
Table 4.3 A comparison between the published gas performance data for as-cast polyaniline membranes with the results of the present work................................................................. 132
Table 4.4 Mechanical properties of PANi hollow fiber membranes.......................................... 139

Table 5.1 Summary of poly(o-anisidine) dope compositions and hollow fiber membrane spinning parameters..................................................................................................................... 150
Table 5.2 Effect of spinning air gap lengths on internal and external diameters, wall and skin layer thickness of POAn hollow fiber membranes............................................................... 156
Table 5.3 Pressure-normalized fluxes of N₂, O₂, CO₂ and H₂ and the ideal gas pair selectivities for silicone coated POAn hollow fiber membranes tested by soap bubble meter.................................................................................................................. 167
Table 5.4 Pressure-normalized fluxes of N₂, O₂, CO₂ and H₂ and the ideal gas pair selectivities for silicone coated POAn hollow fiber membranes tested by pressure drop method.......................................................................................... 168
Table 5.5 Tensile at break, elongation at break and Young's modulus as a function of air gap distance............................................................................................................................................. 173
## List of abbreviations and symbols

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-MA</td>
<td>2-methylaziridine</td>
</tr>
<tr>
<td>4-MP</td>
<td>4-methyl piperidine</td>
</tr>
<tr>
<td>APS</td>
<td>Ammonium peroxydisulfate</td>
</tr>
<tr>
<td>AR</td>
<td>Analytical grade</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>cpc</td>
<td>Critical polymer concentration</td>
</tr>
<tr>
<td>EB</td>
<td>Emeraldine base</td>
</tr>
<tr>
<td>ECP</td>
<td>Electroactive conducting polymer</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>ICP</td>
<td>Intrinsically conducting polymers</td>
</tr>
<tr>
<td>IPA</td>
<td><em>Iso</em>-propanol</td>
</tr>
<tr>
<td>LAG</td>
<td>Length of air gap</td>
</tr>
<tr>
<td>LiCl</td>
<td>Lithium chloride</td>
</tr>
<tr>
<td>NMP</td>
<td>1-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>PAni</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>POAn</td>
<td>Poly(<em>ortho</em>-anisidine)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>WFR</td>
<td>Deionised water flowrate through the centre of spinneret</td>
</tr>
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### Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$J_i$</td>
<td>Permeate flux</td>
</tr>
<tr>
<td>$p$</td>
<td>Partial pressure</td>
</tr>
<tr>
<td>$P$</td>
<td>Permeability coefficient</td>
</tr>
</tbody>
</table>
\( D_i \)  
Diffusion coefficient

\( S_i \)  
Solubility constant

\( L \)  
Membrane effective thickness

GPU  
Gas permeation unit \((1 \times 10^{-6} \text{ cm}^3 \text{ (STP)/cm}^2 \text{ sec cmHg})\)

\( Q_i \)  
Volumetric flowrate of gas ‘i’

\( \Delta P \)  
Transmembrane pressure drop

\( A \)  
Membrane effective surface area

\( D \)  
Fiber diameter

\( l \)  
Effective length of the fiber

\( \text{Å} \)  
Angstrom (unit for kinetic diameter)

\( (P/L)_i \)  
Gas permeance/permeation rate/flux/ of species ‘i’

SD  
Standard deviation

\( M_w \)  
Molecular weight

\( V \)  
volume of the test cylinder

\( R \)  
Gas constant

\( A \)  
Membrane effective surface area

\( t \)  
Temperature (K)

\( p_0 \)  
Initial measured pressures

\( p_f \)  
Final measured pressures

\( \text{o.d./OD} \)  
Outer diameter

\( \text{i.d./ID} \)  
Inner diameter

\( \text{SFV} \)  
Specific free volume

\( \text{MPa} \)  
Megapascal

**Greek symbols**

\( \alpha_{ij} \)  
Selectivity/Ideal separation factor of species ‘i’ over ‘j’

\( \mu \)  
micron
Chapter 1

1. Introduction

1.1. Background

Since the discovery of conjugated polymers ability to conduct electricity upon doping process, numerous researches have been focusing in the area of electroactive conducting polymers (ECPs). Polyaniline (PAni) is probably among the oldest organic polymer known since it was first chemically synthesized in 1840’s [1,2]. However, since it was first reported to possess high conductivity in emeraldine form [3] and after the ‘rediscovery’ as a conducting polymer in 1980 [4], polyaniline has been the most rapidly developing conductive polymer. Polyaniline has also been rigorously studied as a membrane material especially after the remarkable gas separation performance reported by Anderson et al. [5]. Besides known to be thermally and chemically stable, PAni is favourable for the unique ability to alter its morphology and structure upon reaction to acid known as doping technique. In addition, it was easy to synthesize with economical monomer [6-9]. Despite the continuous interest in exploring PAni as membrane material in the membrane gas separation field resulting in numerous interesting gas separation performances [5,7,10-13], the works still remained at the laboratory scale to date. This is probably due to the processability issue of polyaniline especially at high concentration, which is a favourable factor to ensure good gas separation membrane can be developed with high chain entanglement during membrane fabrication that promotes the formation of dense skin layer with high molecular orientation [14,15]. Published studies on gas separation throughout the years have been on PAni films or flat sheet membranes only. These modules have very low effective surface area and packing density as compared to more commercially viable hollow fiber membranes. Thus, the main objective of the current study is to develop polyaniline as a membrane material in a form of hollow fibers for gas separation process.
Since there are no recorded data on hollow fiber membranes for gas separation prior to this work, investigating the spinning parameters that influence PAni membrane formation is an important task to fulfil in order to achieve the overall objective of this study. As compared to films fabrication, spinning of hollow fiber is a more challenging task due to numerous factors controlling the fiber geometry and morphology during phase inversion process. Dope solution formulation is the starting key that will mould the spun fibers structure. Solvent selection is crucial since the molecular sizes of solvents and their solubility differences will directly affect the solvent and non-solvent exchange rate in the precipitation of hollow fiber membranes. The larger the solvent molecular size, the slower the solvent and non-solvent exchange process resulting in a relatively thick skin layer [16]. Secondly, highly concentrated polymer solution is required to induce chain entanglement that will reduce the microvoids in the skin layer thus increasing the separation capabilities of the membrane [14]. As the spinning solution is extruded through an annular spinneret, the bore fluid is co-extruded through a central capillary in the spinneret to prevent the hollow filament from collapsing. The fiber filament is ultimately collected on a wind-up drum. If the tip speeds of the wind-up drum, $V_f$, is faster than the extrusion velocity from the spinneret, $V_o$, the filament diameter will reduce. The path that the filament takes is referred to as the spin line. Fig. 1.1 displays the fundamental principal of fiber spinning process. Another spinning parameter that requires attention is the length of air gap. A greater orientation and tighter molecular packing membrane will form at high air gap distance producing the selective skin layer [17].

![Diagram](image.png)

**Fig. 1.1** Schematic diagram of the fundamental principle of spinning process.
1.2. Scope of thesis

As previously mentioned the main objective of this study is to develop polyaniline hollow fiber membranes with high gas separation performance. Besides, having high selectivity and optimum gas permeability in oxygen enrichment system, the hollow fiber membrane will be chemically stable in facing plasticizing gas in CO\textsubscript{2} removal technology as well as stable for long term gas separation process. In order to achieve the main objective, series of tasks were performed. The relevant methods and analysis required are summarized as follow in the scope of thesis.

Chapter 1 is the introduction to membrane gas separation process and polyaniline as the membrane material. It covers the general background of this area as well as the main objectives of this study.

The fundamental principles of membrane gas separation process that would complement the experimental work are thoroughly discussed in Chapter 2. The progress and basic concept of membranes separation as well as transport mechanisms are reviewed in this chapter. It also includes the understanding of membrane fabrication technique and parameters influencing the membrane formation. The progresses of polyaniline in synthesis and membrane fabrication fields are also presented here.

Prior to membrane fabrication, polyaniline polymerization technique was explored and the spinning dope solution formulation was optimized. Viscosity of the dope solution is the key factor in determining the end performance and morphology of gas separation membrane. High dope viscosity will promote the formation of more defect-free skin membrane, which is favourable for gas separation membrane and this can be achieved by optimizing the molecular weight of the polymer. Thus, Chapter 3 will be initially describing various approaches that have been conducted in obtaining the desired molecular weight with consistent polymer quality. The synthesized PAni molecular weight was measured frequently to ensure the consistency of the polymer. Since polyaniline solubility of concentration higher than 5 wt\% was still a challenge, gel inhibitor was introduced into the spinning solution. Having control over the production and handling of the polymer and PAni dope solution preparation, the hollow fiber
membrane was then fabricated by phase inversion technique, particularly, the hollow fiber dry-jet wet spinning method. Since the development of PANi hollow fiber is new area to explore, the spinning parameters have not been reported in detail before. Chapter 3 will discuss preliminary effort conducted in exploring the spinning parameter. Lengths of air gap were varied during the spinning process. The fibers spun from a high air gap distance may have a greater orientation and tighter molecular packing due to a high gravity-induced elongation stress on the fibers. This was expected to promote the formation of skin layer. The gas permeation properties of the produced hollow fibers were characterized by measuring the pure gases permeation rates with soap bubble method. This will be the standard gas separation performance standard procedure used throughout this study. Although, PANi hollow fiber membrane was successfully spun in Chapter 3, the membrane possessed a very low gas separation performance with undesirable membrane structure and morphology. Since Chapter 3 had presented the foundation of the work, Chapter 4 will explore the continuation of the findings. Generally, the introduction of co-solvent is known to be able to improve the membrane skin formation. The volatile solvent is expected to evaporate before immersion in the non-solvent bath, thus, elevates the polymer concentration at the interface, which upon coagulation should give a dense skin layer. The introduction of new constituent in the dope solution required a further optimization of the spinning solution viscosity to ensure the membrane was developed from a concentration with significant chain entanglement that would suppress defects formation. Morphological study by SEM on the developed membrane was important at this stage to verify the improved skin layer thickness.

Chapter 5 will offer an alternative strategy in polyaniline membrane fabrication by introducing ring substituted PANi derivative as a membrane material. Poly(ortho-anisidine) (POAn) was synthesized ‘in-house’ referring to the method discussed in Chapter 3. The use of POAn was intended to overcome the challenges faced by polyaniline membranes, such as the processability issue (the dope solution needed to be carefully attended most of the time to ensure a more homogeneous solution could be prepared) and low overall gas permeation rates as compared to the other polymer membranes. In addition, it was observed PANi membranes showed possible
deterioration of the gas separation performance since it had been quite a struggle to reproduce the measured data of the same modules after few months.

The ageing and long term stability of the developed and optimized polyaniline and its derivative hollow fiber gas separation membranes will be covered in Chapter 6. In order to ensure that the membrane produced is commercially viable, it is important to understand the durability of the striking gas permeation properties of the developed PAni and POAn membranes. The membrane would age in the normal laboratory environment and the impact on chemical, structural, transport and mechanical properties were examined. Besides the gas permeation measurement that determined the membrane usefulness, extensive characterizations of samples were conducted by FTIR spectroscopy and tensile test. These analyses were important towards understanding and proposing the possible mechanism of chemical degradation induced by ageing. FTIR spectra will elucidate any molecular structure changes in the polymeric membrane, while, the membrane strength is equally important to verify that the membrane can withstand harsh condition such as high pressure separation system for long operational time.

Finally, Chapter 7 summarizes the achievement of this research, followed by a list of recommendation for future research.

References

Chapter 2

2. Literature review

2.1. Introduction

Membrane based separation process; an emerging technology in the commercial separation scene, has demonstrated the potential of saving enormous amounts of energy in the processing industries if substituted for conventional separation systems. In recent years, great efforts have been made in the field and even greater future energy savings should be available when these membrane systems fully substitute conventional separation techniques such as distillation, evaporation, physical filtration, sedimentation and absorption. The system can produce high quality products even be operated at low energy consumption rates, thus, resulting in lower capital costs/spends. In addition, the potential of damaging any thermally sensitive material can also be eliminated since the separation occurs based on molecular size, shape and charge, thus, can be done at room temperature (isothermally) without requiring any phase change [1-6]. Membrane separation is a clean technology with no added waste products where the rejected component from feed can be recovered with ease of operation [7,8]. Since the equipment is modular, designing the membrane system is flexible and allows easy access for future scaling up compared to the conventional separation system [9-11]. All these benefits have made membrane processes very attractive in terms of simplicity, flexibility and economy.

2.2. Progress in membrane separation

Thomas Graham was the first to study gas permeation through membranes when he discovered that a wet pig bladder inflated to bursting point when it was left in a carbon dioxide atmosphere [12,13]. Thus, the report spearheaded the research excitement related to gas permeation through polymers. Mitchell then observed that the shrinking
rates of natural rubber balloons were varied when filled with different gases. He discovered that the porosity of the solid material allowed gas molecules to penetrate through it, in which the balloon filled hydrogen (smaller molecule) was faster than air [14,15]. At about the same time, the “Uber Diffusion” study was then formulated as Fick’s first law for gas diffusion in membranes [14,16,17]. Besides the well-noted discussion of solution theory gas permeation in membranes due to the interaction between permeant and membrane material, Lhermite also reported that theoretically there were two types of membranes in existence; porous and nonporous [18,19]. However, the most remarkable contribution towards understanding the gas permeation in membrane systems was the Graham’s law that proposed solution diffusion. The permeation mechanism was presented in strikingly modern terms and demonstrated experimentally that mixtures of gases can be separated by means of membranes [12,20]. He continued to provide more evidence regarding gas separation possibilities including partial separation of mixed gases leading to the formulation of Graham’s Law [12,21].

During the late 1800s and early 1900s, research in membranes continued but they remained objects of laboratory curiosity. All the early work in gas separation membranes used relatively thick films with very low fluxes and hence there was no commercial interest for any processes [22]. The first systematic studies utilizing synthetic membrane polymers for gas separation were those of Barrer’s in the late 1930’s [23,24]. Despite the early work, no serious attempt to appraise the potential of gas permeation by membranes as a large-scale separation technique until after World War II [25]. Many new types of polymeric membranes were developed and manufactured in sizable quantities for commercial applications. Only in the 1950’s, did the serious examination of the engineering aspects of several gas permeation processes of industrial importance for membrane technology occur; such as enrichment of oxygen from air, recovery of helium from natural gas, and separation of hydrogen from hydrogenation tail gas and refinery gas, removal of carbon dioxide from acid gases and etc [25].

The most influential discovery that transformed membranes from objects of laboratory curiosity to systems of significant commercial interest was the discovery by Loeb and Sourirajan of integrally skinned, high flux, asymmetric reverse osmosis membranes [26,27]. These membranes, which comprised an ultrathin barrier layer supported on a
graded-porosity, micro porous substrate of the same material, produced fluxes that were an order of magnitude greater than those for the dense membranes available up to that time. These membranes could not be immediately used for gas separation because the micro porous substructure collapsed on drying [22]. In 1968, a process was developed that allowed asymmetric cellulose acetate membranes to be dried and used for gas separation [22].

In 1979, American Monsanto Company introduced the PRISM separator for ammonia production processes, which was the first commercial system [28]. The success of the commercialization of the gas permeation system success was a major breakthrough in research and development of membrane technology. Recently, considerable progress has been made in the commercial use of membranes for gas separation, covering many existing and emerging applications. There were more than 10,000 commercial membrane systems operating in industry for various gas separation applications (nitrogen production, oxygen enrichment, hydrogen and helium recovery and purification, acid gas separations, and dehydration systems) by the mid 1990’s and with natural gas processing being the current largest industrial gas separation application, membrane processes have about <5% of the total worldwide market for new natural gas equipment that consists of ~$5 billions per year [29].

2.2.1. Basic concept of membrane separation

The use of membrane separation processes is a well-established technology. The process essentially involves contacting one side of a semi-permeable gas separation membrane with a feed gas mixture containing at least the gas whose enrichment is desired, along with one or more gases. The stream to be separated is fed to the membrane device at an elevated pressure, where it passes across one side of a membrane. The opposite side of the membrane is held at a lower pressure. The pressure difference across the membrane provides the driving force for the diffusion of gas across the membrane [30-32].

Separation is achieved because of differences in the relative transport rates of the feed components. Components that diffuse more rapidly become enriched in the low-pressure permeate stream, while the slower components are concentrated in the retentate
or residue stream. This can be achieved only if the system is not maintained in a state of equilibrium. The typical membrane process for gas separation is shown in Fig. 2.1. A membrane will separate gases only if some components pass through the membrane more rapidly than others. If the membrane contains pores large enough to allow a convective flow, separation will not occur. If the size of the pores is smaller than the mean free path of the gas molecules, then convective flow is replaced by Knudsen diffusion. Low molecular weight gases are able to diffuse more rapidly than heavier ones and separation occurs. If the pores are small enough, large molecules are unable to pass through them and are excluded by the membrane. This molecular sieving is potentially useful in separating molecules of different sizes [32].

![Diagram](image)

**Fig. 2.1** Typical membrane process for gas separation.

Gas permeation is based on the concept that the membrane separation produces permeate enriched in the more permeable species and retentate enriched in the less permeable component. The process requires the pumping of the feed stream tangentially across the appropriate membrane, which is parallel to the membrane surface. As the feed passes through the membrane, it splits into two streams; permeate and retentate. Permeate is the stream consisting of components which are small enough to pass
through the membrane pores while the latter consist of large components that are retained on the surface of the membrane.

The pressure difference provides the driving force for the diffusion of gases and the performance of a membrane-based gas separation is described in term of permeability and selectivity. Permeability indicates flux or permeation rate (productivity) of a desired product while selectivity indicates the degree of separation or degree of enrichment. For the process to be successful, a membrane with a high gas selectivity and permeability is preferred [33].

2.2.2. Classifications of membrane structure

Generally, there are several types of membranes in use today and each has its own set of advantages and disadvantages. Each membrane classification and its applications are simplified in Fig. 2.2. Membranes for gas separation can be classified into four main categories as follow:

i. *Symmetric membranes* are homogenous (nonporous) or porous membranes with a uniform or non-uniform pore size.

ii. *Asymmetric membranes* have top layer made by densified material and supported by porous sublayer. The top layer and sublayer are made of the same material.

iii. *Dynamically formed membrane* involves a coating process of a porous surface with a solution containing additive forming a salt rejecting layer. This additive possesses an ion exchange characteristic that assists the membrane flux and rejection. This membrane is favorable in water and wastewater processes.

iv. *Liquid membranes* utilize a carrier to transport components selectively such as metal ions at relatively high rate across the membrane interface.
Fig. 2.2 Membrane structure classifications and their typical applications.
There is also composite membranes consisting of a thin and dense membrane (A) that is supported by a porous membrane (B; symmetric or asymmetric). A and B are most of the time fabricated from different methods and materials. Among those structures, symmetric and asymmetric membranes are the most studied and developed. Dense and thin film type membranes are among the earliest commercial membranes and are typically used for various dialytic and electrochemical processes [34-36]. Typically, such a membrane is produced by the melting process of polymers, solution casting followed by evaporation, or even by in-situ reaction of monomers into a thin-film polymer form [34,37]. Symmetric membranes with relatively uniform matrix structures are generally produced by phase inversion processes and are typically used for gross filtration and microfiltration (MF) application. Later in the area, they have been used as substrates for fictionalizations to produce active ion exchange and affinity separation membranes [34,35,37].

Asymmetric membranes have received the most attention and development over the years. They have played a significant role in gas separation processes. The development of the first asymmetric phase inversion membranes was a major breakthrough in the development of ultrafiltration and reverse osmosis [38-40]. These membranes typically have 100 to 500 µm thickness and contain porosity in the bottom layer, which determines the type of process in which membrane can be used. The thickness of the top layer will determine the permeation rate, whereas permeation rate decreases with increasing of thickness. Porosity of the sublayer serves as a mechanical support for the top layer and does not give any additional transport resistance [37,41,42]. It should have a regular structure and a high porosity with sufficient interconnection of the pores. Microvoids are present when membranes are formed by immersion precipitation. They appear just below the dense layer and required when high pressure is used [35,37,41].

Typically, asymmetric membranes are produced by solution spinning or casting a solution of the polymer into a coagulation bath composed of a liquid that is miscible with the solvent. Polymer solution concentrations can vary widely, from 10 to 12% up to 40 to 45% of total polymer in some cases. Water is considered the most desirable coagulant and thus, it is widely used. However, any fluid with which the solvent is
miscible and in which the polymer is not soluble is a potential coagulant for the making of such membranes [35,38,41].

2.2.3. Asymmetric membrane

Suitable membranes for gas separation processes require high pressure-normalized flux and selectivity, which can be accomplished by using asymmetric membranes [6,43,44]. Asymmetric membranes consist of a dense and thin skin layer supported by porous sublayer of the same material. It comprises a very thin skin layer (0.1-0.5 µm) on a highly porous thick substructure (100-200 µm) as shown in Fig. 2.3 [45]. Ultrathin-skinned asymmetric membrane implied the asymmetric membrane has an effective skin layer thickness of approximately 1000-5000 angstroms (Å), whereas hyper thin-skinned asymmetric membrane possesses a skin layer with thickness lesser than that [46,47].

![Fig. 2.3 Schematic illustration of the structure of integrally-skinned asymmetric membranes of various configurations; (A) flat sheet and (B) hollow fiber.](image)

The skin layer performs the separation with a high flux since it is thin and with high selectivity due to its high density. The porous substructure provides the mechanical strength for the complete membrane structure, has negligible resistance to mass transfer and prevents the mixing of local permeate fluxes of varying concentrations on the permeate side of the membrane skin surface, regardless of the flow direction of the bulk permeate stream outside the porous layer. In other words, the asymmetric membrane always gives rise to cross-flow permeation irrespective of the feed and bulk permeate
flow pattern [48,49]. For an asymmetric hollow fiber membrane, the surface porosity and pore sizes on its selective layer play an important role to determine the mass transfer process across the membrane [50]. Integrally the skin and thin film composite are two general classes of asymmetric membranes that are universally recognized [51].

The ideal asymmetric membranes produced for gas separation must meet the following requirements [52]:

i. **Porosity of the skin layer:** The selective layer should be defect-free so that gas transport takes places exclusively by a solution/diffusion mechanism to achieve the maximum selectivity, not by poorly selective flow through pores.

ii. **Thickness of the skin layer:** The thickness of the toplayer (skin) determines the permeation rate, and for most of the separation processes this permeation rate is reduced with an increasing skin thickness. The selective skin layer should be as thin as possible to maximize the gas fluxes.

iii. **Porosity of the sublayer:** The substructure should provide sufficient mechanical strength to support the delicate selective layer in higher pressure operation. It should not contribute any additional resistance to gas transport. This means that it should have a regular structure and a high porosity with sufficient interconnection of the pores.

Performance of a membrane-based gas separation process can be described in terms of pressure-normalized flux (productivity) and selectivity (recovery or purity). The pressure-normalized flux indicates flux or permeation rate of the desired product, while selectivity indicates a degree of separation or degree of enrichment. The most important factor to enhance the gas permeance is membrane thickness [33]. Referring to Roman and colleagues, to maximize the flux through membranes, it is essential to minimize the membranes thickness [53]. The skin layer performs the separation with high flux because it is thin and with a high selectivity due to it high density [27,54].

Module design is crucial to the operation of a membrane separation process as this is the unit, which must be operated at a technical scale with large membrane surface areas. Basically, membrane modules are available in five basic designs such as plate and
frame, spiral wound, tubular, capillary and hollow fiber. Good module designs will in general have the following attributes: i) high area packing density, ii) cost effective manufacturing, iii) low pressure drops on feed and permeate sides, iv) good flow distribution and flow pattern, and v) minimal concentration polarization.

For practical gas separation applications, there are two modules that have been widely used such as spiral wound and hollow fiber. Spiral wound modules will typically contain approximately 1000 ft$^2$ of membrane area per cubic foot of pressure vessel volume while hollow fiber permeators have approximately three times as much area per unit volume as the spiral wound unit [35]. A hollow fiber module consists of a bundle of very fine membrane fibers packed into a cylindrical housing or shell. The fibers are arranged parallel to one another and pass through tube at either one or both ends of the device. Seals are provided between the tube exterior and the pressure vessel in order to isolate the high pressure feed from the low pressure permeates. Normally, hollow fiber modules are employed in hemodialysis, large-scale reverse osmosis, and gas separation units, where modules up to 50 cm diameter contain hundreds or thousands of fibers [55].

### 2.2.4. Mechanisms of membrane separation

Fig. 2.4 displays the basic schematic of an ideal gas separation membrane process. The feed stream is separated into permeate and retentate streams during the process. The permeate, which is held at low pressure is enriched in the more permeable species while on the high pressure stream, the retentate is enriched with residue of the less permeable component. The pressure difference provides the driving force for diffusion of gases across membranes, which is maintained by compressing the feed gas or evacuating the downstream side of membrane. Separation occurs because of differences in the relative transport rates of the feed component. Components that diffuse more rapidly become enriched in the low pressure permeate stream, while the slower components are concentrated in the residue stream. The effectiveness of any membrane process is described in terms of the flux (productivity) and selectivity (purity) [35,56,57].
There are two types of membrane that can be used for gas separation. One of them is a “porous” membrane in which the gases are separated based on their molecular size by small pores through the membrane. Generally, the gas permeation rate in porous membranes is affected by three distinct gas flow as follows: i) Poiseuille’s flow; ii) transitional flow and iii) Knudsen’s flow [42,58]. Poiseuille mechanism occurs when the gases collide significantly due to smaller characteristic void passage of the porous structure than the mean free path of the gas molecules. The “no slip” assumption of the viscous flow is voided if the gas-wall collision increases as the mean free path increases relative to the void dimension. Transitional flow happens as the mean free path of the gas molecules is comparable to the size of the pore diameter [59], leading to significant momentum between diffusing molecules and between molecules and the pore wall contributing to the overall flow. As the mean free path is larger relative to the void dimension, the gas transport occurs dominantly due to the collision and bounce of molecules from the pore wall, which is known as Knudsen flow. Flux in this mechanism depends on the molecular weight of the diffusing species [42,60]. These mechanisms as in Fig. 2.5 (A-C) are not commercially useful because of the quite low separation factors that are generally achievable. It should be noted, however, that the world’s first and largest gas separation membrane plant was based on porous membranes [57].

The vast majority of commercial applications are based on nonporous membranes Fig. 2.5 (D). These membranes contain no holes or pores in the conventional sense. The
transport of molecules occurs based on the principle that gases dissolve in and diffuse through solid materials. Gas separation membranes take advantage of this phenomenon with polymers specifically chosen to be highly permeable to the gases of interest. Separation of two gases is possible because different gases exhibit differing rates of transport through the polymer. The ratio of the permeation rates of two gases defines the selectivity of the membrane for those gases [57].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>Convective flow through large pores. No separation occur.</td>
</tr>
<tr>
<td>(B)</td>
<td>Knudsen diffusion through pores. Pores with diameter less than the mean free path of the gas molecules allow lighter molecules to preferentially diffuse through pore.</td>
</tr>
<tr>
<td>(C)</td>
<td>Molecular sieving through small pores. Large molecules are excluded from the pores due to the size.</td>
</tr>
<tr>
<td>(D)</td>
<td>Solution diffusion happens when molecules dissolve into the material and diffuse across it.</td>
</tr>
</tbody>
</table>

Fig. 2.5 Various mechanisms for gas separation membrane process on; (A-C) porous membranes, and (D) dense membranes.

The skin layers can be considered to be essentially defect-free if the transport properties of the asymmetric membranes were predominantly determined by the solution-diffusion mechanism. Skin layer defects form due to incomplete coalescence of polymer in the skin layer [61]. The coalescence process can be caused by the surface tension and the increase in polymer concentration on the outer edge and it prevents the formation of macrovoids near the outer surface.
Polysulfone, polyethersulfone and polyphenylsulfone hollow fibers developed by Fritzsche et al. [62,63] was observed to consists of a dense skin layer and a supporting matrix which composed of loose packing spherical nodule aggregates. It was suggested that fractional free volume of the membranes increased as compared to the polymer used as reflected by an elevated “first heat” glass transition temperature ($T_g$). The membranes spun with 1-methyl-2-pyrrolidone (NMP)/propionic acid (PA) displayed higher pressure-normalized fluxes than those with formylpiperidine (FP)/formamide (FA). As the glass transition temperature of the membranes spun from NMP/PA were found to be larger than those of the membranes spun from the FP/FA solvent system, hence, NMP/PA system had probably greater free volume than FP/PA [62,63].

![Diagram of a quasi-crystalline lattice exhibiting vacancies of holes.](image)

**Fig. 2.6** A quasi-crystalline lattice exhibiting vacancies of holes.

As illustrated in Fig. 2.6, the motion of the molecule occurs when there is a vacancy in the adjacent site, hence, the void will exchange places with the molecule. The same principle can be applied to polymers. However, the motion of the bulk polymer chains can only happen if there is more than one hole available within the same locality. The critical void volume must first exist prior to the jump and these collective vacancies are known as the free volume [64].

(a) **Solution-diffusion mechanism**

This mechanism applies to reverse osmosis, pervaporation and gas permeation in polymer films [27]. The movement of any species across the membranes is caused by
one or more driving forces. This driving force arises from a gradient of chemical potential or electrical potential. A gradient in chemical potential may be due to the concentration gradient or pressure gradient or both [65]. Solution-diffusion separation is based on both solubility and mobility factors. Diffusivity favours the smallest molecules while solubility selectivity favours the most condensable one.

Solubility measures the amount of penetrant passing through the polymer elastomer under equilibrium conditions. Gas solubility through membranes can generally be very low, and is mainly determined by molecule condensation and interaction in the polymer [31]. Larger molecules are more condensed, thus interact better with the polymer to cause higher solubility through the membranes. However, in some cases the diffusivity parameter is higher and is more dominant in influencing the gas pair selectivity than solubility, for example the gas permeation through glassy and crystalline (or semi-crystalline) polymers like polyaniline and polyimide that have a very rigid structure with fixed microvoids. The rigid polymer like PAni has a microstructure (chain intersegmental) which is able to discriminate on a molecular level. These microvoids will trap and immobilize a portion of the permeant gas molecules and this slows down the gas solubility influence on the polymer [66]. In addition, the existence of the openings (free volume) with definite dimensions within the polymer matrix causes the gas molecules of the same size to be easily and consistently separated. Hence, the smaller molecules can go through the thin dense layer faster than the bigger molecules. Thus, this definite rigid structure excludes the larger molecules to a greater extent than smaller molecule gases implying that the separation factor is determined by selective diffusion due to the size of the gas molecules over the specific gas interaction with the polymer [31,67].

The difference in pressure-normalized flux exhibited by a polymer membrane to different gasses can serve as the basis for separating the components of a gaseous mixture. The permeation of a polymer membrane by gas takes place in three steps: (1) the dissolution of the gas at the membrane interface; (2) the diffusion of the gas through the membrane; and (3) the elution of the gas at the opposite interface.
The key properties of a gas separation membrane are pressure-normalized flux and selectivity. According to Fick’s first law, the general flux equation for a pressure-driven process can be written as,

\[
J_i = \frac{P_i \cdot (p_1 - p_2)}{L}
\]  

where \(J_i\) is the permeate flux, \(p\) is the partial pressure of permeating species in the feed \((p_1)\) and product \((p_2)\), where \(P_i = D_i \cdot S_i\) is the permeability coefficient, \(D_i\) is the diffusion coefficient, \(S_i\) is the solubility constant, \(L\) is the membrane resistance to transport, often expressed as membrane-effective thickness.

