

Optimizing the structure and plasticization resistance of asymmetric polyimide hollow fiber membranes for CO2 removal from natural gas

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Optimizing the Structure and Plasticization Resistance of

Asymmetric Polyimide Hollow Fiber Membranes for CO₂ Removal

from Natural Gas

BY

Guangxi Dong



A thesis submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

School of Chemical Engineering

The University of New South Wales

Sydney, Australia

April 2011

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ABSTRACT

Polymeric membrane has been recognized as an energy efficient and economical approach for many industrial gas separation applications, including natural gas purification. Matrimid 5218[®] has been used as a benchmark polymer, due to its combination of high selectivity and acceptable permeance, as well as its excellent mechanical properties and commercial availability.

Based on series of comprehensive experimental studies, we have evaluated many of the critical fabrication parameters and optimized those parameters as regard to the membrane physical and separation properties. Asymmetric hollow fibers with CO_2/CH_4 separation factors up to 67 were successfully fabricated under the optimum fabrication conditions. Our further thermodynamic analysis based on Hansen's solubility parameter and kinetic analysis based on Hayduk and Minhas correlations resulted consistent observations with the experimental results including cloud point experiments, SEM images, and the gas separation properties.

In this study, a nodule structure model was developed based on the nucleation and growth and dual mode sorption model to gain a comprehensive understanding of the plasticization phenomenon and to link the bridge between membrane formation mechanisms with membrane morphology and plasticization phenomenon.

Gas sorption tests were performed on the in-house fabricated Matrimid hollow fibers with various ranges of separation properties, and the Henry's and Langmuir sorption isotherms were decoupled and compared against the pressure. The sorption observations accompanied with the CO_2 conditioning experimental results confirmed that Matrimid

hollow fiber adsorbed more CO_2 gas penetrants in Henry's sites at low-pressure range were prone to the plasticization.

In this study, thermal annealing as a post-treatment to enhance membrane's plasticization resistance was evaluated. CO_2 sorption tests provided solid evidence to prove the suppression of plasticization achieved by thermal annealing was partially because the thermal annealing alters the ratio of Henry's and Langmuir sorption sites and consequently shift the plasticization pressure to a higher level. Other techniques were also adopted in this study to characterize the treated hollow fiber including SEM, DSC measurements as well as dissolution tests.

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PUBLICATIONS

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- G. X. Dong, H. Y. Li, V. Chen, Matrimid hollow fiber membrane for CO₂ removal from natural gas: Fabrication process optimization and thermal annealing aiming to suppress plasticization, Membrane Society of Australasia Student Symposium 2010, Wollongong, Australia.
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NOMENCLATURE

с	Concentration of the gas penetrants in the polymer
S	Henry's solubility constant
р	Gas penetrant pressure
c _D	Gas sorption concentration in Henry's sites
c _H	Gas sorption concentration in Langmuir sites
c _H	Hole saturation constant
b	Hole affinity constant
Q	Permeation flux
D	Diffusion coefficient
L	Membrane thickness/Apparent skin layer thickness
Р	Permeability coefficient
У	Downstream gas mixture mol fraction
X	Upstream gas mixture mol fraction
V_{g}	Specific volume of the polymer material
V_0	Specific volume occupied by polymer chain macromolecules
$D_{\rm H}$	Diffusion coefficient in Langmuir sites
D _D	Diffusion coefficient in Henry's sites
D	Diffusion coefficient
Т	Temperature
ΔG_m	Free enthalpy
ΔH_{m}	Enthalpy of mixing

ΔS_m	Entropy of mixing
V _m	Molar volume fraction of the solution
V_1	Molar volume fraction of component 1
V ₂	Molar volume fraction of component 2
ΔΕ	Energy of vaporization
ΔE_d	London dispersion force
ΔE_p	Dipolar force
ΔE_h	Hydrogen bonding force
E_{coh}	Structure component for the overall solubility parameter
E _{hi}	Structure component for the hydrogen bonding component of the solubility
	parameter
F _{di}	Structure component for the dispersion force component of the solubility
	parameter
F _{pi}	Structure component for the dipolar component of the solubility parameter

GREEK LETTERS

α*	Ideal selectivity (single gas permeation)
α	Separation factor (mixed-gas permeation)
δ	Solubility parameter
δ_d	Solubility parameter due to the dispersion forces
δ_p	Solubility parameter due to polar forces
δ_h	Solubility parameter due to hydrogen bonding

SUBSCRIPTS

A Gas type A in binary gas mixture

В	Gas type B in binary gas mixture
1	Downstream of the membrane
2	Upstream of the membrane
S	Solvent
ns	Non-solvent

ABBREVIATIONS

GPU	Gas permeation unit
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
TGA	Thermo-Gravimetric Analysis
FFV	Fractional free volume
NMP	N-Methyl-2-pyrrolidone
THF	Tetrahydrofuran
DMAc	Dimethylacetamide
GC	Gas chromatography
CED	Cohesive energy density
CTC	Charge transfer complexes

1 INTRODUCTION

1.1 Membrane technology overview

Membrane is a thin barrier that allows certain species transport through in a selective manner. Most of the membranes used in industry are fabricated from either organic (polymers, liquids) or inorganic materials (metals, carbons and zeolites). Membrane separation process can be categorized in terms of the driving forces that they applied: pressure driven process (gas separation, ultra- and micro-filtration, and reverse osmosis), concentration driven process (dialysis), and electrical potential driven process (electrolysis, electro-dialysis). In addition, membrane separation processes can also be classified by the rejected particle and molecular size (Fig.1.1) (Cheryan 1998).



Fig.1.1. Ranges of various membrane separation processes in liquid process (Cheryan 1998)

Membrane can be fabricated either in flat sheet or hollow fiber geometry depending on the considerations of packing density, fouling and concentration polarization tendency, and operation/maintenance costs (Strathmann 2001). Flat sheet membranes are usually packed in plate-and-frame or spiral-wound modules, whereas hollow fibers in tube-inshell module. Membranes either have a symmetric or asymmetric structure; symmetric membranes have a uniform structure through the entire membrane, while asymmetric membranes consist of at least two distinct layers with different structures.

For gas separation, asymmetric hollow fiber membrane is a very competitive membrane configuration compared to other configurations with its large membrane surface area to volume ratio (m^2/m^3) . The cylindrical form and unique asymmetric structure of hollow fibers also allow the modules to withstand higher pressure difference across the membrane.

Membranes can be fabricated via several techniques as shown in Fig.1.2, phase inversion is the most common approach to prepare asymmetric membrane for gas separation, and will be discussed in details in the following chapters, other techniques such as solution casting and extrusion are also commonly adopted for membrane fabrication.



Fig.1.2. Membrane classification in terms of geometry, bulk structure, fabrication method, and application (Pinnau and Freeman 2000)

Membrane technology possesses great advantages over other conventional separation processes (Mulder 1996), for example, it can achieve continuous separation, and consume less energy, its module design makes it easy to scale up and take less footprint. However membrane's application in industry has been limited because of the issues on fouling, concentration polarization, physical aging, plasticization and low efficiency.

Recent development in membrane technology has been focused on the issues including (1) Improvement of the performance of state-of-the-art membranes and development of novel membrane materials such as the thermal re-arranged membrane and the polymers of intrinsic micro-porosity (Budd, Msayib et al. 2005; Mckeown, Budd et al. 2005; Park, Jung et al. 2007; Han, Lee et al. 2010; Jung, Lee et al. 2010; Park, Han et al. 2010), (2) Improvement of the performance of the commonly used membrane module and design of the new module concept such as transverse flow capillary module (Roesink 1989), and (3) Development of the novel membrane processes and applications, such as the development of the ion conductive membranes in fuel cell and battery application (Clochard, Berthelot et al. 2010).

1.2 Gas separation membrane

Gas separation membrane technology has been emerged as a commercial process on the industrial scales since 1980s (Kesting and Fritzschz 1993). The selection of the membrane materials has been the key factor to determine the efficiency of this technology (Yampolskii, Pinnau et al. 2006). During the past thirty years, more than 1000 novel polymer materials have been synthesised with promising physio-chemical and mechanical properties. Yet, only 8 or 9 out of hundreds of these polymer materials have been applied to fabricate commercial gas separation membrane (Baker 2002). The following factors determine the application of membrane technology on gas separation:

- High permeability to maximize productivity,
- High selectivity to increase separation efficiency,
- Tolerant to aggressive feed gas stream,
- Tolerant to various pressure and temperature ranges,
- Mechanical and chemical stability,
- Low manufacturing, operation and maintenance costs,
- Capable of being packed at high density to maximize the surface area per volume.

The revolutionary phase inversion technique was developed by Loeb and Sourirajan to prepare the integrally skinned asymmetric membranes possessing high permeability and selectivity (Loeb and Sourirajan 1962). The ultra-thin selective skin layer of these membranes could maximize the permeation flux, and the micro-porous sub-structure provides mechanical strength meanwhile minimizes the resistance to the gas flux.

Asymmetric hollow fiber membrane is one of the dominating modules in industrial gas separation membrane market due to its high membrane area to module volume ratio $(>1000m^2/m^3)$ compared to the flat sheet and tubular configurations.

1.3 Membrane process in natural gas purification

Natural gas is a fast growing energy source throughout the world, its market is projected to be doubled by 2020 from 2001 level (Barden and Martin 2008). It is a cleaner burning fuel than coal or fuel oils because it produces less carbon dioxide per joule. However the wellhead natural gas contains different levels of impurities including CO_2 , H_2S , water vapour and heavier hydrocarbons which could severely hinder membrane's long-term performance. In Australia, approximately half of its identified natural gas resources have high content of CO_2 which need to be removed prior to transport (Cook 2006).

Removing CO_2 from natural gas is mandatory to meet the pipeline specification because CO_2 presented in the raw natural gas can form corrosive chemical to damage pipeline, or form blocks of dry ice, clogging equipment, most importantly its presence reduces the heat value of the natural gas and increases the transport cost (Wallace 2004; Bernardo, Drioli et al. 2009).

Several techniques have been developed in the past to remove these sour gases from the wellhead natural gas (e.g. amine absorption, pressure swing adsorption, glycol absorption etc.). In the past two decades, membrane technology for gas separation has attracted much attention as a potential candidate to replace the conventional natural gas sweetening techniques due to its environmental friendly nature, small footprint and less energy

consumption. The pressure driven membrane gas separation process eliminates the needs of feed gas compression because of the high pressure of raw natural gas at wellhead (Bhide, Voskericyan et al. 1998).

With the development of the membrane technology on natural gas purification, the market of membrane for natural gas application will continue to grow from 19% of total membrane application in industrial gas separation to 30% in the next decade (as shown in Fig.1.3) (Baker 2002).



(A)



(B)

Fig.1.3. Estimated market share of membrane technology for gas separation (A) in 2000, and (B) in 2020 (Baker 2002)

Membrane units for natural gas purification have already been adopted and installed in oil and gas industry for more than two decades. A CO₂ removal system was commissioned in July 2004 by Petreco incorporated with the PRISM membrane developed by Air Products with a capacity of 8 MMSCFD, capable of reducing CO₂ level from 4.5% to less than 2% (http://www.airproducts.com/Products/Equipment/PRISMMembranes/page06.htm).

SeparexTM cellulose acetate membrane units has been installed by UOP in Pakistan to remove CO₂ from 12% to less than 3% with a capacity of 210 MMSCFD at 90bar (Dortmundt and Doshi 1999). UBE Group has produced CO₂ separation membrane based on polyimide which can bring down CO₂ content from near 10% to less than 2% (http://northamerica.ube.com/content.php?pageid=45).

In addition to the natural gas purification, gas separation membranes have also been successfully adopted in other industrial applications such as nitrogen enrichment from air purification, hydrogen separation, and oxygen enrichment etc (Koros and Fleming 1993; Freeman and Pinnau 1999; Baker 2002). Membrane gas separation technology has also shown great potential in air and natural gas dehydration due to its simple separation process and environmental friendly nature (May-Britt 1998).

1.4 Recent development in gas separation membrane

The separation performance of non-porous gas separation membrane is largely dependent on the choice of the polymer material. The ideal polymer material should deliver not only the maximized fractional free volume but also the optimized distribution of the effective free volume (i.e. interconnected free volume). Under this guideline, large number of novel polymer materials has been synthesized with the desired backbone and side group structure such as PMP, PTMSP, and Teflon AF2400. These polymer materials deliver much higher permeability (2 to 3 orders of magnitude) than the conventional glassy polymers (Hellums, Koros et al. 1991; Story and Koros 1992; Koros and Fleming 1993; Mulder 1996; Cao, Wang et al. 2002; Chung, Ren et al. 2003).

Another significant development of membrane polymer research is the synthesis of the polymers of intrinsic micro-porosity (PIMs) by McKeown et al (Budd, Msayib et al. 2005; Mckeown, Budd et al. 2005). These materials with pore size less than 2nm display superior solubility and processability. Thermally re-arranged polymers was developed by Park et al. with a peculiar free volume micro-structure which can provide high permeability and selectivity (Park, Jung et al. 2007; Choi, Jung et al. 2010).

Mixed matrix membranes containing inorganic molecular sieving materials embedded in a polymer matrix offer great potential to combine the processability of polymers with superior gas separation properties of inorganic molecular sieving materials (Chung, Chan
et al. 2003; Ekiner and Kulkarni 2003; Jiang, Chung et al. 2006). In addition, this new class of gas separation membrane offers enhanced physical, thermal and mechanical stability for harsh operation environments (Hu, Marand et al. 1997).

The carbon nano-tubes have drawn a lot attention recently as a potential material candidate for gas separation membrane (Hinds, Chopra et al. 2003; Majumder, Chopra et al. 2005). Unlike other similar materials such as zeolites with nano-pores, the carbon nano-tubes contain pores on atomic scales which can provide much higher gas flux than conventional membrane materials.

A new class of gas separation membrane called "facilitated transport membrane" has been developed recently. Gas transport through this type of membrane does not solely rely on solution-diffusion mechanism, these membranes comprise metal ions with a special affinity toward a target gas molecule and this interaction controls the rate of transport. These metal ion carriers ensure membrane to achieve high permeability even at low concentration driven force (Ho and Sirkar 1992).

1.5 Challenges for gas separation membrane applications

One of the greatest challenges for the gas separation membrane development is to achieve superior separation performance with high permeability and selectivity at the same time. Robeson (Robeson 1991) has compiled gas separation data from a wide range of gas pairs and polymer materials in 1991, and placed an empirically defined "upper bound" to illustrate the trade-off relation between permeability and selectivity. In 2009, Bernardo et al. (Bernardo, Drioli et al. 2009) reported the latest "Robeson upper bound" which demonstrated all the great efforts have been made by the researchers to push it to a higher level (Fig.1.4).



Fig.1.4. Robeson bounds 1991 vs. 2009 (O_2/N_2 , CO_2/CH_4) (Bernardo, Drioli et al. 2009) For non-porous gas separation membranes, the permeability-selectivity trade-off relation is largely determined by the polymer chain structure itself and polymer chains packing manners (Koros, Fleming et al. 1988), for example, crystalline polymers, which possess large portion of neatly packed folded-chain segments, normally display high selectivity and limited permeability (Kesting and Fritzschz 1993). However the Robeson plot does not reflect how thin the material can be formulated on large scale and actual gas fluxes achievable.

Maintaining membrane's separation properties under harsh and long-term operation conditions at high pressure, high temperature, and the presence of highly sorbing contaminants present another great challenge for membrane gas separation technology. Various researchers have reported dramatic reduction of gas permeability in polymeric membrane over time due to physical aging (Bartos, Muller et al. 1990; McHerron and Wilkes 1993; Rezac, Pfromm et al. 1993; Royal and Torkelson 1993; Pfromm and Koros 1995; Chung and Kafchinski 1996; Chung and Teoh 1999; Dorkenoo and Pfromm 1999; Lin and Chung 2000; Huang and Paul 2004). It was suggested that the severely hindered segmental motions in the glassy polymer could be recovered over time, and this gradual approach to the equilibrium state will reduce the free volume available for gas transport, thus decrease the permeability (Struik 1977). Some polymer materials were reported possessing the physical aging resistance such as Teflon AF2400 (Bernardo, Drioli et al. 2009). Several post-treatment approaches have also been developed to de-age the membrane, for example, electron beam irradiation has been proved to be sufficient to reverse the physical aging effect (McHerron and Wilkes 1993). Unfortunately very little work has been done to investigate the physical aging suppression strategies so far and further investigation is certainly needed.

For the natural gas purification, polymeric membrane's sustainable performance was also jeopardized by another phenomenon other than physical aging: CO₂ induced plasticization (Chiou, Barlow et al. 1985; Jordan, Koros et al. 1987; Maeda and Paul 1987; Jordan, Koros et al. 1989; Bos, Punt et al. 1999; Ismail and Lorna 2002; Kapantaidakis, Koops et al. 2003). Plasticization is a unique phenomenon that could severely deteriorate gas transport properties in membrane (More details of plasticization will be provided in the following chapters) and shorten membrane's life span. Therefore membrane materials must possess robust chemical and mechanical stability to ensure the separation properties can be maintained over long-term operation. Furthermore several suppression strategies have also been established in the past: (1) thermal annealing with or without alteration of polymer structure (Kuroda and Mita 1989; Kuroda, Terauchi et al. 1989; Kawakami, Mikawa et al. 1996; Bos, Punt et al. 1998; Krol, Boerrigter et al. 2001; Chung, Ren et al. 2003; Zhou and Koros 2006), (2) chemical cross-linking with extra cross-linker or polymer material itself (Staudt-Bickel and Koros 1999; Liu, Wang et al. 2001; Tin, Chung et al. 2003; Zhao, Cao et al. 2008; Zhao, Cao et al. 2008), and (3) blending with a secondary polymer material with better plasticization resistance (Wessling, Huisman et al. 1995; Bos, Punt et al. 1998; Bos, Punt et al. 1999; Bos, Punt et al. 2001; Sterescu,

Stamatialis et al. 2008). More details of these plasticization suppression strategies will be presented in Chapter 2.

1.6 Research objectives

The fundamental objective of this study is to develop polyimide hollow fiber membranes with two major characteristics: first it should have defect-free selective skin layer thus provide superior CO_2/CH_4 separation performance for natural gas purification, and secondly it should possess decent plasticization resistance via certain post-treatments thus improve membrane's long-term performance.

To achieve the aforementioned objectives, this dissertation focuses the following subissues:

One of the major objectives of this work is to conduct a systematically evaluation of the fabrication variables in order to develop the optimized spinning protocol so that the defect-free integrally skinned hollow fiber for natural gas purification application can be fabricated without the necessity of the further post-treatment.

The amount of parameters affecting membrane's separation performance makes the evaluation process very time consuming. It would be of great interest to develop an approach to lower the workload. In this dissertation, the Hansen's solubility parameters analysis (Matsuura 1993; Jiang, Chung et al. 2008) is extended from pure component to the mixtures, so that the thermodynamical interaction between dope, bore and coagulation fluid can be evaluated. And the analytical results could be used to guide the selection of the dope and bore composition to reduce the runs of experiments.

It has appeared that very little attempts have been made to connect the existing gas transport mechanism in glassy polymer with plasticization phenomenon. In this dissertation, a nodule structure model which connect both dual-mode sorption model (Vieth, Howell et al. 1976; Koros 1980; Barrer 1984) and membrane formation mechanisms (Kesting 1990; Wienk, Van den Boomgaard et al. 1994) is proposed to interpret the plasticization phenomenon from a new angle.

The classic dual-mode sorption model suggested the existence of two distinct sites in which gas molecules follow different transport principles (Vieth, Howell et al. 1976; Koros 1980; Barrer 1984). However the evidence of the physical existence of such sites remains unclear. The nodules structure model proposed in this dissertation will enable us to visualize these dual-mode sites in the membrane structure. Meanwhile the decoupling of the Henry's and Langmuir sites will make the comparison of the gas sorption behaviour in these two sites possible, the comparison results will be used to interpret the plasticization phenomenon from a different angle.

Plasticization phenomenon on the single CO_2 permeation has been well documented in literature; however it failed to predict the plasticization behaviour in mixed-gas. It was observed that the competitive sorption caused by the introduction of the secondary gas in the gas mixture could suppress or even off-set the plasticization phenomenon, unfortunately only few researchers have touched this area (Sanders, Koros et al. 1984; Story and Koros 1989; White, Blinka et al. 1995), and most of their works were restricted to the dense films. In this dissertation, a comprehensive study on competitive sorption will be carried out on our in-house fabricated Matrimid hollow fibers to gain a better understanding of its relation with plasticization.

Another objective of this work is to establish a thermal annealing protocol to enhance membrane's plasticization resistance based on the following criteria: (1) sufficient to suppress plasticization, (2) less loss of permeability, (3) easy to operate, and (4) economical. The treated membrane will be characterized via different techniques (e.g. membrane densification, cross-linking, or formation of CTC) to investigate the possible mechanisms of the plasticization suppression.

1.7 Organization of the dissertation

This dissertation contains eight chapters:

Chapter 1 provides the introductory information, including the background of the membrane technology, membrane fabrication techniques, and the industrial gas separation applications. Major challenges for gas separation membrane are also presented as well as the recent development and the future directions. This chapter also includes the research objectives and dissertation organization.

Chapter 2 is divided into two parts: Section 2.2~2.8 provides the background of membrane formation mechanisms and characterization. Solution-diffusion model is described in details; the concept of phase inversion is introduced along with the dry-jet, wet spinning fabrication technique. This chapter also provides the details of different characterization strategies, and the formation mechanisms of the skin layer, sub-structure and macrovoids are also discussed. Sections 2.9~2.11 focus on the plasticization phenomenon. The fundamentals of plasticization are discussed in terms of its relations with glass transition temperature, polymer structure and membrane morphology. Three strategies to suppress plasticization are also outlined including thermal annealing, chemical cross-linking and blending.

Chapter 3 provides the information of all the materials used and experimental protocols involved in this work.

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Chapter 4 outlines the approach to fabricate the integral skinned hollow fibers; experiment protocols including fabrication and characterization are provided in details. All the examined operation variables are discussed in terms of their influences on membrane morphology and separation properties. The optimized fabrication protocol is established and presented in this chapter as well.

Chapter 5 presents the Hansen's solubility parameter analysis to connect the thermodynamic properties of dope, bore and coagulation fluid with membrane's final morphology and separation properties.

Chapter 6 discusses the fundamentals of the plasticization phenomenon, a nodule structure model is presented in this chapter to reveal the relations between membrane formation mechanism with membrane morphology and plasticization phenomenon, the evidence is also provided to justify this model. Gas sorption tests were performed and the results will be presented in a way that allow the comparison between Henry's and Langmuir sorption behaviours in glassy polymer. A model is developed to simulate the competitive sorption behaviour in gas mixture; the simulation results will be presented in this chapter to demonstrate the interactions between competitive sorption and plasticization phenomenon under different conditions.

Chapter 7 focuses on the plasticization suppression strategies. The effects of various thermal-annealing protocols (varies from different temperature and time) on CO_2/CH_4 mixed gas separation performance are presented and discussed. The results of several characterization approaches (e.g. sorption tests, dissolution tests, TGA, FTIR, and DSC etc.) are also presented and the possible mechanism behind the suppression of plasticization is discussed.

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Chapter 8 provides a summary of the conclusions of this work, and the recommendations of the future investigation are also discussed.

2 LITERATURE REVIEW

2.1 Organization of the literature review

This literature review covers two main topics:

- 1. Fabrication of integrally skinned hollow fiber membrane (Sections $2.2 \sim 2.8$),
- Plasticization phenomenon investigation and suppression strategies (Sections 2.9 ~ 2.11).

Sections $2.2 \sim 2.4$ provide the background information of the gas transport mechanisms in the polymeric membrane as shown in Fig.2.1, fundamental knowledge of the membrane fabrication (including phase inversion concept, dope development, dry-jet, wet spinning technique etc.) will be provided in Section 2.5; the major membrane characterization techniques will be briefly introduced in Section 2.6. An integrally skinned hollow fiber usually contains two layers: ultra-thin, defect-free skin layer and porous supporting substructure. Section 2.7 presents the detailed formation mechanisms of these two layers.



Fig.2.1. Gas transport mechanisms in polymeric membrane

Plasticization phenomenon will be discussed in Sections 2.8 and 2.9 in terms of its effect on the glass transition temperature, polymer structure, and membrane integrity. Section 2.10 will outline the most common plasticization suppression strategies including thermal annealing, chemical cross-linking and blending.

2.2 Gas transport mechanism in membrane

Membrane gas separation can be achieved by the following three different transport mechanisms: Knudsen-flow separation, molecular sieving and solution-diffusion (Fig.2.2) (Kesting and Fritzschz 1993). These transport mechanisms only apply when the membrane's pore size distribution lies in certain ranges. Knudsen-flow separation applies on the micro-porous membrane with the pore size range (around 10^2 nm) between kinetic diameter of gas molecules and free mean path of gas molecules (λ : the average distance covered by a gas molecule between successive impacts) in the bulk polymer. In such scenario, more collisions would be expected between gas molecules and pore walls than between gas molecules. Gas molecules' momentum is absorbed by the pore wall on each collision, their velocity is therefore slowed down due to the wall collision, and the separation is achieved based on the difference of travel velocity between different gas molecular species. However membrane with such pore size distribution range is not suitable for the gas separation purpose because this transport behavior cannot provide sufficient differences of gas molecules' velocity to make the selective process possible.



Fig.2.2. Schematic representation of three major mechanism of gas transport in membrane

On the other hand, membranes with pore size less than 1 nm can offer gas separation based on the mechanism of molecular sieving. Molecular sieving allows smaller gas molecules permeate through membrane over larger ones only if the gas condensability is negligible so the larger gas molecules will not block the pores. However in most cases, large gas molecules can still accumulate on the membrane surface and foul the membrane, therefore the commercialization of such membrane is still unavailable until the fouling issue is resolved.

In addition to the Knudsen flow and molecular sieving mechanisms, certain membranes also rely on the so called "solution-diffusion" mechanism to achieve separation, for instance, the non-porous polymeric membranes. For gas separation, because the sizes of the gas molecules of different types are in the same magnitude, the conventional porous membrane therefore cannot provide sufficient separation for gas molecules. The nonporous polymeric membranes, on the other hand, achieve separation via "solutiondiffusion" mechanism which make them ideal for gas separation unlike the other membranes with discrete through going pores. In the "solution-diffusion" mechanism, gas molecules first sorb in the upstream side of the membrane, then diffuse through the membrane and eventually desorb at the downstream side of the membrane, as illustrated in Fig.2.3.



Fig.2.3. Schematic representation of the solution-diffusion model on hollow fiber membrane (Shell-side feed configuration, SEM image obtained from in-house fabricated Matrimid hollow fiber)

Instead of offering continuous passage for gas molecules transport, effective solutiondiffusion polymeric membranes rely on the thermally agitated motion of the polymer chain segments to open penetrant-scale gaps which allows gas molecules jump through the polymer chain matrix (Fig.2.4). Theoretically the gas molecules are assumed to jump randomly through the transient gaps, but the majority of the gas molecules will follow the diffusion flux towards the downstream side of the membrane because of the higher chemical potential at the upstream side. The frequency of the agitated motion of polymer chains is measured by diffusion coefficient, the effect of diffusivity in most cases dominates the solution-diffusion process and can provide sufficient differences between species of the gas molecules which makes the separation of gases possible (Mulder 1996). Among all three major mechanisms described above, solution-diffusion membranes are used exclusively in current commercial gas separation devices due to the excellent separation properties they can provide.



