DEVELOPMENT OF HIGH PERFORMANCE AND DEFECT-FREE ASYMMETRIC POLYETHERSULFONE MEMBRANES FOR O_2/N_2 SEPARATION

NORIDA BINTI RIDZUAN

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Gas)

Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia

AUGUST 2004

To arwah Mak and Abah : Halimah Bt Naim& Ridzuan Bin Ibrahim

"I will love you till the end of time"

To my beloved sibling: Kak Ipah, Kak Mia, Kak Iza, Kak Shah,

Kak Ana, Abang Ceri, Abang Lie, Abang Din, Abang Pozi

"Thanks for your blessing"

To SOPIE

"Thanks for everything"

ACKNOWLEDGEMENT

I would like to take this opportunity to express my sincere appreciation to all those people and organizations who contributed to this study. My first thanks and appreciations goes to both my supervisor, Associate Professor Dr.Wan Aizan Bt Wan Abdul Rahman and Professor Dr. Ahmad Fauzi Bin Ismail, for their support, guidance and willingness to teach and share their experience throughout this research project.

I am grateful to University Teknologi Malaysia for funding me generous financial support UTM-PTP fellowship award, that the enabling this work to be successfully. I would also like to thank the following people for their assistance, Mr Ng Be Cheer, who always give me a lot of suggestions and explanations, Mr Sohaimi Bin Abdullah, who provided technical advices, Mr Ayob Bin Abu, who run the Scanning Electron Microscopy, Mr Roslan, who run the Attenuated Total Reflection Fourier Transform Infrared Spectroscopy machine and Mrs. Rosmawati, who always helps me throughout this study.

My sincere to all my colleagues at "Membrane Research Unit" *Miss Suhaina, Miss Suhana, Miss Hasrinah, Miss Noraida, Miss Nawal, Miss Sunarti, Mr Syed Mohd Saufi, Mr Hafiz, Mr Idham, Mr Fazli* , with whom I enjoyed many hours of their company and others who have provided assistance at various occasion. Thanks for given me substantial moral support to finish the study. Above all, I thank Allah the Almighty for His grace, mercy and guidance throughout my life.

ABSTRACT

The objective of this study is to develop high performance and defect-free asymmetric polyethersulfone (PES) membranes for O_2/N_2 separation by manipulation of phase inversion process and rheological factors, including different type of nonsolvent additives, polymer concentration, shear rate and evaporation time. Asymmetric flat sheet membranes were fabricated using a pneumatically-controlled casting machine through a simple dry/wet phase inversion process. 1-methyl–2-pyrolidone (NMP) was employed as a solvent while distilled water (H_2O) and ethanol (EtOH) were used as nonsolvent additives (NSA). For the first stage of this study, three types of casting solution using H_2O as NSA and three types of casting solution using EtOH as NSA had been formulated through titration method. On the next stage, the membranes were fabricated at constant shear rate and evaporation time which is 233.37 s^{-1} and 12s respectively. Consequently, from the pure gas permeation test results, it was found that the optimum weight percent of PES in casting solution were 32.62 wt% and 26.71 wt % when H_2O and EtOH were used as NSA, respectively. Both of the casting solutions were chosen for optimizing the effect of shear rate and evaporation time. Finally, the membranes were fabricated at five different shear rates ranging from 111.67s^{-1} to 744.44s^{-1} and at six evaporation times ranging from 8s to 20s. The results showed that as the shear rate increased, the selectivity and pressure-normalized flux increased until critical shear rate was reached. The best shear rate was found at 233.33s^{-1} and 148.89s^{-1} when H_2O and EtOH were used as NSA, respectively. The rheologicaly induced molecular orientation in asymmetric membranes was observed by analyzing the wave length showed by Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (FTIR-ATR). On the other hand, as evaporation time was increased, the selectivity would increase but the pressure-normalized flux would decrease. The best evaporation time was found at 12s for both casting solution. Thus, the different NSA showed different influence on gas separation characteristics and structures of the produced membranes. The newly developed PES membranes with new casting solution formulation that used H_2O as the NSA, exhibited O_2/N_2 selectivity and pressure-normalized flux at about 7.95 and 9.71 GPU for O_2 respectively. The average skin layer thickness of these membranes was approximately 538.32Å. As for the membranes using EtOH as NSA, the O_2/N_2 selectivity and pressure-normalized flux were 5.01 and 14.07 GPU for O_2, respectively. The calculated average skin layer thickness was about 369.77Å. Therefore, the PES membranes prepared from NMP/H_2O solvent systems proved to provide the best separation characteristics compared to those membranes produced from NMP/ EtOH solvent system. As a conclusion, the combination of phase inversion process and rheological factors had successfully developed high performance, defect-free and hyperthin-skinned layer PES asymmetric membranes for O_2/N_2 separation.