The permeability coefficient will be determined at 25°C. The permeance can be calculated through:

\[
\left(\frac{P}{L}\right)_i = \frac{Q_i}{\Delta p \cdot A} = \frac{Q_i}{\Delta p \cdot n \cdot \pi \cdot D \cdot l}
\]  

where, \((P/L)_i\) is the permeance of the test gas expressed in gas permeation units, GPU \((1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3\text{(STP)/cm}^2\cdot\text{sec} \cdot \text{cmHg})\); \(Q_i\) is the volumetric flowrate of gas ‘i’ \((\text{cm}^3/\text{s})\); \(\Delta P\) is transmembrane pressure drop \((\text{cmHg})\); \(A\) the membrane effective surface area \((\text{cm}^2)\); \(n\) is the number of fibers; \(D\) is the fiber diameter \((\text{cm})\); and \(l\) is the effective length of the fiber \((\text{cm})\).

The ideal separation factor \((\alpha_{ij})\) of an asymmetric membrane can be defined as the ratio of the permeances of two pure gases \(i\) and \(j\);

\[
\frac{\alpha_{ij}}{\alpha_j} = \frac{\left(\frac{P_i}{P_j}\right)}{\left(\frac{P/L}_i\right)} = \frac{\left(\frac{P/L}_j\right)}{\left(\frac{P/L}_j\right)}
\]  

(2-3)
General relative hierarchy of common gases permeabilities is shown in Table 2.1. Table 2.2 shows the kinetic diameter of various types of gases [22,34].

**Table 2.1** General relative hierarchy of common gases permeabilites.

<table>
<thead>
<tr>
<th>Relative permeability</th>
<th>Fast</th>
<th>Medium</th>
<th>Slow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases</td>
<td>H₂O</td>
<td>Ne</td>
<td>C₃H₈</td>
</tr>
<tr>
<td>NH₃</td>
<td>O₂</td>
<td>C₂H₂</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>He</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>Xe</td>
<td>CO</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>CH₄</td>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂H₆</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.2** Estimated kinetic diameter of common gases molecules.

<table>
<thead>
<tr>
<th>Gases molecules</th>
<th>H₂</th>
<th>O₂</th>
<th>N₂</th>
<th>He</th>
<th>CO₂</th>
<th>CH₄</th>
<th>C₂H₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic diameter</td>
<td>2.89</td>
<td>3.46</td>
<td>3.64</td>
<td>2.60</td>
<td>3.30</td>
<td>3.80</td>
<td>3.90</td>
</tr>
</tbody>
</table>

C₂H₄ > CH₄ > N₂ > O₂ > CO₂ > H₂ > He

The major influence on gas transport rate through the membrane is the rigidity or flexibility of the material, and the rates of gases supplied to the skin surfaces of the membrane controlled by feed pressure. Differences between specimen size (*i.e.* hollow fiber diameter) and geometry (*i.e.* hollow fiber diameter), gas mixtures, temperatures, and apparatus may contribute to varying the data and causing possible challenges interpreting results and relating them to other known properties of the membrane.
material [68]. With the possible existence of defects, the effective membrane surface area (membrane geometry and number of fibers) exposed to the test gas is a major factor in determining more consistent data.

Fig. 2.7 Various transport mechanisms involved in an asymmetric membrane.

Gas molecules tend to diffuse from the high pressure to low pressure side when exposed to the asymmetric membrane. Generally, the asymmetric membrane consists of 3 major layers; top dense skin layer, transition layer with narrow pores and support layer with wide pores as shown in Fig. 2.7. As previously explained in detail in Section 2.2.4 on various flow mechanisms in a membrane, it can be clearly seen that the rate determining step controlling the overall gas transfer process is primarily gas transport through the membrane dense skin [31]. Although, the other layers still contribute to some resistance, it is minimal with a low separation factor impact. Membranes with a thicker skin will ensure high gas separation factors while slowing the permeation rate. Thus, in order to ensure that a membrane with desirable gas separation performance can be produced, optimizing the membrane fabrication procedure is the most crucial stage which is widely investigated by many researchers throughout the years.

2.3. **Membrane fabrication by phase inversion process**

In the preparation of synthetic polymeric membranes, one of the popular methods is the phase inversion process [69]. Phase inversion processes were used in the late 1800s.
However, the physical processes involved were not directly identified [52]. The phase inversion process developed by Loeb and Sourirajan is still one of the most important methods of preparing asymmetric membranes. During phase inversion, a combination of nucleation growth and spinodal decomposition controls the formation of membrane morphology [70]. The process involves a phase separation of a polymer solution in polymer rich and lean phases, which can be achieved by the immersion-precipitation technique. A polymer solution is immersed in a nonsolvent bath for the polymer, where a mass transfer process involving interchange of solvent/nonsolvent occurs [71].

Among the various phase inversion techniques are air casting of dope solution, precipitation from the vapour, thermal precipitation and immersion precipitation. In the air casting technique process, the polymer is dissolved in a mixture of a volatile solvent and less volatile nonsolvent. As the solvent evaporates, the solubility of the polymer decreases and then phase separation take places. In the precipitation from the vapour phase process, phase separation of the polymer solution is induced by penetration of nonsolvent vapour in the solution. Thermal induced phase separation (TIPS) technique, involves a demixing process where the solvent quality usually decreases as the temperature decreases. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying. In the immersion precipitation case, a polymer is cast as a thin film on a support or extruded through a die, and subsequently immersed in a nonsolvent bath. Precipitation can occur because the good solvent in the polymer solution is exchanged with nonsolvent in the coagulation bath. The differences between the four techniques originate from differences in the desolvation mechanisms [72]. Among these techniques, immersion precipitation is widely used to produce commercial gas separation membranes and other membrane based-separation.

A major consideration in the phase inversion process lies in whether a wet or a dry casting process has been used. This can be identified by whether the output of the spinneret or casting knife that transfers the polymer solution from a closed reservoir is phase separated in air or submerged directly in a liquid coagulation medium that is a nonsolvent for the polymer. If the solvent and nonsolvent components are removed only by evaporation, membrane formation is defined as a dry phase inversion process. Alternatively the evaporation-induced dry phase inversion process, phase instability and structure formation can also be achieved by immersion of a cast membrane in a liquid
quench medium that is a nonsolvent for the membrane-forming polymer. A membrane can also be fabricated by combining both phase separation known as dry/wet phase inversion process. The technique involves solvent evaporation of the outermost region of the cast membrane followed by precipitation from a nonsolvent vapour phase. Usually in this process, the majority of the membrane structure is formed by solvent-nonsolvent exchange during a quench step in a liquid bath [72,73].

During the immersing process, the solution is cast or extruded into a quench medium, which consists of nonsolvent for the polymer. Nonsolvents diffuse into the nascent membrane, causing spinodal decomposition of the polymer solution into a polymer-rich solid phase, which forms the membrane structure or walls and a solvent-rich liquid phase, which ultimately forms the liquid-filled membrane, pores of the membrane. Temperature may also be used to induce this decomposition or to influence its rate. An evaporation step is usually provided prior to the quench, during which solvent evaporates from what ultimately will be the active layer of the membrane. The quench liquid and any solvent remaining from the membrane formation process must be removed from the membrane before it can be used for gas processing. For some membranes this step is accomplished by water washing and a simple evaporative drying step. For other membranes the quench liquid must be displaced with solvent(s), which are then evaporated. Such solvent displacement is needed in these cases in order to preserve the morphology of the membrane. Drying without the use of the intermediate solvent would result in a collapse or densification of the asymmetric structure, which can greatly reduce membrane productivity. Generally, the pores at the membrane surface where precipitation occurs first and most rapidly are much smaller than those in the interior or the bottom side of the film, and this leads to the asymmetric membrane structure [74].

Two different mechanisms occur during immersion-precipitation that are delayed and instantaneous delayed (liquid-liquid) demixing [75,76]. During delayed demixing, the nonsolvent in liquid medium and the solvent in the casting solution have a poor mutual similarity. In case of delayed demixing there is a certain time interval between the moment of immersion of the polymer solution in the nonsolvent bath and the onset of phase separation. During this interval called delayed time there is a large outflow of
solvent from the solution, while the inflow of nonsolvent is relatively small. These different diffusion rates are caused by an interplay between thermodynamic interaction parameters and friction coefficients [77]. As the solvent evaporates, the local polymer concentration on the outer surface elevates reducing mass exchange rate upon in-contact with the coagulation bath, thus, a dense skin membrane is formed. During instantaneous demixing, the liquid-liquid demixing occurs almost as soon as the polymer solution is in-contact with the coagulation bath. This leads to a strong thermodynamic interaction between the nonsolvent in the liquid coagulation medium with the solvent in the casting solution [76]. Since the liquid-liquid demixing starts instantaneously, a very thin skin layer is forms due to rapid diffusion-driven process. Generally, membranes formed by this mechanism have a very thin microporous skin layer with porous sub layer with a finger or sponge-like open interconnected substructure.

2.3.1 Asymmetric membrane formation by dry-wet phase inversion

Dry/wet phase separation can be described as evaporation-induced phase separation in the outermost regions of nascent flat sheet and hollow fiber membranes prior to coagulation. ‘Dry” phase separation occurs on this outermost membrane region almost instantaneously as the polymer solution is cast or extruded. Upon immersing in the non-solvent bath, the nascent membrane solidifies and the membrane structure is formed and extraction of the remaining solvent begins in the wet phase step. In order to promote the formation defect-free highest performance gas separation membranes, a finer adjustment of the volatile and less volatile solvents used and the duration of wet and dry phase separation are crucial [61].

A process for producing ultrathin and defect-free selecting layers asymmetric membranes using dry/wet phase separation has been reported earlier for organic coagulation media. Pinnau and Koros [78] had successfully eliminated the defects and achieved thinner selective skins by changing the casting solution composition and the addition of a convective evaporation step in the spinning process. However, the flammability, toxicity, difficulties in reclamation of the organic quench media makes it not attractive for commercial use. Hence, it is desirable to have the option to use more convectional aqueous quench media in large scale production operations [78]. A flat sheet polysulfone membrane was produced by aqueous quenched dry/wet system using
organic coagulants [79,80]. Despite the coagulant can have a great effect on morphology, it is believed that the membrane skin and much of the transition region is formed during the dry phase separation step. Under optimum formation conditions, the membrane skin has been found to be much thinner than those formed in traditional wet phase separation processes as well as defect-free without any post-treatment requires [78].

2.3.2 Effects of dope solution formulation on asymmetric membrane formation

(a) Polymer concentration

The addition of an increased amount polymer to the casting solution increases the dope viscosity and tends to promote more selective but less productive membranes in the absence of offsetting casting conditions or other solution component changes. Generally, when polymer concentration increases, the selectivity will increase and permeability will decrease in the separation performance and membranes with higher skin thickness (low porosity) will be produced [81]. According to Pesek and Koros, by increasing the polymer content from 14 to 26 wt% at a constant DMAc/THF solvent ratio of 1/1 in the casting solution of polysulfone membrane, produced an increase in the average $O_2/N_2$ selectivity and a decrease in the average pressure-normalized flux of oxygen. At polymer concentration between 18 to 26 wt%, defect free skin layers less than or equal to 1000 Å was produced. [80] When an increase in the polymer concentration and solvent ratio occur simultaneously, there will be a dramatic increase in the casting solution viscosity while sustaining good membrane performance.

When the polymer concentration decreases, the more dilute polymer solutions require greater amounts of non-solvent to precipitate the polymer. Then, a larger amount of imbibed non-solvent stays in the cast membrane leading to a more porous membrane structure. In addition, the total thickness of the membrane decreases because the film shrinking rate is higher due to increasing solvent outflow at lower polymer concentrations in the casting solutions [80]. Therefore, a thinner skin layer of lower density, a thinner membrane film, and high-porosity sub-layer structure all decrease the membrane resistance to gas flow leading to high permeance whereas the less substantial substructure resistance maintains a high separation factor [82].
Another important factor in formulating a suitable dope solution composition in membrane production is the solvent ratio used. The solvent ratio of less volatile solvent to volatile solvent in the casting solution is a crucial parameter controlling the dry/wet phase separation process. Solvent evaporation and polymer coagulation rate highly influence the formation of a defect-free skin layer. The two parameters can be refined with the use of the two very distinct volatility solvents. Defects on such membranes are expected to be minimal but by optimizing the solvent fraction, thermodynamically better solvent produced an effectively thinner separating skin layer.

As the solvent ratio increases at a constant polymer concentration, the membrane permeability increases. However, the selectivity and the skin thickness of the produced membrane decrease with high porosity [81]. Pesek and Koros reported that as the solvent ratio was increased in the range of 0.5 to 1.5, the effective skin thickness decreased as evidenced by the sharp increase in the pressure normalized flux of oxygen, while only a slight decrease in the O$_2$/N$_2$ selectivity occurred [80]. At a solvent ratio of 2.0, the average effective skin thickness was observed to be close to 350Å. Decreasing the selective skin thickness by increasing the solvent ratio is perhaps most easily explained by lower solvent evaporation, a smaller interfacial dry phase separated region, and therefore a less concentrated outermost skin region in the nascent membrane. On the other hand, there are a few parameters that are affected by the solvent ratio change such as viscosity of the solution, the redissolution rate, and the most importantly the kinetics of the wet phase separations process since water has much stronger affinity for DMAc than for THF. Last but not least, solvent chosen must be a volatile solvent and miscible with water.

Non-solvent additive

Non-solvent plays two important roles in membrane casting. It is used either as an additive in the casting solution or used as external coagulant for solvent exchange, such as tap water. The role of non-solvent additive is controlling the membrane morphology. Wang et al. indicated that the membrane porosity increasing with increasing amount of additives [83]. This is because the addition of large amount of additive would make the casting solution easier to demix and therefore more porous membranes are formed. The
addition of a suitable non-solvent additive into the membrane casting solution accelerates the coagulation process from solution to gel when the casting solution is immersed in a coagulant. As a result, membranes with a thinner skin layer and more uniform structure could be obtained [83].

2.3.3 Spinning parameters in asymmetric membrane production

(a) Effect of shear rate on the membrane fabrication

The rheological conditions such as the degree of shear experienced during membrane casting or hollow fiber spinning were also found to alter the degree of molecular orientation in the skin layer of the asymmetric membranes. The molecular orientation is enhanced by shear during casting and this causes a favourable effect on membrane selectivity [84]. Based on the resistance model of composite hollow fiber membranes and various gas transport mechanisms, Wang and Chung developed a simple approach to estimate surface porosity and mean pore size of asymmetric hollow fiber membranes [50]. The calculations suggested that hollow fiber membranes spun with high shear rates apparently have a thicker or denser selective skin layer and total surface porosity shows an up and down pattern with an increase in shear rate. On the other hand, Chung et al. demonstrated the effect of shear rate on the outer surface morphology of hollow fiber UF membranes by using an atomic force microscope (AFM) [85]. The result from AFM images provided direct proof to support the hypothesis of ‘the higher shear stress in the spinneret may result in a hollow fiber UF membrane with a denser skin due to the greater molecular orientation and the closer package of molecules’.

Manipulation of rheological factors in the membrane formation process provides a potential platform to develop defect-free and ultrathin-skinned asymmetric membranes for gas separation [86]. Therefore, Ismail and Lai, produced a defect-free and ultrathin-skinned asymmetric membrane by optimizing dope formulation or preparation conditions in membrane formation process without any necessity of post-treatments [46]. Besides, both permeability and selectivity of membrane were found to increase with high-sheared casting, which was reflected in a reduction of skin thickness as well as enhancement of molecular orientation in skin layer.
Casting shear rate has a significant effect on the gas separation performance of asymmetric PSF membranes. Using the newly designed casting system, Ismail and his colleagues produced an asymmetric membrane with high permeability and selectivity [87]. It was found that by increasing shear rate, the selectivity of membrane produced was significantly increased. Furthermore, high shear rate membranes tend to exhibit greater molecular orientation in the skin layer.

(b) **Effect of solvent evaporation on the membrane formation**

The evaporation time is considered an important parameter for the formation of the asymmetric membrane. During the evaporation step, it is expected that the most volatile solvent will be removed from the membrane surface, and results in a region with a locally elevated polymer concentration. Basically, the skin layer of asymmetric membranes is generated from the dry phase-separated region [14,79,80,88].

According to Wang et al., at the long air gap, the inner finger like voids nearly reach the outer surface of skin layer and big macrovoids appear under the skin layer [89]. The length of finger like void at the outer surface of fiber depends strongly on the solvent exchange occurring in the air gap region. Previous studies showed that an optimum residence time existed during dry/wet spinning which gives better molecular orientation of the polymer in the skin layer [87]. The influence of the dry phase inversion process as the nascent hollow fibers pass through an air gap is rather complicated and may vary for different membrane forming systems [89]. The formation of the outer skin layer in hollow fiber spinning depends on evaporation and coalescence in the dry process, subsequent phase inversion during the wet process as well as internal coagulation properties.

According to Chung and Hu, there are two mechanisms taking place in the air gap region these are molecular orientation and phase separation [90]. Since the fact that an air gap will introduce elongational stress on the fibers because of gravity, it may generate positive or negative effects on membrane formation and performance. A high elongation stress may pull molecular chains or phase separated domains apart in the early stage of phase separation and creates porosity, while a medium stress may induce molecular orientation and reduce membrane porosity or free volume. During the
extrusion process of polymer solution through the spinneret, elongation stresses caused by gravity and spine line stresses may be responsible for molecular orientation of membrane nascent. These may influence the properties of final hollow fibers. However, these are possible to minimise by employing a wet spinning process and keep a constant ratio of dope extrusion speed to take-up speed during spinning speed scale up (no spin line stress). It is believed that higher air gap between spinneret and coagulation bath would give an impact to formation of hollow fiber membrane. It means that elongation stress caused by gravity becomes more pronounced with increasing air gap [90].

An increase in air gap distance may result in the selective skin with a greater orientation and tighter molecular packing. Thus, selectivity increased while permeability decreased at the same time. On the other hand, the elongational stress caused by spin line stress also affects the hollow fiber formation. Purci clearly states the importance of fine-tuning of the rheological properties of the spinning dope in terms of spinnability and membrane performance [91]. Spinnability relates to stability in the spin line and consistency in the quality of the fiber produced.

2.4. **Defects on asymmetric membrane skin layer**

The development of early gas separation membranes was plagued by the presence of microscopic defects that prevented the intrinsic selectivities of the barrier layer from being achieved in very thin films. These defects could significantly reduce the selectivity of the membrane, often making it virtually useless for practical applications [22]. Formation of defects is very difficult to avoid during membrane preparation and module manufacturing. In preparing asymmetric membranes, the goal is to make the selective layer that performs the separation as thin as possible and defect-free. The defects may be caused by imperfection of membrane skin layer formation, gas bubbles, dust particles and support fabric imperfections but can be very difficult to eliminate. Fig. 2.8 shows a schematic of Loeb-Sourirajan defective anisotropic gas separation membrane [27]. Such defects may not significantly affect the performance of anisotropic membranes used in a liquid separation process but it can be disastrous in gas separation application. Even a single small membrane defect can dramatically decrease the selectivity of gas separation membranes, especially with relatively selective
membranes such as those used to separate hydrogen from nitrogen. For example, a good polymeric hydrogen/nitrogen separating membrane selectivity is greater than 100. A small defect that allows as little as 1 percent of the permeate gas to pass through without separation will double the nitrogen flux and half the membrane selectivity [27].

![Defects on skin layer](image)

**Fig. 2.8** Schematic of defective anisotropic gas separation membrane as proposed by Loeb-Sourirajan.

### 2.4.1. Sealing the defects on the outer surface of asymmetric membrane

Monsanto devised an ingenious solution to the membrane defect problem, which was a critical breakthrough in the commercialization of gas separation membranes; their approach is illustrated in Fig. 2.9 [27,92]. The Monsanto group produced the Loeb-Sourirajan hollow-fiber membranes (principally from polysulfone) and then coated the membranes with a thin layer of silicone rubber. It was explained that the silicone rubber was extremely permeable compared to polysulfone but had a much lower selectivity. Thus, the coating only served to plug defects on the outer surface of the asymmetric membrane without significantly altering the permeability or selectivity of the non-defective portion of the asymmetric skin and eliminated convective flow through these defects. The silicone rubber layer also protected the membrane during handling. The development of silicone rubber-coated anisotropic membranes was a critical step in Monsanto’s production of the first successful gas separation membrane for
hydrogen/nitrogen separations and enabled rapid large-scale production of hollow fiber gas separation membranes, whose defects were sealed in a subsequent post-treatment process.

![Diagram of membrane defect sealing](image)

**Fig. 2.9** Sealing the defects of asymmetric membrane outer surface by silicone coating as proposed by Henis and Tripodi.

Since the Henis and Tripodi effort with Mosanto was known, silicone coating has been the most employed method to overcome these defects on the effective skin layer [67,93,94]. The purpose of silicone coating is to fill any surface pinholes or imperfections, which render the membranes full potential for gas separation [84]. Coating became a standard procedure that allows the membrane to exhibit permeation properties closer to the inherent characteristics of the polymer itself [92,95-97]. Besides, the coating blocks any defects in the selective skin and allows substantial increase of permselectivity without significant reduction of productivity [78,80,84]. Coating differs to other post-treatment techniques since the membrane itself is unaltered. The coating material, polydimethylsiloxane, is a high permeability low selectivity elastomer, which can simply plug the defects but plays no part in the separation of gases. Uncoated membranes show poor selectivities suggesting that surface pores or imperfections prevail. In contrast, coated membrane results are more pertinent since they represent the membranes full potential [95]. The flow of gas through the portion of the silicone
rubber layer over the pore is high compared to the flow through the defect-free portion of the membrane. However, because the area of the membrane defects is very small, the total gas flow through it that plugged defects is negligible [27].

Chung et al. employed the coating technique with 3 wt% PDMS (Sylgard® 184) solution in hexane to his composite polyvinylpyrrolidone/polysulfone (PVP/PSf) hollow fiber membranes [97]. The experimental data showed that the additional coat of PDMS improved the separating properties of the composite hollow fiber membranes tremendously and were able to plug the defects in the PVP layer resulting in improved selectivity. The low selectivity exhibited by the non-coated PVP/PSf hollow fiber suggests the presence of a considerable amount of defects in the PVP intermediate layer. This could be due to the inability of PVP to form a freestanding film, which may result in the PVP coating being unable to cover all pores on the PSf dense layer selectively. Similar results were discovered to the prepared polyethersulfone (PESf) ultrathin skin layer asymmetric hollow fiber membranes made by single polymer and single solvent. The uncoated membranes have an O₂/N₂ selectivity of about 0.96 and this value is significantly improved to 5.8 after a silicone coating [97].

Although, it has been widely reported and accepted that the use of a silicone coating is only to overcome the defects and brings out the intrinsic separation property of the membrane, the remarkable improvement on the separation factor is still debatable. Polydimethylsiloxane (PDMS) that is always used for this purpose is a rubbery polymer that forms a composite-like layer on the outer side of the membrane skin. Generally, gas permeability through a rubbery polymer is much higher than a glassy polymer due to ample thermal energy to promote chain flexibility and interactions. With a high mobility of the chain segments, gas solubility through the membrane will increase, thus promoting a relatively higher permeation rate compared to a glassy polymer. However, this also implies that separation still occurs through the silicone layer prior to the membrane dense surface due to different solubility coefficients among the gases. For example, the oxygen and nitrogen permeabilities through dense PDMS are 600 and 280 barrer, respectively, which indicates the selectivity of ~2.1 [31]. Even though the value is quite low, this goes back to the issue of potentially the silicone coating layer is the initial stage that gas separation occurs. It is recommended that the most possible dilute silicone solution is applied to ensure the layer form upon drying will be as thin as
possible and only acts to plug the defects. Ultimately, further investigations into other factors influencing membrane fabrication is always preferred over silicone coating in order to suppress the formation of defects and ensure more reliable gas permeability and selectivity can be reported without relying on silicone coating repairs.

2.5. Polyaniline: Synthesis and applications

2.5.1. Synthesis of polyaniline

The idea of using plastics as an electrical conductor used to sound impossible. In fact, plastics and polymers have always been synonyms to insulator. Carbon based polymers were rigidly regarded as insulators for the past years and plastics have been extensively used by the electronics industry because of this insulating property. Besides being used as an insulating material, polymers were the favourite option as an inactive packaging. However, the sceptical perception started to change upon the discovery of intrinsically conductive polymer or electroactive polymers. Although this class is in its infancy, much like the plastic industry was in the 30's and 50's, the potential uses of these are quite significant. Interest in π-conjugated polymers has continued for a number of years [98-100]. The extensive delocalization of π electrons is well known to be responsible for the array of remarkable characteristics that these polymers tend to exhibit. These properties include non-linear optical behaviour, electronic conductivity, and exceptional mechanical properties such as tensile strength and resistance to harsh environments [101-104]. Polymers composed of aromatic and heteroaromatic ring structures have been particularly outstanding from a materials perspective [99].

Although it has been over 150 years, there are still continuous research efforts on improving the synthesis technique and exploring the potential applications of polyaniline. Besides being environmentally stable, polyaniline has received the most attention due to the ease of preparation with high yield and low cost of synthesis over the other intrinsically conducting polymers (ICPs) like polyacetylene, polypyrrole etc. [105-108]. Since the first known chemically synthesized in 1840’s by Fritzscche and followed with electrochemically synthesized in 1862 by Letheby, the interest in polyaniline has grown as shown in Fig. 2.12. Pioneering the area, Green and Woodhead suggested that this organic conducting polymer existed in various oxidation states and
with the presence of oxidants or reducing agents these states are interconvertible [109,110].

Fig. 2.10 Basic polyaniline molecular structure in base form.

PAH in base form consists of two main structure units that are the quinoid diamine and the benzoid diamine as Fig. 2.10. It was explained that the $y$-value determined the oxidation state of PAni, which can vary from zero to 1 as they identified five states as in Fig. 2.11. The three primary PAni oxidation states are the completely reduced form ($y=1$), the completely oxidized form ($y=0$) and the equal fraction of both reduced and oxidized forms ($y=0.5$) known as leucoemeraldine, pernigraniline and emeraldine base, respectively.

Fig. 2.11 The three most common oxidation states of polyaniline.
Fig. 2.12 Milestones in the development of polyaniline polymerization [111-116].
Generally, polyaniline is known to be insoluble in common solvents due to the strong π-π interaction between the rigid polyaniline backbones. Understanding the existence of PAni oxidation states, emeraldine base (EB) form turned out to be the most stable and processable polyaniline that is completely soluble in N-methyl pyrrolidone (NMP) and partially soluble in tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) [117-119]. In addition, with the presence of suitable acidic dopant, PAni can be processed in a polar or a non-polar solvent or even water in some cases [119-121]. Due to this behaviour, this study will address only the EB form of polymer.

\[
\begin{align*}
4n \text{NH}_2 + 5n (\text{NH}_4)_2\text{S}_2\text{O}_8 &\rightarrow \text{HA} \\
n \text{SO}_4^{2-} &\rightarrow n \text{NH} - \text{NH} \rightarrow n \text{NH} + 4n \text{H}_2\text{SO}_4 + 5n (\text{NH}_4)_2\text{SO}_4
\end{align*}
\]

**Fig. 2.13** The oxidation of aniline with ammonium peroxydisulfate in aqueous medium yields polyaniline (emeraldine form).

Although throughout the years electrochemical polymerization of aniline had excited the research field immensely in optimizing the reaction conditions and examining the effects on the produced polymer properties, synthesizing PAni chemically has always been the important method. This technique is simple and can be easily employed as well as emerge as the most feasible route for polyaniline production especially in a huge scale [116,117,122,123]. The most common synthesis technique of polyaniline is by oxidative polymerization of the monomer with ammonium peroxydisulfate (APS) as an oxidant (Fig. 2.13) [124-126]. The components are both dissolved in acidic medium, in which aniline exists as an anilinium cation and slowly (the reaction is very exothermic) added to each other. Various selections of organic and inorganic acids of different
concentrations have been utilized in PANi synthesis. The polymer precipitates as small particles and the reaction product is dispersion.

As the year progresses, more work has been done in improving the polyaniline properties as well as varying the molecular weight. Adams et al. discovered that the molecular weight of PANi can be increased as the temperature decreases [113,114,127]. As the temperature reduces to sub-zero level, sufficient amount of lithium chloride was added to keep the reaction mixture mobile. Besides that, longer adding and reaction time were employed to ensure optimized yield achieved. As the reaction temperature reduced to -35.0°C, emeraldine base PANi yielded ranging from 89.6% to 100.5%. A yield of over 100% can be superficial for -27.5°C; they explained that it is possible a certain amount of the ring chlorination and inorganic residue is still present in the filter cake due to incomplete washing of the product. However, they still manage to maximize the amount of EB produced for -27±1°C, which was up to 97.5% with molecular weight of 153000±9000 daltons [113,114]. It was also discovered that the optimum starting pH of the reaction should probably be between +0.2 to +1.0M of HCl since anything less dropped the percentage of yield sharply. In addition, the maximum molecular weight was attained with mole ratio of oxidant to aniline between 1.10 to 1.15:1.0 [114,128]. As the ratio exceeds the range, over-oxidation occurred where the molecular weight of PANi will reduce since the polymer chains began to break up, and the oligomers formed are oxidized to penigraniline [107,116,129].

Although the oxidant adding time affected the percent yield and molecular weight slightly, reaction time is an important factor since it is highly depending on the reaction temperature. A minimum reaction time of 15 hours was required for reaction temperature of -26°C and Cao and his colleagues documented that they employed 4 hours for the PANi polymerization at 0°C [114,116]. However, Jarvinen et al. compared the effects of adding oxidant into the monomer period versus on the produced polyaniline molar mass. They discovered that feeding time of aniline into the oxidant over long period of time (2, 4 and 6 hours) reduced the molecular weight sharply. In contrast, with the reaction temperature of 4°C, 4 hours adding time of oxidant into the monomer was found to be ideal to produced high molar mass PANi. The oxidant was fed to the monomer solution gradually and the polymerization temperature was regulated with appropriate cooling system [130].
Besides preventing the reaction mixture from freezing, lithium chloride apparently induced the charge localization of polyaniline [131]. Although, Chen and Lin found that other ionic salts like LiClO₄, LiBF₄, LiBF₆ and Zn(ClO₄)₂ pseudoprotonation on PAni actually improved EB properties such as the conductivity and mechanical strength, LiCl degree of localization on emeraldine base PAni has the strongest impact [59,132]. It is found that ionic strength of HCl increases as the addition of a salt of a same anion since the total ionic strength of Cl⁻ increases in the polymerization medium [132,133]. Recently, Sengupta and his colleagues [132] further examined the effect of LiCl on the produced polyaniline. LiCl acted as a gel inhibitor to the growing polymer that hindered the molecular aggregation and phased out of the growing polymer. This ensured the polymerization occurred in a homogeneous phase and promoted the polymer growth and chain length. In addition, Cl⁻ incorporation in the polymer chain provided instantaneous nucleation for the growing polymer. Thus, a higher molecular weight polymer was produced and the yield of PAni increased as the amount of LiCl increased [132,134-136]. Hence, not only as an antifreeze in the polymerization process, LiCl also promoted a higher yield of longer PAni chain with improved properties.