Fig.2.4. Gas molecules jump through transient gaps in polymer matrix generated by thermally agitated motion of polymer chain segments

2.3 Solution-diffusion mechanism

Gas transport in non-porous polymeric membrane relies on the "solution-diffusion" mechanism (Wijmans and Bakers 1995) as mentioned in the previous section. The concept of "solution-diffusion" can be simply described by the following equation, i.e.

$$Permeability (P) = Diffusivity (D) \times Solubility (S)$$
(Eqn.2.1)

Eqn.2.1. indicated that the permeability is the product of solubility and diffusivity. Both of these coefficients are critical to determine gas molecule's transport behaviour in the non-porous polymeric membranes.

2.3.1 Sorption

Solubility (S) is a thermodynamic parameter which is dependent on the polymerpenetrants interactions and the condensability of the gas molecule penetrants. It gives a measurement of the amount of the penetrants being sorbed in the polymeric membrane in a steady state. Gas molecule sorption behaves differently in the rubbery and glassy polymers (the definition of the rubbery and glassy polymers will be provided in Section 2.4). In the ideal rubbery state, the gas concentration in the polymeric membrane displays a linear relationship with the gas penetrant pressure which is agreed with Henry's law as shown in Eqn.2.2.

$$\boldsymbol{c} = \boldsymbol{S} \cdot \boldsymbol{p} \tag{Eqn.2.2}$$

Where *c* is the concentration of the gas penetrants in the polymer (cc (STP)/cc polymer), *S* is the Henry's solubility constant (cc (STP)/cc polymer cmHg), and *p* is the gas penetrant pressure (cmHg).

Unlike the linear relation seen in rubbery polymer, the sorption isotherms of certain gas molecules in glassy polymers are convex to the pressure axis as seen in Fig.2.5 (Vieth and Frangoulis 1966; Vieth, Howell et al. 1976). The dual-mode sorption theory was then developed to interpret the deviation from the Henry's Law sorption behaviour.



Fig.2.5 Schematic representation of gas sorption isotherm convex to pressure axis (Vieth and Frangoulis 1966; Vieth, Howell et al. 1976)

The dual-mode sorption model proposed the existence of two types of the sorption sites in the glassy polymer: Henry's sites in which gas penetrants follow Henry's Law and free to diffuse through the polymer structure, and Langmuir sites in which gas penetrants lose their mobility entirely and do not contribute to the gas diffusion.

The dual-mode sorption is simply expressed by the following equation:

$$\boldsymbol{c} = \boldsymbol{c}_{\boldsymbol{D}} + \boldsymbol{c}_{\boldsymbol{H}} = \boldsymbol{S} \cdot \boldsymbol{p} + \frac{\boldsymbol{c}_{\boldsymbol{H}}' \cdot \boldsymbol{b} \cdot \boldsymbol{p}}{1 + \boldsymbol{b} \cdot \boldsymbol{p}}$$
(Eqn.2.3)

The first term of Eqn.2.3 describes the gas penetrant sorption behaviour in Henry's sites, and the second term describes the penetrant sorption behaviour in Langmuir sites. When a glassy polymer is exposed to a given pressure of penetrant (p), gas molecules enter the Henry's site of polymer with a sorption concentration of c_D (the first term of Eqn.2.3). The excess free volume (the Langmuir sites) provides additional low energy berths for penetrants. The additional gas penetrants with a concentration of c_H (the second term of Eqn.2.3) can occupy these Langmuir sites in local equilibrium with the Henry mode gas penetrants concentration c_D . Hole affinity constant (b) accounts for the ratio between the sorption and desorption of penetrants in Langmuir sites. c_H represents the hole saturation constant in the Langmuir sites.

In the low pressure range, where $bp \ll 1$, Eqn.2.3 can be rearranged into a linear expression:

$$\boldsymbol{c} = \left(\boldsymbol{S} + \boldsymbol{c}_{\boldsymbol{H}}^{'} \boldsymbol{b}\right) \boldsymbol{p} \tag{Eqn.2.4}$$

At high pressure range, where $bp \gg 1$, Eqn.2.3 can be rearranged into a different linear expression with an intercept of c'_{H} :

$$\boldsymbol{c} = \boldsymbol{S} \cdot \boldsymbol{p} + \boldsymbol{c}_{\boldsymbol{H}}^{'} \tag{Eqn.2.5}$$

The dual-mode sorption model successfully simulated the gas sorption behaviour in glassy polymer as shown in Fig.2.6 which is in agreement with the commonly observed convex-shaped gas sorption isotherms.



Fig.2.6. Schematic representation of dual-mode sorption model

The Dual Mode Sorption equation can be easily extended to include gas mixtures. The equations for the mixed gas sorption are expressed as a function of partial pressure:

$$\boldsymbol{C}_{A} = \boldsymbol{S}_{A} \cdot \boldsymbol{p}_{A} + \frac{\boldsymbol{C}_{HA} \cdot \boldsymbol{b}_{A} \cdot \boldsymbol{p}_{A}}{1 + \boldsymbol{b}_{A} \cdot \boldsymbol{p}_{A} + \boldsymbol{b}_{B} \cdot \boldsymbol{p}_{B}}$$
(Eqn.2.6)

and,

$$\boldsymbol{C}_{\boldsymbol{B}} = \boldsymbol{S}_{\boldsymbol{B}} \cdot \boldsymbol{p}_{\boldsymbol{B}} + \frac{\boldsymbol{c}_{\boldsymbol{H}\boldsymbol{B}}^{'} \cdot \boldsymbol{b}_{\boldsymbol{B}} \cdot \boldsymbol{p}_{\boldsymbol{B}}}{1 + \boldsymbol{b}_{\boldsymbol{A}} \cdot \boldsymbol{p}_{\boldsymbol{A}} + \boldsymbol{b}_{\boldsymbol{B}} \cdot \boldsymbol{p}_{\boldsymbol{B}}}$$
(Eqn.2.7)

The subscript A and B represent the different gas types in the gas mixture. The above equations illustrate that the concentration of a certain gas molecules decrease as the partial pressure of another gas is increased.

2.3.2 Nodule structure and dual-mode sorption

The dual-mode sorption model is entirely based on the postulation of the two sites existing in the polymer membrane. However, the solid link between the theory and actual physical structure in the polymeric membrane remains unclear. Several attempts have been made to connect the dual-mode sorption sites with the membrane structure in the past. Among them, Kesting et al. (Kesting 1990; Kesting, Fritzschz et al. 1990; Kesting and Fritzschz 1993) proposed a four tier structure theory (macromolecules, nodules, nodular aggregates, and super-nodular aggregates) based on the nodule structure observed on the integrally skinned membrane. The nodule structure (Fig.2.7A) contains both crystalline and amorphous portions of the polymer chains which grow out from the crystal nucleus and form the spherical structure i.e. *nodule* (Wienk, Van den Boomgaard et al. 1994).



(A)



(B)

Fig.2.7. (A) Schematic representation of polymer chains displacement in a nodule, and (B) nodule structure model interpretation of the dual-mode sorption sites(Kesting and Fritzschz 1993)

As shown in Fig.2.7, Kesting's nodule structure model assumed that the large interstices between nodules could be associated with the Langmuir sites whereas the amorphous portions within the nodules represent the Henry's sites. Kesting's model described the possible relationship between the nodule structure and the dual-mode model; however no solid data were available to validate the model and the theoretical ground of this model still remains unclear. Further investigation on Kesting's nodule structure model is necessary to gain a better understanding of the membrane morphology and the gas transport behaviour within the membrane structure.

2.3.3 Diffusion

While sorption on both rubbery and glassy polymers can be described in simple expressions as mentioned above, diffusion, on the other hand, it is a much complicated matter, especially for glassy polymers.

For the rubbery polymers, gas penetrant diffusion behaviour can be well described by the Fick's first law (Eqn.2.8):

$$\boldsymbol{Q} = -\boldsymbol{D} \cdot \frac{dc}{dx} \tag{Eqn.2.8}$$

Where Q represents the permeation flux, D is the diffusion coefficient; c is the local concentration of the gas penetrant in the membrane at the permeation coordinate direction of x. Eqn.2.8 can be rearranged in the following form under low pressure, steady-state condition:

$$\boldsymbol{Q} = \boldsymbol{D} \cdot \frac{\boldsymbol{c}_{A2} - \boldsymbol{c}_{A1}}{L} \tag{Eqn.2.9}$$

where C_{A1} and C_{A2} are concentrations of gas penetrant in the downstream and upstream faces of the membrane respectively and *L* is the membrane thickness. Substituting Eqn.2.2 into Eqn.2.9 will yield:

$$\boldsymbol{Q} = \boldsymbol{D} \cdot \boldsymbol{S} \cdot \frac{\boldsymbol{p}_{A2} - \boldsymbol{p}_{A1}}{L}$$
(Eqn.2.10)

where p_{A1} and p_{A2} are the external partial pressures of the gas species in the downstream and upstream faces of the membrane respectively. Eqn.2.8 illustrated that the gas flux in the polymer is dependent on the diffusion coefficient *D* and solubility coefficient *S*.

Substituting Eqn.2.1 into Eqn.2.10 will yield:

$$\boldsymbol{P} = \boldsymbol{Q} \cdot \frac{L}{p_{A2} - p_{A1}} \tag{Eqn.2.11}$$

According to Eqn.2.11, permeability *P* can be considered as the permeation flux *Q* normalized by the trans-membrane pressure p_{A2} - p_{A1} and membrane thickness *L*. The unit of permeability is Barrers, where 1Barrer = 10^{-10} (cm³ [STP]*cm)/ (cm² *sec*cmHg). Permeability can only be used on dense films where the whole film thickness is effective to separation and can be measured. In asymmetric membranes where the active membrane thickness (*L*) remains unknown, the concept of permeance is introduced which is given by Eqn.2.12.

$$P/_L = \frac{Q}{p_{A2} - p_{A1}}$$
 (Eqn.2.12)

The unit of permeance is Gas Permeation Unit (GPU), where 1GPU = 10^{-6} cm³ [STP]/(cm² *sec*cmHg).

For glassy polymers, the diffusion model is more complicated and the most common model was developed by Vieth et al. (Vieth and Sladek 1965; Vieth and Frangoulis 1966; Vieth, Howell et al. 1976). The fundamental concept of this model is that only the gas penetrants sorbed in Henry's sites are free to diffuse through the membrane, and it is driven by its concentration gradient. On the other hand, the gas penetrants sorbed in Langmuir sites are entirely immobilized and do not contribute to the diffusion flux. And the local equilibrium between mobile gas molecules and immobilized gas molecules is always maintained throughout the polymeric membrane. The detailed description of the model can be found in the literature (Kesting and Fritzschz 1993) and Chapter 6.

The ideal selectivity is a good measurement to characterize the efficiency of the membrane separation only when the downstream pressure is much less than the upstream pressure. The ideal selectivity, which is given by Eqn.2.13, is simply the ratio of the permeability or permeance of the pure gases.

$$\alpha^* = \frac{P_A}{P_B} \tag{Eqn.2.13}$$

For the mixed gases permeation, the selectivity can be defined as the ratio between the compositions of the upstream and downstream sides of the membrane as seen in Eqn.2.14:

$$\alpha = \frac{y_{A/y_B}}{x_{A/x_B}}$$
(Eqn.2.14)

2.4 Free volume theory

The most common material to be used for non-porous gas separation membrane is polymer. The state of the polymers is one of the key factors to determine membrane's separation properties. Glass transition temperature, the temperature at which the polymer thermal energy is just sufficient to overcome the restriction in rotation due to the bulky side groups and the interactions between polymer chains (Mulder 1996) has been used to distinguish the state of the polymer materials. Above the glass transition temperature, polymer is in rubbery state that the polymer chain segments can rotate along the main chain bonds without much restriction, hence showing high polymer chain mobility. Below the glassy transition temperature, the motion of the polymer chains is restricted with the declined temperature; polymer is thereby in a glassy state where the segments of the polymer chain are not able to rotate freely.



Fig.2.8. The relationship between specific volume and temperature in the glass transition region, where V_g is the specific volume of the glassy polymer and V_l is the extrapolated specific volume of the polymer in a hypothetical liquid state (Kesting and Fritzschz 1993) The most significant transformation during the shift between rubbery and glassy state is the alteration of the fractional free volume of polymer materials. Free volume of polymer materials was defined as "the volume unoccupied by macromolecules" by Mulder (Mulder 1996), while Bernardo et al. (Bernardo, Drioli et al. 2009) considered the free volume as "the fraction of the volume not occupied by the electronic clouds of the polymer". Below the glass transition temperature, most of the specific volume associated with the microvoids and excessive free volumes are fixed in the glassy state, the fractional free volume is thereby less sensitive to the increased temperature. On the contrary, significant increase of the fractional free volume is observed in the rubbery state as shown in Fig.2.8 because sufficient thermal energy is provided to free those fixed volumes in the glassy states. These changes in the free volume will affect the gas sorption and diffusion behaviours in both rubbery and glassy polymers.

For glassy polymers, the thermal energy is not sufficient below the glass transition temperature to allow the polymer chain segments to rotate around the main chain. The limited mobility of the polymer chains results in the fixed volume such as microvoids. Above the glass transition temperature, the frozen microvoids are released due to the increasing mobility of polymer chains and the amount of free volume will be significantly shifted to a higher level. As a consequence, higher permeability is expected for the rubbery polymers. Therefore the amount of free volume presented in the polymeric membrane plays a critical role to determine the permeability. The above consensus leads to the development of free volume theory.

Fractional free volume (FFV) is calculated via Eqn.2.15:

$$FFV = \frac{V_g - V_0}{V_0} \tag{Eqn.2.15}$$

where *FFV* is the fractional free volume, and V_g is the specific volume of the polymer material at a certain temperature, V_0 is the specific volume occupied by the polymer chain macromolecules.

The core of the free volume theory is the following equation:

$$\boldsymbol{P} = \boldsymbol{A} \cdot \boldsymbol{e}^{\left(\frac{-B}{FFV}\right)} \tag{Eqn.2.16}$$

which correlates the permeability P with the fractional free volume FFV, where A and B are the constants for a particular gas. This equation demonstrates that the diffusion behaviour of the gas penetrants from one place to another place in glassy polymer requires sufficient free volume. For a particular type of gas, if the fractional free volume increases, the permeability increases.

2.5 Fabrication of asymmetric hollow fiber membranes

2.5.1 Asymmetric hollow fiber fundamentals

Typical asymmetric hollow fiber membranes consist of a very thin $(0.1 \sim 1 \mu m)$, nonporous selective skin layer, combined with a much thicker micro-porous $(100 \sim 200 \mu m)$ layer to provide mechanical support for skin (Fig.2.9). The defect-free skin layer ensures the efficient separation of different gas species; meanwhile its ultra-thin skin and porous support layer guarantee to minimize the gas transport resistance, thus the permeability will not be compromised.

Asymmetric membranes can be classified into two categories in terms of their morphology: integrally skinned membrane and thin composite membrane. The skin and support layer of the integrally skinned membranes are prepared with the same material and dope solution at the same time. Thin composite membranes, on the other hand, are prepared via separate steps with same or different materials. Most of the integrally skinned membranes are prepared by phase inversion technique, which will be discussed later in the next section.



Fig.2.9. SEM image of skin layer and porous support layer of in-house fabricated Matrimid asymmetric hollow fiber membrane

To achieve good separation, the skin layer must be defect-free. An asymmetric membrane can only be considered as "defect-free" if its gas selectivity is above 95% of the intrinsic dense polymer film value, otherwise it will be considered as defect membrane. Although it is impossible to measure the exact thickness of the skin layer, the apparent skin layer thickness can be calculated via the following equation.

$$L = \frac{\text{permeability of the polymeric dense film}}{\text{permeance of the polymeric asymmetric membrane}}$$
(Eqn.2.17)

It is noteworthy that Eqn.2.17 can only be applied on defect-free asymmetric membrane, for the asymmetric membranes with defects, gas transport is not solely governed by the solution-diffusion model, and therefore Eqn.2.17 is not valid.

2.5.2 Phase inversion

Phase inversion is a revolutionary technique to prepare the asymmetric membranes, especially hollow fiber membranes. Phase inversion refers to a process which converting a liquid into a three-dimensional macromolecular solid network in a controlled manner. This solidification process is usually initiated by the liquid-liquid demixing process, the morphology of the asymmetric membranes can be controlled by manipulating the phase inversion process variables.

Phase inversion can be induced either thermally or by non-solvent. Thermally induced phase inversion membrane tends to have a rather thick skin layer which makes it less attractive to gas separation due to its low gas permeation flux. Non-solvent induced phaser inversion technique, on the contrary, is the most common approach to prepare asymmetric hollow fiber membranes. In this process, phase separation is induced by introducing non-solvent into a single, homogeneous binary polymer solution. This process can be easily visualized with the assistance of ternary phase diagram (Fig.2.10).



Fig.2.10. Schematic representation of different membrane formation mechanisms and their relations with the membrane morphology (Koros and Fleming 1993)

Ternary phase diagram provides a qualitatively understanding of the phase inversion in membrane formation (Strathmann and Kock 1977; Altena and Smolders 1982). The three vertices of the triangle represent each of the pure components: polymer, solvent, and nonsolvent, and each point within the triangle represent individual ternary composition. The diagram is divided into three regions: a stable single phase region, a meta-stable twophase region, and an unstable two-phase region. The boundaries that separate these three regions are called binodal and spinodal curves, and the point where two boundaries intersect represents the critical point. The critical point divides the meta-stable region into two parts: polymer rich meta-stable region (above the critical point), and polymer lean meta-stable region (below the critical point). A fourth region commonly called "vitrified region" lies on the top of the triangle diagram. With very high polymer concentration in this region, the polymer chain mobility is too low to allow the macromolecular rearrangement. Liquid-liquid demixing takes place when the ternary composition locates in the meta-stable two-phase region or unstable two-phase region, two separated equilibrium phases are connected by "tie line" and the two intersects of the tie line and binodal curve represent the compositions of the two separated equilibrium phases.

Fabrication of the asymmetric hollow fibers starts with the preparation of the polymer solution with the composition located in the stable single-phase region in the ternary phase diagram. The initial polymer solution can move into either the meta-stable two-phase region or the unstable two-phase region via different paths (Path A and Path B in Fig.2.10 respectively) depending on the solvent out-flow and non-solvent in-flow during the mass transfer. Path A can be achieved when the solvent out-flow exceeds the non-solvent in-flow, and Path B usually occurs while the non-solvent in-flow dominates the mass transfer. As shown in Fig.2.10, the final solution composition lies in the polymer rich meta-stable two-phase region when the composition trajectory follows Path A, while Path B leads to the unstable two-phase region.

The dope composition trajectory determines the actual phase inversion processes which affect membrane's final morphology. For Path A, the phase inversion will follow the so called "nucleation and growth" process (Broens, Koenhen et al. 1977; Koenhen, Mulder et al. 1977) because of the high polymer concentration of the local dope composition when the L-L demixing takes place. During the nucleation and growth process, a series of nucleus of polymer lean phase start to form and grow in the continuous polymer rich phase. Given sufficient time, the dispersed polymer lean cells grow larger and intersect with other similar structure and create interconnectivity. The membranes formed via such

mechanism display a closed-cell structure if the vitrification of polymer rich phase takes place before polymer lean phase getting connected (Fig.2.10); otherwise an open-cell structure is more likely to form due to the high interconnectivity in the polymer lean phase. The open-cell structure provides more passage for gas penetrants than the closedcell structure, and the phase inversion membrane with such structure can observe much improvement in permeation flux.

For Path B, the polymer solution enters the unstable two-phase region, and the phase inversion will take place via the so called "spinodal decomposition" mechanism (Pinnau and Koros 1993; Mulder 1996). It has been reported that the spinodal decomposition could take place when the polymer rich phase takes up more than 15% of overall polymer solution (Koros and Fleming 1993). During the spinodal decomposition, because the amount of the polymer rich phase and polymer lean phase are in the same magnitude, bicontinuous three-dimensional structures could be formed with completely interconnected polymer rich- and lean-phase (Fig.2.10). The interconnectivity of the two phases produces an open cell structure which reduces the gas transport resistance. Therefore spinodal decomposition controlled phase inversion process is favoured for the formation of the low resistance support layer.

The liquid-liquid demixing path proceeds via either "nucleation and growth" or "spinodal decomposition" is dependent on the solvent/non-solvent exchange kinetics. With sufficient exchange between solvent and non-solvent, the dope composition trajectory could enter the spinodal envelope and induce spinodal decomposition (Fig.2.11, from A to C). Insufficient solvent/non-solvent exchange, on the contrary, leads the dope composition trajectory to a meta-stable region and induces the L-L demixing via "the

nucleation and growth" mechanism (Fig.2.11, from A to B) (Pinnau and Koros 1993; Wang, Li et al. 1996).



Fig.2.11. The possible dope composition trajectory in ternary phase diagram

2.5.3 Dope development

A typical polymer solution (often called "dope") usually contains three components: polymer, solvent, and non-solvent, or in some cases only two components: polymer and solvent (McKelvey, Clausi et al. 1997; McKelvey and Koros 1997; Clausi and Koros 2000; Ekiner and Vassilatos 2001). The polymer concentration ranges from 20% to 40% for gas separation membranes to guarantee the sufficient polymer chain density for the non-porous defect-free skin layer. Solvent and non-solvent should be miscible with each other and also with the chosen coagulation medium. Sometimes certain additives are also considered in order to modify the property of the dope solution, such as the so called "viscosity enhancers" and "pore formers" (Kesting and Fritzschz 1993; Koros and Fleming 1993).

The dope composition should be chosen based on two criteria: spinnability and ability to phase separate in a desired manner. A dope which can ensure stable spin line at various operation conditions is considered with good spinnability. Dope's spinnability is largely determined by its extensional viscosity which can be tailored by altering the dope composition.

As discussed in the previous section, membrane's final morphology is strongly affected by the dope composition trajectory in the ternary phase diagram while phase inversion takes place (Fig.2.10). Therefore one of the most crucial tasks for dope development is to ensure the phase inversion take place via the desired mechanism thus to produce hollow fiber with superior morphology and separation property.

Numerous studies on the dope development have been carried out and the common agreement is that the polymer concentration needs to be higher than what is used in casting dense film membranes in order to achieve a higher viscosity to allow the extrusion for hollow fiber fabrication (Clausi and Koros 2000), furthermore higher polymer concentration can also promote the formation of the defect-free skin layer. The addition of non-solvent is also a common approach to modify the property of the dope solution although the role of non-solvent additives (NSA) still remains unclear. It was reported that the addition of non-solvent shifted the dope composition closer to the binodal curve, so that the as-spun fiber can be coagulated quickly which led to a thinner effective separation skin layer (Fritzschz, Murphy et al. 1989; Chung, Kafchinski et al. 1992; Kosuri and Koros 2008). As a result, the separation performance of the membrane was improved. In contrast, Niwa and Kawakami (Niwa and Kawakami 2000) observed that the higher content of NSA in the dope solution promoted the formation of macro-voids and consequently hindered fiber's separation performance.

The rationale for the selection of solvent and NSA also remains somewhat unclear. Pinnau et al. (Pinnau and Koros 1993) suggested that the solvent should have a lower volatility than NSA in order to induce the phase separation during the evaporation steps. By contrast, Wang et al. (Wang, Li et al. 1996) suggested higher volatility of NSA for rapid vaporization could increase the local solvent power and move the dope composition at the membrane surface away from the phase inversion point to form the membranes with dense and thick skin layer. Conversely, quicker loss of solvent component from the membrane surface tends to form thin and porous skin layer.

The addition of an extra solvent with different volatility in the polymer solution has also been adopted in order to gain a finer control of the phase separation process by tuning the evaporation rate of the solvent in the air gap (Pesek and Koros 1994). Clausi et al. (Clausi and Koros 2000) reported a nearly 25% increase in O_2/N_2 ideal selectivity by introducing a solvent mixture of 10% more volatile THF and 90% less volatile NMP in the Matrimid solution, however it was accompanied with a dramatic 70% loss in O_2 permeance.

2.5.4 Dry-jet, wet spinning technique

Polymeric membranes can be prepared via either dry phase inversion, wet phase inversion or dry-wet phase inversion techniques. Flat sheet membrane cast from the dry phase inversion without coagulation step shows a very thick and dense symmetric structure which proves the liquid-liquid demixing process is essential for the formation of asymmetric membrane with ultra-thin skin layer, and a sponge like, supporting structure (Pinnau and Koros 1991). Asymmetric membrane cast from the wet-phase inversion without air gap or forced convective evaporation usually possesses a very defect skin layer (Pinnau and Koros 1991). Small-size macrovoids were also observed underneath the skin layer which could be attributed to the intrusion of the coagulant caused by the defect skin layer. Asymmetric hollow fiber membrane prepared via dry-wet phase inversion on the other hand, display an ultra-thin defect-free skin layer on the top of porous support layer.



Fig.2.12. Schematic representation of the dry-jet, wet spinning technique Dry-jet, wet spinning is the most common technique to prepare asymmetric hollow fiber membranes. The fabrication process involves the co-extrusion of the dope and bore fluid from the spinneret into the air gap with ambient conditions or under forced convective evaporation. Once passing through the air gap (dry phase), the nascent fibers immerses into a coagulation bath filled with coagulation medium at room temperature or elevated temperature (wet phase). After passing over one wheel-guide, fibers are collected on a take-up drum and ready for the subsequent post-treatments. The schematic representation of the dry-jet, wet spinning technique is shown in Fig.2.12.

While passing through the air gap, volatile solvent could evaporate through the nascent hollow fiber to the surrounding environment, thus the polymer concentration at the outermost region of the fiber could increase significantly. Depending on the humidity of the ambient environment, water vapour or other non-solvent vapours could be absorbed into the nascent fiber. As a consequence, phase inversion could take place due to the mass transfer in the air gap. Even if the fabrication process is carried out in a very dry atmosphere, the phase separation could still be induced if NSA presented in the dope solution is less volatile than solvent, then the evaporation of the solvent from the outermost region of the fiber will produce a critical non-solvent additive concentration in the area and induce the dry-phase inversion (Pinnau and Koros 1991).



Fig.2.13. Schematic representation of the mass transfer during the dry-wet phase inversion

After passing through the air gap, the nascent hollow fibers descend into the coagulation bath. The coagulation medium should not only be a non-solvent for the polymer material but also be miscible with the solvent and non-solvent additive in the polymer solution. Once the nascent hollow fiber immerse into the coagulation bath, complex mass transfer takes place simultaneously including the coagulant diffuse into the nascent fiber and solvent diffuse into the coagulation bath (Fig.2.13). Depending on the operation conditions, liquid-liquid demixing takes place via either nucleation and growth or spinodal decomposition, which determines the distribution of the polymer rich and polymer lean phase in the membrane structure as discussed previously.

2.5.5 Dehydration

Water-wet hollow fibers need to be dried prior to further post-treatment or permeation tests. However inappropriate dehydration approach could damage the porous structure and reduce the passage for penetrants, a significant decrease of gas flux could be expected as a result. It was reported that the asymmetric cellulose acetate membrane collapsed into a dense film upon drying (Kesting 1973). Capillary force which is responsible for the collapse of the pores is proportional to the surface tension of the coagulation medium. Water, with high surface tension, could easily damage the small pores in the membrane structure upon drying.