ABSTRAK

Objektif penyelidikan ini adalah untuk menghasilkan membran asimetrik polyethersulfona (PES) berprestasi tinggi dan bebas kecacatan bagi proses permisahan O_2/N_2 dengan pengolahan proses fasa balikan dan faktor reologi, yang merangkumi bahan tambah bukan pelarut yang berbeza, kepekatan polimer, kadar ricih dan masa penyejatan. Membran asimetrik kepingan rata dihasilkan menggunakan mesin penuangan bersistem kawalan-pneumatik melalui proses fasa balikan kering/ basah. 1-methyl-2-pyrrolidona (NMP) digunakan sebagai pelarut, manakala air suling (H_2O) dan ethanol (EtOH) digunakan sebagai bahan tambah bukan pelarut (NSA). Pada peringkat pertama kajian, tiga jenis larutan tuangan menggunakan H_2O sebagai NSA dan tiga jenis larutan tuangan menggunakan EtOH sebagai NSA disediakan melalui kaedah penitratan. Peringkat berikutnya, membran disediakan pada kadar ricih dan masa penyejatan malar iaitu pada 233.37 s^{-1} dan 12s. Seterusnya, daripada keputusan ujian kebolehtelapan gas tulen, didapati peratus berat PES yang optimum dalam larutan tuangan adalah 32.62 wt% dan 26.71 wt % PES apabila H_2O dan EtOH digunakan sebagai NSA. Kedua-dua larutan tuangan tersebut kemudiannya dipilih untuk mengoptimumkan kesan kadar ricih dan masa penyejatan. Akhirnya, membran dihasilkan pada lima kadar ricih yang berbeza dalam julat 111.67s^{-1} hingga 744.44s^{-1} dan pada enam masa penyejatan yang berbeza iaitu dalam julat 8s hingga 20s. Keputusan menunjukkan bahawa apabila meningkatnya kadar ricih, kememilihan dan fluks tekanan-ternormal akan meningkat sehingga kadar ricih kritikal dicapai. Kadar ricih yang terbaik adalah pada 233.33s^{-1} and 148.89s^{-1} apabila H_2O dan EtOH digunakan sebagai NSA. Reologi penghalaan molekul teraruh pada membran asimetik boleh dianalisa dengan panjang gelombang yang ditunjukkan oleh Pemantulan Jumlah Terkecil-Spektroskopi Infra-Merah Penukaran Fourier (FTIR-ATR). Selain dari itu, dengan meningkatnya masa penyejatan, kememilihan membran turut meningkat tetapi fluks tekanan-ternormal menurun. Masa penyejatan yang terbaik diperolehi pada 12s bagi kedua-dua larutan tuangan. Oleh itu, NSA yang berbeza menunjukkan pengaruh yang berbeza kepada ciri-ciri pemisahan gas dan struktur membran yang terhasil. Penghasilan PES membran dengan formulasi larutan tuangan terbaru menggunakan H_2O sebagai NSA menunjukkan kememilihan O_2/N_2 dan fluks tekanan-ternormal untuk O_2 adalah 7.95 dan 9.71 GPU. Purata ketebalan lapisan kulit membran ini dianggarkan 538.32Å. Untuk membran yang menggunakan EtOH sebagai NSA, kememilihan O_2/N_2 dan fluks tekanan-ternormal untuk O_2 adalah 5.01 dan 14.07 GPU. Purata ketebalan lapisan kulit yang dikira adalah 369.77Å. Oleh itu, PES membran yang disediakan dari sistem pelarut NMP/H_2O telah terbukti menunjukkan ciri-ciri pemisahan yang lebih baik berbanding dengan PES membran yang disediakan dari sistem pelarut NMP/EtOH. Sebagai kesimpulan, penggabungan proses fasa balikan dan faktor reologi telah berjaya menghasilkan PES membran yang bebas kecacatan dan berkulit hipernipis bagi permisahan O_2/N_2.

