

NATURAL GAS PURIFICATION BY ZEOLITE FILLED
POLYETHERSULFONE BASED MIXED MATRIX MEMBRANES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ÜLGEN ÇAKAL

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

OCTOBER 2009

Approval of the thesis:

**NATURAL GAS PURIFICATION BY ZEOLITE FILLED
POLYETHERSULFONE BASED MIXED MATRIX MEMBRANES**

submitted by **ÜLGEN ÇAKAL** in partial fulfillment of the requirements for the degree of **Master of Science in Chemical Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Gürkan Karakaş
Head of Department, **Chemical Engineering**

Prof. Dr. Levent Yılmaz
Supervisor, **Chemical Engineering Dept., METU**

Assoc. Prof. Dr. Halil Kalıpçılar
Co-supervisor, **Chemical Engineering Dept., METU**

Examining Committee Members:

Prof. Dr. Hayrettin Yücel
Chemical Engineering Dept., METU

Prof. Dr. Levent Yılmaz
Chemical Engineering Dept., METU

Prof. Dr. Birgül Tantekin Ersolmaz
Chemical Engineering Dept., ITU

Assoc. Prof. Dr. Göknur Bayram
Chemical Engineering Dept., METU

Assoc. Prof. Dr. Halil Kalıpçılar
Chemical Engineering Dept., METU

Date: 23.09.2009

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Ülgen Çakal

Signature :

ABSTRACT

NATURAL GAS PURIFICATION BY ZEOLITE FILLED POLYETHERSULFONE BASED MIXED MATRIX MEMBRANES

Çakal, Ülgen

M.Sc., Department of Chemical Engineering

Supervisor : Prof. Dr. Levent YILMAZ

Co-supervisor : Assoc. Prof. Dr. Halil KALIPÇILAR

October 2009, 90 pages

This research investigates the effect of feed composition on the separation performance of pure polyethersulfone (PES) and different types of PES based mixed matrix membranes (MMMs) in order to develop high performing membranes for CO₂/CH₄ separation. MMMs were prepared by solvent evaporation method using PES as the polymer matrix with SAPO-34 particles as fillers, and 2-hydroxy 5-methyl aniline (HMA) as the low molecular weight additive. Four types of membranes were used throughout the study, namely pure PES membrane, PES/HMA (4, 10%w/w) membrane, PES/SAPO-34 (20%w/w) MMM, PES/SAPO-34 (20%w/w)/HMA (4, 10%w/w) MMM. The effect of CO₂ composition on the performance of the membranes was investigated in detail with a wide feed composition range changing between 0 and 100%. In addition to separating CO₂/CH₄ binary gas mixtures, the separation performances of these membranes were determined by measuring single gas permeabilities at 35°C, with a feed pressure of 3 bar. Moreover, the membranes were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and thermal gravimetric analyzer (TGA).

The separation selectivities of all types of membranes generally observed to be independent of feed composition. The composition independency of these membranes

eliminates the need of investigating at which feed gas composition the prepared membranes are best performing for practical applications. PES/SAPO-34/HMA MMMs with HMA loading of 10% and SAPO-34 loading of 20% demonstrated the highest separation selectivity of about 40, and the ideal selectivity of 44, among the used membranes.

Keywords: Mixed Matrix Membrane, CO₂/CH₄ Separation, Binary Gas Mixtures, Polyethersulfone, SAPO-34.

ÖZ

ZEOLİT KATKILI POLİETERSÜLFON KARIŞIK MATRİSLİ MEMBRANLAR İLE DOĞAL GAZIN SAFLAŞTIRILMASI

Çakal, Ülgen

Yüksek Lisans, Kimya Mühendisliği Bölümü

Tez Yöneticisi : Prof. Dr. Levent Yılmaz

Ortak Tez Yöneticisi : Doç. Dr. Halil Kalıpçılar

Ekim 2009, 90 sayfa

Bu çalışmada besleme kompozisyonunun saf polietersulfon (PES) ve farklı türde katkı PES karışık matrisli membranlarının performansına olan etkisi incelenmiştir. Böylece, CO₂/CH₄ ayırımında kullanılacak performansı yüksek membranların geliştirilmesi amaçlanmıştır. Karışık matrisli membranlar, çözücü buharlaştırma yöntemiyle, polimer matrisi olarak PES, dolgu maddesi olarak SAPO-34 tanecikleri ve düşük molekül ağırlıklı katkı maddesi olarak 2-hidroksi 5-metil aniline (HMA) kullanılarak hazırlanmıştır. Tüm çalışma boyunca, sırasıyla saf PES membran, PES/HMA (4, 10% w/w) membran, PES/SAPO-34 (20% w/w) MMM, PES/SAPO-34 (20% w/w)/HMA (4, 10% w/w) MMM olmak üzere dört farklı türde membran kullanılmıştır. Besleme kompozisyonunun membranların performansına olan etkisi, 0 ile 100% CO₂ arasında değişen geniş bir kompozisyon aralığında ayrıntılı olarak incelenmiştir. CO₂/CH₄ karışımlarının yanı sıra, membranların tek gaz geçirgenlik performansları da 35°C ve 3 bar besleme basıncı koşullarında incelenmiştir. Membranlar, ayrıca, taramalı elektron mikroskobu (SEM), diferansiyel taramalı kalorimetre (DSC), ve termal gravimetrik analiz (TGA) cihazı ile karakterize edilmiştir.

Farklı besleme gaz kompozisyonlarının kullanılan farklı türdeki membranların ayırım performansını etkilemediği gözlenmiştir. Bu tip membranların ayırım performansının gaz kompozisyonundan etkilenmemesi, özellikle ticari uygulamalarda kullanılacak membranların gaz kompozisyonu bağımlılığının incelenmesi gerekliliğini de ortadan kaldırmaktadır. PES/SAPO-34 (20%)/HMA (10%) membranı, 40 civarındaki ayırım seçicilik değeri ve 44 olan ideal seçicilik değeri ile kullanılan membranlar arasında en yüksek performansı göstermiştir.

Anahtar Kelimeler: Karışık Matrisli Membran, CO₂/CH₄ Ayırımı, İkili Gaz Karışımları, Polietersülfon, SAPO-34.

To My Family

ACKNOWLEDGEMENTS

I would first and foremost like to thank my supervisor, Prof. Dr. Levent Yılmaz, and my co-supervisor Assoc. Prof. Dr. Halil Kalıpçılar for all of their support, guidance and encouragement that they have given me during this study. I have learned so much about research and life under their tutelage.

I would also like to convey my gratitude to Prof. Dr. Birgül Tantekin Ersolmaz for willing to be my reference and encouraging me for a graduate education, and helped to get me started in the right direction. I also thank to the colleagues at Chemical Engineering Department in ITU. They provided the results of IGA analysis.

I would like to thank thermal analysis specialist Mihrican Açıkgöz for her helps in differential scanning calorimetric and thermal gravimetric analysis. I would like to thank Central Laboratory specialists for their helps in Scanning Electron Microscopic analysis. I am also thankful to Machine Shop and all staff of Department of Chemical Engineering for their helps throughout the study.

I also gratefully acknowledge the financial support provided by the Scientific and Technological Research Council of Turkey (TUBITAK) as a graduate scholarship. This research was partially supported by METU Research Fund (Grant No: BAP-07-02-2009-00-01) and TUBITAK Research Fund (Grant No: 106M179).

I would like to thank to the colleagues in my lab, for their patience and friendship; especially, to Ceyda for not only her advice, and support as a colleague but also being a great friend during my stay in Ankara.

Finally, I thank my mother and sister for inspiring me with the greatest motivation to learn and unceasing love and support throughout my childhood and academic career.

