Development of novel hydrophobic hollow fiber membranes intended for gas-liquid membrane contactor application

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**DEVELOPMENT OF NOVEL HYDROPHOBIC HOLLOW
FIBER MEMBRANES INTENDED FOR GAS-LIQUID
MEMBRANE CONTACTOR APPLICATION**

ZHANG YUAN

**SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
2013**

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MEMBRANE CONTACTOR APPLICATION**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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- [1] **Y. Zhang**, R. Wang, S. Yi, L. Setiawan, X. Hu, A.G. Fane, Novel chemical surface modification to enhance hydrophobicity of poly(amide-imide) (PAI) hollow fiber membranes, *Journal of Membrane Science*, 380 (2011) 241-250.
- [2] **Y. Zhang**, R. Wang, L. Zhang, A.G. Fane, Novel single-step hydrophobic modification of polymeric hollow fiber membranes containing imide groups: Its potential for membrane contactor application, *Separation and Purification Technology*, 101 (2012) 76-84.
- [3] **Y. Zhang**, J. Sunarso, S. Liu, R. Wang, Current status and development of membranes for CO₂/CH₄ separation: A review, *International Journal of Greenhouse Gas Control*, 12 (2013) 84-107.
- [4] **Y. Zhang**, R. Wang, Gas-Liquid Membrane Contactors: Recent Advances and Future Challenges, *Current Opinion in Chemical Engineering*, 2 (2013) 255-262.
- [5] **Y. Zhang**, R. Wang, Fabrication of novel polyetherimide-fluorinated silica organic-inorganic composite hollow fiber membranes intended for membrane contactor application, *Journal of Membrane Science*, 443 (2013) 170-180.
- [6] **Y. Zhang**, R. Wang, Novel method for incorporating hydrophobic silica nanoparticles on polyetherimide (PEI) hollow fiber membranes for CO₂ absorption in gas-liquid membrane contactor, *Journal of Membrane Science*, (2013), in press.

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[1] **Y. Zhang**, R. Wang, S.L. Yi, L. Setiawan, X. Hu, A.G. Fane, Novel chemical surface modification to enhance hydrophobicity of poly(amide-imide) (PAI) hollow fiber membranes intended for the use in gas-liquid membrane contactor, International Congress on Membranes and Membrane Processes, Amsterdam, Netherland, 23-29 July 2011 (Oral presentation).

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LIST OF SYMBOLS

Nomenclature

A	Gas-liquid contact area (m^2)
$C_{g,in}$	CO_2 concentration in gas phase at inlet (mol/m^3)
$C_{g,out}$	CO_2 concentration in gas phase at outlet (mol/m^3)
$\Delta C_{l,m}$	Logarithmic mean driving force based on liquid phase concentration (mol/m^3)
$C_{b,out}$	CO_2 concentration in liquid phase at outlet (mol/m^3)
$C_{l,in}$	CO_2 concentration in liquid phase at inlet (mol/m^3)
d_i	Inner diameter of the membrane (m)
d_{ln}	Logarithmic mean diameters of the membrane (m)
d_{max}	Maximum pore diameter (m)
d_o	Outer diameter of the membrane (m)
D	Density (g/cm^3)
$D_{g,eff}$	Effective diffusion coefficient of gas in the gas-filled pores (m^2/s)
$D_{g,m}$	Bulk diffusion coefficient of gas (m^2/s)
$D_{g,kn}$	Knudsen diffusion coefficient of gas (m^2/s)
D_l	Diffusion coefficient of the gas in the liquid-filled pores (m^2/s)
H	Henry's constant, 0.831
k_g	Gas mass transfer coefficient (m/s)
k_l	Liquid mass transfer coefficient (m/s)
k_m	Membrane mass transfer coefficient (m/s)
K_{ol}	Overall mass transfer coefficient (m/s)
l_m	Thickness of the membrane(m)
M	Gas molecular weight (g/mol)
ΔP	Minimum pressure or breakthrough pressure (Pa)
Q_l	Liquid volume flow rate (m^3/min)
R	Gas constant, reaction rate ($\text{mol}/\text{m}^3\text{s}$)
r_p	Pore radius of hollow fibers (m)
R_{mg}	Resistance of the membrane sections filled with gas (s/m)
R_{ml}	Resistance of the membrane sections filled with liquid (s/m)

$R_m(t)$	Time-dependent total resistance of the membrane sections (s/m)
$R_{mg}(t)$	Time-dependent resistance of the membrane sections filled with gas (s/m)
$R_{ml}(t)$	Time-dependent resistance of the membrane sections filled with liquid (s/m)
R_{total}	Overall mass transfer resistance (s/m)
T	Temperature (K)

Greek

σ_l	Liquid surface tension (dyn/cm)
θ	Contact angle
μ	Gas dynamic viscosity (pa s)
Ω	Dimensionless function of temperature
ε_m	Porosity of the membrane (%)
ω	Weight of the membrane (g)

SUMMARY

Gas-liquid membrane contactor (GLMC) process has been gaining popularity in recent years as a potential alternative for CO₂ separation from various gas streams, such as biogas, natural gas, and flue gas. However, no commercial CO₂ removal process using GLMC technology is presently in operation. The main technical barrier is the lack of desirable membranes which exhibit anti-wetting property during the long-term operation. Membrane wetting caused by the penetration of liquid absorbent into the membrane surface pores would result in a decline of CO₂ absorption flux of the GLMC system and hence make this technology less efficient and economically unattractive. Therefore, the development of highly hydrophobic and chemical resistant membranes with optimized substrate structure to avoid wetting has become a critical issue to facilitate membrane contactor practical application in CO₂ separation.

In this study, a hydrophobic surface modification method for Torlon[®] poly(amide-imide) (PAI) membrane was explored, which has not been reported previously. Asymmetric microporous PAI hollow fiber membranes were fabricated and followed by a simple surface modification using a silane coupling agent, (3-aminopropyl)trimethoxysilane (APTMS), and a perfluoro-compound, Fluorolink[®]S10 (FS10) to produce the PAI hollow fiber membrane with a hydrophobic surface. The reactions between PAI and the modification reagents have been confirmed by experiments. Optimal modification conditions were investigated by varying the modification parameters, such as APTMS treatment temperature, APTMS concentration, APTMS treatment time, and FS10 treatment time. The newly developed PAI hollow fiber membranes showed much higher hydrophobicity compared with the original PAI substrate, the contact angle was improved from 76 °to 108 -117 °and the liquid entry pressure (LEP_w) was improved from 0.7 -0.8 bar to 2.1 -4.0 bar. Moreover, the modified PAI hollow fiber membranes showed reasonably high CO₂ flux by using water as a physical absorption liquid in GLMC. The modified PAI membranes were investigated in GLMC for the long-term stability test. The membrane showed a stable performance for up to 42 days by using a 2 M sodium taurinate as the liquid absorbent and pure CO₂ as the feed gas. The results indicated that the modified PAI membranes

have a good potential to be used in the GLMC application.

It is well known that both fluoro-compounds and long-chain alkyl groups as low surface energy compounds can generate hydrophobic surface (X. M. Li, D. Reinhoudt, & M. Crego-Calama, 2007; Mecinović et al., 2011; Nishino, Meguro, Nakamae, Matsushita, & Ueda, 1999; X. Zhang, Shi, Niu, Jiang, & Wang, 2008). As a continuous effort of exploring the hydrophobic modification of PAI hollow fiber membranes, we explored a new modification method using an amine compound terminated with a long alkyl chain, e.g. octadecylamine, as the modification reagent to generate long alkyl chains onto the PAI membrane surface and over the cross section. The modification conducted in this study was a single step treatment, differentiating from the previous work which involved two-step chemical modification. Thus, the new method was more convenient and easier to handle. The modification mechanism was confirmed by experiments. Optimal treatment time was also explored. The octadecylamine were single small molecules in the solution and could penetrate deeply into the membrane matrix. The treated membranes showed high hydrophobicity with an improvement in contact angle of around 30°. The LEP_w also increased greatly from 7 psi (0.7 bar) to 63 (4.2 bar) after modification due to the grafting and anchoring of octadecylamine molecules on the membrane surface and pore walls. A stable performance of the modified PAI membranes in GLMC for CO₂ absorption for 15 days was attained by using a 2 M sodium taurinate aqueous solution and pure CO₂.

Hydrophobic surfaces can be produced in two ways. One is to modify the surface with low surface energy compounds; another one is to create a rough surface on the hydrophobic materials (X. Zhang, et al., 2008). In the previous works, the membranes were modified by the perfluoro-compounds and long-chain alkyl as the low surface energy compounds, which rendered a high surface contact angle. In the following works, it was proposed to increase the membrane surface roughness, and meanwhile combine the hydrophobic compounds to achieve a highly hydrophobic membrane surface. To alter the membrane surface roughness, the incorporation of an inorganic layer on the membrane surface was proposed.

A novel method to form a highly hydrophobic inorganic-organic composite hollow fiber membrane by fluorinated silica (fSiO₂) incorporation on the polyetherimide (PEI) substrate was explored. The incorporation of fSiO₂ layer on the membrane surface was examined and confirmed. Ultrasonication test was conducted to test the structural stability of the composite membrane. The experimental results revealed that the fSiO₂ layer was tightly bonded to the PEI substrate through the silane reactions. The incorporation of fSiO₂ layer on the membrane surface could enhance the surface roughness and greatly reduce the surface free energy due to the fluorinated hydrophobic compound (perfluorodecyltriethoxysilane, PFTS). The hydrophobicity of the composite membrane surface was dramatically elevated, as evidenced by the dynamic contact angles increment, e.g. from original 66.7 ° to 124.8 ° for advancing values, and from 49.5 ° to 100.6 ° for receding values. The contact angle hysteresis was 24.2 °. Moreover, it was observed the mechanical property of the composite membrane was better than some of the conventional polymeric membranes such as polyethersulfone (PES), and polyvinylidene fluoride (PVDF). In addition, the composite membrane was also not as brittle as the pure inorganic membrane. The CO₂ absorption flux of the composite membranes was investigated in terms of both physical and chemical absorptions in a GLMC system. The membrane contactor showed a reasonably stable performance with around 20% flux drop throughout the 31 days long-term operation using a 2 M sodium taurinate aqueous solution as the absorbent and pure CO₂. The chemical compatibility test indicated that after the long-term constant contact with sodium taurinate, the hydrophobicity of the fSiO₂-PEI composite membrane still maintained and was much higher than that of original PEI and conventional hydrophobic polymeric membranes such as PVDF. The incorporation of the fSiO₂ inorganic layer not only offered high hydrophobicity, but also would protect the polymeric substrate from the attack of chemical absorbents, making the membrane a longer lifespan. This study offered a novel approach to produce the inorganic-organic composite membranes which combines the advantages of both polymeric and inorganic membranes. To the best of our knowledge, this approach has not been reported for the contactor applications previously.

The properties and performance of the inorganic-organic composite membrane are directly associated with the membrane substrate structure. Asymmetric hollow fiber

membranes prepared from NIPS process usually exhibit a dense skin layer which contributes most of the mass transfer resistance of the membrane part. However, an increase in the pore size may reduce the membrane anti-wetting ability as indicated by Young's equation, which has been explained in details in Chapter 2, Session 2.1.4. Thus, the pore size is always limited by the concern of membrane wettability when fabricating the membranes for contactor applications. As a breakthrough, we fabricated a porous PEI substrate with high surface porosity and large pore sizes of the outer skin layer to minimize the membrane mass transfer resistance by using a solvent-dope solution co-extrusion approach in the hollow fiber spinning process, followed by a novel fSiO₂ nanoparticles treatment to make the membrane surface highly hydrophobic and chemical resistant to prevent the membrane from wetting caused by the large pore size. The triple-orifice spinneret was used in the co-extrusion approach with the solvent as the external liquid flowing in the outer channel, extruded simultaneously with the dope solution and bore fluid in the spinning process. It was observed the resultant membrane exhibited an extremely open and porous outer skin layer with cellular structure. It is worth mentioning that the open cellular surface morphology would effectively reduce the mass transfer resistance, and meanwhile, it also played an important role in the SiO₂ nanoparticles incorporation as the nanoparticles were allowed to embed deeply in this type of structure so that the membrane would hold the nanoparticles through both chemical and physical interactions. It was also observed the resultant membrane had a higher surface roughness and better mechanical properties in terms of rigidity, toughness and elongation compared with the membrane fabricated without using co-extrusion approach. The newly developed composite PEI hollow fiber membranes showed the advancing contact angle value of 123.3°, receding contact angle value of 107.2°, and contact angle hysteresis of only 15.9°, indicating the high water resistant property. Furthermore, the composite membranes showed superior CO₂ absorption performance in GLMC as compared with other commercial and in-house made hydrophobic membranes. Moreover, a stable CO₂ absorption performance by using sodium taurinate as the absorbent was attained over a 60-day long-term GLMC test. The results demonstrated the important role of membrane fabrication and modification techniques in facilitating the commercialization of membrane contactor technology.

In conclusion, this thesis presents the development of novel hydrophobic hollow fiber membranes in terms of the studies of the chemical modification mechanisms, formation of inorganic-organic composite membranes, membrane characterizations and GLMC application for CO₂ absorption. This work contributes to the development of membrane fabrication and modification technology and facilitates the practical application of GLMC process in CO₂ capture.

CHAPTER 1

Introduction

1.1. Background

Carbon dioxide (CO₂) is one of the largest contributors to global warming. In the year of 2011, there were more than 30 billion metric tons global CO₂ emissions from the consumption of energy with an increasing trend ("International Energy Statistics," 2011). CO₂ is commonly found in biogas from anaerobic digestion, natural gas stream, flue gas from fossil fuel combustion and the product of coal gasification. The presence of CO₂ and other acid gases reduce the calorific value and make the gas streams become acidic and corrosive, which in turn cause difficulties for gas compression and transportation. Pipeline specifications for natural gas usually require CO₂ concentrations below 2% (Othman, Tan, & Bhatia, 2009). One major step to treat the various gas streams is to remove acid gases such as CO₂, H₂S and SO₂ before they are compressed and delivered. The separation of CO₂ is important in many industrial processes such as natural gas sweetening, biogas upgrading, oil recovery enhancement and landfill gas purification (H. Yang et al., 2008). Therefore, economic and effective techniques for CO₂ removal from various gas streams and capture at a wide range of CO₂ concentration levels and flow rates are highly desirable and have attracted great interest.

Conventional industrial methods employed for such purpose include chemical absorption by reactive solvents in packed towers, spray towers, scrubbers and bubble columns, pressure swing adsorption and cryogenic separation (Basu, Khan, Cano-Odena, Liu, & Vankelecom, 2010). Regardless of the full maturity of the absorption process, the phase dispersion which occurs during the process frequently causes problems such as flooding, excessive loading, weeping, foaming and entrainment (Peng et al., 2005; R. Wang, Li, Zhou, Liu, & Liang, 2004). Moreover, those conventional methods usually involve substantially complicated equipment, high

energy consumption and large capital cost. As an alternative, membrane-based separation technology has shown promising features and accordingly, attracting increasing attention from the scientific community with research specialized in CO₂ separation and capture due to its energy efficiency, simple process design, ease of scale-up and module construction as well as small footprint (Bernardo, Drioli, & Golemme, 2009; N. N. Li, 2008). Membrane gas separation technology has been proven its commercial availability for acid gas removal in the 1980s (natural gas purification) (Drioli & Barbieri, 2011). Over the years, tremendous progress in gas separation studies using membranes has been made in terms of membrane fabrication, improving chemical and physical properties of the membrane, process design and module configuration, etc. Various membranes for CO₂ capture have been explored. Based on the materials of the membranes, three major categories exist, e.g. polymeric membranes, inorganic membranes and mixed matrix (composite) membranes. In general, polymeric membranes exhibit gas selectivity ~5–10 fold lower than those of inorganic membranes. The polymeric membranes, however, currently dominate the gas separation membrane market because they can be easily processed into both flat sheet and hollow fiber configurations. In addition, their low manufacturing cost is of great interest for industrial applications. Inorganic membranes are attractive for CO₂ separation processes at high temperatures; considering their robust thermal, chemical and mechanical stability. However, more studies need to be performed to improve the reproducibility and reliability and to reduce cost (Y. Zhang, Sunarso, Liu, & Wang, 2013).

Polymeric membranes can be further classified into three types based on the transport mechanism, e.g. dense gas permeation membranes, facilitated transport membranes and microporous hollow fiber membranes used in gas-liquid membrane contactor (GLMC). For the dense gas permeation membrane, gas molecules are transported based on the principle of solution diffusion mechanism. The gas selectivity is regulated by the polymer molecular structure that allows preferential passing of certain gas molecules based on their sizes (Xiao, Low, Hosseini, Chung, & Paul, 2009). The facilitated transport membrane also belongs to dense membrane. The gas transport in a facilitated transport membrane is based on the reversible reactions between reactive carriers and CO₂ in the membranes. CO₂-reactive carriers are incorporated in the

membrane which can create the carrier-mediated CO₂ facilitated diffusion mechanisms in addition to the solution-diffusion mechanism. Thus, facilitated transport membrane can achieve higher permeation flux than gas permeation membrane (Huang, Zou, & Ho, 2008; Zou & Winston, 2006). On the other hand, in a GLMC, CO₂ absorption is achieved when the liquid absorbent is in contact with the gas streams flowing on the other side of the hollow fiber membranes. Compared to the dense gas permeation membranes which have the selectivity advantage, the porous membranes in the membrane contactor are non-selective and only serve as an interfacial barrier between the gas and liquid phases. The role of selectivity is fulfilled by liquid absorbents via physical absorption, chemical reaction or a combination of these two processes. Thus, membrane contactor is able to provide a higher permeation flux due to the lower membrane mass transfer resistance (Qi & Cussler, 1985a, 1985b).

The focus of this research work is on developing highly hydrophobic microporous hollow fiber membranes for the use in a GLMC. The GLMC offers several advantages over the conventional non-membrane devices such as packed towers or bubble columns used in past decades: (1) High surface area per unit volume and less energy-consuming so that it is more economic; (2) The gas and liquid phases flow independently at the different sides of the membrane (lumen and shell), and hence can be manipulated separately; (3) The modularity of the hollow fiber membranes makes the device being easily scaled-up; (4) The membrane area is known and does not depend on the operational conditions such as temperature and liquid flow rate so that the performance of the system can be predicted easily (J. L. Li & Chen, 2005; Mansourizadeh & Ismail, 2009). However, no optimized membranes that can fulfil the requirement of GLMC for CO₂ removal are commercially available. The main problem is membrane wetting due to the penetration of liquid absorbent into the membrane pores, which can significantly reduce the efficiency of the system. Hydrophobic and chemical resistant membrane is an option for overcoming membrane wetting. This is because aqueous absorbent solutions tend to be repelled at the pore openings of hollow fiber membranes made of hydrophobic materials. Meanwhile, to achieve high energy efficiency, the membrane structure should be well-tailed to minimize the mass transfer resistance of the membrane part. Therefore, desirable membrane properties for GLMC application should be: high hydrophobicity, high surface porosity with small pore size,

low mass transfer resistance and good resistance to the chemical liquid absorbents (Mansourizadeh, Ismail, Abdullah, & Ng, 2010).

1.2. Objectives

This study aims at developing highly hydrophobic and efficient porous hollow fiber membranes with strong chemical resistance for GLMC application. The primary objectives of the project are to:

- fabricate porous hollow fiber substrates with desired surface morphology and structure by non-solvent induced phase separation (NIPS) method specifically via dry-jet wet spinning technique, suitable for further surface treatment;
- enhance membrane anti-wetting property by developing novel membrane surface modification techniques;
- develop novel highly hydrophobic inorganic-organic composite membranes through sol-gel process intended for the use in GLMC process;
- investigate the mechanisms of the chemical surface modification and formation of the composite membranes through understanding the reaction between imide and amine functional groups, silane chemistry and its interactions with polymeric membrane substrates;
- assess the CO₂ absorption performances of the newly developed membranes in GLMC and monitor their long-term performances.

1.3. Thesis outline

This thesis includes 7 chapters, which are highlighted as follows:

- Chapter 1: ***Introduction*** - Background information, the objectives and outline of the study are provided.
- Chapter 2: ***Literature review*** - This chapter is divided into two parts. The first part reviews the GLMC technology, including the working principles, mass transfer in GLMC, challenges in the practical applications, state-of-the-

art of hydrophobic membranes and liquid absorbents used. The second part is about the development of highly hydrophobic membranes by membrane modification. The preparation of asymmetric membranes by phase inversion specifically for hollow fiber membrane fabrications via dry jet-wet spinning technique was firstly introduced, followed by the review of various modification methods for developing the hydrophobic membranes.

- Chapter 3: ***Novel chemical surface modification to enhance hydrophobicity of poly(amide-imide) (PAI) hollow fiber membranes*** – Microporous PAI hollow fiber membranes were fabricated and followed by a two-step surface modification to produce the hydrophobic membrane surface. The discussions on the optimal modification conditions, characterizations of the modified membranes and the CO₂ absorption performance of the modified membranes in GLMC are presented.
- Chapter 4: ***Novel single-step hydrophobic modification of PAI hollow fiber membranes*** – PAI hollow fiber substrates were further treated by a single step hydrophobic modification through imide and amine functional groups interactions. Optimal treatment time was investigated. The properties of the PAI membranes before and after modification were characterized. The modified membranes were investigated in the GLMC system for CO₂ absorption.
- Chapter 5: ***Fabrication of novel fluorinated silica-polyetherimide (PEI) inorganic-organic composite hollow fiber membranes intended for GLMC application*** – The formation of a highly hydrophobic inorganic-organic composite hollow fiber membrane was explored by incorporation of fluorinated silica (fSiO₂) layer on the polyetherimide (PEI) substrate via silane chemistry. A series of experiments were performed to characterize the composite membranes and the GLMC performance was examined.
- Chapter 6: ***Novel method for incorporating hydrophobic silica nanoparticles on PEI hollow fiber membranes for CO₂ absorption in GLMC*** – The pore size is always limited by the concern of membrane wettability when fabricating the membranes for contactor applications. To make the

breakthrough, a highly hydrophobic PEI substrate with high surface porosity and large pore size was obtained by using a triple-orifice spinneret through a novel solvent-dope solution co-extrusion approach in the spinning process, and followed by a novel approach of inorganic nanoparticle incorporation to make the membrane surface highly hydrophobic and chemical resistant to prevent the membrane from wetting caused by the large pore size on the membrane surface. The modified membranes were investigated in the GLMC system for CO₂ absorption.

Chapter 7: ***Conclusions and recommendations*** – The important findings of this study and recommendations for future work are presented in this chapter.

CHAPTER 2

Literature Review

This chapter starts with the review of gas-liquid membrane contactor (GLMC) technology, including working principle, mass transfer in GLMC, challenges in the practical application, state-of-the-art of hydrophobic membranes and liquid absorbents used. After this, the development of highly hydrophobic membranes by membrane modification method was presented with the beginning of preparation of asymmetric membranes by phase inversion specifically for hollow fiber membrane fabrications via dry jet-wet spinning technique and followed by the various modification methods for developing the hydrophobic membranes.

2.1. Gas-liquid membrane contactor (GLMC)

2.1.1. *Working principles*

GLMC is increasingly seen as a promising alternative to traditional contacting equipment such as packed towers or bubble columns in past decades. In particular, CO₂ capture from flue gas or biogas using GLMC has attracted intensive interest in recent years. In a GLMC system, a gas stream and a liquid solution normally flow counter-currently in both sides of the membrane. If the gas stream contains CO₂, for example, CO₂ capture is achieved when CO₂ transports through the microporous membrane matrix and is absorbed by the liquid absorbent, as illustrated in Figure 2.1. The microporous membrane serves as a non-selective barrier to provide an interface between the gas and liquid phases. Therefore, GLMC is expected to have potential to overcome the disadvantages of conventional contacting equipment because of its unique feature of non-dispersive gas-liquid contact that allows manipulating the two phases separately. In addition, its compact modular structure provides the flexibility for scale up or down with much larger gas-liquid interface on a small foot-print, leading to significantly enhanced mass transfer efficiency. Moreover, GLMC is able to

operate at nearly atmospheric pressure, which allows low-cost construction of the system. It has been reported that hollow fiber contactors are about 30 times more efficient for gas absorption than conventional equipment (E.L Cussler, 1994). Consequently, the size of the absorber and stripper units can be reduced by 65% (Herzog, 2001), resulting in the potential cost reduction of up to 25% which is below the best available packed column technology (V. Y. Dindore, Brilman, & Versteeg, 2005).

