Development and theoretical analyses of polymeric membranes and mixed matrix membranes for gas separation

Shen, Yi

2012

Shen, Y. (2012). Development and theoretical analyses of polymeric membranes and mixed matrix membranes for gas separation. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/49507>

<https://doi.org/10.32657/10356/49507>

DEVELOPMENT AND THEORETICAL ANALYSES OF POLYMERIC MEMBRANES AND MIXED MATRIX MEMBRANES FOR GAS SEPARATION

SHEN YI

**SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

August 2011

**DEVELOPMENT AND THEORETICAL
ANALYSES OF POLYMERIC
MEMBRANES AND MIXED MATRIX
MEMBRANES FOR GAS SEPARATION**

Submitted by

SHEN YI

School of Mechanical and Aerospace Engineering

**A thesis submitted to the Nanyang Technological University in
fulfillment of the requirements for the degree of Doctor of Philosophy**

August 2011

Acknowledgements

First and foremost, I wish to express my deepest appreciation and gratitude to my supervisor, Professor Lua Aik Chong, for his excellent guidance, constructive suggestions, patient encouragement and continuous support during the study and research.

Next, I would like to thank Mr. Yuan Kee Hock, Higher Laboratory Executive in the Thermal and Fluids Research Laboratory, MAE, for his valuable assistance. I am also grateful to my friends for their help whenever needed.

Last but not the least, I would like to express my sincere appreciation to my family. All successful results in my research are from their support and understanding.

Abstract

Polymeric membranes play a vital role in many industrial separation processes. A considerable amount of work is presently in progress to improve the performance of polymeric membranes for gas separation. Many research efforts are devoted to the development of membranes that exhibit both high selectivities and permeabilities to specific gases. In this thesis, motivated by the idea that the combinations of polymer matrices and inorganic fillers could obtain the desirable properties of the individual components and probably achieve better separation performance in terms of high permeabilities and selectivities, the work focused mainly on the study of organic-inorganic mixed matrix membranes (MMMs). A comprehensive study on the effects of membrane thickness and heat treatment, the selection of inorganic fillers and the preparation methods, on the properties of the resulting membranes, is presented. Various instruments such as TGA (thermogravimetric analysis), DSC (differential scanning calorimetry), XRD (X-ray diffraction), SEM (scanning electron microscope) and TEM (transmission electron microscope) were used to characterize the membranes. The main objective of this research programme was to determine the relationship between the membrane structures and the gas separation performance. Besides the mixed matrix membranes, it was also desirable to study asymmetric membranes, researching into the effects of the preparation conditions on the separation properties of the resulting asymmetric membranes. The thesis consists of the following five parts:

- (1) The effects of membrane thickness and heat treatment on the gas transport

properties of P84 membranes were investigated. The results showed that the single gas permeability increased with increasing membrane thickness whilst the selectivity was independent of the membrane thickness and that the membrane annealed at low temperatures showed higher permeabilities but lower ideal selectivities.

- (2) Three types of inorganic fillers - fumed SiO_2 , MCM-41 and zeolite 4A, were incorporated into the P84 matrix to prepare MMMs and the effects of filler structures on the gas separation performance were comparatively studied. This work is the first systematic comparison of the effects of nonporous (SiO_2), microporous (zeolite 4A) and mesoporous (MCM-41) materials on the gas transport properties of P84 polymer. Results indicated that nano- SiO_2 particles proved to be the most effective inorganic filler in terms of the enhancement of the performance of gas separation. Subsequently, the effects of the modification of SiO_2 surface and the content of SiO_2 on the gas transport properties of the resulting MMMs were investigated. The permeability of the composite membranes was well matched with the predictions given by the free volume theory except that a large discrepancy was observed for the permeability of the composite membranes with higher SiO_2 loadings.
- (3) Polyimide-silica MMMs were also prepared using the sol-gel technique. However, with the introduction of the silica, there was no significant enhancement of the gas separation in the resulting polyimide-silica MMMs due to the strong interaction between the polymer chains and the inorganic phase.

Instead, the derived carbon-silica composite membranes prepared by the pyrolysis of the polyimide-silica MMMs at 900 °C under vacuum exhibited better gas separation properties. The highest permeances of 1042.18, 991.21, 296.03 and 155.26 Barrer/cm for He, CO₂, O₂ and N₂, respectively, were obtained by the C-Si 28% composite membranes and the highest selectivities of 37.57, 36.61 and 7.09 for He/N₂, CO₂ /N₂, and O₂/N₂, respectively, were produced by the C-Si 11% composite membranes.

(4) Nano-silica, MCM-41 and zeolite 4A were also incorporated into polyvinylidene fluoride (PVDF) matrix to prepare MMMs. Unexpectedly, the experimental permeabilities of the MMMs showed that there were no significant differences for these three types of MMMs although the inorganic fillers, *i.e.*, SiO₂, MCM-41 and zeolite 4A, had distinct properties such as pore structures and particle sizes. The gas (He, CO₂, O₂ and N₂) permeabilities of the three types of MMMs, *i.e.*, PVDF/SiO₂, PVDF/MCM-41 and PVDF/4A MMMs, were experimentally measured and theoretically predicted using Maxwell model, Higuchi model, Bruggeman model and Bottcher-Landauer model. However, these models failed to give good predictions on the gas permeation results. By taking the effects of crystallinity on the gas permeability into consideration, a model was proposed and this model gave good predictions on the gas permeabilities of the resulting MMMs, indicating that the model did capture the essence of the gas transport behaviours through the MMMs.

(5) Asymmetric membranes based on P84 were prepared by the wet phase inversion

technique. The thermodynamic and kinetic properties of the ternary nonsolvent/NMP/P84 systems were studied and correlated with the membrane structures. The effects of the membrane preparation conditions such as nonsolvent type, polymer solution concentration, casting solution thickness, evaporation time and coagulation temperature, on the resulting membrane structures were investigated in detail. The asymmetric membranes with several hundred nanometres of dense selective skin layers were successfully prepared.

Table of Contents

Acknowledgements	I
Abstract.....	II
Table of Contents	VI
List of Figures.....	XI
List of Tables.....	XXI
List of Symbols and Abbreviations.....	XXIV
Chapter 1 Introduction.....	1
1.1 Research background	1
1.2 Objectives and Scope	3
Chapter 2 Literature Review	7
2.1 History of polymer membranes for gas separation	7
2.2 Membrane materials.....	9
2.2.1 P84 polymer	9
2.2.2 Poly(vinylidene fluoride) (PVDF).....	21
2.3 Organic/inorganic composite membranes	25
2.3.1 Introduction	25
2.3.2 Optimisation of composite membranes	26
2.3.3 Morphology of inorganic/organic composite membranes.....	36
Chapter 3 Structure and Transport Mechanism of Membranes	42
3.1 Poiseuille flow	42
3.2 Knudsen diffusion	43
3.3 Molecular sieving.....	43
3.4 Capillary condensation.....	44
3.5 Surface diffusion	44
3.6 Fundamentals of transport in polymeric membranes.....	45
3.6.1 Gas sorption and transport in rubbery polymers	48
3.6.2 Gas sorption and transport in glassy polymers.....	48
Chapter 4 Experimental Set-up and Procedures for Preparation and	

Characterisation.....	54
4.1 Materials	54
4.2 Membrane preparation procedures	56
4.2.1 Fabrication of pure P84 membranes using a spincoater	56
4.2.2 Heat treatment of P84 membranes	57
4.2.3 Synthesis of MCM-41 silica.....	58
4.2.4 Fabrication of pristine P84 dense membranes.....	58
4.2.5 Fabrication of P84/SiO ₂ , P84/4A and P84/MCM-41 MMMs	59
4.2.6 Modification of the surfaces of nano-SiO ₂ particles	59
4.2.7 Synthesis of MMMs based on P84 and modified SiO ₂	60
4.2.8 Fabrication of pure PVDF membranes and MMMs.....	61
4.2.9 Preparation of pure polyimide membrane and composite membranes	62
4.2.10 Preparation of carbon and carbon-silica composite membranes	64
4.2.11 Preparation of asymmetric membranes based on P84	64
4.3 Membrane characterisation	65
4.3.1 TGA characterisation	65
4.3.2 DSC characterization.....	66
4.3.3 Density measurement	67
4.3.4 Scanning electron microscopy.....	67
4.3.5 Transmission electron microscopy	67
4.3.6 X-ray diffraction (XRD).....	68
4.3.7 N ₂ adsorption-desorption tests.....	68
4.3.8 Tensile stress-strain tests	68
4.3.9 Contact angle measurements	69
4.3.10 Cloud point determination.....	69
4.3.11 Diffusivity of NMP in nonsolvent coagulation bath.....	69
4.3.12 AFM characterisations.....	70
4.3.13 Porosity measurement	70
4.3.14 Single gas permeation measurements.....	71
4.3.15 Mixture gas permeation measurements	74

Chapter 5 Effects of Membrane Thickness and Heat Treatment on the Gas Transport Properties of P84 polyimide Membranes.....	75
5.1 Introduction.....	75
5.2 Results and Discussion	75
5.2.1 TGA and DSC results	75
5.2.2 P84 membranes with various thicknesses	76
5.2.3 Effect of heat treatment on the properties of P84 membranes	77
5.2.4 Morphology of membranes	78
5.2.5. Effect of membrane thickness on transport properties of membranes	81
Chapter 6 Influence of Inorganic Fillers on the Structural and Transport Properties of Mixed Matrix Membranes	87
6.1 Introduction.....	87
6.2 Results and discussion	87
6.2.1 Characterisation of inorganic fillers	87
6.2.2 Morphology of membranes	89
6.2.3 Membrane characterisation	93
6.3.4 Gas permeation results	99
6.3 Summary.....	101
Chapter 7 Structural and Transport Properties of BTDA-TDI/MDI Co-polyimide (P84)-Silica Nanocomposite Membranes for Gas Separation.....	104
7.1 Introduction.....	104
7.2 Results and discussion	104
7.2.1 Characterisation of the modified nano-SiO ₂ particles	104
7.2.2 Membrane morphology characterisations	106
7.2.3 Mechanical properties of membranes.....	109
7.2.4 DSC and density test results	113
7.2.5 Single gas permeation results	116
7.3 Summary.....	121
Chapter 8 Preparation and Characterisation of Polyimide-Silica Composite Membranes and Their Derived Carbon Composite Membranes for Gas	

Separation.....	123
8.1 Introduction.....	123
8.2 Results and discussion	123
8.2.1 Thermal stability of polyimide/silica composite membrane	123
8.2.2 Mechanical properties of polyimide/silica composite membranes	125
8.2.3 Morphology of the resulting membranes	126
8.2.4 XRD patterns of PI-silica and carbon-silica composite membranes	129
8.2.5 Gas transport properties of PI-silica composite membranes	132
8.2.6 Single gas transport properties of carbon-silica membranes	134
8.2.7 Mixed gas separation of carbon-silica composite membranes	137
8.3 Summary	139
 Chapter 9 Preparation and Characterisation of Mixed Matrix Membranes	
Based on PVDF for Gas Separation	140
9.1 Introduction.....	140
9.2 Results and discussion	140
9.2.1 TGA results.....	140
9.2.2 DSC results.....	143
9.2.3 Morphology	147
9.2.4 Mechanical properties	150
9.2.5 Contact angles	153
9.2.6 XRD patterns	154
9.2.8 Single gas transport properties	160
9.3 Summary	163
 Chapter 10 Theoretical and Experimental Studies on the Gas Transport	
Properties of Mixed Matrix Membranes Based on PVDF	165
10.1 Introduction.....	165
10.2 Modelling work.....	165
10.2.1 Maxwell model [130]	165
10.2.2 Higuchi Model [131]	167
10.2.3 Bruggeman Model [132]	167

10.2.4 Bottcher-Landauer Model [67, 131]	168
10.2.5 Modified Maxwell model	169
10.2.6 Modified Maxwell model for PVDF MMMs	172
10.3 Results and discussion	173
10.4 Summary	188
Chapter 11 Preparation and Characterisation of Asymmetric Membranes Based on Nonsolvent/NMP/P84	190
11.1 Introduction	190
11.2 Results and discussion	191
11.2.1 Thermodynamic properties of nonsolvent/solvent/polymer systems	191
11.2.2 Kinetic properties of nonsolvent/solvent/polymer systems.....	195
11.2.3 Effect of the nonsolvent type	198
11.2.4 Effect of the concentration of the polymer solution	204
11.2.5 Effect of the thickness of the casting solution	210
11.2.6 Effect of the evaporation time	213
11.2.7 Effect of the temperature of the coagulation bath	217
11.3 Summary	221
Chapter 12 Conclusions and Future Work	224
12.1 Conclusions.....	224
12.2 Recommended Future work	227
References.....	229
Appendix I	243
Appendix II.....	245
Appendix III	248
Appendix IV	249

List of Figures

Fig. 2.1 Chemical structure of BTDA-TDI/MDI (P84) co-polyimide	10
Fig. 2.2 Trade-off curves of polymeric O ₂ /N ₂ selectivity and O ₂ size selective regions	37
Fig. 2.3 Summary of the relationship between mixed matrix membrane morphologies and transport properties.	
Fig. 2.4 Flowchart of the chemical modification of zeolite surface by Li <i>et al</i>	39
Fig. 3.1 Schematic diagram of penetrant transport across a membrane	45
Fig. 4.1 Schematic diagram of the test rig for the single gas permeation	71
Fig.4.2 Photograph of the gas permeation testing rig	71
Fig. 5.1 TGA curve of P84 powder	75
Fig. 5.2 DSC curve of P84 powder	76
Fig. 5.3 Relationship between the membrane thickness and the number of coats for porous stainless steel substrates and PMMA substrate	77
Fig. 5.4 SEM micrographs of the cross-section of P84-118 membrane annealed at (a) 80 °C, and (b) 200 °C. (c) A digital photograph together	79

with the SEM micrograph of top surface (insert) of P84-118 annealed at 315 °C

Fig. 5.5 SEM micrographs of the cross-section (labelled as “a”) and the top surface (labelled as “b”) for the membranes P84-6 (1), P84-13 (2), P84-42 (3), P84-118 (4), P84-174 (5), P84-219 (6) and P84-309 (7). 80

Fig. 5.6 Permeabilities of helium of various membranes subjected to various feed pressures 81

Fig. 5.7 Permeability of membranes with various thicknesses 84

Fig. 5.8 Permeance of membranes with various thicknesses 85

Fig. 5.9 Selectivity of membranes with various thicknesses 85

Fig. 6.1 XRD pattern of synthesised MCM-41 88

Fig. 6.2 N₂ adsorption-desorption curve of synthesized MCM-41 88

Fig. 6.3 TEM micrographs of fumed nano-SiO₂ (A), synthesised MCM-41 (B) and zeolite 4A (C) 89

Fig.6.4 Surface (A), cross-section (B) and a higher magnification of the cross-section (C) of SEM micrographs of P84 membrane (1), P84/ SiO₂ membrane (2), P84/MCM-41 membrane (3) and P84/4A membrane (4) 91

Fig. 6.5 TEM micrographs of cut sections of (1) P84/SiO ₂ membrane, (2) P84/MCM-41 membrane and (3) P84/4A membrane	91
Fig. 6.6 Dependence of He permeability on the feed pressure through the membranes	92
Fig. 6.7 X-ray diffraction patterns of the membranes and P84 powder	93
Fig. 6.8 DSC curves of the membranes and corresponding T _g	97
Fig. 7.1 FTIR spectra of the APTES-modified SiO ₂ particles	105
Fig. 7.2 TGA curves of the modified SiO ₂ and the pristine SiO ₂	105
Fig. 7.3 SEM micrographs of cross-sections of (1) pure P84 membrane, (2) P84/4%SiO ₂ , (3) P84/8%SiO ₂ , (4) P84/14%SiO ₂ , (5) P84/20%SiO ₂ , (6) P84/25%SiO ₂ , (7) P84/Un-4%SiO ₂ , (8) P84/Un-8%SiO ₂ , and (9) the surface of P84/Un-14%SiO ₂ composite membranes	107
Fig. 7.4 TEM micrographs of the cross-sections of (1) P84/4%SiO ₂ , (2) P84/8%SiO ₂ , (3) P84/14%SiO ₂ , (4) P84/20%SiO ₂ , (5) P84/25%SiO ₂ (low magnification) and (6) P84/25%SiO ₂ (high magnification) composite membranes	108
Fig. 7.5 Stress-strain curves of resulting membranes	110
Fig. 7.6 Effects of modified SiO ₂ loading on tensile modulus and tensile stress	110

Fig. 7.7 DSC curves of various membranes	112
Fig. 7.8 Effects of volume fraction of modified SiO ₂ particles on the fractional free volume and void volume fraction of the nanocomposite membranes	115
Fig. 7.9 Effects of the volume fraction of inorganic fillers on permeability	120
Fig. 7.10 Effects of volume fraction of modified SiO ₂ particles on the selectivity	120
Fig. 7.11 Comparisons of selectivities among P84/4%SiO ₂ , P84/Un-4%SiO ₂ P84/8%SiO ₂ and P84/Un-8%SiO ₂ composite membranes	121
Fig. 8.1 TGA curves of the PI and PI-silica composite membranes	124
Fig. 8.2 Tensile stress and tensile modulus of pure PI and PI-SiO ₂ composite membranes	126
Fig. 8.3 Elongation strain at break of pure PI and PI-SiO ₂ composite membranes	126
Fig. 8.4 Digital pictures of the PI and PI-silica composite membranes and the resulting carbon membranes	128
Fig. 8.5 SEM micrographs of (1) pure PI membrane, (2) PI-SiO ₂ 7.2% composite membrane and (3) PI-SiO ₂ 13.7% composite membrane, (A) cross-section view with lower magnification, (B) cross-section view with higher magnification and (c) derived carbon membranes	129

Fig. 8.6 XRD curves of pure PI membrane and PI-silica composite membranes	131
Fig. 8.7 XRD curves of pure carbon membrane and carbon-silica composite membranes	131
Fig. 8.8 Single gas permeabilities of pure PI membrane and PI-silica composite membranes	134
Fig. 8.9 Ideal selectivities of pure PI membrane and PI-silica composite membranes	134
Fig. 8.10 Single gas permeabilities of pure carbon membrane and carbon-silica composite membranes	136
Fig. 8.11 Ideal selectivities of pure carbon membrane and carbon-silica composite membranes	137
Fig. 8.12 Mixed gas selectivities of pure carbon membrane and carbon-silica composite membranes	138
Fig. 9.1 TGA curves of (a) PVDF/SiO ₂ , (b) PVDF/MCM-41 and (c) PVDF/4A composite membranes. The TGA curve of the pure PVDF membrane is also included for comparison purpose	142
Fig. 9.2 Decomposition temperatures of the composite membranes as a function of filler content	143
Fig. 9.3 Complete DSC thermogram of pure PVDF membrane	144
Fig. 9.4 DSC curves for the second cycle for (a) PVDF/SiO ₂ , (b) PVDF/MCM-41 and (c) PVDF/4A composite membranes. The DSC curve	146

of the pure PVDF membrane is also included for comparison purpose	
Fig. 9.5 Crystallinity of the membranes as a function of inorganic filler content	147
Fig. 9.6 SEM micrographs of (1) pure PVDF, (2) PVDF/SiO ₂ 8%, (3) PVDF/SiO ₂ 32%, (4) PVDF/MCM-41 8%, (5) PVDF/MCM-41 32%, (6) PVDF/4A 8% and (7) PVDF/4A 32% composite membranes. Micrographs (i) A lower magnification and (ii) B higher magnification	149
Fig. 9.7 Relationship between the mechanical properties and varying inorganic filler contents for (a) tensile stress, (b) modulus, and (c) elongation strain at break of the composite membranes	152
Fig. 9.8 Contact angles of membranes with different inorganic filler contents	154
Fig. 9.9 XRD patterns of the pure PVDF membranes and composite membranes of (a) PVDF/SiO ₂ , (b) PVDF/4A and (c) PVDF/MCM-41	157
Fig. 9.10 Permeability of the membranes as a function of inorganic filler content	162
Fig. 9.11 Selectivity of the membranes as a function of inorganic filler content	163
Fig. 10.1 Permeability model results of PVDF/SiO ₂ MMMs as a function of SiO ₂ nominal volume fraction.	174
Fig. 10.2 Permeability model results of PVDF/MCM-41 MMMs as a function of MCM-41 nominal volume fraction	176
Fig. 10.3 Permeability model results of PVDF/4A MMMs as a function of	178

zeolite 4A nominal volume fraction for (a) He, (b) CO ₂ , (c) O ₂ and (d) N ₂	
Fig. 10.4 P_{eff} of PVDF/SiO ₂ , PVDF/MCM-41, PVDF/4A MMMs and P_v as a function of void thickness	180
Fig. 10.5 Permeability model results based on modified Maxwell equation for (a) PVDF/SiO ₂ , (b) PVDF/MCM-41 and (c) PVDF/4A as a function of the inorganic filler nominal volume fraction	182
Fig. 10.6 Void volume fraction as a function of inorganic filler nominal volume fraction	183
Fig. 10.7 Void thickness as a function of inorganic nominal volume fraction for (a) PVDF/SiO ₂ , (b) PVDF/MCM-41 and (c) PVDF/4A	184
Fig. 10.8 Amorphous polymer volume fraction as a function of inorganic filler nominal volume fraction	185
Fig. 10.9 Permeability experimental——and modelling..... results for (a) PVDF/SiO ₂ , (b) PVDF/MCM-41 and (c) PVDF/4A MMMs	187
Fig. 11.1 Phase diagrams of ternary nonsolvent/solvent/polymer systems.	195
Fig. 11.2 Viscosity of P84/NMP solution as a function of the mass concentration of P84	196
Fig. 11.3 NMP concentration in the vicinity of the P84 solution immersed into the nonsolvent coagulation baths as a function of time	197
Fig. 11.4 SEM micrographs of the cross-sections of the asymmetric membranes prepared using (1) water, (2) ethanol, (3) IPA and (4) acetone as nonsolvent. (A) The overall cross-section, (B) the top layer, and (C) fine pore structure. Membrane preparation conditions: P84 concentration 25.6 wt%; the evaporation time 10 s, the casting solution thickness 300 μ m and the temperature of coagulation bath room temperature	199

Fig. 11.5 3D AFM micrographs of the top layer of the asymmetric membranes prepared using (1) water, (2) IPA, (3) ethanol, and (4) acetone, as nonsolvent. Membrane preparation conditions: P84 concentration 25.6 wt%, the evaporation time 10 s, the casting solution thickness 300 μm and the temperature of coagulation bath at room temperature	201
Fig. 11.6 N_2 adsorption-desorption curves of the asymmetric membranes	202
Fig. 11.7 O_2 permeance and O_2/N_2 selectivities of asymmetric membranes	202
Fig. 11.8 SEM micrographs of the asymmetric membranes prepared using (1)25.6%, (2) 23.1%, (3) 19.4% and (4) 16.7% P84/NMP solution. Preparation conditions: water as the nonsolvent, evaporation time 10 s, casting solution thickness 500 μm and the temperature coagulation bath at room temperature	205
Fig. 11.9 SEM micrographs of the asymmetric membranes prepared using (1) IPA and (2) acetone as a nonsolvent. (A): the overall cross-section view, (B): the top layer view and (C): the pore structure view. Preparation conditions: P84/NMP solution 16.7%; evaporation time 10 s, casting solution thickness 500 μm and the temperature coagulation bath at room temperature.	206
Fig. 11.10 3-dimensional AFM micrographs of the asymmetric membranes prepared using (1)25.6%, (2) 23.1%, (3) 19.4%, and (4) 16.7% P84/NMP solution. Preparation conditions: IPA nonsolvent, evaporation time 10 s, casting solution thickness 500 μm and the temperature coagulation bath at room temperature	207

Fig. 11.11 Effects of varying P84 solution concentration on gas permeance and selectivity of the asymmetric membranes prepared from (a) water/NMP/P84, (b) ethanol/NMP/P84, (c) IPA/NMP/P84 and (d) acetone/NMP/P84	209
Fig. 11.12 SEM micrographs of the asymmetric membranes prepared with casting solution thickness of (1) 1500 μm , (2) 1000 μm , (3) 500 μm and 300 μm . Preparation conditions: nonsolvent water, polymer solution concentration 25.6%, evaporation time 10 s temperature coagulation bath at room temperature.	211
Fig. 11.13 3-dimensional AFM micrographs of the asymmetric membranes prepared with different casting solution thicknesses of (1) 1500, (2) 1000, (3) 500 and 300 μm . Preparation conditions: nonsolvent water, polymer solution concentration of 25.6%; evaporation time 10 s and temperature coagulation bath at room temperature.	212
Fig. 11.14 Effects of varying casting solution thickness on the O_2 permeance and O_2/N_2 selectivity of the asymmetric membranes prepared from water/NMP/P84	212
Fig. 11.15 SEM micrographs of the asymmetric membranes prepared with evaporation times of (1) 10 s, (2) 60 s, (3) 120 s and (4) 300 s. Preparation conditions: water nonsolvent, 500 μm thicknesses, polymer concentration of 25.6% and the temperature coagulation bath at room temperature.	214
Fig. 11.16 3-dimensional AFM micrographs of the asymmetric membranes prepared with different evaporation times (1) 10s, (2) 60s, (3) 120s and (4) 300 s. Preparation conditions: acetone nonsolvent, polymer concentration of 25.6%; 500 μm thickness and temperature coagulation bath at room temperature	215

Fig. 11.17 O ₂ permeance and O ₂ /N ₂ selectivity of the asymmetric membranes prepared from acetone/NMP/P84 for varying evaporation time	216
Fig. 11.18 SEM micrographs of the asymmetric membranes prepared with different coagulation bath temperatures of (1) 0, (2) 25, (3) 60 and (4) 80 °C. Preparation conditions: water nonsolvent, evaporation time 10 s, polymer concentration of 16.7% and casting solution thickness of 500 µm	219
Fig. 11.19 SEM micrographs of the asymmetric membranes prepared from (1) IPA and (2) acetone, (A) overall cross-section view, (B) top layer view and (C) fine pore structure. Preparation conditions: evaporation time of 10 s, polymer concentration of 25.6%, coagulation temperature of 0 °C and casting solution thickness of 500 µm	220
Fig. 11.20 3-dimensional AFM micrographs of the asymmetric membranes prepared with coagulation temperatures of (1) 0, (2) 25, (3) 60 and (4) 80 °C. Preparation conditions: water nonsolvent, polymer concentration of 25.6%, thickness of 500 µm and evaporation time of 10 s	221

List of Tables

Table 1.1 Membrane market share	3
Table 2.1 Summary of membranes based on P84 in the literature review	20
Table 2.2 Summary of membranes based on PVDF in the literature review	25
Table 4.1 Chemical agents	54
Table 4.2 Process parameters for spin-coating	57
Table 4.3 Syntheses of pure PI membrane and PI-silica composite membranes	64
Table 5.1 Transport properties of P84-118 membrane annealed at 80 and 200 °C	78
Table 5.2 Single gas permeability and selectivity of gas pairs for various membrane thicknesses	82
Table 5.3 Single gas permeance for membranes with various thicknesses	82
Table 6.1 Properties of the inorganic fillers	88
Table 6.2 Densities and calculated fractional free volume of membranes.	95
Table 6.3 Results of gas permeation tests and ideal selectivity of gas pairs	99
Table 7.1 Mechanical properties of various membranes	110
Table 7.2 Densities and calculated fractional free volumes of membranes.	114
Table 7.3 Single gas permeability and ideal selectivity of gas pairs	118

Table 8.1 Mechanical properties and decomposition temperatures of the PI and PI-silica composite membranes	124
Table 8.2 Results of elemental analyse for the carbon and carbon-silica composite membranes	128
Table 8.3 Results of XRD analyse and d spacing values for the various membranes	132
Table 8.4 Single gas permeabilities and ideal selectivities of pure PI membranes and PI-silica composite membranes	133
Table 8.5 Single gas permeabilities and ideal selectivities of pure carbon membranes and carbon-silica composite membranes	136
Table 8.6 Comparison of pure gas selectivity and mixed gas selectivity of O ₂ /N ₂	138
Table 9.1 Decomposition temperature (T_d), melting temperature (T_m), crystallizing temperature (T_c), fusion heat (ΔH), crystallinity (χ) and contact angle (CA) of the various membranes	147
Table 9.2 Theoretical density (ρ_c), measured density (ρ_m), void volume fraction (ϕ_v) and modified void volume fraction of membranes	160
Table 9.3 Single gas permeability and ideal selectivity of the membranes	162
Table 11.1 Molar volume (V), boiling temperature (T_b), density (ρ) and solubility parameter of solvent, non-solvents and P84 polymer	192
Table 11.2 Interaction parameters in nonsolvent/solvent/P84 systems at room temperature	194
Table 11.3 Surface tension, viscosity and diffusion coefficients of solvent and nonsolvents	196
Table 11.4 Effects of nonsolvent and polymer concentration on the physical characteristics of the asymmetric membranes	200
Table 11.5 Effects of varying thickness of the casting solution on the physical characteristics of the asymmetric membranes prepared from	209

water/NMP/P84

Table 11.6 Physical characteristics of the asymmetric membranes prepared from water/NMP/P84 and acetone/NMP/P84 for varying evaporation times before immersion. 214

Table 11.7 Properties of the asymmetric membranes prepared from water/NMP/P84, IPA/NMP/P84 and acetone/NMP/P84 with varying temperature of the coagulation bath. 219

List of Symbols and Abbreviations

a	Activity (mole/cm ³)
b	Hole affinity constant (1/atm)
c	Concentration (cm ³ (STP)/cm ³ (polymer))
C_H'	Hole saturation constant (cm ³ (STP)/cm ³ (polymer))
D	Diffusion coefficient (cm ² /s)
D^*	Diffusion coefficient of amorphous polymer (cm ² /s)
d	Average pore diameter (m)
D_{AB}	Diffusion coefficient of A at a lower concentration of B ((cm ² /s))
D_{AK}	Diffusion coefficient in the voids of MMMs (cm ² /s)
D_D	Henry's diffusion coefficient (cm ² /s)
d_g	Diameter of gas molecule (Å)
D_H	Langmuir diffusion coefficient (cm ² /s)
E_{hi}	Hydrogen bonding force (N)
F	Diffusive ratio
F_{di}	London dispersion force (N)
F_{pi}	Dipole force (N)
g_{ij}	Interaction parameters
h	Membrane thickness (μm)
J	Flux (cm ³ /cm ² s)
J_k	Knudsen diffusion flux (cm ³ /cm ² s)

J_p	Poiseuille flow flux ($\text{cm}^3/\text{cm}^2 \text{ s}$)
k	Henry's law constant
L	Thickness (μm)
l	Void thickness ($\text{\AA}$)
M	Molecular weight (g/mole)
n	Structure factor
P	Permeability (Barrer) 1 Barrer = $1 \times 10^{-10} \text{cm}^3(\text{STP}) \text{ cm/s cm}^2 \text{ cmHg}$
$\bar{P}$	Permeance (Barrer/cm)
p	Pressure (Pa)
P_c	Permeability of continuous phase (Barrer)
P_c/P_0	Permeability enhancement
P_d	Permeability of dispersed phase (Barrer)
P_{eff}	Effective Permeability of two phases (Barrer)
P_v	Permeability of voids (Barrer)
P_{3MM}	Permeability of the three-phase MMMs (Barrer)
R	Universal gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$)
R_a	Mean roughness (μm)
R_q	Root mean square of height (μm)
r	Size of crystals (m)
r_k	Kelvin pore radius (m)
S	Solubility coefficient ($\text{cm}^3 (\text{STP})/\text{cm}^3 (\text{polymer}) \text{ Pa}^{-1}$)

S^*	Solubility coefficient of amorphous polymer (cm ³ (STP)/cm ³ (polymer) Pa ⁻¹)
S_v	Solubility coefficient for voids (cm ³ (STP)/cm ³ Pa ⁻¹)
T	Temperature (K)
T_b	Boiling temperature(K)
T_c	Crystallizing temperature (K)
T_d	Decomposition temperature (K)
T_g	Glass transition temperature (K)
T_m	Melting temperature (K)
T_m^0	Equilibrium melting point of the crystals (K)
V	Specific volume (cm ³ /g)
V_A	Molar volumes of A molecule (cm ³ /mole)
V_a	Specific volume of α amorphous PVDF (cm ³ /g)
V_c	Specific volume of α crystalline PVDF (cm ³ /g)
V_g	Polymer specific volume in glassy state (cm ³ /g)
V_l	Polymer specific volume in glassy state in rubbery state (cm ³ /g)
V_m	Molar volume of the gas adsorbate (cm ³ /mole)
V_s	Specific volume of the sample (cm ³ /g)
V_p	Volume of polymer (cm ³)
V_v	Volume of voids (cm ³)
V_w	van der Waals volume (cm ³ /mole)
V_0	Specific volume at 0K ((cm ³ /g))

v_i	Molar volume (cm ³ /mole)
W_{dry}	Weight of dense P84 membrane before swelling process (g)
W_{wet}	Weight of dense P84 membrane after swelling process (g)
α	Amorphous polymer fraction
β	Immobilisation factor
γ	Surface tension of the gas adsorbate (mN/m)
ΔH	Latent heat of fusion (J/mole)
ΔH_m^0	Melting enthalpy of a fully crystalline polymer (J/mole)
δ_h	Solubility parameter of hydrogen bonding force component (J/cm ³) ^{1/2}
δ_d	Solubility parameter of London dispersion force component (J/cm ³) ^{1/2}
δ_p	Solubility parameter of dipole force component (J/cm ³) ^{1/2}
δ_{sp}	Overall solubility of polymers (J/cm ³) ^{1/2}
η_B	Viscosity of species B (mPa s)
θ	Contact angle of the gas adsorbate and the pore wall (degree)
λ	Mean free path of the gas penetrant (Å)
ε	Porosity
ρ	Density (g/cm ³)
ρ^*	Molar density (g/mole)
ρ_{am}	Density of α amorphous crystalline (g/cm ³)
ρ_{cr}	Density of α crystalline PVDF (g/cm ³)
ρ_m	Measured density (g/cm ³)

ρ_t	Theoretical density (g/cm ³)
ρ_l	Density of the nonsolvents (g/cm ³)
ρ_3	Density of polymer P84 (g/cm ³)
σ_A	Surface tension of A species (mN/m)
σ_B	Surface tension of B species (mN/m)
τ	Tortuosity factor
Φ	Volume fraction
φ_p	Volume fraction of the P84 polymer
χ	Crystallinity
ϕ	Volume fraction of filler in the combined two phases
ϕ'	Volume fraction of inorganic filler and voids
ϕ_d	Volume fraction of dispersed phase
ϕ_f^N	Inorganic filler nominal volume fraction
ϕ_v	Void volume fraction

Abbreviations

AFM	Atomic force microscopy
APDEMS	3-aminopropyl-diethoxymethyl silane
APTES	3-Aminopropyltriethoxysilane
CA	Contact angle
ATR	Attenuated total reflectance
CMS	Carbon molecular sieve
CNT	Carbon nanotube
CTAB	Cetyltrimethylammonium bromide
CTC	Charge transfer complexes
DCMD	Direct contact membrane distillation
DMAc	N, N-Dimethyl acetamide
DSC	Differential scanning calorimetry
EDA	Ethylenediamine
FFV	Fractional free volume
FS	Fumed silica
FTIR	Fourier transformed infrared spectroscopy
GC	Gas chromatograph
IPA	Isopropanol
MCNT	Multi-walled carbon nanotube
MMMs	Mixed matrix membranes
MSU-J	Mesostructured silica

List of symbols and abbreviations

MTMOS	Methyl trimethoxysilane
NMP	N-methyl-2-pyrrolidinone
ODA	4, 4'-oxydianiline
P84	3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride and 80% methylphenylene-diamine+20% methylene diamine)
PAA	Polyamic acid
PAH	Poly (allylamine hydrochloride)
PBI	Polybenzimidazole
PD	Packing density
PDMS	Polydimethylsiloxane
PEI	Polyetherimide
PES	Polyethersulfone
PI	Polyimide
PMDA	Pyromellitic dianhydride
PMMA	Poly(methyl methacrylate)
PMP	Poly(4-methyl-2-pentyne)
PP	Polypropylene
PPO	Polyphenyleneoxide
PSF	Polysulfone
PTMSP	Poly(1-trimethylsilyl-1-propyne)
PV	Pervaporation
PVAc	Polyvinyl acetate
PVDF	Poly(vinylidene fluoride)

List of symbols and abbreviations

PVP	Polyvinylpyrrolidone
PTFE	Polytetrafluoroethylene
SCNT	Single-walled carbon nanotube
SEM	Scanning electron microscopy
SFV	Specific free volume
TFP	Tetrafluoropropanol
TEOS	Tetraethyl orthosilicate
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
VMD	Vacuum membrane distillation
XDA	p-xylenediamine
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

Chapter 1 Introduction

1.1 Research background

For more than 20 years, membrane separation has been of interest because of its vital role in the modern industry. Compared with the traditional separation technologies, such as cryogenic techniques and absorption and pressure swing adsorption technology, membrane separation possesses significant advantages. Firstly, energy requirements and capital investment costs are much lower. Secondly, the necessary process equipment is simple, compact and relatively easy to operate and control. In addition, the equipment can be modular and can be easily scaled up or operated at partial capacity.

Generally, membranes for gas separation can be categorised as inorganic membranes and organic membranes depending on the constituent materials. Inorganic membranes, such as zeolite membrane and carbon molecule sieving membrane, exhibit excellent selectivity because of their regular pore structures. However, most inorganic membranes are very brittle and difficult to process. Comparatively, gas separation based on polymeric membrane has attracted more attention because of its ease in processability and much lower capital investment.

As a permselective barrier between two homogenous phases, polymeric membranes can be favourably permeated by some gas components of the mixture while significantly rejecting the other components. Generally, the gas separation properties of membranes are dependent on the membrane materials and membrane structures. An ideal gas separation membrane should exhibit the following characteristics: (1)

high selectivity for a given pair of gases, (2) high gas fluxes for the more permeable gas component, (3) resistance to high temperature, (4) mechanical strength for assembly into modules, (5) tolerance to contaminants, (6) manufacturing reproducibility, and (7) low production cost [1]. Among these criteria, high selectivity and high gas fluxes are the basic requirements for a feasible gas separation process: the higher selectivity results in higher separation efficiency and lower operating cost of the membrane system whilst the higher fluxes give rise to smaller membrane area required and therefore lower capital cost of the membrane system.

Recently, commercial interest in membrane-based gas separation has greatly increased with the development of new membrane materials and novel membrane structural designs. Until now, polymeric membranes have been successfully used in several gas separations such as oxygen/nitrogen enriched air, hydrogen recovery from purge steam in ammonia plants or hydrogenation processes, natural gas dehydration, acid-gas treatment and hydrocarbon recovery [2]. Table 1 presents the membrane market share predicted by Baker [3], which shows a remarkable increase during the last two decades. A considerable amount of work is presently in progress in research laboratories to improve the performance of extant membrane process for gas separation as well as to extend the range of applications of this technology. The “heart” of any membrane separation process is the membrane itself. Therefore, much research work is being devoted to the development of membranes that exhibit both high selectivity and a high intrinsic permeability to specific gases.

Table 1.1 Membrane market share [3]

Separation	Membrane market (US\$ million)		
	2000	2010	2020
Nitrogen from air	75	100	125
Oxygen from air	<1	10	30
Hydrogen	25	60	100
Natural gas	30	90	220
Vapour/Nitrogen	10	30	60
Vapour/Vapour	0	30	125
Other	10	30	100
Total	150	350	760

1.2 Objectives and Scope

This research study consists of two main aspects, which are the fabrication of mixed matrix membranes (MMMs) and asymmetric membranes for gas separation. Two types of polymers, *i.e.*, rubbery PVDF and glassy P84, were used as the matrix and three types of inorganic fillers, *i.e.*, nonporous SiO₂, mesoporous MCM-41 and microporous zeolite 4A, were used as the dispersed inorganic fillers. The main objective of this work is to investigate the relationship between the membrane structures and the separation performance of the membranes. Emphases are placed on the selection of the inorganic fillers, the modification of SiO₂ surface and the membrane preparation methods to achieve good separation performance of the resulting MMMs. The variables of interests such as the effect of membrane thickness and heat treatment, the inorganic filler type and the surface modification and the content of SiO₂ on gas separation performance of MMMs were discussed. For MMMs, the interaction between polymer matrix and molecular sieve phases was carefully examined to investigate the gas transport mechanism in MMMs. On the other hand, the development of asymmetric membranes with an ultrathin

dense-selective layer was also a major interest in this research study.

To achieve the above objectives, the scope of this study is outlined as follows:

1. Investigation of the effect of membrane thickness and heat treatment on the properties of polyimide P84 membranes for gas separation.
2. Preparation of MMMs based on P84 polyimide by incorporating three types of inorganic fillers - nano-SiO₂, zeolite 4A and MCM-41.
3. Study of the effects of the surface modification of SiO₂ and the content of SiO₂ on the gas separation performance of the resulting MMMs.
4. Preparation of a series of PI-silica MMMs by the sol-gel method.
5. Experimental and theoretical study of MMMs based on PVDF matrix.
6. Preparation of asymmetric membranes based on P84 polyimide by phase inversion technique.

This dissertation is organized and structured into twelve chapters and four appendices.

Chapter One is an introductory chapter of this dissertation. It gives the introduction of the membrane separation characteristics, basic concepts, important industrial applications and transport mechanisms of gas separation membranes. The research objective and outline of this dissertation are also presented in this chapter.

Chapter Two presents a literature review which summarises the historical development of membrane technologies, the basic concepts and the transport mechanisms of different membranes, and the applications of two types of membrane materials, *i.e.*, P84 and PVDF. The advantages, the development of MMMs and the

models for the prediction of the gas separation performance of MMMs were also introduced in this chapter.

The general experimental approaches and methodologies, along with the materials involved in all areas are documented in Chapter Four. The details of the membrane preparation and membrane physical characterisation techniques are addressed. The constant volume-variable pressure method for both pure gas and mixed gas permeation tests of membranes are also reported in this chapter.

As a preliminary work, Chapter Five reported the effect of membrane thickness and heat treatment on the gas transport properties of P84, which provided guidance for the further preparation of MMMs. In Chapter Six, the three types of inorganic fillers, SiO₂, mesoporous MCM-41 and microporous zeolite 4A, were comparatively studied as the dispersed phase to improve the gas performance of P84 polymer. Results indicated that SiO₂ nanoparticles were the most effective in terms of the enhancement of gas separation performance. Subsequently, in Chapter Seven, the P84/SiO₂ MMMs were preferentially selected and the effects of the surface modification and the content of SiO₂ on the gas separation performance were investigated in detail. For a comparison purpose, in Chapter Eight, a series of PI-silica MMMs were also prepared by using the sol-gel technique. Compared with MMMs prepared by the direct mixing method, the PI-silica MMMs prepared by the sol-gel technique showed much stronger interaction between the polymer phase and the inorganic phase. However, no significant enhancement of gas separation performance was obtained from these PI-silica MMMs. Alternatively, carbon-silica

composite membranes prepared by the pyrolysis of the PI-silica MMMs showed excellent gas separation performance. In Chapter Nine, a rubbery polymer PVDF was selected as the matrix to prepare MMMs. Unexpectedly, there was no significant difference in the gas separation performance of the resulting MMMs although the structural characteristics of the inorganic fillers such as pore size and particle size were different. In Chapter Ten, in order to provide a good explanation of the results, the single gas transport properties were theoretically predicted using Maxwell, Higuchi, Bruggeman and Bottcher-Landauer models. By taking the effects of crystallinity on the gas permeability into consideration, a model was developed which produced good predictions of the gas permeabilities of the resulting MMMs. Chapter Eleven reports the preparation of asymmetric membranes based on P84 polymer. The effects of the type of nonsolvents, evaporation time, concentration, casting membrane thickness and the temperature of the nonsolvent bath on the separation performance of the symmetric membrane were investigated.