TABLE OF CONTENTS

ABSTRACT.....	iv
ÖZ	vi
ACKNOWLEDGEMENTS	ix
TABLE OF CONTENTS.....	x
LIST OF TABLES	xii
LIST OF FIGURES	xiv
LIST OF SYMBOLS	xvi
CHAPTER	
1. INTRODUCTION	1
2. LITERATURE SURVEY	4
2.1 Gas Separation Membranes	4
2.2 Mixed Matrix Membranes	7
2.3 Separation of Binary Gas Mixtures	12
2.3.1 Mixed and Pure Gas Permeation Variation for Polymeric Membranes	12
2.3.2 Mixed and Pure Gas Permeation Variation for MMMs	16
3. EXPERIMENTAL.....	21
3.1 Membrane Preparation Materials	21
3.2 Membrane Preparation Methodology	21
3.3 Membrane Characterization.....	24
3.4 Gas Permeability Measurements	24
3.4.1 Experimental Set-up	24
3.4.2 Experimental Procedure	25
3.4.3 Permeability and Selectivity Calculations	28
4. RESULTS AND DISCUSSION	29
4.1 Material Selection.....	29
4.1.1 Polymer Selection.....	29
4.1.2 Filler Selection.....	29
4.1.3 LMWA Selection.....	31
4.2 Membrane Characterization.....	31

4.2.1 DSC Results.....	31
4.2.2 TGA Results	34
4.2.3 SEM Results	35
4.3 Single Gas Permeation Results.....	40
4.4 Binary Gas Permeation Results	43
4.4.1 Binary Gas Permeation Results of Dense Homogenous PES Membranes	45
4.4.2 Binary Gas Permeation Results of PES/HMA Membranes.....	46
4.4.3 Binary Gas Permeation Results of PES/SAPO-34 MMMs	49
4.4.4 Binary Gas Permeation Results of PES/SAPO-34/HMA MMMs.....	52
4.4.5 General Performance Comparison of Membranes	55
4. CONCLUSIONS	56
REFERENCES	57
APPENDICES	67
A. CALIBRATION OF GC.....	67
B. CALCULATION OF SINGLE GAS PERMEABILITIES.....	69
C. SAMPLE CALCULATION FOR THE DETERMINATION OF PERMEABILITY- ES AND SELECTIVITIES OF BINARY GAS MIXTURES OF CO ₂ /CH ₄	71
C.1 Feed side analysis	71
C.2 Permeate side analysis	72
C.3 Permeability Calculation of CO ₂ -CH ₄ binary gas mixture.....	73
C.4 Evaluation of the selectivity and permeability using CH ₄ and CO ₂ composi- tion based method.....	75
C.4.1 CH ₄ composition based.....	76
C.4.2 CO ₂ composition based.....	77
C.4.3 Separation Selectivities.....	77
D. SAMPLE DSC THERMOGRAMS OF THE PREPARED MEMBRANES	79
E. SAMPLE TGA THERMOGRAMS OF THE PREPARED MEMBRANES	82
F. REPRODUCIBILITY EXPERIMENTS FOR SINGLE GAS PERMEATION ...	85
G. THE COMPOSITIONS AND SEPARATION SELECTIVITIES OF USED MEM- BRANES.....	87

LIST OF TABLES

TABLES

Table 2.1 Single gas permeabilities and ideal selectivities of glassy polymer MMMs	9
Table 4.1 Glass transition temperatures of different type of membranes used in this work	33
Table 4.2 the weight losses of different type of membranes used in this work	34
Table 4.3 Single gas permeability and ideal selectivity results of PES, PES/HMA, PES/SAPO-34, and PES/SAPO-34/HMA MMMs	41
Table 4.4 Effect of feed composition on permeabilities and selectivities of CO ₂ /CH ₄ binary gas mixture through pure PES membrane (measured at 35°C, with a pressure difference of 3.0 bar).....	47
Table 4.5 Effect of feed composition on permeabilities and selectivities of CO ₂ /CH ₄ binary gas mixture through PES/HMA(4%) membrane (measured at 35°C, with a pressure difference of 3.0 bar)	47
Table 4.6 Effect of feed composition on permeabilities and selectivities of CO ₂ /CH ₄ binary gas mixture through PES/SAPO-34(20%) MMM (measured at 35°C, with a pressure difference of 3.0 bar)	50
Table 4.7 Effect of feed composition on permeabilities and selectivities of CO ₂ /CH ₄ binary gas mixture through PES/SAPO-34(20%)/HMA(4%) MMM (measured at 35°C, with a pressure difference of 3.0 bar)	53
Table 4.8 Effect of feed composition on permeabilities and selectivities of CO ₂ /CH ₄ binary gas mixture through PES/SAPO-34(20%)/HMA(10%) MMM (measured at 35°C, with a pressure difference of 3.0 bar)	53
Table C.1 The results for feed side	72
Table C.2 The results for permeate side	73
Table C.3 Feed and permeate side compositions for constant CH ₄ composition	76
Table C.4 Feed and permeate side compositions for constant CO ₂ composition	77
Table C.5 Feed and permeate side compositions and separation selectivities calculated using compositions.....	78

Table C.6 Permeabilities of the gases and separation selectivities calculated using these permeabilities.....	78
Table F.1 Reproducibility data for pure PES membrane	85
Table F.2 Reproducibility data for PES/HMA membrane.....	85
Table F.3 Reproducibility data for PES/SAPO-34 MMM.....	86
Table F.4 Reproducibility data for PES/SAPO-34/HMA MMM	86
Table G.1 Feed and permeate side compositions and separation selectivities of pure PES membrane.....	88
Table G.2 Feed and permeate side compositions and separation selectivities of PES/HMA (4%) membrane.....	88
Table G.3 Feed and permeate side compositions and separation selectivities of PES/SAPO-34 (20%) MMM	89
Table G.4 Feed and permeate side compositions and separation selectivities of PES/SAPO-34 (20%) HMA (4%) MMM.....	89
Table G.5 Feed and permeate side compositions and separation selectivities of PES/SAPO-34 (20%) HMA (10%) MMM.....	90

LIST OF FIGURES

FIGURES

Figure 2.1 Polymer specific volume as a function of temperature	6
Figure 2.2 Upper-bound trade-off curves of various glassy and rubbery polymeric membranes for CO ₂ /CH ₄	8
Figure 3.1 The repeating unit of PES (a), and the chemical structure of HMA (b)	22
Figure 3.2 Flowchart of the preparation methodology of PES/HMA/SAPO-34 MMM..	23
Figure 3.3 Schematic representation of the gas permeation set-up.....	26
Figure 4.1 Adsorption isotherms for CO ₂ and CH ₄ at 35°C on SAPO-34 powder	30
Figure 4.2 Adsorption isotherms for CO ₂ and CH ₄ at room temperature for pure PES membrane.....	32
Figure 4.3 Adsorption isotherms for CO ₂ and CH ₄ at room temperature for PES/SAPO-34 (20%) MMM.....	32
Figure 4.4 TGA graph of HMA	36
Figure 4.5 TGA graph of PES/SAPO-34(20%) MMM	36
Figure 4.6 SEM images of the cross-section of pure PES (a, b), PES/HMA (4%) (c), and PES/HMA (10%) (d) membranes, respectively	37
Figure 4.7 SEM images of cross-section at low magnification (a, and c), and cross-section at high magnification (b, d, e, and f) of PES/SAPO-34 (20%) MMMs.....	38
Figure 4.8 SEM images of cross-section at low magnification (a, and c), and cross-section at high magnification (b, and d) of PES/SAPO-34/HMA MMMs at constant SAPO-34 loading of 20%, and HMA loading of 4% and 10%, respectively	39
Figure 4.9 H ₂ /CH ₄ selectivity and H ₂ permeability of used membranes on a Robeson's upper bound trade-off curve.....	43
Figure 4.10 Effect of feed composition on permeability and selectivity for CO ₂ /CH ₄ binary gas mixture through PES membrane (a), and PES/HMA membrane (b).....	48
Figure 4.11 Effect of feed composition on the separation selectivity of CO ₂ /CH ₄ through PES/SAPO-34(20%) MMMs.....	50