Among various approaches to reduce the capillary force during dehydration, solvent exchange is the most common method where water is replaced with another non-solvent possessing lower surface tension. The most common solvent exchange process involves three steps: first water is replaced by some low molecular weight alcohols (e.g. ethanol, methanol etc.), then the alcohol is washed out by volatile hydrocarbons (e.g. hexane, heptane etc.), at the end the hydrocarbon-wet hollow fibers are allowed to dry either in air or in vacuum oven to remove the residuals. By following the above dehydration steps, most of the porous structure in the asymmetric hollow fibers will be well preserved.

2.6 Hollow fiber characterization

The common approaches for asymmetric hollow fiber membrane characterization can be classified into two main categories: the macroscopic and microscopic properties. Scanning electron microscopy (SEM) is often applied to observe the macroscopic properties of the hollow fibers (e.g. macrovoids, porous structure in supporting layer, bore concentricity, ovality etc.). Hollow fiber's microscopic properties (gas separation performance: permeability and selectivity) are the most important properties to directly evaluate the quality of the membrane, pure and mixed gas permeation tests provide the most direct measurements of these properties.

2.6.1 Macroscopic properties

SEM technique is usually applied as an approach to quick screen the good quality hollow fibers. The information SEM images provided could be used to briefly evaluate the mechanical strength and separation performance of the hollow fibers. Hollow fibers with perfect ovality and bore concentricity usually display good mechanical strength while fibers with irregular bore, large macrovoids or poor concentricity, cannot withstand high pressure operation in most cases.

The preparation of the hollow fiber's cross section requires cryogenically fracturing of fiber samples under liquid nitrogen to preserve the macroscopic morphology of the cross-section. The fiber samples need to be coated with conductive metal materials (e.g. gold, chromium etc.) prior to taking SEM images.

2.6.2 Microscopic properties

To conduct the pure/mixed gas permeation test, asymmetric hollow fibers must be mounted in a module to make the separation practicable and produce large membrane surface area per unit volume to ensure a maximized permeate flux. Therefore it is desirable to accommodate hollow fibers as many as possible in one single module. To fabricate hollow fiber module with such properties, technique skills are required to optimise the flux distribution and not to damage the outer-skin of the hollow fiber. Li et al. (Li, Wang et al. 2004) has developed a simple approach to fabricate lab scale hollow fiber module.



(B)


(E)



Fig.2.14. Schematic representation of hollow fiber module configurations: (A) Countercurrent shell-side feed, (B) Co-current shell-side feed, (C) Permeate discharge both ends shell-side feed, (D) Counter-current bore-side feed, (E) Co-current bore side-feed, (F) Permeate discharge both ends bore-side feed.

Tube-in-shell is the most common module design for hollow fiber membrane. Six different gas flux configurations can be achieved in tube-in-shell modules as shown in Fig.2.14. These gas flux configurations can be classified into two categories: shell-side feed and bore-side feed. Shell-side feed is commonly applied in high pressure application although concentration polarization in the bore-side could present a challenge. Bore-side feed, on the other hand, does not have the concentration polarization issue, and is perfect for moderate pressure application. In this project, we adopt the counter-current shell-side feed configuration considering the high pressure applied on the feed.

Gas permeation properties can be measured by several ways: constant pressure, variable volume, or constant volume, variable pressure. Constant pressure method has been developed for decades; however it has its own limitations (Kruczek and Matsuura 2000). Constant volume variable pressure method, on the other hand, gains more popularity in the past because it allows straightforward measurements of membrane's permeability and selectivity over a wide range of pressure (Pye, Hoehn et al. 1976; O'Brien, Koros et al.

1986; Moore, Damle et al. 2004). The constant volume variable pressure gas permeation apparatus is depicted in Fig.2.15. Counter-current shell-side feed module configuration is adopted in this design, and a valve is installed on the retentate line to make it easy to switch between single gas and mixed-gas permeation tests. For the single gas permeation tests, the retentate valve is closed, so the whole module is working in a dead-end configuration. For the mixed-gas permeation tests, the retentate valve remains open in order to keep the stage cut below 1% to eliminate the effect of concentration polarization (Kesting and Fritzschz 1993).



Fig.2.15. Schematic representation of the gas permeation apparatus

The permeation and retentate gas compositions are analysed by the gas chromatography (GC) and the flux is measured by a digital bubble flow meter. The results are used to calculate the permeance (*P*/*l*) and selectivity (α) of asymmetric hollow fiber membranes based on Eqn.2.12, 2.13 and 2.14.

2.7 Formation of the integrally skinned membrane

2.7.1 Solidification mechanisms

The solidification of nascent hollow fiber during phase inversion can proceed via different mechanisms (i.e. crystallization, gelation, and vitrification) depending on the nature of the polymer materials.

Crystallization

Polymers can be pure crystalline, partially crystalline or amorphous. Crystallization takes place when pure crystalline or semi-crystalline polymer is used as membrane material, it results in the formation of the spherulites composed of the polymer chains folded in crystal form (Kesting and Fritzschz 1993). The membranes fabricated from these polymers usually display densely packed nodule structures. However, only the polymer materials which are capable of crystallizing rapidly (e.g. PE, PP etc.) can ensure the phase inversion proceed via crystallization mechanism (Mulder 1996).

Gelation

For the polymer materials with low crystalline portion or completely amorphous, solidification usually takes place via another mechanism: gelation (Koenhen, Mulder et al. 1977). Gelation can be considered as the formation of a three-dimensional network with infinite viscosity. It displays a highly elastic, rubber like behaviour and it can be induced either physically or chemically. The formation of the skin layer was suggested to be attributed to the gelation process because the high viscosity in this layer due to the high polymer concentration kinetically limits the opportunity of the liquid-liquid demixing (Wijmans, Kant et al. 1985; Gaides and McHugh 1989).

Vitrification

An amorphous polymer can undergo vitrification process in the absence of crystallization and gelation. Vitrification will proceed when the out-flow of the solvent exceeds the inflow of the non-solvent, in which case, the polymer concentration of the outer-most region of the membrane can easily surpass the vitrification line as shown in Fig.2.10.

2.7.2 Formation of the skin layer

Fabricating asymmetric hollow fibers with defect-free ultra-thin skin layer still remains a great challenge for the researchers. Uncertainty about the skin layer formation mechanism contributes to the fabrication difficulties within the complex phase inversion process. In this section, some of the most popular skin layer formation mechanisms will be reviewed.

Pinnau et al. (Pinnau and Koros 1993) proposed that the phase inversion could take place during the air gap and induce the formation of the skin layer. However such scenario could only occur when the boiling point of the non-solvent is lower than solvent. Therefore the relatively higher evaporation rate of non-solvent will increase the nonsolvent composition to reach the threshold and force the composition of nascent fiber to cross the binodal curve. In this case, the spinodal decomposition usually takes place prior to the entrance of the coagulation bath. The fine-mazed three dimensional spinodal structure presented in the outer-region of the nascent fiber are usually micro-porous. Pinnau et al. suggested that the capillary force presented in the spinodal structure pulls the polymer rich nodules together via a coalesce process and eventually results in a homogenous skin layer during the evaporation step. This skin layer formation mechanism has been examined both on flat sheet (Pesek and Koros 1993) and hollow fibers (Pesek and Koros 1994; Clausi and Koros 2000) with different polymer materials such as polysulfone (Pesek and Koros 1993; Pesek and Koros 1994) and Matrimid (Clausi and Koros 2000) and proved to match experimental observations.

One of the challenges of fabrication of hollow fiber via the above mechanism is that the evaporation during the air gap is usually extremely short compared to flat sheet casting, therefore evaporation time for non-solvent is strictly limited and the phase inversion might not be induced within that time frame. Pesek's solution (Pesek and Koros 1994) to this problem is to reduce the take-up speed to allow the nascent fiber pass through the air gap for longer time, this approach has been successful in the formation of the defect-free skin layer on PSf hollow fiber membranes.

Van't Holf et al. (van't Holf, Reuvers et al. 1992) has developed a dual bath technique to decouple of the formation of the skin layer and rest of the membrane structure. Two non-solvents possessing different affinity with solvent were used as coagulation medium in two baths in series. The first bath contains non-solvent possessing weak affinity with solvent, the solvent out-flow exceeds the non-solvent in-flow in this bath, therefore the polymer concentration in the outer-most region of the nascent fiber will increase to a level which is sufficient to push the outer layer into a gel state. The second bath contains very strong non-solvent therefore the actual phase inversion will take place in this bath where the remaining structure of the hollow fiber precipitates. One of the disadvantages of this process is that the asymmetric membrane it produced usually contains rather thick skin layer (van't Holf, Reuvers et al. 1992; Li, Koops et al. 1994). Furthermore the nascent membrane does not have any mechanical stability while leaving the first bath, maintaining the membrane structure without damaging it becomes a great challenge when transferring the membrane between baths.

Pinnau's approach relies on the coalesce of the nodule structures to form the defect-free skin layer while the fundamental basis of van't Holf's method is based on the gelation formation in the first of a series of baths. Both mechanisms can produce defect-free skin layer yet with certain technical flaws. The fundamentals of the skin layer formation, unfortunately still remains uncertain and further investigation is required to gain the insight of this process.

2.7.3 Formation of the support layer: Type I and Type II membrane

The structure of the support layer is mainly formed after the immersion of the nascent membrane into the coagulation bath. The liquid-liquid demixing responsible for the formation of the supporting structure can either take place instantaneously upon immersion or delays for several seconds to half a minute after immersion. Membranes fabricated via these two routes display different morphology and are named "Type II" and "Type I" membranes (Reuvers and Smolders 1987; Reuvers, Van den Berg et al. 1987; Mulder 1996).

For "Type I" membrane, liquid-liquid demixing takes place several seconds to half a minute after immersion. During this "delay time", a larger outflow of the solvent and a relative small inflow of the non-solvent cause a net loss of solvent from the membrane. The polymer concentration at the outer-most region of the hollow fiber continues to increase until the liquid-liquid demixing commences. As shown in Fig.2.16 (A), the polymer concentration at the onset of phase separation could be pushed to a quite high level depending on the delay time, therefore the nascent fiber composition is more likely to enter the meta-stable two-phase region, nucleation and growth will proceed as a result and a sub-layer with closed cell structure is therefore expected (Fig.2.10). Delayed demixing takes place when the solvent and non-solvent has a low affinity, for those

common solvents such as NMP, DMF, or DMAc, high alcohols are the ideal non-solvent to induce delayed demixing, and for THF and acetone, water is the ideal non-solvent candidate.



(B)

Fig.2.16. Schematic representation of the membrane composition trajectory during fabrication: (A) Delayed demixing, "Type I" membrane, and (B) Instantaneous demixing, "Type II" membrane

For "Type II" membrane, phase inversion takes place instantaneous upon immersion (Fig.2.16B), the local polymer concentration at the onset of the phase separation is more moderate compared to the delayed demixing as shown in Fig.2.16A. Therefore the phase inversion proceeds via spinodal decomposition and results in an open cell sub-structure. Instantaneous demixing takes place while the solvent and non-solvent has a strong affinity (e.g. NMP, DMF, and DMAc as solvent, and water as non-solvent).

Although the "Type II" membrane possesses a very desirable open cell supporting structure which could minimize the gas transport resistance, the formation of the defect-free skin layer is somehow prevented due to the "extraordinary rapidity" of the spinodal decomposition onset that overrides the diffusion process (Reuvers and Smolders 1987; Reuvers, Van den Berg et al. 1987; Tsay and McHugh 1991; Tsay and McHugh 1991). Therefore the combination of both mechanisms is favourable for the optimum membrane structure. The best strategy to achieve this goal is to manipulate the delay time by adjusting the dope and coagulation medium composition, therefore an increase in polymer concentration over a short period of the delay time is guaranteed to obtain a dense skin layer. This can then be rapidly followed by the instantaneous demixing to obtain an open-cell structure in sub-layer.

2.7.4 Formation of the macro-voids

Macro-voids are often observed in the asymmetric membranes as seen in Fig.2.17. The mechanisms of the macro-void formation remain controversial; it might be initiated by the surface tension gradients or mechanical stresses as suggested by Strathmann et al (Strathmann, Kock et al. 1975), or formed by the growth of nuclei, according to other researchers (Broens, Altena et al. 1980; Smolders, Reuvers et al. 1992).



Fig.2.17. SEM cross-section image of an in-house fabricated Matrimid hollow fiber with macro-voids

The presence of the macro-voids, in most cases, is not favourable because they represent the weak points in the membrane. For high pressure application (e.g. gas separation), the membranes could easily collapse due to the existence of these macro-voids. It was suggested that the membranes with macro-voids are formed via the instantaneous demixing, while the membranes without macro-voids are formed via the delayed demixing (Smolders, Reuvers et al. 1992). Therefore the operation conditions which favour the formation of "Type I" membrane may also favour the suppression of the macrovoids. By employing a duo-solvent system with a solvent possessing lower affinity with the coagulant, liquid-liquid demixing process can be delayed; therefore the formation of macro-voids can be avoided. Increasing the viscosity of the polymer solution (e.g. increase the polymer concentration in the dope solution) can also reduce the tendency of the macro-voids formation, meanwhile choosing a NSA with higher volatility than solvent might also benefit the suppression of the macro-voids as well (Wang, Li et al. 1996). Addition of the solvent in the coagulation bath will decrease the difference of chemical potential between the coagulation medium and the nascent fiber, therefore reduce the rate of solvent/non-solvent exchange and eventually suppress the formation of the macrovoids (Strathmann, Kock et al. 1975; Wijmans, Baiij et al. 1983; Van de Witte, Dijkstra et al. 1996).

2.8 Plasticization overview

Polymeric membranes have demonstrated promising separation performance for the industrial gas separation application. However its sustainable performance is largely hindered by the so called "plasticization phenomenon". Carbon dioxide, as a very condensable gas, usually causes the swell of the polymer matrix which reduces the interaction between the adjacent segments of the polymer chains, consequently increases the segmental mobility and free volume. As a result an increase in permeability is commonly observed. In terms of the CO₂ removal from the natural gas, this increase in permeation of both CO₂ and CH₄ takes place in such a fashion that it allow CH₄ permeate at a larger extent than CO₂, which causes the loss in selectivity and methane productivity (Chiou, Barlow et al. 1985; Sanders 1988; Wessling, Huisman et al. 1995; Bos, Punt et al. 1999).

Most of the glassy polymers display a decrease in CO_2 permeability with increasing pressure in the low feed pressure range (Koros, Chan et al. 1977; Sanders 1988; Bos, Punt et al. 1999), which was well explained by Eqn.2.18 derived from dual-mode diffusion model (Vieth, Howell et al. 1976; Chiou and Paul 1986).

$$\boldsymbol{P} = \boldsymbol{S} \cdot \boldsymbol{D} \left(\mathbf{1} + \frac{\frac{\boldsymbol{D}_{H} \cdot \boldsymbol{b} \cdot \boldsymbol{C}_{H}}{\boldsymbol{D}_{D} \cdot \boldsymbol{S}}}{1 + \boldsymbol{b} \cdot \boldsymbol{p}} \right)$$
(Eqn.2.18)

where D_D and D_H represent the diffusion coefficients in Henry and Langmuir environments respectively.

However, the decrease in CO_2 permeance over pressure ends when the feed pressure exceeds a certain value and the CO_2 permeability starts to increase as the feed pressure is further increased due to plasticization. The pressure at the flex point is called the "plasticization pressure" as depicted in Fig.2.18 (Wessling, Huisman et al. 1995; Bos, Punt et al. 1999).



Fig.2.18. CO₂ permeation isotherm as a function of the feed pressure

In the natural gas purification industry, the plasticization phenomenon is undesirable due to the loss of selectivity and methane productivity it causes. However, in certain industries, plasticization has been applied due to its positive and practical effects. For instance, plasticizers have been used in PVC production to increase the polymer chain mobility hence to improve the flexibility of PVC (Selinger 1991). Koros et al. (Koros, Jordan et al. 1988) patented their work of utilizing CO_2 as a plasticizer to improve the permeability of certain gas separation membrane.

2.9 Fundamentals of the CO₂ induced plasticization

2.9.1 Plasticization effect on the glass transition temperature (T_g) of polymers

As described in Section 2.4, the permeability can be considered as the combination of solubility and diffusivity according to the solution-diffusion mechanism (Eqn.2.1). Lifting the feed pressure usually causes the increase in diffusivity and decrease in solubility. Therefore the plasticization induced increase in permeability is more likely to be caused by the rapid increase of diffusivity, in other words, an enhanced polymer segmental mobility (Bos, Punt et al. 1998). Furthermore many studies have illustrated the strong correlation between polymer segmental mobility and the glass transition temperature (T_g) (Chiou, Barlow et al. 1985; Sanders 1988; Paul and Yampolskii 1994; Wessling, Huisman et al. 1995; Bos, Punt et al. 2001), therefore the depression of T_g can be used to quantify the degree of plasticization. Chiou et al. (Chiou, Barlow et al. 1985) reported the decrease in T_g of 32°C for polystyrene, 18 °C for PVC, and 51 °C for polycarbonate after exposing the membrane with CO₂ under the pressure of 20 bar. In addition, Sanders et al. (Sanders 1988) reported a T_g depression of 76 °C for PES after CO₂ conditioning at 7.8atm.

2.9.2 Plasticization effect on the polymer structure

The essence of the plasticization phenomenon is the interaction between CO_2 gas molecules and the polymer chains. Several researchers (Sanders 1988; Raymond and Paul 1990; Ghosal, Chern et al. 1995) indicated that CO_2 is more soluble in polymers with polar and flexible pendant groups, such as -COOCH₃ group in cellulose acetate (CA) or other polymers with a polar matrix. It is assumed that CO_2 has a quadrupole moment which can have dipolar interactions with polar groups presented in the polymer chains. Koros et al. (Koros 1985) reported that the incorporation of the active groups such as carbonyl and sulfone on the side chains, may have an undesirable effect on CO_2/CH_4 selective solubility which increases the tendency of the polymer to exhibit the plasticization behaviour. For cellulose acetate, one of the most commonly used polymer materials in natural gas purification (e.g. UOP, Cynara-NATCO etc.), a reduction in CO_2/CH_4 selectivity of more than 50% compared to the intrinsic dense film value due to plasticization was reported (Houde, Krishnakumar et al. 1996; Baker 2002).

The above studies gave an insight of the interaction between gases and certain functional groups in the polymer chain structure, and provide crucial information not only to prescreen the suitable membrane material from existing polymers, but also to assist tailoring novel polymer structure with desirable plasticization resistance.

The plasticization pressure of several glassy polymers commonly used as membrane materials have been reported in the following order: Polysulfone (PSF) > bisphenol A polycarbonate (BPA-PC) > polyetherimide (PEI) > polyethersulfone (PES) > bisphenol Z polycarbonate (BPZ-PC) > copolyimide (P84) > poly(2,6-dimethyl-*p*-phenylene)oxide (PPO) > tetramethyl bisphenol A polycarbonate (TMBPA-PC) > Matrimid[®] 5218 (BTDA-DAPI) > cellulose acetate (CA) > cellulose triacetate (CTA) (Bos, Punt et al. 1999).

2.9.3 Plasticization effect on membrane integrity

The membrane thickness dependence of plasticization has been well documented both on dense and asymmetric membranes (Jordan, Henson et al. 1990; Pfromm and Koros 1995; Wessling, Lopez et al. 2001; Punsalan and Koros 2005; Huang and Paul 2007). It was observed that membranes with different thickness respond to plasticization differently by displaying the plasticization curves with different shapes as shown in Fig.2.19 (Ismail and Lorna 2002; Wallace 2004).



DEGREASE IN WIEWDRAINE THICKINESS

Fig.2.19. Schematic representation of the thickness dependence of plasticization As shown in Fig.2.19, asymmetric hollow fiber membranes usually display a much lower plasticization pressure than dense film, and sometimes exhibit an instantaneous increase in CO_2 permeance with pressure (Jordan, Henson et al. 1990; White, Blinka et al. 1995). White et al. (White, Blinka et al. 1995) attributed this phenomenon to the loosely packed polymer chains presented in the skin layer of asymmetric membranes compared to those in a dense film. However, higher selectivities in asymmetric membranes (10% above dense film value) were reported for various polymer materials which indicates that there is a higher polymer chain packing density in skin layer of asymmetric membranes than in dense films (Ismail and Shilton 1998; Ismail, Dunkin et al. 1999; Niwa and Kawakami 2000; Niwa, Kawakami et al. 2004). The inconsistent interpretations of these behaviours indicates that the dependence of plasticization on thickness should not simply be attributed to the polymer chain packing density; a more sophisticated model therefore needs to be developed to obtain a consistent explanation of all the experimental observations.

Kesting et al. (Kesting 1990; Kesting and Fritzschz 1993) has suggested that polymer chains in the surface layer of integrally skinned membrane were packed in a different manner (compact blackberry-shaped nodule aggregates in the surface of integrally skinned hollow fibers) compared to those in a dense film. This observation led to the speculation that the difference in polymer chain packing may contribute to the different plasticization behaviour between asymmetric membranes and dense films.

Plasticization occurs during the gas transport process. While several gas transport mechanisms in glassy polymers have been proposed in the past and widely accepted (e.g. dual-mode model, free volume theory etc.) (Vieth, Tam et al. 1966; Vieth, Howell et al. 1976; Koros 1980; Curro and Lagasse 1981; Curro and Lagasse 1982; Barrer 1984), very few attempts have been made to link these transport mechanisms to plasticization. Connecting membrane morphology, membrane formation mechanism, gas transport mechanism and plasticization using theoretical reasoning would provide useful strategies to obtain membrane morphology with desired plasticization resistance by manipulating the membrane fabrication process.

2.9.4 Single gas versus mixed gases permeation

Plasticization phenomenon on single CO_2 permeation has been well documented in literature; however it failed to predict the decrease in selectivity for mixed gases permeation, since the increase of the secondary gas permeability caused by plasticization is overlooked. Sanders et al. (Sanders, Koros et al. 1984) reported a significant reduction of CO_2 solubility in the gas mixture compared to single gas solubility at equivalent partial pressure due to the competitive sorption effect. Story and Koros (Story and Koros 1989) suggested that the competition between two gas types can result in lower penetrant concentration, reduce driving force across the membrane and consequently lower the gas permeability. Furthermore the reduction of CO_2 permeability with increased feed pressure is more pronouncedly than that of CH_4 ; therefore a reduced selectivity is expected as a result. Similarly White et al. (White, Blinka et al. 1995) reported a lower selectivity of mixed-gas permeation compared to single gas on the 6FDA-DMB asymmetric membranes.

The above observations by various researchers are attributed to the so-called "competitive sorption" effects, in which the permeability of the primary gas decreases by the introduction of the secondary gas. The decrease in permeability of the both gas types takes place in such a way that makes the membrane lose its selectivity. Therefore a decrease in selectivity is not a sufficient condition to predict the occurrence of plasticization in CO_2/CH_4 mixed gas permeation since both plasticization and competitive sorption could cause the reduction in selectivity.

In terms of the changes in permeability during the CO₂/CH₄ mixed-gas permeation, plasticization usually causes the increase in permeability while competitive sorption leads to a decrease in permeability. Therefore a counterbalance effect in permeability could exist in the mixed-gas permeation between competitive sorption and plasticization. Visser et al. (Visser, Koops et al. 2005) reported a suppression of plasticization caused by the competitive sorption from increasing the secondary gas content in the gas mixture for a Matrimid/PES (80/20) blend hollow fiber (apparent skin layer thickness of 0.27µm). Kapantaidakis et al. (Kapantaidakis, Koops et al. 2003) reported a similar depression of CO₂ and N₂ permeance with partial pressure for PES/PI blend hollow fibers which indicated the suppression of plasticization by competitive sorption. On the other hand, Bos et al. (Bos, Punt et al. 1998) reported an increase in CO₂ permeability above 15 bar CO₂ partial pressure for a dense Matrimid film which indicated that the plasticization has not been entirely masked by competitive sorption. These inconsistent observations indicate that further investigation of competitive sorption is necessary to understand its behaviour for membranes with different properties and its relation to plasticization.

2.10 Plasticization suppression strategies

Undesired plasticization should be minimized. Several suppression strategies have been developed in the past including (1) thermally annealing with or without alteration of the polymer structure, (2) chemical cross-linking with extra cross-linker or polymer material itself, and (3) blending with a secondary polymer material with higher plasticization pressure.

2.10.1 Thermal annealing

Thermal annealing is an easy approach to enhance membrane's plasticization resistance; it could be carried out either above or below glass transition temperature (T_g) for various period of time.

Chung et al. (Chung, Ren et al. 2003) reported that by thermal annealing of 6FDA-2,6DAT hollow fibers at a range of temperatures between 150 and 320°C, plasticization phenomenon was successfully suppressed. Without the evidence of the cross-linking (observed via NMR), they suggested that the better packed polymer chains and denser skin layer was the cause of enhanced plasticization resistance. On contrast, the crosslinking was evidenced by GPC measurements and TMA on a series of aromatic polymers during heat treatment by Kuroda et al. (Kuroda and Mita 1989; Kuroda, Terauchi et al. 1989). In addition, the formation of the charge transfer complexes (CTC) during thermal annealing at mild and high temperature was suggested by several researchers (Kawakami, Mikawa et al. 1996; Bos, Punt et al. 1998; Krol, Boerrigter et al. 2001; Zhou and Koros 2006) to explain the suppression of plasticization. However the formation of CTC is difficult to assess for asymmetric hollow fibers in contrast with dense thin film.

2.10.2 Chemical cross-linking

Chemical cross-linking makes it possible to suppress plasticization at the ambient condition. It can be done either at the early stage of the dope preparation (cross-linking of the polymer material) or more commonly, at the late stage of the membrane fabrication process as a post-treatment.

Diamino based chemicals have been widely applied as the cross-linkers to modify the polyimide membrane and proved to be sufficient to suppress plasticization (Shao, Chung et al. 2005; Shao, Chung et al. 2005; Powell, Duthie et al. 2007; Shao, Liu et al. 2008). For example, a simple chemical cross-linking modification of 6FDA-Durene dense films at room temperature (Liu, Wang et al. 2001) changed the chemical structure of imide groups into amide groups while immersing the dense film in a *p*-xylenediamine methanol solution. Using the same cross-linking reagent, Tin et al. (Tin, Chung et al. 2003) observed the suppression of plasticization on Matrimid dense film in CO₂ single gas permeation test. Zhao et al. (Zhao, Cao et al. 2008; Zhao, Cao et al. 2008) reported an improvement in the chain mobility and solubility selectivity while cross-linking Matrimid with cross-linker containing poly (ethylene oxide) (PEO). Unlike other common crosslinkers, this cross-linking reaction produced enhanced gas permeability and selectivity at the same time. Cross-linking could also be induced by UV-irradiation (Hsu, Nataraj et al. 1993; Kita, Inada et al. 1994; Meier, Langsam et al. 1994), Staudt-Bickel et al. (Staudt-Bickel and Koros 1999) have investigated UV-light photochemical reaction on 6FDA (4, 4'-(hexafluoroisopropylidene) diphthalic anhydride), however this modification method is difficult to perform on the hollow fibers.