Figure 2.1. CO₂ absorption in a GLMC

Membrane contactors were first studied as a blood oxygenator in the mid-1970s (Esato & Eiseman, 1975). Since then, its application has been extended to many fields, including the capture of acid gases (CO₂, SO₂, H₂S), removal of organic vapour, production of ultrapure water by deoxygenation, air humidity control, etc. (Gabelman & Hwang, 1999). Qi and Cussler were the pioneers in introducing membrane contactors for CO₂ removal, which led to extensive investigations on this topic later (Qi & Cussler, 1985a). An excellent review on hollow fiber membrane contactors was made by Gabelman and Hwang in 1999 (Gabelman & Hwang, 1999). Pilot-scale hollow fiber membrane contactor units have also been developed by some companies, such as Kvaerner Oil & Gas, W.L Associates GmbH, and TNO Environment Energy and Process Innovation (Aresta, 2003).

2.1.2. Mass transfer in GLMC

Membrane gas absorption process uses porous hydrophobic membranes which permit mass transport between the two phases while without phase dispersion. Generally,

three consecutive steps are involved in the mass transfer process: 1). diffusion from the bulk gas phase to the membrane surface; 2). diffusion through the membrane pores; 3). transfer from the membrane liquid interface to the bulk liquid and followed by liquid phase diffusion and/or chemical reaction. Therefore, three individual mass transfer coefficients are associated with the process, e.g. k_l , k_m and k_g in liquid phase, membrane and gas phase, respectively. Figure 2.2 illustrates the mass transport of the interested gas in the membrane contactor.

Figure 2.2. Mass-transfer regions and resistance-in-series in non-wetted membrane contactors (Atchariyawut, Feng, Wang, Jiraratananon, & Liang, 2006).

The overall resistance, defined as the reciprocal of overall mass transfer coefficient for a non-wetted (gas-filled pores) membrane contactor can be expressed by a resistance-in-series model as shown in Equation (1):

$$R_{total} = \frac{1}{K_{ol}} = \frac{1}{Ek_l} + \frac{Hd_o}{k_m d_{ln}} + \frac{Hd_o}{k_g d_i} = R_l + R_m + R_g \quad (1)$$

where K_{ol} is the overall mass transfer coefficient, H (-) represents Henry's constant, indicating the ratio at equilibrium of the gas concentration in the liquid to the concentration above the liquid (Atchariyawut, Jiraratananon, & Wang, 2007; Mansourizadeh & Ismail, 2009). E (-) is the enhancement factor due to chemical reaction. d_o , d_i , and d_{ln} are the outer, inner and logarithmic mean diameters of membrane, respectively. As can be seen from this equation, the overall mass transfer

resistance is the summation of individual mass transfer resistance. The overall mass transfer coefficient K_{ol} can also be calculated based on the experiment which gives:

$$K_{ol} = \left(\frac{Q_l}{A} \right) \left(\frac{C_{l,out} - C_{l,in}}{\Delta C_{l,m}} \right) \quad (2)$$

$\Delta C_{l,m}$ is the logarithmic mean driving force based on liquid phase concentration:

$$\Delta C_{l,m} = \frac{(HC_{g,in} - C_{l,out}) - (HC_{g,out} - C_{l,in})}{\ln(HC_{g,in} - C_{l,out}) / (HC_{g,out} - C_{l,in})} \quad (3)$$

where Q_l is the liquid volume flow rate, $C_{l,out}$ and $C_{l,in}$ are CO_2 concentration in liquid phase at outlet and inlet. A is the gas-liquid contact area; $C_{g,out}$, and $C_{g,in}$ are CO_2 concentration in gas phase at outlet and inlet, respectively.

In the gas-liquid contacting process, the liquid absorbent flow velocity is one of the most important operational parameters. In the case of physical absorption such as CO_2 in water, the mass transfer resistance of gas diffusion from the bulk gas phase to the external membrane surface is negligible compared with the resistance connected with the liquid phase (V.Y. Dindore, Brilman, Feron, Versteeg, & 2004; Karoor & Sirkar, 1993; Rangwala, 1996). The liquid phase resistance depends on experimental hydrodynamics and needs to remain unchanged for a constant liquid flow rate (Mavroudi, Kaldis, & Sakellariopoulos, 2006). The gas absorption flux increases with the increase in the liquid flow velocity while the gas velocity has little influence in the absorption flux. In the case of chemical absorption, the gas absorption flux is found increases with the velocity of liquid flow as well. This is because there are significant depletions of chemical absorbents at the liquid–gas interface; increase of the liquid velocity could accelerate the supply of the active amines and mitigate the depletion effectively (H. Y. Zhang, Wang, Liang, & Tay, 2006). The concentration of interested gas in bulk gas phase also serves as a rate-limiting factor due to the instantaneous absorption of CO_2 in the liquid phase (H. Y. Zhang, et al., 2006).

The mass transfer resistance in the membrane varies with the membrane operation mode, e.g. non-wetted, partially wetted, and completely wetted. Non-wetted condition means the membrane pores are fully filled by gas and the interface between the gas and

liquid phase is immobilized at the membrane pore mouth on the liquid side. Membrane resistance is minimized at this condition. The membrane resistance for non-wetted case R_{mg} can be calculated using Equation (4) (Feron, Jansen, & Klaasen, 1992):

$$R_{mg} = \frac{l}{k_{m,g}} = \frac{\tau_m l_m}{D_{g,eff} \varepsilon_m} \quad (4)$$

where $k_{m,g}$ is the mass transfer coefficient in the membrane. $D_{g,eff}$ is the effective diffusion coefficient of gas in the gas-filled pores, which is determined by two types of diffusion coefficients: bulk diffusion and Knudsen diffusion. Bulk diffusion is caused by collisions of molecules with other molecules. While Knudsen diffusion occurs when the gas molecules collide with pore walls. $D_{g,eff}$, is expressed in the following equations (E.L. Cussler, 1984; M. Mulder, 1996; Reid, Prausnitz, & Sherwood, 1977; Versteeg & van Swaaij, 1988):

$$D_{g,eff} = \left(\frac{l}{D_{g,m}} + \frac{l}{D_{g,Kn}} \right)^{-1} \quad (5)$$

where $D_{g,m}$ and $D_{g,Kn}$ are bulk diffusion coefficient and Knudsen diffusion coefficient, respectively, as shown in Equation (6) and Equation (7) below:

$$D_{g,m} = 1200 \left(\frac{RT}{MP} \right) \left(\frac{\Omega_\mu}{\Omega_D} \right) \mu \quad (6)$$

$$D_{g,Kn} = 0.97 r_p \left(\frac{T}{M} \right)^{0.5} \quad (7)$$

Where M is the gas molecular weight and μ is the gas dynamic viscosity. The Ω_μ and Ω_D are the dimensionless functions of temperature and can be calculated from Neufeld et al. empirical equations (E.L. Cussler, 1984). r_p is the pore radius of hollow fibers. The diffusion coefficient resistance for completed wetted case (the pores filled with liquid), R_{ml} , is expressed as

$$R_{ml} = \frac{l}{k_{m,g}} = \frac{D_l \varepsilon_m}{\tau_m l_m} \quad (8)$$

where τ_m , l_m , and ε_m are the tortuosity, thickness and porosity of the membrane, respectively. D_l is the diffusion coefficient of the gas in the pores filled with liquid, and can be determined by the interactions between the molecules. VersteegVan Swaaij equation can be used to estimate D_l (Versteeg & van Swaaij, 1988):

$$D_l = 2.35 \times 10^{-6} \exp\left(-\frac{2119}{T}\right) \quad (9)$$

For partially wetted pores, the membrane resistance is a function of the resistance of pores filled with gas R_{mg} , the resistance of pores filled with liquid R_{ml} , and the wetting ration, x^* , i.e. the pore length wetted by liquid, x to the overall pore length, shown schematically in Figure 2.3. When the liquid intrusion into the membrane pores increases with time, the ration x^* also changes, and consequently, the membrane resistance, R_m , will change according to (Mavroudi, et al., 2006)

$$R_m(t) = R_{mg}(t) + R_{ml}(t) = (1 - x^*(t))R_{mg} + x^*(t)R_{ml} \quad (10)$$

where $R_{mg}(t)$ and $R_{ml}(t)$ are time-dependent resistance of the membrane sections filled with gas and liquids, respectively. R_{mg} and R_{ml} are resistances of the completely gas-filled and liquid-filled membrane pores. When the partial wetting occurs, the gas-liquid interface is shifted with time from the pore mouth to variable location inside the membrane pores.

Figure 2.3. Membrane pore partial-wetting by liquid (Mavroudi, et al., 2006)

It is worth mentioning that the above equations are based on the assumption that the membrane is uniform with respect to those parameters. When the membrane has a

large pore size distribution, it may lead to a large error to predict membrane mass transfer resistance by using those equations. Noda and Grete (Noda & Gryte, 1979) demonstrated that for a membrane with a smaller average pore size and a higher standard deviation of pore size distribution, a significant error in estimating mass transfer coefficient could be caused. This can be explained by Knudsen diffusion. As the average pore size decreases, the diffusion mechanism is governed by Knudsen diffusion. Under this regime, the pore size distribution plays an important role in determining the mass transfer coefficient.

2.1.3. Challenges of GLMC

High-performance membrane contactor should exhibit a minimal total mass transfer resistance. Obviously, the non-wetted mode of operation is preferred, i.e., the membrane pores are filled with gas to minimize the mass transfer resistance in the membrane, as shown schematically in Figure 2.3. It has been reported that once the membrane is getting wetted or even partially wetted, the mass transfer resistance will increase significantly due to the stagnant liquid phase in the membrane pores (S. Khaisri, deMontigny, Tontiwachwuthikul, & Jiratananon, 2010). Even a less than 2% margin wetting could cause an increase in a membrane resistance as high as 60% of the total mass transfer resistance (Rangwala, 1996).

On the other hand, it is a fact that the polymeric membranes in the membrane contactor have to be in direct contact with an absorbent and the absorbents with a high CO₂ loading capacity are highly corrosive. These conventional absorbents include monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and their mixtures, as well as sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP). The chemical attack of the absorbents resulted in poor performance of the system (R. Wang, et al., 2004). The membrane mass transfer coefficients were found to be much lower than theoretically calculated values for completely non-wetted pores of polypropylene (PP) membranes in aqueous sodium hydroxide (NaOH) and DEA solutions (Rangwala, 1996). Celgard X40-200 and X50-215 PP hollow fibers were observed to suffer changes in terms of pore structure and surface roughness after being exposed to DEA aqueous solutions (R. Wang, et al., 2004). Falk-Pedersen et al.

reported that PP performed poorly and PP or polyethersulfone (PES) coated with polydimethylsiloxane failed after 7 days operation (Falk-Pedersen & Dannström, 1997). Commercially available porous polyolefin membranes were not compatible with the usual aqueous solutions of ethanolamines, as evidenced by liquid seepage through the membranes in the course of operation (P.S. Kumar, 2002). All these studies indicated that performance deterioration is associated with wetting of the membranes used. Thus, the membranes used in GLMC must exhibit highly hydrophobic properties as well as high chemical resistance.

Secondly, the enhancement factor in Equation (1), E , describes the effect of chemical reaction on the mass transfer rate, and Henry's law constant indicates gas solubility. Apparently, instantaneous chemical absorption is favorable. Conventional alkanolamine solutions such as MEA, DEA, MDEA and their mixtures, as well as sterically hindered amines AMP, have been widely used for CO₂ absorption (R. Wang, Zhang, Feron, & Liang, 2005; H. Y. Zhang, Wang, Liang, & Tay, 2008). However, on top of their low surface tension that may result in high tendency of surface wetting, alkanolamine solutions can chemically react with most of polymeric membranes, leading to morphological change and gradual membrane wetting (Lv, Yu, Tu, Yan, & Dahlquist, 2010; Porcheron & Drozd, 2009; H. Y. Zhang, et al., 2008). Another problem associated with this type of absorbents is the evaporative loss in the heating recovery step due to their volatile character (Patricia Luis, Van Gerven, & Van der Bruggen, 2012), which imposes not only economic constraint of the technology, but also adverse impacts to the environment.

Therefore, to achieve a breakthrough of preventing the membrane from wetting, the key opportunities are (a) the development of novel membranes with excellent compatibility to the absorbents used, (b) the utilization of new effective absorbents with low cost for regeneration.

2.1.4. Membrane wetting in GLMC

Several possible reasons responsible for membrane wetting have been considered, including capillary condensation of water vapor in the pores (Mahmud, Kumar,

Narbaitz, & Matsuura, 2000; Nishikawa et al., 1995), change in membrane surface characteristics due to contacting with absorbents (Rangwala, 1996) or pressure difference between the shell side and the lumen side (V. Y. Dindore, Brilman, Feron, & Versteeg, 2004; Malek, Li, & Teo, 1997). Franken et al. investigated the criteria for the wetting of microporous membranes in details (Franken, Nolten, Mulder, Bargeman, & Smolders, 1987). Generally, the membrane wetting depends on the properties of the liquid as well as the membrane material. If the liquid absorbent is water or an inorganic solution which has a high surface tension, it usually cannot wet the hydrophobic membranes. On the other hand, if the liquid contains organic solutes, its surface tension value drops rapidly. There is a critical concentration of the organic solution, above which, the contact angle between the liquid and membrane surface will become less than 90° (Franken, et al., 1987). As a result, the liquid will wet the membrane surface and consequently penetrate into the microporous membrane. Franken et al. were the first to recommend that when using microporous hydrophobic membranes as the permeable barrier between the two phases, the concentration of the active organic compounds could not exceed the Maximum Allowable Concentration (MAC) to avoid wetting (Franken, et al., 1987). However, the liquid may also penetrate into the membrane at the concentration less than MAC due to the pressure exerted on the liquids due to pumping. For a given liquid absorbent, the minimum pressure or breakthrough pressure to be applied on the liquid phase to enter the membrane pores can be estimated by Laplace equation (Franken, et al., 1987; P. S. Kumar, Hogendoorn, Feron, & Versteeg, 2002):

$$\Delta p = \frac{4\sigma_l \cos\theta}{d_{\max}} \quad (11)$$

where σ_l is the liquid surface tension, θ is the contact angle between the liquid and membrane surface, and $d_{\max}$ is the maximum pore diameter in the microporous membrane. As can be seen from this equation, the factors affecting the value of breakthrough pressure are liquid surface tension, membranes hydrophobicity and the maximum membrane pore size. A high breakthrough pressure requires the membrane as hydrophobic as possible with small pore size and narrow pore size distribution.

2.1.5. State-of-the-art of the hydrophobic membranes used in GLMC

Commonly used hydrophobic materials include polytetrafluoroethylene (PTFE), PP, polyethylene (PE), and polyvinylidene fluoride (PVDF). Those polymer structures are shown in Table 2.1. PTFE, PP and PE cannot dissolve in common solvents, thus they are usually produced by stretching or thermal methods, which restrict the gas absorption flux due to the low porosity of the fabricated membranes. PVDF membranes offer good chemical and thermal resistances. Unlike symmetric PTFE, PP and PE membranes, PVDF can be fabricated by non-solvent induced phase separation (NIPS) method with an integrally asymmetric structure, e.g. a relatively dense skin layer and a porous substrate, which provides a good compromise between membrane pore wetting and mass transfer resistance (Atchariyawut, et al., 2006; J. Ren et al., 2006). In addition, PVDF membranes can also be fabricated by thermal induced phase separation (TIPS) (Rajabzadeh, Maruyama, Sotani, & Matsuyama, 2008). Khaisri et al. systematically studied the performance of PTFE, PVDF and PP membranes in GLMC for CO₂ separation from flue gas, and observed that the CO₂ absorption performance can be ranked as PTFE > PVDF > PP (Sakarin Khaisri, deMontigny, Tontiwachwuthikul, & Jiraratananon, 2009). The stability of PTFE and PVDF membranes was examined continuously over 60 h of operation by using MEA as the absorbent. The PTFE membranes maintained their absorption performance, while the PVDF membranes failed over the operating time.

Table 2.1. List of hydrophobic polymer structures.

Name	Chemical structure
Polyethylene (PE)	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$
Polypropylene (PP)	$\left[\begin{array}{cc} \text{H} & \text{CH}_3 \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$
Polyvinylidene fluoride (PVDF)	$\left[\begin{array}{cc} \text{F} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{H} \end{array} \right]_n$
Polytetrafluoroethylene (PTFE)	$\left[\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{F} \end{array} \right]_n$

The reported pore size of the membranes used in gas absorption membrane contactors ranges from a few nanometers (Atchariyawut, et al., 2006; Mansourizadeh, et al., 2010) to a few hundred nanometers (Rajabzadeh, Yoshimoto, Teramoto, Al-Marzouqi, & Matsuyama, 2009; Simons, Nijmeijer, & Wessling, 2009), depending on the fabrication method. Membranes formed by the NIPS process usually exhibit small pore sizes of a few nanometers while membranes formed by the TIPS process or commercially available membranes usually possess relatively larger pore sizes. Polymer dope chemistry and membrane fabricating process have been studied extensively to tailor the morphology and structure of resultant membranes used in membrane contactors. For instance, the effect of different additives was studied on the improvement of the PVDF hollow fiber membrane structure for CO₂ absorption (Naim, Ismail, & Mansourizadeh, 2012). Different membrane morphologies were also examined for wetting resistance and gas permeability (Mansourizadeh & Ismail, 2012). Feng et al. fabricated porous PVDF membranes with double-skin and single-skin structures by using different N-methyl-2-pyrrolidone (NMP) concentrations as an inner coagulant (Feng, Wang, Zhang, & Shi, 2011). It is found that the membranes without an inner skin present higher permeability and lower mass transfer resistance than the membrane with a double skin structure. Same phenomenon was reported by Xu et al. (A. Xu, Yang, Young, deMontigny, & Tontiwachwuthikul, 2008). Moreover, Rajabzadeh et al. reported PVDF membranes made by the TIPS method with considerably different structures and compared their performance in GLMC for CO₂ separation (Rajabzadeh, et al., 2009).

The co-polymer of poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is also a good candidate. The addition of an amorphous phase of hexafluoropropylene (HFP) into the main constituent VDF blocks modified the properties of the homopolymer with increased fluorine content, making PVDF-HFP more hydrophobic than PVDF. Wang and her co-workers published a series of papers on the fabrication of PVDF-HFP asymmetric microporous hollow fiber membranes (L. Shi, R. Wang, & Y. Cao, 2009; L. Shi et al., 2007; Lei Shi, Wang, Cao, Liang, & Tay, 2008; Wongchitphimon, Wang, Jiratananon, Shi, & Loh, 2011). Recently, Bakeri et al. reported the fabrication of polyetherimide (PEI) hollow fiber membrane for CO₂ absorption in GLMC (Bakeri, Ismail, Shariaty-Niassar, & Matsuura, 2010; Bakeri,

Matsuura, & Ismail, 2011). The effects of PEI concentration and different types of additives as phase inversion promoters were investigated on the membrane structures and contactor performance by using water as the absorbent. However, the long-term stability of such less hydrophobic membranes remains uncertain if chemical absorbents are used. Asymmetric poly (phenylene oxide) (PPO) hollow fiber membranes were applied with MEA as the absorbent in membrane contactor for studying the real process consisting of absorption and desorption of CO₂ under practical conditions with CO₂/CH₄ mixtures (Simons, et al., 2009). It was found that the PPO membrane with a dense and ultrathin skin layer showed more stable performance at different feed pressures and the liquid loss at elevated temperature could be restricted by the ultrathin top layer.

In addition to the direct fabrication of hydrophobic hollow fiber membranes, membrane surface modification is a good approach to obtain even highly hydrophobic membranes. This approach is to apply a more hydrophobic surface coating/modification layer on the existing hydrophobic membranes to further enhance the membrane hydrophobicity. A number of surface modification studies have been reported by utilizing a variety of surface modification techniques. This part will be reviewed particularly in Session 2.2.3.

2.1.6. Development of liquid absorbents

TNO of the Netherlands developed a class of solvents, CORAL, based on the mixtures of salts and amino-acids, which have a higher surface tension and thus is able to reduce the tendency of membrane wetting (P.S. Kumar, 2002). The driving force for CO₂ absorption can be maintained even with high CO₂ loadings due to its unique feature of solid precipitation. In addition, amino acid salt solutions have lower vapor pressures due to the ionic nature. These characteristics make amino-acid salt solutions an interesting and promising candidate for effective CO₂ capture (P. S. Kumar, et al., 2002). Yan et al. investigated aqueous potassium glycinate (PG) solution as the absorbent. The membrane under continuous steady operation for 40 hours could still maintain CO₂ removal efficiency of 90% (Yan et al., 2007). Lu et al. added activating agents such as piperazine (PZ), phosphate or borate into the aqueous glycine salt

solution to form amino acid salt-based complex absorbents. The results showed the activated glycine salt solution was evidently better than that of the non-activated glycine salt solution in the membrane contactor for CO₂ capture (Lu, Ji, Zhang, & Chen, 2010; Lu, Zhang, Ji, Fan, & Liu, 2010).

An attempt of utilizing ionic liquids for acid gas capture was also reported recently. The physical absorption of CO₂ offers the advantage of easy desorption of CO₂ from used ionic liquids (Cadena et al., 2004). The applicability of ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate for acid gas removal in a GLMC was demonstrated (P. Luis, Garea, & Irabien, 2009). However, at the current stage, the main bottleneck of ionic liquids for industrial applications is their high viscosity which leads to as high as over 97.8% of the overall mass transfer resistance (Patricia Luis, et al., 2012). Therefore, improving the fluid dynamics of the system in order to enhance the mass transfer rate in the ionic liquid phase is crucial. Parallel flow and transverse flow have been reported in membrane contactor for analysing mass transfer phenomena in the ionic liquid phase (Fallanza, Ortiz, Gorri, & Ortiz, 2011; Ortiz, Gorri, Irabien, & Ortiz, 2010). Other limitations include high investment cost and the scarce experience on their long-term compatibility with polymeric membranes (Patricia Luis, et al., 2012). The use of ionic liquids is still in early-stage of research.

2.1.7. Summary

GLMC, which integrates the absorption process with membranes, is an emerging membrane technology that is of particular interest to acid gas absorption. However, optimized membrane contactor technology for large-scale practical applications is not yet available. To achieve a breakthrough, the key challenges are (a) the development of novel membranes with excellent anti-wetting, chemical and thermal resistances; (b) the utilization of new effective absorbents with low cost for regeneration and excellent compatibility to the membrane used. The current research focuses on the aspect of the novel membrane development. In practical operations, long-term stability of the membranes in GLMC is crucial which will also be addressed in this research.

2.2. Development of highly hydrophobic hollow fiber membranes by surface modification

2.2.1. Phase inversion technique for asymmetric membrane preparation

The most commonly used method for the fabrication of asymmetric membranes is the phase inversion method developed by Loeb and Sourirajan who used made cellulose acetate membrane for reverse osmosis process in the late 1950s (Loeb & Sourirajan, 1963). Since then, membrane fabrication has been ceaselessly cultivated. Compared with flat sheet membranes, hollow fiber membranes are more favored due to the larger membrane area per volume, good flexibility and easy handling in the module fabrication.

Generally, asymmetric hollow fiber membranes are prepared via the phase inversion process which relies on induced thermodynamic demixing of a homogeneous polymer-solvent solution into a polymer-rich phase and a polymer-lean phase, usually by either exposure of the solution to a non-solvent or by cooling the solution below a binodal solubility curve. Non-solvent induced phase separation (NIPS), which as stated previously, is the main membrane manufacturing technique used currently. In this technique, by adjusting different thermodynamics and kinetics parameters, different porous membrane structures can be obtained. The essence of this process is to introduce a nonsolvent to the polymer dope system to induce the solvent and nonsolvent exchange. After a certain time of exchange, the dope solution gradually becomes thermodynamically unstable, leading to demixing. The final membrane with an asymmetric structure will be formed after the whole process.