TABLE OF CONTENTS

CHAPTER	TITLE		PAGE
	TITLE PAGE		i
	DECLARATION		ii
	DEDICATION		iii
	ACKNOWLEDGEMENT		iv
	ABSTRACT		v
	ABSTRAK		vi
	TABLE OF CONTENTS		vii
	LIST OF TABLES		xi
	LIST OF FIGURES		xiv
	LIST OF SYMBOLS		xxi
	LIST OF APPENDICES		xxvi
I	**INTRODUCTION**		1
	1.1	Membrane Formation for Gas Separation	1
	1.2	Problem Statement	4
	1.3	Objectives of the Study	4
	1.4	Scopes of Research	5

II	**LITERATURE REVIEW**			6
	2.1	Membrane Separation Technology		6
	2.2	Historical Background and Current Status of the Technology		10
	2.3	Advantages of Membrane Technology		12
	2.4	Asymmetric Membrane		13
	2.5	Fundamental of Gas Permeation		17
	2.6	Terminology of the Gases		19
		2.6.1	Solution-Diffusion Mechanism	20
	2.7	Asymmetric Membrane Formation		25
		2.7.1	Phase Inversion	25
		2.7.2	Wet Phase Inversion Process	30
		2.7.3	Dry /wet Phase Inversion Process	31
			2.7.3.1 Mechanism of Dry/wet Phase Inversion Process	33
	2.8	Membranes Formation Mechanism		34
	2.9	Effect of Coagulation Medium		35
		2.9.1	Demixing Processes	35
			2.9.1.1 Instantaneous Liquid–Liquid Demixing	36
			2.9.1.2 Delayed Liquid-Liquid Demixing	37
	2.10	Improving the Separation Characteristics		37
		2.10.1	Membrane Coating	38
		2.10.2	Rheological Effect	39
	2.11	Effect of Nonsolvent Additive on the Structure and Separation Performance		40

		2.11.1	Solubility Parameter Approach	44
III	**METHODOLOGY**			46
	3.1	Materials		46
		3.1.1	Polyethersulfone	46
		3.1.2	1-Methyl-2-Pyrrolidone	47
		3.1.3	Physical Properties of Nonsolvent Additives and Coagulation Bath	47
		3.1.4	Physical Properties of Gases	48
	3.2	Research Design		49
	3.3	Turbidity Titration Test		50
	3.4	Preparation of Casting Solution (Dope)		52
	3.5	Measurement of Casting Solution Viscosity		52
	3.6	Membrane Casting		53
	3.7	Membrane Coating		54
	3.8	Gas Permeation Tests		55
	3.9	Membrane Characterization Methods		62
		3.9.1	Scanning Electron Microscope (SEM)	62
		3.9.2	Attenuated Total Reflection Fourier Transform Infrared	63
IV	**RESULTS AND DISCUSSION**			64
	4.1	Effect of Polyethersulfone Concentration on Viscosity of Casting Solution and Membrane Morphology		64

	4.1.1	Effect of Polyethersulfone Concentration on Gas Separation Membrane Performance	73
		4.1.1.1 Performance of Uncoated Polyethersulfone Membranes	73
		4.1.1.2 Performance of Coated Polyethersulfone Membranes	77
	4.1.2	Effect of Polyethersulfone Concentration on Morphology of Uncoated and Coated Membranes	82
4.2		Effect of Shear Rate on Membrane Properties and Morphologies	92
4.3		Effect of Evaporation Time on Membrane Properties and Morphologies	115
V	**CONCLUSIONS AND RECOMMENDATIONS**		125
5.1		Conclusions	125
5.2		Recommendations	128
LIST OF PUBLICATIONS			130
REFERENCES			131
APPENDICES A-C			141-159

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Membrane processes	6
2.2	Major membrane processes applications	7
2.3	Principle characteristics of commercialized membranes separation processes (Sirkar and Winston Ho, 1992; Koros, 1995)	8
2.4	The characteristics of membranes used in different membrane separation processes and process driving	9
2.5	Historical background and current status (Pandey and Chauhan, 2001; Baker, 2000)	10
2.6	Gas separation membrane applications	13
2.7	General hierarchy of permeabilities of common gases (Prasad *et al.*, 1994; Stern, 1994)	24
2.8	Estimated diameter of common gas molecules (Baker, 2000)	24
3.1	Physical, mechanical and thermal properties of polyethersulfone (www.polymerprocessing.com)	47
3.2	Physical properties of nonsolvent additives and coagulation bath	48
3.3	Properties of pure oxygen (O_2) and nitrogen (N_2)	48