2.5.2. Progress in polyaniline derivatives

PAni processability is still an issue for further applications due to difficulty in preparing a stable viscous polymer solution. Although emeraldine base form PAni has been found to be somewhat soluble in strong polar solvents like m-cresol [137], N-methyl-2-pyrrolidone (NMP) [138] dimethyl sulfoxide (DMSO) [139] and N,N'-dimethylpropyleneurea (DMPU) [140,141], the amount of polymer can be dissolved could not be more than 6 wt% since rapid gelation of the solution occurred with the gelation could started at as low as 1 wt% of polymer content [141-143]. As the effort progressed, it was discovered that it was possible to dissolve polyaniline (doped emeraldine salt) to a certain extent in few concentrated acids like formic acid, acetic acid, sulfuric acid [138,144,145]. Upon doping with organic acid dopant, PAni can be dissolved in wider range of organic solvents [120,137,146].

When polyaniline derivatives were electrochemically synthesized in 1910, a new method to improve PAni processability was discovered [109]. However, the study on
polymerization and characterization of ring-substituted polyaniline really took off in 1980’s, when Shenglong et al. [147] had chemically polymerized m-toluidine and o-chloroaniline and halogen-substituted derivatives was electrochemically synthesized by Snauwaert et al. [148]. The following years, various dimethyl derivatives of polyaniline were synthesized [149]. In the late 1980’s, a new soluble polyaniline derivative was polymerized and poly-o-methoxyaniline showed good solubility in numerous inorganic and organic solvents like dimethylformamide (DMF) [150,151]. In 1990, Wei et al. had successfully copolymerized aniline with alkyl ring-substituted anilines. The produced polymer inherited the strong PANi traits like the conductivity [152]. Later, it was shown choosing a longer alkyl substituent resulted in decrease in polymer average molecular weight and yield. However, those polyaniline derivatives were soluble in much wider choices of solvents including chloroform and acetone [153,154].

With the increase in solubility, the synthesized polyaniline became more processable to becoming transformed into films or fibers [155-157]. Polytoluidine prepared by chemical oxidation was dissolved in NMP and its free-standing film with good mechanical properties was successfully prepared by evaporating the solvent and cured at 70-90 °C [155]. A poly(aniline-co-o-ethylaniline) film was easily formed due to high solubility towards various solvents. This acid-catalyzed oxidation copolymer was shown to be 2-7 times more soluble in methanol and acetone and 20 times more soluble in tetrahydrofuran as compared to polyaniline [158]. The Langmuir-Schaefer (LS) horizontal lifting technique was successfully employed to fabricate consistent poly(o-anisidine) films with control film structure, thickness and molecular packing, which is highly desirable in order to further exploit its excellent optical, electrical and electrochemical properties [159-161]. Poly-o-toluidine synthesized, was dissolved in NMP at a high concentration of ~33% and the solution showed no indication or tendency to gel soon. The stable prepared solution was spun into a fiber through a single-hole spinneret into a water bath [156,157]. Since the derivatives of polyaniline have proven to be more soluble, thus, this has made it more possible for transforming polyaniline into more desirable shapes and structures for further applications like membranes.
2.5.3. **Polyaniline based gas separation membrane**

Most of the current polymer research for new membrane material is based on improving either the solubility or diffusivity of the desired component over other permeants. Solubility can be improved by modifying or adding pendant groups to the polymer backbone which interacts strongly to the desired permeant. As for diffusivity it is majorly regulated by size exclusion, where the polymer matrix acts like a molecular sieve to allow easy passage of small penetrants and retards the passage of large ones. So, when Anderson and his fellow researchers reported their extraordinary findings of polyaniline gas separation membranes with selectivities of 30 for O$_2$/N$_2$, 336 for CO$_2$/CH$_4$, 3590 for H$_2$/N$_2$ and 4075 for He/N$_2$, PANi caught world wide researchers’ attention and became an exciting material for gas separation membrane [162].

Among the conducting polymers, polyaniline has attracted the most attention in membrane gas separation area due to the remarkable selectivity of gas pairs done by various group in the past [162-164]. With H$_2$/N$_2$ selectivity increased by approximately tenfold than the previously recorded by other polymer, PANi became a promising substitute for the current industrial gas separation system [162]. They reported the novel method in polymeric membrane fabrication where the morphologies of the produced membrane can be modified after fabrication to cater and optimize to any specific applications. This interesting discovery may solve all the troubles related to gas separation membranes since usually it is hard to predict a polymeric membrane performance prior to fabrication and it is impossible to alter once the membrane is cast.

Kuwabata and his colleagues had also found that polyaniline seems to be more promising and interesting membrane material over the other conductive polymers that they have been working on, which is poly (N-methyl-pyrrole) [163,165,166]. In addition to the potential of doping-dedoping techniques that enable one to tailor PANi membranes to suit the separation task, polyaniline is also known to be chemically stable towards plasticizing gases such as CO$_2$ as well as thermally and air stable and can even reach high thermal stability up to 425ºC in nitrogen [104,167-170]. This is an added advantage for potentially excellent chemical and heat post-treatment for further improving the fabricated membranes performance.
Although the doping technique was common for conducting polymers in improving the conductivity since the first reported by Shirakawa et al. in 1977 [171], Anderson et al. were the first to report the remarkable effect of the doping technique on gas separation membrane selectivity [162]. The polyaniline dense films were fully doped in 4.0M HCl for 15 hours, undoped in 1.0 M ammonium hydroxide for 24 hours and finally redoped for 12 hours in 0.0175 M HCl solutions. The membrane performance was tested at each stage of the doping process beginning with the as-cast film. Upon doping, the hydrogen permeation rate reduced while H\textsubscript{2}/N\textsubscript{2} selectivity improved from 207 to 208. This happened since chloride dopant counterions is believed to be filling up the free volume of the membrane. However, they were completely removed after dedoping in base solution yet the expanded morphology was retained and this increased both H\textsubscript{2} and N\textsubscript{2} permeabilities. Consequently, the selectivity reduced sharply to 41. After the final step of redoping, the new retained free volume of the membrane was again filled up but moderately due to the use of mild acid solution. However, this affected larger gases tremendously since the large pathway was reduced and this led to a very high H\textsubscript{2}/N\textsubscript{2} selectivity of 3590, since the nitrogen permeability reduced by approximately 1000 times from the previous step of dedoping. They also found that the bigger the size of the acid counterions used for doping treatment, the higher the selectivity will be. They managed to improve the CO\textsubscript{2}/CH\textsubscript{4} selectivity from 336 using HCl to 640 using HBr with the same molarity and conditions throughout the process [162].

Although Anderson’s work was an act that is really hard to follow or even to repeat, the polyaniline has been an important material for gas separation membrane ever since. Rebattet et al. [172] followed the doping method by Anderson et al. with additional step of annealing prior to doping with strong acid. They cured the membrane for 2 hours at 120 °C to ensure NMP was completely removed. Despite their unsuccessful efforts to repeat and improve Anderson’s, they managed to increase the smaller gases fluxes by 15% and reduce the larger gases permeability by 45% with the highest selectivity of O\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} of 14 and 78, respectively. In this study, they identified that H\textsubscript{2}, O\textsubscript{2} and CO\textsubscript{2} could be categorized as smaller gases and N\textsubscript{2} and CH\textsubscript{4} were in larger gases group with respect to doping treatment. Although it was not clearly stated by Anderson, both works observed that smaller gases permeabilities were improved while the larger gases permeabilities reduced upon doping-undoping-redoping treatment [162,172].
Kuwabata and Martin prepared polyaniline films to investigate the effects of doping level and number of doping-dedoping cycles as well as film curing time and temperature on the gas pairs membrane selectivity and gases rate of permeation. They found that doping level was the only factor that has a great impact on the membrane gas separation performance. As the doping level increased from 13 to 38%, the selectivities of $O_2/N_2$ and $CO_2/CH_4$ were improved by 50% and 22%, respectively [163]. Later in 1995, Rebattet et al. produced PANi film as done by Anderson with the same doping-dedoping-redoping conditions and produced PANi films with selectivities of $H_2/N_2$, $O_2/N_2$ and $CO_2/CH_4$ of 343, 11 and 88, respectively. They also discovered the same effects on smaller versus larger gases permeability after redoping stage [172].

Carbon dioxide is known to be quite an interesting gas to study. Its plasticization effect on most polymers makes it difficult to choose the suitable material for membrane development. Polyaniline has been proved to be chemically stable in this condition and offers high selectivity with $CO_2/CH_4$ gas pair [162, 163, 172-174]. When Hachisuka et al. doped the membrane with high molecular weight acid polyvinyl sulphonnic acid (PVSH), the polymer dopants; they improved $CO_2/CH_4$ selectivity to over 2000. By comparing the membrane with several acids of 2 different categories; the small dopants; i.e: $HCl$ and methane sulphonnic acid; and large dopants; PVSH, polypisoprene sulphonnic acid (PISH) and polyvinyl sulfate (PVS); it was clearly presented that high molecular acid was able to improve the selectivity more than small molecule acids without compromising the permeability of carbon dioxide. The increasing rate of PANi film conductivity of each different dopant resulted in PVSH having lower rate than $HCl$ and MS due to molecular size that made it difficult for the polymer dopant to diffuse into the film. Consequently, the polymer dopants densified on the surface of the film. Thus, the bigger gas is sieved on the ‘skin’ layer yet the pathway of the inner part of the film is cleared out for the smaller gas to diffuse easily. The wide-angle x-ray diffraction (WAXD) data supported this understanding where the $d$-spacing of both dopants category were approximately the same which implied why the permeability of $CO_2$ in both cases is not much different [175].

An unsupported polyaniline film was prepared by Illing et al. [176] following Anderson’s earlier approach. However, instead of polymerizing their PANi in-house, readily available PANi dispersed in $N$-methyl-pyrroldone (NMP) was procured from
ORMECON, Germany. Their reason was to avoid the potential property variations of PANi coming from different synthesis batches. The thin film was cast on a dust-free glass that was intensively cleaned with acetone or iso-propanol. The defect-free membranes were produced by evaporating the solvent at 80 °C for 8 hours and followed by further tempering at 125 °C for 1 hour. Although it has been suggested that it was almost impossible to produce defect-free [163] films thinner than 10 µm, they managed to produce a film as thin as 8 µm. The produced films showed very good gas separation properties with selectivity of 10 for the gas pair H₂/CO₂, 6 for O₂/N₂ and 200 for H₂/N₂ in the case of the redoped membrane. However, the average gas permeabilities were still very low for the redoped PANi films in this study with the highest value for the smallest gas tested, hydrogen, was found for membrane with thickness, \( l = 9 \) µm of approximately 0.067 GPU [176].

The earlier research on measurement of PANi gases flux can be slightly difficult to control and replicate probably due to the highly sensitive polyaniline preparation procedure and handling. However, PANi is still a desirable material for commercial gas separation processes where high selectivity and high permeability are the main concerns. Orlov et al. [177] prepared a more ingenious composite film with polyvinyltrimethylsilane (PVTMS) as the substructure made of 5 wt% polymer in toluene supported onto the cellophane. The film was dried in vacuum upon solvent removal. Then, polyaniline (PAni) was coated onto the surface of 50 µm thick PVTMS film by borderline polymerization of aniline. Various membrane morphologies were produced due to different PANi coating growth and quality on the surface of PVTMS. PANi synthesized in the study was influenced by the ratio and concentration of the reagents, mixing rate, reaction time, and condition of support surface. The PANi coating layer thickness formed on the PVTMS outer layer was \(~0.5-1 \) µm. The produced PANi/PVTMS composite membranes (doped in 0.1 M HCl) showed no significant improvement on selectivity of O₂/N₂, CO₂/CH₄, He/N₂ and He/CH₄, initially but approximately 6 times lower flux than the PVTM only film. As the membrane was undoped (NH₄OH), it was understood that the dopant (0.1 M HCl) started to migrate from PANi structure and the free volume grew. This resulted in favourable membranes with improved selectivities between 2-6 times higher of PVTMS film with slightly lower gases permeabilities. As the composite membrane underwent another cycle of undoping and redoping with the same solutions, although theoretically a more
productive yet higher separation factor should be obtained, the reality was the process caused tension to the layers thus led to the formation of microdefects [177].

It has been widely reported that polyaniline derivatives are more processable, Chang et al. prepared 100 µm membranes made from highly soluble polymethoxyaniline (PMANi) and polyethoxyaniline (PEANi) in NMP. The fabricated polyaniline derivative films showed significant improvement on the permeabilities for all test gases (He, H₂, CO₂, O₂ and N₂) over polyaniline films with selectivities close to or even higher for some gas pairs. This was due to the intra- and interchain hydrogen bonding in the PANi substituents that led to improvement in the molecular free volume [178]. 4 years later, a series of terpolymers were synthesized by oxidative polymerization of aniline (AN), o-toluidine (OT) and 2,3-xylidine (XY). The synthesized terpolymers were soluble in numerous common solvents including chloroform, tetrahydrofuran, ethylene chloride and benzene. A casting solution of 1.6 wt% polymer blend of the terpolymers (AN/OT/XY=50/30/20) with ethyl cellulose in chloroform was prepared for film fabrication. The produced thin film exhibited good air separation ability with the highest oxygen permeation rate being \(6.1 \times 10^{-7}\) cm³ (STP)/cm²s⁻¹cmHg⁻¹ with oxygen concentration of 43.1% at the pressure difference of 640 kPa [179]. Prior to the work, Li et al. had fabricated thin composite films with the blend of ethyl cellulose (EC) and synthesized poly(aniline-co-ortho-toluidine) or poly(ortho-toluidine) on various porous supports of EC, polysulfone (PS), polyethersulfone (PES) and polysulfone amide (PSA). EC/poly-o-toluidine (80/20) blend top layer on EC support layer composite membrane showed the best stability during actual air separation with oxygen enriched stream flux of \(4.78 \times 10^{-5}\) cm³(STP)/s.cm² and oxygen concentration of 46% [180].

Recently, a new approach was conducted in order to take advantage of the gas permeabilities properties of polyaniline. A well structured polyimide (P84)-polyaniline blend hollow fiber membrane that was thermally stable up to 500 °C was developed. It was observed that the gases permeabilities increased tremendously (60-600 times) as compared to P84 hollow fiber membranes due to the increase of the membrane free volume. However, the significant increment in permeation rates had suffered the gas separation factors of H₂/CH₂, He/N₂, H₂/N₂ and H₂/CO₂ with by factor of 1 to 10. However, a good improvement of CH₄/CO₂ and N₂/CO₂ could be seen, which is a good news to the natural gas processing industry as an alternative material [181].
Although throughout the years, development of PAni gas separation membranes has been active, there is very limited published information regarding hollow fibers. Up to present day, even the produced hollow fiber membrane was claimed to be morphologically suitable for gas separation, there is no recorded data on the performance to support it. Norris et al. [182] spun PAni hollow fibers with an acetone/water mixture as the bore fluid with residence time of 2 s between spinneret and the coagulation bath. The godet bath was filled with 1 M of a different kind of acid (phosphoric acid, HBF₄, HCl, pyruvic acid and acrylic acid) and the spun fiber was immersed in it for at least 10 minutes. Besides slowing the rate of solvent exchange, the membrane was doped simultaneously. Hence, a doped membrane with visibly thick dense layer with minimum macrovoids was fabricated. However, there is no gas performance data reported.

2.5.4. Preparation of highly viscous PAni emeraldine base solution

Although studies showed a processable polyaniline could be produced, some solvents were indentified as being capable of dissolving the emeraldine base polyaniline completely, though it is still a problem to dissolve PAni of high concentration. Since gas separation processes require defect free skin membranes, this usually can only be achieved for concentrations of higher than 15 wt% of most polymers for the development of asymmetric membranes. However, polyaniline begins to aggregate at 1 wt% even in the strongest solvent, which was NMP [136,183-186]. Rapid gelation occurs if PAni concentration employed is approximately more than 6 wt% [139,142,185,187]. This happens due to the strong hydrogen bond between secondary amine hydrogens on one polymer chain and imine nitrogen atoms on the nearest neighbouring chain [185,188].

Mattes group conducted comprehensive studies on choices and effects of secondary amine additives in polyaniline dissolved in organic solvents [185,189]. They discovered that majority of the cyclic amines including the pyrrolidine and piperidine derivatives used, prolonged the gelling time more than 300 hours as compared to dialkyl and bicyclic ring amines that prevent gelation from occurring up to 1 and 11 hours, respectively [189]. Besides having a pKa of higher than 7.7, the suitable amine’s width
and depth were identified to be less than 4.53 Å. The addition of gel inhibitor was shown to prolong the gelation time when the secondary amines hydrogens bond with EB imine nitrogens. However, the presence of the secondary amines caused the chemical reduction of the polyaniline emeraldine base. This degradation decreased the conductivity and ultimately reduced the mechanical strength of EB to an extent that they could not produce any film from the EB/NMP solution [189]. Norris et al. continued the group work by developing an asymmetric hollow fiber membrane using 4-methyl piperidine (4-MP) [182]. As compared to 2-methylaziridine (2-MA), 4-MP was a better choice for hollow fiber spinning solution because it reduced the polyaniline oxidation states at relatively slower rate than the 2-MA [182,190].

2.6. Summary of literature review

Membrane gas separation has shown tremendous progress throughout the years since the fundamental understanding was first discovered by Thomas Graham in 1829. Various membrane configurations like flat sheet, spiral wound and hollow fiber were developed for this purpose. Research has been widely conducted in improving the membrane formulation and fabrication method especially for the favourable asymmetric membranes. Membrane gas separation performance is evaluated based on gas permeability (productivity) and gas pair selectivity (efficiency) and one of the crucial factors determining the membrane quality is the choice of material.

Ever since Anderson et al. reported the excellent gas separation factors, polyaniline has become one of the front runners among conjugated polymers as a membrane material. Besides the high gas permeation properties, polyaniline is easy to synthesis and possesses exceptional mechanical properties with high tensile strength and thermal resistance. Although the highly viscous polyaniline that is required in developing gas separation membranes, has the tendency to gel, numerous efforts has been done and the use of gel inhibitor proved to be able to solve the problem. In addition, more soluble derivatives of polyaniline have emerged as another solution to the concentrated polymer gelling problem. Hence, with the extensive information and understanding of polyaniline, further investigation can be conducted in fabricating the polyaniline membrane for gas separation including into hollow fiber modules.
References


Chapter 3

3. Polyaniline synthesis and hollow fiber membrane fabrication

Abstract

This chapter laid the foundation for the development of emeraldine base form of polyaniline (PAni) based gas separation membrane. Prior to the membrane fabrication, PAni powder was synthesized in-house in order for the fresh batch could be used with consistent molecular weight and quality throughout the study. Since PAni oxidative polymerization is an exothermic reaction, the reaction temperature was decreased to sub-zero to improve the polymer molecular weight, Mw. As predicted, reducing the temperature to -15 °C increased the average molecular weight up to 133,000 g·mol\(^{-1}\). Higher polymer molecular weight contributed to greater dope solution viscosity, which is desirable in producing defect free gas separation membranes. Gel inhibitor was added to stabilize the viscous PAni dope solution for membrane casting. Concentrated dope solution exhibited greater polymer chain entanglement that promoted the formation of thicker and denser effective skin layer, more obvious transition layer and finely porous substructure with smaller macrovoids. The effect of spinning air gap distance was also investigated in this study in order to improve the formation of the membrane structure. The produced membranes showed significant improvement on both performance and the morphology. Present work discovered that hollow fibers spun with PAni synthesized at – 15 °C with air gap distance of 50 cm showed a selectivity of 1.9 for O\(_2\)/N\(_2\) and 7.4 for H\(_2\)/N\(_2\) with the N\(_2\), O\(_2\) and H\(_2\) permeance of approximately 0.36, 0.69 and 2.7 GPU, respectively.
3.1. Introduction

The demand for gas separation process for industrial applications is increasing over the years. Conventional established method such as cryogenic distillation, pressure swing adsorption and thermal swing adsorption (TSA) that are energy intensive have been used by industries for decades [1]. However, due to the current demand for more efficient, environmental friendly and economical technology, gas separation membrane has become an interesting alternative. To cater for wide range of applications including oxygen enrichment system, carbon dioxide removal and even in the development of novel combined reaction separation system that involved relatively high temperature, study has been channelled in finding the suitable new material for membrane fabrication. However, in recent years, membrane-based gas separation is becoming increasingly popular due to its inherent advantages over those more traditional methods. These include low capital and operating costs. A comparison between an ethyl cellulose membrane system with a standard PSA revealed that for 35% oxygen enrichment of air reduced 47% in capital costs and 38% in operating costs for the membrane based process [2]. Since it does not require any phase transformation, membrane is a viable energy-saving alternative for gas purification. Furthermore, the membrane system is compact and simple, maintenance-free since there is no moving part, highly flexible that any additional membrane modules can be easily installed for future expansion and highly reliable and durable since it can withstand high pressure and temperature operation [3-7].

An important concern in membrane gas separations is to produce a membrane process that is economically feasible while maintaining a high permeability and selectivity with good mechanical and thermal stability [6]. Since the last few decades, remarkable progress has been made in the development of high-performance polymers for gas separation. The potential application of a polymer as a separation membrane depends upon the possible throughput and the purity of the product. This means that both the permeability coefficient for the gas that is transported more rapidly and the selectivity should be as large as possible [8]. Thus, interest in selecting the most suitable membrane material is a crucial initial step in membrane fabrication. Criteria for selecting good membrane materials can be varied; nonetheless, durability, mechanical integrity at the operating conditions, productivity and separation efficiency are
important conditions that must be balanced against cost in all cases. However, the most basic criteria that must be fulfilled by membrane materials are selectivity (or separation efficiency) and permeation rate (or productivity).

Polyaniline is known to be thermally stable at high temperature and chemically stable towards plasticizing gas, CO\textsubscript{2} and the most desirable attributes are ease of synthesis with economical monomer. In addition, polyaniline membrane possesses an added advantage over other polymeric membrane because it has the ability to alter the morphology and structure even once the membrane has been formed upon doping method [9-15]. However, one of the concerns related to PANi was the stability in air over period of time. Due to that, it is always favourable to use a fresh batch of the polymer for the dope solution preparation. Polyaniline polymerization has been a great research interest since it was first synthesized by Runge in 1834 and further investigated in 1840 by Fritzsche [16-24]. In the earlier years, the major interest in studying polyaniline was contributed to its electrical conducting property. As the investigation of this conjugated polymer property progressing, the discovery by Chiang and MacDiarmid made huge impression on the area as the conductivity of the polyaniline produced improved by 10 folds upon doping with hydrochloric acid [25,26]. This excellent finding was well exploited by Anderson et al. that reported a remarkable gas separation result in 1991 [27]. This led to a growing interest in the research of polyaniline as a membrane material.

The dope solution formulation is a crucial stage in fabricating asymmetric membranes with an ultrathin selective layer [28]. Integrally skinned asymmetric membrane can be developed with highly concentrated solution. The cast solution acts as a transient ‘template’, which then dissociates rapidly into its constituent moieties upon contact with coagulant. This accelerates the phase inversion kinetics and facilitates the removal of dissociated moieties from the formed membrane. Since the transformation from sol-to-gel occurs so fast, polymer molecules of effective separating layer are hindered from approaching equilibrium as the polymer packing is further rearranged before concomitant compression and distortion occur. As a result, membrane with high free volume skin layer is produced that increases the gas transport rates [28,29].
The main aim for the current work was to explore the basic parameters in the development of polyaniline hollow fiber membranes for gas separation process. Formulating the dope solution composition and altering the solution viscosities are the most crucial stage prior to membrane casting. Thus, polyaniline with various molecular weights was polymerized in order to vary the polymer solution viscosity. With this in control, the membrane fabrication technique was explored particularly the phase inversion process. Preliminary work was conducted to study the effect of dry-jet wet spinning parameter (air gap distance) on the membrane morphology in later part of the chapter. Besides measuring the membrane gas separation performance, the membrane structure was examined to evaluate the developed membrane overall behaviour.

3.2. Experimental

3.2.1. Materials

For PAni synthesis, analytical grade (AR) aniline, ammonium persulfate (\(\text{NH}_4\text{S}_2\text{O}_8\)) and hydrochloric acid (37%) were procured from Sigma Aldrich. Lithium chloride (LiCl) anhydrous (99%, Acros Organics), ammonia solution (35%, Fisher Scientific) and reagent grade acetone (VWR) were used as supplied for the polymerisation. The refrigerant circulating the reactor jacket was made of AR ethanol from VWR chemicals and ethylene glycol (antifreeze) from Fisher Scientific.

The solvent for dope solution mixture was HPLC grade \(N\)-methyl-2-pyrrolidone (NMP) obtained from Rathburn Chemicals was used as received, which was also the mobile phase for GPC testing. Amine 4-methyl piperidine (4MP) procured from Sigma Aldrich was utilised to inhibit the gelation of PAni dope solution.

The silicone coating solution was prepared with polydimethylsiloxane (PDMS), Sylgard 184, purchased from Dow Corning and AR n-pentane from VWR Chemicals. Deionised water utilised throughout the study was the in-house supply and the membrane gas permeations were measured with pure gases (>99.8% purity) of nitrogen, oxygen and hydrogen supplied by BOC UK.
3.2.2. PANi synthesis

Polymerization of emeraldine base was conducted according to the well-established method developed in our group [30] scaled up according to study by Adams et al. [31]. The monomer solution was prepared by adding and well-mixing 37.25 g (0.4 mol) of AnalaR aniline to 400 ml of HCl solution (1.0 M). For sub-zero system, 66.8 g of LiCl was added to prevent the mixture from freezing. In this study, the reaction temperature was varied between +15 to -15 ºC. The mixture was then poured into a 1 litre jacketed glass beaker through which a coolant solution (40 wt% antifreeze, 40 wt% water, 20 wt% ethanol) was cooled and circulated by a Grant R3 circulating chiller with a GR150 thermostat. In order to minimize heat leak to the surroundings, the jacketed beaker was well insulated using neoprene rubber.

In the mean time, an oxidant solution was prepared by dissolving 91.26 g (0.4 mol) of ammonium persulfate (NH₄)₂S₂O₈ in 256.0 ml of 1.0 M HCl solution. For sub-zero system, 39.8 g of LiCl was added to prevent the mixture from freezing during addition. As the monomer solution reached the desired synthesis temperature, the oxidant solution was then added dropwise using Gilson Minipuls 3 peristaltic pump at approximately 20 ml·h⁻¹ to allow control over the reaction temperature and so that the total oxidant addition time was about 18 hours. The reactions for above and below zero degree Celsius were left running for a total of 24 hours and 48 hours, respectively. Throughout the experiment, the reaction mixture was stirred using an overhead mechanical mixer fitted with a Teflon coated impeller. Fig. 3.1 shows the reactor setup diagram and picture.

Then, the solution was filtered and washed with 1 litre of deionised water to remove any leftover reactants and followed by 200 ml of acetone. At this point, the greenish blue filtered product was the PANi doped with HCl. The filter cake was taken and placed in 200 ml of ammonia (NH₃) solution and left to stir for 24 hours to completely deprotonate the emeraldine salt to its base form that was dark purplish blue. The ammonia solution containing the emeraldine base was then refiltered using 1 liter of deionised water to remove the ammonia and followed by 500 ml of acetone to remove any low weight polyaniline oligomers presented and displaced the water to speed up the drying time.
Fig. 3.1 (A) Schematic diagram and (B) photo of polyaniline synthesis reaction system.
Next, the polymer filtered cake was placed in a vacuum chamber for drying for at least 24 hours. To further assisting the dissolution of PANi (hereafter referred as emeraldine base form) in solvent and improving the homogeneity of the dope solution, the dried polymer cake was sieved through a mesh size of 160 µm to produce finer polymer powder. Samples from at least 5 different batches for each synthesis temperature were chosen to determine the average yield of PANi produced and the data measured were presented in Table 3.2.

### 3.2.3. Infrared spectroscopy analysis of the produced polymer

Fourier Transform Infrared (FTIR) spectroscopy is a very useful tool to detect the existence of the functional groups in the polymer or membrane produced. At least 5 samples were placed on the sample holder of the Perkin Elmer Spectrum One spectrometer equipped with an attenuated total reflection (ATR) attachment. All spectra were recorded in the wave number range of 600 to 4000 cm\(^{-1}\) by accumulating 8 scans at a resolution of 2 cm\(^{-1}\).

### 3.2.4. Molecular weight measurement of polyaniline powder

The average molecular weight of the polymer is a good indicator of the length of the polymer chain and the possible membrane morphology formed using the polymer. Besides that it will ensure that the polymer used for the dope formation is of the approximately the same chain length and consistent throughout the study. Therefore, it is a good practice to check the average molecular weight of each batch of polymer produced.

PAni powder synthesized throughout the study was characterized for its molecular weight properties (i.e: weight average, Mw, number average, Mn, and polydispersity) by gel permeation chromatography (GPC) with AR NMP as the mobile phase. Sample of 0.05 wt% PAni thoroughly dissolved in NMP was prepared for the GPC system controlled by Waters Millenium\(^{32}\) software. 50 µl of the prepared sample was injected into the system that integrated the Waters components that were a 600 Multisolvent Delivery System, a system interface module, a 600E System Controller, a temperature controller, a 717 autosampler and a 996 Photodiode Array Detector. The column used was Styragel HT4 column (4.6 mm × 300 mm, Waters, Hertfordshire, UK) operated at
100 °C. Four monodisperse polystyrenes (316500, 143400, 38100 and 8450 Da) procured from Polymer Laboratories made the polystyrene standard used for the calibration with $R^2$ fit of always higher than 99.5%. Samples from at least 5 different batches for each synthesis temperature were chosen to determine the average molecular weight, MW, of the PAni produced, and the data measured were presented in Fig. 3.7.

3.2.5. Preparation of high concentration polyaniline dope solution

Gas separation process requires a defect free skin membranes, this usually can only be achieved for concentration of higher than 15 wt% of most polymer for the development of asymmetric membrane [32-35]. The polymer concentration decided for the dope making of this study was 20 wt%. Thus, it was hypothesized that rapid gelation would occur to the polyaniline solution. A considerable effort had been conducted by Yang et al. [36-39] towards the investigation of various secondary amines as an additive for PAni processing. The secondary amine gel inhibitors are known to chemically attack the polymer backbone and lower its oxidation state. The gel inhibitor 4-MP, was shown to be a better choice for hollow fiber spinning solution because it reduced the polyaniline oxidation states at relatively slower rate than the 2-MA [40].

A solvent mixture of NMP containing 4MP (1 mole per tetramer repeat unit of PAni for inhibiting gelation in PAni/NMP mixtures) [30,40] was first stirred in a properly sealed glass container. PAni powder was then added gradually in the system using a funnel while mechanically stirring the mixture at high speed (200 to 300 rpm). The polymer solution was stirred further for another 15 hours to ensure that homogeneous dope solution was formed. Then, the mixing was stopped and the dope solution was degassed by leaving it to stand for at least 5 hours.

3.2.6. Measurement of dope solution viscosity

Approximately 4 ml of the homogeneous dope solution was taken out to measure the viscosity. The Cannon MV-2020 rotary viscometer with spindle number 16 was used to measure the viscosity of the dope solution at ambient temperature. Samples from at least 5 different batches for each synthesis temperature were chosen to determine the average viscosity of PAni produced and the data measured were presented in Fig. 3.8.
3.2.7. **Polyaniline hollow fiber spinning process**

A degassed dope solution (as described above) was transferred to a stainless steel reservoir and pressurized with nitrogen to channel the solution into the spinneret (Fig. 3.3). A tube-in-orifice spinneret with outer diameter/inner diameter of the tube of 1.0/0.7 mm was used to spin the hollow fibre membranes. The internal coagulant was introduced through the inlet tube to create and to control the bore structure of the hollow fiber. The dope was then forced out of the orifice through an air gap allowing the polymer to gel up while removing the solvent, before dropping into a coagulant bath for full precipitation. In this study, tap water at ambient temperature was used to coagulate the nascent fiber. The bath also permitted further removal of solvents from the membrane. This phase inversion process produced an asymmetric membrane, with a much thicker wall comprising of a thin dense selective skin layer of low permeability and a thick porous layer of high permeability which provides support. The general schematic diagram of spinning system is presented in Fig. 3.2.