Figure 2.4 shows the phase diagram which represents thermodynamic properties of a ternary system including a solvent, a nonsolvent and a polymer. The initial procedure for membrane fabrication from a ternary system is always to prepare a thermodynamically stable and homogeneous polymer solution. This corresponds to a point on the polymer/solvent axis if no nonsolvent is added into the polymer solution. It is also possible to maintain thermodynamically stable when adding some nonsolvents to such an extent that all the components are still miscible. Then the initial dope solution prior to spinning is in Region I, which is the homogenous region with

one phase liquid state. Region II is a liquid-liquid two-phase solution and is in between the binodal curve and gelation boundary. Two curves, e.g. bimodal and spinodal curves are in this region. Two sub-regions are in Region II, e.g. metastable and unstable regions, which are separated by the spinodal line. The metastable region is between the binodal and spinodal curves and the unstable region is under the spinodal curve ADE. Region III refers to the liquid-solid two-phase swelling. It is confined to gelation and swelling boundary. Region IV is the last region in the phase diagram, where the polymer solution is in its glass state or swelling state (Jizhong Ren & Wang, 2010). Region IV is separated from region I and III by the vitrification boundary and swelling boundary, respectively.

Figure 2.4. Phase diagram of a ternary system in diffusion induced phase separation (DIPS) method. Adapted from (Jizhong Ren & Wang, 2010)

Membrane structures are significantly affected by the different demixing processes during membrane formation, e.g. instantaneous liquid-liquid demixing and delayed onset of liquid-liquid demixing. Instantaneous demixing refers to the immediate gelation and solidification which result in a membrane with a dense skin layer, while the substrate beneath the skin layer is porous with macrovoids (Barzin & Sadatnia, 2008; Jizhong Ren & Wang, 2010; Schafer, Fane, & Waite, 2005). On the other hand, in the case of delayed demixing, the composition of the entire solution remains in the homogeneous region e.g. region I of the phase diagram for a certain period of time. This would form a thinner membrane skin layer. The macrovoids in the substrate are reduced dramatically, which are replaced by the sponge-like structures (Barzin & Sadatnia, 2008; Marcel Mulder, 1996).

2.2.2. Asymmetric hollow fiber membranes preparation via spinning technique

Both wet and dry-jet wet spinning processes are the commonly used techniques for fabrication of asymmetric hollow fiber membranes. In summary, the formation of asymmetric hollow fiber membranes includes a few steps: a) dope preparation, b) degas, c) metering, d) spinning, e) evaporation, f) coagulation and g) solvent exchange. During the spinning process, the dope container was connected with a N₂ gas cylinder. The dope was dispensed under pressure through a spinneret at a controlled rate, and went through an air gap before immersing into a coagulation bath. Tap water is most often used as external coagulant. The nascent hollow fibers were taken up by a roller at a free falling velocity and stored in a water bath to remove residual solvent for at least 2 days. The hollow fiber spinning process is shown in Figure 2.5.

Figure 2.5. Hollow fiber membranes spinning system

Different spinning parameters affect the formation of the hollow fiber membranes. Four important parameters, e.g. polymer concentration, coagulant, air gap and types of additives, are discussed here. In phase inversion process, polymer concentration in casting solution is one of important factors affecting membrane structure. The membranes with a denser skin layer, smaller average pore radius and lower porosity can be prepared from casting solutions with a higher polymer concentration, while the

membranes with a thinner skin layer, larger average pore radius and higher porosity are fabricated from a lower polymer concentration (Bakeri, et al., 2010).

The coagulant is used as bore fluid and also in the external coagulant bath to induce the liquid-liquid demixing and solidify the membrane matrix. Thus, the coagulant plays an important role in controlling the membrane morphology and structure. Water is a strong coagulant. When using water as the bore fluid, the resultant hollow fiber membranes usually have a dense inner layer with macrovoids beneath due to the instantaneous demixing mechanism. However, in the application of GLMC, removing inner layer can significantly reduce the mass transfer resistance and enhance the gas absorption, thus the existence of the inner layer may not be preferred (Feng, et al., 2011; A. Xu, et al., 2008). The addition of solvent into the bore fluid can result in a delayed onset of liquid-liquid demixing, and make the dense skin of the resultant membrane gradually disappear while the skin pore size increases. Shi et al. investigated the effect of bore fluid using a mixture of water/NMP (L. Shi, et al., 2007). It was reported that with the increase of NMP concentration in the bore fluid, the cavities under the inner layer of the hollow fiber gradually diminished. This was attributed to the increase in the softness of the bore fluid which reduces the polymer precipitation rate in the phase inversion. Similarly, for the external coagulant, addition of solvent into the coagulant bath is also able to suppress the formation of macrovoids and hence control the membrane structures.

Air gap is the distance between the spinneret and the external coagulation bath. It plays an important role in determining macrovoids formation during membrane fabrication via phase inversion. The air gap has several effects on (1) the gravity induced elongational drawing, (2) the moisture-induced partial phase separation in the air gap region, and (3) the evaporation of the solvent during the dry jet-wet spinning process (Widjojo & Chung, 2006). Wet-spun fibers experience vigorous and almost instantaneous coagulations; it results in the formation of hollow fiber skins with a long-range random, un-oriented chain entanglement. Deformation of the inner contour of PVDF-HFP membrane during wet spinning process was observed by Shi et al. (L. Shi, et al., 2007). The inner contour deformation can be eliminated with an increase in air gap because of the extra exposure time in air which allows the polymer chains to

re-arrange. On the other hand, the skin pore size and porosity can be controlled by varying the air gap in dry-jet wet spinning process. Khayet et al. reported the effect of various air gaps from 0 to 25 cm on the structure and performance of ultrafiltration poly(vinyl chloride) (PVC) hollow fiber membranes (Khayet, García-Payo, Qusay, & Zubaidy, 2009). It was observed that the inner and outer diameters of the PVC fiber membranes decreased with the increase of the air gap distance due to the gravitational force effect. Meanwhile, it was found the outer pore size and the pure water permeation flux both increased with the increase of the air gap distance.

Various additives have been used in membrane fabrication. The roles of different additives vary in different polymer/solvent/non-solvent systems. Generally, they can serve as pore formers to control the membrane structures and morphologies, and eventually affect the resultant membrane properties and performance. Additives that commonly used can be categorized into (Lei Shi, et al., 2008): (a) polymeric additives such as poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG); (b) low-molecular-weight chemicals, including salts such as lithium chloride (LiCl) and lithium perchlorate (LiClO₄), inorganic acids (acetic acid, phosphoric acid) and organic acids (propionic acid); (c) weak co-solvents such as ethanol and acetone; (d) weak non-solvents such as glycerol, ethylene glycol; (e) strong non-solvent, water. Shi et al. studied the effect of different types of additives including PVP (15,000 Da), glycerol and LiCl on the formation of PVDF-HFP asymmetric hollow fiber membranes (Lei Shi, et al., 2008). It was found that the addition of additives made the binodal curve shifted towards the polymer-solvent axis. When using a strong coagulant as the bore fluid such as water, larger macrovoids developed over the cross section with the increase of LiCl concentration due to the good affinity between LiCl and water. On the other hand, when a weak bore fluid was used, the dimension of macrovoids reduced with the increase of LiCl concentration. It was observed that when using PVP as the additive, the resultant membranes exhibited a broader pore size distribution compared to the addition of LiCl and glycerol. Recently, Wongchitphimon et al. systematically studied the effects of PEG with different molecular weights from 200 to 600 and 6000 kDa and different loadings as the additive on the fabrication of PVDF-HFP hollow fiber membranes (Wongchitphimon, Wang, Jiraratananon, Shi, & Loh, 2011). It was found that with the increase of PEG molecular weight and

concentration, the size of finger-like macrovoids, pore size, pure water permeability and MWCO of the resultant membranes increased in parallel.

2.2.3. Development of highly hydrophobic membranes by surface modification

Membrane technology has experienced substantial developments over the past decades. The extension of the scope for various practical applications attributes not only to the advances of membrane fabrication techniques, but also to various supplementary methods to modify and enhance membrane properties. For example, membrane surface modification has been recognized as a simple approach to functionalize the membrane surface and/or to alter the surface property so that the membrane is able to accommodate different applications. In GLMC, the selective layer of the membrane governs the contactor performance because the selective layer is in direct contact with the liquid absorbents. The membrane is ideally expected to be gas filled over the long operation period of time. Thus, the hydrophobicity of the membrane surface has a significant effect on its long-term operation stability.

The hydrophobicity of a surface, as expressed as the contact angle of between the solid phase and liquid phase, is governed by Young's equation:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (12)$$

Where γ_{SV} , γ_{SL} and γ_{LV} are the interfacial surface tensions with S, L and V as solid, liquid and gas, respectively. The contact angle is a result of thermodynamic equilibrium of the free energy at the solid–liquid–vapor interphase (X.-M. Li, D. Reinhoudt, & M. Crego-Calama, 2007). A hydrophobic surface is defined when the contact angle is larger than 90 °. A higher contact angle means a higher water resistance of the surface. The schematic diagram of the contact angle of a liquid droplet deposited on a solid surface is shown in Figure 2.6. It is well known that the increase of a surface hydrophobicity can be achieved by reducing the surface free energy or enhancing the roughness or a combination of both (X. Zhang, et al., 2008). With this in mind, different chemical and physical methods have been used for modifying the membrane surface to enhance the surface hydrophobicity. Several commonly modification methods are described in the following:

Figure 2.6. Contact angle of a liquid droplet deposited on the surface of a solid (Kallioinen & Nyström, 2008)

A. Surface modification by surface modifying macromolecules (SMMs)

The synthesized surface modifying macromolecules (SMMs) have an amphipathic structure with a hydrocarbon tail containing fluorine. SMMs can migrate to the membrane surface during the nonsolvent-solvent exchange process, rendering the membrane surface more hydrophobic than the bulk membrane. Ho et al. reported the surface modification of PES membranes by adding the SMMs additives into the casting polymer solution (Y. Ho, Matsuura, & P. Santerre, 2000). The PES membranes modified by SMMs exhibited lower surface energies, higher chemical resistance and better mechanical strength. As a continuation of membrane surface modification by SMMs, Khayet et al. applied another two novel SMMs incorporated into PVDF membrane for the separation of volatile organic compounds (VOCs) (Khayet, Chowdhury, & Matsuura, 2002). The structures of the two SMMs are illustrated in Figure 2.7. The results showed the contact angle increased remarkably from 78 ° to 109 °, and the chloroform separation factor increased with the increased in SMMs concentration in the PVDF casting solution.

Figure 2.7. Chemical structures of SMMs

B. Surface coating

Surface coating is a simple physical method to improve the surface hydrophobicity of membranes by coating a thin layer onto the membrane surface, aiming to either reduce the surface energy or to create the surface roughness. Gugliuzza et al. (Gugliuzza & Drioli, 2007) fabricated a superhydrophobic PVDF membrane simply by surface coating of a thin layer of tetra-fluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TIT) (Hyflon AD X60). The resultant membrane presented strong hydrophobicity with contact angle as high as 147° . Jin et al. (Jin, Yang, Zhang, & Jian, 2008) modified poly (phthalazine ether sulfone ketone) (PPESK) hollow fiber membrane by surface-coated method using a hydrophobic material: silicone rubber. Both the contact angle and LEPw of modified membranes were higher than that of the unmodified membrane, indicating that the improved hydrophobicity of the modified membranes was attributed to the presence of hydrophobic material on the PPESK membranes surface. Recently, Lv et al. (Lv et al., 2011) fabricated a superhydrophobic PP membrane fiber by depositing a rough layer of dissolved granulated PP on the membrane surface. The contact angle increased from 122° to 158° after the modification. However, the potential drawback of this technique is the instability of the coating layer because of the weak physical adsorption interaction of the coating layer.

C. Chemical grafting

Several types of hydrophobic compounds are commonly used, for instance, 1H, 1H, 2H, 2H-perfluorooctylethoxysilane (FAS) (Koonaphapdeelert & Li, 2007), 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFTS) (Hendren, Brant, & Wiesner, 2009) and a group of perfluoropolyether materials (Fluorolink[®]) developed by Solvay Solexis, aiming at producing hydrophobic surfaces on various materials. Those compounds can be grafted onto the membrane surface through chemical reactions. A highly hydrophobic PVDF-HFP membrane was fabricated by Wongchitphimon et al. with 10% NaOH, and subsequently modified with the mixture solution of tetraethoxysilane (TEOS) and Fluorolink[®] S10 (FS10), which showed an increase in contact angle of around 30° (Wongchitphimon, Wang, & Jiratananon, 2011). The mechanism of

dehydrofluorination of PVDF-HFP membrane by NaOH was proposed as shown in Figure 2.8. Fang et al. reported the development of hydrophobic porous alumina ceramic hollow fiber membrane for membrane distillation process (H. Fang, Gao, Wang, & Chen, 2012). The hydrophilic alumina membrane was modified by FAS, the contact angle increased from original 48 °to 130 °after grafting.

Figure 2.8. The possible reaction pathway of dehydrofluorination onto the PVDF–HFP membrane surface (Wongchitphimon, Wang, & Jiratananon, 2011)

On the other hand, in the graft polymerization process, the surface of a membrane can be activated by chemical initiators or irradiation such as γ -rays and UV, which can cause the generation of free radicals on the backbone of the membrane surface. Next, the activated membrane surface is exposed to the desired monomer. The graft polymerization of the monomers is then initiated at the membrane surface. Wu et al. modified cellulose acetate membrane by irradiation induced graft polymerization of styrene and turned the membrane from hydrophilic to hydrophobic (Wu, Kong, Lin, Liu, & Xu, 1992).

D. Plasma and laser treatment

Plasma is a low pressure gas containing various ions, radicals, electrons, and molecules, formed in the glow discharge. When a membrane is placed in the plasma, the surface of the membrane will be etched and subjected to various changes corresponding to the property and chemistry of the plasma. Plasma treatment may also be used to pretreat the membranes to generate the active sites where surface graft polymerization can occur (Khulbe, Y., & Takeshi, 2008). Lin et al. modified PP

membrane by glow-discharge plasma in CH₄ gas to enhance the water contact angle and roughness of the PP membrane (Lin, Tung, Chen, & Chang, 2009). PES membrane was subjected to surface modification using hexamethyldisiloxane (HMDSO) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) in radio frequency plasma system to improve its hydrophobic property (Tur, Onal-Ulusoy, Akdogan, & Mutlu, 2012). Yang et al. modified PVDF membrane by plasma treatment using the monomer 1H, 1H, 2H, 2H-perfluorodecyl acrylate. The contact angle of the membrane increased from 88 ° to 105 ° (X. Yang, Wang, Shi, Fane, & Debowski, 2011).

Laser irradiation is also an effective method to alter the membrane surface property. Liu et al. studied the effect of KrF excimer laser irradiation on the hydrophobic properties of PVDF membrane (Liu, Wei, Jiang, & Nie, 2010). It was found that the laser cleave C–H and C–F bonds formed C–CF₂ and C–F which reduced the PVDF surface energy while the residual macromolecules could rearrange to achieve a thermodynamic equilibrium, resulting in a rough irradiated surface area. By the both effects, the surface morphology formed and surface chemical construction changed caused the resultant super-hydrophobic PVDF surfaces with a contact angle of approximately 170 °.

E. Other methods

The membrane surface roughness can be significantly altered during membrane fabrication process. Li et al. prepared a super-hydrophobic poly(vinyl chloride) (PVC) surface with a contact angle higher than 150 ° (X. Li et al., 2006). They prepared PVC film at ambient temperature and dried in the air. The nonsolvent ethanol was added at different amounts into the PVC-solvent solution to enhance the phase inversion process, and thus increasing the surface roughness of the resultant PVC film. When ethanol added was at the same amount of the solvent in the PVC solution, the formed film exhibited the highest contact angle of 154 °. This was because when the amount of ethanol in the solution increased, PVC would precipitate out of the polymer solution and formed some PVC aggregates or particles. The more ethanol was added, the more and smaller PVC nanoparticles would form. Thus, a lotus-leaf-like super-hydrophobic film can be formed. A possible formation process of the lotus-leaf-like surface

structure of the porous PVC film is shown in Figure 2.9. Peng et al. prepared very hydrophobic PVDF membranes by two methods (Peng, et al., 2005). The first one was the modified phase inversion method using a water/solvent mixture instead of pure water as the coagulant bath. The second method was letting the PVDF casting film underwent gelation in the open air rather than being immersed into a precipitation bath. It was found that both membranes exhibited certain micro- and nano-scale hierarchical roughness on the membrane surface, which caused the enhanced hydrophobicity of the membrane. The membrane contact angle obtained by the second method could reach as high as 150°.

Figure 2.9. A possible formation process of the lotus-like surface structure of the porous film of PVC (X. Li, et al., 2006)

2.2.4. Summary

This part provides a basic understanding of the membrane formation mechanism by phase inversion method and specifically for hollow fiber membranes fabrication via dry-jet wet spinning technique. Different spinning parameters can affect the formation of the hollow fiber membranes. A few important parameters such as polymer concentration, coagulant, air gap and type of additives, are discussed. Lastly, a review of various modification techniques to develop hydrophobic membranes was presented.

CHAPTER 3

Novel Chemical Surface Modification to Enhance Hydrophobicity of Poly(amide-imide) (PAI) Hollow Fiber Membranes

3.1. Introduction

Membrane surface modification has been recognized as a simple approach to functionalize the membrane surface and/or to alter the surface structure so that the membrane is able to accommodate different applications. Overall, two modification strategies are adopted (Albrecht et al., 2003). In the first strategy, the membrane is usually treated by plasma (Inagaki, Tasaka, & Hibi, 1992; Tur, et al., 2012; Zhu, Iwata, Hirata, & Ikada, 2000), ion beam etching (Minamisawa, Zimmerman, & Ila, 2008), UV laser ablation (Z. W. Dai, Wan, & Xu, 2008; Jen, Hung, & Chun, 2008), and polymerization (Bhut, Conrad, & Husson, 2011; Worthley et al., 2011; S. Yang et al., 2011) to directly alter the surface property or to generate radicals on the membrane surface to make the surface chemically reactive for further treatment. Another strategy is the surface treatment with a chemical solution (wet-chemical) initiating surface-selective reactions (Albrecht, et al., 2003; Santoso et al., 2003). In this technique, the membrane itself contains reactive chemical groups. Imide and amine functional groups involved reactions have been explored in wet-chemical membrane modification for a long time (Lee, Kowalczyk, & Shaw, 1991; Thomas, Buchwalter, Buchwalter, & Chao, 1992). During this reaction, the amine modifier can react with the imide group under certain environments to open the imide ring system.

Many studies have utilized this reaction as the guide of membrane modification to treat imide group contained polymeric membranes. Albrecht et al. systematically investigated the pore opening process during the functionalization of poly(etherimide) (PEI) flat sheet membrane by aliphatic aminic modifiers, and successfully turned the membrane from ultrafiltration characteristics to microfiltration characteristics

(Santoso, et al., 2003). Chinpa et al. prepared PEI based ultrafiltration membranes with low fouling property by surface modification with an amino terminated poly(propylene oxide)/poly(ethylene oxide) block copolymer (PEG-amine) (Chinpa, Quénener, Bèche, Jiraratananon, & Deratani, 2010). Albrecht et al. studied the di- and multivalent amine treatment on PEI membranes, the amine functionality and the distribution of amine functions across the membrane were characterized (Albrecht, et al., 2003). Moreover, Albrecht et al. also investigated the effect of 2-step amine treatment, e.g. diethylenetriamine (DETA) and followed by high molecular poly(ethyleneimine), on different membrane structures and characterized and tested the modified membrane performance (Albrecht et al., 2007). Liu et al. modified polyimide (PI) membrane by p-xylenediamine crosslinking for gas separation (Liu, Chung, Wang, Li, & Chng, 2003a; Liu, Wang, & Chung, 2001). The modified membrane showed enhanced permselectivity for several gas pairs. Very recently, Setiawan et al. reported the surface modification of poly(amide-imide) (PAI) hollow fiber membrane by amine terminated polyelectrolyte post-treatment using poly(ethyleneimine) for forward osmosis process (Laurentia Setiawan, Wang, Li, & Fane, 2011). The treated membrane carrying positive charges showed both high rejection and water permeability.

However, to the best of our knowledge, the exploration of the imide involved modification work regarding the membrane surface hydrophobic modification is still in its infancy. Membrane surface hydrophobicity is important in membrane contactor processes. In a membrane contactor, CO₂ absorption is achieved when CO₂ penetrates through a microporous membrane and is in contact with the liquid absorbent flowing on the other side of the membrane. If the membrane is not water resistant enough, the membrane pores can be filled or partially filled by the liquid. As a result, the mass transfer resistance increases significantly due to the additional resistance brought by the stagnant liquid phase inside the pores. Thus, in order to ensure an efficient mass transfer process, the membrane used should possess highly hydrophobic property for membrane contactor application. The breakthrough pressure or liquid penetrating pressure is used to characterize the membrane in terms of wetting resistance, above which the liquid can penetrate into the membrane pores, as estimated by the Laplace equation (Franken, et al., 1987), shown in Equation (11). In order to obtain a high breakthrough pressure, the membrane material has to be hydrophobic with a contact

angle as high as possible and the membrane should have a well-tailored surface pore structure, i.e., a relatively small maximum pore size and a narrow pore size distribution. In addition, the membrane should also have a high overall porosity to minimize the membrane resistance since the presence of membrane itself introduces an extra resistance to the mass transfer process.

Poly(amide-imide) (PAI, Torlon[®]), have been used to make membranes for vapor permeation and pervaporation (Wanng, Jiang, Matsuura, Chung, & Hong, 2008; Yoshikawa, Higuchi, Ishikawa, Guiver, & Robertson, 2004), gas separation (Cha & Yang, 2007; Kosuri & Koros, 2008), and FO process (W. Fang, Wang, Chou, Setiawan, & Fane, 2012; Laurentia Setiawan, et al., 2011). PAI is a copolymer, thus it possesses unique characteristic properties of both polyamide and polyimide materials. It has exceptional mechanical, thermal and chemical resistant properties.

However, so far no any report is available using PAI membrane in membrane contactor applications because this polymer material is less hydrophobic in nature with the contact angle of $\sim 76^\circ$ and can be wetted easily. The present work explores a simple approach to make highly hydrophobic PAI hollow fiber membranes by utilizing the unique feature of PAI, that is, the imide group in PAI can react with an amine-functionalized silane coupling agent and hence to impart the hydroxyl groups on the PAI membrane surface, which makes the resultant membrane being chemically activated to further react with the silane perfluoro-compound. To the best of our knowledge, there is no similar method reported previously to obtain hydrophobic PAI membranes. The chemical modification mechanism were examined by attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR), and modified membranes were characterized in terms of contact angle, mechanical strength, membrane porosity and liquid entry pressure (LEP_w). Preliminary tests of modified membrane used in the membrane contactor for CO₂ absorption were conducted.

3.2. Experimental

3.2.1. Materials

The membrane material, the commercial polymer poly(amide-imide) (PAI) (Torlon[®] 4000T-MV) was purchased from Solvay Advanced Polymers. *N*-Methyl-2-Pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck chemicals, Singapore) was used as a solvent. Lithium chloride (LiCl, anhydrous, CAS#7447-41-8, MP Biomed) was used as the membrane pore former. (3-aminopropyl)trimethoxysilane (APTMS, 97%, CAS#13822-56-5, Aldrich, Singapore) and Fluorolink[®]S10 (FS10, Solvay Solexis, Singapore) were used as membrane surface modification reagents. Iso-propanal (IPA, 99.9%, CAS#67-63-0, Merck) was used for preparing the modification reagents solutions. Milli-Q deionized water was used in all aqueous solutions (18MΩcm). Some dextran (C₆H₁₀O₅)_n samples with different molecular weights (molecular weight from 1500 to 400,000 D, CAS# 9004-54-0, Sigma, Singapore) were used to characterize the molecular weight cut-off (MWCO) of the as-spun hollow fiber membranes. Taurine (C₂H₇NO₃S, 99%, CAS#107-35-7, Acros) and sodium hydroxide (NaOH, CAS#1310-73-2, Merck) were used to prepare the 2 M sodium taurinate solution as the CO₂ absorbent used in GLMC test. The chemical structures of Torlon[®] 4000T, APTMS and FS10 are given in Figure 3.1.