3.4	The solubility parameter of polyethersulfone, 1-methyl-2 pyrolidone, water, ethanol and methanol (Grulke, 1999; www. engnetbase.com)	51
4.1	Composition of casting solution at different polyethersulfone concentration	65
4.2	Solubility parameter difference for studied systems	67
4.3	Viscosity of various casting solutions	68
4.4	Separation properties of uncoated membranes at different polyethersulfone concentration	74
4.5	Separation properties and skin thickness of coated membranes at different polyethersulfone concentration	78
4.6	Membrane shear rate calculation	93
4.7	Average separation properties of uncoated membranes at different shear rate using water as NSA	94
4.8	Average separation properties of coated membranes at different shear rate using water as NSA	95
4.9	Average separation properties of uncoated membranes at different shear rate using ethanol as NSA	95
4.10	Average separation properties of coated membranes at different shear rate using ethanol as NSA	95
4.11	Comparison of polyethersulfone membrane performance prepared from binary and ternary system for gas applications from various workers	101
4.12	Infrared bands of functional groups in polyethersulfone	107

4.13	Flat sheet asymmetric membrane casting condition	115
4.14	Average separation properties of uncoated membranes at different evaporation time using water as NSA	117
4.15	Average separation properties of coated membranes at different evaporation time using water as NSA	117
4.16	Average separation properties of uncoated membranes at different evaporation time using ethanol as NSA	117
4.17	Average separation properties of coated membranes at different evaporation time using ethanol as NSA	118
4.18	Fine structural details of coated membranes at different evaporation time and different nonsolvent additive	121

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	A schematic illustration of the structure of integrally-skinned asymmetric membranes (Tan, 1999)	14
2.2	Process steps for the preparation of dry/wet phase inversion membranes (Pinnau *et al.*, 1990)	15
2.3	Membrane-based gas separation process	17
2.4	A quasicrystalline lattice exhibiting vacancies of hole. Circles represent molecules; arrow indicates molecular motion (Sperling, 1986)	19
2.5	Porous membranes	20
2.6	Solution-diffusion membranes	20
2.7	The solution-diffusion mechanism	23
2.8	Cross section view of asymmetric membrane	25
2.9	Phase inversion techniques	26
2.10	Ternary phase diagram	28
2.11	Schematic course of composition	29
2.12	Coagulation path of a polymer film	30
2.13	Schematic representation of wet phase inversion process	30
2.14	Steps involved in the preparation of integrally-skinned asymmetric membrane by using dry/wet phase	31

	separation process (Pesek and Koros, 1993)	
2.15	Dry process mechanism (Pesek and Koros, 1993 and 1994)	32
2.16	Membranes formation by immersion precipitation from ternary system: nonsolvent (1), solvent (2) and polymer (3)	34
2.17	Asym metric membrane with silicone rubber coating	39
3.1	Molecular structure of the polyethersulfone (Barth *et al.*, 2000)	46
3.2	Research design	49
3.3	Apparatus for turbidimetric titration	50
3.4	Casting solution preparation system	52
3.5	Pneumatically-controlled casting machine (Ng, 2003; Ismail *et al.*, 2003b)	54
3.6	Gas permeation system	55
3.7	Permeation cell	56
4.1	Viscosity versus polymer concentration	68
4.2	Scanning electron micrographs of membrane cross section at different polymer concentration using water as NSA (i) 23 wt.%, (ii) 27.74 wt.%, (iii) 32.62 wt.% (Magnification: 5000X)	71
4.3	Scanning electron micrographs of membrane cross section at different polymer concentration using ethanol as NSA (i) 18.30 wt.% (ii) 22.44 wt. % (iii) 26.71 wt.% (Magnification: 5000X)	72
4.4	Pressure-normalized flux and selectivity of uncoated membrane using water as NSA at different polymer concentration at 1 bar	76

4.5	Pressure–normalized flux and selectivity of uncoated membrane using ethanol as NSA at different polymer concentration at 1 bar	76
4.6	Pressure–normalized flux and selectivity of coated membrane using water as NSA at different polymer concentration at 1 bar	79
4.7	Pressure–normalized flux and selectivity of coated membrane us ing ethanol as NSA at different polymer concentration at 5 bar	79
4.8	Apparent skin thickness, mean pore size and surface porosity of membrane at different polymer concentration using water as NSA	80
4.9	Apparent skin thickness, mean pore size and surface porosity of membrane at different polymer concentration using ethanol as NSA	81
4.10	Cross section of uncoated membrane micrographs at different polymer concentration using water as NSA at 300X magnification (i) 23 wt.% (ii) 27.74 wt.% and (iii) 32.62 wt.%	83
4.11	Surface layer of uncoated membrane micrographs at different polymer concentration using water as NSA at 6000X magnification (i) 23 wt.% (ii) 27.74 wt.% and (iii) 32.62 wt.%	84
4.12	Cross section of coated membrane micrographs at different polymer concentration using water as NSA at 300X magnification (i) 23 wt.% (ii) 27.74 wt.% and (iii) 32.62 wt.%	85
4.13	Surface layer of coated membrane micrographs at different polymer concentration using water as NSA at 6000X magnification (i) 23 wt.% (ii) 27.74 wt.% and	86