General conclusions drawn from this research study are summarized in Chapter Twelve. Inclusive in this ending chapter are some recommendations/suggestions for future research related to this work. Appendix I showed the calculation of some constants which were used in the modelling work. Appendix II represented a typical data sheet for the measurement of permeability of the sample. Appendix III showed the calibration of GC-MS for the measurements of the concentrations of the solvents and the nosolvents. The publications arising from this project were listed in Appendix IV.

Chapter 2 Literature Review

2.1 History of polymer membranes for gas separation

In 1830, Mitchell [4] discovered that balloons of natural rubber filled with hydrogen which had ascended in his lecture room would descend after a period of time because of the escape of hydrogen. Mitchell further tested the rates of escape of many different gases and found that there was a hundred-fold range between CO₂ and ammonia.

The foundation for gas separation was laid by Graham [5]. He performed the first recorded experiment in the transport of gases and vapours in polymeric membranes and published concepts for gas permeation in terms of a “solution-diffusion” mechanism which was considered to be one of the two most important model concepts for the understanding of gas diffusion phenomenon. The other one was the first Fick’s law proposed by Fick in 1855.

In 1907, Benchoh [6] devised a technique to prepare nitrocellulose membrane with controllable pore size structure. Subsequently, with the development of the concept of “pore size distribution”, Karplus [3] improved the technique and as a result, microporous nitrocellulose membranes became commercially available in the 1930s

By 1960, the elements of modern membrane science had been developed and considerable work had focused on the relationship between structures and performances in gas separation membranes. However, the available membranes suffered some problems, such as low fluxes and selectivity, high cost and unreliability, which restricted their widespread use.

Discoveries by Loeb and Surirajan [7] in the 1960s of the means to produce asymmetrically skinned cellulose acetate membrane for reverse osmosis were finally applied to gas separation in 1970. This was the first successful example which transferred membrane separation from a concept to an industrial process. As a result, further progress in membrane science and technology gradually established the foundation of commercial membranes for microfiltration, ultrafiltration and electrodialysis. At the same time, the separation of gas mixtures of industrial interest with membranes became economically competitive in the late 1970s for certain applications, *e.g.*, the separation of hydrogen from the stream of ammonia [8].

Soon after DuPont's discovery of melt spun polyester hollow fine fibres for high pressure hydrogen application, Monsanto Inc., USA, announced a revolutionary concept of the "resistance composite" membrane that could be formed from hydrophobic materials. The good performance exhibited by the Monsanto system in hydrogen separation led to a favourable impression of the technology and promoted its extension into more demanding areas [9].

The progress in membrane science and technology was accelerated during the 1980s by the development of synthetic polymeric membrane materials in several companies including Dow, DuPont, Air Products, Allied Signal as well as smaller research firms such as Bend Research, Membrane Technology and Development. Universities also became strongly involved in this field. During this period, significant progress was made in virtually every aspect of membrane science and technology, including improvements in membrane formation process, chemical and

physical structure, configuration and applications [10].

By the 21st century, membrane-based gas separation has become an indispensable chemical process in industry which competes successfully with well established traditional gas separation processes. Membrane-based gas separation has been employed in more and more industrial processes including acid gas separation, natural gas treatment and gasoline vapour recovery.

2.2 Membrane materials

For the last three decades, remarkable progress has been made in polymer synthesis with numerous novel polymeric materials being made commercially available. Moreover, with the understanding of the mechanism of gas transport in polymeric membranes and their structure/performance relationship, many polymers with special structures can be designed and successfully synthesised as membrane materials for gas separation. These novel “tailor-made” polymers possess dramatically higher selectivity and permeability for given applications as compared with the traditional polymers.

2.2.1 P84 polymer

In this project, P84 (BTDA-TDI/MDI, co-polyimide of 3, 3' 4, 4' benzophenone tetracarboxylic dianhydride and 80% methylphenylene- diamine + 20% methylene diamine) was chosen as one of the membrane materials for gas separation. P84 is a recent commercially available polyimide and has received significant attention for applications as a novel membrane material in ultrafiltration [11], nanofiltration [12], gas separation [13-28] and as a precursor in the preparation of carbon molecular

sieve membranes [29-31]. The chemical structure of P84 is shown in Fig. 2.1. This polymer possesses excellent chemical resistance, high mechanical strength, thermoxidative stability and particularly high selectivity with superior anti-plasticisation properties against CO₂ in gas separation.

Fig. 2.1 Chemical structure of BTDA-TDI/MDI (P84) co-polyimide

Chung and his research group in the National University of Singapore focused mainly on P84 as a novel material for pervaporation involving the preparation, the characterisation and applications of P84 membranes. Many novel P84 membranes with different structures including dense flat P84 membranes, asymmetric P84 membranes and P84 hollow fibre membranes were originally prepared [13-23].

The first study of sorption, swelling and permeation of aqueous ethanol, 2-propanol (IPA) and tert-butyl alcohol through P84 dense membranes was conducted by Qiao and Chung [13]. Among the three alcohol/water systems, P84 membranes were most seriously swollen by ethanol because of their strong affinity and consequently both water permeability and ethanol permeability were the highest while the selectivity was the lowest. However, P84 membranes exhibited much better separation performance in IPA/water and tert-butyl alcohol/water systems. As suggested by Qiao and Chung [13], this superior separation performance resulted from four factors: (1) rigid P84

chains with a small d-space, (2) the lesser affinity of P84/IPA and P84/tert-butyl alcohol, (3) a high sorption selectivity, and (4) steric hindrance induced by bulky IPA and tert-butyl alcohol molecules.

Asymmetric membranes, based on P84 polymer with superior selectivity and high flux, were prepared by Qiao *et al.* [14] for the pervaporative dehydration of IPA by a dry-wet phase inversion method. It was observed that the performance of P84 membranes was greatly dependent on the thickness and the thermal history. Heat treatment effectively enhanced selectivity but reduced permeability by reducing the defects of the membrane skin layer. The best separation performance had a flux of 432 g/m² h and a separation factor of 3508 at 60 °C for a feed stream consisting of 85 wt.% IPA.

Integrally, skinned P84 hollow fibres for pervaporative dehydration of IPA were prepared by phase inversion process and the effects of spin conditions and silicone rubber modification on fibre formation, morphology and pervaporation performance were investigated by Liu *et al.* [15]. It was found that hollow fibres prepared by wet-spinning at a higher dope/bore fluid flow speed and a lower coagulation temperature showed better separation performance, and that both silicone rubber coating and heat treatment could greatly enhance the separation factor of the membranes. A very impressive separation performance, *i.e.*, flux 883.5 g/m² h and separation factor 10585, was obtained with hollow fibres spun from optimisation conditions for dehydration of 85 wt% IPA in water mixture at 60 °C.

Zeolite 5A and 13X incorporated into P84 matrix to prepare MMMs with enhanced

permeability and selectivity for the pervaporation dehydration of IPA was reported by Qiao *et al.* [16]. The effects of annealing temperature on the interaction between zeolite and polymer and the effects of zeolite 13X loading on membrane formation and pervaporation separation performance for dehydration of IPA were investigated. It was found that a higher annealing temperature was more favourable for improving the adhesion between zeolite and polymer phase and enhancing charge transfer complexes (CTCs) formation. These resultant MMMs had comparably high selectivity. The P84/zeolite 13X MMMs had much higher permeability than P84/zeolite 5A MMMs owing to their bigger pore size, larger pore volume, higher sorption capacity and better adhesion properties of the interface. The addition of zeolite 13X reduced activation energy for water permeation through the membrane but increased that for IPA permeation. In contrast, the addition of zeolite 5A increased the activation energy for both water and IPA permeation. Both permeability and selectivity of P84 membranes were significantly improved after the addition of zeolite 5A and 13X. Pervaporation permeability increased with increasing zeolite 13X loading while the selectivity achieved a maximum at 30 wt% zeolite 13X loading. With further increases in the zeolite 13X loading, the adhesion between zeolite and polymer became poor and the membrane selectivity declined. A comparison between pervaporation and gas separation results revealed that pervaporation membranes could tolerate a higher degree of interstitial defects than gas separation membranes because of the stronger molecular interactions between the feed and the polymer and the larger molecular size difference between the penetrants in the pervaporation.

P84 membranes, chemically modified by two cross-linking agents, *i.e.*, p-xylenediamine (XDA) and ethylenediamine (EDA), were prepared by Qiao *et al.* [17] for pervaporation dehydration studies and the effects of cross-linking on the performance of dense and asymmetric membranes were investigated. The cross-linking reaction induced by EDA was much faster than that by XDA. EDA cross-linked membranes showed a closer chain packing and stronger amide peaks. The pervaporation tests showed that P84 membranes with increasing cross-linking intensity exhibited an increasing separation factor with the compensation of lower flux for pervaporation dehydration of IPA. However, a further increase in the degree of cross-linking could swell up the polymeric chains and result in lower separation performance. Furthermore, the effects of heat treatment after p-xylenediamine cross-linking had been studied. It was confirmed that post heat treatment after cross-linking reaction dramatically enhanced the performance of membranes due to the formation of charge transfer complexes (CTCs). A low-temperature heat treatment may develop pervaporation membranes with high flux and medium separation factor whereas a high-temperature heat treatment may produce membranes with high separation factor with medium flux. The study presented a novel method by which one could easily tailor the membrane performance with high flux and reasonable separation factor or high separation factor with reasonable flux through the proper control of cross-linking time and heat treatment temperature.

Dual-layer asymmetric P84 hollow fibre membranes with PES/zeolite beta mixed matrix dense selective layers had been successfully fabricated by Li *et al.* [18]. The

effects of spinning rate, heat treatment and silicone rubber coating modification on the morphology and performance of resultant membranes were investigated. It was found that heat treatment together with silicon rubber coating modification proved to be an effective method to eliminate the defects on the outer layer surface of dual-layer hollow fibres membranes or reduce voids induced by the unfavourable interaction between polymer and zeolite phases. The resultant dual-layer hollow fibres showed comparable permeability and selectivity of O_2/N_2 and CO_2/CH_4 in both pure and mixed gas tests compared with that of neat polyethersulfone (PES) dense films, which was explained from the polymer chain rigidification and partial pore blockage of zeolite beta.

P84/PES dual-layer hollow fibre membranes were fabricated by the co-extrusion phase inversion process for the dehydration of IPA and the effects of spinning conditions *e.g.* air gap distances, outer and inner layer dope flow rates, and post-treatments including heat treatment and cross-linking modifications, on membrane morphology and pervaporation performance were investigated by Liu *et al.* [19]. They found that the intrusion of non-solvent from the outer-layer may propagate the formation of macrovoids into the inner-layer and that macrovoids in the outer-layer were significantly suppressed in the dry-jet wet-spun fibre as compared to the wet-spun dual-layer hollow fibres. Heat treatment at 200 °C and chemically modification of p-xylenediamine significantly increased separation factor with slight decrease in flux, It was demonstrated that the dual-layer hollow fibre membranes exhibited a comparable separation performance with much less polymer materials.

The material cost of P84/PES dual-layer hollow fibre was nearly half that of P84 single-layer hollow fibre membranes.

Widjojo *et al.* [20] prepared dual-layer Ultem/P84 hollow fibre membranes by using dual coagulation baths and different spinneret designs, and investigated the effects of first external coagulant and bore fluid chemistry as well as air-gap distance on the outer and inner layer morphology of the dual-layer hollow fibres. They found that dual-layer hollow fibre membranes spun with a longer air gap showed a larger size closed cell structure as compared with those spun at a shorter air gap possibly due to the partial phase inversion induced by water vapour at 65% relative humidity. In addition, the outer layer of hollow fibres spun using water or methanol in the first coagulation bath showed mostly an open-cell structure whereas those spun using ethanol or 2-propanol exhibited mostly a closed-cell structure. To fulfill the delamination free requirement for an ideal dual-layer hollow fibre for pressure-driven separation processes, two novel methods were proposed in their work: (1) the addition of aluminium oxide (Al_2O_3) nanoparticles in the inner layer followed by heat treatment, and (2) the introduction of early convective premixing with the aid of an indented and heated dual-layer spinneret. The first method had reduced the degree of shrinkage of the inner layer during heat treatment. Consequently, it lowered the heat-treatment temperature to avoid any delamination, *e.g.*, from 175 °C for 1 h to 150 °C for 2 h. The second method facilitated interlayer molecular diffusion and thus eliminated delamination during the spinning process [20].

Wang *et al.* [21] fabricated novel dual-layer hollow fibre membranes with

polybenzimidazole (PBI) selective layer and P84 supporting layer by the dry-jet wet phase inversion process for the dehydration pervaporation of tetrafluoropropanol (TFP). The pervaporation tests showed that PBI/P84 membrane possessed superior water selectivity as well as high permeation flux. At 60 °C, the PBI/P84 dual-layer hollow fibre membrane showed a permeation flux of 332 g/ (m² h) and a separation factor of 1990 for a feed solution containing of 85 wt% TFP. It was suggested that the high separation factor was attributed to the preferential water sorption and the significant diffusivity difference between TFP and water because of the strong water affinity of PBI and a much smaller molecular size of water. Further investigation revealed that an increase in feed temperature would greatly increase the permeation flux but seriously deteriorate the water selectivity.

Using a precursor of dual-layer polyethersulfone (PES)-zeolite β /P84 composite hollow fibres, Li *et al.* [22] fabricated a novel dual-layer carbon/zeolite nanocomposite hollow fibre membrane by pyrolysis at 800 °C. These dual-layer carbon/zeolite nanocomposite membranes with novel structure possessed a combined effect of carbon molecular sieve (CMS) and zeolite materials, which resulted in a remarkable improvement of dual layer hollow fibre membranes in the performance of oxygen enrichment and natural gas separation through the molecular sieving mechanism. The gas permeation tests showed that these nanocomposite membranes exhibited a significantly enhanced O₂/N₂ and CO₂/CH₄ selectivity of 11.3 and 152, respectively.

Blends of Torlon/P84 with cross-linking of p-xylenediamine were investigated by

Teoh *et al.* [23] as new materials for the dehydration of isopropanol (IPA). It was confirmed that Torlon/P84 blends were miscible with a single glass transition temperature detected by differential scanning calorimetry (DSC). The amidation reaction between the cross-linking agent and the polymer imide rings was verified by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. A tighter chain packing after chemical modification was confirmed by X-ray diffraction (XRD) spectra. Torlon/P84 blended membranes cross-linked with p-xylenediamine had enhanced water selectivity with comparatively high permeation flux. It was suggested that the p-xylenediamine induced cross-linking reactions resulting in greater chain packing and the reduction of free volume.

Wessling and his research group [24-28] mainly focused on P84 as membrane materials for gas separation because of its high selectivity and excellent resistance of CO₂ plasticization. P84 membranes including dense P84 membranes and P84 hollow fibre asymmetric membranes were prepared and particularly the behaviour of CO₂ plasticisation was investigated.

Bos *et al.* [24] prepared Matrimide/PSF and Matrimide/P84 blending membranes and investigated their CO₂ plasticisation behaviour from mixed gas experiments. It was found that the homogeneous blending of Matrimide/PSF stabilised the single gas permeation properties of polymers and improved plasticisation behaviour, but reduced permeation and separation performance. Blending the polyimide Matrimid with P84 stabilised the polymer against plasticisation while simultaneously improving the separation performance.

The transport properties and the separation performance of flat sheet and hollow fibre membranes based on P84 polyimide were investigated by Barsema *et al.* [25]. The permeabilities of He, CO₂, O₂ and N₂ were measured at different feed pressures and temperatures. The achieved ideal selectivity coefficients were 285–300 for He/N₂, 45–50 for CO₂/N₂, and 8.3–10 for O₂/N₂, which were in the range of the highest values reported ever for polymeric membranes. The permeability of CO₂ was relatively low and independent of feed pressure indicating that the P84 dense membranes were of excellent resistance to CO₂ plasticisation. To the contrary, the permeance of CO₂ through the asymmetric P84 hollow fibre membranes increased with pressure, indicating the plasticisation behaviour of asymmetric membranes. However, no evidence of plasticization was observed when a CO₂/N₂ (80/20) mixture was fed to the hollow fibre membranes for pressures up to 30 bar. These results indicated that P84 was a promising material for the preparation of gas separation membranes with extremely high selectivity coefficients. Its relatively low permeability can be compensated by the optimisation of the spinning procedure and the formation of ultra-thin asymmetric hollow fibres.

The transport properties of five asymmetric membranes including pure Matrimid, blends of Matrimid/polyethersulfone, blends of Matrimid/P84, cellulose acetate and polyphenyleneoxide (PPO) were comprehensively investigated by Visser *et al.* [26] for the separation of carbon dioxide/methane mixtures. Competitive sorption and plasticisation were confirmed to be two critical mechanisms for the analysis of the experimental data. Of all asymmetric membranes investigated, P84/Matrimid

membranes exhibited the most promising CO₂/CH₄ separation performance. The separation performance improved with decreasing CH₄ fugacity, which was interpreted because strong competitive sorption effects and plasticization effects did not influence the mixed gas separation performance too much. However, at the lowest CH₄ fugacity and higher CO₂ fugacity, the separation properties started to decline due to significant plasticization.

The transport properties of two asymmetric hollow fibre membranes based on pure Matrimid and the blend of Matrimid/P84 were investigated by Visser *et al.* [27] using single, binary and ternary C₃H₆/C₃H₈. From the single gas permeation tests, it was found that C₃H₆ was a much stronger auto-plasticiser than C₃H₈. For the Matrimid/P84 membranes, the plasticisation of propylene resulted in increasing permeance of propane but kept propylene permeance constant in the binary mixture tests. The presence of 50 vol.% methane in the feed gas diminished the effect of C₃-plasticization in the ternary mixture tests. Plasticisation influenced the separation performance of both asymmetric pure Matrimid membranes and Matrimid/P84 blending membranes, but for the latter, the effect was much less pronounced.

Sterescue *et al.* [28] prepared P84 dense polymer films doping with aliphatic hyperbranched polyester, Boltorn (H40), with various concentrations and investigated their permeation properties. The dispersion of various concentrations of H40 (1, 5 and 10 wt%) in P84 membranes decreased gas permeability in comparison to pure P84 while the selectivity generally remained constant. The decrease of gas permeability was attributed to the increased intersegmental mobility of the polymer chain,

clustering of H40 and phase separation between the polymer and H40 [28].

Table 2.1 Summary of membranes based on P84 in the literature review

Membrane type	Application	Performance	Reference
Dense flat P84 membrane	Alcohol/water	Na	13
Asymmetric flat P84 membrane	IPA/water	A flux of 432 g/m ² h and a separation factor of 3508	14
P84 hollow fibre membrane	IPA/water	A Flux of 883.5 g/m ² h and a separation factor of 10585	15
P84/13X and P84/5A dense flat membranes	IPA/water	Na	16
P84 dense flat and asymmetric membranes	IPA/water	A flux of 1015 g m ⁻² h ⁻¹ and a selectivity of 170	17
P84 hollow fibre with PES/zeolite beta selective layers	O ₂ /N ₂ ; O ₂ /CH ₄	Comparable permeability and selectivity with neat PES membrane	18
P84/PES dual-layer hollow fibre membranes	IPA/water	Na	19
Dual-layer Ultem/P84 hollow fibre membranes	O ₂ /N ₂	O ₂ permeance of 0.9×10 ⁶ cm ³ (STP)/cm ² s cmHg and O ₂ /N ₂ selectivity of 6.34	20
Dual-layer P84/PBI hollow fibre membranes	TFPA/water	A flux of 332 g/(m ² h) and a separation factor of 1990	21
Dual-layer carbon/zeolite nanocomposite hollow fibre membrane	O ₂ /N ₂ and CO ₂ /CH ₄	O ₂ /N ₂ selectivity of 11.3 and CO ₂ /CH ₄ selectivity of 152	22

Torlon/P84 blend membrane	IPA/water	A separation factor of 185 and flux of 1000 g/m ² h.	23
Matrimide/P84 blending membranes	CO ₂ /CH ₄ separation	Improved resistance to plasticization and selectivity	24
P84 flat sheet and hollow fibre membranes	Gas separation (He, N ₂ , O ₂ and CO ₂)	Selectivity: 285–300 for He/N ₂ , 45–50 for CO ₂ /N ₂ , and 8.3–10 for O ₂ /N ₂ .	25
Matrimid/P84 asymmetric membranes	O ₂ /N ₂ , C ₃ H ₆ /C ₃ H ₈) and CH ₄ /C ₃ H ₆ /C ₃ H ₈	O ₂ permeability: 0.49; O ₂ /N ₂ selectivity: 7.9	26, 27
P84 dense polymer films doping with polyester	Gas separation (N ₂ , O ₂ and CO ₂)	Decreased permeability with slight increases in selectivity	28

2.2.2 Poly(vinylidene fluoride) (PVDF)

El-Hibri and Paul [32] first reported the gas sorption and transport properties of poly(vinylidene fluoride) (PVDF) and investigated the effects of uniaxial drawing and processing temperature on these properties. Solubility and diffusion coefficients were measured for He, H₂, Ar, O₂, N₂, CH₄ and CO₂ and correlated with the Lennard-Jones potential and mean molecular diameter of the gas, respectively. It was found that the permeability coefficient and the diffusion coefficient decreased significantly with uniaxial drawing and that the magnitude of this effect was much more pronounced with increasing molecular diameter of the penetrants and with decreasing drawing temperature. The permeability coefficients and the diffusion coefficients of PVDF films annealed above 75 °C showed an increase in these properties as opposed to the effect of drawing. In contrast, the solubility coefficients were almost independent of the processing treatments such as drawing and

annealing.

Li and his research group [33-35] prepared poly(vinylidene fluoride) (PVDF) hollow fibre membranes by dry/wet and wet phase inversion methods. Dimethylacetamide (DMAc) was used as a solvent for PVDF. Poly(vinyl pyrrolidone) (PVP) and lithium perchlorate (LiClO_4) were individually used as additives. The membranes were characterised in terms of the water flux, molecular weight cut-off, gas permeation fluxes, and effective surface porosity. The effects of polymer concentration, air-gap, additive properties and coagulant properties on the permeation properties and membrane structures were examined in detail. It was found that highly permeable PVDF hollow fibre membranes could be prepared from a polymer dope containing low molecular weight PVP and using ethanol as the internal coagulant. The resulting PVDF hollow fibre membranes had been applied for the removal of ammonia from water and a mathematical model was proposed to simulate the ammonia removal in PVDF hollow fibre modules, which matched well with the experimental results. It was found that the hydrophobicity and the effective surface porosity of the resulting PVDF hollow fibre membranes significantly affected the ammonia removal and that the higher pH value of water was favourable for the removal of ammonia. In contrast, the initial concentration of ammonia and the feed velocity of the acid stripping solution had negligible effects on the ammonia removal. The experimental data agreed well with the modelling results [36].

Matsuura and his research group [37-38] prepared PVDF hollow fibre membranes by the dry/wet spinning technique using N, N-dimethylacetamide, ethanol aqueous

solution and 1, 2-ethanediol as the solvent, nonsolvent and the additive, respectively. The effect of the additive concentration on the morphological properties of the hollow fibres was studied using atomic force microscopy (AFM) and scanning electron microscopy (SEM). The liquid entry pressure of water (LEP_w), the porosity and the pore sizes of the hollow fibres were evaluated. They also applied PVDF flat-sheet membranes with different pore sizes and pore size distribution for the separation of chloroform–water mixtures by pervaporation (PV) and vacuum membrane distillation (VMD). For the VMD process, a more general theoretical model that considers the pore size distribution, the solution-diffusion contribution through nonporous membrane portion, and the gas transport mechanisms through the membrane pores was developed and was based on the kinetic theory of gases. The contribution of each mechanism was analyzed. A comparative study was made between both membrane separation technologies [37, 38]

Chung and his research group [39, 40] applied the co-extrusion technique for the fabrication of dual layer hydrophilic–hydrophobic hollow fibres for the direct contact membrane distillation (DCMD) process. The effect of nonsolvents on the morphology of the PVDF membranes was investigated. They found that weak coagulants could induce a three-dimensional porous structure in the PVDF membranes with high surface and bulk porosities, big pore size, sharp pore size distribution, high surface contact angle and high permeability but rather weak mechanical properties. The resulting hollow fibres with flux as high as 55 kg/(m² h) at 90 °C for the DCMD process was achieved. They further explored the fundamental

principles of fabricating poly(vinylidene fluoride) (PVDF) hollow fibre membranes and elucidated the correlation among membrane morphology, crystallinity and mechanical properties as functions of non-solvent additives and dope rheology in the phase inversion process. It was found that the phase inversion of semicrystalline PVDF membranes was dominated by liquid–liquid demixing or solid–liquid demixing accompanying crystallisation, depending on the strength of the non-solvent. As a result, the membrane morphology transformed from an interconnected-cellular type to an interconnected-globule transition type with lower mechanical strengths when adding water, methanol, ethanol or isopropanol into the spinning dopes or into the coagulation bath. The crystallinity and size of spherulitic globules in the morphology were controlled by the amounts of non-solvents present in the systems. PVDF hollow fibre membranes with inner skinless structures were fabricated by Xu *et al.* [41] using phase inversion technique for CO₂ separation and absorption in gas–liquid membrane contactors. The spinning dope solution was prepared with DMAc as the solvent, lithium chloride and polyvinylpyrrolidone (PVP) as the non-solvent additives. The investigation results indicated that the composition of internal coagulants had significant impacts on the thickness and structures of the inner skin layer and that an inner skinless surface could be formed using a 30 wt% water–DMAc mixture. Gas permeation tests showed that PVDF hollow fibres with an inner skinless surface had a higher CO₂ absorption rate than other PVDF and polypropylene (PP) membranes and attained performance levels equivalent to a polytetrafluoroethylene (PTFE) membrane. It was suggested that PVDF membranes

could be a cost-effective alternative for gas–liquid membrane contactors in applications of CO₂ separation and absorption.

Table 2.2 Summary of membranes based on PVDF in the literature review

Membrane	Application	Performance	Reference
PVDF dense membrane	Gas separation(He, N ₂ , O ₂ H ₂ and CO ₂)	Permeability of 7.16, 2.15, 0.344 and 0.093 Barrer for He, CO ₂ , O ₂ and N ₂ , respectively	32
PVDF Hollow fibre membranes	Water/ammonia	N ₂ permeance of 0.562 cm ³ cm ⁻² s ⁻¹ cm ⁻¹ Hg	33-36
PVDF hollow fibre membranes	Water/CCl ₄ by PV and VMD	PV: 6.54×10 ⁻⁹ kg m ⁻¹ s ⁻¹ VMD: 4.78×10 ⁻³ kg m ⁻¹ s ⁻¹	37, 38
Dual layer hollow fibres and flat sheet	Water/methanol by DCMD	A flux of 55 kg/(m ² h) at 90 °C	39, 40
PVDF hollow fibre membranes	CO ₂ separation and absorption	Na	41

2.3 Organic/inorganic composite membranes

2.3.1 Introduction

In 1991, for gas separation based on polymeric membranes, Robeson [63] firstly proposed the “upper bound” trade-off relationship of permeability and selectivity, based on data of over 300 polymeric membranes. As shown in Fig. 2.6, the crosshatch regime was identified as commercially attractive gas transport properties for N₂ enriched air production. It is clear that most of polymeric materials lie below the upper limit line and few membranes are commercially attractive enough for this process. However, molecular sieving materials, such as zeolites and carbon

molecular sieve, lie well above the upper bound trade-off curve and in or near the commercially attractive regime. It is widely accepted that most polymeric materials have desirable mechanical properties and good processability, but lower permeability and selectivity; while zeolites materials and carbon sieving materials show higher selectivity and permeability owing to their narrow distribution of pore size. With their inherent advantages, an attempt to prepare membranes with the combination of polymeric materials and inorganic materials has recently been popular.

Fig. 2.2 Trade-off curves of polymeric O_2/N_2 selectivity and O_2 size selective regions [64].

2.3.2 Optimisation of composite membranes

Composite membranes with inorganic phase incorporated into polymeric matrix are most often called as mixed matrix membranes (MMMs). To get an optimised combination of the properties of polymers and inorganic fillers, it is necessary to make an elaborate selection for polymer matrices as well as inorganic fillers.

Among the various inorganic fillers, zeolites are always preferentially used due to

their special properties for gas separation. Zeolites are crystalline alumina-silicates composed of AlO_4 and SiO_4 tetrahedral, which build up a network of channels and cavities. The microcrystalline interconnected voids and channels are responsible for the very specific properties of these adsorbents. The aperture size is typically in the range of molecular dimensions, *i.e.*, 3 Å to 10 Å. Since the aluminium atom is trivalent, an excess of negative charge is introduced in the network when Si is replaced by Al in the tetrahedral. This charge is compensated by non-framework cations, located near the negative charges. The most common ones are Na^+ , K^+ and Ca^{2+} . The number of cations is thus determined by the number of aluminium atoms in the framework. Due to the presence of cations, these zeolites are polar adsorbents. This means that molecules such as water, ammonia, carbon dioxide, nitrogen and aromatic hydrocarbons are adsorbed more strongly than non-polar species of comparable molecular weight. Zeolites with a high Si/Al ratio are hydrophobic and the adsorption is mainly governed by van der Waals forces. Therefore, four main factors influence the properties of a zeolite as follows.

- (1) Pore size which acts on the ability of a molecule to enter and diffuse through the zeolite framework.
- (2) Si/Al ratio which determines the number of cations and thus the hydrophilicity of the zeolite framework.
- (3) Type of cation (valence and size).
- (4) Direction of the pores (1, 2 or 3D porous network).

Due to their good adsorption and selectivity for many gas mixtures, some zeolites,

such as silicate-1, NaA and NaX, were preferentially incorporated with many polymer matrixes to prepare composite membranes. These microporous materials show some ideal topology structure and proper opening size. Silicalite-1 is a zeolite with MFI topology characterised by a hydrophobic character, due to the absence of Al in the structure and two different types of channels: straight channels having an opening size of (5.4 Å-5.6 Å) that intersect with sinusoidal channels with opening size of (5.1 Å-5.5 Å). NaA zeolite, with LTA topology, presents a hydrophilic nature and pore dimension of 4 Å. This zeolite, capable of discriminating between molecules as O₂ and N₂, is used in air separation by virtue of narrow pore openings. NaX zeolite, with FAU topology, is used commercially as an adsorbent and catalyst. This zeolite is usually synthesised in the sodium form with a Si/Al ratio in the range 1.0-1.5, which confers a strong hydrophilic character. NaX has pores and super cages of 7.4 Å and 13 Å, respectively.

The investigation of mixed matrix membranes for separation was first reported in 1970s with the discovery of a delay diffusion time lag effect for CO₂ and CH₄ when 5A zeolite was added into polydimethylsiloxane (PDMS) [65]. In this work, Kemp and Paul [65] found that the addition of 5A into the polymer matrix caused very large increases in the diffusion time lag but had only minor effects on the steady-state permeation. Researchers at UOP Inc. [66] were the first to report that mixed matrix systems of polymer/adsorbent might yield superior separation performance as compared to that of pure polymeric system. They observed an enhanced O₂/N₂ selectivity from 3.0 to 4.3 with increasing silicate content in the

polymer cellulose acetate matrix.

The work involving the application of zeolite 4A in composite membranes was conducted by Mahajan *et al.* [67, 68]. They incorporated zeolite 4A into polyvinyl acetate (PVAc), Ultem polyetherimide (PEI) and Matrimid polyimide polymer matrix to prepare mixed matrix membranes. It was found that PVAc/40% 4A and Ultem/35% 4A had better O₂/N₂ selectivity with some sacrifice in the O₂ permeability. However, Matrimide/20% 4A zeolite can greatly improve the permeation of O₂ without decreasing O₂/N₂ selectivity. They suggested that it was critical to control the interphase between the filler and the matrix for the preparation of mixed matrix membranes.

Pechar *et al.* [69] fabricated mixed matrix membranes without interfacial defects by using 6FDA-6FpDADABA and amine-functionalised zeolite L. They found that at 4.05×10^5 Pa, oxygen, nitrogen and methane permeabilities through the mixed matrix membranes increased in accordance with the observed higher gas solubility in the zeolite L while those of He and CO₂ decreased. The permeability of CH₄ and CO₂ decreased with increasing pressure in both the mixed matrix and pure polymer systems, suggesting that the gases were not accessing the zeolite pores. This might be due to the partial blockage of the zeolite pores by the surfactant.

Suer *et al.* [70] prepared mixed matrix membranes of polyethersulfone (PES) incorporated with hydrophilic zeolites 13X and 4A. The permeations of N₂, O₂, Ar, CO₂ and He were measured at different zeolite loadings. They found that the type of zeolite in the matrix was very important: for PES/zeolite 13X membranes,

permeability showed a recovery above 8 wt% zeolite loading. However, for PES/zeolite 4A membranes, permeability showed a recovery only above 25 wt% zeolite loading. The reason for this could be the different chemical interactions of polar gases with the different zeolites and the state of zeolites in the matrix (agglomeration of 4A crystals existed whereas 13X crystals remained as discrete entities). The increasing selectivity with increasing filler content could not be due solely to a molecular sieving mechanism, considering the kinetic diameters of the gases. The shape selective properties of zeolites, the polarity of gases and the microstructure of the membranes could also play a role in increasing permselectivity. Clarizia *et al.* [71] used PDMS as matrix to prepare hybrid membranes by a dry phase inversion process, where fillers with different surface and molecular sieving properties had been dispersed. Compared with pure PDMS membranes, these composite membranes showed higher selectivity for some gas pairs. Silicalite-1 played the role of a molecular sieve in the hybrid membranes by facilitating the permeation of smaller molecules and hindering that of larger molecules. Thus, the permeability of the helium with smallest kinetic diameter increased whereas the permeability of methane with biggest molecule size decreased. Carbon dioxide permeability remained around constant due to the combined effect of sorption on the crystal surface and permeation through the matrix. NaX zeolite in the polymeric matrix lowered the permeability of all species. In this case, NaX zeolite did not exhibit molecular sieving effect because the polymeric chains completely filled the zeolite pores. In NaA/PDMS hybrid samples, carbon dioxide tended to strongly

adsorb in NaA zeolite crystals because of their high affinity. This behaviour implied a further decay of the permeability with respect to the pure PDMS. At fixed zeolite content, the CO₂ permeability remained constant. Graphite particles behaved as non-permeable obstacles to the transport for all gases and consequently lowered the permeability without any influences on their ideal selectivity.

Wang *et al.* [72] demonstrated a novel process strategy for incorporating zeolite nanocrystals into a polymer matrix with homogeneous dispersion. Zeolite A nanocrystals with an average particle size of 100 nm and good dispersibility were synthesised. Polysulfone/zeolite A nanocomposite membrane with up to 25 wt% zeolite nanocrystal loading (PSFA/25%) had been successfully prepared. Addition of 25 wt% zeolite A nanocrystals into the polysulfone matrix increased the O₂/N₂ selectivity from 5.9 to 7.7 and O₂ permeability from 1.3 to 1.8 Barrers. However, the synthesis of the zeolite A crystals was complicated and tedious, which limited its wide applications for gas separation.

Li *et al.* [73] fabricated polyethersulfone (PES)/zeolite 3A, 4A and 5A mixed matrix membranes (MMMs) with a modified solution casting procedure at high temperature close to the glass transition temperatures of polymer materials. The permeability of all gases for the resulting composite membranes increased with increasing zeolite pore size, which was consistent with the molecular sieving mechanism. The permeability of all gases for PES/zeolite 4A and PES/zeolite 5A membranes decreased with an increase in zeolite loading, which was opposite to the prediction by the Maxwell model. They suggested two possible hypotheses: one was the

polymer chain rigidification near the zeolite and the other was the partial pore blockage of zeolites by the polymer chains. In considering these two factors, a new modified Maxwell model was proposed. The predicted permeability and selectivity showed good agreement with experimental data.

After a comprehensive study on microporous zeolites/polymer composite membranes, some other novel inorganic fillers, such as mesoporous materials [74-76] and carbon nanotubes [77] were also widely investigated to prepare composite membranes.

Since the discovery of the M41S family of mesoporous molecular sieve by Kresge *et al.* [78], these materials have received considerable interest as catalysts, adsorbents and membranes because of their high surface area and tunable channel size (2-50 nm). MCM-41 is of a hexagonal structure and possesses well-ordered one-dimensional channel pores, which are large enough to allow the penetration of polymer chains, resulting in better wetting and dispersion. Therefore, MCM-41 has potential for preparing mixed matrix membranes for gas separations. Reid *et al.* [74] incorporated the siliceous MCM-41 into polysulfone (PSF) polymer to enhance its gas permeation properties. They found that the hydroxyl groups present in the surface of MCM-41 provided the necessary functionality for hydrogen bond and that the 4 nm pore size was enough to readily enable the penetration of the polymer chains. Consequently, the addition of MCM-41 into polymer matrix dramatically increased the permeability of the composite membranes as compared to pure PSF membranes. For example, the addition of 30% MCM-41 to PSF resulted in a 155%

increase in permeability of O₂ (1.50 to 3.83 Barrers) and a 192% increase in permeability of N₂ (0.257 to 0.753 Barrers). Similarly, the addition of 30% (w/w) MCM-41 to PSF resulted in a 172% increase in the permeability of CO₂ (7.53 to 20.5 Barrers) and a 169% increase in the permeability of CH₄ (0.389 to 1.05 Barrers). Importantly, only a moderate decrease in O₂/N₂ selectivity was observed (O₂/N₂ selectivity decreased from 5.84 to 5.08) and CO₂/CH₄ selectivity remained virtually unchanged.

As compared with MCM-41 of one dimensional structure, MCM-48 possesses three dimensional interconnected cubic pore structures and is more attractive than MCM-41 for potential application in mixed matrix membranes. Kim *et al.* [75] synthesised MCM-48 by a template method and mixed with PSF to fabricate mixed matrix membranes. Helium permeation data and SEM images of as-synthesised MCM-48/PSF MMMs suggested that MCM-48 silica particles adhered well to PSF and no defects or holes were detected in the composite membranes. Mesoporous MCM-48 materials offered the favourable effect of a large increase in gas permeability in MMMs without sacrificing selectivity. The addition of 10 wt % MCM-48 to PSF resulted in 85% increase in the permeability of all gases tested. At 20 wt % MCM-48 silica loading, the permeability increased dramatically by 300% for He and CO₂ and 320% for O₂, N₂ and CH₄. The separation factor decreased only slightly or remained virtually unchanged.

Park *et al.* [76] used as-made and calcined mesostructured silica (denoted MSU-J) with large pores (5.3 nm), to fabricate rubbery epoxy mesocomposites. They found

that the oxygen permeability of the mesocomposites prepared from as-made MSU-J silica increased dramatically at loadings $>5.0\%$ (w/w) whereas the composites made from the calcined silica showed no permeation dependence on silica loading. For instance, the oxygen permeability of the mesocomposites containing 12% as-made MSU-J silica was 6 folds higher than that of pure epoxy membrane. The increase in oxygen permeability was correlated with the partitioning of curing agent between the as-made mesostructure and the liquid polymer, which led to coronas of permeable polymer with reduced chain cross-linking in the vicinity of the silica particles. Mesocomposites made from calcined forms of the mesostructured silica did not allow for curing agent partitioning and the oxygen permeability was not significantly influenced by the silica loading.

Since its discovery in 1991 [79], carbon nanotubes (CNT) have been of interest due to its mechanical, thermal and electrical properties. It was also investigated as inorganic filler for the preparation of composite membranes. Cong *et al.* [77] incorporated single-walled carbon nanotubes (SCNTs) and multi-walled carbon nanotubes (MCNTs) into bominated poly (2, 6-diphenyl -1, 4-phenylene oxide) (BPPO_{dp}) to prepare composite membranes. They found that the composite membranes had an increased CO₂ permeability but of similar CO₂/N₂ selectivity as compared with the corresponding pure polymer membrane. The CO₂ permeability increased with increasing CNT content and reached a maximum of 155 Barrers at 9 wt% of SWNT or 148 Barrers at 5 wt% of MWNTs. The CO₂/N₂ separation performance was insensitive to the MWNT diameter or length. The pristine CNT

enhanced gas permeability was attributed to the formed nanogaps surrounding the CNT. Carboxylic acid-functionalized SWNT dispersed more uniformly in BPPO_{dp} but neither increased permeability nor deteriorated gas separation performance.

Unlike the aforementioned mixed matrix membranes consisting of porous fillers and polymer matrices, a novel mixed matrix membrane based on nonporous nano-size particles had recently been investigated [80-84].

Merkel *et al.* [80] found that the physical dispersion of nonporous fumed nano-silica particles in amorphous poly (4-methyl-2-pentyne) (PMP) simultaneously enhanced both permeability and selectivity for some organic gases. The permeability of all gases (CH₄, C₂H₄, C₃H₆, *etc.*) in PMP systematically increased with increasing fumed silica loading. At 50 wt% fumed silica, the PMP/fumed silica (FS) nanocomposite membrane permeability was more than 240% greater than that of pure PMP. They suggested that these highly unusual property enhancements, in contrast to results obtained in conventional filled polymer systems, were attributed to the disruption of polymer chain packing and an accompanying subtle increase in the size of free volume through which molecular transport occurred, as discovered by positron annihilation lifetime spectroscopy. Further studies by Merkel *et al.* [81] showed that the increased flux in the PMP/FS nanocomposites was attributed to the increase of penetrant diffusion coefficients and that the incorporation of FS into PMP had little impact on gas and vapour solubility coefficients. With the addition of FS, the permeability of large penetrants increased more than that of small gases, resulting in favourable increases in vapour selectivity of the nanocomposites.

Zhong *et al.* [83] prepared supported polyimide/silica hybrid membranes based on polyamic acid (PAA) by sol–gel technique. The bond linkage between minerals and polymer chains in the hybrid membranes were responsible for their excellent properties. The gas permeation tests showed that the resultant composite membranes exhibited outstanding hydrophilic property and high gas permeability with a small increase in the permselectivity of $\text{H}_2\text{O}/\text{N}_2$ and $\text{H}_2\text{O}/\text{CH}_4$.

Gomes *et al.* [84] synthesised poly(1-trimethylsilyl-1-propyne) (PTMSP)/silica nanocomposite membranes by the copolymerisation of tetraethoxysilane (TEOS) with organoalkoxysilanes in the solutions of PTMSP. The butane permeability and the butane/methane selectivity increased simultaneously when high silica conversion was obtained. For the sake of comparison, they also prepared nanocomposite membranes by dispersing silica particles with different functional groups into PTMSP casting solution. These nanocomposite membranes showed a further increase in butane permeability and butane/methane selectivity as compared with the nanocomposite membranes prepared by sol–gel process.

2.3.3 Morphology of inorganic/organic composite membranes

It is widely accepted that the incorporation of inorganic particles into polymer matrices resulted in an improvement of gas separation properties. This improvement may be attributed to the perfect combination of the properties of polymer phase and the inorganic phase. However, in fact, depending on the interaction between polymers and the surface of the inorganic particles, there will be totally different membrane morphology unfavourable for gas separation.