Figure 4.12 Effect of feed composition on permeability and selectivity for CO ₂ /CH ₄ binary gas mixture through PES/SAPO-34 (20%)/HMA (4%) MMM (a), and PES/SAPO-34 (20%)/HMA (10%) MMM (b).....	54
Figure A.1 Calibration plot of CO ₂ for GC analysis.....	68
Figure A.2 Calibration plot of CH ₄ for GC analysis.....	68
Figure B.1 Algorithm for single gas permeability calculation.....	70
Figure C.1 Pressure difference vs. time graph for CO ₂ -CH ₄ binary gas mixture through PES/ SAPO-34 (20%)/HMA (10%) MMM.....	74
Figure D.1 The DSC graph of pure PES membrane (2 nd scan).....	79
Figure D.2 The DSC graph of PES/HMA (4%) membrane (2 nd scan).....	79
Figure D.3 The DSC graph of PES/HMA (10%) membrane (2 nd scan).....	80
Figure D.4 The DSC graph of PES/SAPO-34 (20%) MMM (2 nd scan).....	80
Figure D.5 The DSC graph of PES/SAPO-34 (20%)/HMA (4%) MMM (2 nd scan).....	81
Figure D.6 The DSC graph of PES/SAPO-34 (20%)/HMA (10%) MMM (2 nd scan).....	81
Figure E.1 The TGA graph of pure PES membrane.....	82
Figure E.2 The TGA graph of PES/HMA (4%) membrane.....	82
Figure E.3 The TGA graph of PES/HMA (10%) membrane.....	83
Figure E.4 The TGA graph of PES/SAPO-34 (20%) MMM.....	83
Figure E.5 The TGA graph of PES/SAPO-34 (20%)/HMA (4%) MMM.....	84
Figure E.6 The TGA graph of PES/SAPO-34 (20%)/HMA (10%) MMM.....	84

LIST OF SYMBOLS

D	: Diffusion coefficient
N	: Flux ($\text{cm}^3/\text{cm}^2.\text{s}$)
P	: Permeability (Barrer)
R	: Ideal gas constant
S	: Solubility coefficient
T	: Temperature ($^{\circ}\text{C}$)
T_g	: Glass transition temperature ($^{\circ}\text{C}$)
V_d	: Dead volume (cm^3)
V_g	: Actual glassy specific volume (cm^3/g)
V_1	: Equilibrium specific volume of densified glass (cm^3/g)
x_i	: Mole fraction of gas component i in the feed side
y_i	: Mole fraction of gas component i in the permeate side

Greek Letters

α	: Selectivity
ℓ	: Membrane thickness (μm)
Δp	: Pressure difference (cmHg)

Abbreviations

ABS	: Acrylonitrile–butadiene–styrene copolymer
AC	: Activated carbon
CMS	: Carbon molecular sieve
DMF	: Dimethylformamide
DSC	: Differential scanning calorimetry
GC	: Gas chromatograph
HBPI	: Hyperbranched polyimide
HMA	: 2-hydroxy 5-methyl aniline
IGA	: Intelligent gravimetric analyzer
LMWA	: Low molecular-weight additive

MgO : Magnesium oxide nanoparticles
MMM : Mixed matrix membrane
MOF-5 : Metal-organic framework-5
PC : Polycarbonate
PDMC : Propane diol monoester crosslinkable polymer
PEI : Polyetherimide
PES : Polyethersulfone
PI : Polyimide
pNA : p-nitroaniline
PPO : Poly(phenyleneoxide)
PPZ : Polyphosphazene
SEM : Scanning electron microscopy
TAP : 2,4,6-triamino pyrimidine
TCD : Thermal conductivity detector
TEM : Transmission electron microscopy
TGA : Thermal gravimetric analyzer

CHAPTER 1

INTRODUCTION

As the worldwide attention has focused on shifting toward cleaner energy sources in recent years, natural gas has emerged as an important energy source of the future. Natural gas is an economical and environmentally friendly energy source [1].

Although raw natural gas varies in composition from source to source, methane is the key component, typically 75%-90% of the total [2]. It may also contain considerable amounts of impurities including carbon dioxide, water, nitrogen, hydrogen sulfide and other hydrocarbons [3, 4]. Removal of these impurities, especially CO₂, is mandatory to meet pipeline specifications since CO₂ reduces the heating value of natural gas, and it is very corrosive, and freezes at a relatively high temperature, forming blocks of dry ice that can clog equipment lines and damage pumps [5]. Because of the already high pressures present in natural gas process streams, membrane technology is ideal for CO₂ removal, since membranes rely on a pressure-driving force for the separation [6, 7].

Membranes are selective barriers between two phases and have the ability to transport certain molecules from a mixture much faster than any other molecules [8]. Membranes may separate the fast permeating impurities (CO₂, H₂S, and H₂O) into the *permeate* side, while natural gas is enriched on the *retentate* side with negligible pressure loss, which is an important advantage to minimize recompression costs before sending the natural gas into the pipeline [5, 7].

Membranes can be classified as polymeric and inorganic according to their material of construction. Polymeric materials provide a variety of desirable properties that are significant for gas separation processes including low cost, desirable mechanical stability, and ease of processability [9]. However, they cannot withstand high temperatures and

aggressive chemical environments [5]. Moreover, they show a trade-off between permeability and selectivity which was noted by Robeson [10]. In contrast, inorganic materials generally possess superior thermal and chemical stabilities. Nevertheless, they have poor processability and cannot be fabricated in an economically feasible way with current membrane manufacturing techniques for large-scale applications [9]. In view of this situation, a new approach is needed to provide membranes that combine the properties of both polymeric and inorganic materials.

Mixed matrix membranes (MMMs), composed of an insoluble phase dispersed in a continuous polymer matrix, emerged as excellent candidates for challenging membrane applications [11]. However, the gas transport behavior of MMMs is substantially influenced by a variety of factors such as properties of matrix and filler materials and their compatibility, and the type of polymer-filler morphologies [12-16]. Partial incompatibility between polymeric and dispersed phases may cause an undesirable void at the interface, which is likely to reduce the gas separation performance of the membrane [13]. To overcome this problem, several methods are suggested to optimize the transport properties of MMMs [17-21]. One of these methods which is also used in this study is to use low molecular-weight additives that may act as compatibilizer. The incorporation of certain types of additives into polymer matrix to enhance the separation properties of MMMs by eliminating the interfacial defects has been investigated as a promising alternative [22-25].

Membrane separation and permeation characteristics for a particular mixed gas system are typically calculated from single-component permeation measurements or from the multiplication of single-component transport parameters, namely, diffusion coefficients and solubility constants [26]. However, the transport mechanism of one component in a mixture may be affected from the presence of other penetrants or there may be an interaction of one component with the polymer matrix which may affect the interaction of the others [26-30]. In such a case, these calculations will cause incorrect estimations of the membrane separation properties. Therefore, to evaluate the true separation performance of membranes, binary or multicomponent gas permeability measurements should be carried out. Besides, the studies carrying out binary or multicomponent gas permeability measurements for MMMs are very limited. Moreover, the ones investigating

the separation performance of membranes for a mixed gas system use a very limited number of composition, and very seldom systematic evaluations are carried out [31, 32].