2.10.3 Blending

Commonly used polymer materials possess different anti-plasticization properties; blending polymers with different plasticization characteristics enable the researchers to fine tune the plasticization resistance of the membranes. Furthermore this approach can also be used to tailor a specific separation performance by manipulating the blend composition (Bos, Punt et al. 2001). In addition to these, blending also presents an opportunity to reduce the cost of the membrane by blending with cheap polymers.

Bos et al. (Bos, Punt et al. 2001) reported that the blended dense film of Matrimid and P84 (copolyimide of 3,3'4,4'-benzophenone tetracarboxylic dianhydride and 80% methylphenylene-diamine + 20% methylene diamine) not only suppressed the plasticization effects but also increased the selectivity by a slight relaxation in permeability. The plasticization behaviour on PSF/Matrimid blend dense film has been investigated by Kapantaidakis et al. (Kapantaidakis, Kaldis et al. 1996) and the plasticization pressure was shifted to 20 atm by using a moderate PSF concentration (50/50 PSF/PI). Chung et al. (Chung, Guo et al. 2006) reported that blending a small amount of PBI with Matrimid can efficiently overcome the plasticization of Matrimid at high temperature operation. The suppression of plasticization is attributed to the fact that the interactions between the carbonyl group of Matrimid and the N-H group of PBI make the polymer chains interpenetrate closely and decrease the interstitial chain space.

2.11 Conclusions

The formation mechanism of the integrally skinned membrane is covered in this chapter in great details. The theoretical path leading to a perfect membrane with desired morphology and superior separation performance has been described. Although various theories have been proposed, the formation mechanism of the skin layer still remains cloudy regarding to its relation with the experimental observation. Most of the strategies aiming for the fabrication of defect-free integrally skinned membranes possess certain technical flaws. One of the greatest challenges of membrane fabrication is to ensure the composition of the nascent hollow fibers follow the optimized trajectory in the ternary phase diagram to guarantee the phase inversion taking place via the desired mechanisms (spinodal decomposition, nucleation and growth).

Although plasticization phenomenon has been intensively investigated, most of the work still only focused on its effect on the gas separation properties of the membranes, very little attention has been paid on the mechanism of the plasticization itself, or its relation with the membrane morphology and gas transport mechanism in the membrane structure. Kesting's nodule structure model (Section 2.3.2) presents a possible link between the membrane structure and dual-mode gas sorption model. However the theoretical ground of this model remains unclear. In this work, the nodule structure model will be further explored with theoretical reasoning and experimental justification. Furthermore the improved nodule structure model will also be applied to interpret the plasticization phenomenon in terms of its relation with the membrane structure, and several plasticization related phenomenon will also be interpreted through this model.

In the past, the investigation of plasticization phenomenon has been carried out mostly on dense film with single CO_2 gas due to the limitations described in Section 2.9. Investigation in asymmetric membrane with mixed-gas is therefore essential to gain a complete understanding of the plasticization phenomenon. Furthermore, a thorough investigation of competitive sorption effects is also necessary to reveal its relation with plasticization phenomenon.

Thermal annealing as post-treatment has been proved to be sufficient to suppress plasticization; however the mechanism behind this treatment remains uncertain particularly to asymmetric hollow fibers where changes in morphology (skin layer and substructure support) may be affected, and it requires further exploration to understand the mechanism of the plasticization suppression by thermal annealing.

3 MATERIALS AND METHODLOGY

3.1 Materials

Polymer

Matrimid[®] 5218 used in this work, was generously supplied by Huntsman Advanced Materials Americas Inc. It was chosen because of its superior CO_2/CH_4 separation properties and its robust mechanical, chemical, and thermal stability. The glass transition temperature (T_g) of Matrimid is 319.52°C (measured with Differential Scanning Calorimetry). Its chemical structure is shown in Fig.3.1 and major properties are listed in Table.3-1.



Fig.3.1. Chemical structure of Matrimid[®] 5218 **Table.3-1.** Properties of Matrimid[®] 5218 (Ekiner, Hayes et al. 1992)

P _{O2} (Barrer)	P _{N2} (Barrer)	$\alpha_{O2/N2}$	$T_{g}(^{\circ}C)$	ρ(g/cc)	$M_{ m W}$
1.32~1.35	0.185	7.2	305~320	1.2	86,000

Solvents

All solvents *N*-Methyl-2-pyrrolidone (NMP), Dimethylacetamide (DMAc), Tetrahydrofuran (THF), ethanol, methanol, and hexane were purchased from Scharlau and used as received, absolute ethanol was also used.

Gases

All gases used in this study were purchased from Coregas. Single gases of nitrogen, oxygen, methane, carbon dioxide and helium (used as carrier gas for GC) were all ultrahigh purity grades and were used without further purification. The composition of the CO_2/CH_4 gas mixture was 19.85% carbon dioxide balanced with 80.15% methane.

3.2 Dope development

Cloud point experiment

Cloud point experiment (rapid titration) was applied in this study to construct the Matrimid/NMP/H₂O and Matrimid/NMP/EtOH ternary phase diagrams.

Different amount of Matrimid in NMP (varies from 1~25%) were prepared by mixing desired amounts of these materials in sealed bottles. To achieve homogeneous polymer solutions, these mixtures were stirred for up to 72 hours with a magnetic stirrer.

To perform the rapid titration, Milli-Q water or absolute ethanol were slowly added into the polymer solution by a micropipette with 5 μ l accuracy under agitation. In the case of polymer solution with high Matrimid concentration, NMP was added into the Milli-Q or ethanol to reduce the chance of fast precipitation due to the high non-solvent concentration in the local area. During titration, the solution temperature was controlled at $25^{\circ}C$ with a magnetic hot plate stirrer. The addition of Milli-Q water and ethanol were continued until the clear polymer solution visually turned to a cloudy solution.

After observation of the first sign of turbidity, the addition of Milli-Q water and ethanol were stopped and the cloudy solution was agitated for an additional 30 min to see whether the turbid solution turns to a clear solution, more Milli-Q water or ethanol were added, otherwise the determined point was considered as the onset of cloud point.

The composition of cloud point was then determined by the amount of Milli-Q water/ethanol, NMP, and Matrimid presented in the bottle and the results were mapped on the ternary phase diagram to assist the selection of the dope formula.

Dope preparation

Matrimid[®] 5218 was placed in the oven at 120°C for 12 hours to remove the moisture. Polymer, solvent and non-solvent additives were then mixed in a glass vessel and allowed to sit for half an hour prior to agitation. The dope mixture was stirred at the ambient temperature for 24 hours to obtain the homogenous solution, and then transferred to the dope reservoir 12 hours before the fabrication process to allow degas. Fraction of the dope solution was used to measure the shear viscosity which was measured by a controlled-stress rheometer (AR1500ex, TA Instruments) with a parallel plate. Shear rates in the range of 1000~2000 s⁻¹ under steady-shear conditions were applied and the resulting shear stress was measured at 25°C.

3.3 Integrally skinned hollow fiber fabrication

Dry-jet, wet spinning technique was adopted in this work. The dope solution was pumped into the spinneret via a Motovario pump coupled with a flux controller (TECO FM50 Flux Master), the bore fluid was pumped into the spinneret through a syringe pump (TELEDYNE ISCO 500D), dope and bore fluid were then co-extruded from the spinneret into the air gap with the ambient conditions. Once passing through the adjustable air gap, the nascent fibers were immersed into a coagulation bath filled with tap water at room temperature. After passing over several wheel-guides, the hollow fibers were collected on a take-up drum with a speed controller (RS components low voltage DC reversing speed controller). A picture of the fabrication apparatus is given in Fig.3.2. In all cases, the spinning process was carried out at room temperature (between 20 and 23°C) and a tube-in-orifice spinneret with an outer diameter of 1.2 mm and an inner diameter of 0.4 mm was used (Fig.3.3).



Fig.3.2. Dry-jet, wet spinning fabrication apparatus

The fabrication variables examined in this study include the dope and bore compositions, dope and bore flow rates and air gap distance. Four dope solutions with different compositions were prepared (detailed compositions in Chapter 4), the dope flow rates ranged from 4.2 to 4.8 ml/min. Four bore fluids with different compositions ranging from pure water to 80% NMP in water were also prepare (detailed compositions in Chapter 4),

and bore fluid flow rates varied from 0.8 to 2.0 ml/min. The spinneret sat on a movable stand and the air gap distance can be adjusted between 5 and 30 cm. All the fibers were cut in 1m in length prior to wash and dehydration process.



Fig.3.3. Tube-in-orifice spinneret during fabrication

After the spinning, the wet fibers were immersed in the fresh tap water for 3 days (water changed every day) to allow the dissolution of the solvent residuals from the fiber. After that, a solvent exchange process suggested by previous works (Minhas, Matsuura et al. 1985; Vasarhelyi, Ronner et al. 1987) was performed by immersing the wet fibers in 3 methanol baths for 20 minutes each, followed by immersion in 3 hexane baths for 20 minutes each before drying the hollow fibers in air overnight. The dried fibers were then stored for one month to eliminate the physical aging effect prior to further testing (It was

observed that gas permeance was stabilised 3 weeks after fabrication due to physical aging). A picture of the Matrimid hollow fibers is given in Fig.3.4.



Fig.3.4. Matrimid[®] 5218 hollow fiber samples

3.4 Membrane characterization

3.4.1 Scanning Electron Microscopy (SEM)

The cross-section of the hollow fibers was observed using a Scanning Electron Microscopy (SEM), the cross-section was prepared with the cryogenically fracture of the hollow fiber in liquid nitrogen to preserve its microscopic morphology, then the fiber sample was sputter coated with conductive metal materials such as gold and chromium prior to imaging with a Hitachi S3400. $100 \times$ is adequate to obtain the whole cross-section image depending on the outer diameter of the fiber sample, while $5000 \times$ is usually sufficient to observe the skin layer structure.

3.4.2 Gravimetric sorption

Gravimetric sorption tests were applied to obtain the sorption isotherms of CO₂, CH₄ and N₂ in different hollow fiber samples. These sorption isotherms were used to determine the sorption parameters (*S*, C_{H} ' and *b* as described in Chapter 2) which will be applied in

Chapter 6 to decouple the dual-mode sorption sites and to simulate the mixed-gas transport behaviour in the Matrimid membrane.

The sorption isotherms of single gases (N_2 , CO_2 , and CH_4) on hollow fiber samples were constructed by Colin Scholes and Wendy Tao at the University of Melbourne, and the experiments were performed at 25°C using a Gravimetric High Pressure (GHP-300) analyser with a Cahn microbalance (VTI Corporation, USA).

The samples were placed in a chamber, and buoyed by gas. Sample's weight changes with increasing pressure up to 20 bar were measured and corrected for buoyancy. Likewise, desorption isotherms were constructed by measuring the weight change with decreasing pressure.

3.4.3 Module fabrication

The dried hollow fibers were potted in a double-ended 20 cm long stainless steel module with the membrane area ranging from 15 to 45 cm² (Fig.3.5), the calculation of the area is based on the OD of the hollow fiber membranes since the effective selection layer is located at the outer-most region of the fibers. Matrimid hollow fibers were sealed in the tube with 5mins epoxy (GC QUIK STIK[®]), each module housed 3~6 fibers depending on the OD of the hollow fiber. Two identical modules were prepared from the same batch of the hollow fibers for the parallel permeation tests. After potting, membrane modules were put aside for 30 mins prior to testing to allow the epoxy to cure.



Fig.3.5. Tube-in-shell hollow fiber module

3.4.4 Single and mixed-gas permeation

The permeation properties of the hollow fibers were measured in a high pressure set up by using the variable pressure method (Fig.3.6). This type of apparatus allows a straightforward determination of membrane permeability and selectivity over a wide range of feed pressure and composition (Sanders, Koros et al. 1983; Moore, Damle et al. 2004), and it can be applied on both single gas and mixed-gas permeation (O'Brien, Koros et al. 1986). Permeate flow rate was measured by an Agilent Technologies Optiflow570 digital flow-meter while feed and permeate pressures were measured by MKS Barathron750B and 722A respectively. Gas mixture compositions were measured by a Shimadzu GC-8A gas chromatograph with a silica gel column. The injector temperature was set at 200°C, and the column temperature was fixed at 150°C.



Fig.3.6. Gas permeation apparatus

The membrane modules were tested in a shell-fed configuration at room temperatures from 20 to 23° C (Fig.3.7). Single gas (O₂/N₂) permeation tests were conducted under the pressure of 10 bar, and 15 bar for mixed-gas (CO₂/CH₄) permeation.



Fig.3.7. Shell side feed configuration

Dead end configuration (no retentate flux) was applied on single gas permeation by closing the retentate valve. For relatively "inert" single gas (O_2 , N_2 and CH_4) permeation, fibers were allowed to equilibrate over 30 mins, then the permeate flow-rate was measured, at least three readings were taken and the mean value was used to calculate the permeance. Permeate flux was double-checked after another 30 mins to ensure the fluctuation of permeance results was less than 5% (Fig.3.8). A parallel test was also performed on another module with same batch of hollow fibers to check the consistency.



Fig.3.8. Single gas (O₂, N₂ and CH₄) permeation experimental protocol

For the single gas permeation, the permeance was calculated via Eqn.3.1 and the ideal selectivity was calculated via Eqn.2.13:

$$\frac{P}{l} = \mathbf{10}^{6} \cdot \frac{\text{permeate flux}\left(\frac{ml}{min}\right) \cdot 273.15}{\Delta p \,(\text{psi}) \cdot T(\text{kelvin}) \cdot Area(\text{cm}^{2}) \cdot 5.17 \cdot 60} \tag{Eqn.3.1}$$

where *permeate flux* is measured by the bubble flow-meter, Δp is the pressure difference between downstream and upstream face of the membrane, *T* is the permeation temperature, here is the ambient temperature, and *Area* is the effective membrane area in the module.

The standard error of the ideal selectivity was calculated via Eqn.3.2 and Eqn.3.3 (Harris 2007):

$$z = \frac{y}{x}$$
(Eqn.3.2)

and,

$$error_{z}(\%) = \sqrt{error_{x}^{2} + error_{y}^{2}}$$
 (Eqn.3.3)

For the mixed-gas permeation, concentration polarization effect severely affects membrane's separation properties and should be limited. Kesting et al. (Kesting and Fritzschz 1993) suggested that concentration polarization becomes negligible if the stage cut (ratio between permeate and feed molar flow rates) is kept less than 1%. Therefore in this study, the retentate valve was open during the mixed-gas permeation tests to lower the stage cut. The permeance was then calculated via Eqn.3.4 and the separation factor was calculated via Eqn.2.14:

$$\frac{P}{l} = \mathbf{10}^{6} \cdot \frac{permeate flux\left(\frac{ml}{min}\right) \cdot Y_{A} \cdot 273.15}{(p_{X} \cdot X_{A} - p_{Y} \cdot Y_{A}) (psi) \cdot T(kelvin) \cdot Area(cm^{2}) \cdot 5.17 \cdot 60}$$
(Eqn.3.4)

where Y_A is the permeate mole fraction, X_A is the upstream mole fraction, p_X and p_Y are the upstream and downstream total pressure, it is noteworthy that the partial pressure is used in this equation instead of fugacity since all the fugacity coefficients are close to 1. Similar to the single gas permeation tests, three readings (pressure and flux) were taken

each time except the GC results due to the limitation of the equipment, and the mean values of the pressures and fluxes were used to calculate the partial permeance.

3.5 Plasticization investigation

Plasticization phenomenon was investigated with single and CO_2/CH_4 gas mixture. O_2/N_2 single gas permeation was always performed prior to CO_2 single gas test to provide membrane's initial separation properties as a reference. CO_2 permeances were measured as a function of pressure (increase step-wisely, from 5bar to around 25bar) to construct the CO_2 permeation isotherm to demonstrate the plasticization phenomenon. The time intervals between pressure increasing steps were set ranging from 5 mins to 1 hour to observe the time dependence of plasticization. The CO_2 conditioned fibers were then allowed to degas over night before conducting another O_2/N_2 single gas tests to compare with the permeation results from the virgin fibers.

All the mixed-gas permeation tests were performed under ambient condition (ranging from $20 \sim 23^{\circ}$ C). Two identical membrane modules were measured under the same condition to check the reproducibility. The mixed gases permeation protocol is described as follows:

1. Conduct O_2/N_2 single gas permeation tests at 10 bar to examine the membrane quality and obtain the initial separation properties as the baseline,

2. Allow fibers to de-gas for 1 hour,

3. Conduct the CO₂/CH₄ mixed gas permeation test at 5 bar for approximately 1 hour,

4. Increase the pressure to a higher value and repeat step 3,

5. Repeat step 4 until the pressure reaches 60 bar (depending on the quality of each membrane module),

- 5. Allow fibers to de-gas over night,
- 6. Conduct O_2/N_2 single gas permeation tests at 10 bar to compare with virgin membrane.

3.6 Thermal annealing

A vacuum oven equipped with a temperature controller (maximum: 400°C) was used to anneal hollow fiber samples. The fiber samples were heated to the required temperatures (100, 150, 200, 250, 300, 350 and 380°C) under vacuum (target temperature usually reached in less than 5 mins), then the fiber samples were kept under that temperature for a certain period of time (15, 30, 45mins, 1, 2, 3, 4 and 12 hrs). After the desired time was reached, fiber samples were taken out of the oven immediately and air cooled for 1h prior to further testing.

3.7 Characterization of the treated membrane

Besides single and mixed-gas permeation tests, several other techniques were also adopted in this work to characterize the annealed membranes:

Differential Scanning Calorimetry (DSC)

The evolution of the glass transition temperature indicates the effect of thermal annealing since any change in the polymer chain segmental mobility would affect the glass transition temperature (Kawakami, Mikawa et al. 1996; Bos, Punt et al. 1998; Bos, Punt et al. 1998; Bos, Punt et al. 1999; Bos, Punt et al. 2001; Dudley, Schoberl et al. 2001). TA Instruments DSC2010 was used to measure the glass transition temperature of both virgin and annealed membranes. DSC was also applied on the plasticized membranes because the change of the glass transition temperature indicates the degree of plasticization. The

glass transition temperature of sample polymers is commonly determined on the second run in order to remove the thermal history in polymeric material.

To perform the DSC tests, approximately 10mg of the fiber samples were cut into small pieces, sealed in an aluminum pan and placed in the sample chamber along with the reference pan. All the samples were heated to 350°C at a heating rate of 10°C/min. The glass transition temperature was usually measured at the second round of testing to ensure the accuracy.

Thermo-Gravimetric Analysis (TGA)

TGA measurements (White, Blinka et al. 1995; Kawakami, Mikawa et al. 1996; Dudley, Schoberl et al. 2001; Krol, Boerrigter et al. 2001; Chung, Ren et al. 2003; Barsema, Klijinstra et al. 2004) provide a powerful tool to analyse the residual components remaining in the membrane (water, residual solvent), the decomposition temperature derived from the TGA measurements can be used to indicate the thermal stability of the membrane sample.

TA Instruments Hi-Res Modulated TGA 2950 was used to analyse the weight loss of both treated and untreated membrane during the heating process. Membrane samples were loaded in the sample pan, subsequently heated from 50 to 1000° C at a heating rate of 20°C/min under N₂ environment to ensure the oxidization did not take place. The weight loss of the residual water and solvents was recorded by the Thermal Analysis Control Software, and the decomposition temperature was also measured.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR has been widely applied to investigate the change in the polymer chain structure (Kawakami, Mikawa et al. 1996; Bos, Punt et al. 1998; Tin, Chung et al. 2003; Barsema,
Klijinstra et al. 2004; Zhou and Koros 2006; Jiang, Chung et al. 2008; Kosuri and Koros 2008). It has been reported that the wave-number (v (cm⁻¹)) of the infrared spectrum is proportional to the energy and vibration frequency of the absorbing unit, therefore any change in the chemical structure of polymer chains will reflect on the alteration of the wave-number (Straughan and Walker 1976; Colthup, Daly et al. 1990). FT-IR (Thermo Nicolet 5700 FT-IR) was used in this work to probe the membrane structure in order to detect any chemical structural changes during the thermal annealing.

To obtain the FT-IR spectrum of the Matrimid hollow fiber, background spectrum was collected first on the empty sample stage to eliminate the spectrum of CO_2 and water vapour. Matrimid hollow fiber samples were then cut into 0.5 cm in length, and mounted on the diamond sample stage, the fiber samples were compressed by a metal tip to ensure all the laser beams was reflected back and received by the detector. The laser beam was running under 30 times scan, and the final spectrum was collected from the average value.

Dissolution test

Thermal annealing has a potential to cross-link the polymer chain structure which make it less likely to dissolve in the organic solvent. Therefore the dissolution tests present a good indicator of the cross-linking degree of the polymer chains during the thermal annealing (Wallace 2004).

All the annealed samples (with different annealing temperature) were cut into 3 cm in length and immersed into several glass vials filled with NMP for the same period of time, subsequently, the degrees of dissolution were compared. The time required to fully dissolve the annealed samples were also recorded and compared to indicate the degree of plasticization.

4 FABRICATION OF MATRIMID ASYMMETRIC HOLLOW FIBER MEMBRANE

4.1 Introduction

As described in chapter 1, one of the major objectives of this study is to develop the optimized spinning protocol to prepare the defect-free integrally skinned hollow fiber membranes. In this chapter, the major spinning operation parameters will be examined in terms of their influence on the membrane's morphology and separation properties, the optimized fabrication condition and the separation performance of the hollow fibers spun under this condition will be presented. The experiments were organized in the following manner to reduce the workload: the permeation tests are carried out on O_2 and N_2 single gases first during the optimization process. Once the optimized spinning condition is determined, CO_2/CH_4 mixed-gas permeation tests will be performed to examine whether the hollow fiber obtains a defect-free thin skin layer to deliver the optimized gas separation performance for natural gas purification.

4.2 Dope development

The first step of the dope development is to construct the ternary phase diagrams. The cloud point experiments (rapid titration) were conducted at 25° C on both Matrimid/NMP/H₂O and Matrimid/NMP/EtOH ternary systems and the results were mapped on the ternary phase diagrams (Fig.4.1).



Fig.4.1. (A) Matrimid/NMP/H₂O and (B) Matrimid/NMP/EtOH ternary phase diagrams

The binodal curve in Fig.4.1 was shifted to the right side of the ternary phase diagram when EtOH was used as the non-solvent compared to water. This result indicates that water is a stronger non-solvent than ethanol, and homogenous polymer solution might require longer time to undergo phase inversion in ethanol than in water. Hence the polymer concentration at the outer-most region of the hollow fiber is allowed to increase with the prolonged phase separation time. Therefore a typical "Type I" membrane with a thick and dense skin layer due to the delayed demixing is expected when ethanol is used as the coagulation medium. Although ethanol might be a better candidate for coagulation medium for the above reason, water is still chosen as the coagulant due to the economic concerns, ethanol is added to some of the dope formulas as the non-solvent additive.

With the assistance of the ternary phase diagrams, four dope formulations were developed as shown in Table.4-1. The shear viscosity of these dope solutions were measured at 25° C and ranged from 11,348 to 15,660 cP (shear rate from 1000~2000 s⁻¹). Compared to the dope solution for the flat sheet membrane casting, much higher concentration of the polymers was applied for hollow fiber fabrication in order to increase the shear viscosity to make the dope suitable for spinning.

4.3 Integrally skinned hollow fiber fabrication

The Matrimid hollow fibers were fabricated under different conditions (all shown in Table.4-1) and then characterized via both scanning electron microscopy (SEM) and O_2/N_2 single gas permeation tests to investigate their morphology and separation performance, the results are presented in the following sections.

	M1: 32% Matrimid, 68% NMP
Dope composition	M2: 26% Matrimid, 59.2% NMP, 14.8% EtOH
	M3: 26% Matrimid, 52.7% NMP, 6.5% THF, 14.8%
	EtOH
	M4: 26% Matrimid, 39.5% NMP, 19.7% THF, 14.8%
	EtOH
	Pure water
Dom composition	40% NMP, 60% H ₂ O
bore composition	60% NMP, 40% H ₂ O
	80% NMP, 20% H ₂ O
Dope flow rate	4.2ml/min ~ 4.8ml/min
Bore flow rate	0.8ml/min ~ 2.0ml/min
Air gap distance	5cm ~ 30cm
Temperature	Ambient

Table.4-1. Hollow fiber fabrication conditions

4.3.1 Influence of the dope composition

The effects of the dope composition on membrane's final morphology and separation properties were examined first. O_2/N_2 single gas permeation tests were carried out on hollow fibers fabricated with four dope formulations (shown in Table.4-1) while other spinning conditions maintained constant. The permeance and selectivity results are shown in Fig.4.2. In all the formulations, M1 represents the simplest composition with only the Matrimid and solvent NMP. Non-solvent EtOH is added into M2, M3 and M4 with the same concentration. THF, as a more volatile solvent, is added into M3 & M4 with different ratio.

Fibers fabricated with the simplest dope composition (M1) showed very low O_2 permeance and acceptable O_2/N_2 selectivity. M1 dope contained no non-sovent additives,

it loacated on the polymer-solvent axis which was far away from the binodal curve in the ternary phase diagram, hence the nascent membrane required much longer time to enter the two-phase region. During this delayed time, two factors controlled the trajectory of the nascent fiber's composition:

1. The evaporation of the solvent during the air gap,

2. The solvent and non-solvent exchange rate in the coagulation bath.

The evaporation of the solvent increases the polymer concentration at the outer-most region of the hollow fiber, whereas the effects of the solvent and non-solvent exchange prior to the phase inversion depends on the type of the solvent and non-solvent being used and their interaction. If the solvent out-flow is higher than the non-solvent in-flow, then Path A will be followed as shown in Fig.4.3, and an increase in polymer concentration at the outer-most region of the fiber is expected, otherwise, Path B will be followed and the decrease in polymer concentration could take place.



Fig.4.2. O₂/N₂ permeance and selectivity results of hollow fibers fabricated from different dope compositions (see Table.4-1 for detailed dope conditions).

For M1 dope solution, considering the high boiling point of the NMP (204.3 °C), the evaporation of the solvent was negligible, hence the solvent and non-solvent exchange in the coagulation bath dominates the change of the polymer concentration profile in the nascent membrane. Hollow fibers spun from M1 dope displays acceptable O_2/N_2 selectivity (Fig.4.2), however it is still much lower than the intrinsic selectivity of the Matrimid dense film which illustrates the possbile defects on the skin layer. On the other hand, both O_2 and N_2 permeances appears to be very low, indiciating the huge resistance to the gas transport in skin and transition layer. The above results indicates that the solvent and non-solvent exchange in this case is not sufficient to shift the polymer concentration to a level which produces the defect-free skin. In addition, the delayed demixing allows a prolonged solvent and non-solvent exchange to produce a very thick relatively concentrated polymer layer, therefore a thick yet defective skin layer was created as a result.

The addition of the EtOH (M2) shifts the dope composition closer to the binodal curve and accelerates the phase inversion process, consequently reduces the skin layer thickness and increases the permeance which is evidenced by the thermodynamic analysis presented in Section 5.3.2. On the other hand, the solvent and non-solvent exchange still dominatingly controlls the polymer concentration profile, therefore the polymer concentration at the outer-most region of the fiber could not reach a very high level to produce defect-free skin, as a result only a slight increase of the selectivity is observed as shown in Fig.4.2.