Figure 3.1. Chemical structures of (a) Torlon[®] 4000T; (b) APTMS; (c) FS10

3.2.2. Fabrication of PAI hollow fiber substrates

Two batches of asymmetric PAI hollow fiber membranes were fabricated by a dry–jet wet spinning technique. PAI and LiCl were dried in a 50 °C vacuum oven for 24 h prior to the dope preparation. Desired amounts of the dry polymer, additive, and solvent were mixed in a jacket flask equipped with an overhead stirrer and connected to a circulator bath at a controlled temperature of 60 °C. The detailed compositions of the polymer dope solution are shown in Table 3.1. After the polymer mixture became a homogeneous solution, the solution was cooled down to room temperature, filtered by using a 15 µm stainless steel filter, transferred to a dope tank, and subsequently degassed under vacuum at ambient temperature overnight prior to spinning.

Table 3.1. Spinning conditions and parameters

Parameters	PAI-A	PAI-B
Dope composition (PAI/LiCl/NMP) (wt%)	12/3/85	14/3/83
Dope flow rate (g/min)	6	6
Bore fluid (NMP/H ₂ O) (vol%)	0/100	25/75
Bore fluid flow rate (ml/min)	7	7
Air gap (cm)	15	5
Take up speed	free fall	free fall
External coagulant	tap water	tap water
Spinning temperature (°C)	23	23
Spinneret diameter (mm)	1.5	1.5
ID of bore fluid needle (mm)	0.7	0.7

In the spinning process, the dope solution was connected to a high pressure nitrogen gas cylinder and extruded through the outer channel of the spinneret at a controlled rate. The bore fluid was extruded using a high precision syringe pump through the inner channel of the spinneret. The nascent fibers went through an air gap before immersing into a coagulation bath containing tap water. They were collected at free-falling take-up speed and subsequently stored in a water bath for at least 2 days to remove residual solvent. The spinning system is shown schematically in Session 2.2.2, Figure 2.5. The spinning conditions are also summarized in Table 3.1.

3.2.3. Surface hydrophobic modification

The chemical modification involved the hydroxylation of the PAI membrane by using a silane coupling agent APTMS followed by grafting and crosslinking of FS10, which is a perfluoro-compound containing ethoxysilane terminal groups. The reaction mechanisms were confirmed by the ATR-FTIR. Firstly, the as-spun PAI membranes were immersed into a 2 % (wt/vol) APTMS solution in a mixture of IPA and distilled water (vol 1:1) at 50 °C to 70 °C for varied time ranging from 0.5 to 2 h. The membranes were then rinsed several times by the IPA and DI mixture solution (vol 1:1) to the residue APTMS molecules. After the APTMS treatment, the membranes were then immersed into the FS10 solution at 60 °C for 2 h. The solution was prepared by dissolving 1 wt% acetic acid, 1 wt% FS10 in 4 wt% distilled water and 94 wt% IPA. The modified membranes were then rinsed with IPA and dried. The dried membranes were cured at 100 °C for 0.5 h. The optimal modification conditions were determined by varying different modification parameters, such as APTMS treatment temperature, APTMS concentration, APTMS treatment time, and FS10 treatment time.

3.2.4. Membrane characterizations

The dimension of the hollow fiber membranes was measured by a Keyence VHX 500F Digital Microscope. Three different fibers were taken and a mean value was calculated for each sample measurement. To observe the morphology of PAI hollow fiber membranes, the membrane samples were broken in liquid nitrogen and then sputtered with a thin layer of gold using EMITECH SC7620 sputter coater. The cross-section and outer surface of the hollow fiber membranes were examined using a Zeiss EVO 50 Scanning Electron Microscope (SEM). Images were obtained using an accelerating voltage 20 kV.

Pure water permeability (PWP) and molecular weight cut-off (MWCO) were performed to characterize the as-spun PAI membranes. Every membrane module consisted of four fibers with an effective length of 25 cm. The experiment was carried out in a cross flow filtration set up. Mili-Q ultrapure water was circulated to test the pure water flux at a constant pressure of 14.7 psi (1 bar). PWP was measured after 1

hour of starting the test to eliminate the influence of membrane compaction on flux measurement.

The membrane pore size was assessed by MWCO. The MWCO of asymmetric hollow fiber membranes is defined as the molecular weight at 90% rejection. It was tested using a 2000 ppm dextran aqueous solution with molecular weight ranging from 1,500 to 400,000 Da. The gel permeation chromatography (GPC) on a Polymer Laboratories-GPC 50 plus system was used to determine the dextran molecular weight distribution in feed and permeate solutions. The detailed procedure was described elsewhere (L. Shi, et al., 2007).

The membrane porosity, ε_m , is defined as the volume of the pores divided by the total volume of the membrane. It is usually determined by gravimetric method, measuring the weight of isopropyl alcohol (IPA, analytical grade from VWR Co Ltd) contained in the membrane pores:

$$\varepsilon_m = \frac{(\omega_1 - \omega_2) / D_i}{(\omega_1 - \omega_2) / D_i + \omega_2 / D_p} \quad (13)$$

where ω_1 is the weight of the wet membrane; ω_2 is the weight of the dry membrane; D_i is the isopropyl alcohol density; D_p is the polymer density.

The mechanism of chemical modification was confirmed by ATR-FTIR. The spectra were collected at room temperature with a total of 45 scans performed over a scanning range of 650–4000 cm^{-1} with a resolution of 4.0 cm^{-1} , using an IR Presitige-21 FT-IR (Shimadzu, Japan). The spectrometer was installed with a deuterated triglycine sulphate doped with L-aniline (DLATGS) detector and KBr beamsplitter. Spectral analysis was performed using FT-IR software (IR Solution, Shimadzu).

A tensiometer (DCAT11 Dataphysics, Germany) was used to perform the dynamic contact angle measurement to determine the hydrophobicity of the fibers. A sample fixed by the sample holder was hung from the arm of an electro-balance, and then it experienced three cycles of immersion into DI water and successive emersion. The contact angle was calculated from the wetting force based on the Wihelmy method.

The membrane mechanical property was measured by a Zwick 0.5 kN Universal testing machine. The sample was clamped at the both ends and pulled in tension at constant elongation velocity of 50mm/min. Tensile modulus and strain at break were tested to indicate the membrane's mechanical strength and the degree of deformation that could be expected under a given load. The test was carried out at room temperature and 75% humidity.

Liquid entry pressure of water (LEP_w) was tested to measure the membrane wetting resistance. Distilled water was pumped to the lumen side of the dried hollow fiber membrane and the pressure was increased gradually. The pressure at which the first droplet of water appeared on the outer surface of membrane was recorded as LEP_w , which was the minimum pressure required to drive water through the membrane pore.

3.2.5. GLMC test

The modified PAI hollow fiber membranes were subjected to a preliminary study in a GLMC for CO₂ absorption. A PTFE membrane contactor module was made to test the CO₂ absorption flux of the modified PAI membranes. For each sample, at least two membrane contactor modules were tested to ensure the results were consistent. The characteristics of the membrane contactor modules are given below as in Table 3.2.

Table 3.2. Characteristics of the membrane contactor module

Module ID (mm)	6.4
Module length (cm)	25
Fiber OD (mm)	1.4
Fiber ID(mm)	1.1
Effective fiber length (cm)	17
Contact area (cm ²)	15
Number of fibers	2

Pure CO₂ was employed as the feed gas and the distilled water/ 2 M sodium taurinate aqueous solution were used as the liquid absorbents in order to measure the CO₂ absorption flux. The liquid passed through the shell side and the gas flowed counter-

currently through the lumen side of the hollow fibers, as the hydrophobic layers of the modified membranes were in the outer surfaces. In a typical experiment, a digital variable flow peristaltic pump (MasterFlex) was used to control the liquid flow and pumped the liquid into the shell side of the hollow fibers from a 10L container. The pressures at the inlet and the outlet of the shell side were recorded. The liquid flow rate was also checked at the outlet at regular intervals. The feed gas was introduced into the system from a compressed gas cylinder and the flow rate was adjusted by mass flow controllers (Cole-Parmer). The gas pressures were indicated by the pressure gauges at the lumen inlet and outlet. The gas volume flow rates at the inlet and the outlet of the module were measured by digital bubble meters (Bios Defender 510L). The CO₂ flux was calculated by the difference of CO₂ flow rate before and after the membrane module. The system was completely stabilized for at least one hour before testing the CO₂ flow rate. CO₂ flow rate was recorded after the bubble meter readings were being stabilized and the average of all the stabilized flow rate readings was only used to calculate the CO₂ flux. The system is schematically shown in Figure 3.2.

Figure 3.2. Experimental setup of the GLMC for CO₂ absorption

3.3. Results and Discussion

3.3.1. Characterizations of the as-spun PAI hollow fiber substrates

The cross section morphologies of the as-spun PAI-A and PAI-B hollow fiber membranes are shown in Figure 3.3. It can be seen that both PAI-A and PAI-B hollow

fibers exhibited finger-like structures which were developed simultaneously beneath the inner and outer surfaces of the fibers. The properties of PAI hollow fiber substrates in terms of dimension, PWP, MWCO and porosity are listed in Table 3.3. It shows that both the PAI-A and PAI-B membranes fall in the category of UF membranes. These two hollow fiber membranes exhibited high water flux and small MWCO which suggested a narrow pore size distribution, as compared to the other UF membranes reported in literature that were used in membrane contactors (Atchariyawut, et al., 2006; L. Shi, R. Wang, & Y. M. Cao, 2009). A higher polymer concentration was used for fabricating PAI-B membranes. Increasing in polymer concentration would result in a higher viscosity of the dope solution (L. Shi, et al., 2007), and tended to delay the dope precipitation rate by slowing down the solvent non-solvent exchange process, leading to a denser and thicker skin layer (Bakeri, et al., 2010). Figure 3.3 showed the skin layer thickness of PAI-A and PAI-B was 4.2 μm and 5.6 μm , respectively. Therefore, it was observed that PAI-B showed a lower flux and smaller MWCO as compared to PAI-A. On the other hand, both PAI-A and PAI-B exhibited a high porosity larger than 80%, which was favorable for reducing the mass transfer resistance of the membrane when it was used in the membrane contactor after surface modification. The PAI-A was used as the model substrate for the surface modification to identify the optimized modification conditions, which will be discussed later.

Figure 3.3. Cross section morphology (enlarged at 300X) of (a) PAI-A hollow fiber membrane and (b) PAI-B hollow fiber membrane.

Table 3.3. Properties of the as-spun PAI membranes

Properties	PAI-A	PAI-B
Outer diameter (mm)	1.38	1.43
Inner diameter (mm)	1.05	1.10
Fiber wall thickness (μm)	165	165
Pure water flux ($\text{L}/\text{m}^2 \text{ h bar}$)	125	90
MWCO (kDa)	34	20
Porosity (%)	85	83

3.3.2. Reaction mechanisms of the surface modification

The chemical structures of the original PAI-A membrane before and after the APTMS modification were examined by ATR-FTIR, as illustrated in Figure 3.4 (a). For the original membrane, the typical imide transmission bands were observed at 1778 cm^{-1} (symmetric C-O stretching), 1719 cm^{-1} (asymmetric C-O stretching) and 1379 cm^{-1} (C-N-C stretching). As the chemical reaction progressed, the transmission peaks of the imide bands gradually diminished. The peaks of the 1778 cm^{-1} and 1719 cm^{-1} disappeared altogether after 1 hour APTMS modification. On the other hand, the amide peaks 1644 cm^{-1} (C=O stretching) and 1547 cm^{-1} (C-N stretching) became stronger gradually. This indicated that the imide rings were opened and transformed into amide bonds, which confirmed that the modification reaction by APTMS had taken place effectively. Moreover, the peaks due to O-H stretching variations occurred in the regions of 3200 cm^{-1} to 3600 cm^{-1} became boarder with the increase of APTMS treatment time, which suggested the successful imparting of hydroxyl groups onto the PAI surface. Figure 3.4 (b) shows the typical transmission bands of the original PAI, FS10 and APTMS-FS10 modified PAI membranes. It can be observed that APTMS-FS10 modified membranes showed transmission bands at 1708 cm^{-1} , 1195 cm^{-1} and 1086 cm^{-1} , which are the peaks associated with the pure FS10. 1708 cm^{-1} could be due to the C=O stretching that appears in the FS10. 1195 cm^{-1} and 1086 cm^{-1} are in fingerprint region. They could be attributed to the C-F and Si-O-Si stretching. The results indicated that the FS10 was successfully grafted onto the membrane surface.

Figure 3.4. ATR-FTIR spectra of (a) PAI-A membranes modified by APTMS with different modification time; (b) PAI-A membranes modified by APTMS-FS10 with different APTMS modification time

Based on the ATR-FTIR spectra of the original PAI membrane, APTMS modified PAI membrane and APTMS-FS10 modified PAI membrane, the possible mechanisms of PAI membranes reacting with APTMS, and further reacting with FS10 could be deduced. As shown in Figure 3.5 (a), the APTMS compound was hydrolyzed first in the aqueous solution to form polysiloxane (Kathi & Rhee, 2008). The hydrolyzed APTMS have a chemical structure comprising both primary amine and hydroxyl functional groups, in which the amine functional group can react with the imide group from PAI. Figure 3.5 (b) shows the chemical reaction between the PAI and APTMS, which is confirmed by the ATR-FTIR spectra. It could be seen that after the reaction, the hydroxyl functional groups were imparted onto the membrane surface, which made the secondary treatment by FS10 possible. FS10 molecules were apt to chemically

bond to the hydroxyl sites (X. Yang, et al., 2011). The proposed reaction mechanism between the APTMS treated PAI membrane and FS10 is shown in Figure 3.5 (c).

Figure 3.5. Reaction mechanisms of (a) hydrolysis of APTMS; (b) reaction between PAI and APTMS; (c) grafting and crosslinking of FS10.

3.3.3. Optimal conditions of the surface modification

Optimal APTMS treatment temperature: The optimal APTMS treatment temperature was determined by varying the temperature from 50 °C to 70 °C using the PAI-A hollow fiber membranes as the model substrate while the ATPMS concentration was fixed at 2 % (wt/vol) and the treatment time was controlled at 1 h, followed by the FS10 grafting and crosslinking at 60 °C for 2 h. The temperature effect on the mechanical property and surface hydrophobicity of the modified PAI-A membrane were listed in Table 3.4. It can be seen that the tensile modulus of the membrane increased significantly with the temperature increased. A high tensile modulus suggests a high rigidity of the membrane. The strain at break (ductile behavior) of the membrane dropped continuously. When the temperature increased to 70 °C, the strain at break was very low, indicating the membrane became very brittle due to the harsh reaction condition. On the other hand, the contact angle increased dramatically from original 76° to 112° at 50 °C APTMS treatment. It increased further to 117° when the temperature increased to 60 °C. The increase in contact angle was because of the presence of the perfluoro-compound FS10 layer on the membrane surface. In addition, the contact angle of the modified membrane at 60 °C was similar with that of the membrane treated at 70 °C. Therefore, the APTMS treatment temperature of 60 °C was selected as an optimal condition applied for the treatment of PAI hollow fiber substrates.

Table 3.4. Effect of APTMS treatment temperature on the modified PAI-A membrane properties*

APTMS treatment temperature (°C)	Tensile modulus (MPa)	Strain at break (%)	Dynamic contact angle (2 nd cycle)
-	86 ± 4.7	31.1 ± 0.8	76
50	97.7 ± 0.5	27.1 ± 0.5	112
60	108.5 ± 6.5	21.2 ± 0.7	117
70	101.1 ± 7.9	12.1 ± 1.8	118

*Modification condition: 2 % (wt/vol) APTMS solution for 1 h, followed by 1 wt% FS10 solution for 2 h at 60 °C

Optimal APTMS concentration: In order to determine the optimal APTMS concentration, three APTMS solutions with APTMS 0.5 %, 2 % and 5 % (wt/vol) in a mixture of IPA/DI water (vol 1:1) were prepared. The results of modified PAI-A membrane are showed in Table 3.5. As observed, the tensile modulus increased after the modification, indicating the modified membrane became more rigid, while the strain at break decreased with the increase in APTMS concentration. The contact angle increased considerably after the modification. Surprisingly at 5 % (wt/vol) APTMS, the contact angle was even less than that of 0.5 % (wt/vol) and 2 % (wt/vol) treated membranes. This was possibly because of the self-condensation of APTMS in the aqueous solution due to the high concentration, which may hinder the reaction between the amine group and PAI. Therefore, the APTMS solution with 2 % (wt/vol) was selected for the modification.

Table 3.5. Effect of APTMS concentration on the modified PAI-A membrane properties*

APTMS concentration (% wt/vol)	Tensile modulus (MPa)	Strain at break (%)	Dynamic contact angle (2 nd cycle)
0.0	86 ± 4.7	31.1 ± 0.8	76
0.5	111.5 ± 3.5	23.3 ± 2.0	107
2.0	108.5 ± 6.5	21.2 ± 0.7	117
5.0	108.5 ± 5.5	28.3 ± 0.8	105

*Modification condition: APTMS solution at 60 °C for 1h, followed by 1 wt% FS10 solution for 2 h at 60 °C

Optimal APTMS modification time: Optimal APTMS modification time was determined by using the as-spun PAI-A hollow fibers under the treatment of APTMS for varied period of time. Table 3.6 shows the effect of different APTMS modification time on the properties of the modified PAI-A membranes. With the APTMS modification reaction progressed, the modified PAI-A membranes presented higher tensile modulus. On the other hand, the strain at break continuously decreased with the modification time. In other words, the modified membranes exhibited more rigidity property but less ductile ability compared to the original membrane. Moreover, it was

observed that that with a longer modification time by APTMS, the contact angle became higher. This was because more reaction sites (hydroxyl groups) were generated on the PAI membrane surface, and hence more FS10 molecules were able to graft and crosslink, leading to a higher hydrophobicity.

Table 3.6. Effect of APTMS modification time on the modified PAI-A membrane properties*

Membrane Code	Tensile modulus (MPa)	Strain at break (%)	Dynamic contact angle (2 nd cycle)
PAI-A	86 ± 4.7	31.1 ± 0.8	76
PAI-A#1 (0.5 h APTMS treated)	98 ± 2.0	24.8 ± 2.3	108
PAI-A#2 (1 hr APTMS treated)	108.5 ± 6.5	21.2 ± 0.7	117
PAI-A#3 (2 h APTMS treated)	141 ± 12.0	13.4 ± 4.1	118

*Modification condition: 2 % (wt/vol) APTMS solution at 60 °C, followed by 1 wt% FS10 solution for 2 h at 60 °C

Based on the previous ATR-FTIR results, it was known that the imide groups on the membrane surface were fully consumed around 1 h APTMS modification. Further modification had no significant effect on the surface hydrophobicity. Moreover, prolonged modification also imposed an adverse effect on the membrane mechanical property. Thus, it is concluded that APTMS modification time ranging from 0.5 to 1 h are appropriate for PAI hollow fiber membranes by considering these factors.

The PAI-A hollow fiber membrane after the 2 % (wt/vol) APTMS modification at 60 °C for 1 h was used to investigate the effect of different FS10 treatment time, e.g. 2 h, 6 h, and 24 h. The membrane treated with FS10 for different duration showed similar contact angle ranging from 117° to 119° and similar mechanical properties as well. This was because the FS10 treatment was just grafting and crosslinking FS10 molecules at the APTMS treated membrane surface, without the reaction with polymer matrix. The amount of FS10 that could be reacted depended on the hydroxyl groups available on the membrane surface which were generated from APTMS treatment step. Therefore, 2 h was selected as the optimal FS10 modification time. Further treatment

may increase the thickness of FS10 layer on the membrane surface, leading to an increase of mass transfer resistance.

3.3.4. PAI membrane properties after the surface modification

The modified membranes were observed by SEM. Figure 3.6 displays the morphology observations of the cross-section and outer surface of the original and the APTMS-FS10 modified PAI-B membrane based on 1 h APTMS modification. The modified PAI-B with 0.5 h APTMS modification showed the similar morphology. In addition, the SEM images of the modified PAI-A look similar. It can be seen that there was no visible difference on the cross-section morphology for the modified and unmodified membranes. The porous structures under the dense skin layer remained integrity after modification. However, the difference in the outer surface morphology for modified and unmodified membranes can be observed. The original membrane surface was very smooth. After modification, the surface morphology was altered and became much rougher. It was possible that the membrane surface was covered by a thin layer of APTMS and FS10.

Figure 3.6. Membrane cross section morphology (a) before and after the modification* (enlarged at 300X) and outer surface morphology (b) before and after the modification (enlarged at 1000X) and (c) before and after the modification (enlarged at 10,000X) (*PAI-B: APTMS 2 % (wt/vol) at 60 °C for 1 h, followed by 1 wt% FS10 solution for 2 h at 60 °C)

The mechanical properties, porosity, contact angle and LEP_w of the modified PAI-A and PAI-B membranes are summarized in Table 3.7. Overall, the modified membranes showed enhanced rigidity but weaker ductile properties. It is worth mentioning that although there was no significant difference on cross section structure from SEM image in Figure 3.6, the mechanical property changed which could be due to the diffusion of the modification reagents into the membrane substrate and reacted with the bulk matrix. The membrane porosity decreased after the surface modification. A longer modification time rendered a lower porosity. This was due to the diffusion of APTMS and FS10 macromolecules into the membrane pores which restricted some of the big pores and blocked off some of the small pores during the modification process. Similar phenomenon was reported elsewhere (Ba, Langer, & Economy, 2009). PAI-A#2 and PAI-B#2 presented a much higher LEP_w than PAI-A#1 and PAI-B#1, because PAI-A#2 and PAI-B#2 experienced longer modification time, which led to higher hydrophobicity and denser skin layers. As a result, it is expected that PAI-A#2 and PAI-B#2 membranes would be less vulnerable to pore-wetting but have correspondingly lower CO_2 flux as compared to PAI-A#1 and PAI-B#1 membranes in the membrane contactor experiments.

Table 3.7. Mechanical properties, porosity and LEP_w of the APTMS-FS10 modified membranes

Membrane category	Tensile modulus (MPa)	Strain at break (%)	Porosity (%)	Dynamic contact angle (2 nd cycle)	LEP_w (bar)
PAI-A	86 ± 5	31.1 ± 0.8	85	76	0.7

PAI-B	182 ± 4	28.6 ± 0.3	83	76	0.8
PAI-A#1 (0.5 h APTMS treated)	98 ± 2	24.8 ± 2.3	78	108	2.1
PAI-A#2 (1 h APTMS treated)	109 ± 7	21.2 ± 0.7	72	117	3.7
PAI-B#1 (0.5 h APTMS treated)	199 ± 15	24.5 ± 0.2	73	110	2.7
PAI-B#1 (1 h APTMS treated)	259 ± 7	22.4 ± 1.9	67	117	4.0

3.3.5. Preliminary study of the modified PAI hollow fiber membranes used in GLMC for CO₂ absorption

The modified membranes were subjected to a preliminary study that used as a membrane contactor for CO₂ absorption, and the results are shown in Figure 3.7. It can be seen that the CO₂ flux increased with the increase in liquid velocity. This was because when the distilled water was supplied at a higher speed, the consumed water was replaced by more fresh water, resulting in a lower CO₂ concentration in the liquid phase. Thus, the driving force for CO₂ transfer was increased, leading to a higher CO₂ absorption flux. This is a well-recognized behavior of membrane contactors, which implies the mass transfer resistance mainly exists on the liquid side in the case of physical CO₂ absorption.

Figure 3.7. CO₂ absorption flux of the modified PAI membranes (pure CO₂- distilled water system, atmospheric pressure, absorbent temperature at 25 °C, gas velocity at 0.06 m/s)

It was observed that the CO₂ absorption performance was in sequence of the modified PAI-A > modified PAI-B (PAI-A#1>PAI-B#1; PAI-A#2>PAI-B#2) with respect to the same order of water permeation flux and MWCO of the as-spun PAI-A and PAI-B membranes. Membranes prepared with different dope solutions and spinning conditions showed different substrate performances, would in turn to affect CO₂ absorption performance of the modified membranes. In addition, although the modified PAI-B showed smaller CO₂ absorption flux, they exhibited stronger anti-wetting resistance which was reflected by LEP_w values. Furthermore, the CO₂ absorption flux of PAI-A#1 was obviously higher than that of PAI-A#2, and this was because PAI-A#2 experienced a longer modification time, which resulted in higher hydrophobicity and a denser top layer. This result was consistent with the change in LEP_w as discussed in Table 3.7. In addition, PAI-B#1 and PAI-B#2 membranes showed the similar trend.