	(iii) 32.62 wt.%	
4.14	Cross section of uncoated membrane micrographs at different polymer concentration using ethanol as NSA at 300X magnification (i) 18.30 wt.% (ii) 24.44 wt.% and (iii) 26.71 wt.%	88
4.15	Surface layer of uncoated membrane micrographs at different polymer concentration using ethanol as NSA at 6000X magnification (i) 18.30 wt.% (ii) 24.44 wt.% and (iii) 26.71 wt.%	89
4.16	Cross section of coated membrane micrographs at different polymer concentration using ethanol as NSA at 300X magnification (i) 18.30 wt.% (ii) 24.44 wt.% and (iii) 26.71 wt.%	90
4.17	Surface layer of coated membrane micrographs at different polymer concentration using ethanol as NSA at 6000X magnification (i) 18.30 wt.% (ii) 24.44 wt.% and (iii) 26.71 wt.%	91
4.18	Pressure–normalized flux and selectivity of uncoated membrane using water as NSA at different shear rate at 1 bar	96
4.19	Pressure–normalized flux and selectivity of coated membrane using water as NSA at different shear rate at 1 bar	96
4.20	Pressure–normalized flux and selectivity of uncoated membrane using ethanol as NSA at different shear rate at 1 bar	97
4.21	Pressure–normalized flux and selectivity of coated membrane using ethanol as NSA at different shear rate at 1 bar	97

4.22	Upper bound relationship for O_2/N_2 separation (Robeson, 1999)	100
4.23	Cross section of coated membrane micrographs at different shear rate using water as NSA at 300X magnification (i) 744.44 s^{-1} (ii) 446.67 s^{-1} (iii) 223.33 s^{-1} (iv) 148.89 s^{-1} (v) 111.67 s^{-1}	103
4.24	Cross section of coated membrane micrographs at different shear rate using ethanol as NSA at 300X magnification (i) 744.44 s^{-1} (ii) 446.67 s^{-1} (iii) 223.33 s^{-1} (iv) 148.89 s^{-1} (v) 111.67 s^{-1}	104
4.25	Plane-polarized infrared spectra parallel (dark line) and perpendicular (lighter line) to shear direction using water as NSA (111.67 s^{-1})	108
4.26	Plane-polarized infrared spectra parallel (dark line) and perpendicular (lighter line) to shear direction using water as NSA (148.89 s^{-1})	108
4.27	Plane-polarized infrared spectra parallel (dark line) and perpendicular (lighter line) to shear direction using water as NSA(223.33 s^{-1})	109
4.28	The normalized difference (a linear dichroism) spectrum among the different shear rate (111.67 s^{-1}, 148.89 s^{-1}, 223.33 s^{-1}) of polyethersulfone flat sheet asymmetric membrane using water as NSA	109
4.29	Plane-polarized infrared spectra parallel (dark line) and perpendicular (lighter line) to shear direction using ethanol as NSA (111.67 s^{-1})	110
4.30	Plane-polarized infrared spectra parallel (dark line) and perpendicular (lighter line) to shear direction using ethanol as NSA (148.89 s^{-1})	110

4.31	Plane-polarized infrared spectra parallel (dark line) and perpendicular (lighter line) to shear direction using ethanol as NSA (744.44 s^{-1})	111
4.32	The normalized difference (a linear dichroism) spectrum among the different shear rate (111.67 s^{-1}, 148.89 s^{-1} and 744.44 s^{-1}) of polyethersulfone flat sheet asymmetric membrane using ethanol as NSA	111
4.33	Scanning electron micrographs of membrane cross section at different shear rate using water as NSA (i) 111.67 s^{-1}, (ii) 148.89 s^{-1} and (iii) 223.33 s^{-1} (Magnification: 5000X)	113
4.34	Scanning electron micrographs of membrane cross section at different shear rate using ethanol as NSA (i) 111.67 s^{-1}, (ii) 148.89 s^{-1} and (iii) 744.44 s^{-1} (Magnification: 5000X)	114
4.35	Pressure–normalized flux and selectivity of uncoated membrane using water as NSA at different evaporation time at 1 bar	118
4.36	Pressure–normalized flux and selectivity of coated membrane using water as NSA at different evaporation time at 1 bar	119
4.37	Pressure–normalized flux and selectivity of uncoated membrane using ethanol as NSA at different evaporation time at 1 bar	119
4.38	Pressure–normalized flux and selectivity of coated membrane using ethanol as NSA at different evaporation time at 1 bar	120
4.39	Apparent skin thickness, mean pore size and surface porosity of membrane at different evaporation time using water as NSA	121