Fig.4.3. Demonstration of the solvent, non-solvent exchange effects on polymer concentration trajectory prior to the phase inversion.

Fibers with the dope compositions of M3 and M4 achieves better O_2/N_2 selectivities than with M2 as seen in Fig.4.2. The M3 and M4 dope solutions contain different amount of volatile solvent THF which possess a much lower boiling point than NMP. The evaporation of THF in the air gap increases the polymer concentration at the outer-most region of the nascent hollow fiber to a much higher level prior to the phase inversion compared to the dope solution without the volatile solvent component, therefore the formation of a denser and possible defect-free skin layer is expected, because M4 contains more THF than in M3, a higher selectivity is observed.

4.3.2 Influence of the bore fluid composition

The role of the bore fluid in the hollow fiber membrane fabrication is to take up the space and prevent the fiber collapsing from the bore side (Wallace 2004). It is widely accepted that the bore fluid should remain "neutral" (Chung, Kafchinski et al. 1992; Pesek and Koros 1994; Ismail, Dunkin et al. 1999; Kapantaidakis, Koops et al. 2002; Li, Chung et al. 2002; Tasselli and Drioli 2007) which means it should not interact with the dope solution. The solvent and non-solvent exchange between dope and bore should be minimized. There is a consensus that drawing certain amount of the solvent from the nascent hollow fiber into the bore fluid might be beneficial for membrane's final morphology. Therefore considering the above two factors, the bore fluid composition should be carefully developed in order to optimize membrane's performance.

In this study, four different bore fluid compositions were prepared (A: Pure water, B: 40% NMP/60% H₂O, C: 60% NMP/40% H₂O, and D: 80% NMP/20% H₂O), and the four batches of hollow fibers were fabricated from these bore fluids with the same dope composition (26% Matrimid, 39.5% NMP, 14.7% THF, and 14.8% EtOH, same as the M4 in Table.4-1). The SEM images of these four batches of hollow fibers are shown in Fig.4.4. Image A was fabricated with pure water as bore fluid, and huge macrovoids are observed in the membrane structure. From image B to C, the quantity and size of these macrovoids are decreasing with the increased solvent content in the bore fluid. In image D, the macrovoids are completely vanished when the solvent content in bore fluid reaches 80%.



Fig.4.4. SEM images of the Matrimid hollow fibers' cross-sections with different bore fluid compositions: (A) pure water, (B) 40% NMP/60% H₂O, (C) 60% NMP/40% H₂O, (D) 80% NMP/20% H₂O

The SEM image of the hollow fiber with pure water as bore fluid in Fig.4.5A shows finger like macro-voids from near outer to the almost inner wall of the hollow fiber while very thin skin layers are observed on both inside and outside of the hollow fiber, thin skin is also observed on the wall of finger like macro-voids (Fig.4.5A). Hollow fibers fabricated with a bore fluid contains 80% NMP and 20% H₂O exhibits a much thicker skin layer at the outer layer, and the sponge-like substructure is observed in Fig.4.5B.



Fig.4.5. SEM images of Matrimid hollow fibers asymmetric structure fabricated with different bore fluid compositions: (A) pure water, (B) 80% NMP/20% H₂O

Matrimid hollow fibers fabricated with pure water as bore fluid (Fig.4.6) shows very low O_2/N_2 ideal selectivity indicating the possible formation of the defective skin layer. The high precipitation tendency of the pure water could quickly solidify the inner-most region of the hollow fiber membrane, form an inner skin layer (confirmed by SEM images on Fig.4.4 and Fig.4.5) and impede the mass transfer between the solvent and bore fluid. Therefore the insufficient removal of the solvent within the nascent fiber leads to a defective skin layer and a very low selectivity. A significant increase in the selectivity is observed while increasing the NMP content in the bore fluid from 40% to 60%, however it is at the expense of the dramatic loss of permeances of both gases. Since the solvent concentration in the dope is higher than in bore fluid, the chemical potential difference between the solvent and bore could draw certain amount of the solvent away from the dope into the bore side, which increase the polymer concentration in the transition and support layers, consequently introduce the extra resistance to the gas transport. Bore fluid with 80% NMP produces hollow fibers with selectivity slightly below the intrinsic O_2/N_2 selectivity of the Matrimid dense film, which indicates the formation of the defect-free skin layer.



Fig.4.6. O₂/N₂ permeance and selectivity of the hollow fibers with different bore fluid compositions (Dope composition: 26% Matrimid, 39.5% NMP, 14.7% THF, and 14.8% EtOH)

The above results indicate that the composition of the bore fluid plays a significant role on the formation of the selective skin layer. Increased solvent content in the bore fluid may affect fiber's gas separation performance in the following possible ways:

- Reduce the water coagulant activity in bore fluid, which would slow the coagulation of the polymer from the inner wall of the fiber, and avoid the formation of finger like macrovoids,
- Reduce the solvent migration speed so the polymer concentration at the outer-most region of the fiber will not increase too quickly therefore reduce the difference of chemical potential within the fiber wall. This effect allows the re-dissolution of the polymer in the fiber wall and reduces the thickness of the transition layer and consequently lowers the substructure resistance and improves the gas separation performance.

In order to decide the exact bore fluid composition, Wallace et al. (Wallace 2004) suggested that the optimised bore fluid composition can be determined by extrapolating a line tangent to the binodal line at the polymer concentration of the dope to the solvent-non-solvent axis. According to the results from the cloud point experiment (Fig.4.1), the optimised bore fluid composition should be around 90% ~95% NMP in water in Matrimid/NMP/H₂O ternary system. However it is difficult to maintain the spinning line in our set-up when solvent content in the bore fluid exceeds 80%.

4.3.3 Influence of the dope and bore flow-rates

Dope and bore flow-rates not only affect the shape of the hollow fiber, but also influence the separation properties of the membrane since the mass transfer between the dope, coagulation medium and bore fluid accelerates when the dope and bore fluids are extruded at high speed.

In this study, flow rate of bore fluid in the range of 0.8 ml/min to 2 ml/min has been used in order to maintain the fibers with regular bores. As a rule of thumb, a ratio between dope and bore flow rate around 3 has been suggested by McKelvey et al. (McKelvey, Clausi et al. 1997) and was adopted in our study; therefore, the dope flow rate was first tested between 2.4 to 6 ml/min and then determined to range between 4.2 and 4.8 ml/min to maintain the shape of the hollow fibers.

Hollow fiber dimensions (OD and ID of the hollow fibers were measured with the assistance of SEM images of cross-section) and the gas separation properties (O_2/N_2 single gas permeation tests) are presented in Table.4-2, and the skin layer thickness is calculated based on the O_2 permeability of Matrimid dense film (as shown in Table.3-1). For the fibers fabricated with the dope flow rate of 4.2 and 4.8 ml/min, the change of the outer and inner diameters seems somehow random with the increased bore flow rate.

However the general decrease trends have been seen in the fiber wall thickness. If fixing the bore flow rate, OD, ID and the fiber wall thickness displayed the increasing trend with the increased dope flow rates only with little exceptions. O_2/N_2 single gas permeation results show that the O_2 permeance is lowered with increasing bore flow rate while the O_2/N_2 selectivity increases.

Changing the dope flow rate also alters its shear rate within the spinneret, the increase of the shear rate within the spinneret has been suggested as the cause of a very high selectivity (almost three times the intrinsic values for the dense films) for polysulfone hollow fibers by Ismail et al. (Ismail, Dunkin et al. 1999). Similarly, significant increase above the intrinsic dense film values has also been reported on fluorinated polyimide, 6FDA-6FAP (Niwa and Kawakami 2000; Niwa, Kawakami et al. 2004) at high shear rates during spinning. In this study, Matrimid hollow fibers fabricated under high shear rates (shown in Table.4-2 and calculated based on the method described by Bird et al (Bird, Stewart et al. 2007)) generally display thicker skin layers and higher O_2/N_2 selectivity, which is in agreement with the reported papers (Chung, Lin et al. 2000; Qin, Wang et al. 2000; Niwa, Kawakami et al. 2004). This observation has been interpreted as the result of the improved molecular orientation at high shear stress before the dope exit the spinneret, although, the orientation may experience some degree of the relaxation in the air-gap. However, due to the high viscosity of the dope, this shear stress improved molecular orientation may still affect the skin layer structure, which could lead to the low permeance and high selectivity. The increased bore flow rate, which increases the jet velocity inside the nascent fiber, seems to increase the bore side diameter and reduce the fiber outside diameter, therefore reduces the fiber wall thickness.

Skin layer	thickness	(Å)	1,010	1,180	1,270	1,390	1,280	1,310	1,440	1,450
O_2/N_2	selectivity		5.1	5.8	5.6	6.5	5.4	5.8	6.2	6.7
N_2	permeance	(GPU)	2.6	1.9	1.9	1.5	1.9	1.8	1.5	1.4
O_2	permeance	(GPU)	13.2	11.3	10.5	9.6	10.4	10.2	9.3	9.2
Shear	rate	(s^{-1})	1,495	1,495	1,495	1,495	1,710	1,710	1,710	1,710
Wall	thickness	(mn)	150	140	110	80	160	150	130	06
Inner	diameter	(mn)	410	580	500	530	610	530	500	680
Outer	diameter	(mn)	710	860	720	069	930	830	760	860
Bore flow	rate	(ml/min)	0.8	1.2	1.6	2.0	0.8	1.2	1.6	2.0
Dope flow	rate	(ml/min)	4.2	4.2	4.2	4.2	4.8	4.8	4.8	4.8

Table.4-2. Hollow fibers with different dope and bore flow rates and their dimensions.

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4.3.4 Influence of the air gap distance

Air gap plays a crucial role in the formation of the defect-free skin layer with desired thickness. Evaporation of the solvent and possible intake of water vapour (relative humidity ranging from 49~57%) within the air gap could dramatically alter the final morphology of the hollow fiber membranes. In some cases, the phase inversion inside the nascent hollow fibers could take place during the air gap prior to the immersion into coagulation bath as described in Chapter 2.

In this study, Matrimid hollow fibers were fabricated under a variety range of the air gap distances (from 5 cm to 30 cm), all the fibers were spun from the same dope composition with volatile solvent component THF (26% Matrimid, 39.5% NMP, 19.7% THF, and 14.8% EtOH). Fibers with 5 cm air gap distance display very high permeance and low selectivity indicating the existence of the defects in the skin layer as shown in Fig.4.7. The selectivity is significantly improved once the air gap is lifted to 10 cm; meanwhile the permeance of O_2/N_2 drops dramatically. Elevating the air gap from 10 cm to 15 cm sees a steady increase in the selectivity and decrease in permeance. Further increasing the air gap from 15 cm to 30 cm, only slight improvement is observed in selectivity. The apparent skin layer thicknesses (calculated by dividing the Matrimid dense film intrinsic permeability over the fiber's permeance) range from 950 to 1500Å and display an increase with the air gap distance from 5 cm to 15 cm and stabilized after 15 cm.



Fig.4.7. O_2/N_2 permeance and selectivity results of the hollow fibers with different air gap distances (Dope composition: 26% Matrimid, 39.5% NMP, 19.7% THF, and 14.8% EtOH) Unlike the fibers fabricated with duo-solvent dope shown in Fig.4.7, fibers fabricated with single solvent dope with the composition of 26% Matrimid, 59.2% NMP and 14.8% EtOH exhibits different trends as shown in Fig.4.8. The permeances of O₂ and N₂ display a minimum value at the air gap of 10 cm and increase steadily from 10 cm onwards. The ideal selectivity of O_2/N_2 gas pair, on the contrary, shows the highest value at the air gap of 10 cm then decrease dramatically. Accordingly the apparent skin layer thickness also shows the highest value of 1280Å at the air gap of 10 cm, and then drops sharply to 990Å at the air gap of 20 cm.



Fig.4.8. O₂/N₂ permeance and selectivity results of the hollow fibers with different air gap distances (dope composition: 26% Matrimid, 59.2% NMP and 14.8% EtOH)

Different trends in Fig.4.7 and Fig.4.8 could be explained by the difference in moisture adsorption with and without the addition of volatile solvent in the dope solution. Without the addition of volatile solvent in the dope solution, the evaporation of solvent and the intake of water vapour could be in the same magnitude, the polymer concentration in the nascent fiber could only reach a certain level prior to the precipitation and probably not high enough to produce defect free skin (Path A in Fig.4.9), therefore the selectivity drops significantly as the air gap distance increases because the longer air gap allows more moisture intake therefore lowering the polymer concentration at the outer-most region of the membrane. On the other hand, volatile solvent (THF) presented in the dope solution amplifies the solvent evaporation during the air gap, which may suppress or offset the effects of water vapour intake, hence increases the polymer concentration to a higher level

compared to the other scenario (Path B in Fig.4.9), thus promotes the formation of the defect-free skin layer.



Fig.4.9. Demonstration of the effects of moisture intake during the air gap prior to the precipitation

4.4 CO₂/CH₄ mixed-gas permeation

Based on the systematic evaluation of the fabrication conditions and their effects on the formation of the defect-free asymmetric hollow fiber and the O_2 and N_2 single gas separation properties, optimised fiber spinning protocol is then determined. The Matrimid hollow fibers were fabricated under this optimized condition for subsequent CO_2/CH_4 mixed-gas permeation tests.

Dope composition was selected as 26% Matrimid, 39.5% NMP, 19.7% THF and 14.8% EtOH. NMP was added in the bore fluid (80% wt. NMP 20% wt. H_2O), dope and bore flow rates were set at 4.8 and 2.0 ml/min respectively. And the air gap distance was set at

20 cm. Matrimid hollow fibers fabricated under this optimised condition displays a defect-free thin skin layer and a sponge like support layer as shown in Fig.4.10.



Fig.4.10. SEM image of the Matrimid hollow fiber showing the morphology with a defect-free skin layer and sponge-like support layer

A model mixed-gas of 20% CO₂/80% CH₄ was used to simulate natural gas composition for the mixed-gas permeation tests. Two batches of Matrimid hollow fibers (Batch A and B) were fabricated following identical spinning protocol (Dope composition: 26% Matrimid, 39.5% NMP, 14.7% THF, and 14.8% EtOH, Bore composition: 20% H₂O, 80% NMP, Dope and bore fluid extrusion rates: 4.8 and 2.0ml/min, Air gap distance: 20cm) to examine the reproducibility. Fibers fabricated at this optimized condition displayed a high CO₂/CH₄ separation factor (separation factor as high as 67 with corresponding CO₂ permeance of 11GPU). Meanwhile O₂/N₂ pure gas permeation test was also conducted, and an O₂/N₂ selectivity of 6.9 was obtained which is slightly lower than Matrimid's intrinsic O₂/N₂ selectivity of 7.2. For evaluation of the membrane performance in the gas separation process, Robeson's upper bound (Robeson 1991) is one of the most popular benchmarks for flat sheet membranes to compare films casted with different polymer materials and/or different film formation conditions. However, permeances are more relevant for asymmetric hollow fibers. To make a similar comparison of our in-house fabricated hollow fiber membrane with published results, a range of gas separation performance data of different polymeric hollow fiber membranes from various literatures (Chung, Kafchinski et al. 1992; Pesek and Koros 1994; Wang, Li et al. 1996; Ismail, Shilton et al. 1997; Ismail, Dunkin et al. 1999; Sharpe, Ismail et al. 1999; Clausi and Koros 2000; Niwa and Kawakami 2000; Wang, Li et al. 2000; Li, Chung et al. 2002; Barsema, Kapantaidakis et al. 2003; Carruthers, Ramos et al. 2003; Chung, Ren et al. 2003; Jiang, Chung et al. 2004; Syrtsova, Kharitonov et al. 2004; Qin, Chung et al. 2005; Visser, Koops et al. 2005; Ismail and Yaacob 2006; Wallace, Staudt-Bickel et al. 2006; Wallace, Williams et al. 2006; Sridhar, Veerapur et al. 2007; Visser, Masetto et al. 2007; Kosuri and Koros 2008) were compiled in Fig.4.11. A rough upper bound is shown in O_2 permeance versus O_2/N_2 selectivity in a normal scale (instead of a log-log plot in Robertson plot for dense film).

It is noteworthy to point out that the permeance of the asymmetric hollow fiber is skin layer thickness dependent, therefore unlike the "Robeson upper bound", the upper bound of the hollow fibers constructed here does not represent the intrinsic separation properties of the polymer materials. Nevertheless it is still an effective measurement to compare the quality of the integrally skinned hollow fibers fabricated from different materials or different spinning conditions.



Fig.4.11. Literature data and present work for O₂/N₂ selectivity versus O₂ permeance for a range of polymeric membranes (temperature range: 20-35°C) (Chung, Kafchinski et al. 1992; Pesek and Koros 1994; Wang, Li et al. 1996; Ismail, Shilton et al. 1997; Ismail, Dunkin et al. 1999; Sharpe, Ismail et al. 1999; Clausi and Koros 2000; Niwa and Kawakami 2000; Wang, Li et al. 2000; Li, Chung et al. 2002; Barsema, Kapantaidakis et al. 2003; Carruthers, Ramos et al. 2003; Chung, Ren et al. 2003; Jiang, Chung et al. 2004; Syrtsova, Kharitonov et al. 2004; Qin, Chung et al. 2005; Visser, Koops et al. 2005; Ismail and Yaacob 2006; Wallace, Staudt-Bickel et al. 2006; Wallace, Williams et al. 2006; Sridhar, Veerapur et al. 2007; Visser, Masetto et al. 2007; Kosuri and Koros 2008)
The CO₂/CH₄ separation performances from various membrane materials and configurations were also compiled in this work and presented in Table.4-3. Results in Table.4-3 indicate that our in-house fabricated hollow fibers displays one of the highest separation factors (highest 67, average 47) compared to other Matrimid membranes and other polymer materials found in literature. The CO₂ permeance of this work (average

11.3) is also slightly higher than other Matrimid fibers although the values are lower than the hollow fibers with other polymer materials.

Interestingly, the separation factors for a mixed-gas CO_2/CH_4 feed also exceed those intrinsic values commonly reported for Matrimid films (approximately 30 to 40), our inhouse fabricated Matrimid fibers show CO_2/CH_4 separation factor up to 67 under certain conditions. It is worth noting that most of the homogenous dense films were cast from the dope solution with much lower polymer concentration (e.g. 2% (w/w) polymer solution was prepared by Tin et al. (Tin, Chung et al. 2003) and 10% by Sterescu et al. (Sterescu, Stamatialis et al. 2008) to cast Matrimid dense film) compared to 26% Matrimid solution we prepared for hollow fiber fabrication.

The effect of aging on the ultrathin films can also result in more rapid shift to higher selectivity and lower permeance as illustrated by recent work by Huang and Paul (Huang and Paul 2007). In our work, all the Matrimid samples were tested one month after fabrication to ensure all the fibers are comparable with similar physical aging history. The lower selectivity reported by Visser et al. (Visser, Masetto et al. 2007) on Matrimid hollow fibers (Table.4-3) could be attributed to the higher permeation temperature which usually leads to an significant increase of diffusivity coefficient and a reduction in selectivity (Koros and Fleming 1993).

roymer matrix cmgutatous c0, cH, selectivity operation condutons Matrinid Hollow fiber 11.0 0.16 67 (Highesi) 15sar, 20°C, 2080 Matrinid Hollow fiber 11.8 0.35 34 (Lowesi) ³ 15sar, 20°C, 2080 Matrinid Hollow fiber 8.5 0.23 37 10bar, 35°C, 2080 Matrinid Hollow fiber 8.5 0.25 59.6 Pure gas at 20har, 30°C Matrinid Dense film 8.9 Barrer 0.33 Barrer 31.6 10bar, 35°C, 2080 Matrinid/PES Dense film 8.9 Barrer 0.22 Barrer 40 Pure gas at 1.3 bar, 20°C Matrinid/PES Dual layer 9.5 0.24 40 C0,CH, Matrinid/PES Dual layer 9.5			Permeanc	e (GPU)			3- U
$ \begin{array}{c ccccc} Hollow fiber & Hollow fiber & Hollow fiber & 11.0 & 0.16 & 67 (Highest)^1 & 15har, 20°C, 2080 & 0.35 & 34 (Lowest)^2 & CO_2/CH_4 & 0.35 & 0.23 & 0.23 & 0.23 & 0.20 & 0.206H_4 & 0.000 & 0.200 & 0.200 & 0.000 &$	Polymer Material	Configurations	CO_2	CH_4	Selectivity	Operation conditions	Kei.
Matrinud FILM DIA CO2/CH4 Matrinud Hollow fiber 8.5 0.23 37 $CO2/CH4$ Matrinud Hollow fiber 14.7 0.25 59.6 Pure gas at 20bar, 30°C Matrinud Dense film 7.26Barrer 0.33Barrer 31.6 $10bar, 35°C, 4060$ Matrinud/PES Dual layer 9.5 0.24 40 Pure gas at 1.3bar, 20°C Matrinud/PES Dual layer 9.5 0.24 40 $CO2/CH4$ Matrinud/PES Holow fiber 9.5 0.24 40 $CO2/CH4$ Matrinud/PES	E	11.5.11.5 £34.5	11.0	0.16	67 (Highest) ¹	15bar, 20°C, 20/80	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	INTAUTIONIC	нопом прег	11.8	0.35	34 (Lowest) ²	CO_2/CH_4	FTESEIII WOFK
Matrinu FOLD (1, 1) FOLD (1, 2) FOLD (2, 2)	r:	11.011 fith	8.5	0.23	37	10bar, 35°C, 20/80 CO ₂ /CH ₄	Visser et al. (Visser, Masetto et al. 2007)
Table TrimidTable Trimid<	MAUIIIII		14.7	0.25	59.6	Pure gas at 20bar, 30°C	Sridhar et al. (Sridhar, Veerapur et al. 2007)
Matrinid Matrinid/PESDense film8.9Barrer $0.22Barrer40Pure gas at 1.3bar, 20°CMatrinid/PESDual layer9.50.244010bar, 22°C, 40/60Matrinid/PEShollow fiber110.264210bar, 35°C, 20/80Matrinid/P84 blendHollow fiber110.264210bar, 35°C, 40/60Matrinid/P84 blendHollow fiber591.46402bar, 35°C, 40/60Matrinid/P84 blendHollow fiber591.46402bar, 35°C, 40/60Matrinid/P84 blendHollow fiber591.75362bar, 35°C, 40/60Matrinid/P84 blendHollow fiber591.75362bar, 35°C, 40/60Matrinid/P84 blendHollow fiber591.75362bar, 35°C, 40/60Matrinid/P84 blendHollow fiber591.753620_{20}:Albar, CH4_4Matrinid/P84 blendHollow fiber37319.79020bar, 35°C, 50/50$			7.26Barrer	0.33Barrer	31.6	10bar, 35°C, 40/60 CO ₂ /CH ₄	Tin et al. (Tin, Chung et al. 2003)
Matrimid/PESDual layer hollow fiber9.5 0.24 40 $10bar, 22°C, 40/60$ Matrimid/P84 blendHollow fiber11 0.26 42 $10bar, 35°C, 20/80$ Matrimid/P84 blendHollow fiber59 1.46 40 $2bar, 35°C, 40/60$ 6FDA-2,6-DATHollow fiber59 1.46 40 $2bar, 35°C, 40/60$ 6FDA-2,6-DATHollow fiber63 1.75 36 $C0_{2}:3.4bar, CH_4: 13.8bar, 25°C6FDA-ODA/NDAHollow fiber631.7536C0_{2}:3.4bar, CH_4: 13.8bar, 25°C6FDA-Durene withHollow fiber3731919.7Pure gas at 2.8bar, 25°C$	Matrimid	Dense film	8.9Barrer	0.22Barrer	40	Pure gas at 1.3bar, 20°C	Shishatskiy et al. (Shishatskiy, Nistor et al. 2006)
Matrimid/P84 blendHollow fiber11 0.26 42 $10bar, 35^{\circ}C, 20/80$ $6FDA-2,6-DAT$ Hollow fiber 59 1.46 40 $2bar, 35^{\circ}C, 40/60$ $6FDA-2,6-DAT$ Hollow fiber 63 1.75 36 $20ar, 35^{\circ}C, 40/60$ $6FDA-ODA/NDA$ Hollow fiber 63 1.75 36 $CO_{2}:3.4bar, CH_4: 13.8bar, 25^{\circ}C6FDA-DAA-DABA 2:1Dense film140Barrer4.7Barrer3020bar, 35^{\circ}C, 50/506FDA-Durene withHollow fiber37319.7Pure gas at 2.8bar, 25^{\circ}C$	Matrimid/PES	Dual layer hollow fiber	9.5	0.24	40	10bar, 22°C, 40/60 CO ₂ /CH ₄	Jiang et al.(Jiang, Chung et al. 2004)
6FDA-2,6-DATHollow fiber59 1.46 40 $2bar, 35^{\circ}C, 40/60$ 6FDA-ODA/NDAHollow fiber63 1.75 36 $CO_{2}:3.4bar, CH_4: 13.8bar, 25^{\circ}C$ 6FDA-ODA/NDAHollow fiber63 1.75 36 $CO_{2}:3.4bar, CH_4: 13.8bar, 25^{\circ}C$ 6FDA-DAM-DABA 2:1Dense film140Barrer $4.7Barrer$ 30 $20bar, 35^{\circ}C, 50/50$ 6FDA-Durene withHollow fiber 373 19 19.7 Pure gas at 2.8bar, 25^{\circ}C	Matrimid/P84 blend	Hollow fiber	11	0.26	42	10bar, 35°C, 20/80 CO ₂ /CH ₄	Visser et al. (Visser, Masetto et al. 2007)
6FDA-ODA/NDA Hollow fiber 63 1.75 36 CO ₂ :3.4bar, CH ₄ : 13.8bar, 25°C 6FDA-DAM-DABA 2:1 Dense film 140Barrer 4.7Barrer 30 20bar, 35°C, 50/50 6FDA-Durene with Hollow fiber 373 19.7 Pure gas at 2.8bar, 25°C	6FDA-2,6-DAT	Hollow fiber	59	1.46	40	2bar, 35°C, 40/60 CO ₂ /CH ₄	Cao et al. (Cao, Wang et al. 2002)
6FDA-DAM-DABA 2:1 Dense film 140Barrer 4.7Barrer 30 20bar, 35°C, 50/50 6FDA-Durene with Hollow fiber 373 19 Pure gas at 2.8bar, 25°C	6FDA-ODA/NDA	Hollow fiber	63	1.75	36	CO ₂ :3.4bar, CH ₄ : 13.8bar, 25°C	Ren et al. (Ren, Wang et al. 2003)
6FDA-Durene with Hollow fiber 373 19 19.7 Pure gas at 2.8bar, 25°C silicone contine	6FDA-DAM-DABA 2:1	Dense film	140Barrer	4.7Barrer	30	20bar, 35°C, 50/50 CO ₂ /CH ₄	Wind et al. (Wind, Paul et al. 2004)
Summon Allocation	6FDA-Durene with silicone coating	Hollow fiber	373	19	19.7	Pure gas at 2.8bar, 25°C	Chung et al. (Chung, Lin et al. 2000)

Table.4-3. Performance comparison with literature values

Note:

Obtained from Batch A,
 Obtained from Batch B.