Koros and his research group [67, 68, 85-87] had devoted considerable efforts to dealing with these challenges in successfully preparing inorganic/organic composite membranes. They found that the transport properties of organic–inorganic hybrid membranes were strongly dependent on the nanoscale morphology of membranes. In particular, the morphology of the interface was a critical determinant of the overall transport properties. They summarised the relationship between morphology and transport properties, and showed five different morphologies in composite membranes and their corresponding transport properties [67].

Fig. 2.3 Summary of the relationship between mixed matrix membrane morphologies and transport properties. Circles represent calculated values; squares represent experimental in Ultem data. Solid markers are 35 vol.% zeolite 4A; open markers are 15 vol.% 4A [67].

In Fig. 2.4, Case 0 represented an ideal Maxwell model. Case I behaviour was attributed to the effect of a rigidified polymer region around the zeolite. This region

showed significant lower permeability. The morphology of case I was not always the norm and only existed in a few systems including the incorporation of zeolite 4A in Ultem, PVAc and a partially hydrolysed PVAc. Cases II and III had voids at the interface and case III was just a special case of case II, where the effective void size was of the order of the size of the penetrants. These voids which were formed in these two cases could be due to the inhomogeneous contraction of polymer chains and inorganic fillers during the drying processes. The presence of such voids would dramatically deteriorate the selectivity of membranes. Cases IV and V were both caused by sorption of a strongly held molecule. In case IV, the strongly held molecule completely prevented the penetrants of interest from entering the zeolites, whereas in case V, the penetrants of interest entered or passed through the zeolite slower than usual. Both of these two cases would show decreased permeability.

As mentioned above, there are several types of undesirable morphology during the membrane fabrication processes because of the inhomogeneous properties of the interface between the polymer chains and the surface of the inorganic particles. To avoid this undesirable morphology, it is desirable to prepare membranes in such a manner that the stress at the organic/inorganic interface is minimised to suppress the tendency to form undesirable voids at the interface. Furthermore, processing steps which result in clogging of the zeolites should be avoided. Unfortunately, no “fail-safe” preparation protocol is available. However, some feasible approaches are helpful for the preparation of defects-free membranes:

- (1) Maintain polymer chain to be flexible during membrane formations, for example,

cast polymer solutions at an elevated temperature or even prepare membranes using melt process to minimise stress [67, 68, 85-87].

(2) Modify the surface of inorganic particles, usually using a silane coupling agent, to improve the properties of the interface [69, 73, 77]

(3) Use alternative synthesis method, such as sol-gel and self-assembly method [88, 89].

Li *et al.* [73] used a novel silane coupling agent, (3-aminopropyl)-diethoxymethyl silane (APDEMS) to modify zeolite surface for the preparation of mixed matrix membranes. The results indicated that the interface between the polymer and zeolite phases was better when modified zeolite was used. Both permeability and selectivity of MMMs made from APDEMS modified zeolite were higher than those of MMMs made from unmodified zeolite at 20 wt% zeolite loading.

Fig. 2.4 Flowchart of the chemical modification of zeolite surface by Li *et al.* [73]

Cong *et al.* [77] modified the surface of silica with trimethylsilyl and triphenylsilyl group before mixing with the matrix polymer. Pechar *et al.* [69] first modified the surface of zeolite L with aminopropyl-triethoxysilane (APTES) and then the inorganic particles were covalently linked with the polymer chains by the chemical

reaction of carboxylic acid groups of polymers and amine groups on zeolites. It was demonstrated that the morphology of the interface was better when modified inorganic filler was used.

Sullivan and Bruening [88] prepared ultrathin polyimide membranes on porous alumina substrates by alternating electrostatic deposition of poly (amic acid) salts and poly (allylamine hydrochloride) (PAH) following by heat-induced imidisation. Films about 35-40 nm free of defects were successfully prepared. Permeability and selectivity (O_2/N_2 up to 6.9 and CO_2/CH_4 up to 68) of imidised poly (amic acid)/PAH membranes were comparable to literature values for the corresponding bulk polyimides.

Tamaki *et al.* [89] synthesised organic/inorganic hybrid membranes by sol-gel method. The membranes were prepared by dip coating a methanol solution of poly (N-vinylpyrrolidone) (PVP) and methyl trimethoxysilane (MTMOS) on porous glass tubes. Permeabilities of N_2 , CO_2 and He in these composite membranes were investigated. They found that the permeability of tested gases in the hybrid membranes increased with increasing temperature. In particular, the permeability of He increased at a much greater rate with temperature, resulting in high selectivity against N_2 .

As mentioned above, numerous reports are available for the preparation of the MMMs using various polymer matrices and inorganic fillers for gas separation. The gas separation performance of the resulting MMMs is highly dependent on the interfacial properties between the polymer matrix and the inorganic filler. To the best

of the author's knowledge, no systematic study has been reported on the effects of heat treatment, the polymer matrix, the inorganic filler and the preparation method on the interfacial properties and the gas separation performance of the resulting MMMs. Therefore, two types of polymers, a glassy polyimide and a rubbery PVDF, were typically selected as the matrices and three types of inorganic fillers, i.e., non-porous SiO_2 , microporous zeolite 4A and mesoporous MCM-41, were preferentially used as inorganic fillers due to their distinct pore structures. Two preparation methods, namely, direct mixing and sol-gel technique, were comparatively employed to prepare MMMs. The effects of surface modification and the weight content of the inorganic filler were also explored in detail.

Chapter 3 Structure and Transport Mechanism of Membranes

In this chapter, several transport mechanisms for gas transport were discussed. In particular, many efforts were paid to the transport behaviours of gas penetrants through rubbery and glassy polymer membranes. Two theoretical models including dual mode sorption theory and free volume theory were studied in detail.

3.1 Poiseuille flow

Generally, the pore sizes of the membranes and the molecules play a decisive role on the transport mechanism. In the kinetic theory, the mean free path λ of gas molecules is defined as the average distance between collisions of gas molecules, which can be calculated using

$$\lambda = \frac{3\eta}{2P} \sqrt{\frac{RT}{2M}} \quad (3.1)$$

where η is the viscosity, P is the pressure, R is the universal gas constant, T is the absolute temperature and M is the molecular weight. When the average pore diameter d is much larger than the mean free path of the gas penetrant λ , the Poiseuille flow which is also known as viscous flow is the dominant transport mechanism. This transport mechanism is usually observed for the porous membranes with pore sizes of micrometres and the flux J_p follows

$$J_p = \frac{1}{8} \frac{r^2 \varepsilon}{\tau \eta} \frac{P}{RT} \frac{\Delta P}{L} \quad (3.2)$$

where r is the radius of the pore, ε is the porosity, τ is the tortuosity factor, ΔP is the pressure difference and L is the thickness of the membrane.

3.2 Knudsen diffusion

Knudsen diffusion is the dominant diffusion mechanism for porous membranes, whose pore sizes are much smaller than the mean free path of the gas molecules. By Knudsen diffusion, gas molecules transport through porous membranes by a series of collisions and the flux J_k can be calculated using

$$J_k = D_k \frac{\varepsilon}{\tau} \frac{M \Delta P}{LRT} = \frac{4r\varepsilon}{3\tau} \sqrt{\frac{2RT}{\pi M}} \frac{\Delta P}{LRT} \quad (3.3)$$

where D_k is the diffusion coefficient. Knudsen diffusion usually occurs in porous membranes with pore size of several nanometres. The selectivities of gas pairs based on Knudsen diffusion are inversely proportional to the ratio of molar weight. Consequently, this transport mechanism is not attractive in general for standard application due to their relative low selectivity.

3.3 Molecular sieving

Molecular sieving refers to the selective diffusion of molecules with certain sizes and shapes while strictly blocking the passages of molecules with larger sizes. This mechanism is widely observed in the gas transport of zeolite and carbon molecular sieving membranes with pore sizes of several angstroms, which are of great importance for the separation of mixture gases due to their higher permeability and selectivity. The excellent selectivities of gas pairs based on molecular sieving are achieved from the effective size and shape separation between gas species when the pore diameters are small enough to allow the permeation of smaller molecules while obstructing the larger molecules. Moreover, even though both can enter the pores when the size difference of the two gas molecules is small, the larger one would

experience stronger repulsive forces and therefore lower diffusivity.

3.4 Capillary condensation

At appropriate pressure and temperature, some gases will condense within the pores by capillary condensation and flow through the pores as a condensed phase under a capillary pressure gradient. This behaviour can be described by the Kelvin equation:

$$\ln\left(\frac{P}{P_o}\right) = -\frac{2\gamma V_m \cos\theta}{RT r_k} \quad (3.4)$$

where P_o is the saturation pressure, γ is the surface tension of the gas adsorbate, V_m is the molar volume of the gas adsorbate, θ is the contact angle of the gas adsorbate and the pore wall and r_k is the Kelvin pore radius. Capillary condensation usually occurs when the diameter of the pores are in the range of 40-100 angstroms. During the separation of gas mixtures, the condensation of gas molecules blocks the pores and prevents the diffusion of non-condensable gases. The efficient removal of a component from a gas mixture is often very low even though a relative high separation factor can be achieved.

3.5 Surface diffusion

It is well known that gas molecules can adsorb on the surfaces of solids and the concentration of the adsorbate is dependent of the pressure of the surface sites. Surface diffusion refers to the diffusion of the adsorbates through the pores by the concentration gradient on the surface of the pore walls. The concentration of the adsorbate is a function of the temperature, the pressure and the properties of the solid surfaces. Generally, the stronger is the interaction between the adsorbates and the

pore walls, the harder is the transport of the adsorbates; the lower is the temperature, the faster is the diffusion, and vice versa. Surface diffusion occurs in the membranes, whose pore sizes are in the range of 4-15 angstrom, which is usually larger than the sizes of gas molecules, but less than four times the size of gas molecules.

3.6 Fundamentals of transport in polymeric membranes

The transport of gas molecules through polymer membranes occurs due to the random molecular motion of individual polymer chain, which is usually described by a solution-diffusion mechanism. The solution-diffusion mechanism consists of three steps: (1) the absorption or adsorption at the upstream boundary, (2) activated diffusion through the membrane, and (3) desorption at the permeate side. The transport of a gas is driven by a difference in the thermodynamic activities existing upstream and downstream of the membrane [42].

Fig. 3.1 Schematic diagram of penetrant transport across a membrane [43]

According to the solution-diffusion mechanism, permeation depends on the diffusivity, solubility and concentration gradient of the penetrant in the membrane. Fick's First law, Equation (3.5), is most often used to describe the flux J of gas molecules through the membrane

$$J = -D \left(\frac{\partial c}{\partial x} \right) \quad (3.5)$$

where D is the diffusion coefficient, c is the concentration and x is the distance. Equation (3.5) is applicable to the diffusion in the steady state, *i.e.*, when the concentration does not vary with time. In this case, the diffusion flow is constant and diffusion coefficient is independent of concentration. Then Equation (3.5) may be integrated to give

$$J = \frac{D(c_1 - c_2)}{h} \quad (3.6)$$

where h is the membrane thickness and c_1 and c_2 are the concentrations of penetrant at upstream and downstream side of the membrane, respectively. The concentration of penetrant in the polymer, c_1 and c_2 , can be calculated by

$$c = S \times p \quad (3.7)$$

where S is the solubility coefficient and p is the pressure. The combination of Equations (3.5) and (3.6) gives the well-known permeation equation:

$$J = \frac{DS(p_1 - p_2)}{h} \quad (3.8)$$

where p_1 and p_2 are the ambient pressures on two sides of a membranes of thickness h . According to Equation (3.8), in order to obtain a high flux, or in other words high membrane productivity, a membrane should be as thin as possible. The permeability coefficient P is defined as the product of D and S :

$$P = D \times S \quad (3.9)$$

In terms of permeability, the flux in Equation (3.5) can be written as:

$$J = \frac{P(p_1 - p_2)}{h} \quad (3.10)$$

Permeability is a material property whereas the flux is a membrane property or more

precisely a membrane system property since it depends on the membrane thickness, the pressure difference over the membrane, as well as the diffusivity and the solubility.

Equations (3.5-3.10) are applicable to the transport in the steady state. For non-steady state transport processes, Fick's second law can be used. These equations are still valid by substituting S and D with a mean or integral solubility coefficient and diffusion coefficient. The detailed descriptions can be found in Gorge and Thomas [44].

For a binary gas mixture permeating through a polymer membrane, the separation factor for component A relative to component B, α_{AB} , is defined as

$$\alpha_{AB} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right) \quad (3.11)$$

where D_A/D_B is the ratio of the diffusion coefficients of components A and B and is referred to as the diffusivity selectivity. S_A/S_B is the ratio of solubility coefficients of components A and B and is called the solubility selectivity. In addition to operating conditions (*i.e.* temperature, pressure and composition), gas solubility also depends on factors such as penetrant condensability, polymer-penetrant interactions and polymer morphology (*i.e.* crystallinity, orientation, etc.). Gas diffusivity depends on the ability of the diffusive jumps of the gas molecules; this occurs when random polymer segmental chains form transient gaps, large enough to accommodate penetrants. Like solubility, diffusivity depends on membrane operating conditions, moreover, gas diffusivity is also sensitive to properties such as penetrant size, polymer morphology and polymer segmental dynamics.

3.6.1 Gas sorption and transport in rubbery polymers

The sorption of gases in rubber polymers is similar to the sorption of gases in low molecular weight liquids and gas concentration C in the polymer often obeys Henry's law [45, 46]:

$$C = k \times p \quad (3.12)$$

where k is Henry's law constant and p is the gas pressure in contact with polymer. For rubbery polymers, solubility coefficient S corresponds to the Henry's law constant k . At low penetrant concentrations, diffusion coefficient is often independent of gas concentration [47]. In this case, gas permeability is independent on pressure.

For highly adsorbed penetrants, such as organic vapours, or gases at high pressures, penetrant concentration in the polymer may deviate from Henry's law [48]. Under these circumstances, penetrant concentration in the polymer can often be satisfactorily represented by the Flory-Huggins equation [49]:

$$\ln a = \ln \varphi + (1 - \varphi) + \chi(1 - \varphi)^2 \quad (3.13)$$

where a is the penetrant activity and is equal to p/p_0 for ideal gases (p and p_0 are the penetrant pressures in contact with the polymer and penetrant vapour pressures, respectively). The volume fraction of penetrant dissolved in the polymer is φ , and χ is the Flory-Huggins interaction parameter. In such cases, the diffusion coefficient may also change considerably with penetrant concentration, typically increasing with increasing penetrant concentration [50].

3.6.2 Gas sorption and transport in glassy polymers

Many differences between the sorption and transport properties of rubbery polymers and glassy polymers are due to the non-equilibrium nature of glassy polymers. Unlike rubbery polymers, physical properties of glassy polymers including sorption and transport properties drift over time towards a seemingly unattainable equilibrium. The mechanism of gas transport in glassy polymers is a topic of debate but two models, *i.e.*, the dual mode sorption theory and the free volume theory, are generally used to study the behaviours of gas transport in glassy polymers. Gas sorption and transport in glassy polymers are traditionally described by the dual mode sorption theory. The free volume theory, which is older and was originally developed for rubbery polymers, has however gained much interest lately since in most cases gas transport in glassy polymers can be successfully described by this theory [51].

3.6.2.1 Dual mode sorption theory

The dual mode sorption theory postulates the existence of two populations of gas molecules present in the polymer matrix [52]:

(1) Gas molecules dissolved according to Henry's law. The concentration of the molecules C_D is related to the pressure p by Equation (3.14), where k_D is the solubility constant.

$$C_D = k_D \times p \quad (3.14)$$

(2) Gas molecules absorbed in microcavities "frozen" into the polymer matrix. The concentration of these molecules C_H is related to the pressure p by the Langmuir isotherm. In Equation (3.15), C_H' is the hole saturation constant and b is the hole affinity constant and it represents the ratio of rate constants of gas adsorption and

desorption in the micro-cavities.

$$C_H = C'_H \frac{bp}{(1+bp)} \quad (3.15)$$

The Langmuir sorption capacity is related to the unrelaxed non-equilibrium volume in glassy polymers as shown below [53]:

$$C'_H = \left[\frac{V_g - V_l}{V_g} \right] \rho^* \quad (3.16)$$

where V_g and V_l are the polymer specific volumes in the glassy and hypothetical rubbery states, respectively. ρ^* is the molar density of the condensed penetrant.

The total concentration of a gas adsorbed in a glassy polymer is then represented by

$$C = C_D + C_H = k_D p + C'_H \frac{bp}{(1+bp)} \quad (3.17)$$

Initially, it was assumed that gas molecules in the microcavities were totally immobilised. Petropoulos *et al.* [54] and Paul and Koros [55] modified the dual mode sorption theory by assuming that the molecules adsorbed in the microcavities possessed limited mobility and participated in the permeability. The modified dual mode sorption theory is given by Equation (3.18), where $K = C'_H b / k_D$ is the relative amount of gas adsorbed in the two modes, $F = D_H / D_D$ is the diffusivity ratio, which is a measure of the degree of immobilisation. D_D and D_H are the diffusivities of the gas molecules dissolved and adsorbed in the Langmuir mode in the holes, respectively. D_D is typically much larger than D_H .

$$P = k_D D_D \left(1 + \frac{KF}{1+bp} \right) \quad (3.18)$$

Furthermore, the dual mode model provides the following expression for the

concentration dependent, effective gas diffusion coefficient D , in glassy polymers [53].

$$D = D_D \left\{ \frac{1 + F \frac{K}{(1 + bp)^2}}{1 + \frac{K}{(1 + bp)^2}} \right\} \quad (3.19)$$

In this equation, gas diffusivity increases with increasing gas concentration because the Langmuir mode becomes saturated at higher gas concentrations and therefore, much of the gas added to the polymer at higher penetrant pressures partitions into the higher mobility Henry's law mode.

An extension of the dual mode model permits the description of sorption and permeation of binary, non-interacting penetrant mixtures [53]. The modified expressions are:

$$C_A = k_D p_A + C'_{HA} \frac{b_A p_A}{1 + b_A p_A + b_B p_B} \quad (3.20)$$

where the subscripts A and B refer to the penetrants A and B , respectively. In binary mixtures, there is competitive adsorption between the two penetrants for the fixed amount of unrelaxed volume in the polymer.

3.6.2.2 Free volume theory

The free volume model was originally proposed by Fujita *et al.* [56] for rubbery polymers. However, it is now also widely used to describe the transport of gases in glassy polymers. It correlates diffusivity D to the polymer free volume, using

$$D = D_0 \exp\left(\frac{-B}{FFV}\right) \quad (3.21)$$

where D_0 and B are constants characteristic of the polymer-penetrant system. FFV ,

the polymer fractional free volume is the fraction of the total polymer specific volume which is not occupied by polymer molecules and is available to participate in penetrant molecule transport. Free volume is often estimated by [57]

$$FFV = \frac{V - V_0}{V} \quad (3.22)$$

where V is the specific volume of the polymer at temperature T and V_0 is its hypothetical specific volume at 0 K. V is determined from the polymer density and V_0 is estimated from [58]:

$$V_0 = 1.3V_w \quad (3.23)$$

where V_w is the van der Waals volume of the polymer which can be obtained by a group-contribution method [59].

The specific free volume (SFV) is defined by [60]:

$$SFV = (V - V_0) / M \quad (3.24)$$

where M is the molecular weight (in g/mol) of the polymer repeat unit. The units of SFV are cm^3/g . SFV is the free volume potentially available for gas transport in a repeat unit of polymer.

Chern *et al.* [61] discovered that gas diffusivity in glassy polymers could be correlated with the packing density PD , which, like free volume, provided a measure of the accessibility of the polymer to the penetrant. The packing density is defined as

$$PD = \frac{V}{V - V_w} \quad (3.25)$$

Stern [62] has further modified the free volume theory and showed the desired separation properties of polymers in terms of the hypothetical free volume and the free volume distributions. He proposed that, in the separation of gas pair A/B, certain

volume in a polymer was available only to small penetrant molecules A while other volume was available to both molecules A and larger molecules B. The free volume distribution should be narrowed by structural modifications of the polymer so as to increase area A relative to area B. This will increase the selectivity of the polymer for penetrant A relative to penetrant B. In order not to simultaneously decrease the permeability of the polymer to the smaller penetrant molecules, area A for the “desired” polymer should remain unchanged and preferably be increased by structural modifications.

Chapter 4 Experimental Set-up and Procedures for Preparation and Characterisation

This chapter described the materials involved in this work, the membrane preparation methods and various membrane characterisation methods. Two types of membranes including MMMs and asymmetric membranes were prepared and two types of polymer matrices including a glassy polyimide and a rubbery PVDF were used to prepare MMMs. The membrane preparation procedures and characterisation technique were introduced in this chapter in detail.

4.1 Materials

The materials including the chemicals that were used in this project are listed in Table 4.1. The chemical name, chemical structure and the supplier are given.

Table 4.1 List of materials

Chemical agent	Chemical structure	Company
P84		HP Polymer, GmbH, Austria
Poly(vinylidene fluoride) (PVDF)		Mw=534000, Sigma Aldrich, Singapore
Pyromellitic dianhydride (PMDA)		Purity>97%, Sigma Aldrich, Singapore
4, 4'-oxydianiline (ODA)		Purity≥98%, Sigma Aldrich, Singapore

3-Aminopropyltriethoxysilane (APTES)		Purity ≥ 98% Sigma Aldrich, Singapore
Tetraethyl orthosilicate (TEOS)		Purity, 98%, Sigma Aldrich, Singapore
Cetyltrimethylammonium bromide (C ₁₆ TAB)		Purity > 98%, Sigma Aldrich, Singapore
N-methyl-2-pyrrolidinone (NMP)		Purity > 99%, Sigma Aldrich, Singapore
N, N-Dimethyl acetamide (DMAc)		Purity ≥ 99%, Sigma Aldrich, Singapore
Isopropanol (IPA)		Purity > 99%, Sigma Aldrich, Singapore Purity > 99%,
Acetone		Sigma Aldrich, Singapore
Zeolite 4A powder	$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$	Sigma Aldrich, Singapore
Nano-silica powder	SiO_2	Amorphous, Sigma Aldrich, Singapore

Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	Purity>99%, Sigma Aldrich, Singapore
Toluene		Purity, 99%, Sigma Aldrich, Singapore
Deionised water	H_2O	Home-made

4.2 Membrane preparation procedures

4.2.1 Fabrication of pure P84 membranes using a spincoater

The P84 powder was degassed under vacuum at 373 °C overnight to remove any moisture prior to the preparation of the membranes. 8 g of P84 powder was dissolved in 20 ml of N-methyl-2-pyrrolidinone and the mixture was stirred at 60 °C for three days. The solution was then cooled to ambient temperature and left standing for several hours to remove any gas bubbles before spin coating.

A spincoater was used to prepare the membranes with various thicknesses by varying the number of coats. During spin coating, two types of substrates, *i.e.*, porous stainless steel substrates (Average pore size = 5 µm and diameter = 1.7 cm) and poly(methyl methacrylate) (PMMA) substrates were used to prepare defects-free membranes with thicknesses ranging from 6 to 310 µm. Before spin coating, the porous stainless steel substrates were ultrasonic-cleaned in ethanol for 5 minutes and rinsed with ethanol for several times to remove any surface contaminants. They were

then immersed into a solution of 2 wt % cetyltrimethylammonium bromide (C₁₆TAB) and ethanol for 10 minutes and rinsed with ethanol for three times. Finally, they were dried in an oven at 100 °C overnight. For the PMMA substrates, they were cleaned with ethanol but without immersing into a solution of C₁₆TAB and ethanol, and then dried at 60 °C in an oven overnight.

During its operation, the spin coating system was evacuated by a vacuum pump and the working chamber was purged by a stream of nitrogen gas to ensure an inert condition. All the spin coatings were conducted under ambient temperature. The process parameters for the spin-coating are shown in Table 4.2. During each spin-coating, 0.4 ml P84 solution was injected onto the substrate with a syringe. After each coating, the substrate together with the coating membrane was taken from the spincoater and dried in a vacuum oven under ambient temperature. The thicknesses of the coating membranes were varied by the number of separate coats applied.

Table 4.2 Process parameters for spin-coating

Stage	1	2	3	4
Speed (rpm)	1000	2000	6000	0
Ramp (s)	5	5	10	10
Time (s)	10	10	20	–

4.2.2 Heat treatment of P84 membranes

To study the effects of heat treatment on the morphology and gas transport properties of the membranes, membranes with thickness of 118 µm were annealed under vacuum at three different temperatures, *i.e.*, 80, 200 and 315 °C. For the annealing temperatures of 80 and 200 °C, it was conducted using a vacuum oven (C3000, France Etuves) while for that at 315 °C, the annealing was conducted using a furnace

(Eurotherm 2416CG, Carbolite) with a temperature controller. For each annealing process, the temperature was increased at the rate of 0.5 °C/min to the preset temperature and kept at that temperature for 24 hours. Finally, the samples were cooled to room temperature at the same rate.

4.2.3 Synthesis of MCM-41 silica

Mesoporous MCM-41 silica was synthesised as follows [90]: Typically, 11 g (0.03 mol) of C₁₆TAB was dissolved in distilled water, aqueous ammonia and ethanol solution by stirring for 15 min. 21 g (0.1 mol) of tetraethyl orthosilicate (TEOS) was then added. A solution with a molar composition of 1 TEOS: 0.3 C₁₆TAB: 13 NH₃: 60 ethanol: 142 H₂O was obtained. After stirring for 30 min, the solution was transferred into a Teflon-lined autoclave and aged at 100 °C for 24 h. The resulting solid was collected by filtration and washed with distilled water. The dried precursor powder was calcined at 550 °C for 10 h to remove the template and MCM-41 was produced. The other two inorganic fillers, nano-silica and zeolite 4A, were directly obtained from Sigma Aldrich, Singapore.

4.2.4 Fabrication of pristine P84 dense membranes

P84 powder was degassed at 373 °C overnight under vacuum to remove any moisture present. 4 g of P84 was then dissolved in 20 g of NMP and the mixture was stirred for 48 h at room temperature. After the removal of gas bubbles, the solution was cast onto glass substrates and dried at 110 °C in an oven for 12 h. Once it was dry, the membrane was clamped between two Teflon plates in a vacuum oven and the temperature was raised to 180 °C and dwelled for 24 h.

4.2.5 Fabrication of P84/SiO₂, P84/4A and P84/MCM-41 MMMs

The composite membranes were prepared using the following procedure [16]: A predetermined amount of inorganic filler was added to the NMP solvent and the mixture was ultrasonicated for 30 min. At first, 4% of the total amount of P84 was then added into the solution. After the initial loaded polymer was totally dissolved by stirring for 12 h and followed by a period of 30 min ultrasonication, the remaining P84 polymer was added to the solution and the mixture was stirred for a week at room temperature. Before casting, the mixture was sonicated for 30 min to remove any gas bubbles. The drying and heat treatment were identical to those for the pristine dense membrane. Three inorganic fillers - nonporous nano-silica, MCM-41 and zeolite 4A, were used to prepare the composite membranes and these were designated as P84/SiO₂, P84/MCM-41 and P84/4A, respectively. Four different weight percentages of inorganic fillers, *i.e.*, 4, 8, 12 and 15%, were used to prepare the composite membranes. However, the composite membranes with 12 and 15% inorganic fillers, especially for the 12 and 15% zeolite 4A, were brittle and cracked easily, resulting in erroneous permeability values. Consequently, the weight percentage of the inorganic filler was kept at a highest possible value of 8% for all the composite membranes.

4.2.6 Modification of the surfaces of nano-SiO₂ particles

The modification of the surfaces of nano-SiO₂ particles was carried out according to the method as follows [91]: 2.2 g of SiO₂ was suspended in 70 ml of toluene and thoroughly dispersed by ultrasonication for 30 minutes. 2 ml of silane coupling agent

APTES was dissolved in 10 ml of toluene and then added into the mixture slowly under stirring. The chemical reaction was carried out at 110 °C for 16 h under nitrogen atmosphere. Afterwards, the mixture was cooled down to room temperature and centrifuged to separate SiO₂ particles. The resulting particles were washed and centrifuged twice again with toluene to get rid of the unreacted silane agent, and then dried in a vacuum oven under 80 °C overnight. The presence of the silane agent was confirmed by Fourier transform infrared spectroscopy (FTIR) spectra and X-ray photoelectron spectroscopy (XPS). Thermal gravimetric analysis (TGA) was also performed on the pristine SiO₂ and the modified SiO₂ particles.

4.2.7 Synthesis of MMMs based on P84 and modified SiO₂

The nanocomposite membranes were prepared using a method as follows. Typically, a predetermined amount of the modified SiO₂ was added into 15 ml of NMP and the mixture was ultrasonicated for 30 min. At first, 1.0 g of P84 powder was added into the mixture. After the initially loaded polymer was totally dissolved by stirring for 12 h and followed by a period of 30 min ultrasonication, the remaining P84 polymer powder was added to the solution and the mixture was stirred for over 3 days at room temperature. After the removal of gas bubbles by ultrasonication, the solution was cast onto glass substrates and dried at 110 °C in an oven for 12 h. Once it was dry, the membrane was clamped between two Teflon plates in a vacuum oven, and the temperature was raised to 200 °C and dwelled for 24 h. Both the pristine SiO₂ and the modified SiO₂ were used to prepare composite membranes and five different weight percentages (4%, 8%, 14%, 20% and 25%) of the inorganic filler were

obtained in the resulting composite membranes. However, the composite membranes based on the pristine SiO_2 are so brittle that they have no practical value when the weight percentage of the inorganic filler is over 8%. For convenience, the composite membranes based on the modified SiO_2 were designated as P84/X SiO_2 while the composite membranes based on the pristine SiO_2 were designated as P84/Un-X SiO_2 , where X is the weight percentage of the inorganic filler. For a good comparison, pure P84 membrane was also prepared.

4.2.8 Fabrication of pure PVDF membranes and MMMs

PVDF powder was degassed at 120 °C overnight under vacuum to remove any moisture present. 4 g of PVDF was then dissolved in 36 g of NMP and the mixture was stirred for 48 h at room temperature. After the removal of gas bubbles, the solution was cast onto glass substrates and dried at 80 °C in an oven for 8 h. The resulting membranes were transferred into a vacuum oven and the temperature was raised to 120 °C and dwelled for 24 h to remove the residue solvent.

Three types of inorganic fillers, *i.e.*, nano- SiO_2 , mesoporous SiO_2 and zeolite 4A were incorporated into PVDF matrix to form MMMs and the resulting membranes were designated as PVDF/ SiO_2 , PVDF/MCM-41 and PVDF/4A, respectively. The composite membranes were prepared using a similar method used for the preparation of P84 composite membranes. The typical procedures of the preparation of PVDF/ SiO_2 were as follows: A predetermined amount of inorganic fillers was added to the NMP solvent and the mixture was ultrasonicated for 30 min. At first, 2% of the total amount of PVDF was then added into the solution. After the initial loaded

polymer was totally dissolved by stirring for 12 h and followed by a period of 30 min ultrasonication, the remaining PVDF polymer was added to the solution and the mixture was stirred for at least two days at room temperature. Before casting, the mixture was sonicated for 30 min to remove any gas bubbles. The drying and heat treatment were identical to those for the pristine dense membrane. Five different weight percentages (4%, 8%, 16%, 24% and 32%) of SiO₂ were obtained in the resulting membranes, which were designated as PVDF/ X SiO₂, where X equals to 4%, 8%, 16%, 24% and 32%, respectively. Similarly, composite membranes based on MCM-41 (PVDF/X MCM-41) and zeolite 4A (PVDF/X 4A) with five different weight percentages (4%, 8%, 16%, 24% and 32%) were also prepared.

4.2.9 Preparation of pure polyimide membrane and composite membranes

40 ml of DMAc solvent was poured into a 100 ml flask and N₂ was injected to remove the air. 15 mmol (3.0036 g) of ODA was dissolved in the solvent by magnetic stirring for 30 minutes. 15 mmol (3.2718 g) of PMDA was gradually added into the solution in 10 minutes. About 30 minutes later, the solution became transparent with a golden yellow colour. The solution was stirred at room temperature under N₂ atmosphere for 12 h to obtain the product of poly(amic acid) solution. Before casting, the solution was ultrasonicated for 30 minutes to remove the gas bubbles. The poly(amic acid) solution was cast on a silicon wafer and dried at room temperature for 30 minutes. The membrane was transferred into an oven and dried at 60 °C for 2 h, at 120 °C for 1 h and at 150 °C for 1 h. For thorough imidisation, the membrane was peeled off from the substrate and put into a vacuum furnace. The

furnace temperature was increased with a heating rate of 5 °C/min and dwelled at 350 °C for 4 h.

The composite membranes were prepared using the sol-gel technique [92]. The detailed procedures are as follows: A predetermined amount of ODA was dissolved in DMAc solvent by stirring for 30 minutes. A calculated amount of PMDA was slowly introduced into the solution in 10 minutes under stirring. The total polymer content in DMAc was 12%. After 1 h, the mixture of APTES in DMAc with volume ratio of 1:1 was added into the solution. The amount of APTES was set to be the value, which enabled the complete consumption of –OH groups from the remaining PMDA monomers. After the solution was stirred for 10 h, the mixture of TEOS in ethanol with volume ratio of 1:1 was injected into the solution by droplets using a pipette. The molar ratio of TEOS to APETS was set to be 2:1. The solution was stirred for another 10 h. The reaction was carried out at room temperature under N₂ atmosphere. The resulting mixture was ultrasonicated for 30 min to remove any bubbles and then casted on a silicon wafer. The drying and heat treatment for imidization were identical to those for the pure dense polyimide membrane. The composition of the resulting membranes is shown in Table 4.3. For convenience, PI-silica composite membranes were denoted as PI-SiO₂ *x*%, where *x* was the silica content in the composite membranes.

4.2.10 Preparation of carbon and carbon-silica composite membranes

The synthesised pure polyimide membrane and polyimide-silica composite membranes were used as precursors to prepare carbon membrane and carbon/silica composite membranes. The preparation process was similar to the method reported by Lua and Su [93]. The detailed procedures are as follows: The polymer membranes were cut into circular pieces of approximately 30 mm diameter. These samples were sandwiched between round graphite discs and placed inside a furnace (CTF 12/75/700, Carbolite®). Before heating, the furnace was evacuated for 60 min. The samples were heated from room temperature at a heating rate of 5 K/min to 673 K and held at this temperature for 60 min and then continued to be heated at a rate of 0.5 K/min to temperatures of 1173 K. Subsequently, the membranes were cooled to ambient temperature at a rate of 2 K/min. The samples were carbonised under vacuum.

Table 4.3 Syntheses of pure PI membrane and PI-silica composite membranes

Sample	ODA (mmol)	PMDA (mmol)	APTES (mmol)	TEOS (mmol)	SiO ₂ content (wt %)	Si content (wt %)
Pure PI	15	15	0	0	0	0
PI-SiO ₂ 1.5%	19.5	20	1	2	1.5	1.0
PI- SiO ₂ 5.2%	9	10	2	4	5.2	3.6
PI- SiO ₂ 7.2%	8.5	10	3	6	7.2	5.0
PI- SiO ₂ 8.9%	16	20	8	16	8.9	6.2
PI- SiO ₂ 11.6%	7	10	6	12	11.6	8.1
PI- SiO ₂ 13.7%	12	20	16	32	13.7	9.6

4.2.11 Preparation of asymmetric membranes based on P84

Asymmetric membranes were prepared using a wet phase inversion technique. NMP was used as the solvent for the P84 polymer and water, ethanol, IPA and acetone

were used as nonsolvents. The detailed procedures are as follows: A predetermined amount of P84 powder was dissolved in NMP under stirring for 12 h at room temperature to form a homogeneous solution. After the removal of gas bubbles, the solution was cast onto glass substrates. After the evaporation of the cast solution at room temperature for a given time, it was immersed into a nonsolvent coagulation bath maintained at a fixed temperature for one day. The membranes were first dried at room temperature for one day and finally dried at 150 °C under vacuum for 24 h to remove the residual solvent.

4.3 Membrane characterisation

4.3.1 TGA characterisation

To investigate the thermal stability of the P84 polyimide, a thermogravimetric analyzer (TGA 7, Perkin-Elmer) was used. The thermogravimetric analyzer (TGA) was operated at a temperature range of 25 to 900 °C using a heating rate of 20 °C/min under nitrogen atmosphere.

To confirm the success of grafting APTES onto the nano-SiO₂, another thermogravimetric analyzer (DTG-60H, Shimadzu) was used. For this verification, the TGA was operated at a temperature range of 25 to 600 °C using a heating rate of 20 °C/min under nitrogen atmosphere.

The DTG-60H TGA was used to investigate the thermal stability of the composite membranes based on PVDF. The TGA was operated at a temperature range of 40 to 700 °C using a heating rate of 20 °C/min under nitrogen atmosphere. The decomposition temperature (T_d) was determined as the point where 5% weight loss

occurred. For each sample, at least three measurements were carried out.

4.3.2 DSC characterization

A differential scanning calorimeter (DSC 7 Sub-Amb, Perkin Elmer) was used to determine the glass transition temperature (T_g) of the P84 polyimide. The differential scanning calorimetry tests were conducted at a temperature range of -20 to 400 °C using a heating rate of 20 °C/min.

The differential scanning calorimeter (DSC) was used to determine the glass transition temperature T_g of P84/SiO₂, P84/4A and P84/MCM-41 composite membranes. These calorimetry tests were conducted for a temperature range from -20 to 400 °C at a heating rate of 20 °C/min. Taking the points of intersection as the onset and endpoint of the transition in the DSC curve, the T_g was located at one half the change in heat capacity between the onset and endpoint.

The DSC was also used to determine the T_g of the membranes based on polyimide. The DSC tests were conducted over a temperature range of 30 to 400 °C using a heating rate of 20 °C/min.

Another differential scanning calorimeter (DSC Q200 TA Instruments) was used to determine the phase transitions of the composite membranes based on PVDF. The DSC tests were conducted over a temperature range of 40 to 200 °C. Firstly, the samples were equilibrated at 40 °C and then heated to 200 °C using a heating rate of 10 °C/min. After remaining at 200 °C for 5 minutes to completely melt the PVDF polymer, the samples were cooled from 200 to 40 °C at a rate of 10 °C/min. The tests were run at two circles. The melting temperature (T_m), the crystallize temperature (T_c)

and the latent heat of fusion (ΔH) of the samples were determined accordingly.

4.3.3 Density measurement

The density of the sample was measured using an ultrapycnometer (1000 Quantachrome Instruments). Helium was used as the probe gas and the working cell size was medium (volume 50 cm³). For each test, the number of runs was set at 20 and the average value of the last four tests was used on condition that the deviation was less than 0.1%.

4.3.4 Scanning electron microscopy

A scanning electron microscope (JSM-5600LV, JEOL) was used to examine the morphology of the resulting membranes. Before the scans, all the samples were coated with platinum. For the cross-sectional views, the samples were attached to a vertical surface and then coated with platinum.

The scanning electron microscope (SEM) was used to examine the morphology of the membranes and the dispersion of the inorganic fillers on the composite membranes. Before the SEM tests, all the samples were coated with platinum. For the cross-sectional views, the samples were prepared by fracturing the membranes in liquid nitrogen.

4.3.5 Transmission electron microscopy

A transmission electron microscope (JSM2010, JEOL) was used to study the dispersion and size distribution of the inorganic fillers on the composite membranes. The inorganic particle samples for the transmission electron microscopy (TEM) tests were prepared by the ultrasonication of the powdered samples in ethanol and the

evaporation of one drop of the suspension onto a carbon film supported on a mesh copper grid. Nanocomposite samples for the TEM tests were prepared using a Leica Ultracut UCT microtome (Leica Microsystems GmbH, Germany). Thin sections of about 100 nm thickness were cut with a glass knife at room temperature at a rate of 1 mm/s. The cut sections, floating on the water in the boat, were collected with 300-mesh copper TEM grids. Transmission electron microscopy was carried out at an accelerating voltage of 200 kV at room temperature.

4.3.6 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were obtained by a diffractometer (PW1820, Philip) equipped with Cu K α X-ray radiation. The average value of d spacing was calculated from Bragg's law ($\lambda = 2d\sin\theta$).

4.3.7 N₂ adsorption-desorption tests

The N₂ adsorption-desorption isotherms were obtained using the accelerated and surface area porosimetry system (ASAP 2010, Micromeritics). Before the test, the sample was outgassed at 200 °C overnight in a vacuum oven. The pore surface area was calculated using the Brunauer-Emmett-Teller (BET) method; the pore volume and pore size were calculated by the Barret-Joyner-Halenda (BJH) method.

4.3.8 Tensile stress-strain tests

Tensile measurements on samples were performed using an Instron Static Tester Series 5569 System according to the ASTM standard D3039 with a programmed elongation rate of 1 mm/min under room temperature. The dog-bone shaped specimens were 20 mm long and 3 mm wide in the narrow region. For each

membrane, at least three specimen tests were conducted and the results of tensile modulus, tensile strength and maximum elongation shown were the average values.

43.9 Contact angle measurements

In order to examine the surface properties of the membranes, contact angles of all the membranes were measured by an image analyzer (FTA 200) at room temperature. Images of water droplets on the membrane surface were captured by a computer controlled video capture system. At least eight measurements at different sites of each sample were carried out.

4.3.10 Cloud point determination

The cloud point was determined by a titration method [94]. P84 solutions with different concentrations were placed in sealed glass bottles under a constant temperature of 25 °C. NMP/nonsolvent mixture droplets were added into the P84 solution with a syringe and stirred until the initial clear solution became visually turbid. The cloud points were calculated as the composition of the mixture based on the mass balance in the ternary nonsolvent/solvent/P84 systems. The viscosities of the P84 solutions with different concentrations were measured using a viscometer (Contraves, Zurich).

4.3.11 Diffusivity of NMP in nonsolvent coagulation bath

The diffusion rates of the solvent NMP in the nonsolvent coagulation baths were determined to investigate the mass transport of the solvent during the wet phase inversion process. The detailed procedures are as follows: 5 ml of P84/NMP solution with concentration of 25.6% of P84 was spread on a glass substrate and immersed

into the nonsolvent coagulation bath with a predetermined volume of the nonsolvent. The concentration of the NMP in a fixed position of the coagulation bath, which was 1.5 cm from the bulky solution, was analysed using a gas chromatograph (Agilent 6890, USA). The NMP concentration was recorded as a function of time.

4.3.12 AFM characterisations

The surface morphology of the asymmetric membranes was examined using tapping mode atomic force microscopy (AFM) equipped with a scanner (Model 1553, Digital Instruments). Membrane samples were cut into small pieces, glued onto flat metal substrates which were then placed on the sample holder. All the AFM tests were carried out in air under room temperature and two different scanning areas of $2 \times 2 \mu\text{m}$ and $500 \times 500 \text{ nm}$ were captured. The surface morphology of the asymmetric membranes was quantitatively characterised by the mean roughness, R_a and the root mean square of the height R_q . For each membrane sample, at least five different locations were measured and the average values of R_a and R_q were reported.

4.3.13 Porosity measurement

The porosity ε of the resulting membrane was measured using the following equation [95]:

$$\varepsilon = \frac{\frac{(W_w - W_d)}{\rho_w}}{\frac{(W_w - W_d)}{\rho_w} + \frac{W_d}{\rho_p}} \quad (4.1)$$

where W_w is the weight of wet asymmetric membrane which was immersed into water for 3 days and W_d is the weight of dry membrane which was dried at 150°C under vacuum for 12 h. The symbols ρ_w and ρ_p are the densities of water and P84

polymer, which are 0.997 and 1.339 g/cm³, respectively.

4.3.14 Single gas permeation measurements

Single gas permeation tests on the membranes were conducted using a constant volume test rig as shown in Figures 4.1 and 4.2.