4.40	Apparent skin thickness, mean pore size and surface porosity of membrane at different evaporation time using ethanol as NSA	122
4.41	Cross section of coated membrane micrographs at different evaporation time using water as NSA at 8000X magnification (i)8 s (ii)10 s (iii)14 s (iv)16 s (v)20 s (a: skin layer thickness, b: transition layer, c: substructure)	123
4.42	Cross section of coated membrane micrographs at different evaporation time using ethanol as NSA at 8000X magnification (i)8 s (ii)10 s (iii)14 s (iv)16 s (v)20 s (a: skin layer thickness, b: transition layer, c: substructure)	124

LIST OF SYMBOLS

Abbreviations

NSA	-	Nonsolvent additive
TPX	-	Poly (4-methyl-1-pentene)
SEM	-	Scanning Electron Microscope
FTIR-ATR	-	Attenuate Total Reflection Fourier Transform Infrared Spectroscopy
PES	-	Polyethersulfone
NMP	-	1-Methyl-2-pyrrolidone
MW	-	Molecular weight (g/mol)
$\bar{v}$	-	Molecular speed (cm/s)
EtOH	-	Ethanol
H_2O	-	Water
MeOH	-	Methanol
PVDF	-	Polyvinylidene difluoride
TIPS	-	Thermal Induced Phase Separation
$R_{a/s}$	-	Mass ratio of nonsolvent additive to solvent
PEG	-	Poly (ethylene glycol)
DMAc	-	*N*,*N*-dimethylacetamide
THF	-	Tetrahydrafuran
DegOH	-	Diethyl glycol

EgOH	-	Eethyl glycol
O_2	-	Oxygen
N_2	-	Nitrogen
He	-	Helium
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
GPU	-	Gas permeation unit
FP	-	Formylpiperidine
FA	-	Formamide
PA	-	Propionic acid
PSF	-	Polysulfone
$ZnCl_2$	-	Zinc chloride

Parameters/ Symbols

rpm	-	Rotation per minute
d	-	Kinetic diameter (Å)
J_i	-	Flux of the component i
D_i	-	Diffusion coefficient(cm^2/s)
S_i	-	Effective solubility coefficient (cm^3(STP)/cm^3.cm.Hg)
D_i	-	Average diffusion coefficient(cm^2/s)
C	-	Concentration of the dissolved gas (cm^3 (STP)/cm^3)
k_i	-	Solubility constant
x	-	Direction coordinate
P_i	-	Partial pressure(cm Hg)

D_A	-	Diffusivity selectivity A
D_B	-	Diffusivity selectivity B
S_A	-	Solubility selectivity A
S_B	-	Solubility selectivity B
cP	-	Centrepoise
Tg	-	Glass transition temperature
→	-	Shear rate (s^{-1})
v	-	Velocity of casting knife
g	-	Gap setting of casting knife
P	-	Permeability coefficient of gas (cm^3 (STP) cm/ cm^2. s. cmHg)
Q	-	Volumetric flow rate of gas (cm^3/s) at STP
A	-	Membrane structure area(cm^2)
l	-	Membrane thickness or skin layer thickness (cm)
⇆p	-	Pressure difference across membrane (cmHg),
p_{us}	-	Upstream pressure
p_{ds}	-	Downstream pressure
(P/*l*)	-	Pressure–normalized flux (cm^3 (STP)/ cm^2. s. cmHg)
⇨	-	Selectivity (Unitless)
i	-	Component *i*
j	-	Component *j*
1	-	Component *1*
2	-	Component *2*
A	-	Component A
B	-	Component *B*