The PANi solution was extruded through the spinneret (Fig. 3.3) under a nitrogen pressure between 5 to 15 psig as needed to maintain approximately 1.5 ml/min polymer extrusion rate. The internal coagulant, which was deionised water at room temperature, passed through the centre of spinneret at a flow rate (WFR) of 0.5 ml/min. The length of air gap (LAG) varied from 3 to 50 cm in this study. When LAG was changed, the internal water flow rate and nascent fiber velocity were adjusted as well to ensure a well-coagulated fiber with circular concentrated lumen was collected in the final coagulation bath (fiber collecting reservoir).

The ratio of dope flow rate to bore fluid flow rate was kept approximately constant in the spinning processes. To avoid the extension of fibers by drawing, the take up speed of the fiber was adjusted approximately to the same as the free falling velocity of the fiber in the coagulation bath. The spinning process conditions are summarized in Table 3.1.
Fig. 3.2 Schematic diagram of hollow fiber spinning system.

Fig. 3.3 Pictures of spinneret used during spinning process; (A) spinneret, (a) inner diameter (bore fluid), (b) outer diameter (dope solution), and (c) overall lumen geometry.
The resultant hollow fiber membranes were then immersed in deionised water for 2 days to remove any residuals solvents. Then, it was immersed in iso-propanol bath for 3 hours prior to drying in vacuum oven at 50 °C for about 24 hours. The fibers were then used for further characterization.

### Table 3.1 Polyaniine hollow fiber spinning conditions.

<table>
<thead>
<tr>
<th>Spinning parameters</th>
<th>Sample PT1</th>
<th>Sample PT2</th>
<th>Sample PT3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAni synthesis</td>
<td>15</td>
<td>0</td>
<td>-15</td>
</tr>
<tr>
<td>temperature (°C)</td>
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<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Polymer concentration</td>
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<td>20</td>
<td>20</td>
</tr>
<tr>
<td>4-MP (moles for every mole of PAni repeat unit)</td>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Length of air gap (cm)</td>
<td>50</td>
<td>3, 25, 50</td>
<td>50</td>
</tr>
<tr>
<td>Polymer extrusion rate (ml/min)</td>
<td>1.5</td>
<td>1.5 – 2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Injection rate of internal coagulant (ml/min)</td>
<td>0.5</td>
<td>0.5 - 0.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>

#### 3.2.8. Scanning electron microscopy (SEM)

Scanning electron microscope allows a clear view of the morphology of hollow fiber membranes prepared. In addition, the fiber dimension; inner and outer diameters, can be estimated from the micrographs obtained.

For this study, each membrane dense skin layer, porous substructure and cross section were examined by Scanning Electron Microscope JEOL JSM 5610 LV. The chosen fibers were cut to a minimum length possible. The specimen cross section for the SEM were prepared by freezing the dry hollow fiber membrane in liquid nitrogen and subsequently fracturing it cryogenically to ensure even and smoother cross section. The
fractured samples were then mounted on the SEM stubs and gold sputtered under vacuum using Emitech K550 ion sputtering device. The gold coated samples were examined with SEM at approximately 6 mm working distance that utilized Inlens detector with an excitation voltage in the order of 10 to 20 kV.

3.2.9. Gas permeation measurement by soap-bubble method

After drying fibers with a length of 30 cm each were assembled into bundle of 5 fibers. One end of the bundles was sealed with epoxy resin (Araldite ®), while the shell side of the other end was glued onto a stainless steel holder using similar epoxy. To ensure full curing of the epoxy, the module was only being tested after 24 hours.

The modules were then connected to the gas permeation apparatus as shown in Fig. 3.4 and tested using pure gases in the sequence as H\textsubscript{2}, O\textsubscript{2}, and N\textsubscript{2} (supplied by BOC, 99.9% purity). Operating pressures were controlled from 1 to 10 bars using pressure regulator (Omega Eng. Ltd., UK) in all permeation tests.

![Schematic diagram of the gas permeation apparatus by soap-bubble method.](image)

The gas permeation rate was measured at room temperature using soap-bubble meter. The gas permeance, \((P/L)_t\), was calculated using equation 2-2 and the ideal separation
factor \( \alpha_{A/B} \) of an asymmetric membrane can be defined as the ratio of the permeances of two pure gases A and B as in equation 2-3.

Every hollow fiber module was tested by the soap bubble method, and the data measured for all gas permeations for each pure gas were based on at least 5 different pressures between 1 to 10 bars and for each pressure 5-10 consistent readings were collected. Thus, every gas permeance, \((P/L)\)\(i\), and gas pair selectivity \(\alpha_{A/B}\) of each module recorded were consist of at least 25 measurements. The same method was practiced throughout this study for both uncoated and coated fibers.

3.2.10. silicone rubber coating

After the as-spun membranes were tested, they were coated with a 3% (w/w) solution of silicone polymer in n-pentane (Sylgard 184, Dow Corning) for 5 mins [41]. The fibers were then allowed to cure at room temperature for 48h. The purpose of this coating was to repair any possible pinholes or defect on the membrane surface. The gas permeance data for both coated and uncoated fibers was averaged for at least 2 consistent modules. Hence, each point of flux and selectivity recorded in Table 3.4 was based on at least 50 readings.

3.3. Results and discussions

3.3.1. synthesis of polyaniline emeraldine base

Table 3.2 summarized the yield of blackish blue fine powder of emeraldine base polyaniline produced in this study. Based on the mass of monomer (99.9% purity aniline) added to the reaction, the yield of the PAni polymerization was approximately ~80%. Although, varying the polymerization temperatures between -15 to 15 °C did not affect the yield significantly, from observation, qualitatively the particle size of dried PAni produced increased as the polymerization temperature decreased. Hence, the time consumed during manual sieving of the dried filtered cake was the highest for sample synthesized at -15 °C due to the large polymer particles produced. Consequently, it was expected that PAni molecular weight synthesized at sub-zero (-15 °C) condition would be higher than 15 °C as extensively proven by previous researchers that decreasing the
temperature on the oxidative polymerization of polyaniline would result in higher molecular weight PAni [31,42-46].

<table>
<thead>
<tr>
<th>Sample</th>
<th>PAni synthesis temperature (°C)</th>
<th>Mass of PAni produced (g)</th>
<th>Yield based on mass of aniline (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P15_1</td>
<td>+15</td>
<td>28.341</td>
<td>76.16</td>
</tr>
<tr>
<td>P15_2</td>
<td>+15</td>
<td>29.770</td>
<td>80.00</td>
</tr>
<tr>
<td>P15_3</td>
<td>+15</td>
<td>31.056</td>
<td>83.46</td>
</tr>
<tr>
<td>P15_4</td>
<td>+15</td>
<td>27.665</td>
<td>74.34</td>
</tr>
<tr>
<td>P15_5</td>
<td>+15</td>
<td>29.842</td>
<td>80.19</td>
</tr>
<tr>
<td><strong>average P15</strong></td>
<td></td>
<td><strong>29.335 (1.340)</strong></td>
<td><strong>78.83 (3.60)</strong></td>
</tr>
<tr>
<td>P0_1</td>
<td>0</td>
<td>29.883</td>
<td>80.30</td>
</tr>
<tr>
<td>P0_2</td>
<td>0</td>
<td>30.789</td>
<td>82.74</td>
</tr>
<tr>
<td>P0_3</td>
<td>0</td>
<td>31.076</td>
<td>83.51</td>
</tr>
<tr>
<td>P0_4</td>
<td>0</td>
<td>28.459</td>
<td>76.48</td>
</tr>
<tr>
<td>P0_5</td>
<td>0</td>
<td>31.003</td>
<td>83.31</td>
</tr>
<tr>
<td><strong>average P0</strong></td>
<td></td>
<td><strong>30.242 (1.105)</strong></td>
<td><strong>81.27 (2.97)</strong></td>
</tr>
<tr>
<td>Pn15_1</td>
<td>-15</td>
<td>28.767</td>
<td>77.30</td>
</tr>
<tr>
<td>Pn15_2</td>
<td>-15</td>
<td>31.865</td>
<td>85.63</td>
</tr>
<tr>
<td>Pn15_3</td>
<td>-15</td>
<td>29.492</td>
<td>79.25</td>
</tr>
<tr>
<td>Pn15_4</td>
<td>-15</td>
<td>29.084</td>
<td>78.16</td>
</tr>
<tr>
<td>Pn15_5</td>
<td>-15</td>
<td>32.218</td>
<td>86.58</td>
</tr>
<tr>
<td><strong>average Pn15</strong></td>
<td></td>
<td><strong>30.285 (1.629)</strong></td>
<td><strong>81.38 (4.38)</strong></td>
</tr>
</tbody>
</table>

( ): Standard deviation
3.3.2. FTIR spectroscopy analysis on PAni

The chemical structure of the synthesized EB PAni was identified by means of FTIR spectroscopic measurement. Fig. 3.5 represents a typical spectrum of the polyaniline produced in house. Even though there were 3 different synthesized temperatures employed in this study, each spectrum collected displays similar essential peaks with slightly various intensities. The spectrum displays five major vibrational bands at 1593, 1495, 1295, 1166 and 825 cm$^{-1}$. These peaks were observed by earlier researchers as well [47-55]. A minor sharp peak at 3380 cm$^{-1}$ is the free or non-bonded band of a secondary amine N-H stretch [47,56,57]. A major broad band centred at 3290 cm$^{-1}$ is the hydrogen-bonded N-H band between amine and imine sites [45,47,58]. Although the infrared spectra alone is not an accurate quantitative measurement of the hydrogen bond, from Fig. 3.5 the band intensity qualitatively indicates that the non-bonded N-H stretching is significantly lower than hydrogen-bonded N-H band. This implies that this PAni is self-associated via hydrogen bonding. However, this does not differentiate whether the hydrogen bonding is the interchain between different PAni molecules or the intrachain of various “folded back” segments of the same PAni molecules [47,59].

The broad peak at 3028 cm$^{-1}$ represents the C-H stretch in aromatic rings [38,60]. The sharp peaks at 1593 and 1495 cm$^{-1}$ are most likely due to C=C vibrations in imine quinoid (Q) and amine benzenoid (B) rings, respectively [22,49,60,61]. The strong peak at 1295 cm$^{-1}$ is due to vibration emanated by C-N in QBQ sequences [54,55]. The C-H and aliphatic C-N stretching vibrations are presented by high intensity at 1166 cm$^{-1}$ that can be described as the characteristic of the conducting polymer due to the delocalization of electrical charges caused by deprotonation [57,62-64]. An intense peak at 825 cm$^{-1}$ is attributed to out-of-plane deformations of C-H on 1,4-disubstituted phenyl rings [38,50,60,65]. C-H bending vibration of monosubstituted benzene rings at both ends of the molecule represents by bands around the region of 700-750 cm$^{-1}$ [5,49,60]. As for peaks at 970, 956 and around 695 cm$^{-1}$ are most probably due to various stretching and bending of C-N vibrations [61]. Table 3.3 summarizes the significant peak assignments for the polyaniline sample in this study.
Fig. 3.5 Infrared spectrum of polyaniline emeraldine base produced at -15 °C.
Table 3.3 Infrared spectral peak assignments of polyaniline emeraldine base.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Peak assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3380</td>
<td>non-H-bonded N-H stretch</td>
</tr>
<tr>
<td>3290</td>
<td>hydrogen-bonded N-H stretch</td>
</tr>
<tr>
<td>3028</td>
<td>C-H stretch in aromatic rings</td>
</tr>
<tr>
<td>1593</td>
<td>C=C aromatic ring stretch of imine quinoid (N=Q=N)</td>
</tr>
<tr>
<td>1495</td>
<td>C=C aromatic ring stretch of amine benzenoid (N-B-N)</td>
</tr>
<tr>
<td>1295</td>
<td>C-N stretch in QBQ sequences</td>
</tr>
<tr>
<td>1166</td>
<td>C-H and aliphatic C-N stretching</td>
</tr>
<tr>
<td>~950</td>
<td>various stretching and bending of C-N vibrations</td>
</tr>
<tr>
<td>825</td>
<td>C-H out-of-plane bending of disubstituted 1,4 ring</td>
</tr>
<tr>
<td>~750</td>
<td>C-H bending vibration of monosubstituted benzene rings</td>
</tr>
</tbody>
</table>

3.3.3. **Effect of reaction temperature on the molecular weight**

Synthesizing soluble polymer with minimum content of defects is favourable since the ultimate purpose of producing PAni in-house was as a material for producing defect-free asymmetric membranes. Higher molecular weight is known to have lower defects due to the suppression of side reaction (hydrolysis of products) occurred at low temperature and longer polymerization time [31,44,45,66]. Thus, it is important to optimize the oxidative polymerization temperature of polyaniline in order to determine the suitable and practical molecular weight to be handled for the membrane fabrication in this study. The molecular weight of the produced PAni was investigated by mean of GPC and the typical GPC curve is presented in Fig. 3.6.

As mentioned earlier, the synthesis temperature affected PAni molecular weight significantly as can be clearly seen in Fig. 3.7. Commencing the work based on the prior study in our group using PAni as membrane material for nanofiltration, PAni was prepared at +15 °C [67,68]. Fig. 3.7 (based on at least 5 different batches for each temperature) shows that at +15 °C, the average polyaniline Mw is approximately ~59,500 g mol⁻¹ with standard deviation (SD) of 2500 g mol⁻¹. Reducing the polymerization temperature to zero improved the Mw by about 62.5% to 97.0 kDa (SD
As predicted, by further decreasing the reaction temperature to sub-zero condition (-15 °C), the average Mw of PAni shows drastic increment to $133.4 \times 10^3$ g/mol (SD = $4.7 \times 10^3$ g/mol).

Fig. 3.6 A typical GPC curve of polyaniline powder produced at 0 °C (batch P0_1, Mw=96600, polydispersity=5.4).

Aniline polymerization was reported to possess both characteristics of cationic chain polymerization and condensation polymerization reactions. Thus, due to the cationic chain polymerization properties, at sub-zero temperature, initiation and propagation were in favour and side reactions were suppressed that led to the formation of longer polymer chains. As for condensation reaction characteristic, the longer reaction times for this sub-zero condition further promote the production of high molecular weight PAni [31,43,44,66]. In addition, to ensure the reaction mixture remained mobile throughout the polymerization process, LiCl was added into the sub-zero reaction. Interestingly, LiCl also hindered molecules aggregation and phased out the polymer chains improving the growth of polymer chains length [45,69]. The polydispersity of samples P15, P0 and Pn15 were almost similar with average of 4.96 (SD = 0.39), 5.57 (SD = 0.88) and 6.13 (SD = 1.13), respectively. From the data mentioned, it showed that
reducing PANi synthesis temperature affecting the polymer molecular weight significantly with minor effect on the polydispersity.

![Graph showing the effect of oxidative polymerisation temperature on average Mw of polyaniline.](image)

**Fig. 3.7** Effect of oxidative polymerisation temperature on average Mw of polyaniline.

### 3.3.4. Effect of molecular weight on PANi dope solution viscosity

The effect of polymer molar concentration was investigated by varying the polyaniline molecular weight. Fig. 3.7 clearly shows that as the synthesis temperature reduces the molecular weight of polyaniline increases. By fixing the mass concentration of the polymer (20 wt%), increase in molecular weight of polyaniline had actually increased the dope solution viscosity. This trend is in agreement with data reported by prior researchers [70,71]. Thus, varying the molecular weight is expected to give the same impact on the produced membrane as the varying the polymer concentration.
The polymer molecular weight of bulk polymers is generally known to affect the polymer solution viscosity [72,73]. Viscosity had a significant effect on the hollow fiber spinning and flat sheet membrane casting. Too high viscosity of the casting solution will make it almost impossible to cast the membrane, whereas a low viscosity of the casting solution could cause detrimental effect on the membrane formation. Generally, high viscosity casting solutions are desirable for hollow fiber spinning, preferably in the ranges of 50000 to 100000 cP compared to only 1000 cP to 2000 cP for flat sheet casting solutions [74]. Based on Fig. 3.8, the viscosity of dope solution for PANi synthesized at +15 °C (Mw = 59.5 ± 2.5 kDa) and 0 °C (Mw = 97.0 ± 1.7 kDa) at was found to be approximately 1500 cP and 16500 cP, respectively.

As predicted, when the polyaniline polymerization temperature reduced to -15 °C (Pn15), the polymer Mw increased to more than double of P15, the viscosity of PANi dope solution increased by ~20 folds of about 30800 cP. Since PANi is known to be an exothermic reaction, at low temperature the side reactions are depressed, promoting a
greater number of intramolecular interactions. This leads to longer chain polymer with a more compact coil conformation with higher viscosity as discovered in the current study [71]. Thus, polymer synthesized at sub-zero condition was anticipated to produce denser membrane with fewer defects and improved structure and hypothesized to be a good candidate as a gas separation membrane, which would be proven in the coming sub-chapter.

3.3.5. Fabrication and morphological analysis of PAni hollow fiber membrane

(a) Effect of air gap distance on PAni membrane morphology

Rapid coagulation of extruded polymer solution has been reported repeatedly to occur during wet spinning or low air gap distance [75-79]. The length of finger-like void near to the outer surface of fiber depends strongly on the phase separation occurred in the air gap region. Since the nascent fiber solidification occurred almost instantaneously, this resulted in a higher amount of solvent trapped in the contracted polymer chains. Therefore, the fibers may have a longer-range random and less oriented polymeric chain interaction structure with intermolecular voids or high free volume. Long finger-like void characteristics can be clearly seen in Fig. 3.9 (A) that represents the fiber produced at the lowest air gap distance of 3 cm. In addition, there was almost no visible skin layer can be measured from the SEM picture. Fig. 3.9 displays various membrane structures were developed from the same PAni dope solution (PT2) as the air gap lengths were varied. As the LAG increased, the finger-like voids near the outer surface were clearly depreciated in size while the sponge structure formation ascending as a support layer of the membranes.

Spinning air gap also introduced an elongational stress on the fibers formation induced by gravity. Higher air gap allowed tighter molecular rearrangement that led to greater molecular orientation and improved polymer chain packages. Previous studies had showed similar behaviour; given an optimum residence time or a reasonable LAG during dry/wet spinning will improve the orientation of the polymer especially towards the skin layer. This implied that increasing air gap length promoted the skin layer formation with tighter structure, reduced voids and porosity or free volume as clearly presented in Fig. 3.9 (C) [79-82]. Hence, the skin layer became more visible as the air gap reached 50 cm with estimated thickness of ~0.15 µm as compared to the lower air gap.
gap lengths of 3 and 25 cm that were almost negligible with the employed magnification. Thus, the current finding was consistent as the literature proving that various skin layer thicknesses can be obtained by manipulating the evaporation time (dry process) during casting which is comparable to length of air gaps in spinning [34]. As in this case, at higher air gaps skin layer formation was promoted for asymmetric membrane since it is predominantly controlled by evaporation step (dry process-length of air gap). As a consequence, it was predicted that rate of permeation decreased and the gas pair selectivity increased when the air gap was enhanced. However, it is important to highlight that the existence of finger-like close to the skin layer even at the highest air gap (50 cm), the gas pair selectivity in the current section would potentially suffer.

(b) Effect of dope solution viscosity on PAni membrane morphology

Pesek and Koros reported that increase in polymer solution viscosity tend to promote the formation of a more selective but less productive membranes [74]. Highly viscous dope solution is always preferable since it is known to induce chain entanglement and reduces microvoid concentration in the skin layer [35,72]. Therefore, it leads to a denser skin and with reduction in the membrane porosity which is expected to improve the separation properties of the membranes, which is a desirable characteristic for the purpose of this study. For all PAni dope solution viscosities, the HF membrane outer layer cross-sections (samples PT1-PT3) demonstrate an asymmetric structure composed of a thin skin layer over porous finger-like structure layer near the edge and macrovoid layer in the middle as shown in Fig. 3.10.

Fig. 3.10 (A) displays the thinnest skin layer among the samples (PT1-PT3) with ruptured-looking finger-like voids very close to the skin layer and large macrovoids in the fiber sub-structure. Since the solution viscosity was relatively low, most likely, the finger-like structures near the edges of HF membrane was due to phase inversion enhancement due to instantaneous liquid-liquid demixing and this fast mass transfer resulted in the poor membrane structure. This is further supported by previous reports that stated in the instantaneous demixing process, the finger like structure is more likely to form [83-88].
Fig. 3.9 PANi hollow fiber membranes outer layer cross section of PT2 with LAG of; (A) 2 cm, (B) 25 cm and (C) 50 cm.
As the viscosity of PT2 dope solution increased by 10 folds (as compared to PT1), the exchange rate of solvent-non solvent slowed down and improved on the formation of skin thickness as in Fig. 3.10 (B). However, viscosity of 17k cP was still considerably low, thus, as expected; PT2 membrane with a structure composed of finger-like voids beneath the thin outer skin layer of ~0.15 μm was produced.

As a higher molecular weight PAni was used for spinning solution preparation, Fig. 3.10 (C) reveals a thicker skin layer of ~0.40 μm over a relatively porous structure consisted of shorter finger-like voids and sponge pore layer. This is in agreement with Brown et al. [89], whose encountered that high viscosity polymer solution (high polymer concentration) changed the pore morphologies from large disruptive macrovoids to smaller finger-type voids combined with spongy structure. High concentrated solution depressed the phase separation rate of the nascent fiber substructure. Thus, the concentrated outer layer was rapidly solidified to facilitate the formation of dense surface skin layer. Once formed, the dense layer effectively slowed down the diffusion of water into the nascent film and minimized the void formation [89,90]. Hence, the active skin layer thickness increased with the increasing PAni molecular weight that caused the ascending dope solution viscosity.

Fig. 3.10 (A-C) also display that the formation of membrane transition layer was highly affected by dope solution viscosity. Membranes prepared with low PAni Mw (~59500 Da) seems to have very minimum transition layer as opposed to PT3. The transition layer was explained to form during the redissolution stage when solvent evaporation occurred in the dry-jet stage of a spinning process. It is understood that as a more dilute solution (low viscosity) was extruded during spinning process, the redissolution step enhanced. On the other hand, a high viscosity solution would slow down the redissolution rate. Thus, during the drying stage the polymer-rich phase separation was driven to coalesce. There was a weak interfacial tension forces beneath the phase separation region, resulting in less tendency of polymer to coalesce. During this period, the thickness of the dry phase separation region underneath the skin tended to decrease due to the redissolution from the underlaying homogeneous solution. Therefore, the remaining dry phase separation region was transformed to the transition region [74,79,91].
Fig. 3.10 PANi hollow fiber membranes outer layer cross section spun at LAG=50 cm for; (A) Sample PT1, (B) Sample PT2 and (C) Sample PT3.
Since the high polymer solution viscosity would slow down the diffusion processes rate related to redissolution step, PT3 (Fig. 3.10 (C)) prepared by high molecular weight PAni had denser and more visible transition regions as compared to PT1 as in Fig. 3.10 (A). Consequently, it was predicted that the membrane gas permeation productivity would reduce yet the gas pair selectivity improved.

3.3.6. PAni membrane gas separation performance

(a) Effect of air gap distance on PAni membrane gas separation performance

As thoroughly discussed in the previous Section 3.3.5, the morphology obtained proved that the air gap distance during spinning process is one of the important factors that controlled the formation of asymmetric membrane skin layer. The spine line stress on the nascent fiber caused by gravity at higher air gap distance promoted greater molecular orientation that led to tighter polymer packing [74,78,80,92,93]. Since the selectivity of asymmetric membranes prepared through the phase inversion process is generally controlled by the skin layer of the membrane [74,94-96], the study of the spinning air gap distance was conducted to develop asymmetric membranes with high gas separation performance. In the current study, the hollow fiber membranes were spun at various air gaps of 3, 25 and 50 cm with dope solution prepared from PAni synthesized at 0 °C. At least 2 consistent modules were tested for each pure gas permeation rate at room temperature, measured at transmembrane pressure of 1 to 4 bars and upto 10 bars for as spun fiber and coated membranes, respectively. Table 3.4 shows the recorded pure gas permeation rate and gas pair selectivities for both uncoated and coated PAni hollow fiber membranes.

Referring to Table 3.4, a trade-off relationship of gas separation properties occurred for both uncoated and coated membranes. Generally, the gas flux for all gases decreased while the selectivity increased with the increasing air gap distance from 3 to 50 cm. For the as-spun PAni fibers, flux for all the pure gases reduced of about 30-70%. As previously discussed (Section 3.3.5) the long exposure to air, would enhance the skin thickness formation and improved molecular packing of the nascent fibers. Thus, these promoted the gas pair selectivity as proven in the data; which O₂/N₂ increased by almost 40% and H₂/N₂ was doubled. Although the gas pair separation factor improved at air gap length of 50 cm, they were obviously very low (1.3 for O₂/N₂ and 2.9 for H₂/N₂)
most probably due to the contribution of the defects on the membrane surface. In addition, as in Table 3.4, the uncoated membranes had larger value of standard deviation of gas permeation rate as compared to the coated fibers due the defects [32,35,97]. Thus, the defects on the outer surface of the hollow fibers were sealed externally with PDMS. As predicted, by sealing the defects, the silicone coating reduced the pressure-normalized flux substantially while enhanced the gas separation factor [41,96]. From Table 3.4, upon coating, membranes prepared at 50 cm shows the most improvement in selectivity. H₂/N₂ selectivity was doubled to 5.9 while nitrogen and hydrogen permeation rates reduced by almost 70% to 0.93 GPU and 39% to 5.43 GPU, respectively. The oxygen flux reduced from 4.05 to 1.28 GPU as the fibers was coated for sample PT2_50.

The coated PANi membranes prepared at the lowest air gap of 3 cm exhibited the worst selectivity for all gas pair with H₂/N₂ selectivity of 1.6 and O₂/N₂ selectivity of 1.1. The coated membrane gas performance demonstrated the same trade-off gas separation behaviour as the uncoated when the air gap distance varied. As the spinning air gap increased from 3 to 25 cm, fluxes for N₂, O₂ and H₂ had very minimum reductions from 7.96, 8.62 and 12.58 to 3.53, 4.34 and 8.89 GPU, respectively. These decreases (~30 to 55 %) in flux resulted in minor increase of selectivities for O₂/N₂ from 1.1 to 1.2 and for H₂/N₂ from 1.6 to 2.5. The decreasing gas flux with ascending selectivity was in agreement with the morphology produced that was discussed before, where the skin layer thickness improved with shorter finger-like void as the air gap increased.

However, Table 3.4 reveals even the membranes were prepared at the highest LAG (PT2_50) and produced the best selectivity for now (O₂/N₂ = 1.4, H₂/N₂ = 5.9), the values were still considerably low and highly unattractive for any gas processes applications. This implied that the pores/defects on the skin were too big to seal by the dilute solution coating method. As a result, the hollow fiber membranes prepared showed poor gas separation properties. Thus, further modification should be conducted to improve PANi hollow fiber membranes morphology and gas permeation properties.
(b) *Effect of dope solution viscosity on PAni membrane gas separation performance*

As PAni molecular weight increased from 59.5 to 133 kDa, the polyaniline viscosities became 20 times higher of 30800 cP. It is predicted that the gas separation performance of the developed membranes would improve too. Increasing viscosity of polymer solution hinders the diffusional exchange of solvent and non-solvent in a sub layer. As a result of a fast phase separation at outer skin layer and a slow phase separation at the sub-layer occur. The asymmetric membrane with a dense and skin layer supported by a closed cell sub layer was produced. On the other hand, an asymmetric membrane with a thin and porous skin layer and open cell sub layer was prepared by a polymer solution with a lower viscosity dope solution and this occurrence expected to increase gas permeability yet lowered the selectivity of the membranes and vice versa [34,91,98,99].

As predicted, the gas flux for all gases decreased while the selectivity increased with the increasing dope solution viscosity from 1500 to 30800 cP as can be seen in Table 3.4 for both as-spun and coated hollow fiber membranes. The uncoated PAni fiber flux for all the pure gases reduced significantly by between 100 and 300 times for PT2_50 and PT3_50, respectively as compared to PT1_50. On the other hand, as the solution viscosity increased from 1500 (PT1_50) to 16500 (PT2_50) cP, the gas separation factors of O$_2$/N$_2$ increased by 30% upto 1.3 and H$_2$/N$_2$ was improved by 2.5 times to be 2.9. With high viscosity of 30800 cP, PT3 membranes improved the O$_2$/N$_2$ selectivity to 1.5 and H$_2$/N$_2$ to 4.1 while reducing the O$_2$, H$_2$ and N$_2$ permeance to 1.58, 4.28 and 1.06 GPU, respectively. However, all these performance properties were still significantly less than desirable due to potential defects existence on the outer surface even with improvement of the skin thickness from 0.14 µm (PT1) to 0.40 µm (PT3). Thus, the outer surface of the membrane was silicone coated to seal those defects.

With the silicone coatings, all the membranes gas pair ideal separation factors increased with PT3 showed the most significant improvement of O$_2$/N$_2$ = 1.9 and H$_2$/N$_2$ = 7.4 but the permeance of the gases reduced between 35 to 65% as compared to the as-spun fiber leading to O$_2$, H$_2$ and N$_2$ of 0.69, 2.68 and 0.36 GPU, respectively.
Table 3.4 Gas separation performance of uncoated and coated PAni hollow fiber membranes spun at various air gaps (3, 25, 50 cm) and dope solution viscosities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uncoated membrane</th>
<th>Coated membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Permeance, ((P/L)_i) (GPU)</td>
<td>Selectivity, (\alpha_{i/j})</td>
</tr>
<tr>
<td></td>
<td>(N_2)  (O_2)  (H_2)</td>
<td>(O_2/N_2)  (H_2/N_2)</td>
</tr>
<tr>
<td>PT2_3(^a)</td>
<td>10.170 (1.455) 9.598 (0.834) 13.257 (0.350)</td>
<td>0.944 (0.054) 1.304 (0.154)</td>
</tr>
<tr>
<td>PT2_25(^a)</td>
<td>6.414 (1.050) 6.71 (0.696) 11.616 (1.031)</td>
<td>1.046 (0.064) 1.811 (0.138)</td>
</tr>
<tr>
<td>PT2_50(^a)</td>
<td>3.092 (0.134) 4.046 (0.055) 8.849 (0.257)</td>
<td>1.309 (0.039) 2.862 (0.208)</td>
</tr>
<tr>
<td>PT1_50(^a)</td>
<td>303.9 (51.477) 307.1 (48.720) 342.3 (33.248)</td>
<td>1.011 (0.011) 1.126 (0.083)</td>
</tr>
<tr>
<td>PT2_50(^a)</td>
<td>3.092 (0.134) 4.046 (0.055) 8.849 (0.257)</td>
<td>1.309 (0.039) 2.862 (0.208)</td>
</tr>
<tr>
<td>PT3_50(^a)</td>
<td>1.055 (0.043) 1.578 (0.750) 4.283 (1.185)</td>
<td>1.496 (0.651) 4.060 (1.291)</td>
</tr>
</tbody>
</table>

\(^a\): Spinning air gap distance in cm.