Fig. 4.1 Schematic diagram of the test rig for the single gas permeation

Fig. 4.2 Photograph of the gas permeation testing rig

The test rig in Fig. 4.2 consisted of a stainless steel cell (Millipore) in which the membrane was mounted using O-rings, resulting in a high-pressure (H) and a low-pressure (L) sides. Each side consisted of an inlet port, an outlet port and a gas holder (G_1 or G_2) with regulating valves (H_1 and H_2 or L_1 and L_2). An oil-free

molecular vacuum pump (1025, Alcatel) was connected to the gas holders through the valves, H_3 and L_3 . The volume (V) of the low-pressure side was measured by sealing off the high-pressure side using a metal disk having the same thickness as that of the membrane. Helium supply to the low pressure side was from a standard vessel of known pressure.

Before the single gas permeation test, a membrane was placed in the permeation cell and both sides were evacuated to 10^{-5} Torr absolute pressure and the leakage rate of the system was determined to ensure the valid of the experimental results. During the leakage test, all valves were closed to isolate the system from the atmosphere and the pressure of the system was recorded as a function of time.

After the leakage test, the test gas supplied from a compressed gas cylinder was fed to the membrane through valve H_1 and the pressure in p_1 was measured by a differential pressure transducer (DP15, Validyne). During the test, the pressure in the gas holder G_1 was maintained at a constant value (p_1) whilst vacuum was maintained in the low-pressure side of the membrane. The penetrant was pulled through the calibrated volume (V) and the variation of the pressure in the low pressure side was detected by a high resolution absolute pressure transducer (627B, 10 Torr, MKS). The permeance of a single gas through the membrane was determined from the changes in the pressure $P_L(t)$ as a function of time t . The single gas permeability P is defined by

$$P = \frac{VL}{ART\Delta P} \frac{dp}{dt} \quad (4.2)$$

where V is the downstream volume, L is the membrane thickness, A is the effective

membrane area, R is the universal gas constant, T is the absolute temperature in Kelvin, ΔP is the transmembrane pressure difference ($p_1 - p_2$, where p_1 and p_2 are the upstream and downstream pressures, respectively), and dp/dt is the steady rate at which the pressure increases on the downstream side.

The permselectivity (α) is determined by

$$\alpha = P_A / P_B \quad (4.3)$$

where P_A and P_B are the permeability of pure gases A and B, respectively. The gases used in these tests were He, N₂, O₂, and CO₂. Each gas was of purity of 99.99% and was used as received from Soxal (Singapore Oxygen Air Liquid Pte Ltd.). For all the experiments, the tests were carried out under room temperature. The value of gas permeability (P) is reported in the unit of Barrer [1 Barrer = 1×10^{-10} cm³ (STP) cm/(cm² s cm Hg)]. Membranes coated on the porous stainless steel substrate were used directly for the gas permeation tests while membranes coated on PMMA substrate were peeled from the substrate and then assembled into the gas permeation test rig. The thickness of membrane was measured by a micrometer. For each membrane, eight measurements on different sites were conducted and the average value was obtained.

For the asymmetric membranes, the thicknesses of the skin layers of the resulting asymmetric membranes (L) were estimated using the following formula [96]:

$$L = P^* / \bar{P} \quad (4.4)$$

where $\bar{P}$ is the gas permeance of the asymmetric membranes and P^* is the gas permeability coefficient measured from the dense P84 membrane, whose values are

8.6, 0.41, 0.049 and 0.87 Barrer for He, O₂, N₂ and CO₂, respectively. The gas selectivities of the asymmetric membranes were calculated based on the individual gas permeance.

4.3.15 Mixture gas permeation measurements

For binary gas permeation measurements, the pure gas permeation cell was modified accordingly. The cell was connected to a mixing chamber at its upstream end and the downstream end of the permeation cell was connected to a gas chromatograph (GC) system. The mixed gas system, with combination of permeation cell and GC allows straightforward determination of gas concentration. The GC used was an Agilent 6890 Series completed with MS and TCD detector. The GC was calibrated by standard samples with known composition to obtain the GC peak area as a function of gas mole fraction. The mixture gas consisted of oxygen and nitrogen with a volume ratio of 1:4 which was accurately controlled using flowmetres. Before the permeation test, the whole system was evacuated using a vacuum pump.

The sampling process was initiated by evaluating the line from the receiving volume to GC which was connected to a vacuum pump at its outlet. The compositions of the feed and permeate were analyzed by the GC. Based on binary gas permeation tests, the selectivity was measured.

Chapter 5 Effects of Membrane Thickness and Heat Treatment on the Gas Transport Properties of P84 polyimide Membranes

5.1 Introduction

In this part of the project, a series of P84 membranes of thicknesses ranging from 5 to 310 μm were prepared by spin coating. The effects of membrane thickness and heat treatment on the membrane transport properties were investigated.

5.2 Results and Discussion

5.2.1 TGA and DSC results

Figures 5.1 and 5.2 show the TGA and the DSC curve of P84 powder, respectively. In the TGA curve, the decomposition temperature (T_d) of P84 powder is 535 $^{\circ}\text{C}$, indicating excellent thermal stability. The weight loss (about 4%) at temperature of 100 $^{\circ}\text{C}$ is due to the moisture present in the powder. The glass transition temperature (T_g) of P84 can be determined from the DSC curve (Fig. 5.2) and found to be 315 $^{\circ}\text{C}$.

Fig.5.1 TGA curve of P84 powder

Fig. 5.2 DSC curve of P84 powder

5.2.2 P84 membranes with various thicknesses

For the preparation of the membrane, porous stainless steel substrates were initially used because of the ease in processing the membranes for the gas permeation tests. However, it was difficult to obtain defect-free membranes with thickness less than 50 μm using these substrates. Dense PMMA substrates with much smoother surface were subsequently used for preparing thinner membranes. The membrane prepared using PMMA substrate had to be detached from the substrate by immersing it into ethanol/water solution. A total of seven membranes with thickness ranging from 6 to 310 μm were prepared by controlling the spin coating times. The relationship between the membrane thickness and the number of coats is shown in Fig. 5.3. The membrane with a certain thickness L was labelled as “P84- L ”. For example, a membrane with thickness of 309 μm was labelled as P84-309.

Fig. 5.3 Relationship between the membrane thickness and the number of coats for porous stainless steel substrates and PMMA substrate

5.2.3 Effect of heat treatment on the properties of P84 membranes

The study on the effect of heat treatment was carried out on one of the membranes. Membrane P84-118 was annealed under three different temperatures, *i.e.*, 80, 200 and 315 °C, to investigate the effect of heat treatment on its gas transport properties. Membranes annealed at 315 °C were found to be cracked due to the unequal thermal stress generated at the interface between the substrate and the polymer membrane during the heating or cooling process. The membrane had a line crack as shown in Fig 5.4 (c), while the membranes annealed at 80 and 200 °C were defect-free. Table 5.1 shows that P84-118 membrane annealed at 200 °C yields higher selectivity than that at 80 °C but lower permeability for all the single gases (He, N₂, O₂ and CO₂). The permeabilities of P84-118 annealed at 80 °C were 16.2, 0.196, 1.20 and 2.01 Barrers for He, N₂, O₂ and CO₂, respectively. The permeabilities of P84-118 membrane

annealed at 200 °C decreased by 10%, 48%, 26% and 31% for He, N₂, O₂ and CO₂, respectively, as compared to that at 80 °C while the ideal selectivities increased by 30%, 23%, 25% and 18% for O₂/N₂, He/CO₂, CO₂/N₂ and He/O₂, respectively. This gas transport property in P84-118 membranes was due to the different membrane morphologies, resulting from the different annealing temperatures. As shown in Fig. 5.4 (a), there was a distinct lamination structure in the cross-section of P84-118 membrane annealed at 80 °C which was formed due to the separate layers of coating. For the membrane P84-118 annealed 200 °C, the different layers of polymer were sintered together and the lamination lines disappeared due to chain movements. This is reasonable considering the fact that the higher temperature is favourable to chain movements in polymers. This is termed the densification process whereby the excess free volume of the membrane is reduced. This, in turn, enhances selectivity but reduces the permeability of the membrane. Subsequently, to ensure good performance in gas separation, all membranes were prepared and annealed at 200 °C.

Table 5.1 Transport properties of P84-118 membrane annealed at 80 and 200 °C.

Temperature (°C)	Permeability <i>P</i> (Barrer)				Selectivity <i>S</i>			
	He	N ₂	O ₂	CO ₂	O ₂ /N ₂	He/CO ₂	CO ₂ /N ₂	He/O ₂
80	16.2	0.196	1.20	2.01	6.12	8.06	10.26	13.50
200	14.62	0.102	0.89	1.39	8.73	10.52	13.63	16.42

5.2.4 Morphology of membranes

To observe the morphology of the membranes with varying thicknesses and examine the presence of defects and pinholes, SEM tests were carried out. The results are shown in Fig. 5.5. The SEM micrographs labelled as “a” (1-a to 7-a) show the cross-section morphology and those labelled as “b” (1-b to 7-b) show the top surface

morphology. The micrographs of the cross-sections show no crack lines or pinholes that are present in the membranes. This is due to the fact that P84 is a glassy polymer with a high chain packing density and an excellent ability to form membranes. The micrographs of the top surface images show that the surfaces of membranes P84-310, P84-219, P84-174 and P84-118 that were prepared using porous stainless steel substrate were not very even. This could also be verified that the thickness variations for a given membrane could be up to 10 μm when tested in different locations. However, the surfaces of membranes prepared using PMMA substrates (membranes P84-6, P84-13 and P84-42) were smoother, as observed from the SEM micrographs and the thickness measurements.

Fig. 5.4 SEM micrographs of the cross-section of P84-118 membrane annealed at (a) 80 $^{\circ}\text{C}$, and (b) 200 $^{\circ}\text{C}$. (c) A digital photograph together with the SEM micrograph of top surface (insert) of P84-118 annealed at 315 $^{\circ}\text{C}$

Fig. 5.5 SEM micrographs of the cross-section (labelled as “a”) and the top surface (labelled as “b”) for the membranes P84-6 (1), P84-13 (2), P84-42 (3), P84-118 (4), P84-174 (5), P84-219 (6) and P84-309 (7).

5.2.5. Effect of membrane thickness on transport properties of membranes

Gas permeation tests were carried out to investigate the effect of membrane thickness on the transport properties of P84 membranes. Figure 5.6 shows that the helium permeability through the membranes with different thicknesses is independent of pressure. This behaviour is characteristic of the permeation of non-plasticising gases through glassy polymers and also indicates that some non-selective transport mechanisms, such as Knudsen flow, were not present during the gas transport processes. Further, there were no defects or pinholes present in the membranes as verified by the SEM micrographs.

Fig. 5.6 Permeabilities of helium of various membranes subjected to various feed pressures

Table 5.2 Single gas permeability and selectivity of gas pairs for various membrane thicknesses.

Thickness (μm)	Permeability		P (Barrer)		Selectivity S			
	He	N ₂	O ₂	CO ₂	O ₂ /N ₂	He/CO ₂	CO ₂ /N ₂	He/O ₂
6	4.02	0.039	0.26	0.41	6.67	9.66	10.51	15.23
13	5.41	0.051	0.36	0.59	7.06	9.19	11.57	15.06
42	9.20	0.065	0.57	0.92	8.77	10.0	14.16	16.14
118	14.64	0.102	0.89	1.39	8.73	10.52	13.63	16.42
174	15.31	0.117	0.95	1.48	8.12	10.32	12.65	16.07
219	17.09	0.122	1.09	1.66	8.93	10.27	13.61	15.56
309	18.33	0.127	1.13	1.82	8.90	10.06	14.33	16.20

Table 5.3 Single gas permeance for membranes with various thicknesses

Thickness L (μm)	Permeance $\bar{P}$ (Barrer/ μm)			
	He	N	O ₂	CO ₂
6	0.6700	0.0065	0.0433	0.0683
13	0.4162	0.0039	0.0277	0.0454
42	0.2191	0.0015	0.0136	0.0219
118	0.1241	0.0009	0.0075	0.0118
174	0.0880	0.0007	0.0055	0.0085
219	0.0780	0.0006	0.0050	0.0076
309	0.0593	0.0004	0.0037	0.0059

The gas permeation results for helium, nitrogen, oxygen and carbon dioxide and the ideal selectivity of the given gas pairs are shown in Table 5.2. A feed pressure of 4 bars was used for all the tests. For all the single gases (He, N₂, O₂ and CO₂), their permeabilities are highly dependent on the membrane thickness whereby the permeability increases with increasing membrane thickness. The permeability of all the single gases increased by more than 3 times as the membrane thickness increased from 6 to 309 μm . Table 5.2 also shows that the permeability of the single gas increases in the following order: He (2.6 Å) > CO₂ (3.3 Å) > O₂ (3.46 Å) > N₂ (3.64 Å)

with its respective molecular gas diameter given within the parenthesis. These trends are also shown in Fig. 5.7. Hence, the permeability of the gas increases with decreasing size of the gas molecule, as expected. P84 is a partial crystallised polyimide and its crystallinity level, crystallinity orientation and excess free volume are highly dependent on the membrane thickness [97]. Thinner membranes have a lower crystallinity level, smaller excess free volume and a higher molecule chain alignment in a parallel orientation to the membrane surface. These membrane structure and morphology have considerable influences on the gas transport properties through the membrane. Lower crystallinity will lead to increased gas permeability but smaller excess free volume and higher molecule chain alignment will both lead to decreased gas permeability due to increased flow resistance. Of the four single gases studied in this work, Fig. 5.7 shows that the permeability of each single gas decreases with decreasing membrane thickness. For a thinner membrane, the combined effects of a smaller excess free volume and a higher molecule chain alignment in a parallel orientation to the membrane surface are more pronounced than the lower crystallinity effect and therefore result in lower permeability as compared with a thicker membrane. The numerical values of permeability for the various single gases for different membrane thicknesses are given in Table 5.2. The effect of aging on the gas permeability is probably negligible as all the P84 membranes were used soon after they were prepared. To further evaluate the gas permeability through the membranes with varying thicknesses, the relationship between the permeance and the membrane thickness is shown in Fig. 5.8 and Table 5.3. The permeance of single gas (He, N₂, O₂

and CO_2) decreases with increasing membrane thickness. This is due to the fact that the flow resistance through the membrane increases exponentially with increasing membrane thickness due to increasing gas path length. The selectivity of gas pairs (O_2/N_2 , He/CO_2 , CO_2/N_2 and He/O_2) seems to be almost independent of membrane thickness as shown in Fig. 5. 9, although some minor variations could be observed. Such relationship between selectivity and membrane thickness was also reported for other polymer materials, such as polysulfone, polyetherimide and polycarbonate [98]. From Table 5.2, the average selectivities of O_2/N_2 , He/CO_2 , CO_2/N_2 and He/O_2 were found to be about 8.2, 10.0, 12.9 and 15.8, respectively.

Fig. 5.7 Permeability of membranes with various thicknesses

Fig. 5.8 Permeance of membranes with various thicknesses

Fig. 5.9 Selectivity of membranes with various thicknesses

4.3. Summary

P84 polyimide membranes with thicknesses ranging from 6 to 310 μm were fabricated by spin coating. The effects of heat treatment on the membrane morphology and gas transport properties were investigated. It was found that membrane P84-118 (118 μm thickness) annealed at 315 °C for 24 hour, cracked

because of the stress generated in the interface between the substrate and the polymer membrane, resulting in very low or no selectivity. Membrane P84-118 annealed at 200 °C exhibited higher selectivity but lower permeability than that annealed at 80 °C. The permeabilities of P84-118 annealed at 80 °C are 16.2, 0.196, 1.20 and 2.01 Barrer for He, N₂, O₂ and CO₂, respectively. The permeabilities of P84-118 membrane annealed at 200 °C decreased by 9.8%, 48%, 25.8% and 30.9% for He, N₂, O₂ and CO₂, respectively, as compared with those at 80 °C while the ideal selectivities increased by 42.7%, 30.5%, 32.9% and 21.6% for O₂/N₂, He/CO₂, CO₂/N₂ and He/O₂, respectively. The SEM micrographs revealed that the higher annealing temperature of 200 °C was favourable to fuse the lamination lines resulting from the separate coats during preparation and this could reduce excess free volume and densify the membrane. The helium permeability for the membranes with varying thicknesses was found to be independent of the feed pressure, indicating the absence of defects or pinholes in the membranes. The gas permeation tests showed that the permeability of membranes increased significantly with increasing membrane thickness. This is due to the combined effects of larger excess free volume and lower molecular chain alignment in a parallel orientation to the membrane surface which predominate over the adverse effect of higher crystallinity level in a thicker membrane. The selectivity of gas pairs was nearly independent of the variations in membrane thickness.

Chapter 6 Influence of Inorganic Fillers on the Structural and Transport Properties of Mixed Matrix Membranes

6.1 Introduction

Three types of filler particles, fumed nano-SiO₂, synthesised MCM-41 and zeolite 4A, with different particle sizes, surface areas and pore structures were incorporated into the P84 matrix to prepare mixed matrix membranes. The structural characteristics and gas transport properties of the resulting composite membranes were investigated and systematically compared.

6.2 Results and discussion

6.2.1 Characterisation of inorganic fillers

The X-ray diffraction pattern of the synthesised MCM-41 is shown in Fig. 6.1. Three peaks in the $2\theta = 2-6^\circ$ range are clearly shown in the XRD pattern and these peaks are associated to their corresponding *hkl* reflection indices, which confirm the presence of mesoporous structures in the MCM-41 particles. The N₂ adsorption-desorption isotherm of MCM-41 is shown in Fig. 6.2. The curve is a typical Type IV adsorption isotherm that indicates the characteristics of a mixed micro- and meso-porous material. The synthesised MCM-41 had a high surface area of 812 m²/g and a total pore volume of 0.67 cm³/g as shown in Table 6.1. According to the BJH method, the average pore size was about 2.7 nm. The TEM micrograph of MCM-41 particles in Fig. 6.3 showed that they had a very narrow size distribution of 40-70 nm, which were obtained through a long period of hydrothermal aging during the synthesis procedure. The properties of all the three fillers are given in Table 6.1 and their respective TEM

micrographs are shown in Fig. 6.3.

Table 6.1 Properties of the inorganic fillers

Filler sample	Particle size (nm)	Pore size (nm)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Density (g/cm ³)
Fumed-silica	7	NA	390	NA	2.17
MCM-41	56	2.7	812	0.67	2.12
Zeolite 4A	2500	0.38	567	0.21	1.91

Fig. 6.1 XRD pattern of synthesised MCM-41

Fig. 6.2 N₂ adsorption-desorption curve of synthesised MCM-41

Fig. 6.3 TEM micrographs of fumed nano-SiO₂ (A), synthesised MCM-41 (B) and zeolite 4A (C)

6.2.2 Morphology of membranes

The thickness of the pure P84 membrane was 32 μm while the thicknesses of all the composite membranes were almost the same, *i.e.*, $28 \pm 1 \mu\text{m}$, with slight differences due to minor concentration variations in the casting solutions. P84, P84/SiO₂ and P84/MCM-41 membranes were transparent while the P84/4A membrane was slightly cloudy yellow and semi-transparent in appearance.

Figure 6.4 shows the SEM micrographs of P84 membrane which is dense and defect-free and composite membranes which consist of filler particles that are homogeneously dispersed in the polymeric matrix. The morphology of the P84 membrane (1-A, 1-B) is consistent with the properties of the P84 polymer with a high chain packing density and a good ability to form membranes. Based on the SEM micrographs of the top surfaces (2-A, 3-A) nano-SiO₂ and MCM-41 particles were well sub-embedded under the P84 surface. For the P84/4A composite membrane, some zeolite 4A particles were partially exposed on the surface of the membrane because of their larger particle size (2500 nm, Table 6.1) as compared with nano-SiO₂

(7 nm) and MCM-41 (56 nm) particles. From the SEM micrographs of the membrane cross-sections, P84 and P84/SiO₂ membranes were much denser than P84/MCM-41 and P84/4A membranes which appeared to show the presence of porosities. Careful inspections revealed that some cavities existed in the cross-sections of P84/MCM-41 and P84/4A membranes which were formed by the cleaving of MCM-41 and zeolite 4A particles from the polymeric matrix during the liquid nitrogen procedure which was used to fracture the membranes during sample preparation for SEM analyses. From these micrographs, it could be seen that all the filler particles were homogeneously dispersed and no aggregates existed in the composite membranes. However, by mere observations of the SEM micrographs, it was not sufficiently convincing to draw conclusions that these filler particles had good wettability with the polymer chains and that no non-selective voids between the particle-polymer interfaces existed. Hence, to further investigate the wettability of the fillers and the non-existence of voids in the composite membranes, TEM tests were carried out. TEM micrographs of the composite membranes are shown in Fig. 6.5. The dark contrast in the micrographs corresponds to the inorganic particles while the white contrast corresponds to the polymer chains. Figure 6.5 shows that individual particles are well dispersed into the polymer matrix and that no large particle aggregates are formed for the 8% particle loading. It also confirms that the inorganic particles have good compatibility with the polymer chains and that no voids are present between the particle-polymer interfaces.

Fig. 6.4 Surface (A), cross-section (B) and a higher magnification of the cross-section (C) of SEM micrographs of P84 membrane (1), P84/ SiO₂ membrane (2), P84/MCM-41 membrane (3) and P84/4A membrane (4)

Fig. 6.5 TEM micrographs of cut sections of (1) P84/SiO₂ membrane, (2) P84/MCM-41 membrane and (3) P84/4A membrane

Helium permeation through the membranes was also investigated as a function of its feed pressure. Figure 6.6 shows that for pure P84 membrane, He permeation is independent of the feed pressure. This behaviour is characteristic of the permeation of non-plasticising gases through glassy polymers. Similarly, He permeation through the P84/SiO₂ membrane is also independent of the feed pressure while those of P84/MCM-41 and P84/4A membranes show slight increases with increasing feed pressure. Generally, for increasing feed pressure, a sharp increase in permeation will take place when some continuous non-selective voids or defects are present in the membranes. In this study, due to the low content of the fillers and with careful preparations, the filler particles were homogeneously dispersed and no aggregates appeared in the membranes (Fig. 6.4). The slight increases in the He permeation through P84/MCM-41 and P84/4A membranes with increasing feed pressure were not due to the presence of continuous voids between the particle-polymer interfacial areas. The cause of this phenomenon was probably that the MCM-41 and zeolite 4A particles were porous and the permeation of He through them was pressure dependent.

Fig. 6.6 Dependence of He permeability on the feed pressure through the membranes

6.2.3 Membrane characterisation

The X-ray diffraction (XRD) patterns and densities of the membranes and P84 powder were determined. The XRD patterns are shown in Fig. 6.7. It shows that all patterns have diffraction peaks of 2θ in the range of $18-20^\circ$. Pure P84 powder and P84 membrane show a profile with a large peak centred at $2\theta = 18.5^\circ$ and $2\theta = 18.2^\circ$, respectively. The peaks of P84/SiO₂, P84/MCM-41 and P84/4A composite membranes appear at 19.6° , 19.3° and 19.0° , respectively, with the corresponding d spacing values of $4.54 \text{ \AA}$, $4.59 \text{ \AA}$ and $4.66 \text{ \AA}$, respectively, which are smaller than $4.87 \text{ \AA}$ for pure P84 membrane.

Fig. 6.7 X-ray diffraction patterns of the membranes and P84 powder

The density of the composite membranes ρ was measured by an ultrapycnometer and was also calculated from

$$\rho = \frac{1}{\frac{1-w_f}{\rho_p} + \frac{w_f}{\rho_f}} \quad (6.1)$$

where ρ_p is the density of the P84 polymer powder and ρ_f is the density of the

inorganic filler, w_f is the weight fraction of the inorganic filler which is 0.08 (8%) for all the three composite membranes in these experiments. The properties of the inorganic fillers are given in Table 6.1. The calculated density (ρ_c) and measured density (ρ_t) of the membranes are compared in Table 6.2. The ρ_c values are slightly greater than the ρ_t values for the composite membranes; differences are as follows: P84/SiO₂-7.5%, P84/MCM-41-13.7% and P84/4A-7.1%.

In order to understand the influence of the inorganic fillers on the polymer chain packing better, the fractional free volume (FFV) of the pure P84 membrane was estimated using Equations (6.2), (6.3) and (6.4) as follows:

$$FFV = \frac{V - V_0}{V} \quad (6.2)$$

$$V = M / \rho \quad (6.3)$$

$$V_0 = 1.3V_w \quad (6.4)$$

where V is the total molar volume of P84 monomer (cm³/mol), M is the molar mass of P84 monomer which is 423.6 g/mol, ρ is the density of the membrane, V_0 is the volume occupied by the polymer chains (cm³/mol) and V_w is the van der Waals volume which can be estimated by the group contribution method used by Park and Paul [99]. The value of V_w was found to be 194.5 cm³/mol based on the calculations according to Bos *et al.* [100].

For the composite membranes, the specific volume v (cm³/g) can be obtained from the density tests. The volume occupied by the polymer chains as well as the inorganic fillers should be considered. The fractional free volumes (FFV) of the composite membranes were calculated using Equations (6.5) and (6.6) as follows:

$$FFV = \frac{v - [v_0(1 - \varphi_f) + \varphi_f / \rho_f]}{v} \quad (6.5)$$

$$\varphi_f = \frac{w_f}{w_f + \frac{\rho_f}{\rho_p}(1 - w_f)} \quad (6.6)$$

where φ_f is the volume fraction of the inorganic fillers and v_0 (cm³/g) is the specific volume of the polymer chains. The calculated *FFV* values of the membranes are shown in Table 6.2.

Table 6.2 Densities and calculated fractional free volume of membranes.

Sample code	ρ_t (g/cm ³)	ρ_c (g/cm ³)	V (cm ³ /g)	V-V ₀ (cm ³ /g)	FFV
P84 membrane	1.356	NA	312.4	59.5	0.190
P84/SiO ₂	1.285	1.381	336.7	83.8	0.249
P84/MCM-41	1.214	1.379	348.9	96.0	0.275
P84/4A	1.281	1.370	337.7	84.8	0.251

The DSC curves of pure P84 powder, P84 membrane and composite membranes, and their corresponding glass transition temperature T_g are shown in Fig. 6.8. The T_g values of P84 powder and P84 membrane are 315 and 317 °C, respectively, which agree with those of Bos *et al.* [101]. The T_g value of P84/SiO₂ membrane is 295 °C which is 22 °C lower than that of the P84 membrane. In contrast to P84/SiO₂ membrane, the T_g values of P84/MCM-41 and P84/4A membranes are 328 and 347 °C, respectively. Both are much higher than that of P84 membrane.

Using molecular dynamic simulations for both experimental and modelling results, studies [102-104] had shown that the T_g of composite materials could be enhanced or depressed depending on the properties of polymer-particle interfaces. It is widely accepted that a free surface will have an effect on T_g . Some nano-gaps or non-wetting

interfaces between filler particles and polymer chains would decrease T_g while attractive polymer-particle interfacial interaction might increase T_g . For P84/MCM-41 and P84/4A membranes, increases of 11 and 30 °C, respectively, in the T_g over that of P84 membrane were obtained as shown in Fig. 6.8. This could be attributed to the immobilisation of the polymer chains within the filler particle-polymer interaction areas by raising the energy barrier for the intermolecular chain movements. This phenomenon indicates that the MCM-41 and the zeolite 4A particles have good wettability to the polymer chains and supports the thesis that the slight increases in He permeations through P84/MCM-41 and P84/4A membranes in Fig. 6.5 do not result from the non-selective voids. In contrast to P84/MCM-41 and P84/4A membranes, the P84/SiO₂ membrane showed a decrease in T_g as compared with P84 membrane. Generally, a decrease in T_g for nanocomposite membrane is attributed to the large particle/polymer interfacial area which is similar to nano-scale thin films with large surface area to volume ratios [33]. In the P84/SiO₂ membrane, the size of SiO₂ was about 7 nm which was much smaller than those of MCM-41 and zeolite 4A particles (Table 6.1), and this smaller SiO₂ size was much more effective to prevent chain packing and increase the distance between molecular chains. A large number of particle-polymer interface areas existed in P84/SiO₂ membrane and therefore a decrease in T_g was observed (Fig. 6.8).

Fig. 6.8 DSC curves of the membranes and corresponding T_g

Pure P84 powder is a partially crystalline polymer with intermolecular order at short length scale, resulting in a broad peak in the XRD patterns in Fig. 6.7. With the addition of the filler particles, especially for fumed SiO_2 , the peak angle shifted towards a larger angle while the d spacing value shifted towards a smaller one. This verified that the chain structure in the composite membranes was modified by the introduction of filler particles. The filler particles may act as barriers to the chain packing and decrease the crystallinity of the composite membranes. Among the three fillers used, fumed SiO_2 proved to be most effective in preventing the chain packing and therefore the P84/ SiO_2 membrane had the smallest d value. This was also in agreement with the DSC results in Fig. 6.8 in which the P84/ SiO_2 membrane had the lowest T_g amongst the membranes.

The density of pure P84 powder was found to be 1.339 g/cm^3 which was very close to the reported value of 1.336 g/cm^3 by Bos *et al.* [101]. For the composite membranes, the theoretical density estimated by Equation (6.1) was larger than the measured value,

suggesting an increase in the free volume of the polymer with the introduction of filler particles [80, 81]. This was also verified by the calculated fractional free volume values in Table 6.2. The *FFV* of P84 membrane was calculated as 0.19 which was slightly smaller than the previous reported value of 0.20 [100]. This difference could be due to the different casting solvent or thermal treatments. The *FFV* values of composite membranes were larger than that of P84 membrane. This could be explained by the fact that the filler particles changed the chain structure and decreased the chain packing density by disordering the molecular chains. From Table 6.2, the P84/SiO₂ membrane had a smaller *FFV* value than that of P84/MCM-41 membrane. The fumed SiO₂ particles, with much smaller sizes, should be more effective to hinder chain packing and P84/SiO₂ membrane should have larger particle-polymer interface area and *FFV* value than those of P84/MCM-41 and P84/4A membranes. However, the larger calculated *FFV* values of P84/MCM-41 and P84/4A membranes might be attributed to the fact that MCM-41 and zeolite 4A particles were porous. A part of the pore volume of these particles which was not part of the polymer chains, also contributed to the bulk specific volume during the *FFV* analysis. If the particle voids were accounted for and making the assumption that no polymer chains were trapped into the pores of the MCM-41 and the zeolite 4A particles, new *FFV* values of 0.24 and 0.22 should be used for the P84/MCM-41 and the P84/4A membranes, respectively, after subtracting the pore volume of the filler particles from the bulk specific volume.

Table 6.3 Results of gas permeation tests and the ideal selectivity of gas pairs

Sample code	P_{He}	P_{O_2}	$P_{N_2}^*$	P_{CO_2}	α_{He/O_2}	α_{O_2/N_2}	α_{CO_2/N_2}
Pure P84	8.60	0.41	0.049 ± 0.012	0.87	21.0	8.4	17.8
P84/SiO ₂	10.33	0.59	0.078 ± 0.008	1.26	17.5	7.6	16.2
P84/MCM-41	10.81	0.67	0.181 ± 0.005	1.90	16.1	3.7	10.5
P84/Zeolite 4A	8.41	0.38	0.051 ± 0.014	0.81	22.1	7.4	15.9

* Note: As the N₂ permeation was very slow, three tests for each sample were carried out and the average value was obtained.

6.3.4 Gas permeation results

Generally, the physical characteristics of the membranes such as the particle-polymer interfaces, the *FFV* values and the properties of the filler particles are consistent with the transport behaviours of the composite membranes as shown in the gas permeation results in Table 6.3. Table 6.3 shows the permeability and selectivity results for the various gases (He, O₂, N₂ and CO₂) for P84 membrane and the composite membranes. The ideal selectivity (α) of a membrane for gas pair (A/B) is defined as the ratio of the permeability (P) of gas A to that of gas B. For the tests carried out here, the P84 membrane showed slightly lower permeabilities for He, CO₂, O₂ and N₂ as compared with previous reported values [101]. The lower permeability could be due to the long heat treatment time during the membrane preparation. In Table 6.3, the P84/MCM-41 composite membrane yielded the highest permeability value for all the single gases. The permeabilities of He, O₂, N₂ and CO₂ were 10.81, 0.67, 0.181 and 1.9 Barrer, respectively. However, the selectivities of gas pairs (He/O₂, O₂/N₂ and CO₂/N₂) for P84/MCM-41 composite membrane were the lowest amongst all the membranes tested. For example, α of O₂/N₂ and α of CO₂/N₂ resulted in percent reductions of 56% and 41%, respectively, as compared with those of P84 membrane. Some composite

membranes yield high gas permeation but suffer low selectivity due to the presence of non-selective voids in the membranes. However, the MCM-41 composite membrane in this study had been shown to be free of these non-selective voids as verified by the TEM micrograph in Fig. 6.5. In this case, the probable reasons could be two-folds. Firstly, the MCM-41 particles with sizes of about 56 nm could disrupt the chain packing and increase the free volume of the polymer chain. Secondly, the transport of molecules through the channels of MCM-41 (2.7 nm) was much faster than through the P84 polymer chains. These channels were much larger and non-selective for all the test gases. As a result of these combined effects, a lower selectivity for P84/MCM-41 composite membrane was observed as compared with the other composite membranes and P84 membrane.

In contrast to P84/MCM-41 composite membrane, P84/4A composite membrane showed slightly lower permeabilities for He, O₂ and CO₂, and comparable permeability for N₂ as compared with P84 membrane. However, the selectivities of the gas pairs except for He/O₂ showed no improvements over those of P84 membrane. Generally, zeolite particles are incorporated into the polymer matrix membranes to enhance the selectivity of gas separation with their molecular sieving effect. In this study, the reductions in both the gas permeability and selectivity for P84/4A composite membrane could be due to the rigidifications of the polymer chains around the surfaces and pores of the zeolite 4A particle, resulting in the increase of the tortuosity of the transport path of gas molecules. This phenomenon was also reported by Moore and Koros [85], and Mahajan *et al.* [86]. The rigidifications of the polymer

chains could be due to the long thermal treatment time and this deduction is supported by the significant increase of 30 °C in the T_g of P84/4A composite membrane over that of P84 membrane.

In Table 6.3, the permeabilities of He, O₂, N₂ and CO₂ for P84/SiO₂ membrane are 10.33, 0.59, 0.078 and 1.26 Barrer, respectively, corresponding to increases of 20%, 63%, 59% and 45%, respectively, in the permeabilities over those of the P84 membrane. Correspondingly, the selectivities of gas pairs (α He/O₂, α O₂/N₂ and α CO₂/N₂) for P84/SiO₂ membrane showed slight decreases to those of P84 membrane. Merkel *et al.* [80, 81] attributed the high permeation of fumed nano-SiO₂ composite membranes to their large free volumes. They suggested that nano-SiO₂ particles could disrupt the rigid polymer chain packing and lead to a large free volume of polymer chains. The larger free volume enabled the chains to have more space and lower energy barriers to move. It is accepted that the flexible movements of the polymer chains are favourable to the transport of gas molecules. Similarly, the nano-SiO₂ particles could also effectively disorder the glassy P84 chains and create a large free volume in the P84/SiO₂ membrane as indicated by the XRD results (Fig. 6.7) and *FFV* calculations (Table 6.2). Therefore, P84/SiO₂ membrane has a high permeability while maintaining good selectivity.

6.3 Summary

Three types of inorganic fillers, fumed nano-SiO₂, synthesised mesoporous MCM-41 and zeolite 4A, were incorporated into P84 polymer matrix to prepare mixed matrix membranes. The influences of the introduction of these fillers on the structure of the

polymer chains and the gas transport properties had been investigated.

SEM micrographs indicated homogeneous dispersion of the filler particles and the absence of aggregates in the composite membranes while TEM micrographs verified that there were no voids at the particle-polymer interfaces. Increases in the glass transition temperature T_g of 11 and 30 °C were observed for those of P84/MCM-41 and P84/4A membranes, respectively, above that of P84 membrane while a 22 °C decrease was noted for the P84/SiO₂ membrane against that of P84 membrane. Density tests and *FFV* calculations revealed that the introduction of the fillers, especially the fumed nano-SiO₂ particles, changed the polymer chain structure and effectively increased the free volume of the polymer chains. This was also verified by the XRD results giving rise to a smaller d spacing value with the addition of the nano-SiO₂ particles.

Gas permeation tests with He, O₂, N₂ and CO₂ were carried out on pure P84 membrane as well as the composite membranes. It was found that gas permeation was closely related to some inherent properties of the filler particles (such as particle size, pore size and pore volume) and the properties of the particle-polymer interface. P84/4A composite membrane showed slight decreases in the permeability and selectivity as compared to the P84 membrane because of the rigidifications of the polymer chains around the surfaces of the zeolite particles. P84/MCM-41 membrane showed the highest permeability but the lowest gas selectivity due to the faster transport of molecules through the channels of MCM-41 particles with average pore size of 2.7 nm. P84/SiO₂ membrane had better gas separation efficiency with higher

permeability as well as acceptable gas selectivity over the other membranes. In comparison to P84 membrane, P84/SiO₂ membrane showed increases of 20%, 63%, 59% and 45% in permeabilities for He, O₂, N₂ and CO₂, respectively.

Chapter 7 Structural and Transport Properties of BTDA-TDI/MDI Co-polyimide (P84)-Silica Nanocomposite Membranes for Gas Separation

7.1 Introduction

Three types of inorganic fillers - fumed nano-SiO₂, synthesised mesoporous MCM-41 and zeolite 4A, were incorporated into P84 matrix to form MMMs. It had been demonstrated that the composite membrane with 8 wt% of the pristine SiO₂ had high permeability as well as acceptable selectivity. For this part of the project, composite membranes with different weight percentages of the pristine SiO₂ were prepared. For a good comparison, the pristine SiO₂ was modified with a silane coupling agent and the composite membranes based on the modified SiO₂ were also prepared. Fourier transform infrared spectroscopy (FTIR) spectra, thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) were used to confirm the success of bonding the APTES onto the surface of the SiO₂. Physical properties including membrane density, stress modulus, tensile strength and glass transition temperatures of the resulting membranes were characterised. The gas permeation of the resulting membranes were tested and also compared with theoretical predictions based on the Maxwell equation and the free volume theory.

7.2 Results and discussion

7.2.1 Characterisation of the modified nano-SiO₂ particles

The FTIR spectra (Fig. 7.1) of the modified SiO₂ particles with APTES showed the presence of NH₂ groups (N-H stretching at 3424 cm⁻¹), CH₂ groups (C-H stretching at 2923 cm⁻¹ and 2890 cm⁻¹), and Si-O groups (stretching at 1099 cm⁻¹). The NH₂ and

CH₂ groups confirmed the presence of APTES on the SiO₂ particles.

Fig. 7.1 FTIR spectra of the APTES-modified SiO₂ particles

Fig. 7.2 TGA curves of the modified SiO₂ and the pristine SiO₂

The TGA curves of the modified SiO₂ and the pristine SiO₂ are shown in Fig. 7.2. Due to the pyrolysis of the grafted APTES, the weight loss of the modified SiO₂ was higher than that of the pristine SiO₂. The success of bonding APTES onto the surface of SiO₂ was further confirmed by the XPS analysis. It was found that the atomic concentrations of oxygen, nitrogen, carbon and silicon were 49.67%, 4.75%, 19.12% and 26.45%, respectively. Based on the XPS results, the ratio of SiO₂ to APTES was

3.2:1 or 1.3×10^{-5} mol/m².

7.2.2 Membrane morphology characterisations

The SEM micrographs of the cross-sections of pure P84 membrane and the composite membranes are shown in Fig. 7.3. The SEM micrograph of the cross-section of the pure P84 membrane (Fig. 7.3-1) shows a dense and homogeneous structure. The SEM micrographs of composite membranes showed typical mixed matrix membrane morphology which consisted of filler particles dispersed in polymer matrix. The micrographs of the cross-sections of the composite membranes incorporated with modified SiO₂ exhibited crater-like morphology which consisted of cavities located in a number of fibrillated vein closed networks. These fibrillated vein networks consisted of elongated polymer chains and they were formed as a result of plastic deformation [105]. The appearance of cavities was probably due to the debonding of the particles from the matrix during the freeze fracture. In contrast, this type of morphology did not appear in the cross-sections of the composite membranes based on the pristine SiO₂ as shown in the micrographs in Fig. 7.3-7 and 7.3-8. The crater-like morphology could be attributed to the strong interactions between polymer chains and the surfaces of modified SiO₂ particles [106]. Through the modification of SiO₂ with the silane coupling agent ATPES, the surfaces of SiO₂ would become more hydrophobic and the bound ATPES could entangle with the P84 chains, resulting in favourable compatibility and strong interaction between the SiO₂ particles and the P84 matrix. The micrographs of composite membranes showed that the inorganic particles were homogeneously dispersed in the polymer matrix with the exception for

that of P84/25%SiO₂ composite membranes, which showed the presence of some submicron particle aggregates. There were no apparent voids and defects present in the cross-sections. However, for the composite membrane P84/Un-14%SiO₂, the SEM micrograph (Fig. 7.3-9) of its surface showed that some micrometre size particle aggregates were formed and the presence of some voids between polymer matrix and these aggregates, indicating poor compatibility between the polymer matrix and the large particle aggregates. Hence, the P84/Un-14%SiO₂ composite membranes showed no selectivity for the gases for the permeation tests and it was remarkably brittle.

Fig. 7.3 SEM micrographs of cross-sections of (1) pure P84 membrane, (2) P84/4%SiO₂, (3) P84/8%SiO₂, (4) P84/14%SiO₂, (5) P84/20%SiO₂, (6) P84/25%SiO₂, (7) P84/Un-4%SiO₂, (8) P84/Un-8%SiO₂, and (9) the surface of P84/Un-14%SiO₂ composite membranes

Fig. 7.4 TEM micrographs of the cross-sections of (1) P84/4%SiO₂, (2) P84/8%SiO₂, (3) P84/14%SiO₂, (4) P84/20%SiO₂, (5) P84/25%SiO₂ (low magnification) and (6) P84/25%SiO₂ (high magnification) composite membranes

To further examine the compatibility between the P84 matrix and the inorganic fillers, TEM micrographs of the composite membranes are shown in Fig. 7.4. Figure 7.4 (1-4) confirmed that the modified SiO₂ particles were homogeneously dispersed into the P84 matrix and no voids were present in the interface between the particles and the polymer chains for the cross-sections of P84/4%SiO₂, P84/8%SiO₂, P84/14%SiO₂ and P84/20%SiO₂ composite membranes. However, for the P84/25%SiO₂ composite membrane, some particle aggregates of submicrometre sizes were formed as shown in Fig. 7.4-5. The TEM micrograph with a high magnification (Fig. 7.4-6) revealed that some voids of several angstroms were present between the aggregates and the polymer chains.

For the dispersion of nanoparticles in the polymer matrix, nanoparticles will tend to form aggregates due to their high surface energy while polymer chains promote the

homogeneous dispersion of individual nanoparticles. As the content of the inorganic filler increases, the tendency of nanoparticles to form aggregates overwhelms the polymer stabilising effect, resulting in the formation of some micrometre particle aggregates within the composite membranes. Thermodynamically, these large particle aggregates have poor compatibility with the polymer chains, resulting in some voids and defects in the particle/polymer interfaces. Compared with the pristine SiO_2 , the modified SiO_2 particles have a better resistance to form aggregates due to the entanglement of the APTES chains. Based on the studies here, the content of the inorganic filler could be as high as 20% for void-free or defect-free composite membranes with modified SiO_2 while for pristine SiO_2 , the content of the inorganic filler was limited to 8% and below.