Table 3.8 shows the comparison of LEP_w and CO₂ absorption flux of the current modified PAI-A#2 and PAI-B#2 with the membranes reported by different groups in literature at the liquid velocity of 0.3m/s. At liquid velocity of 0.3m/s, PAI-A#2 showed a high CO₂ absorption flux of 8.5×10^{-4} mol/m²·s, while PAI-B#2 showed the flux of 6.4×10^{-4} mol/m²·s. Atchariyawut et al. tested both in-house made PVDF membranes (Atchariyawut, et al., 2006) and commercial PVDF membranes (Atchariyawut, Jiratananon, & Wang, 2008) for the absorption of pure CO₂ with water. The absorption results of both PVDF hollow fibers were similar to that of the PAI-A#2 and PAI-B#2 membranes, respectively. However, the PAI-A#2 and PAI-B#2 exhibited much higher hydrophobicity than PVDF membranes. Mansourizadeh et al. (Mansourizadeh & Ismail, 2010) reported the CO₂ absorption performance of polysulfone (PSf) membranes with different additives. Among those membranes, PSf with glycerol showed the best performance with LEP_w of 4 bar and the CO₂ absorption flux of 7.5×10^{-4} mol/m²·s at V_{liquid} of 0.3m/s. This result is similar to that of the PAI-B#2 membrane developed in the current study. Moreover, Bakeri et al. (Bakeri, et al., 2010) studied the CO₂ absorption flux of PEI hollow fiber membranes. The flux of PEI membrane with 10 wt% PEI concentration showed a high flux of 1.6×10^{-3} mol/m²·s. However, the wetting resistance of this type of membrane seems to be low, as

indicated by its LEP_w which was only 0.7 bar. In summary, both the PAI-A#2 and PAI-B#2 membranes exhibited higher or equivalent hydrophobicity and good CO_2 absorption flux compared to other membranes used in the membrane contactors.

Table 3.8. Comparison of LEP_w and CO_2 flux of various membranes used as GLMC

Membrane	ID/OD (mm)	Porosity (%)	LEP_w (bar)	CO_2 flux ^a (mol m ⁻² s ⁻¹)	Shell side	Manufacturer	Ref.
PAI-A#2	1.1/1.4	72	3.7	8.5×10^{-4}	Water	In-house made	Current work
PAI-B#2	1.1/1.4	67	4	6.4×10^{-4}	Water	In-house made	Current work
PVDF	0.3/0.4	76	NA	1.0×10^{-3}	Water	In-house made	(Atchariyawut, et al., 2006)
PVDF	0.65/1	75	NA	6.5×10^{-4} (extrapolated)	CO_2	Memcor Australia	(Atchariyawut, et al., 2008)
PSf	0.5/1	72	4	7.5×10^{-4}	CO_2	In-house made	(Mansourizadeh & Ismail, 2010)
PEI	0.5/0.8	87	0.7	1.6×10^{-3}	CO_2	In-house made	(Bakeri, et al., 2010)

a. Achieved at liquid velocity of 0.3 m/s.

A long-term CO_2 absorption experiment of PAI-B#2 was conducted for 42 days. 2 M sodium taurinate and pure water were used as the liquid absorbent respectively. Testing of the membrane contactor was carried out periodically to observe the change in CO_2 absorption flux. The membrane contactor module was fully immersed in the liquid absorbents after every experiment to ensure that the outer surfaces of the hollow fibers would be in constant contact with the absorbent. The results are shown in Figure 3.8. The CO_2 absorption flux obtained using both liquid absorbents were stable throughout the running period. This was attributed to the crosslinked dense layer FS10 on the membrane surface, which offered the high hydrophobicity and prevented the membrane substrate from direct contact with the liquid absorbent, leading to a good anti-wetting ability and long-term stability of the modified PAI membranes in a membrane contactor.

Figure 3.8. Long-term performance of the PAI-B#2 in GLMC over 42 days (atmospheric pressure, absorbent temperature at 25 °C, gas velocity at 0.06 m/s, liquid velocity at 0.15 m/s)

3.4. Conclusions

This study provides a simple and effective way to make hydrophobic PAI porous hollow fiber membranes. Asymmetric PAI hollow fiber membranes were fabricated by a non-solvent induced phase inversion process, followed by the surface hydrophobic modification. The following conclusions are drawn from the experimental results.

- Surface hydrophobic modification on the PAI membrane is feasible with the pretreatment of APTMS, which can impart the hydroxyl groups onto the membrane surface, and makes the membrane chemically reactive to the perfluoro-compounds FS10. The reaction mechanisms were proposed based on the FTIR-ATR experiments.
- The optimal modification conditions were investigated using two as-spun PAI substrates by varying different modification parameters, including temperature of APTMS treatment, APTMS concentration, APTMS treatment time and FS10 treatment time. It was found the optimal modification condition was obtained at 2 % (wt/vol) APTMS treatment at 60 °C for 1 h, followed by grafting and crosslinking of 1 wt% FS10 at 60 °C for 2 h.

- The newly developed PAI hollow fiber membranes showed much higher hydrophobicity (improved from 76° to $108 \sim 117^\circ$) and critical water entry pressure (improved from 0.8 bar to 2.1 ~4.0 bar). The results suggest that the modified PAI membranes tend to be highly pore-wetting resistant.
- A preliminary study of CO₂ absorption test indicates the modified PAI membranes presenting reasonably high CO₂ absorption flux compared to the membranes reported in the literature. A long-term membrane contactor performance for CO₂ absorption over 42 days was attained.
- PAI can be used as the membrane material for membrane contactor application although it is not a hydrophobic polymer. This is realized by the novel surface hydrophobic modification approach presented in this study.

CHAPTER 4

Novel Single-Step Hydrophobic Modification of PAI Hollow Fiber Membranes

4.1. Introduction

It is well known that both fluoro-compounds and long-chain alkyl groups as the low surface energy compounds can generate hydrophobic surface (X. M. Li, et al., 2007; Mecinović, et al., 2011; Nishino, et al., 1999; X. Zhang, et al., 2008). In the previous study, we have explored the hydrophobic modification of PAI hollow fiber membranes by a perfluoro-compound (Fluorolink[®]S10, FS10) through silane chemistry. The modified membranes showed greatly enhanced hydrophobicity and promising GLMC performance for CO₂ absorption. As a continuation of hydrophobic modification of PAI membrane, in this session, we demonstrated a modification method using an amine compound terminated with a long alkyl chain, e.g. octadecylamine, as the modification reagent to generate long alkyl chains onto the PAI membrane surface and over the cross section to enhance the membrane hydrophobicity. The modification conducted in this study was a single step treatment, differentiating from the previous work which involved two-step chemical modification. Thus, the new method was more convenient and easier to handle and operate as compared to the previous work. The membranes were observed by Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM). The chemical modification mechanism was examined by Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), and the modified membranes were characterized in terms of contact angle, mechanical strength, membrane porosity and liquid entry pressure (LEP_w). Preliminary tests of modified membrane used in the membrane contactor for CO₂ absorption were conducted.

4.2. Experimental

4.2.1. Materials

Octadecylamine ($C_{18}H_{39}N$, CAS#124-30-1, Acros) was used as a membrane surface modification agent. Other materials have been described in Chapter 3 Section 3.2.1. All the reagents were used as received. The chemical structure of octadecylamine is given in Figure 4.1.

Figure 4.1. Scheme of the PAI hydrophobic modification by Octadecylamine

4.2.2. PAI membrane preparation

The asymmetric hollow fiber membrane substrates were fabricated by a dry-jet wet spinning technique. Dope preparations and membrane spinning process can be found in Chapter 3 Session 3.2.2. The spinning conditions were summarized in Table 4.1.

Table 4.1. Spinning conditions and parameters.

Parameters	PAI
Dope composition (PVDF/LiCl/NMP)(wt%)	14/3/83
Dope flow rate (g/min)	6.0
Bore fluid (NMP/H ₂ O) (vol%)	25/75
Bore fluid flow rate (ml/min)	7.0
Air gap (cm)	10

Take up speed	free fall
External coagulant	tap water
Spinning temperature (°C)	23
Spinneret diameter (mm)	1.50
ID of bore fluid needle (mm)	0.70

4.2.3. Membrane modification

The as-spun membranes were immersed into a 2 % (wt/vol) octadecylamine in a mixture of IPA and distilled water (vol 1:1) in a water bath at 60 °C for different time varying from 0 to 60 min. The modified membranes were then rinsed several times with IPA, and dried in fume hood for future use.

4.2.4. Membrane characterizations and GLMC test

The as-spun membrane samples were observed by digital microscope, SEM, and characterized in terms of PWP, MWCO. The procedures have been described in Chapter 3 Section 3.2.4. The chemical modification of the PAI substrates was confirmed by ATR-FTIR spectrum, as introduced in Chapter 3 Section 3.2.4.

The membrane surface morphology and roughness were analyzed by AFM XE-100 (Park System). The membrane surfaces were imaged in a scan size of 2 μm $\times$ 2 μm . The surface roughness parameters of the membranes which are expressed in terms of the mean roughness (R_a), and the root mean square of the Z data (R_q). The mean difference between the five highest peaks and lowest valleys (R_z) were calculated from AFM images using tapping mode method.

The overall membrane porosity, mechanical stability, dynamic contact angle and LEP_w were tested for the PAI hollow fiber membranes before and after modification. The detailed characterizations information has been described in Chapter 3 Section 3.2.4.

The modified PAI hollow fibers were tested in a GLMC to measure the CO_2 absorption flux by using water and 2 M sodium taurinate as the absorbents and pure

CO₂ as the feed gas. The membranes were assembled into the PTFE modules. The membrane contactor module characteristics are shown in Table 4.2. The liquid passed through the shell side and the gas flowed counter-currently through the lumen side of the hollow fibers, as the hydrophobic layers of the modified membranes were in the outer surfaces. The detailed experimental setup and procedures have been described in Chapter 3 Section 3.2.5.

Table 4.2. Characteristics of the membrane contactor module

Module ID (mm)	7.4
Module length (cm)	25
Fiber OD (mm)	1.4
Fiber ID(mm)	1.1
Effective fiber length (cm)	18.5
Effective contact area (cm ²)	33
Number of fibers	4

4.3. Results and discussion

4.3.1. Properties of the as-spun PAI hollow fibers

The as-spun membranes were used as the substrates for the chemical modification. The properties of the PAI hollow fiber membranes in terms of dimension, PWP, MWCO and porosity are listed in Table 4.3. The PAI membrane demonstrated superior performance with PWP of 178 L/m²·hr·bar and the MWCO of 19 kDa, which suggested the skin layer was highly permeable with small pore sizes as well as a narrow pore size distribution, comparing to the other UF membranes reported in literature that are used in membrane contactors (Atchariyawut, et al., 2006; L. Shi, et al., 2009).

Table 4.3. Properties of the as-spun PAI substrates

Properties	PAI
Fiber OD (mm)	1.4
Fiber ID (mm)	1.1

Fiber wall thickness (μm)	150
Pure water flux ($\text{L}/\text{m}^2 \text{ h bar}$)	178
MWCO (kDa)	19
Porosity (%)	83

4.3.2. Confirmation of the chemical modification

Figure 4.2 showed the ATR-FTIR spectra of the modified PAI membranes with different treatment time. For the original PAI membrane, the typical transmission bands were observed at 1778 cm^{-1} (symmetric C-O stretching, imide I), 1719 cm^{-1} (asymmetric C-O stretching, imide I) and 1360 cm^{-1} (C-N-C stretching, imide II). As the chemical reaction progressed, the transmission peaks of the imide I bands and imide II bands gradually diminished. The peaks of the imide I disappeared altogether after 20 min modification. On the other hand, the amide peaks 1644 cm^{-1} (C=O stretching) and 1532 cm^{-1} (C-N stretching) became stronger gradually. This indicated that the imide rings were opened and transformed into amide bonds, which confirmed that the modification reaction by octadecylamine had taken place effectively. Moreover, the peak in the range of $2700\text{-}3000 \text{ cm}^{-1}$ due to alkane C-H stretch increased gradually, indicating the successful reaction between octadecylamine and the PAI membrane.

Figure 4.2. ATR-FTIR spectra of the modified PAI membranes with different modification time.

The reaction mechanism between imide from PAI and amine from octadecylamine is shown in Figure 4.1, which was proved by the ATR-FTIR spectra. It can be seen that the imide sites in PAI membrane were opened and grafted by alkyl chains containing 18 carbons, which provided a higher hydrophobic polymer backbone. Moreover, those long chains may entangle each other to prevent the membrane pores away from the external liquids.

4.3.3. Membrane morphology observation and surface roughness analysis

The original and selected modified PAI membranes were observed by SEM. Figure 4.3 displays the morphology observations of the cross-section, skin layer and outer surface of the membranes. It can be seen that there was no visible difference on the cross-section morphology for the original and the membrane with 10 min and 30 min modification time. However, when the reaction increased to 60 min, the cross-section structure integrity was deteriorated, due to the overlong reaction that significantly damaged the polymer chains. The change of the skin layer was also observed with 60 min modification. It is clear that with the reaction progressed; the skin layer defined by the distance between the top surface to the most upper side of the macrovoids became progressively thinner. At 60 min, the membrane skin layer was completely destroyed with finger pores directly exposing to the surface, as shown in Figure 4.3 (d). The reason for the reduction of the skin layer thickness and pore opening can be explained by the mechanism proposed by Santoso et al. (Santoso, et al., 2003). Santoso et al. studied the modification process of PEI membrane by various types of aminic modifiers, and found that only amines with aliphatic compounds showed strong pore opening effect and high functionalization degree, while some other modifiers, like aromatic amines, and amines connected to other functional groups such as carboxylic acid, sulphonic acid exhibited no degradative feature. They proposed the reaction mechanism between the PEI membrane and the aliphatic amine modifier as a two-step sequence. In the first step, where functionalization process dominates, the imide ring is opened and transformed into amide without interfering and breaking the polymer chain. In the second step, with the reaction progressing, the polymer functionalization and degradation occur simultaneously resulting in an equilibrium state (Santoso, et al., 2003). Thus, the pore opening and the reduction of the skin layer thickness should be

most probably attributed to the degradation process that accounted for the breaking of the polymer chains.

Figure 4.3. SEM images of membrane cross section, skin layer and surface of the selected PAI hollow fibers (a) original (b) 10 min modified (c) 30 min modified and (d) 60 min modified

Figure 4.4 demonstrates the two- and three-dimensional surface AFM images of the membrane before and after modification at a scan size of $2\ \mu\text{m} \times 2\ \mu\text{m}$. In these AFM images, the bright area indicates the high region of the membrane surface and the dark part presents the valley or membrane pores. It can be seen that the surface morphologies of the membrane were influenced greatly by the modification process. The membrane topography details were further represented by the line profiles, and their changes can be seen clearly. The small perks in the original membranes diminished and gradually turned to a bump-like profile. The surface roughness parameters of the membranes were calculated at a scan size of $2\ \mu\text{m} \times 2\ \mu\text{m}$ by AFM software and presented in Table 4.4. The roughness parameters in terms of R_a , R_q and R_z of the PAI hollow fiber membrane surfaces increased with the time of octadecylamine treatment.

Figure 4.4. 3-D structure, topography AFM images and line profiles of the selected PAI membranes (a) original (b) 10 min modified (c) 30 min modified and (d) 60 min modified.

Table 4.4. Surface roughness parameters of the selected PAI membranes before and after modification

Modification time (min)	Roughness		
	R_a (nm)	R_q (nm)	R_z (nm)
0	0.409	0.471	1.328
10	0.882	1.126	2.650
30	1.555	1.902	3.643
60	3.872	3.394	10.086

4.3.4. Characterizations of the modified PAI hollow fiber membranes

The mechanical property is a very important parameter for membrane practical applications. The tensile modulus, tensile strength and strain at tensile strength of the original and modified PAI membranes are shown in Table 4.5. Tensile modulus was

calculated based on the combination of tensile strength and strain at the tensile strength. A high tensile modulus suggests a high rigidity of the membrane. It can be seen that with modification reaction progressed, the membrane rigidity increased up to 20 min and decreased during the further modification process. The tensile strength, strain at tensile strength decreased gradually after the modification, indicating the membrane became less rigid and more brittle due to the polymer chain interference by the amine modifier. At 40 min modification time, those parameters decreased to a relatively low level. This was due to the over longed reaction time which resulted in breaking of polymer chains and hence deteriorated the membrane structure. Therefore, it was suggested 30 min could be the maximum appropriate modification time.

Table 4.5. Mechanical properties and contact angles of the modified PAI membranes.

Modification time (min)	Tensile modulus (MPa)	Tensile strength (MPa)	Strain at tensile strength (%)	Contact angle (2 nd cycle)
0	114.6 ± 4.0	9.0 ± 0.1	43.8 ± 0.5	75.6 ± 2.4
5	126.3 ± 6.6	9.1 ± 0.2	34.0 ± 2.0	87.5 ± 1.7
10	141.0 ± 8.4	8.4 ± 0.2	19.3 ± 1.0	98.0 ± 2.0
20	150.2 ± 5.5	7.1 ± 0.7	9.2 ± 0.5	105.3 ± 0.8
30	119.5 ± 3.7	6.0 ± 0.2	5.6 ± 0.3	107.6 ± 1.2
40	72.5 ± 3.8	2.5 ± 0.1	2.6 ± 0.1	108.3 ± 1.5
60	49.4 ± 2.7	0.8 ± 0.1	1.5 ± 0.1	106.5 ± 2.3

Octadecylamine is a type of aliphatic aminic modifier. As can be seen from its chemical structure, it composes of an alkyl chain of 18 carbons and an amine functional group at the end. The long carbon chain ensures the hydrophobic character of this compound. Table 4.5 gives the data of membrane contact angles. In general, the contact angle of 1st cycle is the highest, and in 2nd and 3rd cycles, the contact angles are close to each other. This is because the membrane surface is dry before it is immersed in to the DI water in the first loop. Thus, the data of the 2nd and 3rd cycles are considered as the better characterization of the wetted membranes (L. Shi, et al., 2007). We therefore chose the 2nd cycle data to represent the hydrophobicity of the membranes. After the first 20 min of the modification, the membrane contact angle

increased significantly from 76 °to 105 °as the incorporation of long alkyl chains which were prone to repel water. The contact angle increased further to 108 °at 30 min modification time. After 30 min, the further modification had no much effect on the improvement of contact angle. This observation was consistent with the ATR-FTIR spectrum, which shows that the imide groups were fully consumed between 20 min to 30 min. Further treatment would influence the membrane bulk matrix rather than the surface hydrophobicity. Based on the results of mechanical stability and the contact angle measurement, it can be deduced that the best compromise in terms of the membrane mechanical stability and hydrophobicity, was obtained within the reaction time 10 min to 30 min.

The LEP_w results of the original membrane and the modified membrane between 10 min and 30 min are shown in Table 4.6. LEP_w is used to characterize the water resistant ability of the membranes. A higher LEP_w means a higher non-wettability. The original PAI membrane only presented a low LEP_w of 7 psi, which can be easily wetted during the operation of membrane contactor. After the modification, the LEP_w increased significantly and was further increasing with modification time due to the improved membrane surface hydrophobicity. On the other hand, as mentioned earlier, the octadecylamine treatment may result in a pore opening process which would have an adverse effect on the membrane wetting resistance. However, it was observed the LEP_w increased with modification time which suggested the effect of membrane hydrophobicity contributed more to the overall membrane LEP_w than that of pore enlargement in this case. This is because octadecylamine are single small molecules in an aqueous solution with flexible carbon chains entangling each other. They not only react with the membrane surface, but also can enter deeply into the membrane bulk matrix during the modification process. With the modification progressed, more and more long alkyl chains would graft on the membrane surface and anchor onto the membrane pore walls, which imposed strong resistance to the liquid phase, and hence, determined to the improvement of membrane wetting resistance.

Table 4.6. LEP_w and porosities of the original and selected modified PAI membranes

Modification time (min)	LEP _w (psi)	Porosity (%)
0	7.0 ± 1.5	83 ± 1.5
10	29.7 ± 3.3	65.8 ± 1.5
20	55.0 ± 2.5	73.0 ± 2.6
30	63.0 ± 2.7	79.2 ± 2.0

Porosities of the membrane before and after modification are also shown in Table 4.6. It can be seen that, initially, there was a significant drop of the membrane porosity from 83% to 65.8% for the 10 min modified PAI membranes. This was because the functionalization process dominated in this step, anchoring and grafting of octadecylamine molecules onto the membrane surface and bulk matrix took place without breaking the polymer chains. In addition, the porosity measured for the modified membranes was dry membrane porosity, while the as-spun PAI membranes were fully swollen by water. During the membrane drying process, PAI membranes experienced pore shrinkage which would be another factor contributing to the lower porosity. With the octadecylamine modification time increased, the functionalization was accompanied by the degradation process simultaneously; the polymer backbone was interfered and broke down by the aminic modifier, resulted in the pore opening and thinning down of the skin layer, and the degradation of polymer mass. Hence, the porosity increased gradually. The result was consistent with the SEM images which were discussed earlier.

4.3.5. Preliminary study of the modified PAI membranes used in GLMC test for CO₂ absorption

The modified membranes were subjected to the study that used as a membrane contactor for CO₂ absorption. The CO₂ absorption flux of the modified membrane is shown in Figure 4.5. It can be seen that the CO₂ flux increased with the increase in flow rate of the liquid absorbent. This is a well-known behavior in membrane contactor which indicates the main resistance exists in the liquid phase in the case of physical absorption of CO₂. It is worth mentioning that the CO₂ flux increased with

modification time which suggested an enlargement of membrane pore size with a longer treatment time. This was also consistent with the SEM images of the membrane pore opening and thinning down of the upper top skin layer after the modification, so that the mass transfer resistance became less and hence a higher CO₂ flux was achieved. The similar observation was reported in the literature (Chinpa, et al., 2010; Santoso, et al., 2003).

Figure 4.5. Effect of absorbent flow rate on the CO₂ flux of the modified PAI hollow fiber membranes (pure CO₂ -distilled water system, atmospheric pressure, absorbent temperature at 25 °C, gas velocity at 0.06 m/s)

A long-term CO₂ absorption experiment of the 20 min modified PAI membranes was conducted by using 2 M sodium taurinate as the liquid absorbent. Testing of the membrane contactor was carried out periodically to observe the change in CO₂ absorption flux. The membrane contactor module was fully immersed in the liquid absorbents after every experiment to ensure that the outer surfaces of the hollow fibers would be in constant contact with the absorbent. The results are shown in Figure 4.6. It was observed that the membrane showed a stable performance for the 15-day period. However, the CO₂ flux dropped significantly in the further tests. Comparing with the modified PAI membranes in Chapter 3 which showed a stable CO₂ absorption flux in GLMC around 40 days, the less stable performance of the octadecylamine modified PAI membranes was possibly attributed to the larger pore size and lower surface hydrophobicity. Moreover, the crosslinked FS10 dense layer was present on membrane substrate in our previous work (in Chapter 3). It would protect the membrane substrate

and prevent it from the direct contact with the liquid absorbent, which rendered a good anti-wetting ability and long-term stability of the FS10 modified PAI membranes.

Figure 4.6. Long-term study of the 20 min modified PAI membrane by using 2 M sodium taurinate as the liquid absorbent (atmospheric pressure, absorbent temperature at 25 °C, gas velocity at 0.06 m/s, liquid velocity at 0.1 m/s)

4.4. Conclusions

In the present study, a simple and inexpensive single-step modification method to prepare hydrophobic PAI hollow fiber membranes was developed using a long-chain alkyl aminic modifier, octadecylamine. The modification mechanism was confirmed by ATR-FTIR, and the effect of the varied modification time on the treated membrane properties was investigated.

The modification changed the membrane morphology, resulted in surface pore opening and thinning down of the membrane skin layer. As a compromise between the membrane hydrophobicity and mechanical stability, 10 to 30 min modification time was appropriate for the PAI membranes. The treated membranes showed much higher hydrophobicity than the untreated membrane with an improvement in contact angle of around 30°. The LEP_w also increased significantly after the modification due to the grafting and anchoring of long-chain alkyl on membrane surface and pore walls over the cross section.