( ): Standard deviation.
As proven by the morphology analysis, the increase of skin thickness of almost triple for PT3 with increasing spinning solution viscosity, the gas pair ideal selectivity also improved comparing to PT1 O₂/N₂ of 1.0 and H₂/N₂ of 1.3 by 87% and 450%, respectively. This improvement in the gas separation performance proved the viscous solution caused a sign of significant chain entanglement that can minimize defects/surface pores, thus, affecting the membrane morphology and performance [34,100-103].

3.4. Conclusions

This chapter had laid down the foundation for the development of pure polyaniline based gas separation hollow fiber membranes study. With the previously established in-house PAni synthesis facility, high molecular weight PAni was successfully produced to be used as the raw material for the membrane fabrication. PAni with molecular weight ranging from 59500 to 133000 Da were produced by reducing the synthesis temperature from 15 to -15 °C, respectively. This improved the spinning solution viscosity by 20 times upto 30800 cP. To ensure the concentrated dope solution, which is important factor for the gas separation process membrane, could be utilized in the membrane fabrication, gel inhibitor was added to the dope solution. 4MP was chosen because it possessed the ability to prevent the dope solution from gelling instantaneously due to the high viscosity of the dope. Undergoing the gas permeation test, the as–spun fibers showed very high permeation rates with low selectivity contributed to possible defects on the outer layer of the fiber. Thus, the fiber was silicone coated with dilute PDMS solution to seal the potential defects.

Highly viscous PAni dope solution was employed for the membrane spinning to promote the formation of the skin layer required to ensure good gas permeation performance. This initial gas separation testing showed that the gas flux decreased significantly while the selectivity increased with increasing viscosity due to higher Mw PAni was used. However, since developing a membrane could be influenced by numerous factors, the performance recorded was very low and unattractive for real industrial application. Thus, another spinning parameter was exploited in the current work. The air gap spinning distance was varied from 3 to 50 cm. It is predicted high
LAG would increase the molecular orientation and allowed tight molecular packing of the fiber during the dry phase separation. Consequently, an improved PANi membrane was developed with ideal gas separation properties for O$_2$/N$_2$ (1.9) and H$_2$/N$_2$ (7.4).

Conducting this preliminary testing revealed that polyaniline denied that once was claimed to be a difficult polymer to handle in a highly viscous polymer solution. With the assistance of gel inhibitor, concentrated PANi solution made from high molecular weight polymer was possible to be prepared and used for fabricating gas separation membranes. In addition, the earlier produced PANi hollow fiber membranes displayed almost the identical attribute as most polymer that was previously used in gas separation membrane development. By minimum manipulation of the dope solution viscosity and spinning length of air gap, the membrane developed showed improvement in term of morphology and gas separation properties. Based of this interesting finding, other factors were pursued in the coming chapter.

References


Chapter 4

4. Polyaniline hollow fiber membrane for gas separation

Abstract

In this study, integrally-skinned asymmetric hollow fiber membranes have been developed from emeraldine base form of polyaniline (PAni) for gas separation. High molecular weight PAni was synthesized in-house to provide the fresh supply of the polymer. The hollow fiber membranes were prepared using dry-jet wet spinning and the effects of air-gap distance on nascent fiber morphology, their gas permeation and mechanical properties were investigated. The spin-line stresses resulted in the molecular orientation of the polymer which had synergistic effect towards improving the gas performance of the PAni hollow fiber membranes. The induced molecular orientation also resulted in improvement in mechanical properties of the hollow fiber membrane. The use of volatile co-solvent, tetrahydrofuran (THF) assisted in the skin layer formation which showed a substantial improvement in the gas permeation performance of the hollow fiber as the time of evaporation was varied. Present PAni based hollow fibers showed a selectivity of 10.2 for O$_2$/N$_2$, 105.6 for H$_2$/N$_2$ and 7.9 for H$_2$/CO$_2$ with the H$_2$ and O$_2$ permeance of about 5.0 and $0.49 \times 10^{-6}$ cm$^3$ (STP)/cm$^2$ s cmHg respectively.
4.1. Introduction

An important concern in membrane gas separations is to produce a membrane that is economically feasible while maintaining a high permeability and selectivity with good mechanical and thermal stability. Since the last two decades until today, remarkable progress has been made in the development of high-performance polymers for gas separation. The potential application of a polymer as a separation membrane depends upon the possible throughput and the purity of the product. This means that both the gas permeability coefficient and the selectivity should be as large as possible. In order to cater for wide range of applications including oxygen enrichment system, carbon dioxide removal and even in the development of novel combined reaction separation system that involved relatively high temperature, study has been channelled in finding the suitable new material for membrane fabrication. For practical gas separation applications, hollow fiber is one of the modules have been widely used commercially. A hollow fiber module consists of a bundle of very fine membrane fibers packed into a cylindrical housing or shell that provides the desired high packing density [1].

Besides ease of synthesis with economical monomer, polyaniline is thermally stable and chemically stable towards plasticizing gas, CO$_2$ [2-4]. In addition, polyaniline membrane possesses an added advantage over other polymeric membrane because it has the ability to alter the morphology and structure even once the membrane has been formed upon doping method. Ever since Anderson et al. reported the outstanding gas separation results, research on polyaniline as membrane material has been progressive [5]. They discovered a novel possible solution that enable to alter the membrane morphologies after being cast since polymeric membranes are always hard to predict and impossible to modify after casting especially to cater to a specific applications. Although Anderson’s work was an act that is really hard to follow or even to repeat, the polyaniline has been an important material for gas separation membrane ever since.

Later, Rebattet et al. followed the doping method by Anderson et al. with additional step of curing the membrane at 120 ºC for 2 hours prior to doping with strong acid. Although, they did not managed to improve or even replicate Anderson’s work, they reported a remarkable selectivity of O$_2$/N$_2$ and CO$_2$/CH$_4$ of 14 and 78, respectively, with an increase of 15% for smaller gases fluxes and reduce the larger gases permeability by
45% [6]. Prior to Rebattet’s work, Kuwabata and Martin had explored a wide range of factors including types of doping counterion, duration and temperature of membrane annealing as well as membrane doping level. They discovered that doping level is the most important factor in modifying the gas separation performance; as doping level increased from 13 to 38%, the selectivities of O$_2$/N$_2$ and CO$_2$/CH$_4$ were improved by ~43% and ~20%, respectively [7]. Jiping et al. also discovered similar behaviour when their membranes were treated with different doping level [8].

Approaching the new millennium, PAni gas separation research also channelling towards new area. In 1997, Kaner’s group started to developed gas separation membranes based on polyaniline-polyimide blends. The polymer blends improved pure polyaniline thermal stability and increased the pure gas pair fluxes as compared to the homopolymer (i.e. based on pure polyimide or pure polyaniline). The separation factors for all gas pairs were approximately equivalent or slightly lower than the polyaniline membranes, which were a good attempt since the polyaniline membranes had a greater selectivity as compared to polyimide membranes [9]. Since producing asymmetric polyaniline membrane with consistent controlled skin layer thickness can be a challenge, researchers started to employ polyaniline as part of the composite membranes to exploit the high selectivity it possess as a dense membrane. Orlov and his colleagues had prepared composite polyvinyltrimethylsilane (PVTMS) with polyaniline. PAni was coated on the PVTMS film by borderline polymerization of aniline [10]. They found that the O$_2$/N$_2$ and CO$_2$/CH$_4$ selectivities of the undoped composite films were higher than that of PVTMS. Then, in 2005, ultrathin polyaniline on polyvinylidene difluoride (PVDF) as support material was developed by Illing et al. [11]. The produced composite membranes had relatively significant selectivity of H$_2$/N$_2$ and O$_2$/N$_2$ of 120 and 5, respectively. They also mentioned that the composite membranes were more flexible and less brittle, which is more practical for commercial and bulk handling.

Gupta et al. continued to explore the composite membranes as well as producing nanostructured self-supported polyaniline membranes in 2006. They found that although the self-supported membranes selectivity for H$_2$/N$_2$ (348) was three times higher than the composite membranes, it sacrificed the permeation rate by $10^5$ times [12]. Recently, Chatzidaki et al. [13] have carried work similar to earlier study [9] of blending PAni-polyimide for their hollow fiber membrane fabrication and found that by adding
polyaniline into the polyimide matrix, the pure gases permeation rates increased by 60 to 600 times compared to polyimide based membranes. However, the produced hollow fiber membranes had poor selectivity for all gas pairs as \( \text{O}_2/\text{N}_2 \), \( \text{H}_2/\text{CH}_4 \), \( \text{He}/\text{N}_2 \), \( \text{H}_2/\text{N}_2 \) and \( \text{H}_2/\text{CO}_2 \) were 0.92, 6.4, 8.9, 7.7 and 1.47, respectively [13].

The objective of present study was to develop polyaniline based hollow fiber membranes for gas separation. To the best of our knowledge there was no literature available for the gas permeation of emeraldine base (EB) form of PAni asymmetric hollow fiber membrane. Although there had been attempt to produced PAni hollow fiber membrane [14], enough towards gas permeation investigation was not made. We have demonstrated for the first time the path in developing an EB based PAni hollow fiber membranes for gas separation application. The membrane was produced with the use of tetrahydrofuran (THF) as a co-solvent to N-methyl-2-pyrrolidone (NMP). Effect of air gap distance on the performance of the fibers was investigated in the present study.

4.2. Experimental

4.2.1. Materials

Materials used for the synthesis of polyaniline and dope solution chemicals including solvents and gel inhibitor used for membrane fabrication is similar to those presented in Chapter 3. In addition, a co-solvent of analytical grade (AR) tetrahydrofuran (THF) procured from VWR Chemicals was added to NMP-4MP mixture for dope solution preparation and used as supplied.

Chemicals for silicone coating solution are similar as in Chapter 3. Besides the pure gases listed in Chapter 3, the membrane gas permeation system also measured flux of carbon dioxide (>99.8% purity) supplied by BOC UK.

4.2.2. PAni synthesis

Polyaniline (PAni) was synthesized in-house by oxidative polymerisation of aniline by ammonium persulfate in acidic medium (HCL, 1M) using similar method developed in-house previously [15]. The polymerization temperature employed was -15 °C to ensure
high molecular weight PANi was produced. Obtained polymer was deprotonated with ammonia solution from emeraldine salt to base form and washed with deionised water to remove excess ammonia. PANi (hereafter referred as emeraldine base form) was further characterized for its molecular weight by gel permeation chromatography using polystyrene standards. The column used was Styragel HT4 column (4.6 mm × 300 mm, Waters, Hertfordshire, UK). The average molecular weight of PANi polymer was found to be $13.3 \times 10^4$ g mol$^{-1}$.

### 4.2.3. Preparation of dope solution and viscosity measurement

Since the use of two solvents allows finer adjustment of solvent evaporation and polymer coagulation rate, it was decided to use a solvent mixture of NMP and THF. Furthermore, it is also known that addition of more volatile solvent and mixing into the less volatile solvent that usually is a thermodynamically better solvent produced effectively thinner separating skin layer [16,17]. A considerable effort by Yang et al. [18,19] had been taken towards the investigation of different secondary amines as an additive for PANi processing. The secondary amine gel inhibitors are known to chemically attack the polymer backbone and lower its oxidation state [18,19]. The gel inhibitor 4-MP, was shown to be a better choice for hollow fiber spinning solution because it reduced the polyaniline oxidation states at relatively slower rate than the 2-MA [14]. A solvent mixture of NMP and THF (1:1) containing 4MP (1 mole per tetramer repeat unit of PANi for inhibiting gelation in PANi/NMP mixtures) [14,15] was first stirred in a properly sealed glass container, PANi powder was then added gradually in the system using a funnel while mechanically stirring the mixture at high speed (200 to 300 rpm). The polymer solution was stirred further for another 15 hours to ensure that homogeneous dope solution was formed. Then, the mixing was stopped and the dope solution was degassed by leaving it to stand for at least 5 hours.

Chung et al. [20] hypothesized that one of the requirements to obtain an air-separation hollow fiber with minimum defects is to ensure the dope solution to be prepared with concentration exhibiting significant chain entanglement. Based on this hypothesis, in the present study dope solution had been prepared at about the critical concentration. In order to determine the critical concentration dope solution, different dope concentrations were prepared and the viscosity for each concentration was determined.
The Cannon MV-2020 rotary viscometer with spindle number 16 was used to measure the viscosity of the dope solution at ambient temperature. The corresponding polymer dope concentrations and viscosities were plotted and the value for critical concentration was determined by intersecting the slopes of two linear regions as shown in the Fig. 4.1. A dramatic change in the slope of the curve between 15 and 20 wt% implied a significant increase in polymer chain entanglement at concentration approximately 17.5 wt% (known as critical concentration). Thus, in the present case of PAni hollow fiber spinning it was decided to employ the critical concentration (17.5 wt%) for the preparation of dope solution.

![Graph showing the effect of concentration on PAni dope solution viscosity](image)

**Fig. 4.1** Effect of concentration on the PAni dope solution viscosity.

### 4.2.4. Polyaniline hollow fiber spinning process

A degassed dope solution (as described above) was transferred to a 200 ml Harvard stainless steel syringe controlled and monitored by Harvard PHD 22/2000 Hpsi syringe pump and the schematic diagram of the spinning system is presented in Fig. 4.2. As the dope solution is relatively unstable and agglomerated PAni particles are formed with time, the dope solution was forced through a 40-micron Swagelok in-line filter by the
syringe pump. A tube-in-orifice spinneret with outer diameter/inner diameter of the tube of 1.0/0.7 mm was used to spin the hollow fibers.

Fig. 4.2 Schematic diagram of hollow fiber spinning system using syringe pumps.

Table 4.1 Polyaniline hollow fiber spinning conditions.

<table>
<thead>
<tr>
<th>Spinning parameters</th>
<th>Sample L2.5</th>
<th>Sample L30</th>
<th>Sample L50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer concentration</td>
<td>17.5</td>
<td>17.5</td>
<td>17.5</td>
</tr>
<tr>
<td>Dope NMP/THF ratio</td>
<td>1/1</td>
<td>1/1</td>
<td>1/1</td>
</tr>
<tr>
<td>4-MP (moles for every mole of PAni repeat unit)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Length of air gap (cm)</td>
<td>2.5</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Polymer extrusion rate (ml/min)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Injection rate of internal coagulant (ml/min)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Bore fluid composition (H₂O/NMP by wt%)</td>
<td>80/20</td>
<td>80/20</td>
<td>80/20</td>
</tr>
</tbody>
</table>
The dope solution and the bore fluid were extruded at the predefined extrusion rate (Table 4.1). Tap water at ambient temperature was used as the external coagulant. To avoid the extension of fibers by drawing the take up speed of the fiber was adjusted approximately to the same as the free falling velocity of the fiber in the coagulation bath. The spinning process conditions are summarized in Table 4.1. The resultant hollow fiber membranes were then immersed in deionised water for 2 days to remove any residuals solvents. Then, it was immersed in iso-propanol bath for 3 hours prior to drying in vacuum oven at 50°C for about 24 hours. The fibers were then used for further characterization.

4.2.5. Gas permeation measurement

(a) Gas permeation measurement by soap-bubble method

PAAni hollow fiber membrane modules for gas permeation measurement were prepared similar to the method described in Section 3.2.9.

The modules were then connected to the gas permeation apparatus as shown in Fig. 3.4 and tested using pure gases in the sequence as H₂, N₂, O₂, and CO₂ (supplied by BOC, 99.9% purity). Operating pressures were controlled from 1 to 10 bars using pressure regulator (Omega Eng. Ltd., UK) in all permeation tests. The gas permeation rate was measured at room temperature using soap-bubble meter as in Fig. 3.4.

The gas permeation rate was measured at room temperature using soap-bubble meter. The gas permeance, \((P/L)ₚ\), was calculated using equation 2-2 and the ideal separation factor \((α_{A/B})\) of an asymmetric membrane can be defined as the ratio of the permeances of two pure gases A and B as in equation 2-3.

Every gas permeance and gas pair selectivity presented for each module as in Fig. 4.4 and Table 4.2 was based on the replication strategy of data measurement that was described in detail in Section 3.2.9. At least 2-3 modules for each sample were tested for both coated and uncoated fibers.
(b) *Gas permeation measurement by feed pressure drop method*

In order to verify the results especially for low permeating gases the permeation measurement was also carried by the pressure drop method developed previously in our group as shown in Fig. 4.3 [21].

![Fig. 4.3 Schematic diagram of the gas permeation apparatus by feed pressure drop method.](image)

After gluing the hollow fiber membranes on the stainless steel holder (as described above), the module was assembled into a cylinder with a volume capacity of 500 cm$^3$. After ensuring the system was completely leak proof the test gases were pressurized in the cylinder as displayed in Fig. 4.3. The decrease in pressure from the feed side due to diffusion of gas through the membrane was recorded with time. The pressure drop was measured using digital pressure gauge with a resolution of 0.1 psi (Model DPG1000B-10G, supplied by Omega Engineering Ltd., UK). The gas permeance was calculated using the following equation [21]:

$$P = \frac{V}{RT \cdot At} \cdot \ln \left( \frac{p_0 - p_s}{p_f - p_s} \right)$$  \hspace{1cm} (4-1)
where P is the gas permeance; V is the volume of the test cylinder; R is the gas constant; 
A the membrane effective surface area and t is the measured temperature (K). $p_0$ and $p_1$ 
are the initial and final measured pressures.

At least 5 consistent rates of pressure drop were measured for each module tested to 
make out the calculated permeance recorded in Table 4.2.

4.2.6. **Silicone rubber coating**

After the as-spun membranes were tested, they were coated with a 3% (w/w) solution of 
silicone polymer in n-pentane (Sylgard 184, Dow Corning) for 5 mins [22]. The fibers 
were then allowed to cure at room temperature for 48h. The purpose of this coating was 
to repair any possible pinholes or defect on the membrane surface.

4.2.7. **Scanning electron microscopy (SEM)**

Membrane dense skin layer, porous substructure and cross section were examined by 
Scanning Electron Microscope JEOL JSM 5610 LV. Cross section specimens for the 
SEM were prepared by freezing the dry hollow fiber membrane in liquid nitrogen and 
subsequently fracturing it in to small pieces. The samples were then gold sputtered 
under vacuum using Emitech K550 ion sputtering device.

4.2.8. **Mechanical properties measurement**

Five consistent specimens were selected for each sample with different air gap to test 
the membrane tensile strength using Instron 4466 testing equipment. This testing was 
conducted to determine the strength of the fibers and amount of deformation that could 
be expected given at a certain load. In order to avoid the slippage of fibers from the 
grips the end of the fibers were covered with a piece of glue tape. This piece of glue was 
small enough just to hold the sample in between the grips. Clean fiber samples without 
any visual scratches or defects on the surface were selected for the mechanical testing. 
This was necessary because any surface defects might lead to premature failure of the 
sample. The fiber samples without any surface defects usually break at centre at their 
yield points.
The fiber was held by grips at a distance of 40 mm while a movable crosshead containing the load cell of 1 kN pulled the fiber at a constant rate of 3 mm min\(^{-1}\) at room temperature. Care was taken that the samples were mounted vertically straight without any bending or curling. During the testing, the fiber elongation was measured and the stress-strain curve was developed. The fiber mechanical properties viz., tensile stress, elongation at break and Young’s modulus were calculated to determine indirect information about the molecular orientation of the hollow fibers produced.

4.3. Results and discussions

4.3.1. PANi membrane gas separation performance

Evaporation time is one of the important factors among the various parameters that contribute towards the skin layer formation for hollow fiber asymmetric membrane. During the evaporation step, it is expected that the most volatile solvent will be removed from the membrane surface which results in a region with locally elevated polymer concentration. Thus, the skin layer of asymmetric membrane is formed during this dry phase-separated region [23]. Furthermore, an increase in air gap distance may result in the selective skin with a greater orientation and tighter molecular packing due to the elongational stress caused by spin line stress. In order to understand the air gap distance influence on the membrane morphology and its gas permeance performance the hollow fiber membranes were spun at different air gaps, 2.5, 30 and 50 cm.

The as spun fiber modules for different air gap lengths of 2.5, 30 and 50 cm were tested at room temperature and various pressure differences between 1 to 4 bars for uncoated samples and up to 10 bars for coated samples. The data presented were the average of 2-3 different modules. Fig. 4.4 displays the pressure-normalized flux of test gases (H\(_2\), N\(_2\), O\(_2\) and CO\(_2\)) and their ideal gas pair selectivities; H\(_2\)/N\(_2\), CO\(_2\)/N\(_2\), H\(_2\)/CO\(_2\) and O\(_2\)/N\(_2\). It was observed that the gas flux was significantly decreased while the selectivity was increased with increase in air gap. As the air gap distance was increased from 2.5 to 50 cm, flux for all the test gases showed considerable decrease of about 88-94%. A trade-off relationship was observed between permeance and selectivity, with decrease in flux an increase in selectivity was observed.
Fig. 4.4 Gas separation performance of as-spun membranes at different length of air gaps.
The selectivity of CO$_2$/N$_2$, H$_2$/CO$_2$ and O$_2$/N$_2$ were increased by 34-39% and 93% for H$_2$/N$_2$. The lower permeability and higher selectivity of the fibers indicate the formation of denser skin layers with more orientation and closer packing with increase in air gap. The recorded data were clearly in coherent with the explanation presented above.

However, although there were huge improvement on the gas pair ideal selectivities, they were considerably low (4.8 for H$_2$/N$_2$ and 1.8 for O$_2$/N$_2$) and commercially unattractive. This could be because of the surface defects which results in lower separation factor. It has been reported that micro agglomeration of PAni dispersion could be the probable reason for the surface defects [24]. To seal the defects the tested modules were coated externally with silicone rubber (Section 2.6) and then tested for gas permeance at room temperature for various pressures up to 10 bars and the data averaged for 2-3 modules were summarized in Table 4.2.

After the external surface coating, generally, all the membranes displayed substantial decrease in gas permeabilities with corresponding increase in the selectivities. Comparing between Fig. 4.4 and Table 4.1, it can be clearly seen that although, the N$_2$ permeance reduced by 97% to 0.047 GPU, H$_2$ permeance reduced only a little from 7.8 (uncoat) to 5 GPU after coating for fibers with 50 cm air gap (L50). Thus, this increased the H$_2$/N$_2$ selectivity by more than 23 times resulting in gas pair selectivity of more than 100. This exhibits a very interesting potential towards commercial PAni gas separation membranes development.

The coated membranes gas performance still demonstrates the same behavior as the uncoated. The nitrogen flux reduced significantly from 2 to 0.047 GPU for coated fibers as the air gap increased from 2.5 to 50 cm. The same phenomena were observed for other gases as well, as the length of air gap increased from 2.5 to 50 cm fluxes for O$_2$, CO$_2$ and H$_2$ were reduced from 3.5, 2.3 and 14 to 0.5, 0.6 and 5 GPU, respectively. This decrease in flux was associated with tremendous increase in selectivities especially, for O$_2$/N$_2$ from 1.8 to 10.9 and for H$_2$/N$_2$ from 7 to over 100 when the air gap increased. Since N$_2$ flux was very small a minor change in its value would have a considerable impact on O$_2$/N$_2$ and H$_2$/N$_2$ selectivity.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeance, ((P/L)_i) (GPU)</th>
<th>Selectivity, (\alpha_{ij})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N_2)</td>
<td>(O_2)</td>
</tr>
<tr>
<td>L2.5_1(^a)</td>
<td>2.041</td>
<td>3.450</td>
</tr>
<tr>
<td>L2.5_2(^a)</td>
<td>1.970</td>
<td>3.480</td>
</tr>
<tr>
<td>Average</td>
<td>2.006</td>
<td>3.465</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.050</td>
<td>0.021</td>
</tr>
<tr>
<td>L30_1(^a)</td>
<td>0.078</td>
<td>0.402</td>
</tr>
<tr>
<td>L30_2(^b)</td>
<td>0.080</td>
<td>0.400</td>
</tr>
<tr>
<td>Average</td>
<td>0.079</td>
<td>0.401</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>L50_1(^a)</td>
<td>0.040</td>
<td>0.470</td>
</tr>
<tr>
<td>L50_2(^a)</td>
<td>0.060</td>
<td>0.540</td>
</tr>
<tr>
<td>L50_3(^b)</td>
<td>0.040</td>
<td>0.455</td>
</tr>
<tr>
<td>Average</td>
<td>0.047</td>
<td>0.488</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.011</td>
<td>0.045</td>
</tr>
</tbody>
</table>

\(^a\): Permeance determined by soap-bubble method.

\(^b\): Permeance determined by feed pressure drop method.
In order to further verify the data collected, the gas permeance of the module (L50) was also determined by feed pressure drop method. The results obtained (Table 4.2) were consistent with the values obtained by soap-bubble meter method and thus further validated the results.

Current study observed that increase in air gap had caused the permeance to reduce significantly. As Khayet explained, at low air gap length, the fiber was introduced in the non-solvent coagulation bath more rapidly than at higher air gap distance that led to possible higher amount of non-solvent and solvent trapped in the contracted polymer chains. Hence, the produced fibers may have less oriented polymeric chains and high free volume [25]. On contrary, from the results obtained the flux decreased when the air gap length was increased up to 50 cm suggested that the inner and/or the outer surfaces of the final hollow fiber membranes become apparently denser meaning lower free volume with a greater oriented morphology, thus, the selectivity enhanced substantially.

Previous studies have depicted that an optimum evaporation time during dry/wet spinning is required to give better molecular orientation of the polymer in the skin layer [26], which improves polymer chain packing. This implies that increasing air gap length results in hollow fibers with denser skin layer with tighter structure and reduced the finger like voids length. As a consequence, rate of permeation decreased and the gas pair selectivity increased when the air gap was enhanced and this is in agreement with the results.

It would be worth to compare the gas permeance of the present hollow fiber membranes with the literature. From Table 4.3, it can be clearly seen that the membrane performance for this study showed higher permeation rate and comparable ideal gas selectivities to the previously produced flat sheet dense membranes. It was interesting to note that the flux of H₂ and O₂ was about 17-200 folds and 54-488 folds respectively, higher than the reported values with appreciable H₂/N₂ and O₂/N₂ selectivities.
Table 4.3 A comparison between the published gas performance data for as-cast polyaniline membranes with the results of the present work.

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Permeance, $(P/L)_i$ (GPU)</th>
<th>Selectivity, $\alpha_{i/j}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_2$</td>
<td>$O_2$</td>
</tr>
<tr>
<td>Anderson et al. [5]$^a$</td>
<td>0.0001</td>
<td>0.001</td>
</tr>
<tr>
<td>Rebattet et al. [27]$^a$</td>
<td>0.0015</td>
<td>0.009</td>
</tr>
<tr>
<td>Wang and Mattes [28]$^a$</td>
<td>0.0004</td>
<td>0.003</td>
</tr>
<tr>
<td>Illing et al. [11]$^a$</td>
<td>0.0008</td>
<td>0.007</td>
</tr>
<tr>
<td>This work on asymmetric hollow fiber membrane (with silicone coating)</td>
<td>0.047</td>
<td>0.488</td>
</tr>
</tbody>
</table>

$^a$: Permeance values (GPU) were calculated based on available value of film thickness and permeability coefficient (Barrer).
4.3.2. Morphological analysis of the hollow fibers

In general, the skin layer thickness is proven to affect the separation performance of membranes. Basically, skin layer of asymmetric membrane is generated from the dry phase-separated region. As expected, PANi hollow fiber membrane spun at different air gap lengths had revealed different membrane morphologies. The resulted morphologies can be observed from the SEM images as shown in Fig. 4.5. The overall cross section of the as spun hollow fiber membranes revealed that the average membranes wall thickness reduced from 0.27 to 0.14 mm since the outer diameter (o.d.) of the fiber also reduced from 0.61 to 0.48 mm as the air gap distance increased from 2.5 cm to 50 cm. This decrease in o.d. was obvious due to the fact that air gap induces an elongational stress on fibers because of gravity.

According to Chung and Hu, a high elongation stress may pull molecular chains in the early stage of phase separation, resulting in spine line stresses that may be responsible for further stretching on the nascent fiber as well as creating more packed structure with less porosity and free volume [26]. Thus, as the air gap increased during spinning, the fiber became thinner with reduced outer diameter of the hollow fiber. These results were also in agreement with the polysulfone fibers produced by Tsai et al. [29] and polyethersulfone fibers by Chung and Hu [26] where both studies produced thinner wall hollow fibers as the air gap distance increased. However, in the present case between air gap of 30 cm and 50 cm, there is not much difference in the membrane diameter. This is probably because the nascent fibers had reached its optimum stretching between both distances.

Fig. 4.6 clearly shows the array of finger like voids near the outer surface and macrovoids near the inner surface. However, the finger like voids near the outer surface became visibly shorter for membranes produced at higher air gaps 30 and 50 cm as compared to those at 2.5 cm. This is because the fibres at higher air gap have a longer evaporation time to form a dense skin layer due to evaporation of volatile THF. Thus the outer surface of the fiber at higher air gap (30 and 50 cm) experiences volatile solvent evaporation induced phase separation and stress-induced orientation before it reaches the external coagulation bath.
Fig. 4.5 PANi hollow fiber membranes overall cross section; (A) Sample L2.5, (B) Sample L30 and (C) Sample L50.
Fig. 4.6 PAni hollow fiber membranes cross section; (A) Sample L2.5, (B) Sample L30 and (C) Sample L50.
Whereas at shorter air gap (2.5 cm) comparatively the extent of solvent evaporation as well as the stress-induced orientation is not sufficient enough to form a dense layer on the outer surface. As a result when the fiber reaches the external coagulant it immediately undergoes phase separation resulting in larger macrovoids near the outer surface.

From Fig. 4.7, it can be seen that the skin thickness of hollow fiber membrane spun with an air gap of 50 cm was visibly thicker than those of the other hollow fiber membranes spun at lower air gap lengths (at 2.5 and 30 cm). The skin layer thickness of the membrane increased from approximately 0.2 µm for 2.5 cm air gap to about 0.7 µm for Sample L30 and 1.8 µm for Sample L50. This observation is consistent with the trend observed for gas permeance. Thus, the fibers with low air gap of 2.5 cm had the minimum thickness and higher permeance than the fibers with the higher gap of 50 cm with relatively highest thickness.

Investigations by Koros’ group have demonstrated that physical events occurring during dry phase inversion induced by forced convective evaporation may considerably affect membrane formation process. During the dry phase separation, most volatile solvent were removed from membrane surface, and results in a region with locally elevated polymer concentration [30]. Dry phase separation by spinodal decomposition is instantaneously induced at outermost region of membrane [17]. Subsequently, coalescence and fusion of dry phase-separated structure take place due to capillary pressure acting normal at membrane interface. Thus, in the dry phase-separated region, skin layer of asymmetric membrane will be generated [23,30,31]. Therefore, higher and optimum air gaps will promote a better skin layer formation for asymmetric membrane since it is predominantly controlled by evaporation step (such as evaporation time and length of air gaps).

The results obtained in present work were also consistent with the work conducted by Ismail and Lai [30]. They proved that various skin layer thicknesses can be obtained by varying the evaporation time (dry process) during casting which is comparable to length of air gaps in spinning.
Fig. 4.7 PANi hollow fiber membranes top layer; (A) Sample L2.5, (B) Sample L30 and (C) Sample L50.
4.3.3. **Mechanical properties of PAni hollow fiber membranes**

As discussed above the molecular orientation of the fibers increases with an increase in air gap and have considerable effects on their morphology and gas performance. It was anticipated that this molecular orientation should have synergistic effect on the mechanical properties of the fibers. Typical stress-strain curves (e.g. Fig. 4.8) were developed to determine the mechanical strength of different hollow fiber samples.