7.2.3 Mechanical properties of membranes

It is essential for membranes to possess adequate mechanical strength for applications in gas separation. The stress-strain curves of the various membranes prepared in this study are shown in Fig. 7.5. These stress-strain curves displayed similar characteristics as those of thermoplastic polymers which have well defined elastic deformation at small strains and nonlinear stress-strain behaviour at large strains.

Fig. 7.5 Stress-strain curves of resulting membranes

Table 7.1 Mechanical properties of various membranes

Sample	Tensile Stress (MPa)	Tensile Modulus (MPa)	Maximum Elongation (%)
Pure P84	63.8	1820	5.27
P84/4%SiO ₂	70.6	2021	4.89
P84/8%SiO ₂	86.1	2105	6.42
P84/16%SiO ₂	82.4	2132	5.57
P84/24%SiO ₂	69.7	1987	5.51
P84/30%SiO ₂	68.9	1783	5.82
P84/Un-4%SiO ₂	46.0	1007	5.56
P84/Un-8%SiO ₂	34.8	1485	2.42

Fig. 7.6 Effects of modified SiO₂ loading on tensile modulus and tensile stress

The mechanical properties of the various membranes, such as tensile modulus, tensile stress and maximum elongation at break point are shown in Table 7.1 and Fig. 7.6. The tensile modulus, the tensile stress and the maximum elongation at break point of pure P84 membrane were 1820 MPa, 63.8 MPa and 5.27%, respectively, indicating its stiffness and poor ductility. This is consistent with the properties of P84 polymer which is a rigid glassy polymer. Figure 7.6 shows that the loading of the modified SiO₂ had a remarkable influence on the tensile modulus and the tensile stress of the membrane. The tensile modulus increased with increasing modified SiO₂ loading from 4% to 14% and then decreased thereafter. A maximum modulus value of 2132 MPa was obtained for the P84/14%SiO₂ composite membrane. Compared with pure P84 membrane, the P84/4%SiO₂, P84/8%SiO₂, P84/14%SiO₂ and P84/20%SiO₂ composite membranes had higher values of tensile modulus while the P84/25%SiO₂ composite membrane had slightly lower tensile modulus value. Similarly, the tensile stress increased with increasing modified SiO₂ loading from 4% to 8% and then decreased with further increases in modified SiO₂ loading. A maximum tensile stress value of 86.1 MPa was obtained for the P84/8%SiO₂ composite membrane. All composite membranes incorporated with the modified SiO₂ particles had higher tensile stress when compared with the pure P84 membrane. Increasing SiO₂ loading from 4% to 8% increased the value of maximum elongation at break point but decreased to quite steady values for 14% to 25% SiO₂ loading as shown in Table 7.1. The mechanical properties of the P84 composite membrane with pristine SiO₂ particles were also measured and shown in Table 7.1 as well. Table 7.1 also showed

that the tensile modulus values of P84/Un-4%SiO₂ and P84/Un-8%SiO₂ composite membranes were 1007 and 1485 MPa, respectively, which were significantly lower than that of pure P84 membrane. The P84/Un-14% SiO₂ composite membranes were so brittle that they could not be subjected to the mechanical tests. Generally, the enhancement of tensile modulus and tensile stress of composite membranes are attributed to the transfer of mechanical energy from the polymer matrix to the high modulus of the inorganic filler [37]. The transfer of energy is greatly dependent on the properties of the polymer-filler interfaces. Compared with the pristine SiO₂ particles, the SiO₂ particles modified with ATPES have more hydrophobic surfaces and better wettability with P84 polymer chains, resulting in a strong interaction between the P84 polymer matrix and the inorganic particles. However, with increasing modified SiO₂ loading, the morphology of the membranes will change, *i.e.*, some defects or voids may be formed due to the formation of the SiO₂ aggregates as confirmed by the TEM micrograph in Fig. 7.4-6. These defects will reduce the mechanical strength of the composite membranes.

Fig. 7.7 DSC curves of various membranes

7.2.4 DSC and density test results

The DSC curves of the membranes and their corresponding T_g values are shown in Fig. 7.7. The T_g value of pure P84 membrane was 317 °C. The T_g values of the composite membranes incorporated with the modified SiO₂ particles were more than 30 °C higher than that of the pure P84 membrane while the T_g values of the composite membranes incorporated with pristine SiO₂ particles were at least 20 °C lower than that of pure P84 membrane. Generally, the T_g values of composite materials could either increase or decrease depending on the properties of the polymer-particle interfacial properties [33, 39]. Free surfaces, *i.e.*, nano-gaps or non-wetting interfaces between filler particles and polymer chains, would decrease T_g while attractive polymer-particle interfacial interaction would increase T_g . With the addition of nano-SiO₂ particles, more polymer-particle interfaces will be generated in the composite membranes. For the P84/Un-4%SiO₂ and P84/Un-8%SiO₂ composite membranes based on the pristine SiO₂ particles, the interfacial interaction between the polymer chain and the particles was very weak due to poor compatibility and consequently decreased T_g values were observed. However, for the composite membranes based on the modified SiO₂, the interactions between the polymer chains and the particle surfaces were much stronger due to better compatibility and increased entanglement of the silane coupling agent with the polymer chains, resulting in higher T_g values.

The density of the composite membranes ρ was measured by an ultrapycnometer and also calculated using Equation (6.1). The density of the pristine SiO₂ and the modified

SiO₂ were measure to be 2.17 and 2.19 g/cm³, respectively. The calculated density ρ_c and measured density ρ_t of the membranes were compared in Table 7.2.

Table 7.2 Densities and calculated fractional free volumes of membranes.

Sample code	Volume fraction, ϕ_f (%)	Measured density, ρ_t (g/cm ³)	Calculated density, ρ_c (g/cm ³)	Fraction of free volume	T_g (°C)	Void volume fraction, ϕ_v
Pure P84	0	1.36	NA	0.1882	317	0
P84/4%SiO ₂	0.0248	1.36	1.360	0.1927	352	0.0001
P84/8%SiO ₂	0.0485	1.34	1.380	0.2093	357	0.0292
P84/14%SiO ₂	0.0925	1.35	1.412	0.2117	361	0.0478
P84/20%SiO ₂	0.1326	1.34	1.452	0.2251	359	0.0770
P84/25%SiO ₂	0.1693	1.32	1.483	0.2434	359	0.1010
P84/Un-4%SiO ₂	0.0251	1.31	1.360	0.2225	293	0.0367
P84/Un-8%SiO ₂	0.0489	1.29	1.380	0.2386	297	0.0650

In order to understand the influence of the inorganic fillers on the polymer chain packing better, fractional free volume (*FFV*) of the pure P84 membrane was estimated using Equations (6.2), (6.3) and (6.4).

For the composite membranes, the specific volume V can be obtained from density tests. The volume occupied by the polymer chains as well as the inorganic fillers should be considered. The fractional free volumes (*FFV*) of the composite membranes were calculated using Equation (5.5) and (5.6). According to Hosserni *et. al.* [109], the void volume fraction (ϕ_v) of membranes can be calculated using Equation (7.1). The calculated fractional free volume (*FFV*) and void volume fraction values of the membranes are shown in Table 7.2.

$$\phi_v = \frac{\rho_c - \rho_t}{\rho_t} \quad (7.1)$$

Fig. 7.8 Effects of volume fraction of modified SiO₂ particles on the fractional free volume and void volume fraction of the nanocomposite membranes

Table 7.2 shows that the measured density was smaller than the theoretical density for all the composite membranes. The fractional free volume of pure P84 membrane was calculated to be 0.19, which is very close to the value of 0.2 reported by Bos *et. al.* [100]. An increase of fractional free volume was observed with increasing inorganic SiO₂ loading. For the same weight percentage of inorganic filler, the P84/Un-4%SiO₂ and the P84/Un-8%SiO₂ composite membranes had lower density, but higher fractional free volume and void volume fraction than those of the corresponding P84/4%SiO₂ and the P84/8%SiO₂ composite membranes. This may be due to the strong interaction and better compatibility between the polymer chains and the modified surfaces of SiO₂ particles. The fractional free volume and void volume fraction increased linearly with increasing volume fraction of the modified SiO₂ particles as shown in Fig. 7.8. In nanocomposite membranes, nano-particles will disrupt polymer chain packing, resulting in extra free spaces for polymer chain

movements. The addition of nano-particles will inevitably result in some void spaces being formed due to the formation of aggregates, especially when the inorganic filler loading is high. The former extra volume resulting from the disruptions of chain packing is consistent with the strict definition of free volume of polymer chains while the latter void volume in the particle aggregates is dissociated from the polymer chains and is not part of the free volume. However, it is difficult to differentiate between the free volume and the void volume in the particle aggregates.

7.2.5 Single gas permeation results

Mathematically, the Maxwell model, as expressed in Equation (7.2) [110, 111], has been widely used to predict the gas permeation properties of composite membranes.

$$P_c = P_0 \left[\frac{P_f + 2P_0 - 2\phi_f(P_0 - P_f)}{P_f + 2P_0 + \phi_f(P_0 - P_f)} \right] \quad (7.2)$$

where P_c is the permeability of a gas penetrant in a composite membrane with a volume fraction (ϕ_f) of inorganic filler. P_0 and P_f are the permeability of pure polymer membrane and inorganic filler, respectively. In this study, the non-porous SiO_2 particles were used as the inorganic filler and therefore P_f is 0. Equation (7.2) can be written as follows:

$$P_c / P_0 = \frac{1 - \phi_f}{1 + \phi_f/2} \quad (7.3)$$

where P_c/P_0 is defined as the relative permeability enhancement.

The free volume theory is also widely used to describe the gas transport properties of polymer membranes [81, 112]. It correlates diffusion coefficient D to fractional free volume of polymer membranes as

$$D = D' \exp\left(\frac{-B}{FFV}\right) \quad (7.4)$$

where D' and B are constants characteristic of the polymer-penetrant system.

The permeability coefficient is defined as the product of diffusion coefficient D and solubility coefficient S . The relative permeability enhancement of composite membranes can also be calculated as follows:

$$\frac{P_c}{P_0} = \left(\frac{D_c}{D_0}\right) \times \left(\frac{S_c}{S_0}\right) \quad (7.5)$$

where D_c and D_0 are the diffusion coefficients of the composite membrane and pure polymer membrane, and S_c and S_0 are the solubility coefficients of the composite membrane and pure polymer membrane, respectively. For the transport of light gases, *i.e.*, He, O₂, N₂ and CO₂, through the composite membranes, in Equation (7.5), the ratio of diffusion coefficient is always dominant and the ration of solubility coefficient is close to a unit when the volume fraction of the inorganic filler is low [80, 113]. Therefore, in Equation (7.5), the ratio of diffusion coefficient is dominant. The relative permeability enhancement is approximately equal to the ratio of diffusion coefficient as follows:

$$\frac{P_c}{P_0} \approx \frac{D_c}{D_0} = \exp\left(\frac{-B}{FFV_c} + \frac{B}{FFV_0}\right) \quad (7.6)$$

Here, an assumption is made such that the constants D' and B are the same for the composite membranes and the pure polymer membrane.

The single gas permeation test results and the ideal gas selectivity are presented in Table 7.3. The effect of the volume fraction of the inorganic filler on the permeability is shown in Fig. 7.9. The prediction results based on the Maxwell equation and the free volume theory are also shown in the same figure.

Table 7.3 Single gas permeability and ideal selectivity of gas pairs

Sample	Permeability P (Barrer)				Selectivity S		
	CO ₂	O ₂	N ₂	He	O ₂ /N ₂	CO ₂ /N ₂	He/N ₂
Pure P84	0.89	0.52	0.044	8.60	11.82	20.23	195.45
P84/4%SiO ₂	0.92	0.54	0.047	10.38	11.49	19.57	220.85
P84/8%SiO ₂	1.08	0.66	0.067	10.50	9.85	16.12	156.72
P84/14%SiO ₂	1.26	0.69	0.071	13.9	9.72	17.75	195.77
P84/20%SiO ₂	1.60	0.91	0.158	17.43	5.76	10.13	110.32
P84/25%SiO ₂	2.99	2.02	0.752	48.54	2.69	3.98	64.55
P84/Un-4%SiO ₂	1.16	0.51	0.070	9.80	7.29	16.57	140.00
P84/Un-8%SiO ₂	1.29	0.72	0.086	11.62	8.37	15.00	135.12

The permeabilities of pure P84 membrane for CO₂, O₂, N₂ and He were 0.89, 0.52, 0.044 and 8.6 Barrer, respectively, which were lower than those of all composite membranes as shown in Table 7.3. Figure 7.9 showed that the permeabilities of all gases (CO₂, O₂, N₂ and He) increased with increasing volume fraction of the inorganic filler, in particular, a sharp increase in permeability was observed when the modified SiO₂ volume fraction increased from 0.13 to 0.17. The Maxwell equation gave a much lower prediction as compared with the experimental data and the discrepancy increased with increasing modified SiO₂ volume fraction. On the other hand, the free volume theory gave an acceptable prediction except for large discrepancies against the experimental results for the permeabilities of P84/25%SiO₂ composite membranes. A number of SiO₂ aggregates with micrometre sizes were observed in the P84/25%SiO₂ composite membranes as shown in the SEM micrograph (Fig. 7.3-6). The large permeabilities of P84/25%SiO₂ composite membranes might be due to the presence of some non-selective continuous defects and voids in the aggregates. These deficiencies also resulted in lower selectivities of

the P84/25%SiO₂ composite membranes. The effect of volume fraction of modified SiO₂ particles on the selectivities of gas pairs (CO₂/N₂, O₂/N₂, and He/N₂) is shown in Fig. 7.10. The ideal selectivities of pure P84 membrane were 11.82, 20.23 and 195.45, for CO₂/N₂, O₂/N₂, and He/N₂, respectively. With the addition of the modified SiO₂ particles, comparable selectivities were obtained for the P84/4%SiO₂, P84/8%SiO₂ and P84/14%SiO₂ composite membranes. However, with further increases in modified SiO₂ volume fraction, decreases in the selectivities were observed for P84/20%SiO₂ and P84/25%SiO₂ composite membranes. For instance, the ideal selectivities of P84/25%SiO₂ composite membrane were 2.69, 3.98 and 64.55 for CO₂/N₂, O₂/N₂, and He/N₂, respectively, which were respectively 3.39, 5.08 and 3.03 times less than those of pure P84 membrane. With the same weight percentage of inorganic fillers, the composite membranes based on the modified SiO₂ particles had higher selectivities than the membranes based on the pristine SiO₂ particles, as shown in Fig. 7.11. The ideal selectivities of P84/4%SiO₂ composite membrane were 11.49, 19.57 and 220.85, for CO₂/N₂, O₂/N₂ and He/N₂, respectively, which were higher than 7.29, 16.57 and 140.00, respectively, for those of P84/Un-4%SiO₂ composite membrane. The selectivity enhancement of composite membranes based on modified SiO₂ particles is due to the better polymer-filler interfacial properties.

Fig. 7.9 Effects of the volume fraction of inorganic fillers on permeability

Fig. 7.10 Effects of volume fraction of modified SiO_2 particles on the selectivity

Fig. 7.11 Comparisons of selectivities among P84/4%SiO₂, P84/Un-4%SiO₂, P84/8%SiO₂ and P84/Un-8%SiO₂ composite membranes

7.3 Summary

Fumed nano-SiO₂ particles were modified using a silane coupling agent and then incorporated into P84 polymer matrix to prepare nano-composite membranes. The effects of the surface modification on the structural properties and the gas transport properties were examined. The effects of the modified SiO₂ volume fraction on the tensile modulus, tensile stress, permeability and selectivity of the resulting composite membranes were studied. Based on this work, some conclusions can be drawn as follows:

1. The morphology of the composite membranes was highly dependent on the surface properties of SiO₂ particles. The modified SiO₂ particles were more hydrophobic and exhibited better compatibility with P84 polymer chains as compared with the pristine SiO₂ particles which were confirmed by SEM, TEM, stress-strain tests and DSC tests.
2. The permeabilities of all gases (CO₂, O₂, N₂ and He) increased with increasing

volume fraction of inorganic filler, particularly, sharp increases in permeabilities were observed as the modified SiO_2 volume fraction increased from 0.13 to 0.17. Composite membranes with less than 0.14 volume fractions of the modified SiO_2 particles had comparable selectivities for CO_2 , O_2 , N_2 and He as those of pure P84 membrane. A decrease in selectivity was observed with further increase in the modified SiO_2 volume fraction greater than 0.10. With the same weight percentage of inorganic fillers, the composite membranes based on the modified SiO_2 had higher selectivity than the composite membranes based on pristine SiO_2 .

3. The Maxwell equation gave lower predictions against the experimental data while the free volume theory provided acceptable predictions except that large discrepancies were observed for the permeabilities of P84/25% SiO_2 composite membrane.

Chapter 8 Preparation and Characterisation of Polyimide-Silica Composite Membranes and Their Derived Carbon Composite Membranes for Gas Separation

8.1 Introduction

Polyimide (PI)-silica composite membranes were successfully prepared by the sol-gel technique and the derived carbon-silica composite membranes were obtained by the carbonisation of these PI-silica composite membranes at 900 °C under vacuum. The structural characteristics and gas transport properties of the resulting membranes were investigated.

8.2 Results and discussion

8.2.1 Thermal stability of polyimide/silica composite membrane

The TGA curves of the PI and PI/silica composite membranes are shown in Fig. 8.1. The decomposition temperatures were determined at the points where 5% weight loss occurred and these temperatures are shown in Table 8.1. Figure 8.1 and Table 8.1 showed that both pure PI membrane and PI-silica composite membranes exhibited high thermal stability with decomposition temperatures T_d above 500 °C. The pure PI membrane had the highest T_d value of 586 °C. With the addition of silica, the thermal stability of the PI-silica composite membranes decreased. The PI-SiO₂ 13.7% composite membrane had the lowest T_d value of 533 °C. Generally, it is believed that the introduction of the inorganic fillers is favourable for the enhancement of the thermal stability of the composite materials. However, in this part of project, the silica was obtained by the hydrolysis of TEOS and APTES. This

could influence the imidisation reaction during the synthesis of the polyimide matrix at higher temperature, resulting in the presence of small amount of polyamic acid, which could reduce the thermal stability of the PI-silica composite membranes. All TGA curves showed small weight losses of less than 2% at around 100 °C, which was due to the release of small molecules such as water and ethanol.

Fig. 8.1 TGA curves of the PI and PI-silica composite membranes

Table 8.1 Mechanical properties and decomposition temperatures of the PI and PI-silica composite membranes

Sample	Tensile stress MPa	Tensile modulus MPa	Elongation at break (%)	T_d (°C)
Pure PI	58 ± 3	768 ± 12	44 ± 4	586
PI-SiO ₂ 1.5%	75 ± 4	1076 ± 19	35 ± 1	556
PI-SiO ₂ 5.2%	88 ± 3	1135 ± 32	31 ± 3	564
PI-SiO ₂ 7.2%	134 ± 8	1237 ± 24	25 ± 2	544
PI-SiO ₂ 8.9%	143 ± 13	1386 ± 56	24 ± 4	541
PI-SiO ₂ 11.6%	164 ± 10	1620 ± 68	14 ± 3	560
PI-SiO ₂ 13.7%	178 ± 16	1818 ± 102	14 ± 5	533

8.2.2 Mechanical properties of polyimide/silica composite membranes

Tensile stress-strain tests were carried out to investigate the mechanical properties of the PI and PI-silica composite membranes. Values of tensile strength, tensile modulus and elongation strain at break of samples were determined and shown in Table 8.1. Figure 8.2 shows the tensile strength and the tensile modulus of the membranes as a function of silica content. It could be seen that the tensile stress and the tensile modulus increased monotonically with increasing silica content. The tensile strength and the tensile modulus of the PI membrane were 58 and 768 MPa, respectively. PI-SiO₂ 13.7% composite membrane exhibited the highest tensile strength and tensile modulus, which were 178 and 1818 MPa, respectively. Generally, it is believed that the external force on the composite materials will be transferred from the continuous phase (polymer matrix) to the discontinued phase (inorganic phase), and that the mechanical strength of composite membrane is highly dependent on the interface properties between polymer matrix and inorganic fillers [114-116]. The PI-silica composite membranes were prepared using a sol-gel method and a coupling agent, APTES, to bind the polyimide matrix and the inorganic silica. Cross-linked networks between polyimide chains and silica would probably be formed in the composite membranes, resulting in better mechanical properties as compared with the pure PI membranes.

Fig. 8.2 Tensile stress and tensile modulus of pure PI and PI-SiO₂ composite membranes

Fig. 8.3 Elongation strain at break of pure PI and PI-SiO₂ composite membranes

8.2.3 Morphology of the resulting membranes

Digital pictures of the PI and PI-silica composite membranes and the resulting carbon membranes are shown in Fig. 8.4. The pure PI membrane was of a golden yellow colour and fully transparent. The transparency of the PI composite membranes decreased with increasing silica content. The PI-SiO₂ 13.7% composite membrane was slightly cloudy yellow and semi-transparent in appearance. The

morphology of the polymer composite membranes and the derived carbon membranes was observed by SEM and the constituent elements of the samples, *i.e.*, carbon, silicon and oxygen, were analysed by EDX. The SEM micrographs of the pure PI, PI-SiO₂ 7.2% and PI-SiO₂ 13.7% composite membranes and their derived carbon membranes are shown in Fig. 8.5. The EDX scanning results were included in the SEM micrographs where the dispersion of carbon, silicon and oxygen were represented by the red, blue and yellow curves, respectively. All the polymer membranes had a thickness of 80-90 μm and the derived carbon membranes had a thickness of 60-70 μm . The pure PI membrane exhibited a dense homogeneous structure. The PI-silica composite polymer membranes consisted of the nanoscale SiO₂ particles uniformly dispersed in the continuous polymer matrix; this was verified by the homogeneous dispersion of the silicon element. The SiO₂ particle size increased with increasing TEOS content and the SiO₂ particles in the PI-SiO₂ 13.7% composite membrane were roughly 60 nm, which was much less than the value reported by Morikawa *et al.* [115]. The inorganic phase had excellent compatibility with the polymer matrix as indicated by the non-existence of any cavities in the polymer matrix which was due to the cleaving of SiO₂ particles to the polymer matrix during sample preparation. The uniform dispersion of fine SiO₂ particles and the good compatibility between the inorganic phase and the polymer matrix were attributed to the preparation of the PI-silica composite membranes by the in-situ hydrolysis of TEOS and APETS; these characteristics contributed to the enhancement of the stress strength and modulus of the composite membranes. The

derived carbon membrane and the carbon-silica composite membranes exhibited dense morphology and the constituent elements including silicon, carbon and oxygen were uniformly dispersed in the membranes as indicated by the EDX scanning curves. For elemental analyse, five measurements were carried out for each sample and the average values were listed in Table 8.2. For convenience, carbon-silica composite membranes were denoted as C-Si $x\%$, where x is the weight ratio of silicon to carbon.

Fig. 8.4 Digital pictures of the PI and PI-silica composite membranes and the resulting carbon membranes

Table 8.2 Results of elemental analysis for the carbon and carbon-silica composite membranes

Sample	Si	C	O	Si/C
Pure carbon		94.1	5.9	
C-Si 5%	4.3	86.8	8.9	0.05
C-Si 8%	5.9	78.6	15.5	0.08
C-Si 11%	7.9	71.4	20.7	0.11
C-Si 19%	12.4	65.5	22.1	0.19
C-Si 23%	13.8	61.9	24.3	0.23
C-Si 28%	15.4	55.9	28.7	0.28

Fig. 8.5 SEM micrographs of (1) pure PI membrane, (2) PI-SiO₂ 7.2% composite membrane and (3) PI-SiO₂ 13.7% composite membrane, (A) cross-section view with lower magnification, (B) cross-section view with higher magnification and (c) derived carbon membranes.

8.2.4 XRD patterns of PI-silica and carbon-silica composite membranes

The XRD patterns of the pure PI and the PI-silica composite membranes are shown in Fig. 8.6. All the patterns had diffraction peaks of 2θ in the range of 18-21°. These peaks became broader with increasing SiO₂ content. This “broadening effect” as induced by the introduction of SiO₂ phase was also observed by Agag *et al.* [117] and it could be due to the fact that the nanoscale SiO₂ particles inhibited the ordering packing of polymer chains, leading to lower crystallinity. The pure PI membrane

showed a profile with a distinct peak centred at $2\theta = 18.5^\circ$ which corresponded to a d spacing value of $4.79 \text{ \AA}$. The corresponding peaks of the PI-silica composite membranes shifted from 19.09 to 20.2° and therefore the d spacing values decreased from $4.65 \text{ \AA}$ to $4.39 \text{ \AA}$ with increasing SiO_2 content from 1.5 to 13.7% as shown in Table 8.3. It is noted that no evident diffraction peak is observed for the SiO_2 phase.

The XRD patterns of the pure carbon membrane and the carbon-silica composite membranes are shown in Fig. 8.7. The variations of the peak position in the profiles were examined and the corresponding d spacing values are given in Table 8.3. All the XRD patterns of the pure carbon membrane and the carbon-silica composite membranes showed a broad peak of 2θ in the range of 23 to 26° , which could be indexed to (002) reflection, resulting from the stacks of parallel layer planes. In addition, a lower intensity peak in the range of 43 to 45° was observed for the C-Si 11%, C-Si 19%, C-SiO₂ 23% and C-SiO₂ 28% composite membranes, which could be indexed to (100) reflection, resulting from the regular structure within the individual layer plane. These two peaks were characteristics of disordered carbonaceous materials. The pure carbon membrane showed a peak centred at 23.34° , which corresponded to a d_{002} spacing value of $3.81 \text{ \AA}$. The peaks of carbon-silica composite membranes shifted from 24.19 to 25.11° for C-Si 5% to C-Si 28% and therefore the d spacing values decreased from $3.68 \text{ \AA}$ to $3.55 \text{ \AA}$, respectively as shown in Table 8.3. The value of d_{002} can be visualised as the average distance between two parallel layers and it is always used to estimate the graphitisation degree of carbon. In general, it is believed that carbon materials tend to exhibit

increasing ordering with increasing d_{002} values [118]. It was reported that the structures of the carbon materials obtained from the pyrolysis of polymer precursors were highly dependent on the introduction of the inorganic phases and that the value of d_{002} decreased with the introduction of the inorganic phases [119, 120]. This phenomenon would probably be attributed to the fact that the inorganic phase could have an effect on the carbonisation and graphitisation processes.

Fig. 8.6 XRD curves of pure PI membrane and PI-silica composite membranes

Fig. 8.7 XRD curves of pure carbon membrane and carbon-silica composite

membranes

Table 8.3 Results of XRD analyse and d spacing values for the various membranes

Sample	2θ °	d value (Å)	Sample	2θ °	d value (Å)
Pure PI	18.50	4.79	Pure carbon	23.34	3.81
PI-SiO ₂ 1.5%	19.05	4.65	C-Si 5%	24.19	3.68
PI-SiO ₂ 5.2%	19.18	4.62	C-Si 8%	24.35	3.69
PI-SiO ₂ 7.2%	19.43	4.57	C-Si 11%	24.42	3.64
PI-SiO ₂ 8.9%	19.72	4.50	C-Si 19%	24.59	3.62
PI-SiO ₂ 11.6%	19.94	4.45	C-Si 23%	24.83	3.58
PI-SiO ₂ 13.7%	20.20	4.39	C-Si 28%	25.11	3.55

8.2.5 Gas transport properties of PI-silica composite membranes

The single gas permeation tests on the resulting membranes were carried out. The gas permeabilities and the selectivities of the pure PI membrane and the PI-silica composite membranes are presented in Table 8.4. For the pure PI membrane, the permeabilities of He, CO₂, O₂ and N₂ were 14.63, 1.12, 0.46 and 0.09 Barrer, respectively and the selectivities of He/N₂, CO₂/N₂ and O₂/N₂ were 162.56, 12.44 and 5.11, respectively. With increasing silica content, the gas permeabilities of all the tested gases (He, CO₂, N₂ and O₂) decreased initially and then increased afterwards with the further increase of the silica content. The relationship between the permeability and the silica content represented the resemblances of “V” curves as shown in Fig. 8.8. This behaviour could be explained as follows: On one hand, the decrease of solubility coefficients of penetrants with increasing silica content would lead to the decrease of the permeabilities of the membranes. On the other hand, the formation of the organic-inorganic networks could be favourable for the transport of the penetrants which would enhance the permeabilities of the membranes. The

PI-SiO₂ 7.2% composite membrane had the lowest permeabilities of 9.58, 0.86, 0.34 and 0.03 Barrer while the PI-SiO₂ 13.6% composite membrane had the highest permeabilities of 16.59, 1.47, 0.58 and 0.12 Barrer for He, CO₂, O₂ and N₂, respectively. The variations of the ideal selectivities of gas pairs are shown in Fig. 8.9. The PI-SiO₂ 7.2% composite membrane had the highest selectivities of 319.33, 28.67, and 11.33 for He/N₂, CO₂/N₂, and O₂/N₂ which were 1.96, 2.3 and 2.22 times greater than those of the pure PI membranes, respectively. The PI-SiO₂ 13.6% composite membrane had the lowest ideal selectivities of 138.25, 12.25 and 4.83 for He/N₂, CO₂/N₂, and O₂/N₂, respectively which were smaller than those of the pure PI membrane. Clearly, the resulting membranes still suffered a “trade-off” relationship between permeability and selectivity.

Table 8.4 Single gas permeabilities and ideal selectivities of pure PI membranes and PI-silica composite membranes

Sample	Permeability (Barrer)				Selectivity		
	He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂
Pure PI	14.63	1.12	0.46	0.09	162.56	12.44	5.11
PI-SiO ₂ 1.5%	13.7	1.09	0.47	0.09	152.22	12.11	5.22
PI-SiO ₂ 5.2%	9.64	0.92	0.32	0.06	160.67	15.33	5.33
PI-SiO ₂ 7.2%	9.58	0.86	0.34	0.03	319.33	28.67	11.33
PI-SiO ₂ 8.9%	12.3	0.89	0.42	0.08	153.75	11.13	5.25
PI-SiO ₂ 11.6%	14.59	1.32	0.46	0.1	145.9	13.2	4.6
PI-SiO ₂ 13.7%	16.59	1.47	0.58	0.12	138.25	12.25	4.83

Fig. 8.8 Single gas permeabilities of pure PI membrane and PI-silica composite membranes

Fig. 8.9 Ideal selectivities of pure PI membrane and PI-silica composite membranes

8.2.6 Single gas transport properties of carbon-silica membranes

The single gas permeance and the selectivities of the derived carbon membrane and the carbon-silica composite membranes are shown in Table 8.5. The order for the gas

permeance of all the membranes was in accordance to the magnitude of the kinetic diameter, indicating that the molecular sieving transport mechanism played a dominant role in the transport of the gas penetrants. The pure carbon membrane yielded permeances of 37.74, 7.2, 2.87 and 1.08 Barrer/cm for He, CO₂, O₂ and N₂, and selectivities of 36.35, 6.93 and 2.77 for He/N₂, CO₂/N₂ and O₂/N₂, respectively. In comparison with the pure carbon membrane, the carbon-silica composite membranes resulted in higher permeances for all the samples except for the permeances of O₂ and N₂ for the C-Si 5% composite membrane and the permeance of N₂ for C-Si 8% composite membrane. The gas permeance of the carbon-silica composite membranes progressively increased with increasing ratio of Si to C as shown in Fig. 8.10 The C-Si 28% composite membranes yielded the highest permeance of 1042.18, 991.21, 296.03 and 155.26 Barrer/cm for He, CO₂, O₂ and N₂, which were 21.6, 137.7, 103.2 and 150.7 times greater than those of the pure carbon membrane. With increasing addition of the silica, the selectivities of gas pairs increased when the ratio of silicon to carbon was less than 11% but decreased with further increase in the ratio of silicon to carbon as shown in Fig. 8.11. The increased selectivities for Si:C ratios 0.08 and 0.11 might be attributed to the optimal interphase voids between the carbon and silica that provided a good molecular sieving action for the gas pairs but when the ratio increased beyond 0.11, the interphase voids could possibly increase and therefore the selectivities suffered and decreased as shown in Fig. 8.11. The C-Si 11% composite membranes yielded the highest selectivities of 37.57, 36.61 and 7.09 for He /N₂, CO₂ /N₂ and O₂/N₂,

respectively while the C-Si 28% composite membranes exhibited lowest selectivities.

The variations in the gas permeance were highly dependent on the membranes structures. With the introduction of the silica, the structures of the membranes were remarkably different from the pure carbon membrane as confirmed by the XRD results.

Table 8.5 Single gas permeabilities and ideal selectivities of pure carbon membranes and carbon-silica composite membranes

Sample	Permeance (Barrer/cm)				Selectivity		
	He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂
Pure carbon	37.74	7.2	2.87	1.03	36.35	6.93	2.77
C-Si 5%	38.74	9.57	2.47	0.87	44.5	11	2.84
C-Si 8%	64.32	34.82	5.25	0.97	66.24	35.86	5.41
C-Si 11%	142.18	138.56	26.85	3.78	37.57	36.61	7.09
C-Si 19%	225.86	168.19	62.81	21.22	10.63	7.92	2.95
C-Si 23%	683.46	663.23	195.61	91.11	7.05	7.28	2.15
C-Si 28%	1042.18	991.21	296.03	155.26	6.71	6.39	1.90

Fig. 8.10 Single gas permeabilities of pure carbon membrane and carbon-silica composite membranes

Fig. 8.11 Ideal selectivities of pure carbon membrane and carbon-silica composite membranes

8.2.7 Mixed gas separation of carbon-silica composite membranes

To obtain the true membrane performance in industrial applications, mixed gas measurements are highly recommended. The derived carbon membrane and carbon/silica composite membranes were tested using binary mixed gases and the resulting selectivities of the membranes are shown in Fig. 8.12. The binary mixed gases consisting of oxygen (20%) and nitrogen (80%) were selected for separation in this part of project. The feed pressure of the mixed gases was set at 2 atm. In Fig. 8.12, the mixed gas selectivity first increased with increasing ratio of silicon to carbon and a maximum value of 7.01 was obtained for the C-Si 11% composite membrane. The mixed gas selectivity then decreased with further increase in silicon/carbon ratio. Some differences between pure gas and mixed gas separation results were observed as shown in Table 8. 6. This could be due to the competition in sorption among the penetrants, the effect of concentration polarisation and the

non-ideal gas behaviour of the penetrants. Overall, the agreement between the pure gas selectivity and the mixed gas selectivity for O_2/N_2 was good.

Table 8.6 Comparison of pure gas selectivity and mixed gas selectivity of O_2/N_2

Sample	Pure gas selectivity O_2/N_2	Mixed gas selectivity O_2/N_2
Pure carbon	2.77	2.54
C-Si 5%	2.84	3.01
C-Si 8%	5.41	5.73
C-Si 11%	7.09	7.01
C-Si 19%	2.95	3.44
C-Si 23%	2.15	2.92
C-Si 28%	1.90	1.99

Fig. 8.12 Mixed gas selectivities of pure carbon membrane and carbon-silica composite membranes

8.3 Summary

The polyimide-silica composite membranes and the derived carbon-silica composite membranes were successfully prepared. With the introduction of the inorganic silica phase, the thermal stability of the PI-silica composite membrane decreased slightly. The modulus and tensile strength of the membranes progressively increased with increasing silica content. SEM micrographs showed that the inorganic phase had good compatibility with the polymer matrix, and that the silica particles were uniformly dispersed in the polyimide matrix. XRD results showed that the derived carbon-silica composite membranes had larger d_{002} spacing values with the introduction of silica, indicating that an increased ordering packing was obtained for the carbon-silica composite membranes. The gas permeation results showed that there was no significant enhancement in the gas separation in the PI-silica composite membranes which still suffered a “trade-off” relationship between permeability and selectivity. However, the derived carbon-silica composite membranes exhibited better gas separation properties. The C-Si 28% composite membranes exhibited the highest permeance of 1042.18, 991.21, 296.03 and 155.26 Barrer/cm for He, CO₂, O₂ and N₂, which were 21.6, 137.7, 103.2 and 150.7 times greater than those of the pure carbon membrane. The C-Si 11% composite membranes yielded the highest selectivities of 37.57, 36.61 and 7.09 for He /N₂, CO₂ /N₂, and O₂/N₂, respectively.

Chapter 9 Preparation and Characterisation of Mixed Matrix Membranes Based on PVDF for Gas Separation

9.1 Introduction

To prepare mixed matrix membranes, poly(vinylidene fluoride) (PVDF) was chosen as the matrix and three types of inorganic fillers-fumed nonporous nano-silica, synthesised mesoporous MCM-41 and microporous zeolite 4A, were used dispersed as phases. The aim of this part of project was to investigate the effects of fillers on the gas transport properties of mixed matrix membranes. Although PVDF is always used as a gas barrier material, it was used here as a polymer matrix due to the fact that PVDF exhibits flexible chain movements and excellent membrane formability, thus making it ideal to prepare MMMs with high weight content of inorganic fillers. In addition, its complex crystalline structure also provides a material to study the effects of inorganic fillers on the gas transport properties of semi-crystalline polymers. Three types of inorganic fillers, *i.e.*, fumed SiO₂, MCM-41 and zeolite 4A, were used as the dispersed phase in order to exhibit significant variations of pore structure and particle size, which are thought to be highly essential for the success of MMMs. This study would be able to observe the effects of these inorganic fillers on the gas transport properties of MMMs and further capture the physics of gas transport through MMMs by exploring their gas transport behaviour.

9.2 Results and discussion

9.2.1 TGA results

The TGA curves of the pure PVDF membrane and its composite membranes are

shown in Fig. 9.1 (a), (b) and (c). A major weight loss occurred in the range of 450-520 °C for all the samples and this was due to the decomposition of PVDF. Figure 9.2 shows the variation of the decomposition temperatures T_d as a function of the inorganic filler content. The pure PVDF membrane exhibited a T_d value of 474 °C, indicating its excellent thermal stability. With the addition of the fillers, all the composite membranes had lower T_d values than that of the pure PVDF membrane. Moreover, for all the three types of fillers, T_d decreased with increasing filler content. This decreasing trend was more significant for PVDF/MCM-41 and PVDF/SiO₂ composite membranes. For the same percent content of inorganic filler, PVDF/MCM-41 composite membranes yielded the lowest T_d among the three types of composite membranes. PVDF/4%SiO₂ showed higher T_d as compared with PVDF/4% 4A composite membrane. With the inorganic filler content over 4%, the order of T_d was PVDF/4A >PVDF/SiO₂ >PVDF/MCM-41. PVDF/32% MCM-41 composite membrane had the lowest T_d of 384 °C, which was significantly lower as compared with pure PVDF membrane. Generally, polymer-inorganic composites are expected to exhibit better thermal stability with the incorporation of the inorganic fillers. On the contrary, the incorporation of SiO₂, zeolite 4A and MCM-41 decreased the thermal stability of PVDF matrix. This behaviour was probably attributed to the fact that these inorganic fillers might react with the product of degradation of PVDF, *i.e.*, HF, which subsequently accelerated the decomposition process [121]. Figure 9.1 (a) and (b) showed that PVDF membrane had higher residual weight percent than PVDF/SiO₂ and PVDF/MCM-41 composite membranes.

Fig. 9.1 TGA curves of (a) PVDF/SiO₂, (b) PVDF/MCM-41 and (c) PVDF/4A composite membranes. The TGA curve of pure PVDF membrane is also included for comparison purpose

Fig. 9.2 Decomposition temperatures of the composite membranes as a function of filler content

9.2.2 DSC results

The complete DSC thermogram of pure PVDF membrane is shown in Fig. 9.3, which consisted of an endothermic melting process and an exothermic crystallising process. Interestingly, the crystallising curve was perfectly matched for the two cycle results while the melting curve showed some differences. For the first cycle, the melting thermogram consisted of a step and a peak while for the second cycle, the melting thermogram only showed one regular peak which was positioned at a lower temperature. The irregular shape of the melting curve for the first cycle was also reported by others. Xu *et al.* [122] observed this phenomenon in PVDF/carbon nanotube composites and suggested that the step in the melting curve was attributed to the melting peak of the transcrystalline layers between inorganic fillers and matrix, and that the following subsequent peak corresponded to the melting of the semicrystalline polymer matrix. Apparently, this phenomenon was not only restricted

to PVDF composites but also to pure PVDF membrane as shown in this study. It is believed that the irregular peak is due to the broad distribution of α phase crystals based on Thomson–Gibbs equation [123]:

$$T_m = T_m^0 \left(1 - \frac{2\gamma}{\Delta H_m^0 r \rho} \right) \quad (9.1)$$

where T_m is the experimentally determined melting point, T_m^0 is the equilibrium melting point of the crystals, γ is the free surface energy of the lamellar fold surfaces, r is the size of the crystals, ρ is the density of the crystal and ΔH_m^0 is the melting enthalpy of a fully crystalline polymer. The step was due to the melting of small crystals which needed relative lower energy while the peak was due to the melting of the large crystals which needed higher energy. After the first cycle, the size distribution of α phase crystals had been narrowed and therefore only one regular peak was observed in the second cycle.

Fig. 9.3 Complete DSC thermogram of pure PVDF membrane

Figure 9.4 (a), (b) and (c) shows the DSC curves for the second cycle for the pure PVDF membrane and the composite membranes. The melting temperature (T_m), the crystallizing temperature (T_c) and the fusion heat (ΔH) of the samples were determined accordingly. The crystallinity (χ) of the samples was calculated using the following equation:

$$\chi = \frac{\Delta H}{W \times \Delta H^0} \times 100\% \quad (9.2)$$

where W is the PVDF weight content in the composite membranes, ΔH^0 is the latent heat of fusion of PVDF with 100% crystallinity of α phase, which was set to be 90.4 J/mol [124]. The analysis results are presented in Table 9.1. The T_m , T_c , ΔH and χ of the pure PVDF membrane were 158 °C, 133 °C, 23.8 J/g and 26.3%, respectively. With the incorporation of the inorganic fillers, there were only minor changes in the T_m and T_c values for the composite membranes as compared with those of the pure PVDF membranes as shown in Table 9.1. In contrast, the crystallinity of the composite membranes increased significantly with the incorporation of the inorganic fillers. As shown in Fig. 9.5, the crystallinity of the composite membranes increased sharply with the addition of 4% inorganic fillers and then remained fairly constant with further increases in inorganic fillers. Among the three types of inorganic filler and for the same amount of inorganic filler, the PVDF/4A composite membrane resulted in the highest crystallinity, followed by PVDF/SiO₂ composite membrane while the PVDF/MCM-41 had the lowest crystallinity. PVDF/32% 4A composite membrane had the highest crystallinity of 45%, which was significantly higher than that of pure PVDF membrane. The increase in crystallinity with the incorporation of

inorganic fillers probably resulted from the fact that the inorganic fillers could have served as nucleation agents during the crystallisation of PVDF [125].

Fig. 9.4 DSC curves for the second cycle for (a) PVDF/SiO₂, (b) PVDF/MCM-41 and (c) PVDF/4A composite membranes. The DSC curve of the pure PVDF membrane is also included for comparison purpose.