The CO₂ flux of the modified membranes increased with the modification time because of the pore opening and the reduction of the skin layer thickness due to the

interfering and breaking down of polymer chains by the octadecylamine modifier. A stable CO₂ absorption performance of the long-term test in a GLMC for 15 days was attained.

CHAPTER 5

Fabrication of Novel Fluorinated Silica - Polyetherimide (PEI) Inorganic-Organic Composite Hollow Fiber Membranes for Membrane Contactor Application

5.1. Introduction

In the previous two Chapters, we have explored the hydrophobic modification approaches for polymeric hollow fiber membranes, e.g. poly(amide-imide) (PAI). The PAI membranes showed greatly enhanced hydrophobicity and promising CO₂ absorption performance in GLMC. Currently, most of the membranes used in GLMC are polymeric membranes, attributed to their good membrane forming ability as well as the low manufacturing cost. However, they are somehow restricted due to their relatively low thermal and chemical stability. On the other hand, inorganic membranes are considered have robust thermal and chemical resistant property, but they are too brittle to achieve large scale defect-free fabrication. More studies need to be performed to improve the reproducibility and also to reduce the fabrication cost of inorganic membranes (Y. Zhang, et al., 2013). Inorganic-organic composite membranes are expected to combine basic properties of polymeric and inorganic membrane and offer specific advantages of the hybrid membrane, such as excellent separation performance, good chemical and thermal resistance and adaptability to the harsh operation conditions (Y. L. Xu, Yu, & Han, 2009). Inorganic-organic composite membranes have been widely studied in many applications, such as direct methanol fuel cells (DMFCs) (Aparicio & Klein, 2005; Chen, Yu, Lin, & Yeh, 2008; Sahu et al., 2009), gas separations (Y. Dai, Johnson, Karvan, Sholl, & Koros, 2012; Thompson, Chapman, Koros, Jones, & Nair, 2012; T. Yang, Xiao, & Chung, 2011; C. Zhang, Dai, Johnson, Karvan, & Koros, 2012) and membrane filtrations (Majeed et al., 2012; Teow, Ahmad, Lim, & Ooi, 2013). In general, the composite membranes can be fabricated by two ways, one is blending the inorganic filler or its precursor with

polymer dope solution and then cast the membrane, and another approach is the direct incorporation of inorganic phase on the polymeric membrane substrate.

Blending the inorganic filler or its precursor with polymer dope solution is a mature approach to form the composite membranes (Hashim, Liu, & Li, 2011; S. J. Oh, N. Kim, & Y. T. Lee, 2009; Sukitpaneenit & Chung, 2012). Sahu et al. reported the organic–inorganic composite membrane comprising Nafion and inorganic silica formed through sol-gel process for DMFCs application (Sahu, Selvarani, Pitchumani, Sridhar, & Shukla, 2007). The membrane was prepared by mixing the silica sol with the Nafion solution. The mixed solution was dried at high temperature and formed the final Nafion-silica membrane. Hou et al. reported the fabrication of polyvinylidene fluoride (PVDF) composite hollow fiber membrane by dispersing hydrophobically modified calcium carbonate (CaCO_3) nanoparticles into the PVDF casting solution (Hou, Wang, Sun, Ji, & Luan, 2012). The composite membrane showed an increased contact angle due to enhanced roughness and occurrence of hydrophobic compounds on the membrane surface. PVDF ultrafiltration membrane was modified by dispersing nano-sized titanium(IV) oxide (TiO_2) particles in a PVDF solution (Su Jin Oh, Nowon Kim, & Yong Taek Lee, 2009). It was observed the membrane fouling was reduced by changing the membrane surface from hydrophobic to hydrophilic after TiO_2 addition.

Another approach is the direct incorporation of inorganic materials on top of the membrane surface. It seems this approach would be more effective in altering the membrane surface property since the inorganic phase is in exposure without the cover and interference from the polymeric matrix. However, there are limited reports in this area (Meng et al., 2010; Razmjou, Arifin, Dong, Mansouri, & Chen, 2012), probably because of the undesired structural stability due to the poor adhesion ability between the inorganic phase and polymeric substrate. Meng et al. fabricated the hydrophobic nanostructured shirasu porous glass (SPG) membranes by depositing SiO_2 nanoparticles onto the hydroxide rich membrane surface via condensation reactions (Meng, et al., 2010). Razmjou et al. fabricated superhydrophobic PVDF- TiO_2 membranes for the application of membrane distillation (MD) (Razmjou, et al., 2012). The deposition of TiO_2 nanoparticles on PVDF membranes was achieved by a low

temperature hydrothermal process. The composite membrane exhibited a hierarchical structure with multilevel roughness and the contact angle increased from 125 °to 166 °.

In this study, we will report the formation of a novel inorganic-organic composite membrane based on polyetherimide (PEI) substrate. Recently, PEI was firstly used by Bakeri et al. to make membranes used in GLMC, and the PEI membranes exhibited promising CO₂ absorption performance which was much higher than in-house made PVDF membranes (Bakeri, et al., 2010). However, the long-term performance of PEI membrane in GLMC remains unclear as PEI is less hydrophobic in nature. Herein, we report on the fabrication and characterization of a novel fSiO₂-PEI inorganic-organic composite hollow fiber membrane by sol-gel process, intended for GLMC application. The unique feature of PEI material was utilized, that is, the imide group in the PEI polymer chain can react with amine functionalized silane coupling agent and allow the silanol groups to be generated on the membrane surface, making the treated membrane being activated for the reaction with the fSiO₂ precursor solution. The reaction taking place between the imide and amine groups has been demonstrated successfully in many imide-contained membrane modification studies, such as PEI (Albrecht, et al., 2003), PAI (Y. Zhang et al., 2011) and polyimide (PI) (Liu, Chung, Wang, Li, & Chng, 2003b). The formation, microstructures, stability and properties of the prepared composite membranes were investigated symmetrically by ATR-FTIR, SEM, thermogravimetric analysis (TGA), ultrasonication, tensiometer and tensile test instrument. The performance of the composite membranes was evaluated in the GLMC for CO₂ absorption through both physical and chemical absorptions. To the best of our knowledge, the fabrication of silica-PEI inorganic-organic composite hollow fiber membranes has not been reported previously.

5.2. Experimental

5.2.1. Materials

The membrane material, polymer PEI, commercially known as Ultem[®]1000, was purchased from GE Plastic. N-Methyl-2-Pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck) was used as a solvent. Lithium chloride (LiCl, anhydrous, CAS#7447-41-8,

MP Biomed) was used as the membrane pore former. (3-Aminopropyl) trimethoxysilane (APTMS, 97%, CAS#13822-56-5, Aldrich), tetraethyl orthosilicate (TEOS, $\geq 99\%$, CAS#78-10-4, Merck) and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFTS, 97%, CAS#101947-16-4, Aldrich) were used as membrane surface treatment reagents. Iso-propanol (IPA, 99.9%, CAS#67-63-0, Merck), ammonium (26% $\text{NH}_3 \text{H}_2\text{O}$, Merck) and ethanol (CAS#64-17-5, Merck) was used for preparing the solutions. Milli-Q deionized water was used in all aqueous solutions ($18\text{M}\Omega\text{cm}$). Taurine ($\text{C}_2\text{H}_7\text{NO}_3\text{S}$, 99%, CAS#107-35-7, Acros) and sodium hydroxide (NaOH, CAS#1310-73-2, Merck) were used to prepare the 2 M sodium taurinate solution as the CO_2 absorbent used in membrane contactor. All the reagents were used as received. The chemical structure of Ultem[®]1000, APTMS, TEOS and PFTS are shown in Figure 5.1.

Figure 5.1. Chemical structures of (a) Ultem[®]1000; (b) APTMS; (c) TEOS; (d) PFTS

5.2.2. PEI membrane preparation

The PEI asymmetric hollow fiber membrane substrates were fabricated by a dry-jet wet spinning technique. The dope preparations and spinning process have been introduced in Chapter 3 Session 3.2.2. The spinning conditions were summarized in

Table 5.1. The characterizations of the as-spun PEI substrates have been summarized in Table 5.2.

Table 5.1. Spinning conditions for fabricating PEI hollow fiber membranes

Parameters	PEI
Dope composition (PEI/LiCl/NMP) (wt %)	14/3/83
Dope flow rate (g/min)	6.0
Bore fluid (NMP/H ₂ O) (wt %)	80/20
Bore fluid flow rate (ml/min)	5.0
Air gap (cm)	5
Take up speed	free fall
External coagulant	tap water
Spinning temperature (°C)	23
Spinneret diameter (mm)	1.50
ID of bore fluid needle (mm)	0.70

Table 5.2. Properties of the as-spun PEI hollow fiber substrates

Properties	PEI
Fiber OD (mm)	1.1
Fiber ID(mm)	0.8
Fiber thickness (μm)	150
Fiber mean pore size (μm)	0.04
Fiber porosity (%)	81

5.2.3. Formation of the fSiO₂-PEI composite membranes

In the first step, the PEI membranes were treated in a 2 % (wt/vol) APTMS solution in a mixture of IPA and distilled water (vol 1:1) at the water bath of 70 °C for 3 h. The membranes were then rinsed with abundant amount of distilled water to remove APTMS residue. Next, the fSiO₂ precursor solution, e.g. TEOS/PFTS mixture was prepared based on the well-known Stober method (Stöber, Fink, & Bohn, 1968). Briefly, a 20 ml TEOS with appropriate amount of PFTS (mole ratio TEOS: PFTS = 10:1) were dissolved in a 100 ml ethanol solution and mixed well. The solution was

added dropwise to another solution containing 24 ml ammonium in a 100 ml ethanol solution. The hydrolysis and polycondensation reaction routes of TEOS and PFTS are shown in Figure 5.2. Herein, two treatment approaches were investigated.

Hydrolysis (complete hydrolysis assumed for simplicity)

Polycondensation (fluorination)

Figure 5.2 Hydrolysis and polycondensation reaction routes of TEOS and PFTS

In the approach #1, the mixture solution was stirred intensively overnight at room temperature and treated by ultrasonication probe for 20 min before use. The APTMS treated PEI membrane were immersed in the above solution for 2 h. The mechanism of fSiO₂ particles formation in this sol preparation was proposed and examined by Wang et al. (H. Wang et al., 2008). They prepared TEOS and fluoroalkylsilane (FAS) solutions separately so that TEOS and FAS molecules were allowed to hydrolyze independently. It was observed that the TEOS solution quickly turned milky, while the FAS formed a thick and clean resin and phase-separated from the solution. Thus, it was assumed that the co-hydrolysis of these two silane precursors could quickly form SiO₂ particle cores by TEOS with slowly hydrolyzed FAS molecules attached outside of the cores. The adhesion of the fSiO₂ particles to the substrate was assumed to originate from the formation of interfacial chemical bonds, e.g. Si-O-Si or Si-O-C bonds (H. Wang, et al., 2008). In our case, the adhesion force was formed by co-

condensation of partially hydrolyzed TEOS/PFTS and hydroxyl groups on the PEI membrane surface. The reaction route is illustrated schematically in Figure 5.3.

Figure 5.3. Formation of the inorganic-organic composite membranes by Approach #1 and Approach #2.

In approach #2, the APTMS treated PEI substrates were immersed immediately into the prepared mixture solution before TEOS/PFTS start to hydrolyze, so that the silanol groups on the membrane surface also participated in the hydrolysis and condensation reactions and induced vertical polymerization to form grafted polysiloxane on the membrane surface, which was expected to enhance the chemical bonding between membrane surface and the sol molecules. The reaction route is also drawn in Figure 5.3. The membranes were immersed in the solution for 1 h, 3 h and 5 h respectively.

In the last step, the TEOS/PFTS treated membranes from approach #1 and approach #2 were placed in an oven at 100 °C for 2 h. The final inorganic-organic composite membranes were designated as fSiO₂-PEI membranes.

5.2.4. Membrane characterizations and GLMC test

The membrane samples were observed by SEM. The information of SEM has been introduced in in Chapter 3 Session 3.2.4.

The membrane pore size was measured by a capillary flow porometer (CFP 1500A, from Porous Material. Inc. (PMI)). The membrane samples were fixed into the sample holder and immersed in a liquid (Galwick) till the samples were completely wetted. Galwick has a surface tension of 16.0×10^{-3} N/m. During the test, the gas flow rate was increased stepwise and passed through the saturated sample until the applied pressure exceeded the capillary attraction of the liquid in the pores. By comparing the gas flow rates of a wet and dry sample at the same pressures, the percentage of flow passing through the pores larger than or equal to the specified size can be calculated from the pressure–size relationship (Yang, Wang et al. 2011).

The overall membrane porosity ε was measured using a method based on the density measurements (Tang et al., 2012; J. Xu & Xu, 2002). The equation of calculating ε is shown below:

$$\varepsilon = (1 - \frac{\rho_{membrane}}{\rho_{PEI}}) \times 100\% \quad (14)$$

where $\rho_{membrane}$ is the density of the membrane and ρ_{PEI} is the density of the PEI powder. The $\rho_{membrane}$ is calculated by membrane weight and volume. Membrane weight was determined by an analytical balance. The membrane volume was calculated according to the inner/outer diameters and the length of the fiber sample. The ρ_{PEI} is taken as 1.27 g/cm^3 . An average value of the three times of test results was considered as the overall membrane porosity.

The reaction mechanism was examined by ATR-FTIR spectra of the hollow fiber membrane samples before and after APTMS treatment and fSiO₂ incorporation. The details of ATR-FTIR have been introduced in Chapter 3 Session 3.2.4.

Thermal decomposition of the original and composite PEI membrane was measured by TGA. It was conducted on a thermal analyzer (Pekin Elmer Pyris 7) at a heating rate of 10 °C/min in a nitrogen atmosphere.

The stability of the chemical bonding between the fSiO₂ layer and the PEI substrate was examined by ultrasonic treatment. The surface dynamic contact angles and mechanical properties of the composite membranes were characterized. The detailed characterization tests methods have been described in Chapter 3 Section 3.2.4.

The fSiO₂-PEI composite hollow fibers were tested in a GLMC to measure the CO₂ absorption flux by using water and 2 M sodium taurinate as the absorbents and pure CO₂ as the feed gas. The membranes were assembled into the PTFE modules. The membrane contactor module characteristics are shown in Table 5.3. The liquid passed through the shell side and the gas flowed counter-currently through the lumen side of the hollow fibers, as the hydrophobic layers of the composite membranes were in the outer surfaces. The detailed experimental setup and procedures have been described in Chapter 3 Section 3.2.5.

Table 5.3. Characteristics of the membrane contactor module

Module ID (mm)	6.4
Module length (cm)	25
Fiber OD (mm)	1.1
Fiber ID(mm)	0.8
Effective fiber length (cm)	16
Effective contact area (cm ²)	22
Number of fibers	4

5.3. Results and discussion

5.3.1. Formation mechanism of the fSiO₂-PEI composite membranes

The chemical structure of the original PEI membrane, APTMS treated PEI membrane and fSiO₂-PEI composite membrane was examined by ATR-FTIR. As can be seen in Figure 5.4, the typical imide bands can be observed at 1778 cm⁻¹ and 1719 cm⁻¹ which

correspond to the asymmetric and symmetric C-O stretching of the original PEI membrane. The absorption band at 1353 cm^{-1} is assigned to the bond stretching vibration of C-N-C in phthalimide rings. After APTMS treatment, the intense absorption bands between 1000 cm^{-1} and 1200 cm^{-1} are observed due to asymmetric stretching vibration of siloxane groups (Si-O-Si). A band at 1535 cm^{-1} appears due to the deformation of N-H moiety which is associated with amide II band, indicating that the phthalimide rings was opened, and imide group transferred to amide through the reaction with APTMS. For the spectrum of fSiO₂ incorporated PEI membranes, the PEI characteristic peaks became less intense which is attributed to the coverage of an inorganic fSiO₂ layer on the membrane surface. A very intense peak at 1070 cm^{-1} is assigned to the siloxane asymmetric bond stretching of Si-O-Si or Si-O-R groups (R is a hydrocarbon such as -CH₂CH₃) (Irzh, Ghindes, & Gedanken, 2011), which proved the existence of SiO₂ particles on the membrane surface. The peak at 1199 cm^{-1} could be due to the C-F stretching from PFTS. The ATR-FTIR spectra confirmed the formation of the fSiO₂-PEI composite membrane.

Figure 5.4. ATR-FTIR spectra of the original PEI, APTMS modified PEI, and the fSiO₂ incorporated PEI composite hollow fiber membranes

Figure 5.5 shows the TGA curves of the membranes before and after the fSiO₂ incorporation. The thermal decomposition of PEI mainly occurred in a temperature range of 500-700 °C. The fSiO₂ treated PEI membranes showed slightly higher

thermal stability than the original PEI membranes because of the presence of the inorganic fSiO₂ layer on the membrane substrate. This result confirmed the successful formation of the fSiO₂-PEI composite membranes.

Figure 5.5. TGA curves of the membranes before and after the fSiO₂ incorporation.

5.3.2. Membrane morphology observation

The SEM images of the composite PEI membranes formed by two approaches are shown in Figure 5.6 and Figure 5.7, respectively. We can clearly observe the morphology differences. By using approach #1, as shown in Figure 5.6, a single layer of fSiO₂ particles was deposited on the membrane surface with an average particle size of around 150 to 200 nm. However, after the ultrasonic treatment, most of the fSiO₂ particles disappeared. Although this approach was reported applicable on other material surfaces (H. Wang, et al., 2008), in our study by using polymeric membrane as the substrate, the fSiO₂ particles were easily removed by ultrasonic treatment, which implied the weak bonding between fSiO₂ and PEI substrate.

Figure 5.6. SEM images of the fSiO₂-PEI (approach #1) hollow fiber membranes. (a) surface (5,000x- scale bar of 1µm); (b) surface-enlarged (20,000x- scale bar of 1µm); (c) cross section (50,000x- scale bar of 100nm); (d) surface-after ultrasonication (5,000x- scale bar of 1µm).

The SEM images of the membrane treated by approach #2 are shown in Figure 5.7. It can be seen that with an increase in the treatment time of PEI membrane in the TEOS/PFTS solution, a larger amount of fSiO₂ were attached to the membrane surface. At 5 h treatment time, the membrane surface exhibited a typical inorganic membrane morphology, as shown in Figure 5.7 (d and D) (H. Fang, et al., 2012). Ultrasonication was used to examine the stability of fSiO₂ on the membrane surface. It can be observed that the layer of fSiO₂ on the membrane surface was less affected by the ultrasonic treatment, which indicated the good structural stability of the composite membrane. This was probably because the silanol groups on the membrane surface were involved in the hydrolysis and condensation of TEOS/PFTS, which directly induced the vertical polymerization and condensation of silane compounds to form grafted polysiloxane on the membrane surface, leading to a strong interfacial covalent bonding between fSiO₂ layer and the polymeric substrate (H. Fang, et al., 2012).

Figure 5.7. SEM images of the original and composite (approach #2) PEI hollow fiber membranes (scale bar of 1 μ m)
 (A) original surface (20,000x);
 (b) 1 h fSiO₂ treated (5,000x); (B) 1 h fSiO₂ treated-enlarged (20,000x); (B-U) 1 h fSiO₂ treated-after ultrasonication (20,000x);
 (c) 3 h fSiO₂ treated (5,000x); (C) 3 h fSiO₂ treated-enlarged (20,000x); (C-U) 3 h fSiO₂ treated-after ultrasonication (20,000x);
 (d) 5 h fSiO₂ treated (5,000x); (D) 5 h fSiO₂ treated-enlarged (20,000x); (D-U) 5 h fSiO₂ treated-after ultrasonication (20,000x).

Figure 5.8 (a) shows the cross section morphology of the composite membrane with fSiO₂ treatment for 5 h, layers of fSiO₂ particles were deposited on top of the membrane surface. The fSiO₂ layer surface is shown in Figure 5.8 (b), which played an important role in shifting the membrane wettability to highly hydrophobic, as confirmed by the contact angle measurement (discussed in the next section). In addition, for the membranes treated for 5 h, the stacked layers of fSiO₂ were removed after the ultrasonic treatment and the bottom layer which was chemically bonded to the membrane surface remained there, as shown in Figure 5.7 (D and D-U).

Figure 5.8. SEM images of (a) cross-section of the fSiO₂-PEI-5h (approach #2) composite membrane (10,000x, scale bar of 1μm) and (b) surface of fSiO₂ particles (100,000x, scale bar of 100nm)

5.3.3. Surface wettability of the composite membranes

The membrane surface wettability was studied by investigating the dynamic contact angles. Table 5.4 shows dynamic contact angle results of the original PEI and composite membrane with different fSiO₂ treatment time. Advancing contact angle always exceeds or equals to the receding contact angle. The difference between advancing and receding contact angles is called contact angle hysteresis. A high advancing/receding contact angle and low contact angle hysteresis is responsible for the low wetting property of a material surface (X. M. Li, et al., 2007). In addition, the membrane surface was dry before it was immersed into the DI water in the first loop, thus, 2nd and 3rd cycle contact angles were considered as a better characterization of the membrane hydrophobicity (L. Shi, et al., 2007). The contact angles mentioned below therefore are referred to the value from 2nd cycle, unless specified otherwise. For the fSiO₂-PEI composite membranes, the advancing contact angle increased dramatically from 66.7° of the original membrane to 124.8° of the composite membrane at 3 h

treatment. This was believed due to the combination factors of a reduced surface free energy and enhanced roughness generated by the fSiO₂ layer. The receding contact angle was also significantly higher than that of the original membrane, e.g. 100.6 °vs. 49.5 °. Moreover, the contact angle hysteresis decreased from 32.8 °at 1 h treatment to around 24 °at 3 and 5 h treatment due to a larger amount of PFTS existing on the membrane surface.

Table 5.4. Dynamic contact angles of the original and composite PEI hollow fiber membranes

Membrane code	Contact direction	Contact angle (2 nd cycle)	Contact angle hysteresis(°)
Original PEI	Advancing	66.7 ± 2.4	17.2 ± 2.8
	Receding	49.5 ± 0.4	
fSiO ₂ -PEI-1h	Advancing	124.7 ± 1.8	32.8 ± 3.1
	Receding	91.9 ± 1.3	
fSiO ₂ -PEI-3h	Advancing	124.8 ± 1.4	24.2 ± 3.7
	Receding	100.6 ± 2.3	
fSiO ₂ -PEI- 5h	Advancing	124.6 ± 1.8	24.6 ± 3.6
	Receding	100.0 ± 1.8	

5.3.4. Mechanical properties of the composite membranes

The mechanical property is an important parameter for membrane practical applications. The tensile modulus, tensile strength, strain at tensile strength, stress at break and strain at break of the original and composite PEI membranes are shown in Table 5.5. Tensile modulus was calculated based on the combination of tensile strength and strain at the tensile strength. A high tensile modulus suggests a high rigidity of the membrane. It can be seen that with the reaction progressed, the membrane rigidity increased from 1 h to 3 h treatment and decreased during the further reaction process. The increase in the membrane rigidity was due to the presence of the inorganic fSiO₂ particles on the membrane surface. When the treatment time increased to 5 h, although larger amounts of fSiO₂ were expected to be generated, the polymeric substrate became weaker due to the overlong reaction in the alkaline solution. Thus, the membrane rigidity dropped. The membrane tensile strength and stress at break

followed the same trend as the tensile modulus. On the other hand, with the reaction progressed, the membrane ductile property decreased, which was indicated by a drop of both strain at tensile strength and strain at break. This was possibly because of the intrinsic brittleness property of inorganic materials. Thus, the inorganic-organic composite membranes exhibited weaker elongational property. Moreover, the substrate membrane also became less ductile with reaction progressed. Thus, 3 h treatment of fSiO₂ solution was suitable for the PEI membrane by considering the change of mechanical properties. In summary, the inorganic-organic composite membranes showed better mechanical strength compared with the conventional polymeric membrane, such as PES and PVDF (Chung, Qin, & Gu, 2000; P. Wang, Teoh, & Chung, 2011), and also not as brittle as pure inorganic membranes.