The objective in this study is to produce high performing MMMs for CO₂/CH₄ separation. MMMs were prepared using polyethersulfone (PES) as the polymer matrix with SAPO-34 as the dispersed phase. 2-hydroxy 5-methyl aniline (HMA) was selected as the low molecular weight additive. Four types of membranes were used throughout the study; namely pure PES membrane, PES/HMA (4, 10%w/w) membrane, PES/SAPO-34 (20%w/w) MMM, PES/SAPO-34 (20%w/w)/HMA (4, 10%w/w) MMM. The separation performances of these membranes were determined by measuring single gas permeabilities and by separating CO₂/CH₄ binary gas mixtures. In separation of binary gas mixtures, the effect of CO₂ composition in the feed on the separation performance of the membrane was investigated in detail with a wide feed composition range. In addition to gas permeation experiments, the membranes were also characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

CHAPTER 2

LITERATURE SURVEY

2.1 Gas Separation Membranes

Gas separation membranes, ideally, can be regarded as molecular-scale filters separating a feed mixture of A and B into a *permeate* of pure A and a *retentate* of pure B [33]. Transport through the membrane takes place as a result of a driving force which can be established either by applying a high pressure on the feed side and/or maintaining a low pressure or vacuum on the permeate side [8].

Permeability and selectivity are the two main parameters defining the performance of a membrane. Permeability for a penetrant A is defined by the following [8];

$$P_A = \frac{N_A \ell}{\Delta p_A}$$

where N_A is the flux of gas passing through the membrane, ℓ is the membrane thickness and Δp_A is the pressure difference between high and low pressure sides. Permeability is usually given in units of Barrer, defined as:

$$\text{Barrer} = 1 * 10^{-10} \frac{\text{cm}^3 (\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$$

Selectivity reflects the efficiency of a membrane to separate one gas from another. The ideal selectivity, or permselectivity, of a membrane for penetrant A relative to penetrant B is the ratio of the permeabilities of the two penetrants [8, 33]:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

The permeability of the slower gas is used as the denominator, hence conventionally ideal selectivity is greater than or equal to one. This provides a basis to compare different materials, since permeability of a penetrant, and so permselectivity are intrinsic properties of homogeneous materials. Like other intrinsic properties of homogeneous materials, both permeabilities and selectivities are functions of temperature and pressure [17].

In a binary mixture containing gases A and B with gas A as the faster permeating gas, the separation selectivity is used in place of the ideal selectivity. The separation selectivity can be written as the ratio of mole fractions of gases such as [8, 17];

$$\alpha_{A/B} = \frac{(y_A / y_B)_P}{(x_A / x_B)_F}$$

where y_A and y_B are the mole fractions of components A and B at the permeate and x_A and x_B are the mole fractions in the feed. In the case where the components in the gas mixture do not interact with each other or affect the each other's interaction with the membrane material, and when the permeate pressure is essentially zero, the ideal selectivity is equal to the separation selectivity [34].

Polymers are the most frequently used membrane materials in many gas separation applications. Many polymers show adequate gas selectivity and they can be easily processed into membranes. Moreover, they are economical and offer a wide range of functional and structural conformity [35-37]. Current gas separation membranes are formed both from glassy or rubbery polymers.

The glass transition temperature (T_g) at which transition from glassy to rubbery state occurs is an important physical characteristic of polymer chains and is related mainly with polymer chain flexibility and free volume. This transition is demonstrated by the curve of polymer specific volume versus temperature, as shown in Figure 2.1. When the polymer is in rubbery state, motion of the polymer chains is possible, whereas in glassy state, they are restricted. Because of the reduced polymer chain mobility, the polymer exists in a non-equilibrium state having entangled molecular chains with immobile

molecular backbones in frozen conformations where free volume ($V_g - V_l$ in Figure 2.1) is present [7]. The presence of free volume plays an important role in controlling the gas permeation rate and, thereby, the separation of two or more components [26].

Due to the unique reduced chain mobility, diffusion coefficients in glassy polymers are more dependent on molecular size and shape than in rubbery polymers resulting in better selectivities [7, 38]. As a consequence, glassy polymers are favored for many gas separation applications. Commonly used glassy polymeric materials are polycarbonates, polysulfones, polyimides, polyphenylene oxides, and cellulose derivatives [8].

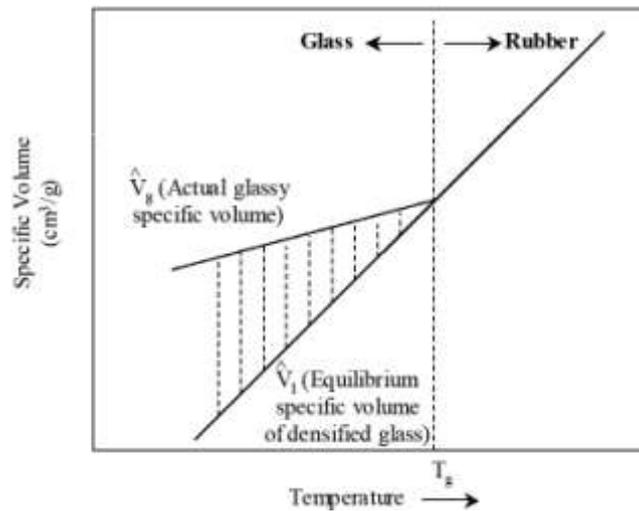


Figure 2.1 Polymer specific volume as a function of temperature (adapted from ref. [7]).

The gas separation through dense polymeric membranes occurs by a coupled mechanism involving sorption and diffusion, hence the permeability equals to the product of the solubility coefficient, S , and diffusion coefficient, D , in a given membrane [8]:

$$P = S * D$$

Solubility coefficient is a thermodynamic parameter and gives a measure of the amount of penetrant sorbed by the membrane under equilibrium conditions. It is related with condensability of the penetrant and interaction between the penetrants and the membrane material. Diffusion coefficient is a kinetic parameter which indicates how fast a penetrant is transported through the membrane. It depends on the penetrants properties (size, shape, and polarity) and nature of the membrane (physical and chemical structure) [8]. In the solution-diffusion mechanism, first the penetrant sorbs and dissolves in the membrane, then diffuses through it and finally desorbs at the other side [8]. Membranes can be selective either due to sorption or diffusion that means the preferred penetrant can be sorbed to a larger extent in the membrane material or it can diffuse faster through the membrane [39].

For gas separation, polymers with both high permeability and selectivity are desirable. Higher permeability reduces the amount of membrane area needed to treat a given amount of gas, by that means decreasing the capital cost of membrane units. Higher selectivity brings about higher purity product gas [38, 40]. Polymeric membranes generally undergo a trade-off limitation between permeability and selectivity. Robeson expressed this relationship by graphing the available data as shown in Figure 2.2, which presents CO₂ permeability and CO₂/CH₄ selectivity for various glassy and rubbery polymers [10]. Polymers with the best performance would be in the upper right-hand corner of this figure, which is denoted as commercially attractive region. However, polymers with permeability/selectivity combinations above and to the right of the line drawn are exceptionally rare [38].

2.2 Mixed Matrix Membranes (MMMs)

In spite of all the advantages, as stated before, polymeric membranes suffer from a trade-off between permeability and selectivity. On the other hand, inorganic membranes exhibit favorable performance on the trade-off curves as compared to polymeric membranes, but have high cost, modest reproducibility and brittleness. Based on the requirement of a more efficient membrane than polymeric and inorganic membranes, mixed matrix membranes have been developed recently [9]. They are composed of an insoluble phase dispersed in a continuous polymer matrix [17]. These materials combine the processability of the polymer phase with the high separation capabilities of the inorganic

phase, thereby resulting in the best of both worlds [18]. The continuous polymer matrices can be selected from either glassy polymers or rubbery polymers, whereas the dispersed phase is microporous molecular sieves (zeolites), mesoporous molecular sieves, carbon molecular sieves, metal-organic frameworks and silicas [7, 19, 21, 41-43].