![Stress versus strain curve for Sample L50.](image)

The calculated tensile stress, elongation at break, modulus of elasticity and standard deviation of each sample are recorded in Table 4.4. It was apparent from the data that the tensile strength, stress at break and Young’s modulus increased but elongation at break decreases with increasing air gap distance. These phenomena was also probably due to the fact that the finger like voids was reduced and thicker skin layer was formed for the hollow fiber membranes produced at higher air gap.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Tensile stress @ break (MPa)</th>
<th>Elongation @ break (%)</th>
<th>Young's Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2.5_1</td>
<td>3.86</td>
<td>3.83</td>
<td>20.53</td>
<td>104.2</td>
</tr>
<tr>
<td>L2.5_2</td>
<td>3.83</td>
<td>3.79</td>
<td>21.95</td>
<td>104.6</td>
</tr>
<tr>
<td>L2.5_3</td>
<td>3.76</td>
<td>3.73</td>
<td>17.30</td>
<td>110.8</td>
</tr>
<tr>
<td>L2.5_4</td>
<td>3.79</td>
<td>3.79</td>
<td>19.70</td>
<td>101.2</td>
</tr>
<tr>
<td>L2.5_5</td>
<td>3.76</td>
<td>3.76</td>
<td>17.76</td>
<td>109.5</td>
</tr>
<tr>
<td>Mean Sample L2.5</td>
<td>3.80</td>
<td>3.78</td>
<td>19.44</td>
<td>106.1</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.04</td>
<td>0.03</td>
<td>1.73</td>
<td>3.5</td>
</tr>
<tr>
<td>L30_1</td>
<td>4.26</td>
<td>4.26</td>
<td>9.38</td>
<td>136.1</td>
</tr>
<tr>
<td>L30_2</td>
<td>4.33</td>
<td>4.26</td>
<td>11.01</td>
<td>118.8</td>
</tr>
<tr>
<td>L30_3</td>
<td>4.33</td>
<td>4.26</td>
<td>11.26</td>
<td>130.3</td>
</tr>
<tr>
<td>L30_4</td>
<td>4.48</td>
<td>4.40</td>
<td>14.63</td>
<td>132.4</td>
</tr>
<tr>
<td>L30_5</td>
<td>4.48</td>
<td>4.48</td>
<td>19.79</td>
<td>98.7</td>
</tr>
<tr>
<td>Mean Sample L30</td>
<td>4.38</td>
<td>4.33</td>
<td>13.21</td>
<td>123.3</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.09</td>
<td>0.09</td>
<td>3.70</td>
<td>13.6</td>
</tr>
<tr>
<td>L50_1</td>
<td>4.48</td>
<td>4.48</td>
<td>12.27</td>
<td>138.2</td>
</tr>
<tr>
<td>L50_2</td>
<td>4.41</td>
<td>4.41</td>
<td>10.58</td>
<td>138.3</td>
</tr>
<tr>
<td>L50_3</td>
<td>4.41</td>
<td>4.33</td>
<td>10.73</td>
<td>126.4</td>
</tr>
<tr>
<td>L50_4</td>
<td>4.41</td>
<td>4.33</td>
<td>11.23</td>
<td>136.8</td>
</tr>
<tr>
<td>L50_5</td>
<td>4.41</td>
<td>4.41</td>
<td>12.38</td>
<td>135.7</td>
</tr>
<tr>
<td>Mean Sample L50</td>
<td>4.42</td>
<td>4.39</td>
<td>11.44</td>
<td>135.1</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.029</td>
<td>0.06</td>
<td>0.76</td>
<td>4.4</td>
</tr>
</tbody>
</table>
The mechanical properties results of this study also further gives an evidence of molecular orientation for the polyaniline hollow fiber membrane produced at higher air gap. It is well known that molecular orientation during fiber spinning results in better chain packing leading to further improvement in its mechanical properties [32]. As the air gap increases from 2.5 to 50 cm, the tensile strength also showed a small increment from 3.7 to 4.4 MPa. This value is quite comparable to other previously reported mechanical strength for other polymeric membrane such as about 5.24 MPa for polysulfone produced by Tsai et al. [29], less than 4 MPa for polyethersulfone [33] and about 3 MPa for PVDF [34].

4.4. Conclusions

Emeraldine base form of PAni were successfully dry-jet wet spun in to asymmetric hollow fiber membrane for gas separation. High molecular weight PAni was synthesized in house by oxidative polymerization. The PAni dope solution formulation using THF as the co-solvent was employed for the membrane spinning in order to promote the formation of the skin layer required to ensure good gas permeation performance. It was observed that the gas flux was significantly decreased while the selectivity was increased with increase in air gap from 2.5 -50 cm. This was attributed to the increased molecular orientation due to elongational stress experienced by the fibers during early stage of fiber dry phase separation. As a result, membrane with higher air gap (50 cm) showed promising ideal gas separation properties for H₂/N₂ (105.6), O₂/N₂ (10.2), CO₂/N₂ (13.3) and H₂/CO₂ (7.9).

The membrane performance for this study showed higher permeation rate and comparable ideal gas selectivities to the previously reported flat sheet dense membranes. SEM confirmed the increase in skin layer thickness with the increase in air gap as anticipated with increase in molecular orientation. The mechanical properties results of this study also further gives an evidence of molecular orientation for the polyaniline hollow fiber membrane produced at higher air gap. Thus, the present study depicts the potential of the polyaniline hollow fiber membrane for gas separation application.
References


Abstract

A more soluble polyaniline substitute was synthesized in-house for this study by introducing a methoxy group on the ortho position of aniline monomer. It was observed that the prepared dope solution was more homogeneous with less visible agglomerates as compared to previously prepared polyaniline solution. Integrally-skinned hollow fiber membranes were successfully prepared by dry-jet wet spinning from poly(ortho-anisidine) (POAn) with N-methyl-2-pyrrolidone and a more volatile tetrahydrofuran co-solvent system for gas separation process. The spinning air gap lengths were varied to promote the formation of the membrane skin layer. POAn membranes prepared at higher air gap were more orientated with more packed structure. This was responsible for substantial improvement in gas separation factors with slight reduction in gases permeance especially for gases with kinetic diameter smaller than 3.4 Å. At air gap distance of 50 cm, POAn based hollow fibers prepared in this study showed very interesting separation factors of O₂/N₂, CO₂/N₂, H₂/N₂ and H₂/CO₂ of about 13.2, 89.3, 370.2 and 4.2, respectively with permeation rates of H₂, CO₂ and O₂ about 10.4, 2.5 and 0.37 x 10⁻⁶ cm³ (STP)/cm² s cmHg, respectively. The results showed that the POAn hollow fiber membranes gases permeation rates was improved as compared to previously prepared polyaniline hollow fiber membranes in our group.
5.1. Introduction

Membrane based gas separation processes have had serious interest for years due to its inherent advantages over those more traditional methods (cryogenic distillation, adsorbent bed processes and adsorption processes, such as pressure swing adsorption and thermal swing adsorption). One of the reasons membranes became an industrial favourite option because the permeation rate of a chemical species through the membrane can be controlled as desired. The current study projected that the combined sales of membrane products in the U.S market for gas separation, pervaporation and other novel processes related processes was $180 million. This was forecast to increase at a compound annual growth rate (CAGR) of 6.6% to $247 million by 2015 [1]. This huge market had definitely intensified the interest in finding new material that was suitable for producing synthetic membrane that can cater for the gas separation related industry.

Over 3 decades ago, the idea of carbon based polymers as conductor would be considered absurd but this perception was rapidly change upon the discovery of the new class polymer known as conductive polymer that supposedly have exceptional mechanical properties such as tensile strength and resistance to harsh environment [2,3]. Among them, polyaniline has been the most studied conjugated polymers especially as the membrane material for gas separation process with many literatures highlight the remarkable gas separation factors it possessed [4-6]. Even it has been widely claimed that polyaniline in emeraldine base form is processable [7-9] into solution to form films or fibers, this is only true upto 6 wt% [10,11] since polyaniline started to aggregate at 1 wt% even in the strongest solvent like NMP. Then, intensive study started to channel their work on the use of secondary amine additives to assist polyaniline dissolution [10,12-15]. Although, secondary amine increased PAni concentration in the dope to more than 15 wt. %, there was still undissolved particle could be seen in solution. Previous researchers tend to filter the dope prior to spinning or used inline filters during extrusion to ensure a more homogenous solution was extruded to minimize any potential defects on the fibers outer layer [14,16].

The other attempts on improving the solubility, some studies had been focusing on modifying PAni on the polymerization stage without causing significant loss of its main
characteristics. This was achieved by introducing bulky alkyl [17-19] or alkoxy groups [7,20-22] onto the aniline ring. Some of the PAni derivatives were found to overcome the solubility difficulty in most organic solvents such as chloroform, dimethylformamide, tetrahydrofuran, 1,4-dioxane, acetone and butanone. Savitha and Sathyarayana synthesized copolymers of aniline with o-toluidine that showed great solubility in 1-methylpyrrolidone, dimethyl sulfoxide, dimethylformamide and tetrahydrofuran and resembled the poly-o-toluidine (POT) homopolymer, especially with higher amount of o-toluidine in the copolymers [19]. Wang et al. had spun POT fibers from 33.2 wt% POT/NMP solution. In addition to preparing considerably high polymer concentration solution, they observed that the mixture did not show any tendency to gel [23], which is not easy to avoid for pure PAni. By substituting methoxy group to the ortho position of the benzene ring, polyaniline substitute that was soluble in chloroform was synthesized [24].

Furthermore, it was anticipated that the PAni derivatives will also be able to improve the gas permeation properties. Chang et al. explained that the torsional angle between the aromatic rings and the polymer interchain distances would be altered upon the methoxy substitution to the aniline ring [25]. They had estimated the specific free volume (SFV) of polyaniline and poly(o-anisidine), (POAn), based on correlations between polymer structure and gas permeability presented by Salame [26] and Lee [27]. They found that POAn’s SFV (0.119 cm$^3$/g) was 3% higher than PAni and it was the major factor that cause big improvement on the gases permeation rates especially for smaller gases (He, H$_2$ and CO$_2$) and increase in most of the gas pair selectivity [25]. However, to the best of knowledge there were no reports available in the literature for the asymmetric POAn membrane.

Present study was aimed at developing the polyaniline derivative hollow fiber membrane with improved processability and gas permeation characteristics. In order to accomplish these objectives, substituted aniline with methoxy group at the ortho position of the aniline ring was used as the monomer for the emeraldine base POAn synthesis. The polymerization was done at sub-zero temperature to ensure high molecular weight POAn was produced. Besides measuring the gases permeance, POAn hollow fiber membranes fabricated in this study was characterised by scanning electron microscope to verify the membrane morphology and structure consistency to the
membrane performance. In addition, the membrane mechanical strength was also studied by means of tensile test.

5.2. Experimental

5.2.1. Materials

Analytical grade (AR) ortho-anisidine and hydrochloric acid (37%) supplied by VWR Chemicals, ammonium persulfate (NH₄)₂S₂O₈ (Sigma Aldrich), lithium chloride (LiCl) anhydrous (99%, Acros Organics) and ammonia solution (35%, Fisher Scientific) were used as supplied for the polymer synthesis. Amine 4-methyl piperidine (4MP) was procured from Sigma Aldrich and the solvents, HPLC grade N-methyl-2-pyrrolidone (NMP) obtained from Rathburn Chemicals and AR grade tetrahydrofuran (THF) and isopropanol (IPA) from VWR Chemicals were used as received. The silicone coating solution was prepared using polymethylsiloxane (PDMS), Sylgard 184, procured from Dow Corning and AR grade n-pentane from VWR Chemicals.

5.2.2. Poly(ortho-anisidine) synthesis and characterization

In order to ensure the polymer used throughout the study is fresh and more consistent in quality, poly(o-anisidine) was synthesized in-house by oxidative polymerisation of 0.4 mol o-anisidine with 0.4 mol ammonium persulfate in acidic medium (HCL, 1M) using similar equipment developed in-house previously for polyaniline synthesis [16,28]. Oxidant mixture was added drop wise into the reactor gradually at about 15 ml/hr for approximately 22 hours to produce less structural irregularity in the polymer chains [29]. Prior to the addition of oxidant mixture, the desired synthesis temperature was achieved and stabilized. The polymer was synthesized at -15 ºC for a total 4.5 days with continuous stirring to ensure high molecular weight POAn was produced. Since POAn was synthesized at subzero temperature, as recommended by Adams et al. lithium chloride was also mixed into the reaction to prevent the reaction mixture from freezing [8]. The amount of LiCl added was approximately 12 wt. % of the total reaction mixture. LiCl presence in the system also hindered the growing polymer aggregation, thus, promoting the formation of longer polymer chain [30]. In order to maintain and inhibit high heat loss to the surrounding, the jacketed beaker was insulated using neoprene rubber.
The dark orange reaction mixture was then filtered and washed with excess deionised (DI) water to remove any unreacted components. At this stage, the filtered cake was in the form of POAn emeraldine salt doped with HCl. Then, the blackish brown filtered cake obtained was deprotonated with ammonia solution, turning the slurry mixture dark red to produce emeraldine base (EB) form of POAn. To ensure complete deprotonation the slurry was further stirred overnight. The EB POAn is a more desirable form since it is known to be highly soluble in organics solvents [31]. The deprotonated mixture was re-filtered and washed with DI water to remove excess ammonia till the waste filtrate turned colourless. Prior to drying the cake in a vacuum chamber, it was washed with iso-propanol to facilitate the drying process by replacing the water in the cake. After drying, the polymer powder was sieved through a 160 µm mesh to ensure a fine lump-free shiny dark brown POAn powder (hereafter referred as emeraldine base form) was prepared and ready for the next task. The chemical structure of the repeat unit of POAn is as shown in Fig. 5.1. POAn was further characterised for its molecular weight by gel permeation chromatography using polystyrene standards. The column used was Styrage HT4 column (4.6 mm × 300 mm, Waters, Hertfordshire, UK). The polymer is also characterised for its chemical structure by $^1$H-NMR using Bruker AV 400 spectrometer and by FT-IR analysis (Perkin Elmer). The samples for H-NMR were prepared by dissolving the polymer in deuterated dimethylsulfoxide (1wt. %). The $^1$H-NMR and FT-IR spectra are given in Fig. 5.2 and Fig. 5.3, respectively.

![Chemical structure of poly(o-anisidine).](image)

5.2.3. Preparation of POAn dope solution

Although the produced POAn showed better solubility than polyaniline, preliminary study showed that at high concentration POAn dope solution tended to gel after an hour as the added polymer concentration exceeded ~ 8 wt.%. Thus, just like polyaniline, gel inhibitor was added to the poly(o-anisidine) dope solution to allow higher polymer
concentration of dope solution [14,28]. Since the previous gas separation polyaniline hollow fiber spinning using amine 4-methyl piperidine proved to be successful, 4MP was again selected as gel inhibitor amine for the current system [16]. A solvent mixture of NMP and THF with weight ratio of 1:1 containing 4MP (1 mole per tetramer repeat unit of POAn) was first stirred in a properly sealed glass container for half an hour. The fine powder was then added gradually into the system using a funnel while mechanically stirring the mixture at high speed (200 to 300 rpm). The polymer solution was stirred further at lower speed of approximately 150 rpm for another 15 hours to ensure that homogeneous dope solution was formed. Then, the stirrer was stopped and the dope solution was then transferred to a gas tight reservoir and was degassed by leaving it to stand for at least 5 hours.

5.2.4. Measurement of dope viscosity

Throughout the years, numerous literatures have discussed the importance of determining optimum polymer concentration in minimizing defects on the developed membranes [32-35]. Thus, the corresponding polymer dope concentrations and viscosities were plotted and the value for critical concentration was determined by intersecting the slopes of two linear regions as shown in Fig. 5.4. The viscosity of dope solution at ambient temperature was measured using Cannon MV-2020 rotary viscometer with spindle number 16. The obtained POAn critical concentration was employed for hollow fiber spinning.

5.2.5. Fabrication of poly(o-anisidine) hollow fiber membrane

A degassed poly(o-anisidine) dope solution (as described in Section 5.2.3) was transferred to a 200 ml Harvard stainless steel syringe controlled and monitored by Harvard PHD 22/2000 Hpsi syringe pumps. In order to remove the agglomerated particles, the dope solution was forced through a Swagelok inline-filter (mesh size of 40 µm) by means of a syringe pump. Then, the solution was passed through a tube-in-orifice spinneret with outer diameter/inner diameter of the tube of 1.0/0.7 mm. The dope solution and the bore fluid were extruded at the predefined extrusion rate (Table 5.1) and the external coagulant used in the bath was tap water. To avoid the extension of fibers by drawing the take up speed of the fiber was adjusted approximately to the same
as the free falling velocity of the fiber in the coagulation bath. The spinning process conditions are summarized in Table 5.1.

**Table 5.1** Summary of poly(o-anisidine) dope compositions and hollow fiber membrane spinning parameters.

<table>
<thead>
<tr>
<th>Spinning parameters</th>
<th>Sample A0</th>
<th>Sample A2</th>
<th>Sample A30</th>
<th>Sample A50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer concentration</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Dope solution NMP/THF ratio</td>
<td>1/1</td>
<td>1/1</td>
<td>1/1</td>
<td>1/1</td>
</tr>
<tr>
<td>4-MP (moles for every mole of POAn repeat unit)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Length of air gap (cm)</td>
<td>0</td>
<td>2</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Polymer extrusion rate (ml/min)</td>
<td>1.5</td>
<td>1.5</td>
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<tr>
<td>Injection rate of internal coagulant (ml/min)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Take up velocity (m/min)</td>
<td>5.1</td>
<td>4.7</td>
<td>4.3</td>
<td>4.2</td>
</tr>
<tr>
<td>Bore fluid composition (H₂O/NMP by wt%)</td>
<td>80/20</td>
<td>80/20</td>
<td>80/20</td>
<td>80/20</td>
</tr>
<tr>
<td>Coagulation (water) bath (°C)</td>
<td>16.0 ± 1</td>
<td>16.0 ± 1</td>
<td>16.0 ± 1</td>
<td>16.0 ± 1</td>
</tr>
</tbody>
</table>

The resultant hollow fiber membranes were then immersed in deionised water for 2 days to remove any residuals solvents. Then, it was immersed in *iso*-propanol bath for 30 minutes prior to drying in vacuum oven at 50 °C for about 24 hours. The fibers were then used for further characterization.
5.2.6. Preparation of testing modules and gas permeation measurement

After drying fibers with a length of 25 cm each were assembled into bundle of 6 fibers. One end of the bundles was sealed with epoxy resin (Araldite ®), while the shell side of the other end was glued onto a stainless steel holder using similar epoxy. To ensure full curing of the epoxy, the module was only being tested after 24 hours. The modules were then connected to the gas permeation apparatus as described previously [16] and tested using pure gases in the sequence as H₂, N₂, O₂, and CO₂ (supplied by BOC, 99.9% purity). Operating pressures were controlled from 1 to 10 bars using pressure regulator (Omega Eng. Ltd., UK) in all permeation tests. The gas permeation rate was measured at room temperature using a soap-bubble meter. The pure gases permeabilities and selectivities were calculated using equation 2.2 and equation 2.3, respectively [16].

Every gas permeance and gas pair selectivity presented for each module as in Fig. 5.8 and Table 5.3 was based on the replication strategy of data measurement that was described in detail in Section 3.2.9. At least 2-3 modules for each sample were tested for both coated and uncoated fibers.

To further verify the gas permeation results especially for low permeating gases the permeation measurement was also carried by the pressure drop method developed previously in our group [16,36]. The hollow fiber membranes module prepared (as described above) was assembled into a cylinder with a volume capacity of 500 cm³. After ensuring the system was completely leak proof the test gases were pressurized in the cylinder. The decrease in pressure from the feed side due to diffusion of gas through the membrane was recorded with time. The pressure drop was measured using digital pressure gauge with a resolution of 0.1 psi (Model DPG1000B-10G, Omega Engineering Ltd., UK). The gas permeance for this pressure drop method was calculated using equation (4-1).

At least 5 consistent rates of pressure drop were measured for each module tested to calculate the permeance recorded in Table 5.4.
5.2.7. Silicone rubber coating

After the as-spun membranes were tested, they were coated with a 3% (w/w) solution of polydimethylsiloxane (PDMS) dissolved in n-pentane for 5 mins [37]. The coated fibers were then allowed to cure at room temperature for 48h. The purpose of this coating was to seal any surface defects of the membrane. The gas permeance for both coated fibers was averaged for 2-3 modules and presented in Table 5.3 (soap-bubble meter) and Table 5.4 (feed pressure method).

5.2.8. Scanning electron microscopy (SEM)

Scanning Electron Microscope JEOL JSM 5610 LV was used to examine membrane dense skin layer, porous substructure and cross section. The hollow fiber membranes were immersed in liquid nitrogen and fractured to obtain its cross sections. The samples were then gold sputtered under vacuum using Emitech K550 ion sputtering device.

5.2.9. Mechanical properties measurement

At least five consistent specimens were selected for each sample to analyze the membrane tensile strength using Instron 4466 testing equipment. This testing was conducted to determine the strength of the fibers and amount of deformation that could be expected at a certain load. The fiber was held by grips at a distance of 40 mm while a movable crosshead containing the load cell of 1 kN pulled the fiber at a constant rate of 3 mm min$^{-1}$ at room temperature. During the testing, the fiber elongation was measured and the stress-strain curve was developed. The fiber mechanical properties viz., tensile stress, elongation at break and Young’s modulus were calculated.

5.3. Results and discussions

5.3.1. POAn synthesis and characterisation

Poly(ortho-anisidine) was synthesized in-house using our previously developed method for polyaniline synthesis [28]. In order to get high molecular weight of POAn, the reaction was carried out at -15 °C for 4.5 days. Mean molecular weight of the polymer as characterised by GPC was $14.5 \times 10^4$ g mol$^{-1}$. 
The polymer was further characterized for its chemical structure by $^1$H-NMR and FT-IR spectroscopy. The $^1$H-NMR spectra (Fig. 5.2) clearly shows the peak for methoxy protons (─OCH$_3$) at ~ 3.8 ppm. The aromatic proton was observed in the range of ~ 6-7.5 ppm.

FT-IR spectra of POAn (Fig. 5.3) shows the characteristic peak around ~2900 cm$^{-1}$ ascribed to ─CH$_3$ group [7]. Various vibrational bands in the spectra of POAn can be observed from Fig. 5.3. The major peaks can be observed around 3370, 3060, 2925, 2830, 1599, 1510, 1460, 1405, 1330, 1260, 1216, 1188, 1030, 954 and 845 cm$^{-1}$ are the characteristic bands of the POAn also observed in the case of PANi [7,22,39]. The bands seen around ~ 3400 cm$^{-1}$ are attributed to N-H stretching [22,40]. The sharp peaks between 1510 and 1595 cm$^{-1}$ are due to C=C vibrations in benzenoid and quinoid rings, respectively [9,39,41]. Additional peaks at 1258 and 1028 cm$^{-1}$ are due to C-O-C asymmetric and symmetric stretching of the alkyl aryl ether linkage, respectively [22,25].
### 5.3.2. Determining the critical polymer concentration of POAn dope solution

Usually, with increase in polymer concentration in the dope solution the viscosity increases and tends to promote more selective but less productive membranes in the absence of offsetting casting conditions or other solution component changes. As polymer concentration increases, the selectivity will increase and permeability will decrease in the separation performance and membranes with higher skin thickness (low porosity) will be produced [33]. On the contrary, a more dilute dope solution produces membranes with low degree of chain entanglement, hence, low gas pair selectivity due to formation of thin and porous skin layer. Thus, preparing the solution with an optimum viscosity is a critical stage prior to membrane preparation for gas separation.
Chung’s et al. [42,43] hypothesis stipulates that one of the key requirements in producing membrane with minimum defects is using the dope solution that exhibits significant chain entanglement. In order to determine the critical polymer concentration (cpc, the concentration at which the sudden increment in viscosity is observed due to significant polymer chain entanglement), the corresponding polymer dope concentrations and viscosities recorded were plotted. The cpc was determined by intersecting the two tangents with substantial slope differences as shown in Fig. 5.4. The cpc value in the present case for POAn was ~18 wt. %. Thus, for the hollow fiber fabrication dope solution was prepared with a concentration of 18 wt. %.

5.3.3. Effect of length of air gap on POAn hollow fiber membrane geometry

Generally, the primary membrane fabrication parameters in establishing the hollow fiber geometry including the inner diameter, wall and skin thickness are the spinneret geometry, dope extrusion rate, bore fluid flow rate and air gap distance. In this study,
the POAn spinning air gap distance was manipulated to produce hollow fiber with various geometries. The cross section dimensions of the spun POAn hollow fiber are recorded in Table 5.2.

Table 5.2 Effect of spinning air gap lengths on internal and external diameters, wall and skin layer thickness of POAn hollow fiber membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Outer diameter (µm)</th>
<th>Internal diameter (µm)</th>
<th>Wall thickness (µm)</th>
<th>Skin thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>997 ± 12</td>
<td>697 ± 24</td>
<td>150 ± 7</td>
<td>0.25</td>
</tr>
<tr>
<td>A2</td>
<td>892 ± 28</td>
<td>644 ± 31</td>
<td>124 ± 25</td>
<td>0.36</td>
</tr>
<tr>
<td>A30</td>
<td>667 ± 10</td>
<td>521 ± 19</td>
<td>73 ± 10</td>
<td>0.60</td>
</tr>
<tr>
<td>A50</td>
<td>639 ± 13</td>
<td>495 ± 5</td>
<td>70 ± 8</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Hollow fiber A0 developed with the lowest air gap distance of 0 cm, which is the wet spun fibers have the biggest overall diameter and wall thickness than the other dry-jet wet spun fibers. As previously explained by Khayet, upon exiting the spinneret, the polymer macromolecules would undergo die swelling due to the viscoelastic properties of the polymer spinning solution [44]. In the case of the wet spinning process (A0), the die swell was expected to be coagulated instantaneously as contacted by the water bath and the orientation induced within the spinneret may be rapidly frozen into the solidified outer skin of the wet spun fiber [45,46]. This resulted in POAn hollow fibers with the largest diameter when spun at zero air gap distance as compared to those fabricated by dry-jet wet spinning process (A2, A30 and A50). It was predicted that during the dry-jet wet spinning process, the die swelling of the nascent fiber may be eliminated since prior entering the water coagulation bath, the shear-induced orientation would undergo relaxation even with an air gap as low as 1 cm [46] (in this study the lowest dry-wet spinning air gap length was 2 cm). Additionally, the nascent fiber also experiences an elongational stress due to gravitational force which further stretches it before entering the coagulation bath.
Based on the data collected in Table 5.2 from the measurements of Fig. 5.5, it could be clearly seen the outer diameter (OD) and the inner diameter (ID) of the fiber reduced from ~ 1.00 to 0.64 mm and ~ 0.70 to 0.50 mm, respectively, as the air gap distance increased from 0 to 50 cm. Simultaneously, the average wall thickness for the fibers reduced by approximately 50% from 0.150 mm (for spinning air gap of 0 cm) to 0.70 mm (for spinning gap of 50 cm). Thinner fibers were produced as the air gap increased since during the dry region (air gap), besides the nascent fiber weight and the take up force, the fiber had moment to relax and elongate due to the gravitational force that caused external spine-line stresses on the nascent fiber. Thus, the higher the air gap, the nascent fiber experienced higher stretching stress that emanated hollow fiber with lesser outer and inner diameter. Similar fiber geometry situation occurred to other polymeric hollow fibers developed like polyvinylidene fluoride (PVDF) by Khayet [44], polyetherimide (PEI) hollow fibers by Khulbe et al. [47] and polysulfone/titanium dioxide (PSF/TiO₂) by Hamid et al. [45]. Same as previously developed PANi hollow fiber [16], for higher air gap of 30 and 50 cm, the POAn hollow fiber dimensions show only slight decrease of 4 to 5% for OD, ID and the wall thickness. This is probably due to the nascent fiber has reached its optimum stretching force.

5.3.4. Morphological and structural analysis of POAn hollow fiber membrane

In order to understand the air gap distance influence on the membrane morphology and its gas permeance performance the hollow fiber membranes were spun at different air gaps, 0, 2, 30 and 50 cm. Fig. 5.5 to Fig. 5.7 show the morphology and structure of the POAn hollow fiber membranes developed in this study. From Fig. 5.6 (A to D), it can be clearly seen that all fibers have a sandwich structure with fiber inner layer, middle layer and outer layer. However, the thickness of each layer and size of the finger like void at the inner and outer layer vary as the air gap length changes.

There are array of finger-like voids near both outer and inner surface of the fibers. Since the same internal coagulant solution was used for all the spinning, it can be visibly seen in Fig. 5.7 that the size of finger-like voids near the inner layer of all the fibers (A0 to A50) are almost of the same length. However, as the air gap increased from 0 to 50 cm, the finger voids approaching the membrane skin layer became shorter.
Fig. 5.5 POAn hollow fiber membranes overall cross section; (A) Sample A0, (B) Sample A2, (C) Sample A30 and (D) Sample A50.
Fig. 5.6 POAn hollow fiber membranes cross section of: (A) Sample A0, (B) Sample A2, (C) Sample A30 and (D) Sample A50.
Fig. 5.7 POA)n hollow fiber membranes top layer of; (A) Sample A0, (B) Sample A2, (C) Sample A30 and (D) Sample A50.
At higher air gaps (samples A30 and A50), the finger-voids are observably shorter due to the formation of thicker denser skin as compared to membranes prepared at low air gaps (A0 and A2). During the dry-jet stage, the longer the time prior the POAn nascent fiber reached the external coagulation bath, the more time for the highly volatile THF to evaporate that created a more concentrated polymer region on the fiber surface. This created a high resistance for coagulant penetration and solvent exchange during phase separation in the wet stage. On the other hand, at zero air gap and even the low air gap length of 2 cm, since solvent exchange and the extruded polymer solution coagulated almost instantaneously, the coagulant jet into the nascent fiber was frozen rapidly, thus, producing hollow fibers with longer finger-like macrovoids [48].

As mentioned before, as the air gap increased, a locally enhanced polymer concentration surface was developed and this promoted the formation of thicker dense layer. This can be seen from Fig. 5.7 and as recorded in Table 5.2, at zero air gap the membrane skin layer is almost invisible with only ~0.25 µm. However, as the air gap distance increases from 2 to 30 cm, the skin layer thickness increases by 67 % up to 0.6 µm. During the dry-jet phase, it was anticipated that the volatile solvent was mostly removed that promoted the formation of polymer enriched dry-phase region, thus, producing nascent fiber skin layer. As previously discussed, the matured nascent skin layer that was formed at the outer layer of the fiber possessed higher resistance towards the counter-diffusion of solvent and non-solvent between the external coagulant and the remaining components (solvents to be removed) in the interior of the nascent fiber as it was immersed in the water bath. As a result the demixing and precipitation of nascent sublayer occurred at relatively slower rate for higher air gap that would restrain the voids formation. Thence, as the air gap distance was increased, the finger-like voids size was reduced and asymmetric hollow fiber membranes with thicker skin layer were produced [33,49,50].

As conjectured, the highest air gap distance in this study, which is 50 cm, has the thickest skin dense layer of 0.8 µm as recorded in Table 5.2. Other researchers had proven evaporation time during casting and air gap lengths in spinning process produced membranes with various skin layer thicknesses and this is in consistent with the membrane skin formation behaviour as observed in the present POAn hollow fiber development [16,33]. With the thicker skin layer formation, it was expected that the gas
pair separation factor would enhance, which is very desirable for this study and this will be further discussed in the subsequent section.