Table 5.5. Mechanical properties of the original and composite PEI hollow fiber membranes and the comparison with other common polymeric membranes

Membrane code	Tensile modulus (MPa)	Tensile Strength (MPa)	Strain at tensile strength (%)	Stress at break (MPa)	Strain at break (%)
fSiO ₂ -PEI- 1h	136.2 ± 0.3	2.4 ± 0.3	2.3 ± 0.1	2.4 ± 0.3	2.3 ± 0.1
fSiO ₂ -PEI- 3h	140.0 ± 3.9	2.7 ± 0.2	2.0 ± 0.1	2.7 ± 0.2	2.0 ± 0.1
fSiO ₂ -PEI-5h	86.6 ± 3.2	1.7 ± 0.1	1.5 ± 0.2	1.7 ± 0.1	1.5 ± 0.2
PES (Chung, et al., 2000)	57.5 – 104.0	–	–	0.9 – 1.7	9.9 – 16.9
PVDF (P. Wang, et al., 2011)	26.9 – 33.5	0.62 – 1.08	74.0 – 116.0	–	–

5.3.5. Application of the composite membranes in GLMC for CO₂ absorption

The performance of CO₂ absorption by using the composite membranes with the change of the liquid velocity was tested. Pure CO₂ and pure water was used in this experiment. It can be seen from Figure 5.9 that the CO₂ flux increased with the increase in flow rate of the pure water. This is a well-known behavior in membrane contactor which indicates the main resistance exists in the liquid phase in the case of physical absorption of CO₂. The change in gas velocity hardly affected the absorption performance (Atchariyawut, et al., 2007). In addition, with increase in fSiO₂

incorporation time, the CO₂ flux became smaller. This result is consistent with the observation from SEM images. With a longer treatment time, a larger amount of fSiO₂ particles and hence thicker fSiO₂ layer was generated on the membrane surface which would hinder the mass transfer of CO₂ gas.

Figure 5.9. CO₂ flux using pure water as the absorbent (atmospheric pressure, absorbent temperature at 25 °C, gas flow rate at 30 ml/min)

The composite membrane fSiO₂-PEI-3h was used to investigate the CO₂ capture performance by chemical absorption. Figure 5.10 shows the CO₂ flux by using amino acid salts as the absorbent liquid, e.g. 2 M aqueous sodium taurinate solution. It was observed that with the increase in liquid velocity, CO₂ absorption flux increased. This was because there was a significant solvent depletion in the shell side due to the high pure CO₂ concentration in the gas phase. Thus, the solvent concentration would drop dramatically at the gas-liquid interface and instantaneous absorption regime took place. Increase in the solvent velocity would reduce its depletion at the interface, and therefore enhanced the mass transfer efficiency (Yan, et al., 2007).

Figure 5.10. CO₂ flux of the composite membrane fSiO₂-PEI-3h using 2 M sodium taurinate as the absorbent (atmospheric pressure, absorbent temperature at 25 °C, gas flow rate at 30 ml/min)

The chemical compatibility between the membrane and CO₂ chemical absorbent was examined by immersing the membrane in the sodium taurinate solution for 50 days. The surface of the fSiO₂-PEI-3h composite membrane was examined by SEM periodically to observe the morphology change during the immersion. The SEM images are shown in Figure 5.11. During the 50-day immersion, the fSiO₂ layer remained on the membrane surface in spite of the direct exposure to the alkaline solvent. The dynamic contact angles of the immersed membranes were also investigated and summarized in Table 5.6. It was found that the contact angles of the immersed membranes reduced gradually over the immersion period. Nevertheless, the hydrophobicity still maintained and was much higher than that of original PEI and conventional hydrophobic polymeric membranes such as PVDF, which was in-house prepared according to Loh et al. (Loh & Wang, 2012).

After the chemical compatibility test, a long-term test of the composite membranes was conducted to observe the CO₂ flux trend in the membrane contactor by using sodium taurinate as the absorbent. Testing of the membrane contactor was carried out periodically to observe the change in CO₂ absorption flux. The membrane contactor module was fully immersed in sodium taurinate solution after every experiment to ensure that the outer surfaces of the hollow fibers would be in constant contact with the absorbent. As can be seen from Figure 5.12, the membrane contactor showed a

reasonable stability throughout the 31-day operation with ~20% drop of the initial CO₂ flux. The drop of the CO₂ flux could be due to the partial wetting of the membrane surface. In this work, fluorination was done in a single step by mixing TEOS and PFTS together to allow the hydrolysis, polycondensation and fluorination reactions occur simultaneously to generate fSiO₂ in the solution. There could be the possible exposure of the hydrophilic TEOS on the inorganic layer surface, which may result in the wetting. In our next work, improvement has been done to further enhance the hydrophobicity of the developed composite membranes to avoid wetting.

Figure 5.11. SEM images (enlarged at 5,000x, scale bar of 1μm) of the composite PEI hollow fiber membranes wo/w immersing in 2M sodium taurinate solution (a) blank; (b) for 10 days; (c) for 20 days; (d) for 30 days; (e) for 40 days; (f) for 50 days

Table 5.6. Dynamic contact angles of the composite PEI hollow fiber membranes after immersion in the chemical absorbent

Membranes wo/w immersion in a 2 M sodium taurinate aqueous solution	Contact direction	Contact angle (2 nd cycle)
Blank	Advancing	124.8 ± 1.4
	Receding	100.6 ± 2.3
10 days	Advancing	120.5 ± 1.7
	Receding	91.3 ± 3.0
30 days	Advancing	115.8 ± 2.6

50 days	Receding	86.7 ± 2.1
	Advancing	114.4 ± 3.6
	Receding	75.8 ± 3.2
PVDF	Advancing	89.8 ± 5.1
	Receding	57.2 ± 2.3

Figure 5.12. Long-term CO₂ flux of the composite membrane fSiO₂-PEI-3h using 2 M sodium taurinate as the absorbent (atmospheric pressure, absorbent temperature at 25 °C, gas flow rate at 30 ml/min, liquid velocity at 0.1 m/s)

5.4. Conclusions

In the present study, a novel method was explored to form the highly hydrophobic organic-inorganic composite hollow fiber membranes by incorporating the fSiO₂ inorganic layer on the PEI organic substrate. The approach #2 was proven to be effective to form the composite membrane with a stronger structural stability, as indicated by the ultrasonication test. The formation of the composite membrane was examined and confirmed by ATR-FTIR, TGA and SEM. The experimental results revealed that the incorporation of fSiO₂ layer greatly enhanced the membrane surface hydrophobicity, as evidenced by the dynamic contact angles increment. The advancing contact angle increased from original 66.7° to 124.8°, and receding contact angle increased from 49.5° to 100.6°. The contact angle hysteresis reached as low as 24.2°. Moreover, the composite membranes showed better mechanical properties compared with the some of the conventional polymeric membranes and also not as brittle as pure inorganic membranes.

The CO₂ absorption performance of the composite membrane was investigated by both physical and chemical absorptions processes in gas-liquid membrane contactor. Moreover, the chemical compatibility test indicated that after the long-term constant contact with the sodium taurinate, the hydrophobicity of the PEI-fSiO₂ composite membrane still maintained and was much higher than that of the original PEI substrate and conventional hydrophobic membranes such as PVDF. Furthermore, the membrane contactor showed a reasonable stability throughout a 31-day long-term operation. The incorporation of the fSiO₂ inorganic layer not only offered high hydrophobicity, but also would protect the polymeric substrate from the attacks of chemical absorbents, making the membrane a longer lifespan.

CHAPTER 6

Novel Method for Incorporating Hydrophobic Silica Nanoparticles on PEI Hollow Fiber Membranes for CO₂ Absorption in GLMC

6.1. Introduction

In the previous chapter, we have successfully fabricated novel fluorinated silica (fSiO₂)-polyetherimide (PEI) inorganic-organic composite hollow fiber membranes for GLMC application. In this study, we will further improve the properties of the composite membranes and CO₂ absorption performance in GLMC by optimizing the PEI substrate structure and improving the approach for fSiO₂ nanoparticle incorporation.

The essential properties of the membranes for contactor applications include: high hydrophobicity, high surface porosity with small pore size, low mass transfer resistance and high chemical resistance to the liquid absorbents (Mansourizadeh, et al., 2010). Asymmetric hollow fiber membrane prepared from the NIPS process usually exhibits a relatively dense skin layer and porous substrate. The most mass-transfer resistance in the membrane comes from the dense skin layer, while the porous substrate only provides mechanical support and fractional resistance. The pore size and pore size distribution of the skin layer significantly affect the CO₂ absorption flux and are associated with membrane wetting problem since the skin layer is in direct contact with the liquid absorbents. Atchariyawut et al. reported that the ratio of the membrane resistance over the overall mass transfer resistance increased with the decrease of the skin layer pore size (Atchariyawut, et al., 2006).

On the other hand, according to Laplace equation as shown in Equation (11), with an increase in the pore size, the liquid entry pressure decreases, indicating high tendency of membrane wetting. Thus, the pore size is always limited by the concern of

membrane wettability when fabricating the membranes for contactor applications. To make the breakthrough, herein, we are going to report a porous PEI substrate with high surface porosity and large pore size to minimize the membrane mass transfer resistance by using a triple-orifice spinneret in the hollow fiber spinning process, and followed by a novel approach of inorganic nanoparticle incorporation to make the membrane surface highly hydrophobic and chemical resistant to prevent the membrane from wetting caused by the large pore size on the membrane surface.

In recent years, a triple-orifice spinneret has been developed mainly for fabricating dual layer hollow fiber membranes by using the second dope solution as the external liquid (Edwie, Teoh, & Chung, 2012; L. Setiawan, Wang, Shi, Li, & Fane, 2012; P. Wang, et al., 2011). The cross section of the triple-orifice spinneret is shown in Figure 6.1. The use of this type of spinneret with a solvent as the external liquid flowing in the outer channel and being extruded simultaneously with the dope solution and bore fluid in the spinning process was also reported. He et al. were the first using this approach to fabricate porous PSf with NMP as the external liquid at the outside orifice of the spinneret (He, Mulder, & Wessling, 2003). It was found that the resultant membranes had a highly open and porous outer skin. Later, Bonyadi et al. fabricated a highly porous and macrovoids free PVDF hollow fiber membrane by using the same approach for membrane distillation (MD) application (Bonyadi & Chung, 2009). An improved water flux of MD was observed. In this study, we intend to use this approach to fabricate PEI hollow fiber membrane with high surface porosity. After obtaining the good substrate, the incorporation of fSiO₂ nanoparticles on the membrane surface was conducted. Compared with the composite membrane formation approach used in Chapter 5, incorporation of fSiO₂ nanoparticles on the membrane surface with improved procedures was explored. The incorporated fSiO₂ nanoparticles were embedded in the highly porous top skin layer of the membrane, leading to the formation of resultant nanostructured architecture with highly hydrophobic fluoro-compounds on the membrane surface. The resultant membranes were subjected to a two-month long-term study in a GLMC to examine the performance stability.

Figure 6.1. Cross section of a triple-orifice spinneret

6.2. Experimental

6.2.1. Materials

The n-hexane (CAS#110-54-3, Merck) was used for preparing the 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFTS) solutions. Other materials have been described in the Chapter 5 Section 5.2.1. All the reagents were used as received. The chemical structures of PEI (Ultem[®]1000), (3-Aminopropyl)trimethoxysilane (APTMS), tetraethyl orthosilicate (TEOS) and PFTS have been shown in Chapter 5, Figure 5.1.

6.2.2. PEI hollow fiber membranes preparation by using a triple-orifice spinneret

The PEI asymmetric hollow fiber membrane substrates were fabricated by a dry-jet wet spinning process using the spinning system as described in details in Chapter 3. The spinning conditions are summarized in Table 6.1.

Table 6.1. Spinning conditions of the fabricated PEI hollow fiber membranes

Parameters	PEI
Dope composition	PEI/LiCl/NMP (14/3/83)
Dope flow rate	3.78 g/min
External liquid	PEI A: - PEI B: NMP
External liquid flow rate	PEI A: 0 PEI B: 1 ml/min
Bore fluid	DI water/NMP (20 wt%/80 wt%)
Bore fluid flow rate	3 ml/min
Length of air gap	5 cm

Take up speed	Free fall
External coagulant	DI water
Spinning temperature	23 °C

6.2.3. *Incorporation of fSiO₂ nanoparticles on the PEI substrates*

The PEI membranes were immersed in a 2 % (wt/vol) APTMS, a silane coupling agent, in the mixture of IPA and distilled water (vol 1:1) at the water bath of 70 °C for 3 h to generate hydroxyl groups on the membrane surface. The membranes were then rinsed with abundant amount of distilled water to remove APTMS residue. The hydroxyl groups served as a bridge link between the PEI substrate and the SiO₂ nanoparticle solution which was prepared in the next step. The SiO₂ precursor solution was prepared based on the well-known Stober method (Stöber, et al., 1968). Briefly, a 20 ml TEOS were dissolved in a 100 ml ethanol solution and mixed well. The solution was added dropwise to another solution containing 24 ml ammonium in a 100 ml ethanol with agitation. The mixture was stirred intensively at room temperature. After stirring for 12 h, the mixture was treated by probe ultrasonication for 20 min to alleviate the SiO₂ nanoparticles aggregation in the solution. The APTMS treated PEI membranes were then immersed in the above solution for 2 h with shaking. The hydroxyl groups on the membrane surface reacted with SiO₂ nanoparticles through condensation reaction. Subsequently, the membranes were rinsed with abundant ethanol to remove loosely bonded and stacked layer of SiO₂ nanoparticles on the membrane surface and placed in an oven at 100 °C for 1 h. Herein, the PEI substrate with nanostructured SiO₂ hydrophilic surface was obtained. To get the nanostructured hydrophobic surface, the membranes were further treated by a 2 wt% PFTS in n-hexane at room temperature for 2 h. The PFTS molecules were opt to react with the hydroxide groups on the membrane surface. The final membranes were then dried in oven at 100 °C for 1 h. APTMS treated membranes were designated as PEI-APTMS and the final membranes were designated as PEI-fSiO₂. The reaction route is schematically shown in Figure 6.2. The ATR-FTIR spectra of the original PEI, PEI-APTMS and PEI-fSiO₂ were similar to that of our previous work, as shown in Chapter 5, Figure 5.4. It should be pointed out that the fluorination of SiO₂ was taken place in the final step in this experiment. While in Chapter 5, fluorination was done in a single

step by mixing TEOS and PFTS together to allow the hydrolysis, polycondensation and fluorination reactions occur simultaneously to generate fSiO₂ in the solution. This may have the potential disadvantages that partial PFTS could be covered beneath the top layer and there was the possible exposure of hydrophilic TEOS on the fSiO₂ layer surface, which may have the tendency towards wetting. A similar situation was also reported by Edwie et al. as well (Edwie, et al., 2012). Fluorination as the final treatment step is favorable to ensure a more uniform coverage of PFTS network on the SiO₂ layer surface.

Figure 6.2. Reaction route of forming inorganic-organic composite membranes

6.2.4. PEI hollow fiber membrane characterizations and GLMC test

The procedures for morphology observation by SEM and pure water permeability measurement have been described in Chapter 3 Section 3.2.4. The membrane pore size was measured by a capillary flow porometer and overall membrane porosity ϵ was characterized, as introduced in Chapter 5 Section 5.2.4.

The membrane surface morphology and roughness were analyzed by AFM. The information of AFM analysis has been introduced in Chapter 4, Session 4.2.4. Surface dynamic contact angle and mechanical properties measurements of the composite PEI-fSiO₂ membranes were conducted. The procedures have been described in Chapter 3, Session 3.2.4.

The composite PEI hollow fibers were tested in a GLMC to measure the CO₂ absorption flux by using water and 2 M sodium taurinate as the absorbents and pure CO₂ as the feed gas. The membranes were assembled into the PTFE modules. The membrane contactor module characteristics are shown in Table 6.2. The liquid passed through the shell side and the gas flowed counter-currently through the lumen side of the hollow fibers, as the hydrophobic layers of the modified membranes were in the outer surfaces. The detailed experimental setup and procedures have been described in Chapter 3 Section 3.2.5.

Table 6.2. Characteristics of the membrane contactor module

Module ID (mm)	6.4
Module length (cm)	25
Fiber OD (mm)	1.0
Fiber ID(mm)	0.7
Effective fiber length (cm)	16
Effective contact area (cm ²)	20
Number of fibers	4

6.3. Results and discussion

6.3.1. *Preparing the porous PEI substrate using the triple-orifice spinneret*

Two approaches can be used to obtain an open and porous skin layer of the membrane. One approach is to use a very low polymer composition in the dope solution. The drawback of this approach is that the dope viscosity would be too low to make the spinning process feasible or make the resultant membranes full of macrovoids with poor mechanical property. Another approach is to induce delayed liquid-liquid demixing. For the delayed demixing, the intrusion of non-solvent to the dope matrix was hindered, thus the membrane skin becomes open and porous and the macrovoids are significantly reduced. Applying a coagulant bath composing of solvent and nonsolvent mixture could a possible method to induce the delayed demixing (Bonyadi, Chung, & Rajagopalan, 2009; Teoh & Chung, 2009; P. Wang, et al., 2011). However, this method would consume a large amount of solvent which is not feasible in the practical membrane fabrication. Moreover, it is not environmentally friendly and also imposes potential health effect as the coagulant bath is usually open to the atmosphere.

The approach of using the triple-orifice spinneret with solvent and dope co-extrusion from the spinneret simultaneously was adopted. Firstly, the solvent contact with the outer layer of the dope effectively reduces the polymer concentration, but has no impact on the bulk dope system. Secondly, after the two-phase flow entering the coagulant bath, the outward diffusion of the solvent hinders the non-solvent inward diffusion and hence slows down the solvent and non-solvent exchange process, resulting in the delayed demixing process. The resultant membrane is expected to exhibit a very open and porous skin layer which is able to decrease the mass transfer resistance significantly.

6.3.2. Characterizations of the as-spun PEI hollow fiber substrates

The SEM images of the two as-spun PEI substrates, e.g. PEI A and PEI B are shown in Figure 6.3. PEI A was spun by using the standard dry-jet wet spinning process without solvent flowing in the outer channel of the spinneret. PEI B was spun with solvent phase extruding from the spinneret simultaneously with the dope solution. The dope of PEI A went through an air gap after extruded from the spinneret and entered the water bath. A relatively dense skin layer was formed. When NMP was applied in the outer orifice, an extremely open and porous skin layer with a lacy structure was obtained for PEI B. This was because the solvent in the outer channel of the spinneret reduced the outer layer polymer concentration of the dope system and also hindered the solvent exchange process with the coagulant of water, resulting in a loose and open cellular structure in the skin layer.

The cross section of PEI A and PEI B are also shown in Figure 6.3 (a3) and (b3), respectively. For PEI A, it can be seen the finger-like structures were developed simultaneously beneath the inner and outer surfaces of the fibers with a thin layer of sponge structure sandwiched in between. This was because of the fast solvent and nonsolvent exchange process so that the dope system gelled and solidified immediately after immersion in water bath which resulted in a membrane with a fine pore skin and finger-like pore structure. On the other hand, the substrate beneath the outer skin layer of the PEI B showed a free and interconnected pore structure. This was because the solvent flowing at the outer layer of the dope solution hindered the inward diffusion of

the nonsolvent, leading to the delayed demixing which made the morphology completely different from that of PEI A. It is worth mentioning that the open cellular surface morphology would effectively reduce the mass transfer resistance, and meanwhile, it also played an important role in the SiO₂ nanoparticles incorporation as the nanoparticles were able to be embedded deeply in this type of morphology so that the membrane would hold the nanoparticles through both chemical and physical interactions.

Figure 6.3. SEM images of the surface and cross-section of the as-spun substrates. PEI A: (a1) 10,000x- scale bar of 1 μ m (a2) 30,000x- scale bar of 10nm and (a3) 600x- scale bar of 10 μ m; PEI B: (b1) 10,000x- scale bar of 1 μ m (b2) 30,000x- scale bar of 10nm and (b3) 600x- scale bar of 10 μ m.

The characteristics of the as-spun PEI A and PEI B substrates in terms of fiber dimension, average pore size, overall membrane porosity and pure water permeability are summarized in Table 6.3. Under the same spinning condition, the thickness of PEI B was 25% less than PEI A. The PEI B exhibited smaller overall membrane porosity because of the replacement of finger-like structures and macrovoids by the interconnected pores. The pure water flux was almost the same for PEI A and PEI B. This was possibly because of the balance between an increased pore size and decreased overall membrane porosity.

Table 6.3. Characteristics of the as-spun PEI hollow fiber membranes

Properties	PEI A	PEI B
Fiber OD (μm)	1042	966
Fiber ID (μm)	736	737
Fiber wall thickness (μm)	153	115
Fiber mean pore size (μm)	0.03	0.09
Overall membrane porosity (%)	81.2	71.2
Pure water permeability ($\text{L}/\text{m}^2 \text{ h bar}$)	662	665

6.3.3. Membrane morphology observation and surface roughness analysis of PEI-fSiO₂ membranes

Figure 6.4 shows the SEM images of the two PEI substrates after APTMS treatment and fSiO₂ incorporation. The nanostructured architecture can be observed clearly on the PAI A-fSiO₂ and PAI B-fSiO₂ membrane surfaces after the incorporation of fSiO₂ nanoparticles on the PEI substrates. For PEI A, the surface was denser compared with PEI B and the fSiO₂ nanoparticles deposited individually on top of the membrane surface. While for PEI B, the surface was so loose with cellular morphology that the fSiO₂ nanoparticles were embedded into the skin layer of the membrane so that the bonding force between the nanoparticles and membrane substrate was expected to be stronger, as the membrane was able to bond with the nanoparticles through both chemical and physical interactions. Moreover, the deposition of SiO₂ nanoparticles was found more uniform on the PEI B surface as observed from the higher magnification surface morphology images. In addition, the skin layer cross section images of PAI B-fSiO₂ are also shown in Figure 6.4. The embedment of the fSiO₂ nanoparticles in the top skin layer of the PEI B-fSiO₂ can be observed from the cross section images.

Figure 6.4. SEM images of the PEI A and PEI B membranes after APTMS treatment (surface, enlarged at 30,000x- scale bar of 100nm) and fSiO₂ nanoparticles incorporation (surface, enlarged at 10,000x- scale bar of 1μm and 30,000x- scale bar of 100nm & cross section, enlarged at 5000x- scale bar of 1μm and 20,000x- scale bar of 1μm)

The three-dimensional surface images and surface roughness parameters of the PEI membranes before and after fSiO₂ incorporation can be observed in Figure 6.5 and Table 6.4. Roughness parameters, the mean roughness (Ra) defined as the arithmetic average of the absolute values of the surface height deviations measured from the center plane, and the root mean square roughness (Rq) representing the standard deviation from the mean surface plane were obtained with the AFM analysis software. Comparing with the two as-spun substrates, apparently the PEI B showed a much higher roughness due to the cellular surface morphology. After the fSiO₂ incorporation, the membrane PEI A-fSiO₂ exhibited enhanced roughness due to the nanostructured architecture on the membrane surface resulted from the presence of fSiO₂ nanoparticles. It is worth mentioning the roughness of the PEI B-fSiO₂ became smaller compared with the PEI B. This was possibly because embedding the

nanoparticles may partially fill the holes of the membrane surface, thus reduced the roughness.

Figure 6.5. 3-D topography AFM images of (a1) PEI A, (b1) PEI B, (a2) PEI A-fSiO₂, and (b2) PEI B-fSiO₂ membranes

Table 6.4. Surface roughness parameters of the PEI membranes before and after fSiO₂ incorporation

Membrane code	Roughness	
	R _a (nm)	R _q (nm)
PEI A	35.80	50.58
PEI B	79.12	99.87
PEI A-fSiO ₂	64.99	79.91
PEI B-fSiO ₂	72.92	92.08

6.3.4. Effect of fSiO₂ incorporation on the surface wettability of the PEI membranes

The membrane surface wettability was indicated by the dynamic contact angle measurement. Table 6.5 shows the dynamic contact angle results of the PEI membrane before and after fSiO₂ incorporation. We can see that for the first cycle advancing value, the PEI B (109.9 ± 1.4) was higher than the PEI A (86.2 ± 1.1) due to the higher

surface roughness of the PEI B which has been demonstrated in Table 6.4. However, the PEI B was getting wetted quickly as indicated by the second and third cycle advancing values which dropped significantly and even became lower than that of the PEI A. This was believed to be caused by the large pore sizes in the skin layer of the PEI B, where water could enter easily and wet the surface. After the SiO₂ nanoparticles were incorporated and hydrophobically treated, the contact angles of the membranes behaved in a different way. It can be seen that the second and third cycle advancing contact angles were almost the same as the first cycle for both PEI A-fSiO₂ and PEI B-fSiO₂ which indicated the membranes were highly hydrophobic and kept completely dry after immersing in the water.