K	-	Total effective permeability
m	-	Mean hydraulic radius or mean pore size
↑	-	Viscosity
p	-	Pressure
$\bar{p}$	-	Mean pressure
$\bar{v}$	-	Mean molecular speed
R	-	Gas constant
T	-	Absolute temperature
M	-	Molecular weight
⇦	-	Numerical factor
k_0	-	Numerical factor account for pore shape(dimensionless)
k_1	-	Numerical factor account for pore shape(dimensionless)
l_r	-	Pore length
c	-	Concentration
B_o	-	Slope
K_o	-	Intercept
d	-	Dispersion interaction
P	-	Polar bonding
h	-	Hydrogen bonding
X	-	Molar fraction
V	-	Molar volume

Greek symbols

⇆ ♥ ♂ $_p$	-	Solubility parameter difference due to solvent and polymer

$\Delta\delta_{NSA-p}$	-	Solubility-parameter difference between the polymer and nonsolvent additives
δ_d	-	Solubility parameter due to dispersion forces in PES, (J/m^3) or $(MPa)^{0.5}$
δ_p	-	Solubility parameter due to polar forces in PES, (J/m^3) or $(MPa)^{0.5}$
δ_h	-	solubility parameter due to hydrogen bonding forces in PES, (J/m^3) or $(MPa)^{0.5}$
δ_T	-	Solubility parameter due to total forces in PES, (J/m^3) or $(MPa)^{0.5}$
Å	-	Amstrong
↘m	-	Micrometer

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Separation properties and fine structural details uncoated and coated membranes with different polyethersulfone concentration	143
B	Separation properties of uncoated and coated membranes at different shear rate using water and ethanol as NSA	148
C	Separation properties and fine structural details of uncoated and coated membranes at different evaporation time using water and ethanol as NSA	153

CHAPTER I

INTRODUCTION

1.1 Membrane Formation for Gas Separation

Membranes have gained an important place in separation technology and are used in a broad range of applications. As a general definition, membrane is regarded as a selective barrier between two phases (Mark *et al.*, 1985; Sirkar and Winston Ho, 1992; Ismail, 1997; Pandey and Chauhan, 2001). Membrane should always be associated with its application according to this definition. These applications can range from desalination, dialysis, filtration to gas separation (Kools, 1998). Membranes are normally classified according to the pore size or the size of the materials they are used to separate.

According to Koros and Fleming (1993), there are three areas which were considered critical issues controlling successful membrane–based gas separation. These areas are material selection, membrane formation and module and system configuration. Material selection is important because it will determine the maximum achievable selectivity for the particular membrane. The membrane formation process is responsible for the production of an optimized skin layer to ensure greater enrichment and higher productivity. Finally, the efficiency of the membrane system is highly dependent on the membrane module design and system configuration. The membrane formation and material selection are the aspects that were considered in this study.

The majority of membrane materials for gas separation are polymeric, however there is a steady growth in the application of inorganic material like ceramic, metal, carbon and glass membranes (Ismail, 1997). Membrane gas separation by polymer membrane is a proven technology that has found a wide range of application. For membrane formation, membrane can be prepared by phase inversion technique and can be further divided into four different techniques namely thermal precipitation, air casting of casting solution, precipitation from the vapor phase and immersion precipitation. Among these techniques, immersion precipitation is widely used to produce commercial gas separation membranes and others membrane-based separation available at present (Van de Witte *et al*, 1996). This process had been used to form ultrathin-skinned and defect-free asymmetric membranes from variety of glassy polymer (Pesek and Koros, 1993; Peinemann and Pinnau, 1988; Pinnau *et al*, 1990). For membrane preparation, the polymer solution generally consists of either a binary mixture of polymer and solvent or a ternary mixture of polymers, solvents, and nonsolvents (Pesek and Koros, 1993). The equilibrium thermodynamic data on ternary system (polymer/ solvent/ nonsolvent additive) can be determined by using turbidimetric titration method. Polymer precipitation curves were obtained by a simple titration to get the exact amount of nonsolvent additive value (Lau *et al.*, 1991).

According to previous researchers, different type of nonsolvent additive (Wang *et al.*, 1997; Lai, 1996; Wang *et al*, 2000), shear rate (Sharpe *et al.*, 1999; Ismail *et al.*, 1997; Ismail and Yean, 2002; Ismail and Lai, 2003c, Niwa *et al*, 2004), polymer concentration (Wood *et al.*, 1993; Lai, 2002; Ismail and Lai, 2003c) and evaporation time (Yamasaki *et al.*, 1999; Lai, 2002, Ismail and Lai, 2003c) are most widely studied since these parameters significantly influence membrane structure and performance.