Uncertainty analysis

Two modules were made from each batch of the hollow fibers, three permeation measurements were taken on each module and the standard errors of CO_2 and CH_4 permeance were within the range of 20%. The standard errors of separation factors were then calculated and within the range of 21% (Harris 2007). Two modules from same batch showed differences in separation factors less than 17%, while the separation factors differences between Batch A and B (fabricated under the same conditions) are less than 28%.

The uncertainty of permeation properties presented above might originate from several sources:

- Membrane fabrication:
 - The air gap environment was not controlled in this study; the fluctuation of humidity can alter the solvent and non-solvent exchange rate during the air gap. The application of the volatile solvent in the dope solution could mask the negative effect of the humidity change at certain extent as described in Section 4.3.4.
 - The change of the solvent concentration in the coagulation medium could also affect membranes' properties. The solvent out-flow into the coagulation bath increases the concentration of the solvent in the coagulation medium over fabrication time. Using a larger size coagulation bath minimizes this effect; the addition of the solvent in the coagulation medium is therefore negligible.
 - Other experimental errors, e.g. the friction between the nascent fibers and guide wheels could alter the nascent fiber's morphology.
- Module fabrication:

- The size of housing material limited the number of the hollow fibers mounted in one module. In this study, no more than five strands of hollow fibers can be potted in the stainless steel tube depending on the OD of the hollow fiber. By increasing the number of the hollow fibers in one module, this type of error could be minimized.
- The uncertainty of effective length of hollow fibers in the module due to the glue technique results in the error in the membrane area calculation.
- Permeation:
 - The concentration polarization effect on the shell side could introduce systematic errors. In this study, the stage cut was lowered to less than 1% to minimize the effect of the concentration polarization.
 - Instrument errors introduced by the pressure transducer, bubble flow-meter, and GC.

4.5 Conclusions

Optimizing the solvent migration on both the shell and lumen sides of the hollow fibers allowed consistent formation of the defect free ultrathin skin layer on sponge like support. Polymer dope composition, which include polymer, solvent, possible volatile solvent and non-solvent additive affects the phase separation process in both the air gap and coagulation medium and can be manipulated to produce fibers with tuneable range of separation properties. Addition of the volatile solvent in the dope formula improved the O_2/N_2 selectivity from 3.6 with single solvent formula to 6.7 while O_2 permeance was reduced from 14.9 to 9 GPU. This was explained as due to the formation of the tighter membrane skin layer caused by a more rapid volatile solvent evaporation in the air gap.

Addition of the solvent in the bore fluid avoided the formation of finger like macrovoids in the fiber's cross section and increasing the solvent content leads to an improved O_2/N_2 selectivity and an increase of selective skin layer thickness. Air gap distance between the spinneret and the coagulation bath is another very important parameter that implicates the fiber skin formation. For a dope formula that includes volatile solvent, the evaporation of the volatile solvent leads to an increased selectivity and reduced permeance with increased air gap distance. In the absence of the volatile solvent, selectivity was optimal at an intermediate air gap distance. The observation was explained by the adsorption of water vapour on the fiber surface in the air gap, which led to the formation of porous skin layer and increased permeance and reduced selectivity. The ratio of the dope fluid and bore fluid flow rates affects the fiber diameter and wall thickness, higher fiber wall thickness was observed at higher dope and bore flow rate ratio.

With optimized spinning parameters, fibers exhibited O_2/N_2 selectivity near the intrinsic value of the Matrimid dense film, and significantly higher than intrinsic CO_2/CH_4 separation factors. This performance indicates that the conformation of the polymers in the surface layers in hollow fibers may quite different from the bulk film; yielding high separation factors even for mixed CO_2/CH_4 feed gases at higher pressures.

5 THERMODYNAMIC ANALYSIS OF PHASE INVERSION PROCESS

5.1 Introduction

As described in Chapter 2, the interaction between the dope solution, bore fluid and coagulation medium, especially the solvent and non-solvent mass transfer during the phase inversion process, greatly affect the final membrane morphology. Chapter 4 presented an experimental evaluation of a wide range of the fabrication variables aiming for spinning the defect-free integrally skinned hollow fiber membranes. The conditions that have been examined included the dope and bore fluid compositions and flow-rates, as well as the air gap distance. Among all of these variables, the dope and bore fluid compositions are the most crucial conditions and the optimization of these two variables requires large amount of time-consuming experiments.

Thus it is important to study the thermodynamic characteristics of the dope solution, bore fluid and coagulation medium in terms of their influences on the mass transfer between the solvent and non-solvent, subsequently on the membrane formation process and membrane separation performance.

Chapter 4 provides a comprehensive investigation to connect the fabrication process with the membrane morphology/separation properties based on the experimental observation. In this chapter, analysis of the solubility parameters is carried out to evaluate whether the theoretical polymer-solvent interactions are consistent with the morphologies observed. In this aspect, Jiang and Chung et al. (Jiang, Chung et al. 2008) applied the Hansen's solubility parameters on the Matrimid for pervaporation dehydration of isopropanol. A simple comparison of the solubility parameters between the polymer and the penetrants was carried out to indicate the plasticization effects of the isopropanol on Matrimid. Vandezande et al. (Vandezande, Li et al. 2009) adopted the same concept to analyze the solubility difference between the solvent, non-solvent and polymer and concluded that kinetics plays a major role in the membrane formation because the morphology of their in-house fabricated asymmetric film did not agree with the thermodynamic analysis. In this study, we extend their approach to the mixture of the solvent system, so the binodal curve of different solvent compositions can be qualitatively illustrated on the ternary phase diagram by comparing the solubility difference between solvents and coagulation medium, therefore membrane's morphology and separation properties can be hypothetically predicted in terms of the position of the binodal curve in the ternary phase diagram.

5.2 Hansen's solubility parameter

5.2.1 Fundamentals of the solubility parameters

When mixing different components together, whether the process takes place spontaneously or not is dependent on the following equation:

$$\Delta \boldsymbol{G}_{\boldsymbol{m}} = \Delta \boldsymbol{H}_{\boldsymbol{m}} - \boldsymbol{T} \cdot \Delta \boldsymbol{S}_{\boldsymbol{m}} \tag{Eqn.5.1}$$

where ΔH_m and ΔS_m are the enthalpy and entropy of mixing respectively, *T* is the temperature, and ΔG_m is the free enthalpy. If the free enthalpy is negative then the mixing will occur spontaneously. For the polymeric system, the entropy of mixing is small and always positive, thus the mixing process is largely dependent on the enthalpy of mixing (Mulder 1996). The enthalpy of mixing can be derived by the following expression developed by Hildebrand (Hildebrand and Scott 1949).

$$\Delta H_m = V_m \left[\left(\frac{\Delta E_1}{V_1} \right)^{0.5} - \left(\frac{\Delta E_2}{V_2} \right)^{0.5} \right]^2 V_1 V_2$$
(Eqn.5.2)

where V_m , V_1 and V_2 represent the molar volume fraction of the solution, component 1 and 2 respectively, ΔE is the energy of vaporization. The term $\Delta E/V$ is called the cohesive energy density (CED), and the solubility parameter δ is determined by the following equation:

$$\boldsymbol{\delta} = (\boldsymbol{C}\boldsymbol{E}\boldsymbol{D})^{0.5} \tag{Eqn.5.3}$$

The cohesive energy density is a measurement of the energy required to remove a molecular from the neighbouring molecular. Inserting Eqn.5.3 into Eqn.5.2, Eqn.5.4 is derived:

$$\Delta H_m = V_m [\delta_1^{0.5} - \delta_2^{0.5}]^2 V_1 V_2$$
 (Eqn.5.4)

Eqn.5.4 indicates that the enthalpy of mixing is always positive and its value is approaching to zero when δ_1 and δ_2 are close. Since the entropy of mixing is small and also always positive, according to Eqn.5.1, the mixing process can only proceed if δ_1 and δ_2 are close (in other words, $\Delta H_m < T\Delta S_m$).

The energy of vaporization (ΔE) can be divided into three components, i.e.

$$\Delta \boldsymbol{E} = \Delta \boldsymbol{E}_{\boldsymbol{d}} + \Delta \boldsymbol{E}_{\boldsymbol{p}} + \Delta \boldsymbol{E}_{\boldsymbol{h}} \tag{Eqn.5.5}$$

where ΔE_d is the London dispersion force, ΔE_p is the dipolar force, and ΔE_h is the hydrogen bonding force (Matsuura 1993). In terms of the solubility parameter, it can also be divided into three contributions (Matsuura 1993):

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{Eqn.5.6}$$

where δ_d is the solubility parameter due to the dispersion forces, δ_p is the solubility parameter due to the polar forces, and δ_h is the solubility parameter due to the hydrogen bonding.



Fig.5.1. 3-Dimensional interpretation of Hansen's solubility parameter

These three solubility parameter components are, in fact, three-dimensional vectors as shown in Fig.5.1. Therefore the Hansen's solubility parameter difference between two components (e.g. polymer and solvent) can be considered as the distance between the endpoint of two vectors, as Δ shown in Fig.5.1, and it can be calculated via the following equation:

$$\Delta = \left[\left(\delta_{d,A} - \delta_{d,B} \right)^2 + \left(\delta_{p,A} - \delta_{p,B} \right)^2 + \left(\delta_{h,A} - \delta_{h,B} \right)^2 \right]^{0.5}$$
(Eqn.5.7)

The affinity increases between components A and B with decreased \varDelta value until it approaches zero. In other words, a lower value of the solubility parameter difference would indicate a closer cohesive energy and a higher mutual affinity between two components. For the solvent/non-solvent system, it translates to a better miscibility between two liquids.

5.2.2 Group contribution method

The Hansen's solubility parameters of all organic compounds with known chemical structure can be calculated via group contribution method (Matsuura 1993). δ , δ_d , δ_p , and δ_h can be obtained by the following equations:

$$\boldsymbol{\delta} = \sqrt{\frac{\sum \boldsymbol{E_{coh}}}{\boldsymbol{V}}} \tag{Eqn.5.8}$$

$$\boldsymbol{\delta_d} = \frac{\sum F_{di}}{V} \tag{Eqn.5.9}$$

$$\boldsymbol{\delta_p} = \frac{\sqrt{\sum F_{pi}^2}}{V} \tag{Eqn.5.10}$$

$$\boldsymbol{\delta_h} = \sqrt{\frac{\sum E_{hi}}{V}} \tag{Eqn.5.11}$$

The value of E_{coh} , F_{di} , F_{pi} , and V of all organic compound functional groups can be found from Matsuura's "Synthetic Membranes and Membrane Separation Processes" (Matsuura 1993). The solubility parameter values of the major functional groups in Matrimid[®] 5218 (chemical structure seen in Fig.5.2) and the common solvent and non-solvent are listed in Table.5-1.



Fig.5.2. Repeat unit of Matrimid[®] 5218

Functional group	$\mathrm{E}_{\mathrm{coh}}$	V_{i}	F_{di}	F_{pi}	E _{hi}	V_{gi}
	(cal/mol)	(cm ³ /mol)	$(cal^{0.5}cm^{1.5}/mol)$	$(cal^{0.5}cm^{1.5}/mol)$	(cal/mol)	(cm ³ /mol)
-CH3	1,125	33.5	205	0	0	23.9
-CH2-	1,180	16.1	132	0	0	15.9
>C<	350	-19.2	-34	0	0	4.6
-CON<	7,050	-7.7	220	479	7,762	24.9
-CO-	4,150	10.8	142	376	478	13.4
Phenylene (o, m, p)	7,630	52.4	621	54	0	65.5
НО-	7,120	10.0	103	244	4,777	9.7
-N-	1,000	0.6-	10	391	1,194	6.7
-0-	800	3.8	49	196	717	10.0

Table.5-1. Solubility parameter component group contributions

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Based on Eqn.5.8~5.11 and the thermodynamic data from Table.5-1, Hansen's solubility parameters for the Matrimid, some common solvents and non-solvents were calculated and listed in Table.5-2.

	δ_d	$\delta_{\rm p}$	$\delta_{\rm h}$	δ_{sp}
	(MPa ^{1/2})	(MPa ^{1/2})	(MPa ^{1/2})	(MPa ^{1/2})
NMP	18	12.3	7.2	23.0
DMAc	16.8	11.5	10.2	22.8
THF	16.8	5.7	8	19.5
H ₂ O	15.6	16	42.3	47.8
MeOH	15.1	12.3	22.3	29.6
EtOH	15.8	8.8	19.4	26.5
Matrimid	18.7	9.5	6.7	22.0

 Table.5-2. Hansen's solubility parameters of Matrimid, some common solvents and non-solvents

Mutual affinity between polymers, solvents and no-solvents can be measured by the difference of the solubility parameters $\Delta \delta_{S-NS}$, $\Delta \delta_{S-POLYMER}$, and $\Delta \delta_{NS-POLYMER}$ calculated via Eqn.5.7.

The above Hansen's solubility parameter calculations limited to the comparison between the pure components (e.g. polymer-solvent, or solvent-non-solvent). The following equation (Van Krevelen and Hoftyzer 1990) has been applied to calculate the Hansen's solubility parameters of the mixture with several components. Such approach enables the comparison between dope solutions as one single system and the bore fluid mixtures or coagulation mixtures.

$$\boldsymbol{\delta} = \frac{\sum_{i} X_{i} V_{i} \delta_{i}}{\sum_{i} X_{i} V_{i}} \tag{Eqn.5.12}$$

where X_i , V_i , and δ_i are mole fraction, molar volume and solubility parameter of a specific component in the mixture respectively.

5.3 Thermodynamic analysis and the experimental observations

5.3.1 Influence of the solvent selection

Hansen's solubility parameter differences between different solvents (DMAc, NMP and THF) and water (as coagulant) were presented in Table.5-3. THF displays the highest solubility parameter difference with water compared to NMP and DMAc. The higher value of $\Delta\delta$ indicates a lower affinity between different solvents and water, thus THF should have the lowest affinity with water. In other words, THF is less miscible with water compared to the other two solvents. Therefore, on the ternary phase diagram, polymer/THF/H₂O binodal curve should be located closer to the water vertex since THF is the least miscible solvent with water. On the other hand, polymer/DMAc/H₂O binodal curve should be the closest one to the polymer/solvent axis (as shown in Fig.5.3). It should be noted that the position of the binodal curves in the ternary phase diagrams are for references only and they do not represent the real binodal compositions.

	$\Delta \delta_{\text{ns-NMP}}$	$\Delta\delta_{ns\text{-}DMAc}$	$\Delta \delta_{ns\text{-}THF}$
	(MPa ^{1/2})	(MPa ^{1/2})	(MPa ^{1/2})
H ₂ O	35.4	32.4	35.8

Table.5-3. Hansen's solubility parameter difference between solvents and non-solvents

For the dope solutions (polymer/solvents/ H_2O) with different solvents but fixed concentration, THF binodal curve is the furthest to the initial dope composition, therefore polymer solution with THF as solvent is more likely to experience the delayed demixing than NMP and DMAc, high polymer concentration can be reached prior to the liquid-
liquid demixing, thus produce "Type I" membrane with dense and defect-free skin layer as described in Section 2.7.3.



Fig.5.3. Binodal curves in ternary phase diagram with different solvents (DMAc, NMP and THF), Matrimid and H₂O

The cloud point experiment reported in the study of the phase separation behaviour in PES/solvent/H2O and PSf/solvent/H2O systems by Lau et al. (Lau 1991) was in agreement with the ternary phase diagram (Fig.5.3) derived from the thermodynamic analysis.

The above thermodynamic analysis indicates that THF is as good as NMP and the addition of THF into NMP will benefit the formation of the defect-free skin layer from the thermodynamic point of view due to its low boiling point.

5.3.2 Influence of the non-solvent additives (NSA)

The role of the non-solvent additives in the dope solution has been well explained in Chapter 2 and the experimental verification was provided in Chapter 4. The addition of the non-solvent could drive the initial dope composition much closer to the binodal curve, thus induce the instantaneous demixing and significantly reduce the skin layer thickness (Fritzschz, Murphy et al. 1989; Chung, Kafchinski et al. 1992; Wang, Li et al. 1996; Niwa and Kawakami 2000; Kosuri and Koros 2008).

In the thermodynamic study, the solubility parameter differences between water and pure NMP or NMP/ethanol mixtures were presented in Table.5-4. The results indicate that the dope solution without NSA possesses a higher value of $\Delta\delta$ and a lower affinity with the coagulation medium (water), therefore the binodal curve should be located closer to the water vertex than binodal curve with EtOH as the non-solvent additive (Fig.5.4).

Table.5-4. Hansen's solubility parameter differences with and without NSA and the gas permeation properties from the corresponding hollow fibers

		Permeance (GPU)		
	$\Delta \delta_{\text{S-H2O}}$	O ₂	N ₂	$lpha_{O2/N2}$
NMP	35.4	8.3	1.6	5.2
80% NMP, 20% EtOH	32.6	11.5	2.2	5.3

Fig.5.4 illustrates that the initial dope composition is much closer to the binodal curve when adding the non-solvent into the dope solution, which is in great agreement with the theory proposed by various researchers (Pesek and Koros 1994; Wang, Li et al. 2000). Matrimid hollow fibers fabricated under such condition should possess thinner skin layer and possible defects. Furthermore, the O_2/N_2 single gas permeation results (Table.5-4) justify the thermodynamic analysis by showing an almost 40% increase in permeance while adding EtOH in the dope solution, meanwhile the ideal selectivity almost remained the same.



Fig.5.4. Binodal curves of two different dope systems (with and without non-solvent additives)

5.3.3 Influence of the coagulation medium

The selection of the coagulation medium has been investigated extensively in the past, it has been reported that for those common solvents such as NMP, DMF, or DMAc, high alcohols are the ideal non-solvent candidates to induce the delayed demixing and prepare membrane with the defect-free skin layer (Kesting and Fritzschz 1993; Koros and Fleming 1993).

In this study, the thermodynamic interaction between three different coagulation media $(H_2O, MeOH, and EtOH)$ and NMP as the solvent were analysed, and the Hansen's solubility parameter differences between solvent and coagulation media were presented in Table.5-5. The results indicate that the higher alcohol (ethanol) possesses the lowest solubility difference, thus the highest affinity with NMP. On the other hand, water displays the highest solubility difference with NMP.

 Table.5-5. Hansen's solubility parameter difference between NMP and different coagulation media

	H ₂ O	МеОН	EtOH
$\Delta\delta_{\rm ns-NMP}({\rm MPa}^{1/2})$	35.4	15.4	12.9

These results were mapped on the ternary phase diagram (as shown in Fig.5.5), which illustrates that alcohols are better coagulation media than water in regards to the fabrication of the defect-free integrally skinned membrane. The cloud point experiments (Fig.5.6) were carried out to construct the ternary phase diagrams of (A) Matrimid/NMP/H₂O, and (B) Matrimid/NMP/EtOH systems, the results were agreed with the trend observed from the thermodynamic analysis.



Fig.5.5. Binodal curves of three different coagulation media (H₂O, MeOH and EtOH) as non-solvents



(A)



Fig.5.6. Ternary phase diagrams of (A) Matrimid/NMP/H₂O, and (B) Matrimid/NMP/EtOH derived from cloud point experiment

Even though the high alcohols appears to be the ideal coagulation media, water was still selected as the coagulation medium in this study due to its less hazardous nature and much less cost.

5.3.4 Influence of the dual-solvent in the dope solution

Addition of the extra solvent with different volatility can significantly modify the membrane morphology and separation performance (Pesek and Koros 1993; Pesek and Koros 1994; Clausi and Koros 2000). The discussion in Chapter 4 revealed that the acceleration of the volatile solvent evaporation in the air gap could mask the moisture adsorption. Therefore the morphology of the hollow fiber membrane could be much less sensitive to the surrounding environment and the fabrication process therefore can be carried out in a much wider operation window.

In this study, three dope solutions were prepared with different volatile solvent contents (Dope A: no volatile THF, B: 9% THF and C: 27% THF). Hansen's solubility parameters differences between these dope solutions and the coagulation medium (water) was presented in Table.5-6.

	٨٥	Permeance (GPU)		0
	$\Delta \sigma_{\text{S-H2O}}$	O ₂	N ₂	u _{O2/N2}
80% NMP, 20% EtOH	32.5	11.5	2.2	5.3
71% NMP, 9% THF, 20% EtOH	32.7	10.7	1.7	6.4
53% NMP, 27% THF, 20% EtOH	32.9	9.2	1.4	6.7

Table.5-6. Hansen's solubility parameter differences between complex solvents system and non-solvents and gas permeation properties from the corresponding hollow fibers

The thermodynamic analysis results indicate that the dope solution with the highest volatile solvent content possessing the highest Hansen's solubility parameter differences

with the coagulation medium although only slight increase was observed, thus this dope solution should be much less miscible with water compared to other dope solutions, and should be the closest to the water vertex (as shown in Fig.5.7). These binodal curves indicate that, by adding the volatile solvent, the delayed demixing can be expected, and a defect-free skin layer can be produced as a result. However it should also be recognised that due to the insignificant change in solubility parameter differences, the improvement observed in separation performance is more likely due to the use of volatile solvent rather than the solubility parameter differences seen in Table.5-6 although it also contribute to the final results.

The O_2/N_2 single gas permeation tests were carried out on the hollow fibers fabricated from these dope solution, and the separation performance (Table.5-6) shows that the dope solution with more volatile solvent content produce membranes with high selectivity (near the Matrimid dense film intrinsic value). This experimental observation is consistent with the thermodynamic analysis.



Fig.5.7. Binodal curves of three different dope compositions with various portion of volatile solvent content

5.4 Conclusions

Thermodynamic analysis through the solubility parameters between polymeric dope solutions bore fluids and coagulants provided very useful tool to indicate the likely rate of demixing which could dictate the formation of the hollow fiber skin layer and supporting sub-structure. The Hansen's solubility parameter analysis provided in this chapter confirmed our experimental observation presented in Chapter 4 in terms of the membrane morphology and separation properties.

For a particular type of the polymer material, the selection of the solvent and non-solvent additives in the dope system, or the selection of the bore fluid and coagulation medium can be achieved through a simple calculation of the Hansen's solubility parameter differences, which significantly simplify the time-consuming fabrication variables optimization process.

The discussion in this chapter proved that the thermodynamic analysis through the solubility parameters could be used in the future for predicting possible relative outcomes of the membrane performance through manipulation of the dope composition, bore fluid content and the coagulation medium. The thermodynamic analysis can also be used for tailoring the polymer material structure aiming for obtaining preferred solubility characteristics, thus desired membrane separation properties.

6 INVESTIGATION OF THE PLASTICIZATION PHENOMENON

6.1 Introduction

Polyimide hollow fiber membrane offers superior gas separation performance as indicated in the previous chapters; however its long-term performance could be severely jeopardized by the aggressive gas feed containing components such as CO_2 . The introduction of CO₂ into the polymeric membrane structure leads to a unique phenomenon: plasticization, which causes the dilation of the polymer chains, thus reduces diffusion selectivity, subsequently compromises membrane's integrity and sustainable separation performance. In addition to the researches on the effects of the plasticization on membrane's gas separation performance, very little work has related the plasticization behaviour with the membrane formation process and the membrane morphology although these crucial information could provide fundamental understanding of the plasticization phenomenon, which could be used to develop the suitable suppression strategies. In this chapter, a nodule structure model based on the nucleation and growth mechanism and dual-mode model (both described in Chapter 2) was developed to visualize the Henry's and Langmuir sites in the membrane structure. This model is subsequently applied to connect the plasticization behaviour with the membrane formation mechanisms and membrane morphology. Single gas sorption isotherms of the Matrimid hollow fibers were decoupled into the Henry's and Langmuir sites, the results are presented in this chapter to illustrate the connection between the dual-mode sorption model and the plasticization phenomenon. This chapter also discusses the thickness and time dependence of plasticization in terms of their relations with the nodule structure model. CO₂/CH₄ mixedgas permeation behaviour was modelled to examine the competitive sorption effects, the

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comparison between modelling and experimental results are presented in this chapter as well.

6.2 Nodule structure model

6.2.1 Nodule structure and dual-mode model

It is a common observation that, unlike the linear sorption isotherm observed for rubbery polymer materials, the CO_2 sorption isotherm obtained with Matrimid, a glassy polymer material, displayed a curved sorption isotherm as shown in Fig.6.1.



Fig.6.1. CO₂ sorption isotherm derived from Matrimid hollow fibers with CO₂/CH₄ selectivity of 66 at 25°C, and corresponding Henry's and Langmuir sites

This distinct sorption behaviour of the glassy polymer was interpreted using the dualmode model (Vieth and Sladek 1965; Vieth, Tam et al. 1966; Vieth, Howell et al. 1976). In the past this model has proved useful; simulation data from this model closely followed the observed experimental trends (Barrer 1984; Sanders, Koros et al. 1984). However the postulated sorption modes were idealized and there was no physical evidence of the dual sorption sites

The first study that observed the physical structure of dual sorption sites was that of Kesting et al. (Kesting 1990) who proposed a four tier structure theory (macromolecules, nodules, nodular aggregates, and super-nodular aggregates) for integrally skinned membranes. A *nodule* is defined as a three-dimensional sphere structure with a diameter around 200Å containing both crystalline and amorphous portions of polymer chains which is the primary construction unit of the membrane structure (Wienk, Van den Boomgaard et al. 1994).

Based on this nodule structure model, Kesting et al. (Kesting and Fritzschz 1993) suggested that the smaller volume between chain segments within the nodule may correspond to the Henry's site in the dual-mode model, whereas the larger free volumes between the nodules may constitute the Langmuir sites. According to the dual-mode sorption and diffusion model, Henry's sites (free volume between polymer chain segments within a nodule) provide the channels for gas molecules to diffuse through whereas the gas molecules sorbed into the Langmuir sites (interstices between nodules) are much less mobile than in Henry's sites, therefore they are completely immobilized and much less likely to contribute to the diffusion at all.

Based on Kesting's nodule structure model, we proposed that the growth of the nodules during the membrane formation process follows a nucleation and growth mechanism (Fig.6.2). The nodules (*spherulite*) extend from the *crystal nucleus*; both the crystalline portion (*lamellar fibrils*) and the amorphous portion of the polymer (Henry's sites) co-exist in the nodule structure, and their ratio is determined by the polymer material itself.



Fig.6.2. Schematic representation of the nodule structure model

Densely packed polymer chains within the nodules provide a large contact surface for gas molecule adsorption, the adhesion behaviour between gas penetrants and polymer chains in this region is similar to gas dissolution in a liquid, therefore Henry's Law can be adopted to describe the linear relation between gas penetrant pressure and gas concentration in this region as shown in the first term of Eqn.6.1. It is also reasonable to postulate that higher polymer chain packing density in Henry's sites leads to more surface area being available for gas sorption and therefore a higher value of Henry's solubility constant (k_D).

$$\boldsymbol{C} = \boldsymbol{C}_{\boldsymbol{D}(\boldsymbol{HENRY})} + \boldsymbol{C}_{\boldsymbol{H}(\boldsymbol{LANGMUIR})} = \boldsymbol{k}_{\boldsymbol{D}} \cdot \boldsymbol{p} + \frac{\boldsymbol{C}_{\boldsymbol{H}} \cdot \boldsymbol{b} \cdot \boldsymbol{p}}{1 + \boldsymbol{b} \cdot \boldsymbol{p}}$$
(Eqn.6.1)

Interstices between nodules are associated with the un-relaxed "frozen" excessive free volume present in glassy polymers. These interstices are not free of matter, they contain a very low density of polymer chain segments (mainly amorphous segments extending out from the nodules). Gas penetrants usually adsorb onto the surface of these voids. The adsorption behaviour in this region is described by the Langmuir isotherm (Perry and Green 2008) as shown in the second term of Eqn.6.1. In most cases, Langmuir sites adsorb a much smaller quantity of gas penetrant than Henry's sites considering that the differences in surface area available in these two sites differ by several orders of magnitude. We can assume that an increase in the size and quantity of the microvoids in the Langmuir sites could boost the contact surface area and increase the amount of the gas adsorbed. In this case, according to the second term in Eqn.6.1, a higher value of the hole saturation constant (C_H) should be expected as a result.