Table 9.1 Decomposition temperature (T_d), melting temperature (T_m), crystallising temperature (T_c), fusion heat (ΔH), crystallinity (χ) and contact angle (CA) of the various membranes

Sample	T_d ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔH (J/mol)	χ	CA ($^{\circ}$)
Pure PVDF	473	158	133	23.8	0.26	90
PVDF/4% SiO_2	471	159	136	31.9	0.37	83
PVDF/8% SiO_2	458	158	136	31.9	0.38	77
PVDF/16% SiO_2	443	157	134	28.8	0.38	72
PVDF/24% SiO_2	422	158	133	24.5	0.36	69
PVDF/32% SiO_2	416	158	133	23.5	0.38	69
PVDF/4% MCM-41	452	159	134	31	0.36	80
PVDF/8% MCM-41	452	158	133	28.5	0.34	76
PVDF/16% MCM-41	439	159	133	25.9	0.34	72
PVDF/24% MCM-41	396	158	132	22.5	0.33	69
PVDF/32% MCM-41	384	157	133	20.5	0.34	67
PVDF/4% 4A	462	159	135	34.1	0.39	83
PVDF/8% 4A	461	159	135	34.0	0.41	82
PVDF/16% 4A	459	159	135	31.9	0.42	82
PVDF/24% 4A	459	159	135	28.2	0.41	77
PVDF/32% 4A	445	159	134	27.6	0.45	70

Fig. 9.5 Crystallinity of the membranes as a function of inorganic filler content

9.2.3 Morphology

Figure 9.6 shows the SEM micrographs of pure PVDF membrane, PVDF/ SiO_2 8%,

PVDF/SiO₂ 32%, PVDF/MCM-41 8%, PVDF/MCM-41 32%, PVDF/4A 8% and PVDF/4A 32% composite membranes. Pure PVDF membrane exhibited homogeneous morphology while the composite membranes showed inorganic particles uniformly dispersed within the polymer matrix. Among the three types of MMMs, PVDF/SiO₂ composite membranes had relative dense structure and there were no particle aggregates with microsize and apparent voids. In contrast, PVDF/MCM-41 and PVDF/4A composite membranes showed many cavities which were formed by the cleavage of particles during sample preparation. In addition, for the PVDF/4A composite membranes, apparent voids between zeolite 4A and polymer chains were seen and the size of the voids increased with increasing content of zeolite 4A. SEM micrographs confirmed that the voids between the filler particles and polymer chains were highly dependent on the size of inorganic filler as well as the weight percent of inorganic filler.

Fig. 9.6 SEM micrographs of (1) pure PVDF, (2) PVDF/SiO₂ 8%, (3) PVDF/SiO₂ 32%, (4) PVDF/MCM-41 8%, (5) PVDF/MCM-41 32%, (6) PVDF/4A 8% and (7) PVDF/4A 32% composite membranes. Micrographs A: lower magnification and B: have higher magnification.

9.2.4 Mechanical properties

In order to investigate the effects of inorganic fillers on the mechanical properties of composite membranes, stress-strain tests were carried out for all the membrane samples. Tensile stress, modulus and elongation strain at break were determined. The variations of tensile stress, modulus and elongation strain at break with inorganic filler content are shown in Fig. 9.7 (a), (b) and (c), respectively. The tensile strength of the pure PVDF was found to be 24.3 MPa which was lower than the value reported due to differences in molecular weight [126]. The modulus and elongation at break of the pure PVDF were 741 MPa and 10.1%, respectively. The tensile strength of PVDF/MCM-41 and PVDF/4A composite membranes decreased with increasing filler content. However, the tensile strength of PVDF/SiO₂ initially increased with an increase of SiO₂ content and a maximum value was attained by the PVDF/24% SiO₂ composite membrane but subsequently decreased with further increase of SiO₂ content as shown in Fig 9.7 (a). The modulus of PVDF/MCM-41 composite membranes decreased with increasing filler content while the modulus of PVDF/4A and PVDF/SiO₂ composite membranes increased with increasing filler content attaining maximum values by the composite membranes with 24% inorganic filler but subsequently decreased with further increases in the inorganic filler. Figure 9.7 (c) shows that for all the three types of MMMs, the elongation strain at break decreased progressively with increasing filler content, indicating that the incorporation of SiO₂, zeolite 4A and MCM-41 deteriorated the ductility of the PVDF chains. The complexities of the mechanical properties of the composite

membranes could be explained as follows. On one hand, the mechanical properties of composite membranes are highly dependent on the polymer/particle interface properties. A poor compatibility between the filler particles and the PVDF polymer matrix would result in the failure of the transfer of the external force from the polymer matrix to the inorganic fillers. As the filler content increased, some particles were prone to form aggregates, thereby aggravating the compatibility between the polymer matrix and the filler particles; all these would reduce the modulus and tensile strength of the composite membranes. On the other hand, the incorporation of the inorganic fillers increased the crystallinity of the composite membranes and this would enhance the mechanical properties. In other words, due to its semicrystalline structure, the composite membranes were not only influenced by the polymer/particles interface properties but also changes in the crystallinity of the composite membranes.

Fig. 9.7 Relationship between the mechanical properties and varying inorganic filler contents for (a) tensile stress, (b) modulus, and (c) elongation strain at break of the composite membranes.

9.2.5 Contact angles

In order to investigate the surface properties of the composite membranes, contact angle tests were carried out and the results are presented in Table 9.1. The contact angle of pure PVDF was 90 °, indicating its excellent hydrophobic property. With the addition of inorganic fillers, the contact angles of the composite membranes reduced. This behaviour was due to the hydrophilic properties of SiO₂, zeolite 4A and MCM-41. Figure 9.8 shows the variations of contact angle with the inorganic filler content. It could be seen that for all the three types of composite membranes, the contact angle decreased with increasing filler content. With the same filler content, PVDF/4A composite membranes produced the smallest contact angle, followed by PVDF/SiO₂ composite membranes, and PVDF/MCM-41 composite membranes had the largest value of contact angle. This trend was attributed to the different properties of the inorganic fillers, such as the hydrophilicity and the particle size. PVDF/32% 4A composite membranes exhibited the lowest value of contact angle of 66° which was very much smaller than that of pure PVDF.

Fig. 9.8 Contact angles of membranes with different inorganic filler contents

9.2.6 XRD patterns

PVDF is a well known semicrystalline polymer with four crystal forms, *i.e.*, α , β , γ and δ [124, 127]. The non-polar α phase exhibits a monoclinic crystal structure and is obtained by crystallisation from melting solution or solution casting films. The polar β phase exhibits an orthorhombic crystal structure and consists of two planar zigzag chains passing through the orthorhombic unit cell. The β phase attracts great interest due to its piezoelectric and pyroelectric properties and is usually obtained by mechanically stretching the α phase. The γ phase is also of monoclinic crystal structure, which can be obtained by crystallisation under high temperature. The δ phase is a polar version of α phase, which can be obtained by the solid transition of α phase under strong electric field. Figure 9.9 (a), (b) and (c) shows the XRD patterns of pure PVDF membrane and the composite membranes. The XRD pattern of pure PVDF membrane showed three distinct peaks centred at 17.8, 18.5 and 20.1 °, which

are the characteristics of the reflection of α phase and can be indexed into α (100), α (020) and α (110), respectively. There were no peaks in the range of 20.2 to 20.8 ° indicating that the β phase was absent in pure PVDF membrane. With the addition of SiO₂, the XRD patterns of the PVDF/SiO₂ composite membranes showed no significant variations as compared with that of the pure PVDF. The three peaks that were attributed to the reflections of α phase of pure PVDF still appeared at almost the same positions but their intensities were lower as compared with those of the pure PVDF and decreased with increasing SiO₂ content as shown in Fig. 9.9 (a). These characteristics were also observed for the XRD patterns of PVDF/4A composite membranes in Fig. 9.9 (b). In addition, the five peaks centred at 12.5, 16.2, 21.7, 23.1 and 24 ° were present for PVDF/16% 4A, PVDF/24% 4A and PVDF/32% 4A composite membranes which were due to the reflections of zeolite 4A. For the PVDF/MCM-41 composite membranes in Fig. 9.9 (c), the XRD patterns exhibited some distinct different characteristics from those of the pure PVDF membrane. For these composite membranes, the two peaks which appeared at 17.8 and 18.5 ° for the pure PVDF membrane merged into a broad peak and the third peak shifted from 20.1 ° to 20.5 °, which was attributed to the characteristic reflection of β phase. The intensity of this peak at 20.5 ° appeared to be independent of the amount of MCM-41 content. It was surmised that the addition of the MCM-41 particles induced the transition of α phase to β phase while the addition of SiO₂ and zeolite 4A did not produce a similar effect. It was widely reported that the incorporation of inorganic particles with nano-scale sizes did achieve the phase transition and that the success

of this phase transition was highly dependent on the surface properties of the inorganic particles [128]. Hence, the results of phase change as mentioned above could be due to the different surface properties of fumed SiO_2 , zeolite 4A and synthesised MCM-41.

Fig. 9.9 XRD patterns of the pure PVDF membranes and composite membranes of
(a) PVDF/SiO₂, (b) PVDF/4A and (c) PVDF/MCM-41

9.2.7 Void volume fraction

The measured values of density (ρ_m) of the various membranes are shown in Table 9.2. For the purpose of comparison, the theoretical density (ρ_c) of the membranes was also calculated using Equation (6.1). The densities of SiO₂, MCM-41 and zeolite 4A were 2.17, 2.12 and 1.91 g/cm³, respectively. Due to its semi-crystalline property, the density of pure PVDF membrane is a function of the crystallinity and can be calculated using

$$\rho_p = \frac{1}{\frac{1-\chi}{\rho_{am}} + \frac{\chi}{\rho_{cr}}} \quad (9.3)$$

where ρ_{am} and ρ_{cr} are the densities of α amorphous and crystalline PVDF, which are 1.68 and 1.92 g/cm³, respectively [129]. The crystallinity of pure PVDF can be calculated using

$$\chi = \frac{V_a - V_s}{V_a - V_c} \quad (9.4)$$

where V_a and V_c are the specific volumes of amorphous PVDF and α crystalline PVDF, which were reported to be 0.596 and 0.521 cm³/g, respectively [129]. V_s is the specific volume of the sample and its calculated value was 0.575 cm³/g which was based on its density value. Hence, the crystallinity of pure PVDF was calculated to be 0.28 which was very close to the value obtained from DSC test.

It could be seen from Table 9.2 that for all the three types of composite membranes, the measured density values were smaller than the theoretical density values. This disparity was due to the presence of voids between the polymer chains and inorganic

filler particles. Generally, the void volume fraction (ϕ_v) can be calculated using Equation (7.1). With the incorporation of inorganic filler particles, the voids between the polymer/particle interfaces resulted in lower density. On the other hand, the presence of the inorganic fillers increased the crystallinity of the PVDF matrix and this would increase the density of the composite membranes. In other words, the density of the resulting composite membranes was dependent on two factors-polymer crystallinity and void volume fraction. From Table 9.2, it could be seen that the void volume fractions of the PVDF/MCM-41 and PVDF/4A composite membranes were much greater than that of the PVDF/SiO₂ composite membranes for the same inorganic filler content. This was due to the porous structures of the MCM-41 and zeolite 4A particles whose pore volumes were considered in the void volume calculations. Assuming that there were no polymer chains trapped into the pores of the MCM-41 and the zeolite 4A particles, new void volume fraction values (denoted as modified ϕ_v in Table 9.2) could be obtained by subtracting the pore volumes of MCM-41 and zeolite 4A particles.

Table 9.2 Theoretical density (ρ_c), measured density (ρ_m), void volume fraction (ϕ_v) and modified void volume fraction of membranes

Sample	ρ_c (g/cm ³)	ρ_m (g/cm ³)	ϕ_v	Modified ϕ_v
Pure PVDF	1.7372	1.7372	0	
PVDF/4% SiO ₂	1.7743	1.7337	0.0229	
PVDF/8% SiO ₂	1.7914	1.7126	0.044	
PVDF/16% SiO ₂	1.8180	1.6775	0.0773	
PVDF/24% SiO ₂	1.8424	1.5726	0.1464	
PVDF/32% SiO ₂	1.8764	1.5123	0.1940	
PVDF/4% MCM-41	1.7703	1.6667	0.0584	0.039
PVDF/8% MCM-41	1.7796	1.6014	0.1001	0.0612
PVDF/16% MCM-41	1.8044	1.4973	0.1702	0.0912
PVDF/24% MCM-41	1.828	1.3581	0.2571	0.1371
PVDF/32% MCM-41	1.8577	1.2189	0.3439	0.1812
PVDF/4% 4A	1.7721	1.6983	0.0417	0.0269
PVDF/8% 4A	1.7809	1.6316	0.0839	0.0541
PVDF/16% 4A	1.7935	1.4902	0.1691	0.1090
PVDF/24% 4A	1.8023	1.3025	0.2773	0.1867
PVDF/32% 4A	1.8196	1.1271	0.3806	0.2587

9.2.8 Single gas transport properties

The single gas permeabilities of the various membranes are shown in Table 9.3. The permeabilities of pure PVDF membrane for He, CO₂, O₂ and N₂ were 3.94, 1.18, 0.14 and 0.04 Barrer, respectively. Figure 9.10 shows the gas permeability of the various membranes as a function of the inorganic weight content. With the incorporation of the inorganic fillers, the permeabilities of the composite membranes showed a similar trend in that the permeabilities of the composite membranes decreased slightly or remained constant for 4% filler content as compared with the pure PVDF membrane. Subsequently, the permeabilities increased with further addition of inorganic fillers. At inorganic filler weight contents of 4%, 8% and 16%, PVDF/SiO₂, PVDF/MCM-41 and PVDF/4A composite membranes produced similar

permeabilities. However, at high loadings over 16%, the permeabilities of PVDF/MCM-41 and PVDF/4A composite membranes were much greater than those of PVDF/SiO₂ composite membranes. The highest permeabilities for He, CO₂, O₂ and N₂ were obtained through PVDF/4A 32% composite membrane, which were 9.65, 3.62, 0.41 and 0.12 Barrer, respectively. The selectivities of gas pairs (He/N₂, CO₂/N₂, and O₂/N₂) are also showed in Table 9.3. For PVDF/SiO₂ composite membranes, the selectivities for gas pairs were higher than those of pure PVDF membrane except that the PVDF/SiO₂ 16% composite membrane had lower selectivities for He/N₂ and CO₂/N₂ as shown in Fig. 9.11. For the PVDF/MCM-41 and PVDF/4A composite membranes with inorganic filler contents less than 16%, the selectivities were higher as compared with the pure PVDF membrane. But with higher inorganic filler loadings, *i.e.*, 24% and 32%, the selectivities deteriorated. PVDF/SiO₂ 4% composite membrane exhibited the highest selectivities of 120.7, 30.7 and 4.7 for He/N₂, CO₂/N₂, and O₂/N₂, respectively.

Table 9.3 Single gas permeability and ideal selectivity of the membranes

Sample		Permeability (Barrer)				Selectivity		
		He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂
Pure PVDF		3.94	1.18	0.14	0.04	98.5	29.5	3.5
PVDF/SiO ₂	4%	3.62	0.92	0.12	0.03	120.7	30.7	4.0
	8%	4.19	1.15	0.17	0.04	104.8	28.8	4.3
	16%	5.42	1.64	0.23	0.06	90.3	27.3	3.8
	24%	8.01	2.45	0.32	0.07	114.4	35	4.6
	32%	8.87	2.65	0.36	0.08	110.9	33.1	4.5
PVDF/MCM-41	4%	3.62	1.04	0.15	0.04	90.5	26	3.8
	8%	4.45	1.26	0.18	0.05	89	25.2	3.6
	16%	6.02	1.84	0.22	0.06	100.3	30.7	3.7
	24%	8.17	2.48	0.29	0.08	102.1	31	3.6
	32%	10.2	2.85	0.41	0.14	72.9	20.4	2.9
PVDF/4A	4%	3.62	0.95	0.12	0.04	90.5	23.8	3
	8%	4.81	1.08	0.15	0.05	96.2	21.6	3
	16%	6.33	1.89	0.2	0.06	105.5	31.5	3.3
	24%	8.76	2.24	0.26	0.09	97.3	24.9	2.9
	32%	9.65	3.26	0.41	0.12	80.4	27.2	3.4

Fig. 9.10 Permeability of the membranes as a function of inorganic filler content

Fig. 9.11 Selectivity of the membranes as a function of inorganic filler content

9.3 Summary

Three types of inorganic fillers, *i.e.*, SiO₂, MCM-41 and zeolite 4A were incorporated into PVDF matrix to prepare composite membranes. The thermal stability of the resulting composite membranes decreased which was probably attributed to the reaction between inorganic fillers and the degradation product of PVDF. The crystallised temperature and melting temperature of composite membranes had no significant variations while the crystallinity of PVDF in the composite membranes was enhanced with the addition of inorganic fillers due to the fact that the inorganic fillers served as nucleation agents during the crystallisation process. The elongation strain at break decreased with increasing inorganic filler content. This was due to the poor compatibility between inorganic fillers and polymer chains, which was also confirmed by the density test and SEM micrographs. The contact angle of composite membranes decreased with addition of inorganic fillers. XRD results showed that the incorporation of SiO₂ and zeolite 4A particles

did not induce the phase change and the crystalline PVDF structure in the PVDF/SiO₂ and PVDF/4A composite membranes was still present as the α phase while in PVDF/MCM-41 composite membranes, phase transformation from α phase to β phase was observed. Although the pores and particle sizes were different for the three types of inorganic fillers, the permeabilities of the three composite membranes showed a very similar behaviour, especially at lower inorganic filler loadings. The selectivities of composite membranes were less systematic and were dependent on the inorganic filler content as well as specific gas pairs.

Chapter 10 Theoretical and Experimental Studies on the Gas Transport Properties of Mixed Matrix Membranes Based on PVDF

10.1 Introduction

Permeabilities for He, CO₂, O₂ and N₂ through three types of MMMs, *i.e.*, PVDF/SiO₂, PVDF/MCM-41 and PVDF/4A MMMs, were theoretically predicted using Maxwell model, Higuchi model, Bruggeman model, Bottcher-Landauer models. By taking the effects of crystallinity on the gas transport properties into consideration, modified Maxwell model gave good predictions on the gas permeabilities of the MMMs, indicating that the model did capture the essence of the gas transport behaviours through the MMMs.

10.2 Modelling work

10.2.1 Maxwell model [130]

Mathematically, several theoretical models have been proposed to predict the gas transport properties of MMMs. Maxwell [130] first developed a model to analyze the steady-state permittivity of a dilute suspension of spheres. Subsequently, this model was analogously employed by Vu *et al.* [131] to predict the gas permeability of MMMs. This model is as follows:

$$P_{eff} = P_c \left[\frac{nP_d + (1-n)P_c - (1-n)\phi_d(P_c - P_d)}{nP_d + (1-n)P_c + n\phi_d(P_c - P_d)} \right] \quad (10.1)$$

where P_{eff} , P_d and P_c are the permeability of the mixed matrix membrane, dispersed phase and continued phase, respectively. When $n = 0$, Equation (10.1) corresponds to parallel transport of penetrants through MMMs and can be expressed as:

$$P_{eff} = (1 - \phi_d)P_c + \phi_d P_d \quad (10.2)$$

When $n = 1$, Equation (10.1) corresponds to serial transport of penetrants through MMMs and can be expressed as:

$$P_{eff} = \frac{P_c P_d}{P_d(1 - \phi_d) + \phi_d P_c} \quad (10.3)$$

When $n = 1/3$, Equation (10.1) corresponds to the most general cases for MMMs and is known as Maxwell equation as follows:

$$P_{eff} = P_c \left[\frac{P_d + 2P_c - 2\phi_d(P_c - P_d)}{P_d + 2P_c + \phi_d(P_c - P_d)} \right] \quad (10.4)$$

Generally, it is assumed in the Maxwell model that the transport of gas penetrants around the filler particles is not affected by the presence of nearby particles. Hence, it is suggested that the Maxwell model can give good predictions only on MMMs with low filler loadings in which the interparticle distance is sufficiently large to ensure that the flow patterns around any one particle is undisturbed by the presence of others. In this part of the project, as P_d for PVDF/SiO₂ MMMs is 0 for the non-porous SiO₂ filler, the Maxwell equation becomes

$$P_{eff} = P_c \frac{2 - 2\phi_d}{2 + \phi_d} \quad (10.5)$$

For PVDF/MCM-41 MMMs, P_d is much larger than P_c . The Maxwell equation (10.4) can then be written as:

$$P_{eff} = P_c \frac{1 + 2\phi_d}{1 - \phi_d} \quad (10.6)$$

For PVDF/4A MMMs, the permeabilities of He and CO₂ can still be calculated using Equation (10.6) due to the fact $P_d \gg P_c$. However, the calculations of the permeabilities of O₂ and N₂ have to be strictly based on Equation (10.4).

10.2.2 Higuchi Model [131]

Higuchi proposed another model as given in equation (10.7) to estimate the permeability of MMMs. The Higuchi model is applied for random dispersion of spherical filler particles but lacks the well-defined mathematical rigour.

$$P_{eff} = P_c \left[1 + \frac{3\phi_d}{\frac{P_d + 2P_c}{P_d - P_c} - \phi_d - K \left[\frac{(1 - \phi_d)(P_d - P_c)}{P_d + 2P_c} \right]} \right] \quad (10.7)$$

where K is an empirical constant and is generally assigned a value of 0.78 on the basis of experimental data. Higuchi indicated that the value of K is exaggerated by an “asphericity factor”. However, no physical basis could be attributed to K .

For PVDF/SiO₂ MMMs, P_d equals to 0 and the Higuchi model *i.e.*, Equation (10.7) becomes

$$P_{eff} = P_c \left[1 - \frac{6\phi_d}{3.22 + 2.78\phi_d} \right] \quad (10.8)$$

For PVDF/MCM-41 MMMs, as $P_d \gg P_c$, the Higuchi model *i.e.*, equation (10.7) can be approximately written as

$$P_{eff} = P_c \left[\frac{0.22 + 2.78\phi_d}{0.22 - 0.22\phi_d} \right] \quad (10.9)$$

For PVDF/4A MMMs, the permeabilities of He and CO₂ can be calculated using Equation (10.9) due to the fact $P_d \gg P_c$. However, the calculations of the permeabilities of O₂ and N₂ have to be based on Equation (10.7).

10.2.3 Bruggeman Model [132]

Based on the effective medium theory, Bruggeman derived equation (10.10) to

estimate the permeability of MMMs. Due to the fact that the effective medium theory treats the local permeability as fluctuations about the effective permeability of a uniform medium, no distinction between continuous phase and dispersed phase is made. In contrast to the Maxwell model, the Bruggeman model considers the effects of the presence of nearby particles on the transport of gases around filler particles by introducing an asymmetrical integration technique. Therefore, the Bruggeman model is particularly recommended for high filler loadings.

$$\left(\frac{P_d}{P_c} - \frac{P_{eff}}{P_c} \right) \left(\frac{P_c}{P_{eff}} \right)^{1/3} = (1 - \phi_d) \left(\frac{P_d}{P_c} - 1 \right) \quad (10.10)$$

Equation (10.10) is a third order algebraic expression in P_{eff} .

For PVDF/SiO₂ MMMs, P_d equals to 0 and the Bruggeman model, *i.e.*, Equation (10.10) becomes

$$P_{eff} = P_c (1 - \phi_d)^{3/2} \quad (10.11)$$

For PVDF/MCM-41 MMMs, as $P_d \gg P_c$, the Bruggeman model, *i.e.*, Equation (10.10) can be approximately simplified to

$$P_{eff} = \frac{P_c}{(1 - \phi_d)^3} \quad (10.12)$$

For PVDF/4A MMMs, the permeabilities of He and CO₂ can be calculated using Equation (10.12) due to the fact that $P_d \gg P_c$. However, the calculations of the permeabilities of O₂ and N₂ have to be based on Equation (10.10).

10.2.4 Bottcher-Landauer Model [67, 131]

Bottcher-Landauer model was originally developed to calculate the electrical resistance of binary metallic mixtures and subsequently analogously applied to

estimate the permeability of MMMs.

$$\left(\frac{P_d}{P_c} + \frac{2P_{eff}}{P_c} \right) \left(1 - \frac{P_c}{P_{eff}} \right) = 3\phi_d \left(\frac{P_d}{P_c} - 1 \right) \quad (10.13)$$

Equation (10.13) is a second order algebraic expression in P_{eff} .

For PVDF/SiO₂ MMMs, P_d equals to 0 and the Bottcher-Landauer model, *i.e.*,

Equation (10.13) becomes

$$P_{eff} = P_c (2 - 3\phi_d) / 2 \quad (10.14)$$

For PVDF/MCM-41 MMMs, due to $P_d \gg P_c$, the Bottcher-Landauer Equation

(10.13) can be approximately written as

$$P_{eff} = \frac{P_c}{(1 - 3\phi_d)} \quad (10.15)$$

For PVDF/4A MMMs, the permeabilities of He and CO₂ can be calculated using equation (10.15) due to the fact that $P_d \gg P_c$. However, the calculations of the permeabilities of O₂ and N₂ have to be based on equation (10.13).

10.2.5 Modified Maxwell model

Koros *et al.* [85] observed some non-ideal behaviour of MMMs induced by interface voids, polymer chain rigidifications and pore blockages and they modified the Maxwell equation according to the polymer/inorganic interface properties.

Considering the influence of interface voids in MMMs, a three-phase system including inorganic filler phase, polymer phase and the interface voids was proposed.

The permeability P_{3MM} of the three-phase membrane is obtained by applying the Maxwell model twice. Firstly, gas flows through the interface voids by Knudsen diffusion, with a slight modification to account for the finite size of the gas molecules and this Knudsen diffusion coefficient is given by Equation (10.16)

$$D_{AK} = 9.7 \times 10^{-5} r \sqrt{\frac{T}{M_A}} \left[1 - \frac{d_g}{2r} \right] \quad (10.16)$$

where r is the effective pore radius, T is the temperature, M_A is the molecular weight, and d_g is the gas molecular size. The solubility coefficient S_v in these voids is assumed to be the same as that in the gas phase, *i.e.*,

$$S_v = \frac{1}{RT} \left(1 - \frac{d_g}{2r} \right)^2 \quad (10.17)$$

where R is the gas constant.

The gas permeability P_v through the voids is the product of D_{AK} and S_v such that

$$P_v = \frac{9.7 \times 10^{-5} r}{RT} \sqrt{\frac{T}{M_A}} \left[1 - \frac{d_g}{2r} \right]^3 \quad (10.18)$$

Secondly, a modified Maxwell equation is used to obtain the permeability of the combined interface voids and inorganic phase with the interface void as the continuous phase and the inorganic phase as the dispersed phase. This modified Maxwell equation is

$$P_{eff} = P_v \left[\frac{P_d + 2P_v - 2\phi(P_v - P_d)}{P_d + 2P_v + \phi(P_v - P_d)} \right] \quad (10.19)$$

where

$$\phi = \frac{V_f}{V_f + V_v} \quad (10.20)$$

Here, P_{eff} is the permeability of the combined sieve and interface void, P_d is the permeability of the dispersed or sieve phase, P_v is the permeability of the interface voids, and V_f and V_v are the volumes of inorganic filler and voids, respectively.

Finally, the value of the permeability of the combined filler and interface void, P_{eff} , can then be used along with the continuous polymer phase permeability, P_c , to obtain a predicted permeability P_{3MM} for the three-phase MMMs by applying the Maxwell equation a second time.

$$P_{3MM} = P_c \left[\frac{P_{eff} + 2P_c - 2\phi'(P_c - P_{eff})}{P_{eff} + 2P_c + \phi'(P_c - P_{eff})} \right] \quad (10.21)$$

where

$$\phi' = \frac{V_f + V_v}{V_f + V_v + V_p} \quad (10.22)$$

and V_p is the polymer volume.

If $P_{eff} \gg P_c$, the permeability P_{3MM} for the three-phase MMMs becomes

$$P_{3MM} = P_c \times \frac{1 + 2\phi'}{1 - \phi'} \quad (10.23)$$

Assuming that the inorganic particles are perfectly spherical and the voids are distributed evenly around the particles, equations (10.20) and (10.22) can be respectively expressed as

$$\phi = \frac{r^3}{(r+l)^3} = \frac{1}{(1+l/r)^3} \quad (10.24)$$

$$\phi' = \frac{\phi_f^N}{\phi_f^N + \frac{1 - \phi_f^N}{(1+l/r)^3}} \quad (10.25)$$

where ϕ_f^N is the inorganic nominal volume fraction, r is the particle size and l is the void thickness. ϕ_f^N is defined as

$$\phi_f^N = \frac{V_f}{V_f + V_p} \quad (10.26)$$

The void volume fraction ϕ_v can be estimated using Equation (10.27)

$$\phi_v = \frac{V_v}{V_v + V_f + V_p} = \frac{(l/r + 1)^3 - 1}{(l/r + 1)^3 + \frac{1 - \phi_f^N}{\phi_f^N}} \quad (10.27)$$

The void volume fraction of the MMM can also be calculated as follows: ²²

$$\phi_v = \frac{\rho_t - \rho_m}{\rho_t} \quad (10.28)$$

where ρ_t and ρ_m are the theoretical and measured densities of the MMMs, respectively.

Based on Equations (10.27) and (10.28), the relationship between l and r can be obtained as follows:

$$l = \left[\left(\frac{a(1 - \phi_f^N) + 1}{1 - a\phi_f^N} \right)^{1/3} - 1 \right] \times r \quad (10.29)$$

where a is the gradient of the line for the void volume fraction ϕ_v versus the inorganic filler nominal volume fraction relation

10.2.6 Modified Maxwell model for PVDF MMMs

It has been known that the permeability of PVDF matrix is closely related to its crystallinity. Generally, crystalline polymer structure can influence the permeability of polymer membranes by two-folds. Crystallinity will decrease the solubility coefficient due to the fact that the crystalline polymer with higher packing density exhibits lower solubility compared with that of the amorphous polymer. The relationship [133] can be expressed as

$$S = S^* \times \alpha \quad (10.30)$$

where S and S^* are the solubility coefficients of semicrystalline polymer and amorphous polymer, respectively, and α is the amorphous polymer fraction. In

addition, crystalline polymer chains also block the diffusion of gas penetrants and decrease diffusion coefficient, and the relationship is given by

$$D = D^* \times \alpha \quad (10.31)$$

where D and D^* are the diffusion coefficients of semicrystalline polymer and amorphous polymer, respectively. The permeability coefficient is the product of solubility coefficient and diffusion coefficient and is given as

$$P = S^* \times D^* \times \alpha^2 = P^* \times \alpha^2 \quad (10.32)$$

Usually, the presence of crystalline polymer will influence the transport properties of the vicinity amorphous polymers. An immobilisation factor, β , is used to represent the degree of tautness in the intercrystalline amorphous segments. Hence,

$$P = P^* \alpha^2 / \beta \quad (10.33)$$

Consequently, the permeability of PVDF matrix is dependent on the filler content because its crystallinity is related to the filler content. According to Polyakova *et. al* [133], the permeabilities of completely amorphous PVDF, P^* , for He, CO₂, O₂ and N₂ were 7.26, 2.15, 0.344 and 0.093 Barrer, respectively. The immobilisation factor, β , of crystalline polymer is dependent on the gas penetrant molecular size. The β values are set to be 1.0, 1.2, 1.4 and 1.5 for He, CO₂, O₂ and N₂, respectively [133]. The volume fraction of the amorphous polymer, α , can be determined by the crystallinity χ of the MMMs as follows:

$$\alpha = 1 - \chi \quad (10.34)$$

10.3 Results and discussion

Relative gas (He, CO₂, O₂ and N₂) permeabilities P_{eff}/P_c of PVDF/SiO₂ MMMs based on the Maxwell model, Higuchi model, Bruggeman model and

Bottcher-Landauer model for varying volume fractions are shown in Fig. 10.1. Due to the nonporous nature of the fumed SiO_2 particles, the permeabilities of PVDF/ SiO_2 MMMs predicted by all four models are smaller than that of pure PVDF membrane and monotonically decreased with increasing SiO_2 nominal volume fraction. This is to be expected due to decreasing polymer content for gas dissolution and diffusion as the SiO_2 volume fraction increases. Among these four models, the Maxwell model predicted the largest values while the Higuchi model resulted in the lowest values of gas permeabilities and the values given by the Bruggeman model and the Bottcher-Landauer model lied between those of the two preceding models. The permeability values followed this order: Maxwell model > Bruggeman model > Bottcher model > Higuchi model. Due to the nonporous properties of SiO_2 , P_d equals to zero in the PVDF/ SiO_2 MMMs. These models except the Maxwell model lack the well-defined physical basis and make some approximations to treat the complexity of the MMMs. For instance, the Bruggman model considers the effects of the presence of nearly particles on the transport of gases around filler particles by introducing an asymmetric integration technique. However, for the non-porous SiO_2 particles, no path is available for the transport of gases through the dense particles. For the Higuchi model, the assigned value of 0.78 for the empirical constant K might not be appropriate for the SiO_2 particles. For the Bottcher-Landauer model, it was developed to calculate the electrical resistance of binary metallic mixtures and therefore the predicted permeabilities of MMMs are only approximate. These approximations could lead to the lower predicted permeability values.

Fig. 10.1 Permeability model results of PVDF/SiO₂ MMMs as a function of SiO₂ nominal volume fraction.

In contrast to nonporous SiO₂, mesoporous MCM-41 exhibited much higher permeabilities of He, CO₂, O₂ and N₂ than that of pure PVDF. In Fig. 10.2, the relative permeabilities P_{eff}/P_c of PVDF/MCM-41 MMMs predicted by all four models were higher than that of pure PVDF membrane and permeability increased with increasing MCM-41 nominal volume fraction due to increased pores. The permeability values for PVDF/MCM-41 MMMs given by the Maxwell model are the smallest while those given by the Higuchi model are the greatest. The order of permeability values is the reversed order to PVDF/SiO₂ MMMs. This reversed trend - Higuchi model > Bottcher-Landauer model > Bruggeman model > Maxwell model, has indicated the increasing dominance of the volume fraction of the MCM-41, ϕ_d , on the overall MMM permeability, P_{eff} , in the models in this sequence. The curves based on Maxwell, Bruggeman and Bottcher-Landauer models show an approximate linear relationship between permeability and MCM-41 nominal volume fraction

while the curve based on Higuchi model exhibit an exponential relationship between permeability and MCM-41 nominal volume fraction due to the predominance of ϕ_d on permeability in the Higuchi model.

Fig. 10.2 Permeability model results of PVDF/MCM-41 MMMs as a function of MCM-41 nominal volume fraction

The permeability values of PVDF/SiO₂ and PVDF/MCM-41 MMMs based on the four models are consistent for all the test gases given that the SiO₂ particles are nonporous and the MCM-41 particles are of pore size of 2.7 nm. These two inorganic fillers showed no selectivities for He, CO₂, O₂ and N₂. On the basis of the four models, the additions of SiO₂ and MCM-41 into PVDF would only affect the permeabilities of the MMMs but their selectivities would be the same as that of the pure PVDF membrane. These results were not manifested for the PVDF/4A MMMs because zeolite 4A particles produced different permeabilities of O₂ and N₂ with the PVDF matrix and consequently resulted in a high selectivity for these two gases. The

He and CO₂ permeabilities of PVDF/4A MMMs based on the four models are shown in Fig. 10.3 (a) and (b), respectively, which are very similar to those of PVDF/MCM-41 MMMs due to the much higher He and CO₂ permeabilities through the zeolite 4A particles than through the PVDF matrix. As the molecule size of the penetrants increased in the following order: He (2.6 Å) > CO₂ (3.3 Å) > O₂ (3.46 Å) > N₂ (3.64 Å) with its respective molecular gas diameter given within the parenthesis, the zeolite 4A particles exhibited higher permeabilities of He and CO₂ as compared with those of O₂ and N₂. For PVDF/4A MMMs, the order of magnitude of O₂ permeability was similar to those of He and CO₂: the permeability values given by the Higuchi model were the largest while those given by the Maxwell model were the smallest, and the values given by Bottcher-Landauer and Bruggeman models lied between the four models. However, the differences in the O₂ permeability values given by the four models narrowed as the four curves became closer. The N₂ permeabilities of PVDF/4A MMMs for the four models showed different characteristics. The N₂ permeability values given by the Maxwell model were the largest while the values given by the other three curves collapsed together.

Overall, the shape of the permeability curves of the MMMs given by the models is determined by the two parameters, *i.e.*, the filler volume fraction and the relative permeability P_d/P_c . Given that all the gases (He, CO₂, O₂ and N₂) for the PVDF/SiO₂ MMMs, $P_d \ll P_c$ whereas for the PVDF/MCM-41 MMMs, $P_d \gg P_c$. Therefore, the order of the permeability values of PVDF/SiO₂ MMMs given by the four models was exactly the reverse of those of the PVDF/MCM-41 MMMs. For the PVDF/4A

MMMs, the relative permeability P_d/P_c is dependent on the type of test gas. For He and CO₂, $P_d \gg P_c$, the results were of similar trends to the PVDF/MCM-41 MMMs. However, for O₂ and N₂, P_c is comparable to P_d , and this led to significant variations of the permeability curves for varying inorganic filler volume fractions.

Fig. 10.3 Permeability model results of PVDF/4A MMMs as a function of zeolite 4A nominal volume fraction for (a) He, (b) CO₂, (c) O₂ and (d) N₂.

Maxwell, Higuchi, Bottcher-Landauer and Bruggeman models ideally treat the MMMs as two phases, *i.e.*, polymer matrix phase and inorganic filler phase. In this part of the project, three inorganic fillers SiO₂, MCM-41 and zeolite 4A were used

without any modifications; these fillers are hydrophilic and show poor compatibility with the PVDF matrix. It is reasonable to assume that some voids may be present between the particle-polymer interfaces and this assumption can be verified if the theoretical density differs from experimental density.

Based on Equations (10.18) and (10.29), the gas permeability through the voids is highly dependent on the thickness of the voids thickness as shown in Fig. 10.4. The O₂ permeability through the voids increased steeply with void thickness and this upward trend gradually diminishes for void thickness greater than 30 Å. The O₂ permeability, P_{eff} , of the MMMs based on Equation (10.19) is also shown in Fig. 10.4. For PVDF/SiO₂ and PVDF/4A MMMs, the O₂ permeability, P_{eff} , showed a similar trend as P_v except that P_{eff} was smaller than P_v for the same void thickness. For PVDF/MCM-41 MMMs, the O₂ permeability, P_{eff} , increases linearly with increasing void thickness. In using the modified Maxwell model, the P_{eff} value based on the Equation (10.19) is much greater than the permeability P_c of PVDF even though the void thickness is as small as 2.5 Å. The fact that P_{eff} is much larger than P_c in Equation (10.21) for all the three MMMs enables the calculations of the permeability, P_{3MM} , of MMMs using Equation (10.23)

Fig. 10.4 P_{eff} of PVDF/SiO₂, PVDF/MCM-41, PVDF/4A MMMs and P_v as a function of void thickness

The permeability results given by the modified Maxwell model are shown in Fig. 10.5 (a), (b) and (c), in which five, six and seven different void thicknesses are plotted for PVDF/SiO₂, PVDF/MCM-41 and PVDF/4A MMMs, respectively. For all the MMMs, the permeabilities were highly dependent on the void thickness and the inorganic filler nominal volume fraction. For smaller void thicknesses, the permeabilities showed an approximate linear relationship with the nominal inorganic filler volume fraction while for larger void thicknesses, a non-linear relationship was observed. For the same nominal volume fraction, the permeability increased with increasing void thickness and the effect of void thickness on the permeability was much more significant for the PVDF/SiO₂ MMM than the PVDF/MCM-41 and PVDF/4A MMMs. For instance, the largest P_{3MM}/P_{eff} value for PVDF/28% SiO₂ MMM was 17.5 for a void thickness of 10 nm while the largest P_{3MM}/P_{eff} value for PVDF/28% MCM-41 and PVDF/30.5% 4A MMMs were 26.2 and 8.6 for void

thicknesses of 100 and 2000 nm, respectively. This indicated that the larger inorganic fillers, *i.e.*, zeolite 4A and MCM-41 with particle sizes of 2.5 μm and 56 nm, respectively, exhibited better tolerance with voids than the smaller inorganic filler, *i.e.*, SiO_2 with particle size of 7 nm. This is due to the fact that for the same void thickness, MMM with an inorganic filler of a larger particle size has lower void volume fraction.

Figure 10.5 shows that the void thickness is a critical parameter but it is assumed to be independent of the nominal inorganic filler volume fraction in the modified Maxwell model. On the contrary, the void thickness is dependent on the properties of the inorganic filler including its particle size, its surface properties and its nominal volume fraction in the resulting MMMs and is closely related to the void fraction. The void volume fraction of the MMMs can be calculated using Equation (10.28).

Fig. 10.5 Permeability model results based on modified Maxwell equation for (a) PVDF/SiO₂, (b) PVDF/MCM-41 and (c) PVDF/4A as a function of the inorganic filler nominal volume fraction

Figure 10.6 shows the relationship between the void fraction and the inorganic filler nominal volume fraction. The void volume fraction of PVDF/MCM-41 and PVDF/4A shown in Fig. 10.6 were obtained after subtracting the pore volumes of MCM-41 and zeolite 4A, respectively. With the same inorganic filler nominal volume fraction, PVDF/SiO₂ and PVDF/MCM-41 MMMs had similar void fractions which were smaller than that of PVDF/4A MMMs. Using straight line fits, the slopes of the curves were obtained as 0.69, 0.67 and 0.82 for PVDF/SiO₂, PVDF/MCM-41 and PVDF/4A MMMs, respectively. Subsequently, the void thickness was estimated using Equation (10.27) and the results are presented in Fig. 10.7. For the three types of MMMs, the void thickness increased with increasing inorganic filler nominal volume fraction. However, the void thickness l showed significant differences due to the different particle sizes r of the inorganic fillers which is supported by Equation (10.29)

Fig. 10.6 Void volume fraction as a function of inorganic filler nominal volume fraction

Fig. 10.7 Void thickness as a function of inorganic nominal volume fraction for (a) PVDF/SiO₂, (b) PVDF/MCM-41 and (c) PVDF/4A.

From the DSC measurements, the crystallinity of the resulting MMM was determined. Figure 10.8 shows the amorphous polymer fraction, α , as a function of the inorganic filler nominal volume fraction. For the three types of MMMs, the addition of inorganic filler increased the crystallinity of the PVDF matrix. The amorphous polymer volume fraction decreased sharply with the addition of inorganic filler volume fraction of 0.03 and this downward trend slowed down with further increases of inorganic fillers.

Fig. 10.8 Amorphous polymer volume fraction as a function of inorganic filler nominal volume fraction

Taking the effect of crystallinity on the permeability into consideration and calculating the void thickness of the MMM, the permeabilities of the MMMs could be determined using the modified Maxwell model in Equation (10.21). The modelling and experimental results are shown in Fig. 10.9 in which the solid symbols represent the experimental results while the hollow symbols represent the modelling results. Pure PVDF membrane had experimental permeabilities of 3.94,

1.18, 0.14 and 0.04 Barrer which are very consistent with the modelling results of 3.78, 1.18, 0.14 and 0.04 Barrer for He, CO₂, O₂ and N₂, respectively. Unexpectedly, the experimental permeability results showed no significant differences among the PVDF/SiO₂, PVDF/MCM-41 and PVDF/4A MMMs although the inorganic fillers *i.e.*, SiO₂, MCM-41 and 4A, had different properties such as particle size and pore structure. This behaviour could be attributed to the fact that the gas penetrants bypassed the inorganic filler particles in the MMMs altogether due to the presence of voids, resulting in no passage through the inorganic fillers. For all the three MMMs, the permeabilities initially decreased when the inorganic fillers were about 4 wt% and then increased with further increases in the inorganic filler content, resulting in minimum values for the MMMs with 4 wt% inorganic fillers. This behaviour can be explained as follows. On one hand, the permeabilities of the MMMs increased with increasing inorganic fillers due to the formation of voids. On the other hand, the addition of the inorganic filler could lead to increase in the crystallinity of the PVDF matrix, which could in turn decrease the permeability of the MMM. Generally, the permeability modelling results matched the experimental results well though some small deviations were observed. The discrepancy between the experimental permeability and the modelling permeability was attributed to two factors: (1) the formation of filler particle aggregates, particularly for the nano-SiO₂ particles with the smallest size, which was not taken into consideration in the modelling work, and (2) the assumption that the filler particles were perfectly spheres. The latter could play a more significant role on the deviations observed in the results for

PVDF/MCM-41 and PVDF/4A MMMs.