Nonsolvent additives have influence the casting solution properties, gas separation characteristics and structures of the resulting membranes, therefore plays an important role in membranes making. The role of a nonsolvent additive is in controlling the membrane morphology and it also used to elevate the porosity of asymmetric membrane. Other attempts to explain the additive effect on membrane

formation have also been made by Kim and Lee. They elucidated that additive could be known as pore former on the structure formation of membranes (Kim and Lee, 1998). The addition of a suitable nonsolvent additive into the membrane casting solution accelerates the coagulation process from solution to gel when the casting solution was immersed in coagulant. As a result, membranes with thinner skin layer and more uniform structure were obtained (Wang *et al.*, 1995a). The addition of a nonsolvent additive in the polymer solution was to bring the solution composition closer to the point of phase separation (Kapantaidakis and Koops, 2002) in order to speed up precipitation of phase- separated structures and reduced relaxation effects on molecular orientation (Chung *et al.*, 2000b; Ismail and Lai, 2003a).

From different perspective, Ismail and co-worker and Shilton and co-worker had identified that rheological factor such as shear rate is an important parameter during membrane fabrication process. Increased shear rate during spinning increases molecular orientation and, in turn, enhance selectivity (Shilton *et al.*, 1997; Ismail *et al.*, 1997; Ismail and Shilton, 1998; Chung *et al*, 2000; Ren *et al*, 2002; Ismail and Lai, 2003a; Ismail *et al.*, 2003b; Niwa *et al*, 2004). From the polymer concentration aspect, polymer solution exhibited a significant chain entanglement which played an important role in the formation of membrane morphology and membrane performance. Increasing polymer concentration of casting solution will form a denser and thicker skin layer, resulting in a more selective but less productive asymmetric membranes for gas separation as described by previous researcher (Lai, 2002; Pesek and Koros, 1993). The optimum polymer concentration of casting solution therefore has to be determined in order to achieve defect-free and hyperthin-skinned asymmetric membranes for gas separation.

The selectivity of asymmetric membrane prepared through the phase inversion process is generally controlled by the thin skin structure of the membrane. The formation of skin structure is due to the evaporation induced by suitable gases during membrane fabrication. Therefore, it is expected that evaporating the solvent from the interface before precipitating the polymer could increased the polymer concentration at the top layer so that the formation of the skin structure could be

expedited. The skin structure is generally formed from the increase polymer concentration at the casting solution or air interface at the point of precipitation.

Thus, the combination all of the parameters mentioned above, it is expected that the produced membrane exhibit the best separation performance which will be suitable for gas separation application.

1.2 Problem Statement

The different type of nonsolvent additive (NSA), rheological effect, polymer concentration and evaporation condition during membrane fabrication played an important role in the morphology and separation performances of polymeric membrane. Different type of nonsolvent additive used in the casting solution result in the different morphology and separation performances. Lai *et al.* reported that nonsolvent additive was shown to play an important role in the gas performance of poly (4-methyl-1-pentene) (TPX) membranes. The porosity of the membrane is affected by types of NSA used where by adding the NSA into polymer solutions an increased in the pressure-normalized flux was observed (Lai *et al.*, 1996). High pressure-normalized flux does not exhibit that the membrane is in a good performance. Therefore, high selectivity is needed to develop membrane with hyperthin-skinned and defect-free. Therefore, this studies focus on the development and optimization of the membrane formation process of asymmetric polyethersulfone membrane for gas separation.

1.3 Objectives of the Study

Based on the problem statement described in the previous section, the following are the objectives of this research:

1. Developing new types of polymer solution formulation to fabricate high performance and defect-free asymmetric polyethersulfone membrane for gas separation application.
2. Improving phase inversion conditions so as to provide a platform for enhancing membrane selectivity.
3. Inducing and controlling molecular orientation during membrane fabrication through rheological conditions.
4. Correlating membrane performance with fabrication conditions hence producing high performance and defect-free membrane.

1.4 Scopes of Research

In order to achieve the above mentioned objectives the following scopes were drawn:

1. To develop an optimum casting solution formulation and casting conditions for the development of high performance and defect-free polyethersulfone membrane.
2. Casting solution which develop from various type of nonsolvent additive (NSA) were then cast through a dry/wet phase inversion technique using pneumatically-controlled casting machine. During the membrane fabrication, two variables were studied there are the evaporation time and the shear rate.
3. Characterization of the developed membrane using pure gases N_2 and O_2 as test gases.
4. Morphological studies of the surface layer and cross section of the developed membrane using Scanning Electron Microscopy (SEM).
5. Direct measurement of molecular orientation in asymmetric membranes using Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (FTIR ATR).