Fig.6.3. Nodules structure observed in both skin and supporting layer

Using high magnification SEM of our in-house fabricated hollow fibers (Fig.6.3), a very high density of nodule structures was clearly observed in the skin layer. Interestingly, the nodule structures were also observed in the supporting sub-structure, and nodules were densely packed to constitute the solid cell wall in the honeycomb-like sub-structure. All the nodules were similar in size with an average diameter of 20 nm.

6.2.2 Nodule structure model and plasticization

To apply the nodule structure model to the plasticization process, it is assumed that CO_2 induced polymer chain dilation takes place immediately after CO_2 gas molecules are introduced into the membrane structure. The swelling of the polymer chains in Henry's sites would be more pronounced than the dilation in Langmuir sites due to the difference in polymer chain density between the two regions. Therefore the onset of plasticization is determined by the ratio between Henry's and Langmuir sites presented in the membrane structure. A glassy polymer with more Langmuir sites can adsorb more CO_2 gas molecules yet show little sign of plasticization while a glassy polymer with a higher proportion of Henry's sites might display instantaneous plasticization due to its high polymer chain packing density and large contact surface available for gas adsorption.

6.3 Experimental justification of the nodule structure model

The gas sorption and permeation tests were carried out under different conditions to support the nodule structure model that we propose in this study. The well-documented effects of factors such as thickness and time on plasticization were interpreted using the nodule structure model. The predictions based on the nodule structure model are compared with the experimental observations in the following sections.

6.3.1 Gas sorption test for glassy polymer

In this study, three batches of hollow fibers with different CO_2/CH_4 selectivity were selected (fabricated under different spinning conditions as reported in (Dong, Li et al. 2010)) to carry out both the sorption and permeation tests in order to compare the influence of membrane microscopic structure predicted using nodule structure model with the gas sorption test results, moreover, the degree of plasticization from membranes with different selectivities were evaluated. All of the sorption parameters (k_D , C_H ', and b) were determined based on the calculation procedure shown in Fig.6.4, the results were presented in Table 6-1. To obtain the sorption parameters, the Langmuir portion of Eqn.6.1 was re-arranged as follows:

$$\frac{p}{c_H} = \frac{1}{c'_H b} + \frac{p}{c'_H}$$
 (Eqn.6.2)

If p/C_H is plotted against p, a linear relationship should be expected according to Eqn.6.2. C_H ' and b were then determined by measuring the slope and intercept of the curve. k_D on the other hand, was determined by measuring the slope of the gas sorption isotherm at the high pressure range.

The sorption parameters calculated in this study were comparable with the previous reports (Punsalan 2001; Madden 2005). Using the linear regression in estimation of the dual-mode sorption parameters, the coefficients of determination (R^2) were found to be between 0.799 and 0.992. This indicated the close fit between the regression model and the experimental results.



(A)



(B)

Fig.6.4. Schematic demonstration of (A) dual-mode sorption parameters calculated with the assistance of CO_2 sorption isotherm and (B) dual mode sites decoupling technique (CO2 sorption isotherm constructed from membrane with $\alpha_{CO2/CH4}$ of 66).

Decoupling the Henry's site sorption from Langmuir site sorption was achieved as shown in Fig.6.1 and Fig.6.4B. The results presented in Fig.6.5B indicate that Matrimid hollow fibers with higher selectivity (66) displayed a larger increase in CO_2 concentration in Henry's sites with pressure than those with lower selectivities. Membranes with higher selectivity usually possess higher polymer chain packing density and larger contact surface for gas molecules adsorption, therefore can adsorb more gas molecules than membranes with lower selectivity.

	Gas type	k _D	C _H '	b	R ²
α _{CO2/CH4} : 66	CO_2	0.110±0.005	13.904±0.385	0.046±0.013	0.971
	CH_4	0.028±0.003	3.843±0.414	0.023±0.029	0.962
	N_2	0.013±0.001	0.658±0.233	0.031±0.008	0.901
α _{CO2/CH4} : 53	CO ₂	0.075 ± 0.008	13.774±0.253	0.184 ± 0.014	0.992
	CH_4	0.027±0.001	4.456±0.186	0.039±0.003	0.976
	N_2	0.012±0.001	0.493±0.103	0.105 ± 0.047	0.799
α _{CO2/CH4} : 36	CO_2	0.062 ± 0.007	14.144±0.157	0.306±0.033	0.980
	CH_4	0.030±0.002	3.422±0.299	0.091±0.016	0.966
	N_2	0.021±0.002	1.960±0.135	0.105±0.096	0.948

Table 6-1. Dual-mode sorption parameters derived from sorption tests

Fig.6.5C indicated that all the hollow fibers displayed a sharp increase in CO_2 sorption at the low pressure range and stabilized afterwards. Furthermore Matrimid hollow fibers with the lowest CO_2/CH_4 selectivity displayed the highest increase in CO_2 concentration with pressure.



(A)



(B)





Fig.6.5. CO₂ modelled sorption results based on dual-mode sorption model (the dualmode sorption parameters obtained from Matrimid hollow fibers with different CO₂/CH₄ separation factors). (A) CO₂ sorption isotherms, (B) Henry's sites sorption component, and (C) Langmuir sites sorption component

This linking of the dual-mode model to the nodule structure model proposed in this study was subsequently applied to explain the sorption behaviour during plasticization.

All the CO₂ sorption isotherms presented in Fig.6.5 were re-organized and presented in Fig.6.6 in order to compare the CO₂ sorption in Henry's and Langmuir sites. In Fig.6.6A, for the hollow fiber with the highest selectivity (CO₂/CH₄: 66), the amount of CO₂ sorbed into the Langmuir sites were slightly higher than in Henry's sites below a pressure of 7 bar. Beyond that pressure the CO₂ sorption in the Henry's sites surpassed that in Langmuir sites. For hollow fibers with a selectivity of 53 (Fig.6.6B), more CO₂ gas molecules were adsorbed in the Langmuir sites than in Henry's sites in the lower pressure range and the intersection of Henry's and Langmuir sorption isotherms also shifted to 12 bar. A similar trend was observed when the selectivity was further lowered to 36 (Fig.6.6C), the size of the enclosed area between the Henry's and Langmuir sorption

isotherm became larger indicating that more CO_2 was adsorbed in the Langmuir sites in the low pressure range, and the intersection was subsequently increased to around 15 bar.



A: CO₂/CH₄ selectivity: 66



B: CO₂/CH₄ selectivity: 53



C: CO_2/CH_4 selectivity: 36

Fig.6.6. CO₂ sorption isotherms from Matrimid hollow fibers with different separation properties

Similar trends (decrease in enclosed area with increased selectivity) were also observed on N_2 and CH_4 sorption isotherms as shown in Fig.6.7. These observations demonstrate that the gas sorption behaviour in polymeric membrane structure is dominated by the distribution manner of the polymer chains in both Henry's and Langmuir sites regardless the types of the gas tested.



A: N₂ sorption modelling results (CO₂/CH₄ selectivity of 36)



B: N₂ sorption modelling results (CO₂/CH₄ selectivity of 53)



C: N₂ sorption modelling results (CO₂/CH₄ selectivity of 66)



D: CH₄ sorption modelling results (CO₂/CH₄ selectivity of 36)



E: CH₄ sorption modelling results (CO₂/CH₄ selectivity of 53)



F: CH₄ sorption modelling results (CO₂/CH₄ selectivity of 66)

Fig.6.7. N₂ and CH₄ sorption experimental data and modelled results from dual mode model analysis

As indicated in the previous sections, CO_2 sorption in Henry's sites is the main contributor to plasticization because the high polymer chain packing density presented in those regions makes it more sensitive to the plasticization than in the Langmuir sites. Since the hollow fiber with higher selectivity adsorbed more CO_2 in Henry's sites than in Langmuir sites compared to hollow fibers with lower selectivity, it is to be expected that hollow fibers with higher selectivity should be more vulnerable to plasticization and hollow fibers with lower selectivities should possess better plasticization resistance. This expectation will be validated in Section 6.3.3.

6.3.2 Thickness dependence of plasticization

The membrane thickness dependence of plasticization has been well documented both on dense and asymmetric membranes (Jordan, Henson et al. 1990; Pfromm and Koros 1995; Wessling, Lopez et al. 2001; Punsalan and Koros 2005; Huang and Paul 2007). It was observed that membranes with different thickness respond to plasticization differently by displaying the plasticization curves with different shapes as shown in Fig.6.8 (Ismail and Lorna 2002; Wallace 2004).



DECREASE IN MEMBRANE THICKNESS

Fig.6.8. Schematic representation of thickness dependence of plasticization

As shown in Fig.6.8, asymmetric hollow fiber membranes usually display a much lower plasticization pressure than dense film, and sometimes exhibit an instantaneous increase in CO₂ permeance with pressure (Jordan, Henson et al. 1990; White, Blinka et al. 1995). White et al. (White, Blinka et al. 1995) attributed this phenomenon to the loosely packed polymer chains presented in the skin layer of asymmetric membranes compared to those in a dense film. However, higher selectivities in asymmetric membranes (10% above dense film value) were reported for various polymer materials which indicate that there is a higher polymer chain packing density in skin layer of asymmetric membranes than in dense films (Ismail and Shilton 1998; Ismail, Dunkin et al. 1999; Niwa and Kawakami 2000; Niwa, Kawakami et al. 2004). The inconsistent interpretations of these behaviours indicates that the dependence of plasticization on thickness should not simply be attributed to the polymer chain packing density; a more sophisticated model therefore needs to be developed to obtain a consistent explanation of all the experimental observations.



Fig.6.9. CO₂ sorption isotherms of Henry's and Langmuir sites in Matrimid dense film, dual mode sorption parameters from Punsalan's work were adopted (Punsalan 2001; Punsalan and Koros 2005)

The nodule structure model proposed in this study can be adopted to interpret the dependence of plasticization on thickness. A CO_2 sorption isotherm for a dense Matrimid film was constructed based on the results from Punsalan et al. (Punsalan 2001; Punsalan and Koros 2005). Similar to the approach applied in the previous section, Henry's and Langmuir sorption sites were de-coupled and plotted in Fig.6.9. It was observed in Fig.6.9 that Langmuir sites in the dense Matrimid film adsorbed much more CO_2 than Henry's sites in the low pressure range and the size of the enclosed area between the Langmuir and Henry's sorption isotherms was much larger than was observed for Matrimid hollow fibers as shown in Fig.6.6A.

It is reasonable to suggest that the size of the nodules is related to the nodule growth time according to the nucleation and growth mechanism, if the growth time is too short to allow the nodules to grow larger, the size of interstices between nodules (Langmuir sites) would also become correspondingly smaller. On the other hand, when nodules are allowed to grow to a much larger size by prolonging the growth time, then the number of Langmuir sites also increases. Casting a dense film using the dry-phase inversion allows a much longer time for nodule growth compared with hollow fiber spinning. Therefore dense films generally display a larger and more loosely packed nodule structure with larger interstices between them (i.e. Langmuir sites) compared to hollow fiber membranes. This nucleation and growth hypothesis is in agreement with the observation of sorption isotherms constructed in this study (Fig.6.9) as well as observations of other researchers (Ismail, Dunkin et al. 1999; Niwa and Kawakami 2000; Niwa, Kawakami et al. 2004). In addition the increased volume of Langmuir sites will also make it possible to accommodate much more CO₂ gas in the low pressure range compared to Henry's sites (Fig.6.9); hence the plasticization effect is negligible for dense films in the lower pressure range. Consequently a delayed plasticization and an elevated plasticization pressure should be expected for dense film compared to hollow fibers which is in agreement with the common observations as shown in Fig.6.8.

6.3.3 Time dependence of plasticization

The CO_2 permeability is not constant over time at a fixed pressure when the glassy polymer material plasticizes. This time dependence of plasticization has been well documented by various researchers (Wessling, Schoeman et al. 1991; Kanehashi, Nakagawa et al. 2007).

It is demonstrated in Fig.6.10 that, while all the normalized CO_2 permeance increases over time under different pressures, the extent of the increasing trend is more pronounced for permeation under pressure above 12 bar. CO_2 conditioned at 20 bar in particular, displays the highest increase in CO_2 permeance during the first 2 hours indicating the highest degree of plasticization. CO_2 conditioned at 4 bar, on the other hand, shows much slower increase in normalized CO_2 permeance compared to those operated under higher pressure.



Fig.6.10. Normalized CO₂ permeance over time under different CO₂ conditioning pressures (CO₂/CH₄ selectivity of 23)

The CO2 conditioning experiments were also performed at elevated pressures (up to 25 bar) from the same batch of the hollow fibers with different time intervals between pressure-increasing steps (Fig.6.11). CO₂ permeation isotherm with 5 mins time interval displays a typical plasticization curve of the dense film with a minimum CO₂ permeance at 12 bar. CO₂ permeation isotherms with time intervals of 30 and 60 mins, on the

contrary, displays an instantaneous increase of CO_2 permeance at the onset of the experiment which is similar to the plasticization curve obtained from the asymmetric membrane with ultra-thin skin layer. Furthermore higher CO_2 permeance is also observed for longer time intervals at the same feed pressure (above 10 bar). It could be explained by the time dependence of plasticization (Wessling, Huisman et al. 1995).

Hollow fibers were subsequently depressurized after reaching 25 bar in order to observe the hysteresis effect of the plasticization. The CO_2 permeance was measured every 30 mins till the pressure is lowered below 5 bar. It is observed that the CO_2 permeance continues to increase despite of the decrease in CO_2 pressure. This hysteresis behaviour could be partially contributed to the alterations of the polymer matrix by CO_2 not capable of relaxing back to their original states within the time scale of the measurements. The extra-created free volume at the previous higher pressures resulted in higher permeances even upon depressurization. Moreover higher CO_2 permeance is observed for the fibers with 30 and 60 mins time intervals compared to 5 mins interval indicating the time dependence of the plasticization during the depressurization.



Fig.6.11. CO₂ permeation isotherms during pressurization and depressurization at temperature of 21°C (CO₂/CH₄ selectivity of 23)

Time dependence of plasticization for Matrimid hollow fibers with different separation properties shown in Fig.6.12A and B indicated that Matrimid hollow fibers with the highest selectivity displayed the lowest initial CO_2 permeance compared to those with lower selectivities. Lower CO_2 permeance was observed for fibers with high selectivity throughout the whole permeation experiment.



(A)



(B)

Fig.6.12. CO₂ permeation isotherms for hollow fibers with different separation properties at 20bar and room temperature (around 23°C) (A: absolute CO₂ permeance and B: normalized CO₂ permeance)

On the other hand, hollow fibers with higher selectivities (53 and 66) displayed much higher normalized CO_2 permeance in the high pressure range than those with lower selectivity (Fig.6.12B). Hollow fibers with selectivity of 53 exhibited higher normalized CO_2 permeance than those with selectivity of 66 in the time frame of the experiment; however, it was observed that the fibers with a selectivity of 66 could display higher normalized CO_2 permeance beyond 400 mins.



Fig.6.13. N₂ permeance decay over time after CO₂ conditioning

 N_2 permeance decay experiments were performed immediately after the CO₂ conditioning experiments to evaluate the degree of the polymer chain network dilation. The pressure of N_2 single gas permeation was set at 10 bar for all experiments, N_2 permeation data were collected every 30 mins for 10 hours. All the N_2 permeances were normalized by the initial N₂ permeance, which is determined prior to CO₂ conditioning. Therefore a value above 1 indicates a higher N₂ permeance after CO₂ conditioning than the N₂ permeance prior to CO₂ conditioning. Fig.6.13 demonstrates that, for hollow fibers with selectivity of 36, the initial N_2 permeance after the CO_2 conditioning is almost 1.6 times of the N_2 permeance prior to CO₂ conditioning. This increase in N₂ permeance is attributed to the dilation of the polymer chain. On the contrary, hollow fibers with higher selectivity displayed lower initial normalized N₂ permeance compared to low selectivity membranes. N_2 permeances of all hollow fibers slowly decline over time and stabilized after 400 mins. None of the normalized permeances could reach the value 1 in the time frame of the experiments indicating the swollen polymer chain matrix caused by plasticization could not recover to their original state. Meanwhile, hollow fibers with lower selectivity display lowest final N₂ permeance compared to hollow fibers with higher selectivity. During the N₂ permeance decay experiments, swollen nodules structures were gradually recover to their original state, for loosely packed nodule structures (usually observed in hollow fibers with lower selectivity), they could more easily consolidate to their original state compared to densely packed nodule structures. As a result, hollow fibers with lower selectivity display a final normalized permeance closer to the value of 1.

6.4 Plasticization phenomenon under single gas permeation

Two different protocols were adopted in CO_2/CH_4 single gas permeation tests to examine the plasticization phenomenon:

Scenario 1: The procedure is described in Fig.6.14. CO_2 permeation tests were carried out first at elevated pressure from 5 to 25 bar with 1 hour time interval between pressure increase steps. The permeation system was then allowed to degas overnight (purged with

 N_2 then left in atmosphere overnight) prior to further testing with CH₄, and CH₄ single gas permeation tests were following the same protocol as CO₂.



Fig.6.14. CO_2/CH_4 single gas permeation tests protocol flow chart (Scenario 1) Scenario 2: Unlike Scenario 1, permeance of CO_2 and CH_4 were measured in an alternate manner with elevated pressure, the protocol is depicted in Fig.6.15. The permeation apparatus was purged when switching between gas types. All the CO_2 and CH_4 permeances were then recorded after 1 hour permeation till they were stabilized.



Fig.6.15. CO_2/CH_4 single gas permeation tests protocol flow chart (Scenario 2) The normalized CO_2 permeances from both scenarios were plotted against feed pressure in Fig.6.16, increase in permeances with pressure is observed on both cases indicating the occurrence of plasticization. Scenario 2 displays lower extent of permeance increase than Scenario 1 because the relaxation of the swollen polymer chain matrix during CH_4 permeation between CO_2 pressure increasing steps in Scenario 2 mitigates the degree of the plasticization.


Fig.6.16. Normalized CO₂ permeances over feed pressure from both scenarios



Fig.6.17. Normalized CH₄ permeances over feed pressure from both scenarios

Significant difference is observed for the normalized CH_4 permeances following different testing protocols (Fig.6.17). CH_4 permeances from Scenario 1 exhibited 20% decrease below 15 bar and stabilized afterwards which is similar to the N₂ permeance decay. The swollen polymer chain matrix slowly recovered towards its original state during the CH_4 permeation, therefore a reduction in permeance is observed. CH_4 permeation following Scenario 2, on the other hand, displays completely different behavior. CH_4 permeances steadily increased with elevated pressure. CO_2 permeation between CH_4 permeance. The steadily increased CH₄ permeances indicates that the plasticization phenomenon became more pronounced at high CO_2 pressure, therefore a higher CH_4 permeance is observed each time after membrane was conditioned with CO_2 at an elevated pressure.



Fig.6.18. Normalized CO₂/CH₄ ideal selectivity over feed pressure from both scenarios

The ideal selectivity was calculated from the CO_2/CH_4 single gas permeance results and depicted in Fig.6.18 against the feed pressure. For Scenario 1, ideal selectivity increases almost 2.5 times compared to the initial value. On the other hand, a slightly decrease in ideal selectivity is observed in Scenario 2. Plasticization induced by CO_2 invasion usually causes the increase in permeability and decrease in selectivity in mixed-gas permeation. Therefore Scenario 1 greatly over-estimated the change in selectivity due to plasticization. The trends observed in Scenario 2 are in agreement with the expected outcome from the mixed-gas plasticization behaviour. However CO_2/CH_4 mixed-gas permeation is still necessary since the interaction and competition between the gas types in mixed-gas permeation could not be simulated via single gas permeation.

6.5 Effect of the competitive sorption in mixed-gas permeation

As the interaction and competition between different gas types could affect the sorption and diffusion behaviour during mixed-gas permeation, results from single gas permeation tests could give misleading predictions about plasticization behaviour (Sanders, Koros et al. 1984; Story and Koros 1989; White, Blinka et al. 1995; Visser, Koops et al. 2005). The so-called "competitive sorption effects" taking place during the CO_2/CH_4 mixed gases permeation could lower the permeability of both gases and mask the plasticization effects to a certain degree.

In this study, a mixed gases permeation model was developed to demonstrate the effects of competitive sorption under different permeation conditions. The simulation model (Eqn.6.3 and 6.4) was originally developed by Vieth et al. (Vieth and Sladek 1965; Vieth, Tam et al. 1966; Vieth, Howell et al. 1976) and subsequently modified by Petropoulos (Petropoulos 1970). These expressions were based on the assumption that some of the gas molecules adsorbed on the Langmuir sites do not entirely lose their mobility and still

contribute to the diffusion. In this study, Petropoulos' model was adopted to simulate the mixed-gas permeation behaviour and the model was described in Eqn.6.4.

$$\boldsymbol{c}_A = \boldsymbol{k}_{\boldsymbol{d}_A} \boldsymbol{p}_A + \frac{\boldsymbol{c}_H' \boldsymbol{b}_A \boldsymbol{p}_A}{1 + \boldsymbol{b}_A \boldsymbol{p}_A + \boldsymbol{b}_B \boldsymbol{p}_B}$$
(Eqn.6.3)

$$P_{A} = k_{D_{A}} D_{D_{A}} \left(1 + \frac{\frac{D_{H_{A}} c'_{H_{A}} b_{A}}{D_{D_{A}} s_{A}} \frac{p_{A2}}{p_{A2} - p_{A1}}}{1 + b_{A} p_{A2} + b_{B} p_{B2}} - \frac{\frac{D_{H_{A}} c'_{H_{A}} b_{A}}{D_{D_{A}} s_{A}} \frac{p_{A1}}{p_{A2} - p_{A1}}}{1 + b_{A} p_{A1} + b_{B} p_{B1}} \right)$$
(Eqn.6.4)

Where D_H and D_D characterize diffusion due to local concentration gradients in the respective Henry and Langmuir sites, k_D represents the Henry's law dissolution constant, b is the hole affinity constant and C_H ' is the hole saturation constant, which measures the sorption capacity of the un-relaxed volume. Subscription A and B represent binary gas components, subscription 1 and 2 represent downstream and upstream of partial pressure of gas A and B. In most of the cases, it is assumed that the downstream partial pressure is negligible, so the above expression can be simplified to:

$$\boldsymbol{P}_{A} = \boldsymbol{k}_{D_{A}} \boldsymbol{D}_{D_{A}} \left(\mathbf{1} + \frac{\frac{D_{H_{A}} \cdot \boldsymbol{C}_{H_{A}} b_{A}}{D_{D_{A}} \cdot \boldsymbol{S}_{A}}}{\mathbf{1} + b_{A} p_{A2} + b_{B} p_{B2}} \right)$$
(Eqn.6.5)

The above expression clearly demonstrates the effects of competitive sorption on gas permeation through glassy polymers. When a second gas component B is introduced into the membrane structure, component B will occupy some of the Langmuir sites (second term in the bracket of Eqn.6.5) which were previously only available for component A (assuming both components A and B are non-interactive gas molecules). Consequently the solubility coefficient for component A will be suppressed, and the concentration driving force of component A will be lowered. As a result, a lower permeability of component A is expected due to the competitive sorption induced by component B. CO₂/CH₄ mixed gases permeations with different feed compositions were modelled and the CO₂ partial permeances were normalized to the permeance at the total pressure of 5 bar and then plotted against the CO₂ fugacity ($D_{DCO2} = 40.86$, and $D_{HCO2} = 3.52$) (Bos, Punt et al. 1999). A similar simulation was carried out by Visser et al. (Visser, Koops et al. 2005), and they suggested that due to the insignificant difference in pressure and fugacity, and the use of either pressure or fugacity will not affect the simulation results. The results presented in Fig.6.19 demonstrate that the gas mixture with the least CH₄ composition (CO₂:CH₄=80:20) exhibits the mildest decline of CO₂ permeance against CO₂ fugacity, only 7% loss of the CO₂ permeance is observed when lifting the CO₂ fugacity to 15 bar. Gas mixture with the highest concentration of CH₄ (CO₂:CH₄=20:80), on the contrary, displays the quickest decrease in CO₂ permeance against CO₂ fugacity, and the drop of CO₂ permeance is almost 13% at the CO₂ fugacity of 15 bar.



Fig.6.19. Mixed gas permeation modeling of CO_2/CH_4 with different gas compositions ($\alpha_{CO2/CH4}$:66)

The mixed gas permeation simulation (Fig.6.19) indicates that the CO_2 permeance is significantly lowered by the presence of the secondary gas (CH₄ in this case) caused by competitive sorption, and the competitive sorption effects are more pronounced with increased concentration of the secondary gas. This phenomenon is typical for binary inert gas mixture permeation without the presence of the plasticization.

The mixed gas permeation rates were also estimated for Matrimid hollow fiber membranes with different separation properties and a gas mixture composition of $CO_2:CH_4=20:80$. Fig.6.20 shows that Matrimid hollow fiber with the highest selectivity would be expected to experience the mildest loss in CO_2 permeance with increasing CO_2

fugacity, whereas the hollow fiber with lowest selectivity would suffer the most severe effect of competitive sorption by displaying an almost 35% decline in CO_2 permeance for an increase in CO_2 fugacity from 1 to 15 bar.



Fig.6.20. Mixed gas permeation modeling of CO_2/CH_4 with different membrane separation properties ($\alpha_{CO2/CH4}$: 66, 53 and 36) and same gas mixture composition ($CO_2:CH_4=20:80$)

The modelling results presented in Fig.6.20 indicate that the counter-effects of competitive sorption and plasticization might make hollow fibers with lower selectivity less sensitive to plasticization.



Fig.6.21. Normalized CO₂ partial permeance against total feed pressure from CO₂/CH₄ (20/80) mixed-gas permeation tests with Matrimid hollow fibers with different selectivity (CO₂/CH₄ selectivity of 39, 23 and 14)

The mixed-gas permeation tests with the Matrimid hollow fibers possessing different selectivity (Fig.6.21) indicate that hollow fiber membranes with lower selectivity were less sensitive to plasticization with a slower increase in normalized CO_2 partial permeance compared to the hollow fiber membranes with higher selectivity. This better plasticization resistance of hollow fibers with lower selectivities could be partially attributed to, according to the modelling results, the stronger competitive sorption effects on hollow fibers with lower selectivity.

6.6 Conclusions

In order to gain a comprehensive understanding of the plasticization phenomenon, a nodule structure model based on nucleation and growth mechanism and dual mode transport model was developed in this study to link membrane formation mechanisms with membrane morphology and plasticization.