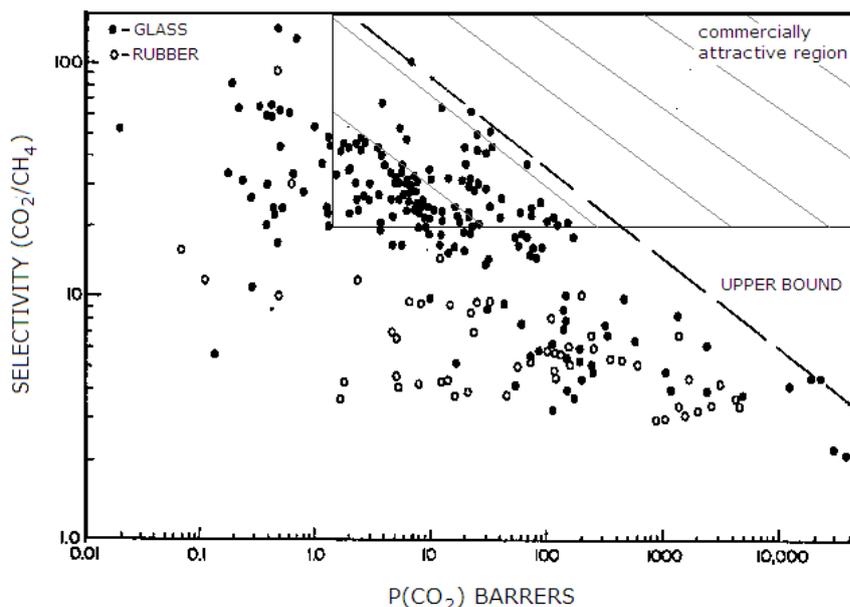


Figure 2.2 Upper-bound trade-off curves of various glassy and rubbery polymeric membranes for CO₂/CH₄ (adapted from ref. [10]).

The potential for MMMs has been investigated for various gas separations, including air separation (e.g., O₂/N₂), natural gas purification (e.g., CO₂/CH₄), hydrogen recovery (e.g., H₂/CO₂, H₂/N₂, and H₂/CH₄), and hydrocarbon separation (e.g., i-pentane/n-pentane, and n-butane/CH₄) [18, 19, 44-48]. Among these, CO₂/CH₄ separation, which was also investigated in this study, has received high attention due to its significance in industrial applications. Studies reporting enhanced gas separation performances for CO₂/CH₄ with MMMs prepared using various glassy polymers and different types of fillers are noted in Table 2.1. Different types of filler with different loadings were tested in order to enhance the gas separation performances. Comparison of these studies showed that a trend does

Table 2.1 Single gas permeabilities and ideal selectivities of glassy polymer MMMs.

Polymer	Filler		Permeability (Barrer)		Ideal selectivity CO ₂ /CH ₄	Ref.
	Type	Loading	CO ₂	CH ₄		
PI (Matrimid)	CMS	0.0	10.0	0.280	35.3	[7]
		17 (vol %)	10.30	0.230	44.4	
		36 (vol %)	12.60	0.240	51.7	
PEI (Ultem)		0.0	1.45	0.037	38.8	[7]
		16 (vol %)	2.51	0.058	43.0	
		35 (vol %)	4.48	0.083	53.7	
PI (Matrimid)	MgO	0.0	7.50	0.225	33.3	[52]
		20(wt %)	8.27	0.278	29.8	
PI (Matrimid)	ZSM-5	0.0	7.29	0.210	34.71	[46]
		10 (wt %)	8.27	0.120	67.19	
		20 (wt %)	8.65	0.130	66.07	
		30 (wt %)	14.61	0.260	56.48	
PI (Matrimid)	Cu-BPY-HFS	0.0	7.29	0.21	34.71	[41]
		10 (wt %)	7.81	0.24	31.93	
		20 (wt %)	9.88	0.36	27.62	
		40 (wt %)	15.06	0.59	25.55	
PES	4A	0.0	3.38	0.112	30.18	[19]
		20 (wt %)	2.32	0.0743	31.22	
PI (Matrimid)	C60	0.0	7.15	0.199	36	[50]
		5 (wt %)	4.54	0.127	36	
		10 (wt %)	3.79	0.109	35	
ABS	AC	0.0	3.43	0.174	19.71	[53]
		38.8 (vol %)	8.43	0.384	21.95	
		45.6 (vol %)	11.44	0.454	25.20	
		62.4 (vol %)	22.64	0.590	38.37	
PES	AgA	0.0	2.7	-	31.4	[54]
		20 (wt %)	1.6	-	39	
		30 (wt %)	1.4	-	48	
		40 (wt %)	1.2	-	54	
		50 (wt %)	1	-	59.6	
HBPI	silica	0.0	7.4	0.098	75	[42]
		10 (wt %)	10	0.092	114	
		20 (wt %)	12	0.080	150	
		30 (wt %)	19	0.080	238	
PC	4A	0.0	8.8	0.374	23.6	[21]
		10 (wt %)	8.2	0.250	32.8	
		20 (wt %)	7.8	0.240	32.5	
		30 (wt %)	7.0	0.186	37.6	
PES	13X	0.0	2.6	-	-	[55]
		16.6 (wt %)	1.8	-	-	
		33.3 (wt %)	2.7	-	-	
		50.0 (wt %)	5.2	-	-	
	4A	16.6 (wt %)	2.3	-	-	
		33.3 (wt %)	2.0	-	-	
		50.0 (wt %)	10.7	-	-	

not exist for the change of both permeabilities and selectivities with different fillers and their loadings. It can be said that gas separation performances either increased or decreased with filler loading. As a consequence, studies reveal that not only suitable combination of polymer-inorganic filler but also filler loading and membrane preparation parameters can be major concerns in the separation properties of MMMs [18, 44, 49-51].

Although these membranes offer promising properties, material compatibility and polymer-sieve morphologies formed at the interface are still challenging in forming successful MMMs [9, 13, 17]. Furthermore, recent researches have indicated that the kind of polymer-sieve morphologies has a direct effect on the gas separation performance of a membrane [13-16]. The nature of the polymer-sieve interaction and the stress encountered during membrane preparation are two key parameters playing an important role in the formation of the interface [18]. Weak polymer-sieve interaction can result in the formation of voids that are much larger than the penetrating gas molecules. These voids allow the transport of both slow and fast gases non-selectively, thus reducing the separation performance of the MMM with respect to the pure polymer [56]. The second factor, the stresses generated during solvent removal, may also result in the formation of voids. During membrane preparation, as the solvent evaporates, the overall film will begin to shrink due to solvent loss. Shrinkage of the matrix can result in considerable stress in the matrix. This stress is probably the reason of a poor contact between the sieve and the polymer on the interface which results in the formation of voids [18, 49]. Different methods such as modification of the zeolite external surface by a silane coupling agent, incorporation of a plasticizer, annealing the membrane above the T_g of the polymer, and using additive with functional groups have been offered for the elimination of the non-selective voids at the interface.

Modification of the zeolite external surface by a silane-coupling agent was proposed to improve polymer-sieve contact and promote compatibility [17, 39, 45, 57-60]. In almost all studies, the adhesion between zeolite and polymer matrix phases has been improved by modifying zeolite surface according to SEM or TEM analyses. However, the performance of their MMMs remained unchanged or decreased compared with those made of polymer-unmodified zeolite.

Alternatively, the incorporation of different plasticizers (RDP Fyroflex, Di-Butyl Phthalate, and 4-Hydroxy Benzophenone) into polyimide (Matrimid)-zeolite 4A MMM was suggested by Mahajan et al. [18]. The results showed that good contact was obtained between the zeolite and the polymer. However the gas separation properties showed no improvement.

As another alternative, Huang et al. [19] used zeolite 4A particles for the preparation of PES membranes which were annealed above the T_g of the polymer. Annealing the membrane above the T_g was able to overcome void formation in some extent. The selectivities for O_2/N_2 and CO_2/CH_4 remained unchanged or increased slightly. However in another study done by Ismail et al. [61], when the (PES/PI)/zeolite 4A MMM was annealed above the T_g of the polymer blend, the ideal O_2/N_2 selectivity was improved by a factor of 5 while the permeability of both gases decreased compared to the membranes which were annealed at temperature below T_g . At temperature above the T_g of the polymer, the polymer chain became more flexible and mobile, thus caused an increasing adherence of zeolite particles to the polymer, providing performance improvement [61].