Table 6.5. Dynamic contact angles of the PEI membranes before and after fSiO₂ incorporation

Membrane code	Contact direction	First cycle (°)	Second cycle (°)	Third cycle (°)	Hysteresis (°)
PEI A	Advancing	86.2 ± 1.1	70.7 ± 2.5	70.4 ± 2.7	23.2 ± 4.1
	Receding	47.6 ± 1.5	47.5 ± 1.6	47.6 ± 1.7	
PEI B	Advancing	109.9 ± 1.4	60.8 ± 1.7	58.3 ± 3.1	12.7 ± 2.5
	Receding	48.0 ± 1.0	48.1 ± 0.8	48.2 ± 0.9	
PEI A-fSiO ₂	Advancing	121.0 ± 2.0	121.0 ± 2.1	120.8 ± 2.2	22.3 ± 3.3
	Receding	98.2 ± 1.0	98.7 ± 1.1	98.7 ± 1.5	
PEI B-fSiO ₂	Advancing	123.2 ± 1.3	123.2 ± 0.7	123.2 ± 0.7	15.9 ± 4.5
	Receding	106.1 ± 3.9	107.2 ± 3.9	107.1 ± 3.8	
PVDF	Advancing	92.3 ± 3.7	89.8 ± 5.1	89.2 ± 5.0	32.6 ± 7.4
	Receding	57.6 ± 2.6	7.2 ± 2.3	57.2 ± 2.4	

Based on the second cycle values, both PEI A and PEI B membrane showed an increase in advancing and receding contact angles of more than 50 ° because of the nanostructured architecture generated by fSiO₂ nanoparticles and highly hydrophobic fluoro-compounds of PFTS on the membrane surface. In particular, the PEI B-fSiO₂ showed a higher advancing contact angle of 123.2 ± 0.7 ° (53 ° increment) and a receding contact angle of 107.2 ± 3.9 ° (60 ° increment) due to the greater surface roughness. The difference between advancing and receding contact angles is called contact angle hysteresis. A high advancing/receding contact angle and low contact

angle hysteresis is responsible for the low wettability of a material surface (X. M. Li, et al., 2007). The contact angle hysteresis here was calculated according the second cycle advancing and receding contact angles. The PEI B-fSiO₂ showed a very low contact angle hysteresis of $15.9 \pm 4.5^\circ$. The inherently hydrophobic membrane PVDF was prepared according to Loh et al. (Loh & Wang, 2012) and the contact angle values were also tested. The newly developed PEI-fSiO₂ membranes showed significantly higher values than PVDF membranes in all contact angle categories.

6.3.5. Effect of fSiO₂ incorporation on the mechanical properties of the PEI membrane

Table 6.6 shows the mechanical properties of the PEI membranes before and after fSiO₂ nanoparticles incorporation in terms of tensile modulus, stress at break and strain at break. The PEI B showed tensile modulus of 233.7 ± 14.3 , which was significantly higher than that of the PEI A (116.9 ± 7.8). A high tensile modulus suggests a high rigidity of the membrane. The stress at break and strain at break of the PEI B reached 10.4 ± 0.2 and 49.4 ± 3.6 , as compared to 5.4 ± 0.1 and 21.1 ± 2.1 of the PEI A, respectively. The combination of high tensile strength and strain at tensile strength makes the membrane have a high toughness. The PEI B had higher rigidity, toughness and elongation properties than that of the PEI A, which was attributed to its more interconnected pore structure, while the PEI A had a finger-like pore structure and macrovoids on its cross section. On the other hand, due to the incorporation of inorganic nanoparticles in the PEI substrate, the composite PEI membranes showed higher rigidity but less elongation properties compared with the as-spun substrates, which was attributed to the intrinsic brittle properties of inorganic materials.

Table 6.6. Mechanical properties of the PEI membranes before and after fSiO₂ incorporation

Membrane code	Tensile modulus (MPa)	Stress at break (MPa)	Strain at break (%)
PEI A	116.9 ± 7.8	5.4 ± 0.1	21.1 ± 2.1
PEI B	233.7 ± 14.3	10.4 ± 0.2	49.4 ± 3.6
PEI A-fSiO ₂	125.6 ± 5.7	5.5 ± 0.1	11.3 ± 0.4
PEI B-fSiO ₂	274.9 ± 16.2	10.6 ± 0.1	19.2 ± 1.0

6.3.6. Application of the PEI-fSiO₂ membranes in GLMC for CO₂ absorption

The PEI A-fSiO₂ and PEI B-fSiO₂ fibers were tested for CO₂ absorption in gas-liquid membrane contactor. The performance of CO₂ absorption with the change of the liquid velocity is shown in Figure 6.6. Pure CO₂ and pure water was used in this experiment. It can be observed that the CO₂ flux increased with the increase in the water flow rate. This is a well-known behaviour in membrane contactor which indicates the main resistance exists in the liquid phase in the case of physical absorption of CO₂ (Atchariyawut, et al., 2007; Y. Zhang, et al., 2013; Y. Zhang, Wang, Zhang, & Fane, 2012). The change in gas velocity hardly affected the absorption performance. As can be seen from Figure 6.6, the PEI B-fSiO₂ possessed much higher CO₂ flux than that of the PEI A-fSiO₂. At a liquid velocity of 0.3 m/s, the PEI A-fSiO₂ showed the CO₂ flux of 1.38×10^{-3} mol/m²·s while the PEI B-fSiO₂ showed the CO₂ flux of 2.65×10^{-3} mol/m²·s, which was almost twice of the PEI A-fSiO₂'s flux. This was most likely due to the higher surface porosity and bigger pore sizes of the PEI B-fSiO₂ membrane which significantly reduced the mass transfer resistance. In contrast, the relatively dense skin layer of the PEI A-fSiO₂ imposed higher mass transfer resistance compared with the PEI B-fSiO₂. Moreover, the high degree of pore interconnectivity in the cross section the PEI B-fSiO₂ was believed to be another factor contributing to its high flux.

Figure 6.6. CO₂ flux using pure water as the absorbent (atmospheric pressure, absorbent temperature at 25 °C, gas flow rate at 30 ml/min)

Figure 6.7 shows the CO₂ flux of the composite PEI-fSiO₂ membranes by using amino acid salts as the absorbent liquid, e.g. 2 M aqueous sodium taurinate solution. It is well

understood that the physical absorption suffers low separation efficiency than chemical absorption. In the case of chemical absorption by using a 2 M aqueous sodium taurinate solution, the CO₂ flux of the PEI A-fSiO₂ was $6.83 \times 10^{-3} \text{ mol/m}^2\cdot\text{s}$ at a liquid velocity of 0.3 m/s; it was 4 times higher than the flux in physical absorption at the same liquid velocity. While the CO₂ flux of the PEI B-fSiO₂ was $2.06 \times 10^{-2} \text{ mol/m}^2\cdot\text{s}$, which was 6.7 times higher than the flux in physical absorption. In addition, the flux of the PEI B-fSiO₂ was three times of the PEI A-fSiO₂'s flux because of its higher surface porosity and pore interconnectivity beneath the top layer. Moreover, it is observed that with the increase in liquid velocity, CO₂ absorption flux increased. This was because there was a significant solvent depletion in the shell side due to the high pure CO₂ concentration in the gas phase. Thus, the solvent concentration would drop dramatically at the gas-liquid interface and instantaneous absorption regime took place. An increase in the solvent velocity would reduce its depletion at the interface, and therefore enhanced the mass transfer efficiency.

Figure 6.7. CO₂ flux using 2 M sodium taurinate as the absorbent (atmospheric pressure, absorbent temperature at 25 °C, gas flow rate at 100 ml/min)

The long-term performance of CO₂ flux of the PEI A-fSiO₂ and PEI B-fSiO₂ membranes by using 2 M sodium taurinate were carried out for 60 days. Measurements were carried out periodically to observe the change in CO₂ absorption flux. The membrane contactor modules were fully immersed in the sodium taurinate solution after every experiment to ensure that the outer surfaces of the hollow fibers would be in constant contact with the absorbent. The experimental results are shown in Figure

6.8. The CO₂ flux of the PEI B-fSiO₂ membrane was consistently higher than that of the PEI A-fSiO₂ membrane. Through the 60 days testing, the PEI B-fSiO₂ membrane was able to maintain a very stable performance with CO₂ flux around 1.4×10^{-2} mol/m²·s while the flux of the PEI A-fSiO₂ decreased gradually from 6.0×10^{-3} mol/m²·s to 4.0×10^{-3} mol/m²·s, suggesting that the PEI A-fSiO₂ was partially wetted by the 2 M sodium taurinate solution. This was probably due to the relatively lower surface hydrophobicity of the PEI A-fSiO₂ membranes as compared with PEI B-fSiO₂. The long-term test indicated the great potential of PEI B-fSiO₂ membranes in GLMC application, and also revealed the important role of membrane fabrication and modification techniques in facilitating the commercialization of membrane contactor applications.

Figure 6.8. Long-term CO₂ flux using 2 M sodium taurinate as the absorbent (atmospheric pressure, absorbent temperature at 25 °C, gas flow rate at 100 ml/min, liquid velocity at 0.1 m/s)

Table 6.7 shows the summary of the CO₂ flux of various membranes used in GLMCs. We can see that the PEI B-fSiO₂ possessed superior CO₂ absorption performance over the other commonly used polymeric membranes. The surface modifying macromolecule (SMM) modified PEI hollow fiber membranes also showed a very high CO₂ flux, but the hydrophobicity was relatively low with contact angle of 95 °and the long term performance of the membrane was not available (Bakeri, Ismail, Rana, & Matsuura, 2012). In fact, it is rare that the in house-made hollow fiber membranes experienced long-term stability investigation, in particular for such a long period of

time -2 months. Both the high CO₂ flux and stable long-term performance indicated the PEI B-fSiO₂ membranes have the great potential to be used practically in GLMC process, which also reveals the important role of membrane engineering in terms of fabrication and modification techniques in facilitating industrial processes of membrane-based separations.

6.4. Conclusions

Aiming to minimize the membrane mass transfer resistance, the study in this Chapter utilized the unique structure of triple-orifice spinneret to fabricate PEI hollow fiber membranes with a highly porous and interconnected surface structure, which is desirable for incorporating fSiO₂ nanoparticles on the membrane surface. The following conclusions can be drawn from this study:

- (1) The solvent-dope solution co-extrusion method using a triple-orifice spinneret for hollow fiber spinning is an effective way to increase the surface porosity, pore size and pore interconnectivity of the membrane.
- (2) The membrane mechanical properties were improved because of the highly porous cellular surface structure and high degree of pore interconnectivity.
- (3) This highly porous and cellular surface structure is favorable for nanoparticle embedment. fSiO₂ nanoparticles were incorporated on the PEI hollow fiber membrane, leading to a significant improvement in surface hydrophobicity, as evidenced by the advancing contact angle value of 123.2 °; receding contact angle value of 107.2 °; and contact angle hysteresis of only 15.9 °.
- (4) The PEI B-fSiO₂ membranes prepared by the solvent-dope solution co-extrusion approach showed a significant flux enhancement and more stable long-term performance through a two-month long-term test compared with the PEI A-fSiO₂ membrane, indicating its great potential for GLMC application.

Table 6.7. Overall comparison of CO₂ flux of various membranes used in GLMCs

Membrane code	Polymer type	ID/OD (mm)	Porosity (%)	CO ₂ flux ^a (mol m ⁻² s ⁻¹)	Shell side	Remarks	Manufacturer	References
#1 (PEI A-fSiO ₂)	PEI	0.7/1	81	1.38 x 10 ⁻³	Water	fSiO ₂ incorporated	In-house made	Current work
#2 (PEI B-fSiO ₂)	PEI	0.7/0.9	71	2.65 x 10 ⁻³	Water	fSiO ₂ incorporated	In-house made	Current work
#3 (fSiO ₂ -PEI-3h)	PEI	0.8/1.1	-	8.68 x 10 ⁻⁴	Water	fSiO ₂ incorporated	In-house made	Chapter 5
#4 (PAI-20min)	PAI	1.1/1.4	73	1.54 x 10 ⁻³	Water	Octadecylamine modified	In-house made	Chapter 4
#5 (PAI-A#2)	PAI	1.1/1.4	72	8.5 x 10 ⁻⁴	Water	APTMS & FS10 modified	In-house made	Chapter 3
#6	PVDF	0.3/0.4	76	1.0 x 10 ⁻³	Water	Phosphorous acid as the additive	In-house made	(Atchariyawut, et al., 2006)
#7	PVDF	-/-	-	8.0 x 10 ⁻⁴	Water	Commercial	Tianjin Motian Membrane	
#8	PVDF	0.3/0.5	-	8.0 x 10 ⁻⁴	Water	Pristine PVDF	In-house made	(Feng, et al., 2011)
#9	PVDF	0.65/1	75	6.5 x 10 ⁻⁴ (extrapolated)	CO ₂	Commercial	Memcor Australia	(Atchariyawut, et al., 2008)
#10	PSf	0.5/1	72	7.5 x 10 ⁻⁴	CO ₂	Glycerol as the additive	In-house made	(Mansourizadeh & Ismail, 2010)
#11	PEI	0.3/0.6	77	1.2 x 10 ⁻³	CO ₂	Pristine PEI	In-house made	(Bakeri, et al., 2012)
#12	PEI	0.35/0.6	81	2.3 x 10 ⁻³	CO ₂	SMMs modified		
#13	PP	0.22/0.23	40	1.4 x 10 ⁻³	CO ₂	Commercial	Celgard Inc.	(R. Wang, et al., 2005)

^a. Achieved at liquid velocity of 0.3m/s

CHAPTER 7

Conclusions and Recommendations

7.1. Overall conclusions

This thesis presents the development of novel hydrophobic hollow fiber membranes intended for the use in GLMC application for CO₂ capture. So far, no commercial CO₂ removal process using GLMC technology is presently in operation. One of the main technical barriers is membrane wetting. The essential properties of the membrane suitable for GLMC application include high surface hydrophobicity and chemical resistance, and appropriate pore sizes so that the membrane can be prevented from wetting and chemical attack by the absorbents.

In this study, the hydrophobic hollow fiber membranes with controlled pore structures were prepared by the means of surface modification, and highly hydrophobic inorganic-organic composite membranes were also fabricated as presented from Chapter 3 to Chapter 6: two-step chemical modification of poly(amide-imide) (PAI) hollow fiber membranes (Chapter 3), single-step chemical modification of PAI hollow fiber membranes (Chapter 4), fluorinated silica (fSiO₂) incorporation on polyetherimide (PEI) substrate to form an inorganic-organic composite membrane (Chapter 5) and optimization of the PEI substrate and fSiO₂ incorporation technique to produce the composite membrane with superior GLMC performance (Chapter 6). The following conclusions can be drawn from this study:

From Chapter 3:

- Asymmetric microporous PAI hollow fiber membranes were fabricated and treated by a two-step surface modification using APTMS and FS10 to produce the membrane with a highly hydrophobic surface.

- Increasing in polymer concentration would result in a higher viscosity of the dope solution, and tended to delay the dope precipitation rate by slowing down the solvent non-solvent exchange process, leading to a denser and thicker skin layer of the as-spun hollow fiber membranes.
- The newly developed PAI hollow fiber membranes showed much higher hydrophobicity. The dynamic contact angle (2nd cycle) improved from 76° to 108~117° and LEP_w improved from 0.8 bar to 2.1~4.0 bar. The results suggested that the modified PAI membranes tend to be highly wetting resistant.
- A preliminary study in GLMC indicated the CO₂ absorption performance of the modified PAI membrane was affected by the substrate structure. The membrane with larger pore sizes had a smaller mass transfer resistance and hence larger CO₂ flux.
- The modified membranes showed a stable CO₂ absorption flux using pure CO₂ as the feed gas and 2 M sodium taurinate and water as the liquid absorbents in a GLMC for up to 42 days.

From Chapter 4:

- A simple and inexpensive single-step modification method by using a long-chain alkyl octadecylamine as the aminic modifier was explored to prepare hydrophobic PAI hollow fiber membranes.
- The treated membranes showed much higher hydrophobicity with an improvement in contact angle of around 30°. The LEP_w also increased significantly after the modification from 0.7 bar to 4.2 bar because of the grafting and anchoring of the alkyl chains on membrane surface and over the cross section.
- The CO₂ flux of the modified membranes increased with the modification time because of the pore opening and the reduction of the skin layer thickness due to the interfering and breaking down of polymer chains by octadecylamine

modifier. A stable performance of the modified membranes in a GLMC by using sodium taurinate as the liquid absorbent was attained for 15 days.

From Chapter 5:

- A novel highly hydrophobic inorganic-organic composite hollow fiber membrane was formed by incorporating of fSiO₂ layer on the PEI substrate through sol-gel process. The ultrasonication test revealed that the fSiO₂ layer was tightly bonded to the PEI substrate via the silane chemical reactions.
- The hydrophobicity of the composite membrane surface was dramatically elevated, as evidenced by the dynamic contact angles increment, e.g. from original 66.7 ° to 124.8 ° for advancing values, and from 49.5 ° to 100.6 ° for receding values. The contact angle hysteresis reached 24.2 °.
- A reasonably stable long-term performance of the fSiO₂-PEI composite membrane was attained by using pure CO₂ as the feed gas and 2 M sodium taurinate as the liquid absorbent in the GLMC. The contactor showed around 20% of the initial flux drop over the 31-day operation.

From Chapter 6:

- Aiming to minimize the membrane mass transfer resistance, a newly porous PEI substrate with high surface porosity and large pore size in the outer skin layer was developed via the solvent-dope solution co-extrusion approach using a triple-orifice spinneret for hollow fiber spinning, followed by the fSiO₂ nanoparticle incorporation to make the membrane surface highly hydrophobic and chemical resistant.
- The PEI membrane (PEI B) spun by the solvent-dope solution co-extrusion approach showed better mechanical properties in terms of rigidity, toughness and elongation, due to the higher degree of pore interconnectivity in the membrane cross section compared with the PEI membrane (PEI A) spun from standard dry-jet wet spinning process.

- The newly developed PEI B-fSiO₂ hollow fiber membranes showed the advancing contact angle value of 123.2°, receding contact angle value of 107.2°, and contact angle hysteresis of only 15.9°, indicating the high water resistant property.
- The PEI B-fSiO₂ showed consistently higher CO₂ flux than that of the PEI A-fSiO₂ in both physical and chemical absorption GLMC tests. This was due to the high surface porosity and big pore sizes as well as the high degree of pore interconnectivity beneath the outer top layer of the PEI B-fSiO₂ membrane, which minimized the mass transfer resistance.
- The PEI B-fSiO₂ membranes showed superior performance in GLMC compared with other commercial or in-house made hydrophobic membranes based on CO₂ absorption process. A stable CO₂ absorption performance by using sodium taurinate as the liquid absorbent was attained over a 60-day long-term test, indicating the great potential of PEI B-fSiO₂ membranes in practical GLMC application for CO₂ capture.

Overall:

To achieve a high performance membrane contactor, there are two requirements on the membrane: high CO₂ absorption flux and stable long-term performance. The stable long term performance is determined by the membrane hydrophobicity and chemical resistance. Most membranes used in GLMC in literature are the end-products of the spinning process without post treatment. The CO₂ absorption flux therefore is determined by the spinning conditions and the hydrophobicity is intrinsically determined by the polymer materials. On the other hand, post chemical treatment can dramatically enhance the hydrophobicity of the membrane, and may also enhance the CO₂ absorption performance. In this thesis, PAI hollow fibers were chemically modified and turned from hydrophilic membranes to highly hydrophobic membranes with good CO₂ absorption performance. The PEI hollow fibers were incorporated with inorganic silica nanoparticles and formed a highly hydrophobic and chemical resistant organic-inorganic composite membrane. Due to the well-designed spinning condition,

the PEI-B substrate showed highly porous and interconnected surface structure which determined its superior performance in CO₂ flux. In summary:

- PAI and PEI are not hydrophobic polymers naturally. They can be used as the membrane materials for GLMC application which is realized by the novel surface hydrophobic modification approaches or through the formation of inorganic-organic composite membranes presented in this study.
- The results of the above studies demonstrated the important role of membrane engineering in terms of fabrication and modification techniques in facilitating commercialization of GLMC applications.

7.2. Recommendations for future research

The recommendations for the future research can be divided into a few parts, as listed below:

- **In-situ generation of silica nanoparticles in the membrane matrix**

In Chapter 6, the formation of the silica-PEI composite membrane was accomplished by direct deposition of the silica nanoparticles on the membrane surface through silane chemical interactions. The silica precursor solution was allowed to hydrolyze and condensate completely to form the silica nanoparticles suspension. Then the membranes were placed in the suspension to allow the deposition of silica nanoparticles on the membrane surface.

On the other hand, in situ formation of silica nanoparticles within the bulk PEI membrane matrix would be another interesting approach to fabricate the inorganic-organic composite membranes. To achieve the in-situ growth of silica nanoparticles, the silica precursor solution can be impregnated into the membrane matrix during the process of the hydrolysis and condensation and allows the formation and growth of the silica nanoparticle cores inside the membrane matrix. The size and morphology of the silica nanoparticles synthesized can be controlled by the confined space within the membrane matrix network. However, prolonged immersion time of the membrane in the

precursor solution would damage the polymer substrate since the solution is strong alkaline. Thus, the silicification process in this study needs to be faster than the conventional sol–gel approach; temperature, concentration and pH of the precursor solution can be adjusted to facilitate the growth of the silica by promoting the condensation process.

- **Bio-inspired mineralization to incorporate nanoparticles onto the membrane surface to develop hydrophobic hollow fiber membranes**

Nature has always been a source of inspiration. The understanding of the underlying formation mechanisms of biomaterials provides ample opportunities for developing new approaches to fabricate new composite membranes. For example, recently, a nanohybrid composite membrane via in-situ generation of inorganic nanoparticles in an ultrathin membrane scaffold was reported (Pan, Jia, Cheng, & Jiang, 2010). A systematic study on biomineralization inspired synthesis of novel composite membranes is recommended. For example, different polymers and in-organic precursor solutions need to be selected carefully based on the design requirement. The thermodynamics and kinetics of nucleation and crystal growth of nanoparticles need to be studied, aiming to control the size, shape, orientation, aggregation and texture of nanoparticles, etc. Fundamental understanding of polymeric and inorganic phase interaction and membrane formation principles are critical for this study.

Bio-inspired mineralization synthesis strategy is recommended to explore the incorporation of the nanoparticles on the membrane surface to enhance the surface roughness. Biomineralization is an extremely widespread natural process, where living organisms produce minerals under a chemical environment to form exquisite mineralized tissues. Specifically, the inorganic phase is usually precipitated by bio-macromolecules such as proteins, polysaccharides or polypeptides, and mediated by the polymeric phase. The resultant materials normally exhibit a hierarchical architecture and possess diverse functions (Aizenberg et al., 2005)

- **Quantifying the extent of chemical modification**

The extent of membrane chemical modification can be examined to better understand the modification process. Testing the gel content is one possible approach. The gel content of the crosslinked membrane (insoluble part) can be determined by immersing the membrane in a solvent, such as tetrahydrofuran (THF). The crosslinked or gelled polymer will not dissolve in the solvent while the rest polymer will dissolve. Therefore, the gel content of a membrane can be obtained by the gravimetric procedure. Alternatively, positron annihilation lifetime spectroscopy (PALS) can also be used to quantify the extent of the membrane chemical modification.

- **Study of mixed gas or industrial gas on the performance of the membranes**

The study of membrane contactor based on the mixed gas or real industrial gases such as biogas, natural gas and flue gas will be investigated. Trace gases such as NO_x , SO_x and H_2S are present in the industrial gas streams which will have interference on the absorption process of CO_2 . Moreover, the absorption process can also be affected under elevated temperature and/or pressure. Those harsh operating conditions will be considered in the future study.

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