Fig. 10.9 Permeability experimental— and modelling..... results for (a) PVDF/SiO₂, (b) PVDF/MCM-41 and (c) PVDF/4A MMMs

10.4 Summary

The permeabilities of the PVDF/SiO₂, PVDF/MCM-41 and PVDF/4A MMMs were modelled using the Maxwell model, Higuchi model, Botthcher-Landauer model, Bruggeman model and modified Maxwell models and then compared with the experimental results. For PVDF/SiO₂ MMMs, the permeability model results followed the following order: Maxwell model > Bruggeman model > Bottcher-Landauer model > Higuchi model, which was different for that of PVDF/MCM-41 MMMs. Based on these four models, the additions of SiO₂ and MCM-41 only changed the permeability but the selectivity will remain the same as the polymer matrix. For the PVDF/4A MMMs, the He and CO₂ permeabilities showed similar trends with those of PVDF/MCM-41 MMMs while the N₂ and CO₂ permeabilities showed different trends for the two MMMs. The permeability values of the modified Maxwell model were highly independent of the void thickness. For all the three MMMs, the permeabilities increased with increasing void thickness and this upward trend was significant for the PVDF/SiO₂ MMMs due to the smaller particle size of SiO₂. Based on the relationship between the void volume fraction and the inorganic filler nominal volume fraction, it was possible to estimate the void thickness using Equation (10.29). Unexpectedly, the experimental permeability results of the MMMs showed no significant differences for the three types of MMMs; the permeabilities decreased initially as the inorganic fillers was about 4 wt% and then subsequently increased with further increases of the inorganic fillers. Using the modified Maxwell model and taking into account the crystallinity effect on the

permeability, the permeability modelling results matched the experimental permeability results very well, indicating the success of capturing the gas transport phenomena of MMMs.

Chapter 11 Preparation and Characterisation of Asymmetric Membranes Based on Nonsolvent/NMP/P84

11.1 Introduction

Asymmetric membranes prepared *via* phase inversion technique have been widely investigated for desalination, filtration and gas separation since the pioneering work of Loeb and Sourirajan [134] in the 1960s. In a typical wet phase inversion process, the polymer solution is cast onto a substrate and immersed into a nonsolvent coagulation bath after a given evaporation time. Due to the exchange of the solvent and nonsolvent, the polymer solution will be vitrified into a polymer-lean phase and a polymer-concentrated phase. It is believed that the membrane structure is highly dependent on both the thermodynamic and the kinetic properties of the ternary nonsolvent/solvent/polymer system [135-137]. For gas separation, asymmetric membranes with a dense selective thin skin layer are favourable to achieve good gas separation performance.

Ren *et al.* [11] prepared asymmetric membranes from water/NMP/P84 system. They found that the approaching ratio of the casting solution played a critical role on the membrane structure and that three types of membrane morphology, *i.e.*, finger-like structure, transition structure and sponge-like structure, were observed. Qiao *et al.* [14] studied asymmetric membranes based on P84 for pervaporative dehydration of isopropanol by a dry-wet phase inversion method. Asymmetric membranes with a flux of 432 g/m^2 and a separation factor of 3508 at 60°C were successfully obtained. Many studies on the applications of P84 dense membrane for gas separation had also

been reported [27]. However, to the best of the author's knowledge, limited work is devoted to develop asymmetric membranes based on P84 for gas separation. In this part of the study, asymmetric membranes based on ternary nonsolvent/NMP/P84 systems have been prepared *via* a wet phase inversion technique. The effects of the membrane preparation conditions, *i.e.*, nonsolvent type, polymer solution concentration, casting solution thickness, evaporation time and coagulation temperature, on the membrane structures were investigated.

11.2 Results and discussion

11.2.1 Thermodynamic properties of nonsolvent/solvent/polymer systems

Thermodynamically, three interaction parameters (g_{12} , g_{13} and g_{23}) are required to explain the formation mechanism of asymmetric membranes and their correlation with the membrane structures. Strictly speaking, these binary interaction parameters are dependent on the concentration of polymer solution. However, due to the lack of data, the solvent/non-solvent (g_{12}) and solvent/polymer (g_{23}) binary interaction parameters are presumably treated to be independent of the solution concentration and calculated using Equation (11.1) with the help of solubility parameters [138].

$$g_{ij} = \frac{v_i}{RT} (\delta_i - \delta_j)^2 \quad (11.1)$$

where δ_i and δ_j are the solubility parameters of component i and j , respectively, R is the universal gas constant, T is the absolute temperature and v_i is the molar volume of the smaller molecule. The solubility parameters of the solvent NMP and nonsolvents were reported by Barton [139] and the solubility parameter of the P84 polymer was calculated by applying the additive rule to the structural components of

the repeat unit of the P84 polymer according to the method reported by Matsuura [140].

$$\delta_p = \sqrt{\sum F_{pi}^2} / V \quad (11.2-a)$$

$$\delta_d = \sum F_{di} / V \quad (11.2-b)$$

$$\delta_h = \sqrt{\sum E_{hi}} / V \quad (11.2-c)$$

$$\delta_{sp} = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (11.2-d)$$

where F_{di} , F_{pi} and E_{hi} are the London dispersion force, the dipole force and the hydrogen bonding force and δ_d , δ_p and δ_h are their corresponding components of the solubility parameters, respectively, V is the total molar volume of all groups included in the structural unit, δ_{sp} is the overall solubility of the polymer. The molar mass, boiling temperature, density and solubility parameter of the solvent, nonsolvents and P84 are shown in Table 11.1.

Table 11.1 Molar volume (V), boiling temperature (T_b), density (ρ) and solubility parameter of solvent, non-solvents and P84 polymer

	V (cm ³ /mol)	ρ (g/cm ³)	T_b (°C)	δ_d (J/cm ³) ^{1/2}	δ_p (J/cm ³) ^{1/2}	δ_h (J/cm ³) ^{1/2}	δ_{sp} (J/cm ³) ^{1/2}
water	18.0	0.997	100	15.5	16.0	42.3	47.8
ethanol	58.5	0.785	78.5	15.8	8.8	19.4	26.5
IPA	76.8	0.781	82	15.8	6.1	16.4	23.5
acetone	74.0	0.784	56	15.5	10.4	7.0	20.0
NMP	96.5	1.026	202	18.0	12.3	7.2	22.9
P84	313.8	1.35	NA	20.4	12.4	7.7	25.1

The nonsolvent/polymer interaction parameters (g_{13}) are calculated by Equation (11.3) [141].

$$g_{13} = \frac{-\{\ln(1-\phi_p) + \phi_p\}}{\phi_p^2} \quad (11.3)$$

where ϕ_p is the volume fraction of the P84 polymer and it can be determined by the swelling experiments as follows: P84 dense membranes were prepared by evaporating the casting P84/NMP solution in an oven at 80 °C for 6 h and then a vacuum oven at 120 °C for 12 h. The dried membranes were immersed into the nonsolvents for at least two days. The weight of the membrane samples was measured before and after the immersion.

$$\phi_p = \frac{\frac{W_{dry}}{\rho_3}}{\frac{W_{dry}}{\rho_3} + \frac{W_{wet} - W_{dry}}{\rho_1}} \quad (11.4)$$

where W_{dry} and W_{wet} are the weights of the dense P84 membrane before and after the equilibrium swelling process, and ρ_1 and ρ_3 are the densities of the nonsolvents and polymer P84, respectively.

The binary interaction parameters g_{12} , g_{23} and g_{13} are shown in Table 11.2. The NMP/P84 interaction parameter g_{23} was calculated to be 0.19. The values of g_{12} and g_{13} play a vital role on the formation mechanism of the asymmetric membranes. A lower value of the interaction parameter indicates a stronger affinity between the two species and vice versa. The values of the nonsolvent/solvent interaction parameters g_{12} were in the order of water > ethanol > acetone > IPA and the values of nonsolvent/polymer interaction parameters g_{13} were in the following order: IPA > water > ethanol > acetone. Among the four types of the nonsolvents, water exhibits the largest g_{12} value of 4.5 indicating its lowest affinity to the solvent NMP

whilst acetone has the lowest g_{13} value of 1.21, indicating its strongest interaction with the P84 polymer.

Table 11.2 Interaction parameters in the nonsolvent/solvent/P84 systems at room temperature

Non-solvent	g_{12}	g_{23}	g_{13}
water	4.50	0.19	1.65
ethanol	0.31	0.19	1.44
IPA	0.01	0.19	1.67
acetone	0.25	0.19	1.21

The experimentally determined binodal demixing curves based on the cloud points for the ternary nonsolvent/solvent/polymer systems are shown in Fig. 11.1. It could be seen that the binodal curve shifted to the lower nonsolvent concentration in the following order: acetone>IPA>ethanol>water. Water appeared to be the most efficient nonsolvent and the introduction of a small amount of water into the P84/NMP solution could cause the polymer solution to be separated into two phases. In contrast, the acetone/NMP/P84 system exhibited the best tolerance for the nonsolvent acetone and a relatively higher amount of acetone was needed for phase separation due to its stronger interaction with the P84 polymer.

Fig. 11.1 Phase diagrams of ternary nonsolvent/solvent/polymer systems.

11.2.2 Kinetic properties of nonsolvent/solvent/polymer systems

Generally, the formation mechanism of the asymmetric membranes was determined by both thermodynamic and kinetic properties of the ternary nonsolvent/solvent/polymer system. The viscosity of the polymer solution is closely related to the exchange rate of solvent and nonsolvent during the phase inversion process and plays a very important role on the precipitation kinetics and therefore the membrane structures. The viscosity of P84/NMP solution as a function of the mass concentration of P84 is shown in Fig. 11.2. It can be seen that the viscosity of the P84/NMP solution increases exponentially with increasing P84 mass concentration. The exchange rate of solvent and nonsolvent at the polymer solution/coagulation bath interface was theoretically estimated by the diffusion coefficient calculated

from the Tyn-Calus equation [142] given as

$$D_{AB} = 8.93 \times 10^{-8} \left(\frac{V_B^{0.267}}{V_A^{0.433}} \right) \left(\frac{T}{\eta_B} \right) \left(\frac{\sigma_B}{\sigma_A} \right)^{0.15} \quad (11.7)$$

where D_{AB} (cm^2/s) is the diffusion coefficient of species A in species B; V_A and V_B (cm^3/mol) are the molar volumes of A and B, respectively; T (K) is the absolute temperature; η_B (mPa s) is the viscosity of species B and σ_A and σ_B (mN/m) are the surface tensions of A and B, respectively.

Fig. 11.2 Viscosity of P84/NMP solution as a function of P84 mass concentration fraction

Table 11.3 Surface tension, viscosity and diffusion coefficients of solvent and nonsolvents.

Chemicals	Surface tension σ (mN/m)	Viscosity η (mPa s)	$D_{NMP \rightarrow NS}$ ($10^{-6} \text{cm}^2/\text{s}$)	$D_{NS \rightarrow NMP}$ ($10^{-6} \text{cm}^2/\text{s}$)
Water	72.5	1.00	8.59	14.2
Ethanol	22.7	1.22	8.11	10.1
IPA	23.0	2.40	4.44	8.9
Acetone	25.2	0.32	33.43	9.0
NMP	40.7	1.65	NA	NA

Table 11.3 shows the results of the diffusion coefficients of the solvent NMP in nonsolvents ($D_{NMP \rightarrow NS}$) and those of non-solvents in NMP ($D_{NS \rightarrow NMP}$). The values of

the $D_{NS \rightarrow NMP}$ were in the range of 8.9 to $14.2 \times 10^{-6} \text{ cm}^2/\text{s}$ and the variations were relatively small. It was believed that the effect of $D_{NS \rightarrow NMP}$ on the phase demixing was insignificant due to the high viscosity of the NMP/P84 solution. The $D_{NMP \rightarrow NS}$ was thought to play a critical role on the exchange rate of solvent and nonsolvent [142]. Generally, a higher value of $D_{NMP \rightarrow NS}$ leads to a faster exchange rate between the solvent and the nonsolvent. In other words, it takes a shorter time before enough NMP solvent diffuses into the nonsolvent coagulation bath to give phase demixing. As shown in Table 11.3, among the four types of non-solvents, the diffusion coefficient of the NMP in acetone coagulation bath $D_{NMP \rightarrow \text{Acetone}}$ exhibited the largest value of $33.43 \times 10^{-6} \text{ cm}^2/\text{s}$ due to the small viscosity of acetone, which was followed by water, ethanol and IPA with diffusion coefficients of 8.59×10^{-6} , 8.11×10^{-6} and $4.44 \times 10^{-6} \text{ cm}^2/\text{s}$ for, respectively.

Fig. 11.3 NMP concentration in the vicinity of the P84 solution immersed into the nonsolvent coagulation baths as a function of time

The diffusivities of the NMP in the nonsolvents baths were also experimentally determined. The NMP concentration in the nonsolvent coagulation baths as a

function time is shown in Fig. 11.3. It was believed that a gelation medium interface could be formed between the polymer solution and the bulk nonsolvent medium and that the NMP molecules had to diffuse through the polymer solution into the gelation medium interface and then into the bulk nonsolvent bath [143]. This reported diffusion behaviour was also observed in this study. As shown in Fig. 11.3, the NMP concentration rapidly increased to a maximum value during the early stage, reached a constant value and then decreased subsequently. The diffusivities of NMP in water and acetone coagulation bath had similar values in the early stage, which were larger than those in ethanol and IPA.

11.2.3 Effect of the nonsolvent type

The SEM micrographs of the cross-sections of the asymmetric membranes prepared from different nonsolvent coagulation baths are shown in Fig. 11.4. All the asymmetric membranes consisted of a top dense layer supported on a porous sub-layer. The thickness of the dense layer and the structure of the sub-layer were significantly affected by the type of nonsolvent coagulation medium. The asymmetric membranes prepared using water as the nonsolvent had the thickest dense top layer and a porous sub-layer characteristic of finger-like macrovoids while the asymmetric membranes prepared using ethanol, IPA and acetone as nonsolvents exhibited a thinner top layer and a fine sponge-like sub-layer. The average pore size of the sub-layer of the asymmetric membrane was in the following order: acetone > ethanol > IPA > water.

Fig. 11.4 SEM micrographs of the cross-sections of the asymmetric membranes using (1) water, (2) ethanol, (3) IPA, and (4) acetone as a nonsolvent. (A): the overall cross-section view, (B): the top layer view, and (C): fine pore structure view.

Membrane preparation conditions: P84 concentration = 25.6 wt%; evaporation time = 10 s; casting solution thickness = 300 μm and temperature of coagulation bath = room temperature

The 3D AFM micrographs of the top surface of the asymmetric membranes with a scanning area of $2 \times 2 \mu\text{m}$ are shown in Fig. 11. 5. The R_q and R_a values are summarised in Table 11. 4. In the AFM micrographs, the vertical height profile of the membrane sample is indicated by colour difference. The light regions corresponded to the high peaks and the dark regions corresponded to the valleys. The asymmetric membrane prepared using water as nonsolvent had the smoothest surface with R_q and R_a values of 2.5 and 2.1 nm, respectively. The roughness of the asymmetric

membrane increased in the following order: acetone > ethanol > IPA > water, which was coincidentally consistent with that of the pore size of the sub-layers.

Table 11.4 Effects of nonsolvent and polymer concentration on the physical characteristics of the asymmetric membranes

Nonsolvent	P84 Concentration	Skin thickness L (μm)	Porosity ε	Roughness (nm)	
				R_a	R_q
water	25.6%	4.9	0.78	2.1	2.5
	23.1%	3.7	0.80	2.2	2.8
	19.4%	3.0	0.84	2.6	3.6
	16.7%	1.6	0.85	4.8	6.1
ethanol	25.6%	2.3	0.73	3.8	4.8
	23.1%	1.9	0.74	4.1	5.2
	19.4%	1.1	0.79	4.9	5.9
	16.7%	0.7	0.81	6.2	7.5
IPA	25.6%	1.6	0.69	2.2	2.7
	23.1%	1.1	0.72	2.2	3.0
	19.4%	0.9	0.76	2.9	3.7
	16.7%	0.5	0.78	4.5	5.7
acetone	25.6%	0.9	0.81	6.6	8.4
	23.1%	0.8	0.84	7.1	8.9
	19.4%	0.5	0.88	8.6	11.0
	16.7%	NA*	0.90	9.0	12.0

*Defective skin due to open pores in the skin layer

Fig. 11.5 3D AFM micrographs of the top layer of the asymmetric membranes prepared using (1) water, (2) IPA, (3) ethanol, and (4) acetone as a nonsolvent. Membrane preparation conditions: P84 concentration = 25.6 wt%; evaporation time = 10 s; casting solution thickness = 300 μm and temperature of coagulation bath = room temperature

The N_2 adsorption-desorption isotherms of the asymmetric membranes are shown in Fig. 11.6, indicating Type II characteristics of the macroporous structures for the resulting asymmetric membranes. The BET surface areas of the asymmetric membranes prepared using water, ethanol, IPA and acetone were 26.6, 13.2, 5.9 and 27.7 m^2/g , and the porosities of these membranes were 0.78, 0.73, 0.69 and 0.81, respectively.

Fig. 11.6 N₂ adsorption-desorption curves of the asymmetric membranes

The O₂ permeances of the asymmetric membranes prepared using water, ethanol, IPA and acetone were 0.08, 0.18, 0.26 and 0.46 Barrer/μm, respectively as shown in Fig. 11.7 and the thicknesses of the skin layer were determined to be 4.9, 2.3, 1.6 and 0.9 μm, respectively, using equation (11.7), which were consistent with the SEM results in Fig. 11.4. The O₂/N₂ selectivities of the asymmetric membranes in Fig. 11.7 were almost the same with that of the dense P84 membrane, indicating the presence of defect-free top layers.

Fig. 11.7 O₂ permeance and O₂/N₂ selectivity of the asymmetric membranes

The structural properties of the asymmetric membranes were determined by two factors: thermodynamics and kinetic properties of the ternary nonsolvent/solvent/P84 systems. Thermodynamically, the water/NMP/P84 system had the smallest miscibility gap as shown in Fig. 11.1 due to the fact that water had the lowest affinity with the solvent NMP as indicated by its largest value of g_{12} . During the phase inversion process, the smaller miscibility gap indicated a lower resistance to phase demixing and therefore upon a very small amount of exchange of solvent with water, the initial P84 solution composition could be moved into the unstable region where phase demixing took place. This instantaneous demixing in water/NMP/P84 system was responsible for the presence of the finger-like structure [144]. Using ethanol, IPA and acetone as the nonsolvents, the nonsolvent/NMP/P84 systems possessed higher resistance to phase demixing, in which delayed demixing occurred and a sponge-like structure was obtained [144]. It was believed that the roughness of the asymmetric membranes was closely related to the size of the nodule or nodule aggregates and there was good correlation between the roughness and pore size of the asymmetric membranes [141]. The lowest R_q and R_a values of the asymmetric membranes prepared with water as the nonsolvent could also be attributed to its largest value of g_{12} . The exchange of solvent and nonsolvent also played an important role on the membrane structures. Acetone had the fastest exchange rate with NMP and this could be responsible for the largest roughness and the thinnest top dense layer of the asymmetric membrane prepared using acetone as the nonsolvent [145]. The porosity of the resulting asymmetric membranes was

presumably related to the exchange rate of solvent and nonsolvent.

11.2.4 Effect of the concentration of the polymer solution

The effects of the concentration of the initial P84 solution on the membrane structure and its gas separation performance were studied. The SEM micrographs of the asymmetric membranes prepared from the water/NMP/P84 system with varying P84 solution concentrations are shown in Fig. 11.8. All the micrographs had similar characteristics of finger-like structures, indicating instantaneous occurrence of demixing regardless of the polymer concentration. However, the thickness of the dense top layer decreased with decreasing polymer concentration. Finger-like macro-voids were present in the SEM micrographs of the asymmetric membranes using a weight concentration of 16.7% of P84 in the polymer solution as shown in Fig. 11.9 (1-A, 2-A). It could be seen that the pore sizes of the sub-layers in Fig. 11.9 (1-C, 2-C) had increased as compared with those of the asymmetric membrane prepared from 25.6% P84 weight concentration as shown in Fig. 11.4 (3-C) and 11.4 (4-C). A lower concentration of polymer casting solution would lead to a lower polymer concentration of the ternary system at the binodal phase demixing point and could result in a more porous structure. Further, a lower polymer solution with lower viscosity would increase the exchange rate of the solvent and the nonsolvent and delay phase demixing, which would result in a thinner skin layer and a more porous sub-layer. The formation of finger-like macrovoids in the symmetric membranes prepared from IPA/NMP/P84 and acetone/NMP/P84 with 16.7% weight concentration of P84 in Fig. 11.9 could also be attributed to the rapid exchange of

solvent and nonsolvent. By decreasing the polymer concentration, a faster disentanglement of the polymer chains took place due to the higher diffusivities of the solvent and nonsolvent. It was believed that the disentanglement process would affect to the pore size and the top layer roughness [146]. The AFM micrographs of the top layers of the asymmetric membranes are shown in Fig. 11.10. The size of the nodule aggregates increased as the polymer concentration decreased, resulting in greater roughness. It was reported that for the systems with lower polymer concentrations, more polymer chains were incorporated into nodules, resulting in larger nodule sizes and greater roughness as compared with the systems with higher polymer concentrations [145].

Fig. 11.8 SEM micrographs of the asymmetric membranes using P84 weight concentration of (1) 25.6%, (2) 23.1%, (3) 19.4%, and (4) 16.7% in the P84/NMP solution. Preparation conditions: nonsolvent = water; evaporation time = 10 s, casting solution thickness = 500 μm and temperature of coagulation bath = room temperature.

Fig. 11.9 SEM micrographs of the asymmetric membranes using (1) IPA and (2) acetone as the nonsolvent. (A): the overall cross-section view, (B): the top layer view, and (C): the pore structure view. Preparation conditions: P84/NMP solution = 16.7%; evaporation time = 10 s; casting solution thickness = 500 μm and temperature of coagulation bath = room temperature

Fig. 11.10 3D AFM micrographs of the asymmetric membranes using P84 weight concentration of (1) 25.6%, (2) 23.1%, (3) 19.4%, and (4) 16.7% in the P84/NMP solution. Preparation conditions: nonsolvent = IPA; evaporation time = 10 s; casting solution thickness = 500 μm and temperature of coagulation bath = room temperature.

The effects of the P84 concentration and solvent type on the physical characteristics of the asymmetric membranes are given in Table 11.4. The porosity and roughness of the asymmetric membranes increased while the thickness of the skin layer decreased with decreasing P84 polymer concentration. Table 11.4 also shows that all

asymmetric membranes had selective dense skin layers except the asymmetric membrane prepared from acetone/NMP/P84 with 16.7% polymer concentration. The gas (He, CO₂, O₂ and N₂) permeance of the asymmetric membranes showed a similar trend in Fig. 11.11. The gas permeance of the asymmetric membranes increased with decreasing polymer concentration, which confirmed that the thickness of the skin layer increased with increasing concentration as shown in Table 11.4. The absence of permeance results for acetone/NMP/P84 with 16.7% polymer concentration was in agreement with the zero skin thickness in Table 11.4. The selectivities of the gas pairs (He/N₂, CO₂/N₂ and O₂/N₂) for the asymmetric membranes prepared from water/NMP/P84 and ethanol/NMP/P84 were independent of the polymer solution although some minor fluctuations were observed whilst the selectivity for He/N₂ of the asymmetric membranes prepared from IPA/NMP/P84 and acetone/NMP/P84 increased slightly with decreasing polymer concentration. In other words, the selectivity for He/N₂ of the asymmetric membranes prepared from IPA/NMP/P84 and acetone/NMP/P84 were weakly dependent on the thickness of the skin layer. It was believed that when the skin thickness decreased into the range of several hundreds of nanometres, the selectivity increased with decreasing skin layer due to the fact that a more compact structure was obtained in a thinner skin layer [147].

Fig. 11.11 Gas permeance and selectivity of the asymmetric membranes prepared from (a) water/NMP/P84, (b) ethanol/NMP/P84, (c) IPA/NMP/P84, and (d) acetone/NMP/P84 with varying P84 solution concentration

Table 11.5 Properties of the asymmetric membranes prepared from water/NMP/P84 with varying thicknesses of the casting solution.

Casting thickness (μm)	Skin thickness L (μm)	Porosity ϵ	Roughness (nm)	
			R_a	R_q
300	4.9	0.78	2.1	2.5

500	14.4	0.65	1.8	2.3
1000	42.3	0.53	1.6	2.0
1500	68.7	0.45	1.5	1.9

11.2.5 Effect of the thickness of the casting solution

The effects of the thickness of the casting polymer solution on the membrane structure and the membrane separation performance were investigated. The SEM micrographs of the asymmetric membranes prepared from water/NMP/P84 with varying thicknesses of the casting solution are shown in Fig. 11.12. With increasing thickness of the casting solution, the resulting asymmetric membranes became denser and the number of finger-like macrovoids reduced. The thickness of the dense top layer also increased with increasing thickness of the casting solution. The thicknesses were calculated as 4.9, 14.4, 42.3 and 68.7 μm for the asymmetric membranes prepared with solution thicknesses of 300, 500, 1000 and 1500 μm , respectively, using Equation (11.8). The roughness of the skin surface of the asymmetric membrane decreased with increasing thickness as shown in Fig. 11.13. With a thicker casting solution, it would take a longer time for the nonsolvent to penetrate into the solution, which would result in more a concentrated polymer solution at the polymer/coagulant interface and delay demixing at the same time. Hence, the resulting asymmetric membrane prepared with a thicker casting solution exhibited denser membrane morphology and a smoother skin surface. The structural properties of the asymmetric membranes prepared from water/NMP/P84 with varying thicknesses of the casting solution are given in Table 11.5. The gas permeation results inferred and thereby indicated that the thickness of the skin layer

increased with increasing thickness of the casting polymer solution but the selectivity of the asymmetric membranes were almost the same with varying thicknesses of the skin layer of the asymmetric P84 membranes as shown in Fig. 11.14.

Fig. 11.12 SEM micrographs of the asymmetric membranes prepared with different thicknesses (1) 1500, (2) 1000, (3) 500 and 300 μm of the casting solution.

Preparation conditions: nonsolvent = water; polymer solution concentration = 25.6%; evaporation time = 10 s and temperature of coagulation bath = room temperature.

Fig. 11.13 3D AFM micrographs of the asymmetric membranes prepared with different thicknesses (1) 1500, (2) 100, (3) 500, and (4) 300 μm. Preparation conditions: nonsolvent = water; polymer solution concentration = 25.6%; evaporation time = 10 s and temperature of coagulation bath = room temperature.

Fig. 11.14 O₂ permeance and O₂/N₂ selectivity of the asymmetric membranes prepared from water/NMP/P84 with varying casting solution thicknesses

11.2.6 Effect of the evaporation time

Figure 11.15 shows the cross-sections of the top layers of the asymmetric membranes prepared under different evaporation times of 300, 120, 60 and 10 s. It could be observed that the thickness of the dense skin layer increased whilst the roughness of the skin surface decreased with increasing evaporation time as shown in Figs. 11.15 and 11.16, respectively. The results were consistent with those reported by Kawakami *et al.* [145]. It is believed that with increasing evaporation time before immersing the casting solution into the coagulation bath, the polymer concentration in the top layer of the casting solution would increase as a result of solvent evaporation. This could then reduce the exchange rate of the solvent and the nonsolvent at the top layer and result in asymmetric membranes with thicker and smoother dense skin layers. As shown in Table 11.6, the thickness of the skin layer of the asymmetric membrane increased with increasing evaporation time. The rate of increase in the thickness was particularly significant for the asymmetric membranes prepared from the acetone/NMP/P84 system. The skin thickness of the asymmetric membrane prepared with 300 s evaporation time before immersion was 9.3 μm , which was almost 10 times greater than that of the membrane prepared with 10 s of evaporation time. This could be due to the relatively higher volatility of acetone as compared with water. As expected, the porosity of the asymmetric membranes prepared from acetone/NMP/P84 for the acetone/NMP/P84 system decreased with

increasing evaporation time as shown in Table 11.6. Fig. 11.17 shows the permeances and selectivities of the asymmetric membranes prepared from acetone/NMP/P84 as a function of evaporation time. As expected, the permeance decreased with increasing evaporation time as a result of increasing skin layer thickness. All the asymmetric membranes had good selectivities, indicating the presence of selective dense skin layers. The asymmetric membrane prepared under an evaporation time of 10 s yielded the highest selectivity and permeance.

Fig. 11.15 SEM micrographs of the asymmetric membranes prepared with different evaporation times (1) 10, (2) 60, (3) 120, and (4) 300 s. Preparation conditions: nonsolvent = water; casting solution thicknesses = 500 μm ; polymer solution concentration = 25.6% and temperature of coagulation bath = room temperature.

Fig. 11.16 3D AFM micrographs of the asymmetric membranes prepared with different evaporation times (1) 10, (2) 60, (3) 120, and (4) 300 s. Preparation conditions: nonsolvent = acetone; polymer solution concentration = 25.6%; casting solution thickness = 500 μm and temperature of coagulation bath = room temperature.

Table 11.6 Properties of the asymmetric membranes prepared from water/NMP/P84
and acetone/NMP/P84 with varying evaporation times before immersion into the
coagulation bath.

Nonsolvent (concentration)	Evaporation time (s)	Skin thickness L (μm)	Porosity ε	Roughness (nm)	
				R_a	R_q
Water (25.6%)	10	4.9	0.78	0.78	2.1
	60	5.3	0.78	0.63	1.6
	120	9.2	0.79	0.54	1.3
	300	9.6	0.80	0.54	1.2
Acetone (25.6%)	10	0.9	0.81	6.6	8.4
	60	5.2	0.78	5.6	7.1
	120	7.6	0.76	5.1	6.5
	300	9.3	0.73	5.0	6.2

Fig. 11.17 O₂ permeance and O₂/N₂ selectivity of the asymmetric membranes prepared from acetone/NMP/P84 with varying evaporation times prepared from acetone/NMP/P84 for varying evaporation time

11.2.7 Effect of the temperature of the coagulation bath

The temperature of the coagulation bath will affect the diffusivity of the solvent and nonsolvent, which will have an impact on the membrane structure. With low temperatures in the coagulation baths, the exchange rate between the solvent and the nonsolvent is relatively slow and will result in delayed demixing. Hence, a denser membrane structure with a thicker skin layer will be obtained. On the other hand, higher temperature will accelerate the exchange between the solvent and the nonsolvent, resulting in a more porous structure. Furthermore, temperature will also affect the viscosity of the casting solution. Lower temperature leads to higher viscosity, resulting in lower exchange rate between solvent and nonsolvent and delays demixing. The SEM micrographs of the cross-sections of the asymmetric membranes prepared using different temperatures of water bath are shown in Fig. 11.18. The membranes immersed into the water bath with 0 and 25 °C exhibited thicker dense skin layers due to delayed demixing and lower porosities as compared with those immersed into higher temperatures of 60 and 80 °C. It was observed that some polymer particles were present in the cross-sections of the membranes prepared with higher coagulation temperatures as shown in Fig. 11.18 (3) and (4). It is surmised that the formation of these polymer particles was attributed to the fast diffusivities of the solvent and the nonsolvent. Figure 11.19 shows the SEM

micrographs of the asymmetric membranes prepared with a temperature of 0 °C for the IPA and acetone coagulation baths. A denser membrane structure with thicker skin layer and smaller pore size was observed as compared with the room temperature conditions in Fig. 11.4-3 and 4-4. The structural properties of the asymmetric membranes prepared from water/NMP/P84 and acetone/NMP/P84 with varying temperature of the coagulation bath are given in Table 11.7. The roughness of the asymmetric membranes increased with increasing temperature of the coagulation bath as shown in Fig. 11.20. The R_a and R_q values of the asymmetric membrane immersed into 0 °C water bath were 1.0 and 1.4 nm, respectively, which were much smaller than the values of 7.3 and 9.5 nm, respectively, for the asymmetric membrane immersed into 80 °C water bath. These smaller roughness values were presumably due to the slower exchange rate between the solvent and the nonsolvent and the higher viscosity of the casting solution at lower temperature.

The porosities of the symmetric membranes prepared at 0, 25, 60 and 80 °C water bath temperatures were 0.75, 0.85, 0.88 and 0.92, respectively, which were consistent with the SEM micrographs in Fig. 11.18. The porosities of the asymmetric membranes prepared from 0 °C IPA and 0 °C acetone coagulation baths were 0.58 and 0.69, respectively, both of which were smaller than the porosities of 0.69 and 0.81 for the asymmetric membranes prepared from 25 °C IPA and 25 °C acetone coagulation baths, respectively. Gas permeation tests indicated that some nonselective cracks or defects were present in the membranes prepared using higher coagulation temperatures of 60 and 80 °C. The skin thickness of the asymmetric

membranes increased with decreasing coagulation temperature.

Table 11.7 Properties of the asymmetric membranes prepared from water/NMP/P84, IPA/NMP/P84 and acetone/NMP/P84 with varying temperature of the coagulation bath.

Nonsolvent (concentration)	Coagulation Temperature (°C)	Skin thickness L (um)	Porosity ε	Roughness (nm)	
				R_a	R_q
Water (16.7%)	0	1.9	0.75	1.0	1.4
	25	1.6	0.85	2.6	3.6
	60	NA	0.88	4.4	6.3
	80	NA	0.92	7.3	9.5
IPA (25.6%)	0	2.4	0.58	1.8	2.2
	25	1.6	0.69	2.2	2.7
Acetone (25.6%)	0	1.3	0.76	5.1	6.3
	25	0.9	0.81	6.6	8.4

Fig. 11.18 SEM micrographs of the asymmetric membranes prepared with different temperatures of coagulation bath (1) 0, (2) 25, (3) 60, and (4) 80 °C. Preparation conditions: nonsolvent = water; evaporation time = 10 s; polymer solution concentration = 16.7% and casting solution thickness = 500 µm.

Fig. 11.19 SEM micrographs of the asymmetric membranes prepared with (1) IPA, and (2) acetone. (A): overall cross-section view, (B): top layer view, and (C): fine pore structure. Preparation conditions: evaporation time = 10 s; polymer solution concentration = 25.6%; coagulation temperature = 0 °C and casting solution thickness = 500 µm.

Fig. 11.20 3D AFM micrographs of the asymmetric membranes prepared with different coagulation temperatures (1) 0, (2) 25, (3) 60, and (4) 80 °C. Preparation conditions: nonsolvent = water; polymer solution concentration = 25.6%; casting solution thickness = 500 μm and evaporation time = 10 s

11.3 Summary

Asymmetric membranes based on P84 were prepared using the wet phase inversion technique. The effects of the membrane preparation conditions such as the nonsolvent type, polymer solution concentration, evaporation time, thickness of

casting polymer solution and temperature of the coagulation bath, on the membrane structures and gas separation performance were studied. Some conclusions are as follows:

1. The nonsolvent type played a critical role on the membrane morphology. The symmetric membranes prepared from water/NMP/P84 system showed a thicker skin layer supported on a finger-like sub-layer whilst the asymmetric membranes prepared from ethanol/NMP/P84, IPA/NMP/P84 and acetone/NMP/P84 systems had thinner skin layers and sponge-like sublayers.
2. Lower polymer solution concentration resulted in a more porous membrane structure with a thinner and smoother skin layer. The membranes prepared from ethanol/NMP/P84, IPA/NMP/P84 and acetone/NMP/P84 systems with low polymer solution concentration showed some finger-like macrovoids.
3. Longer evaporation time and thicker casting polymer solution resulted in a denser membrane structure with a thicker and smoother skin layer. The effect of the evaporation time was more significant for the acetone/NMP/P84 system due to the high volatility of the acetone.
4. Higher temperature of the coagulation bath resulted in a more porous membrane with a thinner and rougher skin layer. The asymmetric membranes immersed into the water bath with temperatures of 60 and 80 °C were very brittle and showed no selectivity for gas pairs due to some cracks or defects.

5. The gas permeation results indicated that the selectivities of the asymmetric membranes increased slightly with decreasing skin thickness when the thickness of the skin layer was less than several hundred nanometres.

Chapter 12 Conclusions and Future Work

12.1 Conclusions

Main conclusions based on this project can be drawn as follows:

- (1) P84 has been verified to be one of the attracting membrane materials for gas separation due to its excellent thermal stability, permeability and selectivity. The permeability of a single gas increased with increasing membrane thickness whilst the selectivity of a given gas pair was nearly independent of the membrane thickness. The average selectivity of O₂/N₂, He/CO₂, CO₂/N₂ and He/O₂ were found to be 8.2, 10.0, 12.9 and 15.8, respectively. The heat treatment increased the selectivity but decreased the permeability of the P84 membranes.
- (2) The physical characteristics of the three types of MMMs based on the pristine fumed SiO₂, synthesised mesoporous MCM-41 and zeolite 4A as inorganic fillers were investigated. Gas permeation tests showed that, among the three synthesised MMMs, P84/SiO₂ membrane had the best performance in terms of gas separation. P84/SiO₂ membrane exhibited a 20%, 63%, 59% and 45% increases in the permeability of He, O₂, N₂, and CO₂, respectively, over those for P84 membrane, besides maintaining comparable good selectivity.
- (3) To improve the compatibility between the polymer chains and the SiO₂ particles, nano-SiO₂ particles were modified with a silane coupling agent and they were subsequently incorporated into P84 polymer matrix to form MMMs. The composite membranes based on the modified SiO₂ showed better bonding morphology at the polymer/particle interfaces, higher stress modulus and tensile strength, and

significantly higher glass transition temperature as compared with those of the composite membranes based on the pristine SiO_2 particles. With the same weight percentage of the inorganic filler, the composite membranes based on the modified SiO_2 had higher selectivity than that of the composite membranes based on the pristine SiO_2 . The permeability of the composite membranes was compared with the theoretical predictions based on the Maxwell equation and the free volume theory. The Maxwell equation predicted lower values than the experimental data while the free volume theory produced acceptable predictions except for a large discrepancy in the permeability value for the P84/25% SiO_2 composite membrane.

(3) Polyimide-silica composite membranes were prepared using the sol-gel technique. The carbon-silica composite membranes were prepared by the pyrolysis of the polyimide-silica composite membranes at 900 °C under vacuum. With the introduction of the silica, there was no significant enhancement of the gas separation in the resulting PI-silica composite membranes, which still suffered a “trade-off” relationship between permeability and selectivity. However, the carbon-silica composite membranes exhibited better gas separation properties. The C-Si 28% composite membranes exhibited the highest permeance of 1042.18, 991.21, 296.03 and 155.26 Barrer/cm for He, CO_2 , O_2 and N_2 , respectively, which were 21.61, 137.67, 103.15 and 150.74 times of those of the pure carbon membrane, respectively. The C-Si 11% composite membranes exhibited the highest selectivities of 37.57, 36.61 and 7.09 for He/N_2 , CO_2/N_2 , and O_2/N_2 , respectively.

(4) Three types of inorganic fillers-fumed nonporous nano-silica, synthesised

mesoporous MCM-41 and micoporous zeolite 4A were incorporated into PVDF matrix to prepare mixed matrix membranes. With the incorporation of the inorganic fillers, the thermal stability of the composite membranes was reduced with lower degradation temperatures while the melting temperatures and crystallising temperatures seemed to be unaffected. The DSC results showed that the crystallinity of the composite membranes was increased as compared with pure PVDF membrane. In addition, the incorporation of MCM-41 had induced PVDF crystalline phase transformation from α phase to β phase. This phenomenon was not observed in PVDF/SiO₂ and PVDF/4A composite membranes as indicated by the XRD results. Beyond expectations, the gas permeabilities of the three composite membranes exhibited similar behaviour, especially at lower inorganic filler loadings, though the inorganic fillers showed different pore structure and particle size. Based on the density measurement results, the void volume fractions of the resulting MMMs can be calculated and subsequently an equation was proposed to estimate the void thickness. By taking the effects of crystallinity on the gas permeability into consideration, the modified Maxwell model gave good predictions on the gas permeabilities of the resulting MMMs, indicating that the model did capture the essence of the gas transport behaviours through the MMMs.

(5) The thermodynamic and kinetic properties of the ternary nonsolvent/NMP/P84 systems were studied and correlated with the membrane structures. The effects of the membrane preparation conditions including nonsolvent type, polymer solution concentration, casting solution thickness, evaporation time and coagulation

temperature played a critical role on the structures and gas transport properties of the resulting membranes. Asymmetric membranes with several hundred nanometres of dense selective skin layers were successfully prepared. Interestingly, the selectivities of gas pairs (He/N_2 , CO_2/N_2 and O_2/N_2) were higher than those of dense P84 membranes and increased with decreasing skin thickness of the asymmetric membranes.

12.2 Recommended Future work

Some experimental and theoretical studies can be considered for further work. The recommendations are as follows:

- 1) Carry out gas adsorption tests and investigate the transport properties of MMMs under different temperatures.**

The gas permeability coefficient of membranes is the product of diffusion coefficients and solubility coefficients. Adsorption tests at varying temperatures should be conducted to obtain solubility coefficients, which could provide useful information to further understand the mechanism of the gas transport. Gas permeation tests under varying temperatures should be conducted to obtain the activation energy of the transport process, which is vital to the understanding of the mechanism of gas transport and the choice of optimised temperatures for the target membranes.

- 2) Investigate novel inorganic fillers, *i.e.*, metal-organic framework materials to fabricate MMMs with better separation performance.**

It has been demonstrated that the performance of MMMs is highly dependent on the

properties of the inorganic fillers. Metal-organic framework materials have recently drawn much interest due to their unique adsorption and selective properties. It has been expected that MMMs based on metal-organic framework materials will show excellent gas separation performance. Therefore, this type of material is highly recommended as the inorganic filler for the preparation of MMMs for gas separation.

3) Investigate some alternative polymers and experimental conditions to prepare carbon/silica composite membranes

Carbon/silica composite membranes have good gas separation performance. However, these membranes are brittle. To address this problem, further studies can be carried out to look for alternative polymer matrices and improve the membrane preparation methods.

4) Model the permeation and separation of gases through asymmetric membranes

Asymmetric membranes with varying membrane structures (top layer thickness, porosity, pore size, surface roughness, etc.) had been successfully prepared in this project. The gas permeation results are closely related to the membrane structural characteristics. Some theoretical models should be considered to study the gas transport behaviour through the asymmetric membranes and compared with the experimental results.