On the other hand, the incorporation of multifunctional low molecular weight additives was investigated as a promising alternative to modify the gas separation performance of polymeric gas separation membranes [20-23, 25, 62]. Yong et al. [20] suggested to use 2, 4, 6-triaminopyrimidine (TAP) as a compatibilizer to reduce the voids between polymer and zeolite. In their study, different types of zeolites (4A, 5A, 13X, NaY and NaSZ390HUA) were dispersed in a Matrimid-polyimide matrix. The permeabilities of all gases tested decreased with addition of TAP into the PI/4A MMM. However, the selectivities of CO_2/N_2 , O_2/N_2 and CO_2/CH_4 increased significantly. Especially the selectivity of CO_2/CH_4 increased to 617 from 2.23 with the addition of TAP to PI/4A MMM. They concluded that TAP enhanced the contact of zeolite particles with polyimide chains.

Recently, Şen et al. [21] used p-nitroaniline (pNA) as the low molecular-weight additive and prepared polycarbonate (PC)/pNA/4A MMMs to examine the effect of pNA on the structure and performance of the membrane. The CO_2/CH_4 selectivities increased significantly from 23.6 to 51.8 for PC/pNA (1%)/4A (20%) MMMs despite a loss in the permeabilities with respect to pure PC membrane. The separation performance of membranes changed because of modification of membrane morphology by zeolite 4A

particles and pNA even at very small concentrations (1-2%w/w). They concluded that pNA acted as a facilitator by improving the interaction between rigid, glassy polymer PC and zeolite 4A particles.

Consequently, the introduction of multifunctional low molecular-weight additives into glassy polymers can be used as a tool to enhance the performance of the polymeric membranes by providing a better interaction [21, 25, 31, 63].

2.3 Separation of Binary Gas Mixtures

Polymeric membranes are usually characterized by single gas permeation experiments as it is a simple technique to evaluate the performance of a membrane. Furthermore, it gives an idea of possible performance of a membrane which is useful for material screening. However, using single gas transport parameters to predict the permeation behaviour of a mixture may cause incorrect estimations of the membrane separation properties [26], since the permeation behaviour of one component in a gas mixture can be affected by the presence of other penetrants or there may be an interaction of one component with the polymer matrix which affect the transport of other components [26-30]. These cannot be taken into account in single gas permeation experiments. Particularly for industrial applications, there is a need to understand whether permeation behaviour of each component in a gas mixture is different from those in the single component system [26, 27, 30, 64-66]. Therefore, for better defining the membrane separation characteristics, permeation of binary or multicomponent gas mixtures should be investigated. Moreover, the studies dealing with the permeation of binary or multicomponent gas mixtures are very rare, and these ones do not investigate the effect of feed composition systematically, they only investigate for a limited composition range.

2.3.1 Mixed and Pure Gas Permeation Variation for Polymeric Membranes

Some studies have been conducted to compare the differences between mixed and pure gas permeations through polymeric dense membranes [27-30, 64-71]. Unfortunately, the reasons for the differences are yet not understood exactly due to experimental lack of data since membrane performances for a particular mixed gas system is typically calculated from single-component permeation measurements or from the multiplication of single-

component transport parameters, namely, diffusion coefficients and solubility constants [26]. The studies carrying out mixed gas permeation experiments are very rare, and about all of these limited studies carry out experiments with a limited composition range.

According to these studies, this variation is believed to arise from the effect of competition in Langmuir sorption sites between the penetrants, plasticization phenomena, concentration polarization, and non-ideal gas behaviour [27, 70, 71]. However, in some studies no difference is observed between mixed and pure gas permeations through polymeric dense membranes which are usually attributed to the non-interactive nature of gas transport through these membranes [26, 31, 32, 64].

As the gas transport in polymers occurs by the solution diffusion mechanism, the gas molecules in a mixture may compete for sorption sites in the membrane matrix. In a binary mixture containing CO₂ and CH₄ molecules, the presence of less permeable gas, CH₄, may reduce the permeability of more permeable gas, CO₂. This then results in a lower separation selectivity compared to the ideal selectivity [72]. This phenomenon was also explained in the study of Tin et al. [71] who investigated the performance of Matrimid membranes for a binary gas mixture containing 40% of CO₂ in CH₄ as the feed gas. They claimed that the reduced CO₂ permeability in the presence of CH₄ is because of the reduced solubility coefficient of CO₂ due to the competition in occupying the unrelaxed volume. Moreover, CO₂ will also decrease the solubility of CH₄ for the same reason. However, they observed that the CH₄ permeability from mixed gas was close to that obtained in pure gas test. It is owing to the presence of CO₂ even though reduced the solubility of CH₄, but also facilitate the transport of CH₄ by increasing CH₄ diffusivity. As a result, the decrease in solubility is compensated by an increase in diffusivity yielding the same permeability as the pure gas test. Consequently, the selectivities of CO₂/CH₄ obtained for mixed gas tests are lower than ideal selectivities.

Similarly, Donohue et al. [73] observed a similar behaviour in cellulose acetate membranes for a binary gas mixture containing 30.6 % and 70.6 % of CO₂ in CH₄ respectively as the feed gas. Differently, in their study, the presence of CO₂ increased the CH₄ permeability due to an increase in the diffusivity of CH₄ whereas the diffusivity of CO₂ decreased due to the presence of CH₄, even though the solubilities of both gases decreased in the presence of each other. Because the diffusivity of CH₄ increases more

than the solubility of CH₄ decreases, the CH₄ permeability is higher in a mixture compared to the pure gas permeability at the corresponding partial pressure and the CO₂ permeability is lower. They ascribed the increase in diffusivity of CH₄ to the plasticization of the membrane. Ismail et al. [74] summarized this phenomena observed for different polymeric membranes used for gas separation, and discussed the alteration of physical properties resulting from the polymer plasticization by the sorbed penetrant molecules. When a membrane is plasticized by CO₂ in a gas mixture of CO₂/CH₄, the diffusivity of the other gas (CH₄) is accelerated because of the swelling of the polymer matrix due to strong interactions between CO₂ and the polymer materials. This may result in significant selectivity losses as compared with ideal selectivities. To overcome this effect, Bos et al. tried heat treatment to stabilize the polyimide membrane [75]. Car et al. [76] also observed lower CO₂/gas separation selectivities than the ideal selectivities due to the plasticization of Pebax/polyethylene glycol (PEG) blend thin film composite membranes, tested with mixed gas experiments which were carried out with 50/50 vol.% CO₂/H₂ and CO₂/CH₄ mixtures, and 25/75 vol.% CO₂/N₂ mixture at 20°C and a total feed pressure of 20 bar.

Another factor causing the deviation of membrane performance in a gas mixture from that of pure gas tests is concentration polarization, which refers to a concentration gradient building up at high feed pressures due to the depletion of the more permeable component and the accumulation of the less permeable species in the boundary layer adjacent to the membrane [65]. It leads to a decrease in the available driving force for the more permeable species across the membrane and an increase for the less permeable species. This causes a decrease in the separation efficiency of the membrane. Different mass transfer models and simulations [65, 70, 77, 78] were established to analyze the concentration polarization.

Apart from these factors, for a gas mixture containing CO₂, the non-ideality of gas behaviour is believed to be one of the reasons causing a difference between mixed and pure gas permeations. In industrial applications, the feed gas stream is always maintained at high pressure values. Hence, the assumption of ideal gas will no longer be valid. Moreover, the fugacity coefficient of one component will be reduced by introducing the other component in the mixture. Therefore, the driving force for each gas component decreases when compared with pure gas tests at equivalent pressures. This brings about a

decrease in the separation selectivity when compared with the ideal selectivity. These findings were observed by Chern et al. [70] for CO₂/CH₄ mixtures for polyimide films. They proposed an alternative model to investigate the effects of gas-phase non-ideality and concluded that “in addition to flux depressions due to dual-mode effects, non-ideality of the gas phase must be accounted for to explain the substantial flux depressions observed for the CO₂/CH₄ mixtures.”