5.3.5. Poly(o-anisidine) hollow fiber membrane gas separation performance

Generally, it has been widely accepted, the longer the evaporation time or as the length of air gap increases, the membrane developed will be more selective or retentive [51] and this has been verified by our previous study for pure polyaniline hollow fiber membranes [16]. As described in Section 5.3.4, at higher air gap (longer solvent evaporation time), the removal of volatile solvent promoted the formation of denser membrane skin layer [52]. Furthermore, with longer period for gravitational force to stretch and elongate the nascent fiber due to its weight; there was longer time for the polymer to aggregate and orient closer together, thus, creating a more pack structure before coagulating in the water bath. Thus, the outer surface of the fiber at higher air gap experiences volatile solvent evaporation induced phase separation and stress-induced orientation before it reaches the external coagulation bath. This was expected to be beneficial in improving the gas pair selectivity.

(a) Effect of air gap on the gas permeance of POAn hollow fiber membrane

POAn hollow fiber spinning length of air gap was varied from 0 to 50 cm (Table 5.1) to develop membranes with good gas separation performance. The spun fibers were tested at room temperature with various pressure differences between 1 to 3 bars for uncoated samples and up to 10 bars for coated samples. Each data presented is the average of 2 to 3 different modules.

Fig. 5.8 clearly shows that flux for all test gases (H₂, N₂, O₂ and CO₂) reduced between 94 to 97% as air gap increased from 0 to 50 cm. On the other hand, in Fig. 5.9 the ideal gas pair selectivities; O₂/N₂, CO₂/N₂, H₂/CO₂ and H₂/N₂ increased by 1.3 to 2.9 times. A general trade-off behaviour was observed between gas permeabilities and selectivities [53-55]. This study showed identical behaviour as Ekiner and Vassilatos’ work which was the development of polyaramide hollow fiber membranes and reported that as the air gap distance increased, the helium (He) permeance decreased dramatically while the He/N₂ selectivity increased [53].
Fig. 5.8 POAn as-spun hollow fiber membrane gases permeabilities prepared at various air gap distances.
According to them, this was due to the increasing amount of solvent removal during dry-jet process that led to thicker skin layer formation and the development of a more defect-free membrane. Although as the air gap increased the POAn membrane displayed improvement for selectivity; 1.1, 1.3 and 7.0 for O₂/N₂, CO₂/N₂ and H₂/N₂, respectively, are very low and undesirable for the industrial application. It has been reported that the probable reason for surface defects could be micro-agglomeration of the PANi dispersion [56]. Thus, the membranes were silicone coated (details in Section 5.2.7) to seal the defects and the pure gas permeabilities were examined again at room temperature at various pressures up to 10 bars.
Since PDMS coating is known to have permeability coefficient of a higher magnitude than the glassy polymeric asymmetric membranes, it will only inhibit the gas to permeate through the defects but not altering the original permeation characteristics of the membranes [57]. After the external coating with a very dilute 3 wt. % PDMS solution, all the POAn membranes showed a significant decrease in the gas fluxes (Fig. 5.10 and Table 5.3). The sealed defects caused significant reduction in permeabilities of bigger gases (N$_2$ and O$_2$) for all samples up to ~ 90%, while, for smaller gases, the fluxes were ~ 90% for A0 and A2 and approximately halved for A30 and A50. For instance, upon coating for sample A0 (Fig. 5.10), H$_2$ permeability reduced from 365.3 to 48.3 GPU, CO$_2$ decreased from 156.5 to 12.5 GPU, O$_2$ reduced from 127.6 to 17.9 GPU and N$_2$ reduced from 149.3 to 16.11 GPU.

As for higher air gap sample, A30, H$_2$ permeance reduced from 17.6 to 11.7 GPU and CO$_2$ permeance was reduced from 6.5 to 2.9 GPU, while bigger gases, O$_2$ and N$_2$ fluxes...
reduced by ~ 90%, to 0.372 and 0.038 GPU, respectively. On the other hand, the ideal gas selectivities improved tremendously with O2/N2 increased between 2 to 12 times for all samples. As mentioned, since the coating layer will not alter the membrane permeation properties, for membranes with thinner skin layer prepared at low air gap, sample A0 and A2 showed only a small improvement on all gas pairs selectivities of only up to 3 times as compared to the as spun hollow fiber membranes. This verifies that the membrane pores on the fiber outer layer were huge, thus, even the coating solution was not able to seal them [58]. On the other hand, samples prepared at high air gap lengths; A30 and A50, showed substantial selectivity increment of over 45 fold for CO2/N2 and H2/N2. This improvement was highly desirable and showed the same trend as the previously developed polyaniline hollow fiber membranes [16].

Table 5.3 shows that as the air gap distance increases, each gas permeability decreases, while gas pair selectivity increases. It is apparent that the coated membranes possess the same behaviour as the as spun (uncoated) fibers. Nitrogen flux reduced dramatically from 16 to 0.028 GPU as the air gap length increases from 0 to 50 cm. Collected data shows similar trend for other gases as well; for oxygen, at zero air gap the flux was 17.9 GPU and this reduced to 10.8 for sample A2, then, further decreased by almost 48 times to 0.372 and 0.367 GPU for air gap of 30 and 50 cm air gap, respectively. For smaller gases, CO2 and H2 fluxes showed moderate decline from 12.5 and 48 GPU to 2.5 and 10 GPU, as the air gap increased from 0 to 50 cm.

During wet spinning, the coalescence of polymer on the surface of the nascent fiber was very minimal caused the formation of bigger pores on the fiber outer layer. Since the fiber coagulated almost instantaneously, promoted higher amount of solvent trapped in the polymer producing less oriented morphology with bigger macrovoids and this led to higher gas permeation [44,59] at lower air gap. It should be noted that even with 5 times lower than zero air gap, the hydrogen permeability of A50 increased more than 50% as compared to the pure polyaniline membranes [16]. Such an increment in permeance was due to the presence of methoxy group which renders looser polymer chain packing in the case of poly(o-anisidine) as compared to polyaniline and will be further discussed in the next section.
Table 5.3 Pressure-normalized fluxes of N$_2$, O$_2$, CO$_2$ and H$_2$ and the ideal gas pair selectivities for silicone coated POAn hollow fiber membranes tested by soap bubble meter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeance, (P/L)$_i$ (GPU)</th>
<th>Selectivity, $\alpha_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_2$</td>
<td>$O_2$</td>
</tr>
<tr>
<td>A0_1</td>
<td>18.438</td>
<td>20.539</td>
</tr>
<tr>
<td>A0_2</td>
<td>13.772</td>
<td>15.210</td>
</tr>
<tr>
<td>Mean A0</td>
<td>16.105</td>
<td>17.875</td>
</tr>
<tr>
<td>Std deviation</td>
<td>3.299</td>
<td>3.768</td>
</tr>
<tr>
<td>A2_1</td>
<td>8.206</td>
<td>11.007</td>
</tr>
<tr>
<td>A2_2</td>
<td>6.381</td>
<td>10.569</td>
</tr>
<tr>
<td>Mean A2</td>
<td>7.294</td>
<td>10.788</td>
</tr>
<tr>
<td>Std deviation</td>
<td>1.290</td>
<td>0.310</td>
</tr>
<tr>
<td>A30_1</td>
<td>0.031</td>
<td>0.255</td>
</tr>
<tr>
<td>A30_2</td>
<td>0.048</td>
<td>0.498</td>
</tr>
<tr>
<td>A30_3</td>
<td>0.036</td>
<td>0.364</td>
</tr>
<tr>
<td>Mean A30</td>
<td>0.038</td>
<td>0.372</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.009</td>
<td>0.122</td>
</tr>
<tr>
<td>A50_1</td>
<td>0.026</td>
<td>0.384</td>
</tr>
<tr>
<td>A50_2</td>
<td>0.030</td>
<td>0.375</td>
</tr>
<tr>
<td>A50_3</td>
<td>0.028</td>
<td>0.342</td>
</tr>
<tr>
<td>Mean A50</td>
<td>0.028</td>
<td>0.367</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.002</td>
<td>0.022</td>
</tr>
<tr>
<td>PAri [15]</td>
<td>0.047</td>
<td>0.488</td>
</tr>
</tbody>
</table>
Table 5.4 Pressure-normalized fluxes of N\textsubscript{2}, O\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2} and the ideal gas pair selectivities for silicone coated POAn hollow fiber membranes tested by pressure drop method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeance, (P/L) \textsubscript{(GPU)}</th>
<th>Selectivity, ( \alpha_{i/j} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N\textsubscript{2}</td>
<td>O\textsubscript{2}</td>
</tr>
<tr>
<td>A30_1</td>
<td>0.031</td>
<td>0.273</td>
</tr>
<tr>
<td>A30_2</td>
<td>0.049</td>
<td>0.495</td>
</tr>
<tr>
<td>A30_3</td>
<td>0.037</td>
<td>0.364</td>
</tr>
<tr>
<td>Mean A50</td>
<td>0.039</td>
<td>0.377</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.009</td>
<td>0.112</td>
</tr>
<tr>
<td>A50_1</td>
<td>0.027</td>
<td>0.377</td>
</tr>
<tr>
<td>A50_2</td>
<td>0.032</td>
<td>0.374</td>
</tr>
<tr>
<td>A50_3</td>
<td>0.027</td>
<td>0.354</td>
</tr>
<tr>
<td>Mean A50</td>
<td>0.029</td>
<td>0.368</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.003</td>
<td>0.013</td>
</tr>
</tbody>
</table>
The reduction in gas permeabilities resulted in significant increment of gas pair selectivity. As the air gap increased to 50 cm, the $O_2/N_2$ increased by about 12 times, from 1.1 during wet spinning to 13, which is a very attractive value. Both $H_2/N_2$ and $CO_2/N_2$ were also increased by more than 100 times at 50 cm air gap as compared to 0 cm air gap. For $CO_2/N_2$, the selectivity increased from about 1 to 78 and 89 at high air gap sample of A30 and A50, respectively. Whereas, $H_2/N_2$ improved to 304 and 370 for high air gap lengths of 30 and 50 cm, respectively, as compared to 3 for A0 and 7 for A2. As discussed before, at higher air gap the nascent fiber experiences molecular orientation due to stretching and elongation before its coagulation in water bath producing more packed structure at the fiber surface layer. Furthermore, higher air gap also results in increased skin thickness due to increased volatile solvent evaporation. Thus, POAn with the highest gas pair selectivities was successfully produced at air gap of 50 cm.

Generally, this study (Table 5.3) showed a great improvement for gas pair separation factors and permeabilities. It should be noted that the $N_2$ flux was less than 1 GPU and a small value would affect the selectivity substantially, even with slight difference on the decimal values. Thus, to further confirm the data reported in the tested fibers were also analyzed by constant volume feed pressure drop method [16] and presented in Table 5.4. Comparing both tables, the consistency with difference of less than $\pm$3%, further validated the data.

(b) Comparison of gas performance of present POAn membrane with the previously developed PAni membrane

It would be interesting to compare the gas permeance data of the present polyaniline derivative membrane with the gas permeance of pure polyaniline membrane previously developed by us (Table 5.3). It could be seen that as compared to PAni hollow fiber membranes POAn membranes showed significant improvement in both permeation rates (especially for smaller gases $H_2$ and $CO_2$) and the gas pair separation factors. Comparing samples prepared at 50 cm air gap distance, although, the bigger gases permeance reduced slightly; $H_2$ permeation rates was doubled from 5.0 to 10.7 GPU and $CO_2$ permeance increased 4 times from 0.6 to 2.5 GPU. Thus, this improvement in permeance of small gases led to significant enhancement in gas pair selectivities with
H₂/N₂ by more than 3 times from 106 (PAni), CO₂/N₂ by 7 times to 89 and even O₂/N₂ improved by 30% from 10 (PAni) to 13.

Such an enhancement in permeabilities with simultaneous increase in permselectivities of POAn based hollow fiber membranes could be attributed to the rigid structure of the POAn. The small and bulky —OCH₃ group makes the POAn chain backbone rigid (high Tg [60]) with more open structure (high free volume, [25]) than the PAni structure. The rigid structure of POAn (Tg = 240 °C, [60]) as compared to PAni (Tg = 170 °C, [60]) gives better discriminating ability for the former polymer towards gas pairs than the later. It is known that bulky group substitution in the case of various polymer families such as polycarbonate [61], polysulphone [62], polyarylate [63] and polyimide [64] led to improvement in permeability as well as selectivity due to their increased rigidity and free volume. Structural alterations on the polymer backbone that inhibit chain packing while simultaneously inhibiting chain mobility tend to increase permeability while maintaining or increasing selectivity. Thus, in the present case of POAn presence of bulky —OCH₃ group increased the permeance (H₂ and CO₂) as well as selectivity as compared to PAni.

(c) Effect of pressure on CO₂ permeance of POAn hollow fiber membrane

Fig. 5.10 displays the pressure-normalized fluxes of N₂, O₂, CO₂ and H₂ for silicone coated POAn fibers spun at zero air gap measured over the range of 1 to 3 bar at room temperature. The average permeabilities of all test gases of sample A0 reduced between 7 to 13 fold with slight increment in selectivities as compared to the as cast fibers. From the figure, a more consistent permeability measurement can be seen when for testing pressure of 2 bar and higher. The permeability of H₂ shows slight decrease of about 2% while N₂, O₂ and CO₂ show minor increment of 5, 13 and 2%, respectively, with increasing pressure between 2 to 3 bars. One of the major advantages of using polyaniline and its derivatives based membranes was due to its plasticization resistance towards carbon dioxide as compared to other polymer such as polyetherimide, polysulfone, polycarbonate and polyestercarbonate [57,58,65]. Although, the curve demonstrated that there was still slight increment in CO₂ permeability of POAn membranes as the testing pressure increase, the change was very minimal. Thus, this further verifies that this polyaniline derivative membrane was indeed chemically stable.
towards plasticization gas, carbon dioxide [5]. For testing pressure above 2 bars, the same CO₂ permeation rates behaviour as A0 was discovered for other samples (A2, A30 and A50) as in Fig. 5.11 with very small change between 7 to 10%, as the pressure increases up to 10 bars.

![Graph showing CO₂ permeability as a function of pressure for different samples.](image_url)

**Fig. 5.11** Average pressure-normalized flux of carbon dioxide for coated POAn hollow fiber spun at various air gaps as a function of pressure.

### 5.3.6. Mechanical properties analysis of POAn hollow fiber membranes

Increase in length of air gap had proved to improve the membrane gas separation performance and affecting the membrane morphology significantly. As previously discussed, the increase in air gap distance increased the membrane molecular orientation. Thus, it is predicted that the mechanical properties of POAn hollow fiber membranes would be affected considerably. Fig. 5.12 shows the engineering stress versus engineering strain curve of poly(o-anisidine) hollow fiber membranes spun at 50 cm air gap. These curves were developed to analyze the mechanical properties of
different hollow fiber samples with different air gaps. Similar stress-strain curves were obtained for other samples too.

![Stress versus strain curve for Sample A50.](image)

**Fig. 5.12** Stress versus strain curve for Sample A50.

Table 5.5 presents the calculated tensile stress at break, elongation at break, modulus of elasticity and standard deviation of each sample. The recorded data based on 5 fiber samples, illustrates the tensile strength at break and Young's modulus of these fibers increase but the elongation at break decreases with increasing air gap distance. As the air gap increases from 0 to 50 cm, tensile strength at break improves from 12.07 to 13.53 MPa and Young's modulus of these fibers improves by 29 % up to 448 MPa. As discussed before, the longer air gap promoted thicker skin layer formation due to solvent evaporation and better chain packing due to molecular orientation. Furthermore this increase in air gap also reduced the finger like voids in the hollow fiber membranes. Thus, this enhanced the molecular orientation and reduced size of finger like voids improved the mechanical properties of the fibers [66]. It is well known that molecular orientation during fiber spinning results in better chain packing leading to further improvement in its mechanical properties [67,68].
Table 5.5 Tensile at break, elongation at break and Young's modulus as a function of air gap distance.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile at break (MPa)</th>
<th>Elongation at break (%)</th>
<th>Young’s Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0_1</td>
<td>12.01</td>
<td>17.16</td>
<td>343.39</td>
</tr>
<tr>
<td>A0_2</td>
<td>11.90</td>
<td>16.50</td>
<td>370.95</td>
</tr>
<tr>
<td>A0_3</td>
<td>12.23</td>
<td>15.92</td>
<td>337.46</td>
</tr>
<tr>
<td>A0_4</td>
<td>12.00</td>
<td>16.40</td>
<td>341.84</td>
</tr>
<tr>
<td>A0_5</td>
<td>12.19</td>
<td>16.85</td>
<td>344.83</td>
</tr>
<tr>
<td>mean sample A0</td>
<td>12.07</td>
<td>16.57</td>
<td>347.69</td>
</tr>
<tr>
<td>std deviation</td>
<td>0.14</td>
<td>0.47</td>
<td>13.29</td>
</tr>
<tr>
<td>A2_1</td>
<td>12.46</td>
<td>15.75</td>
<td>358.37</td>
</tr>
<tr>
<td>A2_2</td>
<td>12.30</td>
<td>15.29</td>
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5.4. Conclusions

Asymmetric hollow fiber membranes from emeraldine base form of substituted polyaniline, poly(o-anisidine), were successfully developed by dry-jet wet phase inversion process. The chemical modification proved to not only improved the polymer solubility in NMP and THF but also enhanced the gas permeation properties. The volatile co-solvent, THF, was used to facilitate the skin layer formation. As anticipated, the POAn hollow fiber membranes morphology showed increment on the skin layer thickness with reduced size of the finger-like voids at higher air gap. Higher air gap led to formation of hollow fiber membrane with outer surface having thicker skin layer and higher molecular orientation. The morphology produced had a crucial effect on gas permeation performance of the hollow fiber produced. The gas flux was reduced while gas pair selectivity increased dramatically as the air gap distance increase from 0 to 50 cm. As compared to the wet spinning membranes, membranes spun at 50 cm air gap showed considerable increase in gas pair selectivity. The selectivities, H₂/N₂ and CO₂/N₂ were increased by more than 100 times to 370 and 89 respectively. While for O₂/N₂ it was increased by 12 times to 13. The gas permeance performance of present POAn fiber was significantly improved as compared to PANi hollow fiber membranes that were previously developed in our group. The H₂ permeance was almost doubled to 10.7 GPU while CO₂ permeance was increased by 4 times to 2.5 GPU. This increase in permeance was associated with the simultaneous enhancement in gas pair selectivities. The H₂/N₂ and CO₂/N₂ selectivities were improved by 3 and 7 times respectively. Such an effect of increase in permeance with simultaneous increase in selectivity was attributed to the rigid and more open structure of POAn as compared to PANi. The POAn hollow fiber membranes also showed an improvement in their mechanical properties with increase in air gap due to induced molecular orientation.

References


Chapter 6

6. Stability analysis of polyaniline and its derivative base hollow fiber membranes

Abstract

The effect of natural aging process on the gas transport properties of polyaniline (PAni) and ring substituted derivative membranes was investigated due to the preliminary challenge to retain the gas separation performance of PAni hollow fiber membranes after certain period of time. FTIR analysis was conducted on the membranes in order to identify any possible molecular structure changes that might affect the mechanical properties of the membranes as well. The aging PAni membrane gas flux for all testing gases started to degrade significantly between 24 to 39% after 84 days and 64 to 80% after 196 days. Comparing the pristine fibers and the fibers aged for 196 days, the gas pair selectivities reduced from 10.4 to 6.4 for O$_2$/N$_2$, 13.9 to 10.9 for CO$_2$/N$_2$ and 109.2 to 58.9 for H$_2$/N$_2$. The FTIR spectra suggested that the aging membranes experienced noticeable physical crosslink and oxidation due to the broadening of the overall bands and the appearance of new peaks at $\sim$1680 cm$^{-1}$, respectively. This led to the reduction of the tensile strength by 40% and Young’s modulus by 53%. On contrary, the polyaniline derivative membranes showed more promising stability with all gas pair separation factors reduction of only 12 to 30% after 196 days with still considerably high values of 9.30 for O$_2$/N$_2$, 85.0 for CO$_2$/N$_2$ and 299.5 for H$_2$/N$_2$. The recorded FTIR spectra and mechanical properties of poly(o-anisidine) membranes were in agreement as the gas separation performance with very minimal changes. This study had shown that even without thermal assistance, the polyaniline membranes still could deteriorate when left aging in the ambient humid conditions with surrounded by laboratory equipment and activities.
6.1. Introduction

Generally, conducting polymers are air unstable but some studies have shown that most of the conducting polymers with aromatic ring like polypyrrole, polythiophene and the most studied polyaniline seem to be stable in air [1-3]. Most studies were focusing on the aging of electrical conductivity of the polymer powder or film at high temperatures. However, it is always a wonder, why did the study on the gas performance of pure polyaniline membranes do not flourish towards asymmetric membranes extensively.

The stability of the gas separation membranes is a crucial factor to ensure the credibility and durability of the membranes for a long period of time before any actual industrial applications. Numerous studies have been devoted to study the possible degradation of polyaniline powder and film due to artificial aging by thermal effect. However, instead of the gas permeation properties, all of these studies have been focusing on the relation of heating temperature and aging duration to sample conductivity, which is very useful for electrical conductor application [3-11]. Rannou et al. [4] proposed that the conductivity decay of PAni films developed was controlled by the defects formed during the thermal aging process of the films. These defects interrupted the conduction path along the chains that led to the decrease of ECP films conductivity and lifespan.

Conducting polymers possess interesting properties such as mechanical strength, electrical conductivity, corrosion stability with ease of synthesis by chemical and electrochemical that making them useful in wide area of applications including electrochemical sensors and capacitors, and in the last few years as protective coatings against corrosion, especially for mild steel [12-14]. Polyaniline and polypyrrole have been the strongest candidate for this purpose and have been studied for many years [12,15-18]. Besides the possible reaction between the oxidized electroactive conducting polymer (ECP) and the coated metal, Kinlen et al. [19] also proposed that ECP can also be oxidized by atmospheric or dissolved oxygen [14]. Considering the potential oxidation of ECP in atmospheric, the structure of the developed PAni and POAn membranes for this study were examined upon aging at room condition for more than 4700 hours.

In order to better understand the gas separation performance stability of the membranes produced in this study, the changes in molecular structure during aging period were
examined by FT-IR spectroscopy. Hobaica [20] reported that the synthesized polyaniline showed lack of variation in the FT-IR spectra suggesting the powder produced was not degrade even after 5 years. However, it is important to note that the sample was only exposed to dry air and kept in a desiccator filled with fresh anhydrous calcium sulfate throughout the aging period with vacuum for the first 120 hours. An oxygen-free atmosphere with high temperature crosslinking mechanism proposed that aromatization of quinoid ring occurred with simultaneous formation of free radicals as the C=N double bond break. These free radicals have the tendency to react with other free radicals of the adjacent chain forming the crosslinked polymer [5,21]. However, in the real conditions with presence of oxygen (air) around, it was suggested that carbonyl linkages were likely to develop as well due to the oxidation of polymer chain as identified by the appearance of IR peak at ~1680 cm\(^{-1}\) [5,22]. However, earlier study on PANi films showed another interesting finding where upon thermal aging, the carbonyl band around ~1675 cm\(^{-1}\) started to disappear due to the lost of carbonyl stretching of the solvent but a new peak around 1705 cm\(^{-1}\) emerged suggesting C=O was forming due to oxidation [9]. Although, many studies agreed that the PANi powder and film degraded rapidly upon heating, these various findings suggested that different samples could age very differently and highly influenced by the nature of the polymers synthesized, the constituent of the as cast films/modules and the surroundings as well as the parameters influencing the aging process.

Preliminary observation of the gas permeation analysis in this study showed that the gas fluxes of PANi hollow fiber membranes changed after few months and it was quite a challenge to obtain a repetitive gas separation performance from the same spinning batch even after 4 months. Even though PANi and its derivative membranes showed a promising gas separation performance, if long term stability is an issue, this might harm the opportunity for the commercialized application. Generally, the fresh PANi membranes possessed defects that potentially assisting the degradation process caused by the surrounding environment. Although, the defects on the PANi derivative membranes were not completely eliminated, the spinning solution was more homogeneous producing POAn membranes with improved gas separation performance and greater mechanical strength. In order to investigate the long term stability of polyaniline membranes, the gas permeations of both PANi and POAn aging membranes were recorded. FT-IR spectroscopy was conducted on the aging membranes to
understand of any possible molecular structure changes during the aging process that might contribute to the deterioration of the membrane gas separation performance. Then, effects of the molecular structure changes on the mechanical properties were examined to further verify the possible membranes deterioration occurred.

6.2. Experimental

6.2.1. Materials

Materials used for the synthesis of polyaniline and poly(o-anisidine) as well as solvents and gel inhibitor used for membrane fabrication are similar to those presented in Chapter 4 and Chapter 5, respectively. Chemicals for silicone coating solution and the pure gases utilized for measuring the gas fluxes through membrane gas permeation system are as listed in Chapter 3.

6.2.2. Synthesis of polyaniline and its derivative

Polyaniline and poly(o-anisidine) were synthesized in-house by oxidative polymerization of monomers aniline and anisidine, respectively. The polymerizations were conducted at sub-zero temperature (-15 °C) according to the method discussed in Chapter 3 (PAni) and Chapter 5 (POAn) to ensure high molecular weight polymers were synthesized.

6.2.3. Preparation of dope solution

Polyaniline and poly(o-anisidine) dope solutions were prepared for membrane dry-jet wet spinning process according to each critical concentration as previously determined in Chapter 3 and Chapter 5 to ensure significant chain entanglement of the polymer solutions.

6.2.4. Fabrication of hollow fiber membranes

The hollow fiber membranes of polyaniline and poly(o-anisidine) were fabricated by dry-jet wet spinning process according to the methods previously presented in Chapter 4 and Chapter 5, respectively. The length of air gap chosen for the spinning process for
both membranes was 50 cm since membranes that were previously spun at that LAG showed the most promising gas permeation performance.

6.2.5. Preparation of testing modules and gas permeation measurement

The pure gases permeation rates through polyaniline and poly(o-anisidine) hollow fiber membranes were measured by soap bubble method as previously presented in Chapter 3. The polyaniline and its derivative membranes were exposed to room temperature and conditions including the average relative humidity of ~73% successively for 196 days. All the membranes tested in this chapter were silicone coated prior to the gas permeation measurement and average permeance of at least 2 consistent modules was recorded. Every gas permeance and gas pair selectivity reported in this chapter was based on the replication strategy of data measurement that was described in detail in Section 3.2.9.

6.2.6. Infrared spectroscopy analysis of hollow fiber membranes

PAni and POAn hollow fiber membranes were examined by mean of FTIR to investigate the aging effect on the polymer molecular structure for the before aging ('pristine' fiber) and after aging process of 14 and 28 weeks. Detailed of the FTIR procedure was as described in Chapter 3.

6.2.7. Mechanical properties measurement

The mechanical strength of PAni and POAn hollow fiber membranes before and after aging were examined by mean of tensile testing. The test was conducted on the before aging ('pristine') fibers and fibers aged after 14 and 28 weeks and the detailed of the analysis procedure was as described in Chapter 4.

6.3. Results and discussions

6.3.1. Degradation study of polyaniline hollow fiber membrane

(a) Gas permeation analysis of the aging PAni membranes

Due to the preliminary observations when the membranes were retested after few months; most of the gas permeation rates of the PAni membranes changed dramatically.
Since PANi hollow fiber spun at 50 cm air gap exhibited the most promising gas separation performance among PANi membranes studied previously in Chapter 4, samples with the same fabrication conditions were prepared to investigate the aging behaviour.

Fig. 6.1 displays the gases permeabilities of polyaniline hollow fiber membranes as the membranes aged up to 28 weeks. The aging membranes were tested every other 28 days up to the 196th day. It can be seen as the membranes aged up to approximately ~1300 hours; the large gases permeabilities were quite plateau with only slight reduction of less than 10% as compared to the ‘pristine’ fibers. Nitrogen permeance reduced only by approximately 5.6% from 0.047 GPU while oxygen reduced by 7.1% from 0.488 GPU. As for the smaller gases, the reduction is slightly more significant with carbon dioxide and hydrogen permeance reduced by 18.1% and 31.0%, respectively. CO₂ permeability reduced from 0.65 to 0.53 GPU and H₂ reduced from 5.13 to 3.54 GPU. As expected, the reductions of gases permeabilities would affect the gas pair selectivity. After 56 days (Fig. 6.2), O₂/N₂ shows minor reductions from 10.4 to 10.1 (3.0%). As for CO₂/N₂, H₂/N₂ and H₂/CO₂, the selectivities were reduced from 13.4, 109.2 and 7.9 to 11.9, 78.7 and 6.6, respectively.

After 98 days, all the gases fluxes started to show substantial reduction of 35 to 55% resulting in decrease of separation factors of O₂/N₂, CO₂/N₂, H₂/N₂ and H₂/CO₂ to 8.0, 11.7, 76.1 and 6.5, respectively. By leaving the fibers to age further, all the gases permeabilities started to show more dramatic reduction. After ~4700 hours, the total permeabilities reductions for all gases of the aged membranes as compared to the ‘pristine’ membranes were in the range of 70-80% for O₂, CO₂ and H₂ and 50% reduction for nitrogen permeance. The permeabilities of nitrogen, oxygen, carbon dioxide and hydrogen were 0.024, 0.11, 0.19 and 1.00 GPU for PANi hollow fiber membranes aged after 28 weeks with reduced separation factors of O₂/N₂, CO₂/N₂, H₂/N₂ and H₂/CO₂ of 4.5, 7.7, 41.9 and 5.4, respectively.

Since it was quite difficult to find any publication discussing the gas permeation of the aging PANi films, thus, the understanding of the dramatic reduction of gas separation performance was compared to the reported sample conductivity behaviour. There have been numerous studies reported that polyaniline powder was stable in air [20,23].
presented in term of the conductivity of the conjugated polymer. However, Jousseaume et al. [3] stressed that PANi stability could differ depending on many factors including the molecular structure due to the polymer dopant and the morphology of the produced samples. Their study showed that even though most samples were generally stable after 500 days at room temperature, PANi-HCl (different hydrogen halide dopant) showed significant reduction of conductivity of ~20% less than 100 days. This implied that the polymer had started to degrade at that point and the reduction was more severe after 500 days [3].

In this study, the gases permeation data (Fig. 6.1 and Fig. 6.2) showed similar declining trend (as conductivity in previous studies [3,4,6,24,25]) for the aging PANi membranes by time with the final permeability and selectivity suffering reductions upto 80% and 60%, respectively. Even though, there was no earlier ratify explanation on the reduction of gas permeation phenomena, it was predicted that any of the following processes probably happened as the fibers were exposed to the room conditions for a long time, that are; (1) oxidation, hydrolysis or chain scission of the polymer chains especially on the outer surface of the membranes due to long term exposure to air and strong humidity of the area, and (2) interchain cross-linking of polymer backbone [3-5,14,22]. These two processes were proposed as chemical modifications promoted by thermal condition.

Although, PANi hollow fibers in this study were not directly heated, it was suggested that being exposed to the chemically and thermally harsh laboratory environment with furnaces, ovens and various heating equipment around, just like one of Jousseaume et al. samples [3] degraded at room condition, would most probably catalyzed the ageing process and possibly the logical explanation for now. Besides, this is probably the reason why the degradation rate was slower than previous studies that were usually only taken hours to see significant degradation [3,4,6,25] and only more significant as the fibers aging for a longer time (upto 196 days). To verify if any of the processes did occur, further investigation were conducted on the molecular structure of the aged membranes by means of FTIR.
Fig. 6.1 Gases (N₂, O₂, CO₂ and H₂) fluxes of PANi hollow fiber membranes aged up to 28 weeks in air at room conditions.
Fig. 6.2 Gas pair selectivity of polyaniline hollow fiber membranes (LAG = 50 cm) aged up to 28 weeks in air at room temperature.