References

1. Pinnau I., Recent advances in the formation of ultrathin polymeric membranes for gas separations, *Polym. Adv. Tech.*, 5 (1994) 733
2. Spillman R.W., Economics of gas separation membranes, *Chem. Eng. Prog.*, 85 (1989) 41
3. Baker R. W., Future Directions of Membrane Gas Separation Technology, *Ind. Eng. Chem. Res.*, 41 (2002) 1393
4. Mitchell J. K., On the permeation of gases, *Am. J. Med.*, 7 (1830) 36
5. Graham T., On the law of the diffusion of gases, *Phil. Mag.*, 32 (1866) 401
6. Benchold H., Membranes for gas ultrafiltration, *Biochem Z.*, 6 (1907) 379
7. Loeb S., Sourirajan S., Sea-water demineralization by means of an osmotic membrane, *Adv. Chem. Ser.* 38 (1962) 117
8. Henis J.M. S, Tripodi M.K., A novel approach to gas separations using composite hollow fibre membranes, *Sep. Sci. Technol.* 15 (1980) 1053
9. Graham T.E., Maclean D.L. Process for hydrogen recovery from ammonia purge gases, U.S. patent 4180552 assigned to Monsanto Inc. Dec., 25, 1979
10. Koros W.J., Fleming G.K., Membrane-based gas separation, *J. Membr. Sci.*, 83 (1993) 1
11. Ren J., Li Z., Wong F.S., Li D., Development of asymmetric BTDA-TDI/MDI (P84) co-polyimide hollow fibre membranes for ultrafiltration: the influence of shear rate and approaching ratio on membrane morphology and performance, *J. Membr. Sci.* 248 (2005) 177
12. White L.S., Transport properties of a polyimide solvent resistant nanofiltration membrane, *J. Membr. Sci.*, 205 (2002) 191
13. Qiao X.Y., Chung T.S., Fundamental characteristics of sorption, swelling, and permeation of P84 co-polyimide membranes for pervaporation dehydration of alcohols, *Ind. Eng. Chem. Res.* 44 (2005) 8938
14. Qiao X.Y., Chung T.S., Pramod K.P., Fabrication and characterization of

- BTDA-TDI/MDI (P84) co-polyimide membranes for the pervaporation dehydration of isopropanol, *J. Membr. Sci.*, 264 (2005) 176
15. Liu R. X., Qiao X.Y, Chung T.S., The development of high performance P84 co-polyimide hollow fibres for pervaporation dehydration of isopropanol, *Chem. Eng. Sci.*, 60 (2005) 6674
 16. Qiao X.Y., Chung T.S., Rajagopalan R. Zeolite filled P84 co-polyimide membranes for dehydration of isopropanol through pervaporation process, *Chem. Eng. Sci.*, 61 (2006) 6816
 17. Qiao X.Y., Chung T.S., Diamine modification of P84 polyimide membranes for pervaporation dehydration of isopropanol, *AIChE J.*, 52 (2006) 3462
 18. Li Y., Chung T.S., Huang Z., Kulprathipanja S., Dual-layer polyethersulfone (PES)/BTDA-TDI/MDI co-polyimide (P84) hollow fibre membranes with a submicron PES–zeolite beta mixed matrix dense-selective layer for gas separation, *J. Membr. Sci.*, 277 (2006) 28
 19. Liu R.X, Qiao X.Y., Chung T.S., Dual-layer P84/polyethersulfone hollow fibres for pervaporation dehydration of isopropanol, *J. Membr. Sci.*, 294 (2007) 103
 20. Widjojo N., Chung T.S., Krantz W.B., A morphological and structural study of Ultem/P84 copolyimide dual-layer hollow fibre membranes with delamination-free morphology, *J. Membr. Sci.*, 294 (2007) 132
 21. Wang K. Y., Chung T.S., Rajagopalan R., Dehydration of tetrafluoropropanol (TFP) by pervaporation via novel PBI/BTDA-TDI/MDI co-polyimide (P84) dual-layer hollow fibre membranes, *J. Membr. Sci.*, 287 (2007) 60
 22. Li Y., Chung T.S., Exploratory development of dual-layer carbon–zeolite nanocomposite hollow fibre membranes with high performance for oxygen enrichment and natural gas separation, *Microporous Mesoporous Mater.*, 113 (2008) 315
 23. Teoh M.M., Chung T.S., Wang K.Y., Guiver M.D. Exploring Torlon/P84 co-polyamide-imide blended hollow fibres and their chemical cross-linking

- modifications for pervaporation dehydration of isopropanol, *Separ. Purif. Tech.* 61 (2008) 404
24. Bos A., Punt I., Strathmann H., Wessling M., Suppression of gas separation membrane plasticization by homogeneous polymer blending, *AIChE J.*, 47 (2001) 1088
 25. Barsema J.N., Kapantaidakis G.C., van der Vegt N.F.A., Koops G.H., Wessling M., Preparation and characterisation of highly selective dense and hollow fibre asymmetric membranes based on BTDA-TDI/MDI co-polyimide, *J. Membr. Sci.* 216 (2003) 195
 26. Visser T., Masetto N., Wessling M., Materials dependence of mixed gas plasticization behaviour in asymmetric membranes, *J. Membr. Sci.*, 306 (2007) 16
 27. Visser T., Wessling M., Auto and mutual plasticization in single and mixed gas C₃ transport through Matrimid-based hollow fibre membranes, *J. Membr. Sci.*, 312 (2008) 84
 28. Sterescue D.M., Stamatialis D.F., Wessling M., Boltorn-modified polyimide gas separation membranes, *J. Membr. Sci.* 310 (2008) 512
 29. Tin P.S., Chun T.S., Hill A.J., Advanced fabrication of carbon molecular sieve membranes by nonsolvent pre-treatment of precursor polymers, *Ind. Eng. Chem. Res.*, 43 (2004) 6476
 30. Tin P.S., Chung T.S., Liu Y., Wang R., Separation of CO₂/CH₄ through carbon molecular sieve membranes derived from P84 polyimide, *Carbon*, 42 (2004) 3123
 31. Barsema J.N., A van der Vegt N.F., Koops G.H., Wessling M., Carbon molecular sieve membranes prepared from porous fibre precursor, *J. Membr. Sci.*, 205 (2002) 239
 32. El-Hibri M.J., Paul D.R., Gas transport in poly(vinylidene Fluoride): effects of uniaxial drawing and processing temperature, *J. Appl. Poly. Sci.*, 31 (1986) 2533

33. Wang D.L., Li K., Teo W.K., Preparation and characterization of polyvinylidene fluoride (PVDF) hollow fibre membranes, *J. Membr. Sci.* 163 (1999) 211–220
34. Deshmukh S.P., Li K., Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fibre membranes, *J. Membr. Sci.* 150 (1998) 75–85
35. Yeowa M.L., Liu Y.T., Li K., Preparation of porous PVDF hollow fibre membrane via a phase inversion method using lithium perchlorate (LiClO_4) as an additive, *J. Membr. Sci.* 258 (2005) 16–22
36. Tan X.Y., Tan S.P., Teo W.K., Li K., Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water, *J. Membr. Sci.* 271 (2006) 59–68
37. Khayef M., Feng C.Y., Khulbe K.C., Matsuura T., Study on the effect of a non-solvent additive on the morphology and performance of ultrafiltration hollow-fibre membranes, *Desalination* 148 (2002) 321–327
38. Khayet M, Matsuura T., Pervaporation and Vacuum Membrane Distillation Processes: Modelling and Experiments, *AIChE J*, 50: 1697–1712, 2004
39. Bonyadi S., Chung T.S., Flux enhancement in membrane distillation by fabrication of dual layer hydrophilic–hydrophobic hollow fibre membranes, *J. Membr. Sci.* 306 (2007) 134–146
40. Sukitpaneenit P., Chung T.S., Molecular elucidation of morphology and mechanical properties of PVDF hollow fibre membranes from aspects of phase inversion, crystallization and rheology, *J. Membr. Sci.* 340 (2009) 192–205
41. Xu A., Yang A.H., Young S., Montigny D., Tontiwachwuthikul P., Effect of internal coagulant on effectiveness of polyvinylidene fluoride membrane for carbon dioxide separation and absorption, *J. Membr. Sci.* 311 (2008) 153–158
42. Pandey P., Chauhan R.S., Membranes for gas separation, *Prog. Poly. Sci.*, 26 (2006) 853

43. Ghosal K., Freeman B.D., Gas separation using polymer membranes: an overview, *Polym. Adv. Tech.*, 5 (1994) 673
44. Gorge S.C., Thomas S., Transport phenomena through polymeric systems, *Prog. Polym. Sci.*, 26 (2001), 985
45. Chern R.T., Koros W.J., Sanders E.S., Chen S.H., Hopfenberg H.B., Implications of the dual-model sorption and transport models for mixed gas permeation, *ACS Symp. Ser.*, 223 (1983).47
46. Paul D.R., Polymer topics- sorption and transport in glassy polymers, *Polym. Eng. Sci.*, 20 (1980) 14
47. Amerongen G.P.V., Swelling behaviour of rubbery materials *Rubber Chem. Tech.*, 37 (1964) 1065
48. Koros W.J., Chern R.T., *Handbook of Separation Process Technology*, R. W. Rousseau, Ed., John Wiley & Sons (1987).
49. Fleming G.K., Koros W.J., Dilation of polymers by sorption of carbon dioxide at elevated pressures. 1. Silicone rubber and unconditioned polycarbonate, *Macromolecules*, 19, (1986) 2285
50. Story B.J., Koros W.J., Sorption and transport of CO₂ and CH₄ in chemically modified poly(phenylene oxide), *J. Membr. Sci.*, 67 (1992) 191
51. Hensema E.R., Polymeric Gas Separation Membranes, *Adv. Mater.*, 6 (1994) 279
52. Vieth W.R., Howell J.M., Hsieh J.H., Dual sorption theory, *J. Membr. Sci.*, 1 (1976) 177
53. Koros W.J., Chern R.T., Stannett V.T., Hopfenberg H.B., A model for permeation of mixed gases and vapours in glassy polymers, *J. Polym. Sci.: Polym. Phys. Ed.*, 19 (1981) 1513
54. Petropoulos J.H., On the dual mode gas transport model for glassy polymers, *J. Polym. Sci. Polym. Phys. Ed.*, 26 (1988) 1009
55. Paul D.R., Koros W.J., Effect of partially immobilizing sorption on permeability and the diffusion time lag, *J. Polym. Sci., Polym. Phys. Ed.*, 14

- (1976) 675
56. Fujita H., The dependence of diffusivity on the polymer free volume, *Fortschr. Hochpolym. Forsch.*, 3 (1961) 1
 57. Lee W.M., Selection of barrier materials from molecular structure, *Polym. Eng. Sci.*, 20 (1980) 65
 58. Bondi A., Free Volumes and Free Rotation in Simple Liquids and Liquid Saturated Hydrocarbons, *J. Phys. Chem.*, 58 (1954) 929
 59. Krevele D.W., *Properties of Polymers*, 3rd ed., Elsevier, Amsterdam, 1990, pp. 72-76.
 60. Lee W.M., Selection of barrier materials from molecular structure, *Polym. Eng. Sci.*, 20 (1980) 65
 61. Chern R.T., Jia, L. Shimoda S., Hopfenberg H.B., A note on the effects of mono-and di-bromination on the transport properties of poly(2, 6-dimethylphenylene oxide), *J. Membr. Sci.*, 48 (1990) 333
 62. Stern S.A., Polymers for gas separations: the next decade, *J. Membr. Sci.*, 94 (1994) 1
 63. Robeson L.M., Correlation of separation factor versus permeability for polymeric membranes, *J. Membr. Sci.*, 62 (1991) 165
 64. Koros W.J., Hellums M.W., Husk G.R. J. Paul D.R., Gas transport in halogen-containing aromatic polycarbonates, *J. Appl. Polym. Sci.*, 43 (1991) 1977
 65. Kemp D.R., Paul D.R., Gas sorption in polymer membranes containing adsorptive fillers *J. Polym Sci. Polym Phys. Ed.*, 12 (1974) 485
 66. Kim T.H., Koros W.J., Husk G.R., O'Brien K.C., Relationship between gas separation properties and chemical structure in a series of aromatic polyimides, *J. Membr. Sci.*, 37 (1988) 45
 67. Mahajan R., Koros W.J., Mixed matrix membrane materials with glassy polymers. Part 1, *Polym. Eng. Sci.*, 42 (2002) 1420
 68. Mahajan R., Koros W.J., Mixed matrix membrane materials with glassy

- polymers. Part 2, Polym. Eng. Sci., 42 (2002) 1432
69. Pechar T.W., Kim S., Vaughan B., Marand E., Tsapatsis M., Jeong H.K., Cornelius C.J., Fabrication and characterization of polyimide–zeolite L mixed matrix membranes for gas separations, J. Membr. Sci., 277 (2006) 195
 70. Suer M.G., Ba N., Yilmaz L., Gas permeation characteristics of polymer-zeolite mixed matrix membranes, J. Membr. Sci., 91 (1994) 77
 71. Clarizia G., Algieri C., Drioli E., Filler-polymer combination: a route to modify gas transport properties of a polymeric membrane, Polymer 45 (2004) 5671
 72. Wang H.T., Holmberg B.A., Yan Y.S., Homogeneous polymer–zeolite nanocomposite membranes by incorporating dispersible template-removed zeolite nanocrystals, J. Mater. Chem., 12 (2002) 3640
 73. Li Y., Chung T.S., Cao C., Kulprathipanj S., The effects of polymer chain rigidification, zeolite pore size and pore blockage on polyethersulfone (PES)-zeolite A mixed matrix membranes, J. Membr. Sci., 260 (2005) 45
 74. Reid B.D., Ruiz-Trevino F.A., Musselman I.H., Balkus K.J., Ferraris J. P., Gas permeability properties of polysulfone membranes containing the mesoporous molecular sieve MCM-41, Chem. Mater., 13 (2001) 2366
 75. Kim S., Marand E., Ida J., Gulians V.G., Polysulfone and mesoporous molecular sieve MCM-48 mixed matrix membranes for gas separation, Chem. Mater., 18 (2006) 1149
 76. Park I., Peng H.G., Gidley D.W., Xue S.Q., Pinnavaia T.J., Epoxy–Silica mesocomposites with enhanced tensile properties and oxygen permeability, Chem. Mater., 18 (2006) 650
 77. Cong H.L., Zhang J.M., Radosz M., Shen Y.Q., Carbon nanotube composite membranes of brominated poly(2, 6-diphenyl-1, 4-phenylene oxide) for gas separation, J. Membr. Sci., 294 (2007) 178
 78. Kresge C.T., Leonowicz M.E., Roth W.J., Beck J.S., Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, Nature,

- 359 (1992) 710
79. Iijima S., Helical microtubules of graphitic carbon, *Nature*, 354 (1991) 56
 80. Merkel T.C., Freeman B.D., Spontak R.J., He Z., Pinnau I., Sorption, transport, and structural evidence for enhanced free volume in poly(4-methyl-2-pentyne)/fumed silica nanocomposite membranes, *Chem. Mater.*, 15 (2003) 109
 81. Merkel T.C., Freeman B.D., Spontak R.J., He Z., Pinnau I., Meakin P., Hill A. J., Ultrapervious, reverse-selective nanocomposite membranes, *Science*, 296 (2002) 519
 82. Cong H.L., Hu X.D., Radosz M., Shen Y.Q., Brominated poly(2, 6-diphenyl-1, 4-phenylene oxide) and its silica nanocomposite membranes for gas separation, *Ind. Eng. Chem. Res.*, 46 (2007) 2567
 83. Zhong S.H., Li C.F., Xiao X.F., Preparation and characterization of polyimide–silica hybrid membranes on kieselguhr–mullite supports, *J. Membr. Sci.*, 199 (2002) 53
 84. Gomes D., Nunes S.P., Peinemann K.V., Membranes for gas separation based on poly(1-trimethylsilyl-1-propyne)–silica nanocomposites, *J. Membr. Sci.*, 246 (2005) 13
 85. Moore T.T., Koros W.J., Non-ideal effects in organic-inorganic materials for gas separation membranes, *J. Mol. Struct.*, 739 (2005) 87
 86. Mahajan R., Burns R., Schaeffer M., Koros W.J., Challenges in forming successful mixed matrix membranes with rigid polymeric materials, *J. Appl. Polym. Sci.*, 86, (2002) 881
 87. Moore T.T., Mahajan R., Vu D., Koros W.J., Hybrid membrane materials comprising organic polymers with rigid dispersed phases, *AIChE J.* 50 (2004) 311
 88. Sullivan D.M., Bruening M.L., Ultrathin, gas-selective polyimide membranes prepared from multilayer polyelectrolyte films, *Chem. Mater.*, 15 (2003) 281
 89. Tamaki R., Chujo Y., Kuraoka K., Yazawa T., Application of

- organic-inorganic polymer hybrids as selective gas permeation membranes, *J. Mater. Chem.* 9, (1999) 1741
90. Grun M., Unger K., Matsumoto A., Tsutsumi K., Novel pathways for the preparations of mesoporous MCM-41 materials: control of porosity and morphology, *Microporous Mesoporous Mater.* 27 (1999) 207.
 91. Ash B.J., Siegel R.W., Schadler L.S.J., Glass-transition temperature behaviour of alumina/PMMA nanocomposites, *Polym. Sci., Part B: Polym. Phys.*, 42 (2004) 4371
 92. Chen Y., Iroh J.O., Synthesis and characterization of polyimide/silica hybrid composites, *Chem. Mater.*, 11 (1999) 1218
 93. Lua A.C., Su J.C., Effects of carbonisation on pore evolution and gas permeation properties of carbon membranes from Kapton polyimide, *Carbon*, 44 (2006) 2964
 94. Wang X.Y., Zhang L., Sun D.H., An Q.F., Chen H.L., Effect of coagulation bath temperature on formation mechanism of poly(vinylidene fluoride) membrane, *J. Appl. Polym. Sci.*, 110 (2008) 1656
 95. Feng C.S., Shi B.L., Li G.M., Wu Y.L., Preparation and properties of microporous membrane from poly(vinylidene fluoride-co-tetrafluoroethylene) (F2.4) for membrane distillation, *J. Membr. Sci.*, 237 (2004) 15
 96. Kawakami H., Nakajima K., Shimizu H., Nagaoka S., Gas permeation stability of asymmetric polyimide membrane with thin skin layer: effect of polyimide structure, *J. Membr. Sci.*, 212 (2003) 195
 97. Sroog, C.E., Polyimide, *Prog. Polym. Sci.*, 16 (1991) 561.
 98. Koops, G.H., Nolten, J.A.M., Mulder, M.H.V., Smolders, C.A., Selectivity as a function of membrane thickness-gas separation and pervaporation, *J. Appl. Polym. Sci.*, 53 (1994) 1639.
 99. Park J.Y., Paul D.R., Correlation and prediction of gas permeability in glassy polymer membrane materials via a modified free volume based group contribution method, *J. Membr. Sci.* 125 (1997) 23.

100. Bos A., Punt I., Wessling M., CO₂-induced plasticization phenomena in glassy polymers, *J. Membr. Sci.* 155 (1999) 67.
101. Bos A., Punt I., Strathmann H., Wessling M., Suppression of gas separation membrane plasticization by homogeneous polymer blending, *AIChE J.* 47 (2001) 1088.
102. Brown D., Marcadon V., Mele P., Alberola N.D., Effect of filler particle size on the properties of model nanocomposite, *Macromolecules*, 41 (2008) 1499.
103. Rittigstein P., Priestley R.D., Broadbelt L.J., Torkelson J.M., Model polymer nanocomposites provide an understanding of confinement effects in real nanocomposites, *Nature Mater.* 6 (2007) 278.
104. Bansal A., Yang H.C., Li C.Z., Cho K.W., Benicewicz B.C., Kumar S.K., Schadler L.S., Quantitative equivalence between polymer nanocomposites and thin polymer films, *Nature Mater.* 4 (2005) 693
105. Zhang M.Q.; Rong M.Z.; Zhang H.B.; Friedrich K., Mechanical properties of low nano-silica filled high density polyethylene composites, *Polym. Eng. Sci.*, 43 (2003) 490
106. Perez E. V.; Balkus K. J.; Ferraris J. P.; Musselman I. H. J., Mixed-matrix membranes containing MOF-5 for gas separations , *J. Membr. Sci.*, 328 (2009) 165
107. Jia X., Li Y.F.; Cheng Q.; Zhang S.J.; Zhang B., Preparation and properties of poly(vinyl alcohol)/silica nanocomposites derived from copolymerization of vinyl silica nanoparticles and vinyl acetate, *Eur. Polym. J.*, 43 (2007) 1123
108. Ash B. J.; Siegel R. W.; Schadler L. S., Glass-transition temperature behaviour of alumina/PMMA nanocomposites, *J. Polym. Sci., Part B: Polym. Phys.*, 42 (2004) 4371
109. Matteucci S.; Kusuma V. A.; Kelman S. D.; Freeman B. D., Gas transport properties of MgO filled poly (1-trimethylsilyl-1-propyne) nanocomposites, *Polymer*, 49 (2008) 1659
110. Maxwell J. C. *Treatise on Electricity and Magnetism*; Oxford University

- Press: London, 1873; Vol. 1
111. Bouma R.H.B., Checchetti A., Chidichimo G., Drioli E., Permeation through a heterogeneous membrane: The effect of the dispersed phase, *J. Membr. Sci.*, 128 (1997) 141
 112. Lee W.M., Selection of barrier materials from molecular-structure, *Polym. Eng. Sci.*, 20 (1980) 65
 113. Ahn J., Chung W.J., Pinnau I., Guiver M. D., Poly sulfone/silica nanoparticle mixed-matrix membranes for gas separation, *J. Membr. Sci.*, 314 (2008) 123
 114. Mascial L., Kioul A., Influence of siloxane composition and morphology on properties of polyimide-silica hybrids, *Polymer*, 36 (1995) 3649
 115. Morikawa A., Iyoku Y., Kakimoto M., Imai Y., Preparation of new polyimide-silica hybrid materials via the sol-gel process, *J. Mater. Chem.*, 2 (1992) 679
 116. Ahmad Z, Mark J.E., Polyimide-ceramic hybrid composites by the sol-gel route, *Chem. Mater.*, 13 (2001) 3320
 117. Agag T., Koga T., Tckeichi T., Study on thermal and mechanical properties of polyimide-clay nanocomposites, *Polymer*, 42 (2001) 3399
 118. Sakintuna B., Yurum Y., Preparation and characterization of mesoporous carbons using a Turkish natural zeolitic template/furfuryl alcohol system, *Microporous Mesoporous Mater.*, 93 (2006) 304
 119. Zarbin A.J.G., Bertholdo R., Oliveira M.A.F.C, Preparation, characterization and pyrolysis of poly(furfuryl alcohol)/porous silica glass nanocomposites: novel route to carbon template, *Carbon*, 40 (2002) 2413
 120. Barata-Rodrigues P.M., Mays T.J., Moggridge G.D., Structural carbon adsorbents form clay, zeolite and mesoporous aluminosilicate templates, *Carbon*, 41 (2003) 2231
 121. Zulfiqar S., Zulfiqar M., Rizvi M., Munir A., Mcneill I.C., Study of the thermal degradation of polychlorotrifluoroethylene, poly(vinylidene fluoride) and copolymers of chlorotrifluoroethylene and vinylidene fluoride, *Polym.*

- Degrad. Stabil., 43 (1994) 423.
122. Xu Y.S., Ray G., Magid B.A., Thermal behaviour of single-walled carbon nanotube polymer–matrix composites, *Composites: Part A* 37 (2006) 114
 123. Lund A., Hagstrom B., Melt Spinning of Poly(vinylidene fluoride) Fibres and the Influence of Spinning Parameters on b-Phase Crystallinity *J. Appl. Polym. Sci.*, 116 (2010) 2685
 124. Hasegawa, R., Takahashi, Y., Chatani, Y., Tadokoro, H., Crystal Structures of Three Crystalline Forms of Poly (vinylidene fluoride), *Polym. J.*, 3 (1972) 600
 125. Costa P., Silva J., Sencadas V., Costa C.M., van Hattum F.W.J., Rocha J.G., Lanceros-Mendez S., The effect of fibre concentration on the α to β phase transformation, degree of crystallinity and electrical properties of vapour grown carbon nanofibre/poly(vinylidene fluoride) composites, *Carbon*, 47 (2009) 2590
 126. Kim J.W., Cho W.J., Ha C.S., Morphology, Crystalline Structure, and Properties of Poly(vinylidene fluoride)/Silica Hybrid composites, *J. Polym. Sci.: Part B: Polym. Phys.*, 40 (2002) 19
 127. Vidhate S., Shaito A., Chung J., D’Souza N.A., Crystallization, Mechanical, and Rheological Behaviour of Polyvinylidene Fluoride/Carbon Nanofibre Composites, *J. Appl. Polym. Sci.*, 112 (2009) 254
 128. Song R., Yang D.B., He L.H., Effect of surface modification of nanosilica on crystallization, thermal and mechanical properties of poly(vinylidene fluoride), *J. Mater. Sci.*, 42 (2007) 8408
 129. Nakagawa K., Ishida Y., Estimation of amorphous specific volume of poly(vinylidene fluoride) as a function of temperature, *Kolloid-Z. u. Z. Polymere*, 251 (1973) 103
 130. Vu D.Q., Koros W.J., Miller S.J., Mixed matrix membranes using carbon molecular sieves II. Modelling permeation behaviour, *J. Membr. Sci.*, 211 (2003) 335

131. Petropoulos J.H., A Comparative Study of Approaches Applied to the Permeability of Binary Composite Polymeric Materials, *J. Poly. Sci. Poly. Phys.*, 23 (1985) 1309
132. Matteucci S., Kusuma V.A., Kelman S.D., Freeman B.D., Gas transport properties of MgO filled poly(1-trimethylsilyl-1-propyne) nanocomposites, *Polymer* 49 (2008) 1659
133. El-Hibri M.J., Paul D.R., Gas Transport in Poly(vinylidene Fluoride): Effects of Uniaxial Drawing and Processing Temperature, *J. Appl. Poly. Sci.*, 31 (1986) 2533
134. Loeb S., Sourirajan S., Sea water demineralization by means of an osmotic membrane, *Adv. Chem. Ser.* 38 (1962) 117.
135. Reuvers A.J., van den Berg J.W.A., Smolders C.A., Formation of membranes by means of immersion precipitation: Part I. A model to describe mass transfer during immersion precipitation, *J. Membr. Sci.*, 34 (1987) 45
136. Reuvers A.J., Smolders C.A., Formation of membranes by means of immersion precipitation: Part II. the mechanism of formation of membranes prepared from the system cellulose acetate-acetone-water, *J. Membr. Sci.*, 34 (1987) 67
137. Yilmaz L., McHugh A.J., Analysis of nonsolvent–solvent–polymer phase diagrams and their relevance to membrane formation modelling, *J. Appl. Polym. Sci.*, 31 (1986) 997
138. Mikawa M., Seki N., Nagaoka S., Kawakami H., Structural and gas permeability of asymmetric polyimide membranes made by dry-wet phase inversion: Influence of alcohol as casting solution, *J. Polym. Sci.: Polym. Phys.*, 45(2007) 2739
139. Barton A.F.M., Solubility parameters, *Chem. Rev.*, 75 (1975) 731
140. Matsuu T., Synthetic membranes and membrane separation processes, CRC Press, Boca Raton, 1994.
141. Shimizu H., Kawakami H., Nagaoka S., Membrane formation mechanism

- and permeation properties of a novel porous polyimide membrane, *Polym. Adv. Tech.*, 13 (2002) 370
142. Van't Hof J.A., Reuvers A.J., Boom R.M., Rolevink H.H.M., Smolders C. A., Preparation of asymmetric gas separation membranes with high selectivity by a dual-bath coagulation method, *J. Membr. Sci.*, 70 (1992) 17
143. Kim H.J., Tyagi R.K., Fouda A.E., Jonasson K., The kinetic study for asymmetric membrane formation via phase-inversion process, *J. Appl. Polym. Sci.*, 62 (1996) 621
144. Smolders C.A., Reuvers A.J., Boom R.M., Wienk I.M., Microstructures in phase-inversion membranes. Part 1. Formation of macrovoids, *J. Membr. Sci.*, 73 (1992) 259
145. Kawakami H., Mikawa M., Nagaoka S., Formation of surface skin layer of asymmetric polyimide membranes and their gas transport properties, *J. Membr. Sci.*, 137 (1997) 241
146. Vandezande P., Li X.F., Gevers L.E.M., Vankelecom I.F.J., High throughput study of phase inversion parameters for polyimide-based SRNF membranes, *J. Membr. Sci.*, 330 (2009) 307
147. Kawakami H., Mikawa M., Nagaoka S., Gas Transport properties of asymmetric polyimide membrane with an ultrathin surface skin layer, *Macromolecules* 31 (1998) 6636
148. Ruthven D., Derrah R., Diffusion of Monatomic and Diatomic Gases in 4A and 5A, *J. Chem. Soc., Faraday Trans.* 71 (1975) 2031

Appendix I

The gas transport through MCM-41 particles is based on Knudsen diffusion and the corresponding permeability is given by Equation (A1.1). The permeabilities of He, CO₂, O₂ and N₂ for the mesoporous MCM-41 particles are founded to be 1.51×10^6 , 3.2×10^5 , 3.8×10^5 and 4.0×10^5 Barrer at 298 K, respectively.

$$P = 97 \left(\frac{r\varepsilon}{\tau} \right) \frac{1}{R\sqrt{TM}} \left(\text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1} \right) \quad (\text{A1.1})$$

where r is the mean pore radius (m), ε is the porosity, τ is the tortuosity, R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature and M is the molecular weight. The r and ε/τ values are 2.7 nm and 0.59, respectively.

The diffusion coefficients of CO₂, O₂ and N₂ through zeolite 4A are calculated to be 8.7×10^{-10} , 3.2×10^{-9} and 3.3×10^{-11} cm²/s at 298 K, respectively, using the Arrhenius formula

$$D_i = D_0 \exp \left(-\frac{E_d}{RT} \right) \quad (\text{A1.2})$$

where pre-exponential factor D_0 and activated energy E_d values are reported by Ruthren and Derrah [148].

The solubility coefficients of CO₂, O₂ and N₂ in zeolite 4A at 308 K are 2.97×10^{-1} , 1.78×10^{-3} and 3.88×10^{-3} mol Pa⁻¹ m⁻³, respectively, as reported by Ruthren and Derrah [148]. The data are adjusted to 298 K using the Arrhenius formula, which are 5.38×10^{-1} , 2.12×10^{-3} and 4.91×10^{-3} mol Pa⁻¹ m⁻³, for CO₂, O₂ and N₂, respectively.

$$S_i = S_0 \exp \left(-\frac{H_s}{RT} \right) \quad (\text{A1.3})$$

The permeability coefficients of CO₂, O₂ and N₂ in zeolite 4A are obtained as the product of the solubility coefficient and the diffusion coefficients at 298 K, which

was 139.5, 2.0 and 0.048 Barrer, respectively.

Due to a lack of He diffusion and sorption data in zeolite 4A, the He permeability of zeolite 4A is estimated to be 1255.5 Barrer in accordance to the selectivity of He/CO₂ for the zeolite 4A membranes.

Appendix II

This appendix presents the details of the experimental procedures for the gas permeation test and the calculations of the permeability coefficient based on the test. The original permeation data sheets for the sample P84/SiO₂ MMMs mentioned in Chapter 5 were included as an example to illustrate the calculations.

In general, the gas permeation test can be divided two parts including the leakage rate test and the gas permeation test. For all the samples, the leakage rates were determined and compared with the gas permeation rates to ensure the valid of the permeability results. The original data sheets were shown in Fig. A2.1 and the variations of pressure as a function of time were shown in Fig. A2.2. Here the calculation of O₂ permeability coefficient was shown as follows. The calculation of permeability coefficient P was based on the following equation

$$P = \frac{VL}{ART\Delta P} \frac{dp}{dt} \quad (\text{A2.1})$$

Where V is the constant volume of the downstream, A is the effective membrane area, L is the membrane thickness, R is the universal gas constant, T is the absolute temperature, and ΔP is the pressure drop between the upstream and downstream. dp/dt is the pressure change rate of the downstream. For the calculation of the O₂ permeability of P84/SiO₂ composite membrane, $V=500 \text{ cm}^3$ (constant); $A=2.27 \text{ cm}^2$; $R=8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$; $T=299.25 \text{ K}$; $\Delta P=4 \times 101325 \text{ Pa}$; $L=32 \times 10^{-4} \text{ cm}$ and $dp/dt = 1.27 \times 10^{-3} \text{ Torr/min}$. The permeability of O₂ for the P84/SiO₂ membrane was calculated to be 0.59 Barrer.

Data 16 Feb 2018
 Sample P10000, Grm No. T=21.1°C
 System vacuum 1.2x10⁻⁴ Torr Oxygen overnight

Leakage test			Sample test		
Time (min)	Pressure (D)	Pressure (R)	Time (min)	Pressure (D)	Pressure (R)
0	2.162 Torr	2.948 Torr	9.5	2.075	2.941 Torr
6	2.163	"	10	2.076	"
16	2.165	"	18	2.077	"
20	2.165	"	100	2.078	"
27	2.166	"	101	2.078	"
25	2.167	"	104	2.080	"
28	2.168	"	105	2.081	"
31	2.167	"	113	2.082	"
38	2.170	"	118	2.082	2.870
42	2.171	"	123	2.084	"
			124	2.085	2.872
			126	2.086	"
			127	2.088	"
			128	2.089	"
			129	2.091	"
			130	2.092	"
			131	2.093	"
			132	2.094	"
			133	2.095	2.879
			136	2.095	2.870
			137	2.096	"
			138	2.096	"

Step 1: 2.1x10⁻⁴ Torr/min
 Step 2: 1.2x10⁻⁴ Torr/min

Data 18 Feb 2018
 Sample P10000, Grm No. T=21.5°C
 System vacuum 1.2x10⁻⁴ Torr Oxygen overnight

Leakage test			Sample test		
Time (min)	Pressure (D)	Pressure (R)	Time (min)	Pressure (D)	Pressure (R)
0	2.077 Torr	2.938 Torr	82	2.085	2.895 V
5	2.078	"	83	2.086	"
12	2.075	"	89	2.087	"
17	2.076	"	91	2.088	"
125	2.077	"	109	2.090	"
121	2.078	"	110	2.091	"
127	2.077	"	113	2.092	2.893 V
128	2.078	"	116	2.092	2.892 V
129	2.081	"	117	2.093	"
137	2.082	"	120	2.094	"
			125	2.095	"
			126	2.097	2.892 V
			128	2.097	"
			129	2.099	"
			130	2.095	2.894 V
			131	2.096	"
			135	2.095	"
			137	2.093	"
			138	2.093	"
			139	2.095	"
			147	2.094	"

Step 1: 2.1x10⁻⁴ Torr/min
 Step 2: 1.2x10⁻⁴ Torr/min

Data 21 Feb 2018
 Sample P10000, Grm No. T=21.3°C
 System vacuum 1.2x10⁻⁴ Torr Oxygen overnight

Leakage test			Sample test		
Time (min)	Pressure (D)	Pressure (R)	Time (min)	Pressure (D)	Pressure (R)
0	2.116	2.906	174	2.086	2.877 V
6	2.117	"	176	2.087	"
16	2.118	"	185	2.088	"
26	2.119	"	194	2.088	2.876
25	2.120	2.908	203	2.089	"
25	2.121	"	209	2.090	"
25	2.122	"	214	2.091	"
26	2.123	"	219	2.092	"
26	2.124	"	225	2.093	"
27	2.125	"	250	2.094	"
27	2.126	"	258	2.095	"
28	2.127	"	260	2.096	"
28	2.127	"	270	2.098	"
29	2.128	"	270	2.097	"
29	2.128	2.912	280	2.097	2.875
29	2.128	"	285	2.098	"
			291	2.097	"
			296	2.097	"
			301	2.098	"
			307	2.098	"

Step 1: 9.5x10⁻⁵ Torr/min
 Step 2: 1.2x10⁻⁴ Torr/min

Data 23 Feb 2018
 Sample P10000, Grm No. T=21.6°C
 System vacuum 1.2x10⁻⁴ Torr Oxygen overnight

Leakage test			Sample test		
Time (min)	Pressure (D)	Pressure (R)	Time (min)	Pressure (D)	Pressure (R)
0	2.116 Torr	2.906 Torr	26	2.092 Torr	2.874 V
2	2.117	"	27	2.093	2.874 V
17	2.118	"	28	2.094	2.874 V
28	2.119	"	29	2.095	2.874 V
32	2.120	"	31	2.096	2.874 V
40	2.121	"	32	2.097	"
			33	2.098	2.874 V
			34	2.099	2.874 V
			35	2.100	2.874 V
			36	2.101	2.874 V
			37	2.102	2.874 V
			38	2.103	2.874 V
			39	2.104	2.874 V
			40	2.105	2.874 V
			41	2.106	2.874 V
			42	2.107	2.874 V
			43	2.108	2.874 V
			44	2.109	2.874 V
			45	2.110	2.874 V
			46	2.111	2.874 V
			47	2.112	2.874 V
			48	2.113	2.874 V
			49	2.114	2.874 V
			50	2.115	2.874 V
			51	2.116	2.874 V
			52	2.117	2.874 V
			53	2.118	2.874 V
			54	2.119	2.874 V
			55	2.120	2.874 V
			56	2.121	2.874 V
			57	2.122	2.874 V
			58	2.123	2.874 V
			59	2.124	2.874 V
			60	2.125	2.874 V
			61	2.126	2.874 V
			62	2.127	2.874 V
			63	2.128	2.874 V
			64	2.129	2.874 V
			65	2.130	2.874 V
			66	2.131	2.874 V
			67	2.132	2.874 V
			68	2.133	2.874 V
			69	2.134	2.874 V
			70	2.135	2.874 V
			71	2.136	2.874 V
			72	2.137	2.874 V
			73	2.138	2.874 V
			74	2.139	2.874 V
			75	2.140	2.874 V
			76	2.141	2.874 V
			77	2.142	2.874 V
			78	2.143	2.874 V
			79	2.144	2.874 V
			80	2.145	2.874 V
			81	2.146	2.874 V
			82	2.147	2.874 V
			83	2.148	2.874 V
			84	2.149	2.874 V
			85	2.150	2.874 V
			86	2.151	2.874 V
			87	2.152	2.874 V
			88	2.153	2.874 V
			89	2.154	2.874 V
			90	2.155	2.874 V
			91	2.156	2.874 V
			92	2.157	2.874 V
			93	2.158	2.874 V
			94	2.159	2.874 V
			95	2.160	2.874 V
			96	2.161	2.874 V
			97	2.162	2.874 V
			98	2.163	2.874 V
			99	2.164	2.874 V
			100	2.165	2.874 V
			101	2.166	2.874 V
			102	2.167	2.874 V
			103	2.168	2.874 V
			104	2.169	2.874 V
			105	2.170	2.874 V
			106	2.171	2.874 V
			107	2.172	2.874 V
			108	2.173	2.874 V
			109	2.174	2.874 V
			110	2.175	2.874 V
			111	2.176	2.874 V
			112	2.177	2.874 V
			113	2.178	2.874 V
			114	2.179	2.874 V
			115	2.180	2.874 V
			116	2.181	2.874 V
			117	2.182	2.874 V
			118	2.183	2.874 V
			119	2.184	2.874 V
			120	2.185	2.874 V
			121	2.186	2.874 V
			122	2.187	2.874 V
			123	2.188	2.874 V
			124	2.189	2.874 V
			125	2.190	2.874 V
			126	2.191	2.874 V
			127	2.192	2.874 V
			128	2.193	2.874 V
			129	2.194	2.874 V
			130	2.195	2.874 V
			131	2.196	2.874 V
			132	2.197	2.874 V
			133	2.198	2.874 V
			134	2.199	2.874 V
			135	2.200	2.874 V
			136	2.201	2.874 V
			137	2.202	2.874 V
			138	2.203	2.874 V
			139	2.204	2.874 V
			140	2.205	2.874 V
			141	2.206	2.874 V
			142	2.207	2.874 V
			143	2.208	2.874 V
			144	2.209	2.874 V
			145	2.210	2.874 V
			146	2.211	2.874 V
			147	2.212	2.874 V
			148	2.213	2.874 V
			149	2.214	2.874 V
			150	2.215	2.874 V
			151	2.216	2.874 V
			152	2.217	2.874 V
			153	2.218	2.874 V
			154	2.219	2.874 V
			155	2.220	2.874 V
			156	2.221	2.874 V
			157	2.222	2.874 V
			158	2.223	2.874 V
			159	2.224	2.874 V
			160	2.225	2.874 V
			161	2.226	2.874 V
			162	2.227	2.874 V
			163	2.228	2.874 V
			164	2.229	2.874 V
			165	2.230	2.874 V
			166	2.231	2.874 V
			167	2.232	2.874 V
			168	2.233	2.874 V
			169	2.234	2.874 V
			170	2.235	2.874 V
			171	2.236	2.874 V
			172	2.237	2.874 V
			173	2.238	2.874 V
			174	2.239	2.874 V
			175	2.240	2.874 V
			176	2.241	2.874 V
			177	2.242	2.874 V
			178	2.243	2.874 V
			179	2.244	2.874 V
			180	2.245	2.874 V
			181	2.246	2.874 V
			182	2.247	2.874 V
			183	2.248	2.874 V
			184	2.249	2.874 V
			185	2.250	2.874 V
			186	2.251	2.874 V
			187	2.252	2.874 V
			188	2.253	2.874 V
			189	2.254	2.874 V
			190	2.255	2.874 V
			191	2.256	2.874 V
			192	2.257	2.874 V
			193	2.258	2.874 V
			194	2.259	2.874 V
			195	2.260	2.874 V
			196	2.261	2.874 V
			197	2.262	2.874 V
			198	2.263	2.874 V
			199	2.264	2.874 V
			200	2.265	2.874 V
			201	2.266	2.874 V
			202	2.267	2.874 V
			203	2.268	2.874 V
			204	2.269	2.874 V
			205	2.270	2.874 V
			206	2.271	2.874 V
			207	2.272	2.874 V
			208	2.273	2.874 V
			209	2.274	2.874 V
			210	2.275	2.874 V

Fig. A2.2 Variation of pressures as a function of time

Appendix III

The GC calibration graphs are shown as follows:

Fig. A3.1 GC calibration graphs for the measurements of the concentrations of the nonsolvent

Appendix IV

Publications arising from this research

- 1) Effects of membrane thickness and heat treatment on the gas transport properties of membranes based on P84 polyimide, Yi Shen; Aik Chong Lua, Journal of Applied Polymer Science, 116 (2010) 2906-2912
- 2) Influence of inorganic fillers on the structural and transport properties of mixed matrix membranes, Aik Chong Lua and Yi Shen, Submitted to Journal of Applied Polymer Science, under revision.
- 3) Structural and transport properties of BTDA-TDI/MDI co-polyimide (P84)-silica nanocomposite membranes for gas separation, Yi Shen and Aik Chong Lua, Chemical Engineering Journal, accepted.
- 4) Preparation and characterization of mixed matrix membranes based on PVDF and zeolite 4A for gas separation, Yi Shen and Aik Chong Lua, Submitted to Polymer Engineering and Science, accepted.
- 5) Preparation and characterization of polyimide-silica composite membranes and their derived carbon composite membranes for gas separation, Yi Shen and Aik Chong Lua, Submitted to Journal of Membrane Science, under review.
- 6) Preparation and characterization of asymmetric membranes based on nonsolvent/NMP/P84 for water treatment and gas separation, Yi Shen and Aik Chong Lua, under preparation.
- 7) Theoretical and experimental studies on the gas transport properties of mixed matrix membranes based on PVDF, Yi Shen and Aik Chong Lua, submitted to

AICHE, under revision

- 8) Preparation and characterization of mixed matrix membranes based on PVDF and three inorganic fillers (fumed nonporous silica, zeolite 4A and mesoporous MCM-41) for gas separation, Yi Shen and Aik Chong Lua, submitted to Chemical Engineering Journal, under review.