Besides the studies dealing with the variation between mixed and pure gas permeation, the effect of operating conditions such as temperature and pressure on the CO₂/CH₄ binary gas mixture permeabilities and selectivities have also been investigated. Since our research is focusing on the effect of feed composition on the separation of CO₂/CH₄ binary gas mixtures, only the studies related with this subject will be considered here.

Typically, permeabilities increase with an increase in CO₂ feed concentration, whereas the selectivities may decrease, increase or stay constant depending on the gas-gas or gas-membrane matrix interactions.

Aminabhavi et al. [79] investigated the performance of sulfonated PC membranes for the separation of CO₂/CH₄ binary mixtures at 30°C with a feed pressure of 20 bar by changing the CO₂ feed concentration. It is observed that an increase in CO₂ concentration from 5 to 40 mol% caused a corresponding increase in flux of the membranes. Moreover, the separation selectivities enhanced because of greater CO₂ sorption. Additionally, Sridhar et al. [80] studied the separation of CO₂/CH₄ binary mixtures at 30°C and 30 bar using pure and modified PPO membranes. They observed increasing permeabilities and separation selectivities with increasing CO₂ concentration in the feed from 5 to 40 mol%, and increasing selectivities were attributed to greater sorption of CO₂ in the membrane due to the availability of more number of gas molecules for interaction with the membrane. They also claimed that the permeation of CH₄ molecules was hindered due to increasing polarization of CO₂ molecules near the membrane surface.

The same group [72] also investigated the effect of varying composition of binary CO₂/CH₄ gas mixture at 20 bar and 30°C, using crosslinked Pebax membrane. They observed similar behaviour; both the separation selectivity and the permeabilities increased, with increasing CO₂ concentration in the feed from 2 to 20 mol%.

However, Şen et al. [31] observed no change in the separation selectivity of CO₂/CH₄ with feed composition for pure PC membranes. The separation selectivities stay constant around the ideal selectivities. Similar conclusions were also made by Battal et al. [32] for pure PES membranes. The independent behavior of the selectivities of pure PC gas composition was ascribed to the non-interactive nature of gas permeation through these membranes.

Dhingra et al. [26] reported interesting results for polyimide membranes which were used in CO₂/CH₄ binary gas system at 35°C and 2 atm with four different compositions, namely, 5%, 25%, 50%, 75% CO₂. They observed higher separation selectivities than the ideal selectivity for all compositions, and they explained these phenomena with ‘the presence of gas-gas and gas-polymer interactions, which drastically alter the transport properties of the gases in the polymer’. In addition, the separation selectivities increased with an increase in CO₂ feed concentration. The increase in separation selectivity of the membrane with increasing CO₂ feed concentration shows the presence of counteracting effects, where the influence of the dominating gas (CO₂) is compensated by the increase in the concentration of CH₄. When CO₂ feed concentration decreased, CO₂ permeability increased due to the increase in CO₂ solubility, whereas the increase in CH₄ permeability can be explained by increasing diffusivity. The increase in solubility observed for CO₂ can be explained in terms of the unsaturated state of the gas sorption in the microvoid volume present in the membrane. In other words, the concentration of CO₂ in the polymer is not sufficient to fill up all the sorption sites at low feed pressures.

2.3.2 Mixed and Pure Gas Permeation Variation for Mixed Matrix Membranes (MMMs)

The studies mentioned up to now demonstrated not only the deviation between CO₂/CH₄ binary and single gas permeability measurements, but also the effect of CO₂ feed concentration on the performance of different types of polymeric membranes. For MMMs, which contain fillers with specific sorption properties, this effect may be more significant due to sorption characteristics of CO₂ in the MMMs. Moreover, the interactive nature of CO₂ is believed to lead to more drastic deviation between binary and single gas permeability measurements for MMMs. Unfortunately, the studies investigating the effect of CO₂ feed concentration on the performance of different types of MMMs are rare.

Hillock et al. [81] observed higher separation selectivity than the ideal selectivity using a 10/90 vol.% of CO₂/CH₄ feed mixture for PDMC/SSZ-13 MMMs which is in contrast with general observation in polymeric membranes. They claimed that in the absence of plasticization, the mixed gas CO₂/CH₄ selectivity is higher than the ideal selectivity, since CO₂ may outcompete CH₄, effectively slowing the transport of the bulkier molecule as it permeates through the matrix.

However, Chung et al. [54] observed no difference between mixed gas and pure gas permeation performances of PES–zeolite AgA MMM with 50 wt % zeolite loading for the CO₂/CH₄ mixed gas with a 47/53% molar fraction. The ideal selectivity of CO₂/CH₄ was 59.6, while the separation selectivity was 58.1.

On the other hand, Battal et al. [32] observed lower separation selectivities than the ideal selectivities. They also studied a wide composition range from 0 to 100% (mol/mol) of CO₂/CH₄, CO₂/Ar and H₂/CH₄ binary mixtures in order to investigate the effect of feed composition on the transport properties of the PES/4A MMMs. They concluded that for all binary mixtures, when the composition of gases with higher single gas permeabilities (CO₂, H₂) increased, the permeabilities of the mixture also increased. They observed that the separation selectivities show a strong concentration dependency. For CO₂/CH₄ and CO₂/Ar binary mixtures, increasing CO₂ feed concentration resulted in lower selectivities. However, in the case of H₂/CH₄ binary mixtures, as H₂ concentrations in the feed increased, separation selectivities also increased. The concentration dependency of the selectivities for all binary mixtures was attributed to the gas-membrane matrix and gas-gas-membrane matrix interactions. Furthermore, they claimed that for CO₂/CH₄ and CO₂/Ar binary mixtures, CO₂ molecules are self-inhibited due to saturation of active sites of zeolite at high CO₂ concentrations. Since the potential of the CO₂ molecules is reduced, the priority for CO₂ to permeate through the membrane may no longer be effective. Therefore, the separation selectivities decreased with increasing CO₂ feed concentration. For H₂/CH₄ binary mixtures, they concluded that CH₄ may impede the permeation of H₂ by blocking the narrow regions of the network, resulting in lower selectivities for CH₄ rich feed mixtures.

Similar arguments were reported by Şen et al. [31] investigating the effect of feed composition on the performance of the PC/4A MMMs by changing the CO₂ feed

concentration from 0 to 100 mol%. The permeability of both CO₂/N₂ and CO₂/CH₄ binary mixtures increased while the selectivities decreased with an increase in CO₂ feed concentration. They concluded that when the faster permeating component of a mixture (CO₂), has a strong interaction possibility with the membrane matrix, selectivities decrease with increasing concentration of this component independent from the type of the relatively less interactive component (CH₄ and/or N₂) in the mixture, indicating the importance of competitive sorption among penetrants.

Contrary to the observed decreasing separation selectivities with increasing CO₂ feed concentration, Jha and Way [82] reported increasing CO₂/CH₄ separation selectivities for MMMs prepared using rubbery polymer, polyphosphazene (PPZ) and molecular sieve, SAPO-34 as the feed volume fraction of CO₂ increased from 0.66 to 0.87. However, these increased separation selectivities are still lower than the ideal selectivity of the membrane. The absence of improvement was attributed to absence of pore blocking effect of CO₂ due to the lower adsorption of CO₂ in SAPO-34 zeolite even at the experimental conditions of higher pressure (4.3 bar) and low temperature (-15°C). They concluded that the experimental conditions of higher pressure and low temperature conditions were still not favourable to restrict the transport of CH₄ through the pores of the SAPO-34 particles by adsorption of CO₂.