(b) FTIR analysis of the aging PANi membranes

The significant decrease in the gas separation is predicted to be caused by corresponding changes in the polymer molecular structure. Thus, FTIR analysis was conducted to assist in describing the possible changes and the resulting spectra are presented in Fig. 6.3 (A-B). Fig. 6.3 (A) shows all the predicted characteristic peaks for pristine and aging PANi fibers including the five major vibrational bands at approximately 1600, 1490, 1290, 1170 and 830 cm\(^{-1}\). In addition, peaks between 3400-3500 cm\(^{-1}\) can also be observed representing N-H stretch. The detailed descriptions on the major characteristic bands for polyaniline molecular structure were previously discussed in Chapter 3.
Fig. 6.3 FTIR analysis of PAni hollow fiber membranes aging in air at room conditions upto 196 days (A) overall spectra and (B) spectra of wavenumber 1000-2000 cm$^{-1}$. 
Fig. 6.3 (A) shows pronounced spectral changes between the fresh fibers and fibers aging up to 196 days. As compared to spectra (a), spectra (b) and (c) show three distinctive spectral changes that implied the fibers experienced three possible aging processes especially between 98 to 196 days. The first major observation is the significant decrease of the infrared bands intensity as clearly shown in Fig. 6.3 (B), in particular the infrared bands associated with quinoid rings (1600, 1370 and 1290 cm$^{-1}$), aromatic structure at 1490 cm$^{-1}$ and tertiary amines stretch at 1240 cm$^{-1}$. The broadening of the peaks was probably due to chain entanglement or chain bonding as previously discussed by Scherr et al. [5,9,21]. Although there was no certain evidence given, they suggested that the physical chain bonding occurred as the nitrogen formed bridges between quinoid-imines.

Another striking observation in Fig. 6.3 (A) is the appearance of broad peak at ~3610 cm$^{-1}$ only after 28 weeks of aging. This band can be associated with O-H stretching [9] that was probably best explained due to the capture of water vapour from the surrounding humidity. There is also a small yet noticeable increase of intensity for the peak around 1680 cm$^{-1}$ as the aging process reached the 196th day. This could be attributed by minor oxidation of the sample that led to the formation of carbonyl groups (quinoid-imine stretching mode). Upon exposure to oxygen (even O$_2$ in ambient air), it was suggested that the PANi surface would allow the effective adsorption of oxygen to the specific sites with strong interaction with mobile polarons [25,26]. Genoud et al. proved this with the fast increase of normalized weight uptake of the PANi sample due to the adsorption as well as the broadening of electron-spin-resonance (ESR) linewidth indicating that oxygen had reached sites with conducting grain surface [25], thus, leading to the decay of PANi sample.

As mentioned earlier, since there was no direct heating of the fibers and only due to the surrounding and laboratory condition influences, the most significant changes only could be seen after 196 days rather than 98 days since the aging process rate was generally slow. It was also suggested that the existing chain defects as well as impurities [9] and contaminants (from the laboratory environment) might be responsible for the physical chain crosslinking and membranes degradation to happen. Hence, it was expected that the mechanical properties of the hollow fibers would suffer as well. In
order to verify this, the tensile test was conducted on the aging PANi membranes and will be further discussed later.

**(c) Mechanical properties study on the aging PANi membranes**

Since polyaniline hollow fiber FT-IR spectra suggested that the fibers possibly experienced physical chain crosslinking that cause physical deterioration, tensile test was conducted on the PANi membranes after the 14\textsuperscript{th} and 28\textsuperscript{th} week of the aging period. Effect of the aging time on the PANi hollow fiber membranes mechanical properties is presented in Fig. 6.4.

As predicted in the previous section, generally, the longer the fibers aged, all the mechanical properties (tensile stress, Young’s modulus and elongation at break) showed noticeable reduction. As the fibers aged upto 14 weeks, tensile strength at break showed minor decrease of 4.8% as compared to the ‘pristine fibers’ from 4.39 to 4.18 MPa and Young's modulus of these fibers degraded by only 15.1% reducing the values to 114.69 MPa. The elongation of the fibers also decreased a little by 4.8% from 11.44 to 10.89% after 98 days. However, as the fibers aged further (over 28 weeks), a more significant reduction on the mechanical properties can be observed as in Fig. 6.4 (A) for tensile stress and Young’s modulus and Fig. 6.4 (B) for fibers elongation percentile. After the 196\textsuperscript{th} day, the tensile stress at break and Young’s modulus of the PANi membranes reduced considerably by 40.1% to 2.63 MPa and 52.7% to 63.94 MPa, respectively. Simultaneously, PANi membrane elongation at break reduced to 9.80%. The recorded mechanical properties had verified the researcher’s observations that the aged fibers had lost the elasticity (reduced in elongation) and more brittle with easier to break upon slight bending. Consequently, the handling of the fibers to form modules became more challenging.

As previously shown by FTIR analysis, the mechanical analysis of aging PANi hollow fibers portrayed similar degradation behaviour. The deterioration of PANi membrane mechanical strength recorded was more prominent after the 28\textsuperscript{th} week than the 14\textsuperscript{th} week. This further supported the suggested explanation that the fibers in this study aged very slowly since there was no assisted heating like most studies conducted by earlier researchers [3,4,20,25], for example Genoud et al. [25] samples degraded after heating.
24 hours at 135°C and Jousseaume et al. [3] reported that the conductivity of the films started to decay even upon heating as low as 100°C for approximately 2 days and the degradation was more significant with higher heating temperature for less than a day.

**Fig. 6.4** Mechanical properties profiles of PAni hollow fiber membranes aging upto 196 days: (A) tensile at break and Young's Modulus, and (B) elongation at break.
6.3.2. Degradation study of poly(ortho-anisidine) hollow fiber membrane

(a) Gas permeation analysis of the aging POAn membranes

The introduction of methoxy group on the ortho position of polyaniline had shown to improve PANi processability as presented in Chapter 5. In addition, a more rigid polymer chain backbone was developed that inhibit chain mobility with increase free volume. Thus, hollow fiber membranes with improved gas permeation properties were developed. However, as the PANi membranes, it was crucial to investigate the stability of the PANi derivative membranes for real condition long term application.

Fig. 6.5 and Fig. 6.6 display the gases permeabilities of poly(ortho-anisidine) hollow fiber membranes as the membranes aged upto 196 days. The aging membranes were tested every other 4 weeks upto 28 weeks. Generally, all gases permeabilities and gas pairs selectivities showed consistent values throughout the testing period with ‘fresh’ POAn hollow fiber membranes fluxes of 0.027 GPU for nitrogen, 0.364 GPU for oxygen, 2.572 GPU for carbon dioxide and 10.273 GPU for hydrogen and selectivites of 13.44 (O\(_2\)/N\(_2\)), 96.28 (CO\(_2\)/N\(_2\)), 379.69 (H\(_2\)/N\(_2\)) and 4.02 (H\(_2\)/CO\(_2\)). Although there were fluctuations in the permeabilities, even after 3360 hours, the difference to the ‘pristine’ POAn membranes was less than 10.6% with standard deviations of 0.001, 0.013, 0.104 and 0.345 GPU for N\(_2\), O\(_2\), CO\(_2\) and H\(_2\), respectively.

There were slight yet more noticeable dropped of permeabilities can be observed after 168 days. However, the minor reductions did not harm the selectivities severely. O\(_2\)/N\(_2\), CO\(_2\)/N\(_2\), H\(_2\)/N\(_2\) and H\(_2\)/CO\(_2\) reduced between 3.0 to 17.3% producing aged POAn membranes with selectivities of 11.1, 87.2, 339.8 and 3.9, respectively. These selectivities were still considerably high and showed that POAn membranes were still stable even after aging for 24 weeks at room conditions. By leaving the fibers to age further, after 28 weeks, all the gases fluxes showed more substantial reduction of 21 to 45% resulting in decrease of separation factors of O\(_2\)/N\(_2\), CO\(_2\)/N\(_2\), H\(_2\)/N\(_2\) and H\(_2\)/CO\(_2\) to 9.3, 85.0, 299.5 and 3.6, respectively. Even with the gas flux reduction as much as 45% and gas pair selectivity reduction upto 31%, the overall gas separation performance of poly(o-anisidine) hollow fiber membranes after 196 days could be considered appreciably high and stable.
Fig. 6.5 Gases ($N_2$, $O_2$, $CO_2$ and $H_2$) fluxes of POAN hollow fiber membranes aged up to 28 weeks in air at room conditions.
Fig. 6.6 Gas pair selectivity of polyaniline hollow fiber membranes (LAG = 50 cm) aged up to 28 weeks in air at room temperature.

From the collected permeation data, by comparing the polyaniline hollow fiber membranes to ring substituted PANi membranes, poly(o-anisidine) hollow fibers appeared to be more stable when aging for 28 weeks in the laboratory condition with high humidity and surrounded by heating equipment as well as dust. However, it was suggested that POAn hollow fiber membranes was less affected and more stable when aging at room condition due to the fact that the ‘pristine’ fibers had less defects to start with as compared to PANi membranes. This was due to the formation of a more desirable consistent fiber from a more homogeneous dope solution since POAn powder was proven to be more soluble. In addition, the rigidity of the backbone chain probably reduced the tendency for the membranes to physically crosslink or oxidized without the high temperature heating assistance. In order to verify this claim, FTIR was conducted on the membranes half way of the testing period (the 14th weeks) and after 196 days.
(b) **FTIR analysis of the aging POAn membrane**

Since the gas separation performance for poly(o-anisidine) hollow fiber membranes proven to stable throughout the aging time and only minor reduction after 28 weeks, it was predicted that the harsh laboratory environment did not severely alter the chemical structure of the membranes. In order to ensure this hypothesis, FT-IR analysis was conducted on the POAn membranes and the resulting spectra are presented in Fig. 6.7 (A-B). Fig. 6.7 (A) displays all the characteristics peaks for the pristine and aging POAn membranes including peaks at approximately ~1250 and ~1025 cm\(^{-1}\) attribute to C-O-C asymmetric and symmetric stretching of the alkyl aryl ether linkage, respectively. The detail descriptions on the major characteristic bands for POAn molecular structure were previously discussed in Chapter 5.

Generally, there are no striking spectral changes between the fresh fibers and fibers aging upto 98 and 196 days as in Fig. 6.7 (A). Spectra (a) and (b) that represent POAn pristine fibers and fibers aging after 98 days, respectively, show almost identical spectra with almost the same peaks intensities throughout the wavenumber 4000 to 600 cm\(^{-1}\). This implied that even if there was physical crosslinking occur, it was probably very minimal and did not affect the peaks intensities prominently. However, as the POAn membranes aged upto 196 days, the spectrum broadened slightly that implied the fibers experienced possible crosslinking at a very slow rate that might reduce the membrane free volume. This is in agreement with the gas permeation data presented earlier that all the gases fluxes showed more prominent decrease only after the 24\(^{th}\) weeks.

However, there are noticeable peaks appearing at wavenumber of approximately ~3600 cm\(^{-1}\) for the aging POAn fibers with increase intensities of the bands as the fibers aged upto 196 days. Since the fibers endured the ambient humidity, this band is best represented by O-H stretch due to the water vapour trapped by the membranes [9], thus, as the membranes aged longer, the peaks became more obvious. Although, it is not that visible in Fig. 6.7 (A), Fig. 6.7 (B) shows a very small peak exist at around ~1700 cm\(^{-1}\) for the fibers aging for 28 weeks. As the pure polyaniline membranes, its derivative membranes in this study may also experienced minor oxidation.
Fig. 6.7 FTIR analysis of POAn hollow fiber membranes aging in air at room conditions up to 196 days (A) overall spectra and (B) spectra of wavenumber 1000-2000 cm$^{-1}$. 
Overall, Fig. 6.7 exhibit that the aging poly(o-anisidine) membranes upto 196 days had very minimal spectral changes, indicating the POAn membranes developed were relatively more stable. This is in agreement with the membrane gas separation performance previously discussed. Since the aging process of membranes in this study was only influenced by the laboratory condition and humidity as well as the surrounding activity and equipment with no assistance by any direct heating, the fibers aged at a very low rate. Hence, the spectral changes can only be seen after 28 weeks. Since generally, the FT-IR spectra and gas separation performance of aging POAn hollow fiber membranes in the current study did not exhibit any major degradation, it was expected that the mechanical properties of the membranes would be stable to. Thus, in the next section data calculated from tensile test analysis will be discussed.

(c) Mechanical properties study on the aging POAn membrane

Gas separation properties and FT-IR analysis demonstrated that POAn hollow fiber membranes were considerably stable upon aging for 28 weeks. In order to further corroborate the POAn membranes stability, the fiber mechanical strength was examined by mean on tensile test. Fig. 6.8 illustrates the calculated ultimate tensile strength (UTS), Young’s modulus and elongation at break of the ‘pristine’ fiber as well as POAn membranes aging for 98 and 196 days.

From Fig. 6.8, UTS, Young’s modulus and elongation at break of the fresh poly(o-anisidine) membranes was found to be 13.53 MPa, 447.89 MPa and 14.1%, respectively. As the membranes aged up to 98 days, the membrane mechanical properties showed consistent values as the ‘pristine’ fibers. However, there were slight reductions in the increasing aging time of the membranes. After the 28th week, the tensile stress at break and Young’s modulus of the POAn membranes decreased by only 15.4% to 11.45 MPa and 13.2% to 388.59 MPa, respectively. Simultaneously, POAn membranes elongation at break reduced to 12.1%. These results were in agreement to the FT-IR spectra that justified the POAn membranes were considerably stable in ambient conditions.
Fig. 6.8 Mechanical properties profiles of POAn hollow fiber membranes aging upto 196 days: (A) tensile at break and Young's Modulus, and (B) elongation at break.
6.4. Conclusions

The current study demonstrated that the characteristic parameters of polyaniline hollow fiber membranes slowly changed with increasing aging time. It has been shown that the permeation rates of nitrogen, oxygen, carbon dioxide and hydrogen were significantly reduced from 0.047 to 0.017 GPU, 0.488 to 0.108 GPU, 0.652 to 0.185 GPU and 5.133 to 1.002 GPU, respectively, as the polyaniline membranes aged for 196 days. The degradation of PAni membranes gas separation properties were predicted due to the change in the molecular structures caused majorly by oxidation and physical chain crosslinking. FT-IR spectra of the aging fibers as compared to the pristine fibers had proven these occurrences with the appearance of new band at ~1680 cm\(^{-1}\) and substantial decrease in the intensity of all adsorption bands. Consequently, the mechanical properties of aging PAni membranes were proven to deteriorate significantly with tensile strength decreased by 40.1% and Young’s modulus reduced by 52.7% as compared to the pristine PAni fibers. Since the aging process was solely influenced by the room conditions and humidity as well as laboratory surroundings with no direct heating of samples involved, POAn membranes slowly showed indication of any degradation only after 196 days. Although, there were slight reductions on the gas pair selectivities of aging POAn membranes (196 days), the values were still considerably high with O\(_2\)/N\(_2\), CO\(_2\)/N\(_2\), H\(_2\)/N\(_2\) and H\(_2\)/CO\(_2\) of 9.30, 85.03, 299.54 and 3.55, respectively. The recorded FT-IR spectra and mechanical properties of these aging modified PAni membranes further justified the stability of POAn membranes with very minimal changes only after aging for 28 weeks. Therefore, the current study showed that polyaniline derivative membranes were proven to be more stable than PAni membranes.

References


Chapter 7

7. Conclusions and future work recommendations

7.1. Conclusions

Due to the demand for more efficient, environmental friendly and economical separation technology, gas separation membrane has become a favourable alternative over the gas separation conventional methods. In order to cater for wide range of applications including oxygen enrichment system and carbon dioxide removal, many studies have been focusing in finding a new suitable membrane material that produces membranes with desirable gas separation performance. Polyaniline has been chosen as the material for this study due to the remarkable findings on the gas separation properties by previous researchers and other various advantages it offered. Hollow fiber module has been developed for this work since it has high area packing density that is desirable for industrial application. The polymer was synthesized in-house to ensure a fresh powder was used every time for dope solution making. Polyaniline hollow fibers were successfully fabricated with the assistance of co-solvent in the dope solution. The membranes demonstrated a respectable gas separation performance indicating that the produced fibers were well orientated due to the spin-line stresses especially at high air gap. Induced molecular orientation also resulted in improvement in mechanical properties of the hollow fiber membrane. Despite to the fact that gel inhibitor assisted the polymer solubility; the dope solution was heterogeneous resulting in the defects on the membrane skin surface which required silicone coatings prior to gas permeation measurement. Alternatively, a more soluble ring substituted polyaniline was synthesized. The produced poly(o-anisidine) was proven to be more soluble in many solvents. However, in order to prepare a highly viscous dope solution for spinning process, gel inhibitor was still required and improved dope solution homogeneity was
formed as compared to PANi solution. Due the rigidity of the polymer chain backbone of POAn, the fabricated fibers possessed high free volume that enhanced the gas separation performance with improved mechanical properties.

The following section presents a concise summary, which expand in Chapter 3 to Chapter 6.

Chapter 3 - Polyaniline synthesis and hollow fiber membrane fabrication

In order to ensure fresh polyaniline was used as membrane material in this study, PANi was synthesized with the established ‘in-house’ synthesis facility. Since gas separation membranes require a high chain entanglement polymer solution, polymer molecular weight is an important factor. The polymerization temperature was varied between 15 to -15 °C in order to alter the polymer molecular weight. It is important to note it was difficult to control the polydispersity of the produced polymer although the molecular weight can be controlled by the synthesized temperature. An average polydispersity of 6.1 for PANi synthesized at -15 °C indicated that the polymer produced had a quite large molecular weight distribution. Thus, the low molecular weight polymer that was incorporated in the batch had the tendency to wash out during coagulation stage of spinning. This was predicted to contribute to the formation of defects on the membrane surface in addition to the agglomerates that were present in the dope solution. To overcome this problem, the synthesized PANi should be thoroughly washed with acetone to remove the low molecular weight oligomers.

The formation of gas separation membranes required a highly viscous dope solution with a high molecular weight polymer of concentration preferably higher than 15%. Hence, the addition of gel inhibitor was necessary in this study as the PANi solution started to gel at concentration of more than 1% and it would gel instantaneously at concentration of more than 6%. However, the use of the diamines would degrade the polymer over time, thus, limiting the time frame for PANi membrane fabrication from the moment the inhibitor was added. Thus, 4MP was chosen since it has been proven that the degradation rate was slow, which allowed adequate time for the hollow fiber to be spun (approximately 24 hours).
As previously discussed, the defects formation on the surface of the fabricated PANi hollow fiber membranes were unavoidable. Thus, the prepared testing modules were silicone coated prior to gas permeation measurement.

This initial gas separation measurement showed that a common trade-off trend among polymeric membranes with gas flux decreased significantly while the selectivity increased with increasing length of air gap for the membrane prepared from PANi synthesized at 0 °C. The membrane gas separation performance was enhanced as a higher dope solution viscosity was prepared using high Mw PANi. However, since the membrane formation can be influenced by numerous factors, it is predicted that the preliminary measurement on the recorded gas permeation performance was slightly unattractive. In other points, minor adjustments on the dope solution viscosity and varying spinning length of air gap showed an improvement on the membrane development in term of morphology and gas separation properties that provided a kick-start on the production of high gas separation PANi membranes.

Chapter 4 - Polyaniline hollow fiber membrane for gas separation

As previously mentioned, dope solution formulation is a key factor in the morphological formation of the membranes. Solvent evaporation and polymer coagulation rate are among the crucial parameters controlling the formation of defect-free skin layer. Since membranes with possibly defect-free skin layer is highly desirable for gas separation process, one of the important factors considered for this study was the addition of volatile solvent in the dope solution. Highly volatile tetrahydrofuran (THF) was selected for this study. Since polyaniline was found to be mildly soluble in THF, it was necessary to retain the use of N-methyl-2-pyrrolidone (NMP) as the co-solvent to ensure the solubility of PANi in the dope solution. Solvent ratio of 1:1 (NMP/THF) was used throughout the study since the higher ratio did not promote the formation of skin layer and lower solvent ratio was not possible as the prepared dope solution gelled after few hours. The dope solution was prepared using the critical concentration determined prior to spinning process.

Since most of the volatile solvent was expected to be removed during the dry stage of the spinning, the air gap distance (LAG) was varied from 2.5 to 50 cm to optimize the
skin layer formation. The morphology of membrane prepared at low air gap displayed that the membrane was porous and the length of the finger-like structure was longer resulting in the membranes with a high flux yet the separation factor for all gas pairs suffered significantly. As the air gap increased to 50 cm, the membrane SEM micrograph showed that the developed fibers skin layer thickness improved by 9-fold. The thicker skin layer was proven to assist on improving the gas separation factor tremendously resulting in the membrane with promising gas separation properties of \( \text{H}_2/\text{N}_2 \) (105.6), \( \text{O}_2/\text{N}_2 \) (10.2), \( \text{CO}_2/\text{N}_2 \) (13.3) and \( \text{H}_2/\text{CO}_2 \) (7.9). Since long air gap allowed a better rearrangement of the polymer packing and improved the polymer molecular orientation, the membranes mechanical properties increased. Although, the gas permeation showed to be higher or comparable to the previous research on flat sheet, it was still considerably low as compared to other polymeric membrane probably due to the thick skin layer of over 1 µm. Due to the low gases fluxes with less than 1 GPU for nitrogen, oxygen and carbon dioxide, there was a possibility of parallax or handling errors during the bubble soap measurement. Thus, a more sensitive pressure drop system was set up to verify the collected readings. This system has been tested to be an important tool to verify the measurement of gas permeation throughout this research.

Besides having low gas permeation rates, other important issue that needed to be addressed for the current task was the challenge in producing a completely homogeneous dope solution. The prepared dope was always had visible agglomerates or undissolved particles. To vacuum filter the solution prior to spinning was not a smart decision since almost 50 % of the viscous solution was lost during the process. Thus, a Swagelok in-line filter (40 micron pore size) was installed prior to the spinneret. A smaller available pore size filter (15 micron) was tried before but the PAni particles clogged the mesh very quickly causing back flushed and consequently, stopped the hollow fiber spinning pump. The gas separation factors implied that a higher concentration solution was required in order to be improved but the current PAni dissolving property making it difficult. Hence, an enhanced soluble polyaniline must be synthesized to ensure that the solution was more homogeneous and possibly increased the polymer concentration of the dope solution.
Chapter 5 - Gas transport properties investigation on ring substituted polyaniline hollow fiber membranes

Since suppressing the formation of agglomerated PANi particles in the dope solution was a predicament, a more soluble polyaniline substitute was polymerized. Methoxy group was introduced onto aniline at the **ortho** position of the aromatic rings and the substituted anilines were used as the monomer for the reaction with the similar procedure as in Chapter 2 for 4.5 days. Although the produced poly(o-anisidine) (POAn) appeared to be more soluble than PANi, the polymer solution started to gel after an hour when the concentration exceeded ~8 wt%. Thus, 4MP was added in order to prepare higher dope solution concentration. The prepared dope solution had very minimal visible undissolved particles and the prepared solution was seen to be more homogenous. Nevertheless, in order to minimize the possible defects formation on the skin layer, similar in-line filter was utilized during POAn hollow fiber spinning process.

The addition of the side group to the backbone of the polymer chain was proven not only enhanced the solubility in solvents but also improved the gas permeation properties of the membranes. The bulky methoxy group was expected to alter the stiffness of chain backbone and the torsional angle between successive aromatic rings and inter-chain distances, which modified the gas permeation rate ultimately. Generally, changes in the chain mobility or the free volume of a polymer will affect the diffusion rate of larger gases more than smaller gases. However, in this study, the permeation rates for both large and small gases were affected significantly but in a different manner. With a higher specific free volume, the smaller gases (H\textsubscript{2} and CO\textsubscript{2}) permeation rates showed remarkable improvement. On the other hand, the larger gases permeations (O\textsubscript{2} and N\textsubscript{2}) were predicted to be highly influenced by the formation intra- and inter-chain hydrogen bonding in POAn that increased the polymer backbone rigidity and this almost negated the influence of the larger free volume that led to the slight decrease of nitrogen and oxygen fluxes. Consequently, as compared to the PANi membranes (Chapter 4), POAn membranes spun at 50 cm air gap showed a drastic improvement on the ideal separation factors for all gas pairs with H\textsubscript{2}/N\textsubscript{2} by over 3 times from 106 (PAni), CO\textsubscript{2}/N\textsubscript{2} by 7 times from 13 (PAni) and even O\textsubscript{2}/N\textsubscript{2} improved by 30% from 10 (PAni) to 13 (POAn).
Chapter 6 - Stability analysis of polyaniline and its derivative base hollow fiber membranes

Although it has been claimed that polyaniline is stable in air, an intriguing phenomenon was encountered when PAni membranes of a same batch showed different gas separation performance when retested after few months especially those fibers that was not kept in a vacuum desiccator. In order to make the membrane desirable for real commercial applications, it should be able to withstand harsh industrial environment for a long period. Thus, both polyaniline and its derivative membranes were exposed to the ambient laboratory condition with a high humidity and possible chemical as well as thermal influences from the laboratory activities and heating equipment around with exposure to room light and sunlight during the day and possible darkness at night.

The gas separation performance of PAni membranes showed a promising consistent performance for the first 8 weeks and only slight decrease towards the 16th weeks. However, when the PAni membranes were aged longer, the depreciation of gas separation factor for all gas pairs was very alarming due to the pronounced decrease of the gas permeation rates. The degradation of membranes was probably best explained due to the change in molecular structure caused by oxidation and physical chain crosslinking. FTIR spectra had concurred that PAni membranes experienced the recommended reactions when aging for 196 days. Although there was no direct heating of the fibers involved, it was suggested that being exposed to oxygen in air on continuous basis and the possible continuous heat from room lights and the surrounding heating equipment might promote those reactions to occur. Consequently, the mechanical properties of PAni membranes had also showed a drastic decrease. On the other hand, POAn membranes perceived to be more stable throughout the aging time and the gas separation performance only had a slight reduction with very minimal changes on the molecular structures and mechanical properties after 196 days. As compared to polyaniline membranes, PAni derivative membranes were proven to be more stable even though was not kept in any control or vacuum condition for 28 weeks. This discovery offered a very promising platform for further investigation on poly(o-anisidine) as a membrane material for gas separation towards commercial applications.
7.2. Future work recommendations

Even though polyaniline membranes in this study showed a very significant degradation, it is important to note that the developed ‘pristine’ fiber skin layer possessed defects to start with and that may contribute to the acceleration of the aging process as compared to POAn membranes. Thus, it is important to further examine other factors that influence membrane formation for both PAni and POAn in order to develop a defect-free gas separation membrane. In addition, the potential of PAni and its derivative hollow fiber membranes for practical application should be investigated. Followings are the recommendations for future works in order to further exploit polyaniline as gas separation membrane material.

(a) Investigation of membrane rheologically induced molecular orientation

An understanding of the effect of fluid rheological behaviour within the spinneret on gas separation hollow fiber membrane formation is essential for a large-scale hollow fiber production. There are probably two dominant mechanisms to induce molecular orientation during the phase inversion of the fiber formation. One is due to elongation stresses (mostly outside the spinneret) because of the gravity and spin line stresses, while the other is due to the shear stress within the spinneret. Many polymer solution are normally exhibited a shear thinning tendency, suggesting a progressive alignment of polymer molecules under shear in flow directions. Shear-induced oriented structures of the fabricated membranes are expected to affect morphology and molecular orientation, hence, the physical properties of the final product. Ultimately it is predicted that the gas pair selectivity will improve. Thus, it is worth to explore this factor in order to improve the current produced membrane. FTIR spectroscopy is a crucial tool to assess the molecular orientation in the active layer of dry-jet-wet spun hollow fibers. Then, the morphology and structure of the produced membrane will be observed with SEM to further support the morphology of the formed membranes.

(b) Screening and developing doping techniques suitable for gas separation hollow fiber membrane

The most common acid doping technique is by immersing the membrane in acid bath. This method is proven to be effective and simple in optimizing the gas separation
performance of PANi membrane. The common doping method involves the acid dopant and base dedoped solution. The membrane usually will be immersed in acid solutions for a certain period of time to yield total doped fiber. Then, it will be undoped with base solution to remove the acid counterion in the membranes. Those membranes are then redoped in the similar acid solution with a lower molarity.

Another available doping technique is by gradually adding a high concentrated acid into the dope solution. It is claimed that by doping the dope solution prior the membrane fabrication, the expansion of the membrane free volume is more stable for a longer period of time and the doping occurs more completely. However, since it is never been done on gas separation membrane, there is a risk of over-expanding the free volume. Thus, this may compromise the gas separation performance of the membrane.

Besides the gas permeation measurement, the effectiveness of both doping methods will only be known by conductivity test that may show the presence/absence of acids in the membrane. Four Probe Method can be employed for measuring conductivity. Doped PANi should have detectable conductivity and the success of dedoping will be known from the decrease or lack of the conductivity. In addition, to elucidate any structural changes in the membrane after doping treatment, WAXD will be performed in order to study the intersegmental distance of the polymeric molecules.

\[(c)\] Determining suitable dopants and optimizing doping condition

A wide range of halide acids (HF, HCl, HBr, or HI) and polymer acids can be chosen to optimize the membrane performance and durability. Although a high molecular weight acid is always favourable for membranes doping, it is important to study the possibility of different effect on hollow fiber membrane. Besides, some acid tend to dope only the surface/skin layer of the membrane rather than the overall structure since the molecules can be too big to diffuse into the membrane. Consequently, the permeability may reduce extremely even though the selectivity may improve. Thus, a proper selection of acid dopant is important in optimizing the membrane performance.

Besides the choice of acid, the doping concentration, period of immersion and number of doping cycles can be investigated as well to determine the possibility of improving
the gas separation performance. Optimizing the doping immersing stage is crucial because in some cases, when the doping ratio and immersing time exceed the optimum value, it might deteriorate the membrane full potential.

FTIR spectroscopy is a great characterization tool to investigate the existence and intensity of each ion in the doped membrane sample. UV spectrophotometer can justify the degree of doping by comparing the UV-visible-near-infrared spectrum. The absorbance peak can further determine if there is a significant structural difference on the membrane.

**(d) Examining the membrane gas separation performance for practical applications**

PAni membranes were developed in this study for gas separation applications. Unfortunately, the present work had been limited to 4 gases only (H₂, CO₂, O₂ and N₂) and it would be very interesting to investigate the gas permeation with wider selection of pure gases (*i.e* He and CH₄) in order to broaden the gas separation potential application in future. In addition, the gas permeation properties of the asymmetric membrane obtained by using pure gases should be verified with gas mixture permeation testing because various other factors could possibly alter the mixed-gas separation results from those tested with pure gases. Long term continuous air separation testing should be conducted on the developed hollow fiber membranes in order to examine the stability of the gas separation performance while determining extraneous effects such as operating pressure, humidity and aging on membrane properties in order to justify the applicability of asymmetric membrane in actual application. Since polyaniline is claimed to be thermally stable, it is worth to further evaluate the gas separation performance of the established PAni membranes at high temperature and ultimately integrating the membranes in membrane reactor system that involved relatively high operational temperature.