The model suggested that the nodule structure is the primary unit constituting the membrane structure. The interstices between nodules are associated with Langmuir sites whereas the amorphous portions within the nodules represent Henry's sites. It is proposed that the CO_2 sorption in Henry's sites is the main contributor to the dilation of the polymer chain and the plasticization, whereas Langmuir site sorption contributes very little to the plasticization. The degree of plasticization is therefore determined by the competition of Henry's and Langmuir site sorption at different pressures. In this study, gas sorption tests were performed on Matrimid hollow fibers with various ranges of separation properties, and the Henry's and Langmuir sorption isotherms were decoupled and compared against pressure. The sorption observations accompanied by CO_2 conditioning experimental results confirmed that Matrimid hollow fiber which adsorbed more CO_2 in Henry's sites in the low-pressure range were prone to plasticization.

The nodule structure model was suitable for interpreting the dependence of plasticization on membrane thickness. The modelling results revealed that thicker films generally display more CO_2 sorption in Langmuir sites than in Henry's sites indicating better plasticization resistance than thin films or hollow fibers with an ultra-thin skin layer, which was in good agreement with reported experimental observations. The nodule structure of our in-house fabricated hollow fibers was observed in SEM images, nodules with an average diameter of 20 nm were observed both in the skin layer and the supporting sub-structure.

A mixed gas permeation model was developed to predict the competitive sorption behaviour. The results demonstrated that membranes with lower selectivity exhibited stronger competitive sorption compared with hollow fibers with higher selectivity; therefore plasticization is more likely to be masked by competitive sorption for hollow fibers with lower selectivity.

7 SUPPRESSION OF PLASTICIZATION

7.1 Introduction

Plasticization phenomenon presents a huge challenge for Matrimid hollow fiber's sustainable separation performance, therefore need to be suppressed. The most common strategies to improve polymeric membrane's plasticization resistance include: chemical cross-linking (Hsu, Nataraj et al. 1993; Kita, Inada et al. 1994; Meier, Langsam et al. 1994; Liu, Wang et al. 2001; Tin, Chung et al. 2003; Shao, Chung et al. 2005; Shao, Chung et al. 2005; Powell, Duthie et al. 2007; Shao, Liu et al. 2008; Zhao, Cao et al. 2008; Zhao, Cao et al. 2008), thermal annealing (Kuroda and Mita 1989; Kuroda, Terauchi et al. 1989; Kawakami, Mikawa et al. 1996; Bos, Punt et al. 1998; Krol, Boerrigter et al. 2001; Chung, Ren et al. 2003; Zhou and Koros 2006) and blending with different type of polymer with higher plasticization resistance (Chiou and Paul 1986; Raymond, Koros et al. 1993; Kapantaidakis, Kaldis et al. 1996; Bos, Punt et al. 2001; Kapantaidakis, Koops et al. 2002; Chung, Guo et al. 2006; Visser and Wessling 2008). Thermal annealing was chosen in this study due to its relative lower cost compared to the other post-treatments. Several characterization techniques were applied in this study to investigate the possible mechanisms behind the suppression of plasticization, and the results will be presented in this chapter.

7.2 Optimization of thermal annealing protocol

7.2.1 Annealing time

Previous studies (Kuroda and Mita 1989; Kuroda, Terauchi et al. 1989; Kawakami, Mikawa et al. 1996; Dudley, Schoberl et al. 2001; Tin, Chung et al. 2003; Zhou and Koros 2006) have suggested that the three factors that influence the effect of the thermal

annealing process are (1) annealing temperature, (2) annealing time, and (3) annealing environment. In this study, all the hollow fibers were thermally annealed in a vacuum oven. Therefore only the effects of the heating temperature and time were considered.

The glass transition temperature (T_g) of the Matrimid is between 305 and 320°C (Ekiner, Hayes et al. 1992), thermal annealing were carried out both above and below T_g . For the hollow fibers annealed at 200°C, the normalized CO₂ permeances were lower than that for the untreated membrane as shown in Fig.7.1. This indicated that the annealed membrane possessed a degree of plasticization resistance. However, CO₂ permeance did not stabilize for all of the treated fibers, indicating that annealing treatment had not been sufficient to entirely suppress plasticization. Since increasing the thermal annealing time over 30 mins could not further improve membrane's plasticization resistance, 30 mins was selected as the heating time in the following thermal annealing tests.



Fig.7.1. Normalized CO₂ permeance of Matrimid membrane over conditioning time at different thermal annealing time (all the fibers were annealed at 200°C, and CO₂ pressure was set at 20 bar, CO₂/CH₄ selectivity: 47)

7.2.2 Annealing temperature

Fig.7.2 shows the normalized CO_2 permeance against CO_2 conditioning time for Matrimid hollow fibers annealed under different temperatures for 30 mins compared to the untreated fibers. CO_2 permeance increased less than 20% for hollow fibers annealed at a temperature above 250°C and stabilized after 2 hours. In particular, the hollow fiber annealed at 380°C, showed only a 10% increase in CO_2 permeance after 6 hr conditioning.



Fig.7.2. Normalized CO₂ permeance of Matrimid membrane over conditioning time at different thermal annealing temperature (all the fibers were annealed for 30mins, and CO₂ pressure was set at 20 bar, CO₂/CH₄ selectivity: 47)

The CO₂ permeation isotherms against feed pressure were also constructed for membranes with different annealing history as shown in Fig.7.3 (30 mins annealing at different temperatures). All the annealed fibers showed lower CO₂ permeances compared to untreated fibers, and CO₂ permeances decreased with increasing annealing temperature. The hollow fibers annealed at 150°C displayed the typical 'dense film' permeation isotherm with a decrease in permeance below 8 bar and a steady increase thereafter. On the other hand, the hollow fiber annealed at 250°C displayed almost constant CO₂ permeance with feed pressure indicating that plasticization was suppressed for an annealing temperature at or above 250°C. CO₂ permeation isotherms for the hollow fibers annealed at 350 and 380°C displayed a similar trend to that for the hollow fibre annealed at 250°C but with lower CO_2 permeance.



Fig.7.3. CO_2 permeation isotherms over feed pressure for membranes treated at different annealing temperatures (all the fibers were annealed for 30mins, CO_2/CH_4 selectivity: 47) Based on the above CO_2 conditioning experimental observations, 250°C 30mins thermal annealing was chosen in this study as the optimized thermal annealing condition not only because it is sufficient to suppress plasticization but also because of its low energy consumption.

7.3 Characterization of annealed membrane

7.3.1 FT-IR analysis

FT-IR analysis was carried out in this work to investigate the possible change in chemical structure during thermal annealing. The FT-IR spectrum of Matrimid derived from untreated hollow fiber is given in Fig.7.4 and corresponds well with Matrimid spectrum obtained by other researchers (Bos 1996; Tin, Chung et al. 2003; Barsema, Klijinstra et al. 2004; Zhou and Koros 2006). Band assignments and wave numbers for IR spectrum of Matrimid hollow fiber were shown in Table 7-1.



Fig.7.4. FTIR absorption spectrum of untreated Matrimid hollow fiber and chemical structure of Matrimid

Number	Wave number (<i>v</i>)	Band assignment
1	2960-2860	v (C-H) stretch of methyl groups
2a	1779	v (C=O) symmetric stretch (imide I)
2b	1725	v (C=O) anti-symmetric stretch (imide
		I)
3	1673	v (C=O)stretch of benzophenone
		carbonyl
4 & 4'	1512 & 1488	v (C=C) aromatic stretching
5	1374	v (CNC) axial stretch (imide II)
6	1096	v (CNC) transverse stretch (imide III)
7	717	v (CNC) out-of-plane bending (imide
		IV)

Table 7-1. Wave numbers (v) and band assignments for IR spectrum of Matrimid hollow fiber with no thermal annealing history



Fig.7.5. FTIR spectra of untreated and treated Matrimid hollow fibers

Comparing the spectrum of an annealed Matrimid hollow fiber with an untreated hollow fiber as shown in Fig.7.5, the most significant difference was the reduced absorption intensity as thermal annealing temperature increased. This is due to the decrease in concentration of functional groups. A significant decrease of the peak intensity for the benzophenone carbonyl group (1673cm⁻¹) was observed while the anti-symmetric stretching peak density of the imide carbonyl group (1725cm⁻¹) was almost remained unchanged. This observation indicated that the concentration of benzophenone carbonyl group decreased compared to the concentration of imide carbonyl group during thermal annealing. The reduced concentration of the benzophenone carbonyl might be attributed to the possible crystallization of Matrimid during thermal annealing which could improve membrane separation properties (Ishida and Huang 1994; Bos, Punt et al. 1998).

7.3.2 Thermo-gravimetric analysis



Fig.7.6. Thermo-gravimetric analysis of hollow fibers treated at various temperatures below T_g

Thermo-gravimetric analysis has also been carried out on the hollow fibers treated at different annealing temperatures, the most significant weight loss observed above 450°C for all the hollow fibers was caused by the polymer degradation (Barsema, Klijinstra et al. 2004). Less than 3% weight loss was observed below 400°C which could be caused by the removal of the residual solvent and water. Among all the hollow fibers, untreated hollow fibers recorded largest weight loss below 400°C (around 3%), and slight difference of the weight loss can be observed from other hollow fibers with different annealing time as shown in Fig.7.6. All the Matrimid hollow fibers were stored for at least one month prior to thermal annealing, majority of the residual water and solvent evaporated during that period, therefore no significant weight loss difference was observed between the untreated and treated membranes. The hollow fibers annealed at 350°C for 4 hours showed only 1% weight loss below 400°C which indicated that most of

the remaining residual solvent and water was removed during the thermal annealing at 350°C. Removal of the residual solvent and water usually creates more free-volume available for the gas sorption and diffusion thus increases the gas permeability(Fu, Hu et al. 2008). However, the experimental observations suggested otherwise as shown in Fig.7.1 to Fig.7.3, further investigation is necessary.

7.3.3 Characterization of membrane morphology



Fig.7.7. The evolution of skin layer thickness as increasing the thermal annealing temperature (A: virgin, B: 150°C 30mins, and C: 300°C 30mins)

The SEM images of hollow fibers at different thermal annealing temperatures (Fig.7.7) suggests that thermal annealing not only results in densification of the polymer chain matrix but also converts part of the transition layer into skin layer. Matrimid hollow fibers treated at 300°C clearly exhibited a collapse in the sponge-like structure, and the walls between honeycomb-like cells also seemed to densify which might also contribute to the extra resistance to gas transport. This suggests that thermal annealing provides extra

energy for polymer chains to gain more mobility and relax from the restricted frozen unequilibrium state towards a more rubbery state with much lower modulus, thus allowing them to pack more densely and efficiently.

7.3.4 Gas sorption test

 CO_2 sorption tests were performed on the hollow fiber with a selectivity of 66 annealed at 250°C for 30 mins. The Henry's and Langmuir sorption isotherms were de-coupled and presented in Fig.7.8. It was observed that in Fig.7.8A that the Henry solubility constant significantly declines after thermal annealing compared to the untreated hollow fiber. Slight difference was observed on the Langmuir sorption isotherms (Fig.7.8B), the hole saturation constant (C_H ') exhibits a little decrease after thermal annealing which indicates that Langmuir sites (interstices between nodules) only reduces to a limited degree as a result of the thermal annealing.



(A)

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(B)



(C)

Fig.7.8. CO₂ sorption simulation results from untreated and annealed Matrimid hollow fibers with CO₂/CH₄ selectivity of 66 (250°C, 30mins) (A) Henry's sites sorption, (B) Langmuir sites sorption, and (C) Henry + Langmuir sorption

In order to investigate the thermal annealing effects on plasticization, Henry's and Langmuir sorption isotherms were decoupled and shown in Fig.7.9B. Compared to Henry's and Langmuir sorption isotherms of the untreated hollow fiber presented in Fig.7.9A, Fig.7.9B displays a significantly larger enclosed area between Langmuir and Henry's sorption isotherms. Furthermore, the intersection between the two isotherms shifted to a much higher pressure. Therefore the thermally annealed hollow fiber should possess better plasticization resistance than the untreated fibers which is consistent with the experiment observations presented in Fig.7.3.



(A)



(B)

Fig.7.9. CO₂ sorption isotherms of Henry's and Langmuir sites from Matrimid hollow fiber with CO₂/CH₄ selectivity of 66 (A) Untreated, and (B) Thermal annealed at 250°C for 30mins

7.3.5 Mixed-gas permeation test

The effects of thermal annealing on plasticization were also investigated with CO_2/CH_4 mixed-gas. Two modules were prepared with the Matrimid hollow fibers (CO_2/CH_4 selectivity around 23), while one without any treatment and the other being post-treated at 250°C for 30 mins. Both modules were tested with CO_2/CH_4 (20/80) mixed-gas at elevated pressure from 10 to 35 bar, and the results were presented in Fig.7.10A and B. The untreated Matrimid hollow fibers display an elevated CO_2 permeance with pressure indicating the effect of plasticization. The annealed hollow fibers, on the contrary, exhibit a typical 'dense film' permeation isotherm. The CO_2/CH_4 separation factors, Fig.7.10B

indicates that the thermal annealing improves membranes' separation factors by around 15%. Moreover for the treated hollow fibers, almost constant separation factors were observed throughout the whole pressure range, while the untreated hollow fibers displayed slight decrease in separation factors with pressure. It is noteworthy that the hollow fiber membranes used in this part of work have a CO_2/CH_4 selectivity of 23 compared to that of 47 used in Fig.7.1 ~ 3. As a result, higher permeance was observed here in contrast to Fig.7.1 ~ 3



(A)



(B)

Fig.7.10. (A) CO₂ partial permeation isotherms and (B) CO₂/CH₄ separation factors as a function of total feed pressure for both untreated and treated membranes (CO₂/CH₄ selectivity of 23)

7.3.6 DSC and Dissolution test

DSC measurement of T_g of both untreated and treated Matrimid hollow fibers demonstrated a slight increase in T_g for the annealed fiber compared to the untreated fiber (from 312°C to 318°C), indicating a constraint of polymer chain mobility caused by annealing. The dissolution tests in NMP revealed that the Matrimid hollow fiber became insoluble after thermal annealing at high temperature indicating the possible cross-linking during the thermal annealing (Fig.7.11). The suppression of plasticization might also be caused by the formation of the Charge Transfer Complexes (CTC) during the thermal annealing (Jiang, Chung et al. 2008). However validation of CTC formation in hollow fiber membranes is difficult. Future research is needed to evaluate the effect of CTC formation on the suppression of plasticization.



Fig.7.11. Images of dissolution tests results (all fibers annealed for 30mins at different temperature)

Thus in addition to the well-documented explanation of the enhanced plasticization resistance due to thermal annealing (e.g. cross-linking, crystallization or the formation of CTC), the re-distribution of the Henry's and Langmuir sites caused by thermal annealing could also contribute to the suppression of plasticization.

7.4 Conclusions

In this study, thermal annealing as a post-treatment to enhance membrane plasticization resistance was investigated. Matrimid hollow fibers were treated under different temperature for various period of time to develop the optimized thermal annealing condition. Matrimid hollow fibers annealed at 250°C for 30 mins possessed superior plasticization resistance since CO_2 permeance remained constant over a wide range of feed pressure with no sign of plasticization.

 CO_2 sorption tests for untreated and treated Matrimid hollow fibers provided support that the suppression of plasticization achieved by thermal annealing may be partially due to the alteration of the ratio of Henry's and Langmuir sorption sites and consequently shifts the plasticization pressure to a larger value.

Other techniques were also adopted in this study to characterize the thermally annealed hollow fiber. Evidence of densification of the skin layer was provided by SEM images which could lead to the suppression of plasticization. DSC measurements indicated the relaxation of the frozen glassy polymer segments back to their original equilibrium state. Dissolution tests, on the other hand, showed that the enhanced plasticization resistance might also be due to cross-linking of polymer chains during thermal annealing or the formation of CTC.

Based on the nodule structure model, the best strategy to suppress plasticization without undesired loss in permeability is to restrain the dilation of polymer chain matrix by intranodule cross-linking. Inter-nodule cross-linking can restrain the mobility between nodules however it possesses no strength to limit the polymer chain swell within nodule. Intranodule cross-linking, on the other hand, can restrain the dilation of the polymer chain segments within module; therefore prevent the growth of the free volumes for gas passage or creating of larger surface area for gas adsorption. Further investigation is required to develop a new strategy to encourage the intra-nodule cross-linking to suppress the plasticization with less sacrifice to gas permeability.

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8 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

8.1 Summary of the conclusions

Membrane gas separation technology offers great potential on natural gas purification application due to its superior separation performance over conventional separation technologies. However, the so called "plasticization phenomenon" could compromise membranes' long-term performance. The current work was focused on two aspects: 1 optimizing the fabrication process for the hollow fibers with desired morphology and superior separation properties, and 2 investigating the plasticization mechanism and developing the proper suppression strategies. This final chapter presents the conclusions of all the observations from this study, the problems arose from the study are also addressed as the potential research angle for the future study.

8.1.1 Fabrication of the defect-free integrally-skinned hollow fiber

One of the main purposes of this study was to investigate the effects of spinning process variables on membrane's final morphology and separation properties. The fabrication parameters have been examined in this study included dope and bore compositions and flow rates, air gap distance etc.

It was recognized through the study that the consistent formation of the defect-free integrally skinned hollow fibers relies on the optimization of solvent migration on both shell and lumen sides of the nascent hollow fibers. All the optimization strategies developed in this study (e.g. the additional volatile solvent or non-solvent additive in the dope solution, increasing the air gap distance to encourage the evaporation of the solvent), all aimed to one goal: manipulating the solvent/non-solvent migration process during fabrication to create the desired polymer concentration gradient within the membrane, eventually to produce hollow fibers with tunable range of separation properties.

Addition of the volatile solvent in the dope formula improved the O_2/N_2 selectivity from 3.6 with single solvent formula to 6.7; meanwhile the O_2 permeance was reduced from 14.9 to 9 GPU. The formation of the tighter membrane skin layer caused by the rapid evaporation of volatile solvent in the air gap was believed to be contributed to the enhanced selectivity.

Addition of the solvent in the bore fluid avoided the formation of finger like macrovoids which was evidenced by the SEM observation. Increasing the solvent content in the bore fluid led to the improved O_2/N_2 selectivity and increase in the thickness of selective skin layer.

Air gap distance between the spinneret and the coagulation bath is another very important parameter that implicates the formation of fiber skin formation. For a dope formula that includes volatile solvent, an increased selectivity and declined permeance were observed as a result of the evaporation of the volatile solvent. In the absence of the volatile solvent, selectivity was optimal at an intermediate air gap distance. This observation indicated that the addition of volatile solvent in the dope solution could amplify the effects of solvent evaporation, subsequently suppress or offset the negative influence from the humidity in the air gap.

The ratio of dope and bore fluid flow rates affected the fiber diameter and wall thickness, higher fiber wall thickness was observed at higher dope and bore flow rate ratio.

With optimized spinning parameters, fibers exhibited O_2/N_2 selectivity near the intrinsic value of Matrimid dense film, and significantly higher CO_2/CH_4 separation factors. This

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observation indicated that the conformation of polymers in the surface layers in hollow fibers may be quite different from the bulk film; yielding high separation factors even for mixed CO_2/CH_4 feed gases at higher pressures.

8.1.2 Thermodynamic analysis

A thermodynamic analysis tool based on the Hansen's solubility parameters was developed in this study to analyse the thermodynamic interactions between the different components in the dope, bore fluid and coagulation bath. For a particular type of polymer material, the selection of the compositions of the dope bore fluid and coagulation medium can be achieved through a simple calculation of the Hansen's solubility parameter differences. The Hansen's solubility parameter differences provided a very powerful tool to indicate the likely rate of demixing which could dictate the formation of hollow fiber structure. The thermodynamic analysis provided in Chapter 5 was in agreement with the experimental observation presented in Chapter 4 in terms of the membrane morphology and separation properties.

The potential of this thermodynamic analysis tool was seen in the development of novel polymer material by tailoring the polymer chain structure to obtain the desired solubility characteristics (e.g. better solubility with the common organic solvents).

8.1.3 Investigation of plasticization phenomenon

In this study, an improved model based on Kesting's nodule structure model was developed to understand the plasticization phenomenon and to connect the plasticization phenomenon with the membrane formation mechanisms and membrane morphology.

The model developed in this study suggested that the nodule structure is the primary unit to constitute membrane's structure. The interstices between the nodules are associated with the Langmuir sites whereas the amorphous portions within the nodules represent Henry's sites. The CO_2 sorption in Henry's sites is the main contributor to the dilation of the polymer chain and the plasticization, whereas the Langmuir sites sorption contributes very little to the plasticization. The degree of plasticization is therefore determined by the competition of Henry's and Langmuir sites sorption. In this study, gas sorption isotherms were constructed for Matrimid hollow fibers with various ranges of separation properties, the Henry's and Langmuir sorption isotherms were decoupled and compared against pressure. The sorption observations accompanied with the CO_2 permeation results confirmed that the Matrimid hollow fiber which adsorbing more CO_2 in Henry's sites than Langmuir sites over low-pressure range were more sensitive to the plasticization. This theory was also used to interpret other plasticization related phenomenon such as thickness and time dependence of plasticization.

The nodule structure was also evidenced by the SEM images of our in-house fabricated hollow fibers, nodules with average diameter of 20nm were observed both in skin layer and supporting sub-structure.

Competitive sorption effects, unique for the mixed-gas permeation, were also investigated with the membranes possessing different separation properties. The results indicated that, other than the distribution of the dual-mode sites, the competitive sorption effect also affects the plasticization phenomenon.

8.1.4 Plasticization suppression strategies

Plasticization suppression strategies have been studied extensively in the past. The most common approaches include chemical cross-linking, thermal annealing and blend with different polymer materials. In this study, thermal annealing was adopted considering its easiness to operate and low costs. It was observed that Matrimid hollow fibers annealed at 250° C for 30mins possessed superior plasticization resistance; CO₂ permeance remained constant over wide range of feed pressure with no sign of plasticization.

 CO_2 sorption tests were applied on untreated and treated Matrimid hollow fibers, and it provided solid evidence to prove the suppression of plasticization achieved by thermal annealing was partially because the thermal annealing alter the ratio of Henry's and Langmuir sorption sites and consequently shift the plasticization pressure to a higher level.

Other techniques were also adopted in this study to characterize the treated hollow fiber. Evidence of the densification of skin layer was provided by SEM images, DSC measurements indicated the relaxation of the frozen glassy polymer segments to their original equilibrium state during annealing. Dissolution tests proved that the enhanced plasticization resistance might be due to the cross-linking of polymer chains.

Sorption tests performed in this study revealed a possible new strategy to suppress plasticization without the involvement of any post-treatments. Membranes with lower polymer chain packing density in Henry's sites possess less surface area to adsorb gas molecules, consequently display less dilation in polymer chain after exposing to CO₂ gas penetrants. Such membranes should exhibit better plasticization resistance than membrane with higher polymer chain packing density in Henry's sites. Therefore fabricating the membrane with loose polymer packing density without need of further post-treatments could be a new strategy to suppress plasticization. However, polymeric membranes with such structure commonly possess low selectivity. Therefore a trade-off relation exists between enhancing plasticization resistance and maintaining adequate selectivity.

8.2 **Recommendations for future work**

It has been shown in the previous chapters that it required very fine control to fabricate defect-free integrally-skinned hollow fibers. Efforts have been made in this study to examine the possibility to widen the operation window. For instance, as demonstrated in the previous chapters, the addition of the volatile solvent in the dope solution could abate the effects of humidity in the air gap. Therefore, defect-free hollow fibers can be prepared in room condition without the additional chamber surrounding the air gap to control the humidity.

The viscosity of dope solution plays a significant role during the membrane preparation not only to the spinnability of the polymer solution, but also affects membrane's morphology and separation performance. It is suggested in this work that a comprehensive and thorough investigation on dope viscosity is essential to gain a better understanding of membrane formation, morphology and separation properties.

A problem arose from the study is that the wheels used in the coagulation bath to guide the membranes could damage the surface of the nascent hollow fibers especially for the high take-up speed, therefore it was suggested in this study to use a series of automotive rotated wheels with motor as the guides instead of the traditional wheels to reduce the friction between the nascent hollow fiber and wheels.

The effects of concentration polarization could present a challenge to obtain the accurate measurement of the hollow fibers' separation properties. The common approach to minimize its effect on the lab scale permeation tests is to maintain a very low stage cut which is, unfortunately, not a very economical strategy. It is suggested in this study, some strategies applied on UF and MF membranes could be adopted in the gas separation

hollow fiber membrane, for example, adding certain fillings or spacers between membranes to guide the gas flux and limit the concentration polarization while cross-flow module configuration is adopted.

Other than the attempts to optimize the fabrication conditions aiming for better separation performance, a lot researches have also been dedicated to the development of the new polymer material, new additives and new post-treatment strategies. For instance, it was suggested that novel custom-made polymers designed for specific applications will be the focus of the membrane research (Baker 2002). The high cost of these novel materials will make the composite membrane with substructure made from cheap polymer materials very desirable compared to conventional integrally-skinned single-material membranes.

It was also realized through this study that the best gas separation membrane should possess the optimized trade-off between permeability and selectivity. Maintaining a reasonable permeability should not be neglected while pursuing a higher selectivity.

Kesting's nodule structure model was borrowed in this study to interpret the dual-mode sorption theory and the plasticization phenomenon; however the drawback of Kesting's nodule structure model should not be neglected. Most of the nodules presented in the membrane structures have a diameter of few hundred angstroms, and the size of interstices between them therefore should be in the same order of magnitude compared to the size of nodules. In this case, these interstices/voids will be more likely act as the extra passages for gas molecules following the Knudsen flow mechanism, thus significantly lower the selectivity. Therefore, in order to achieve the selectivity observed in most of the gas separation membranes, the nodules will have to be compactly packed thus reduce the size of the interstices. Moreover, the interstitial spaces between nodules should not be free

of matter and should be filled with macromolecules but more loosely than inside the nodules.

The suppression of plasticization has been investigated in this study, some solid evidences were provided to interpret the suppression mechanism. However, it still felt that further characterization is needed to investigate the other possible mechanisms behind the enhanced plasticization resistance by thermal annealing, e.g. the formation of Charge Transfer Complexes (CTC). Jiang et al (Jiang, Chung et al. 2008) has reported that the high temperature annealing caused the shift of UV adsorption band which was attributed to the formation of CTC. It was believed that the formation of the intra- and intermolecular CTC in Matrimid (as shown in Fig.8.1) can restrict the mobility of the macromolecules which has a similar effect of the cross-linking modification and could contribute to the suppression of plasticization.



Fig.8.1. Demonstration of the Charge Transfer Complexes (CTC) formation mechanism

It was observed that, through the study, physical aging could counterbalance the effect of plasticization to certain extent. The plasticized Matrimid hollow fibers were stored for a
period of time and then tested with O_2/N_2 again. The O_2/N_2 permeance was significantly lower than those tested right after the plasticization, although still higher than the permeance values prior to plasticization. This observation indicated that the swollen polymer chains caused by the plasticization were allowed to relax back towards their original states during aging. The above observation demonstrated that it would be of great interest to further investigate the counterbalance relations between plasticization and physical aging, and to study the possibility to adopt the physical aging as an approach to suppress plasticization in the future.

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