Similar results were reported in a study of Zhang et al. [46] which used gas mixtures of H₂/CO₂ (75:25, 50:50, and 25:75 mol%), CO₂/CH₄ (75:25, 50:50 and 10:90 mol%) and CH₄/N₂ (94:6, 50:50 and 25:75 mol%) to test Matrimid/ZSM-5 MMMs at 35°C. The separation selectivities for all gas mixtures exhibited no change with respect to feed composition. Furthermore, the selectivities of different gas mixtures are very close to the ideal selectivity which suggests that there is no competitive adsorption of the gases in the mesoporous ZSM-5. They concluded that the separation is mainly determined by the molecular sieving effect.

The same research group [41] also prepared MMMs, using the same polymer, Matrimid with the incorporation of Cu-4,4-bipyridine-hexafluorosilicate (Cu-BPY-HFS) crystals. The membranes were tested using same gas mixtures of H₂/CO₂ (75:25 and 50:50 mol%), CO₂/CH₄ (50:50 and 10:90 mol%) and CH₄/N₂ (94:6 and 50:50 mol%). The separation selectivity of CH₄/N₂ increased 50% for the mixed gases, 1.7 versus the 1.16 for the pure

gases. The selectivity of CO_2/CH_4 decreased from 34 to 22, much lower than the ideal selectivity of 27.6 for CO_2/CH_4 . As for the separation of the CO_2/H_2 mixture, there was not a large difference compared with pure Matrimid, which suggests the Cu-BPY-HFS has no affinity towards H_2 or CO_2 . This result suggests that the Cu-BPY-HFS has strong affinity for CH_4 and the competitive adsorption of CH_4 over N_2 increases the solubility of CH_4 in the membrane selectively in the mixture.

Recently, Perez et al. [43] synthesized metal-organic framework-5 (MOF-5) nanocrystals and added to polyimide-Matrimid polymer to form MMMs for the separation of binary mixtures; H_2/CO_2 (75:25, 50:50, and 25:75 mol%), CO_2/CH_4 (50:50 and 10:90 mol%) and CH_4/N_2 (94:6, 50:50 mol%). The measurements were carried out at 35°C with a feed pressure of 2.7 bar. Permeation experiments with blends of gases showed that the separation selectivity of H_2/CO_2 in the MOF-5/Matrimid MMM did not change with CO_2 feed ratio. However, CO_2/CH_4 separation selectivity decreased with increasing CO_2 feed concentration from 10 to 50%. They explained these phenomena in terms of the extended dual mode transport model for gas mixtures that assumes that the primary effect of the presence of more than one gas in the membrane results in the competition between these gases for the fixed unrelaxed free volume in the polymer. In addition, due to the large solubility of CO_2 in the membrane, the solubility of CH_4 is greatly reduced, rendering CH_4 transport dependent mostly on diffusivity, which is enhanced by the porosity and the uniform surface introduced by the MOF-5 nanocrystals. Moreover, the incorporation of MOF-5 reduced the sorption sites in the polymer for CO_2 which contributed to the reduction of CO_2 transport.

So far, the researchers stated that the presence of a second component in a penetrant system affects the interactions between the gas molecules of the two components and the polymer, resulting in changes in permeability and selectivity, which deviate from the ideal values. In addition, the variation of feed composition in the gas mixture may also affect the separation performance of a membrane. However, reasons to these affects have not been understood clearly due to the lack of systematic experimental data, yet. Therefore, from industrial standpoint, increasing the number of studies on this subject is necessary to determine at which feed gas composition the prepared membranes are best performing for practical applications. Moreover, the effects of feed composition on the performance of MMMs should be investigated by using a wide range of feed composition

of the target gas mixtures. In this regard, this study used ternary membranes (polymer/zeolite/additive) for investigating the effect of feed composition systematically on the performance for CO₂/CH₄ separation. As far as we know, there is no study investigating the effect of feed composition on the separation performance of ternary (polymer/zeolite/additive) membranes using a wide composition range as this study does.

CHAPTER 3

EXPERIMENTAL

3.1 Membrane Preparation Materials

A commercial Radel A-100 polyethersulfone (PES), supplied by Solvay Advanced Polymers, was selected as the continuous phase. Figure 3.1 (a) shows the repeating unit of PES. PES has a glass transition temperature, T_g , of about 220°C [83].

Dimethylformamide (DMF), obtained from Lab-Scan Analytical Sciences, was used as solvent. It has the chemical formula of C_3H_7NO , and boiling point of 153°C.

The filler used was SAPO-34 which was synthesized in our laboratory [84]. Its particle size changes between 1 μm and 2 μm determined by both SEM and optical microscopy.

The low molecular weight-additive was 2-hydroxy 5-methyl aniline, HMA, which was acquired from Aldrich. It has the chemical formula of C_7H_9NO and melting point of 140°C. It was used in the experiments as received without any further treatment. Figure 3.1 (b) shows the chemical structure of 2-hydroxy 5-methyl aniline.

3.2 Membrane Preparation Methodology

Membranes were prepared by solvent-evaporation method. Before using both PES and SAPO-34, they were dried at 250°C overnight.

The membrane preparation methodology of PES/HMA/SAPO-34 MMM was summarized in Figure 3.2. SAPO-34 was dispersed in DMF, and then the mixture was ultrasonicated (Branson 2510, 40 kHz) for 60 min to minimize the agglomeration and to obtain uniform

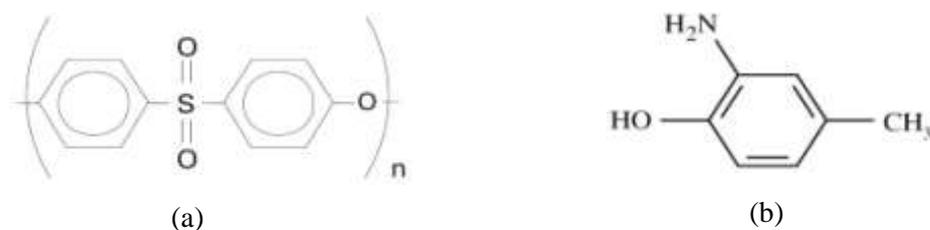


Figure 3.1 The repeating unit of PES (a), and the chemical structure of HMA (b).

dispersion of zeolite particles in the mixture. Then, HMA was added and the mixture was stirred overnight by a magnetic stirrer. In order to promote compatibilization of the sieves with the polymer [7], and not to increase the viscosity of the mixture suddenly, thereby providing ease of stirring, SAPO-34 particles were primed by adding 15w% of total amount of PES, followed with ultrasonication for 60 min. Then, the remaining amount of the polymer was added step by step into the mixture with same ratios as soon as it dissolved. Before blade casting, the mixture was ultrasonicated finally for 60 min. The mixture was blade cast on a glass plate at room temperature in air using a stainless steel film applicator (Automatic Film Applicator, Sheen 1133) with a casting knife of 500 μm , and placed in an oven preheated to 40°C. Then, the temperature was increased to 80°C, and the film was dried at 0.2 bar for 8 h in nitrogen. After that, the film was removed slowly and carefully peeled off to use as membrane. The membrane that was detached from the plate was annealed for 24 h at 100°C in nitrogen at 1 bar to remove the residual solvent. After annealing, the membrane was cooled down to room temperature slowly before taking out of the oven. Similar procedures were also applied to prepare pure PES, PES/HMA and PES/SAPO-34 membranes. All membranes were tested with gas permeation, and prior to and after the experiments they were kept in vacuum desiccator.

The thicknesses of all membranes were measured with a micrometer and those of several membranes were measured from SEM micrographs. The thicknesses changed between 45 and 55 μm .

The concentration of PES in DMF was 20% (w/v). HMA and SAPO-34 loadings were added according to PES loading in the solvent. The concentrations of HMA in the casting solution were 4 and 10% (w/w), while the concentration of SAPO-34 was 20% (w/w).

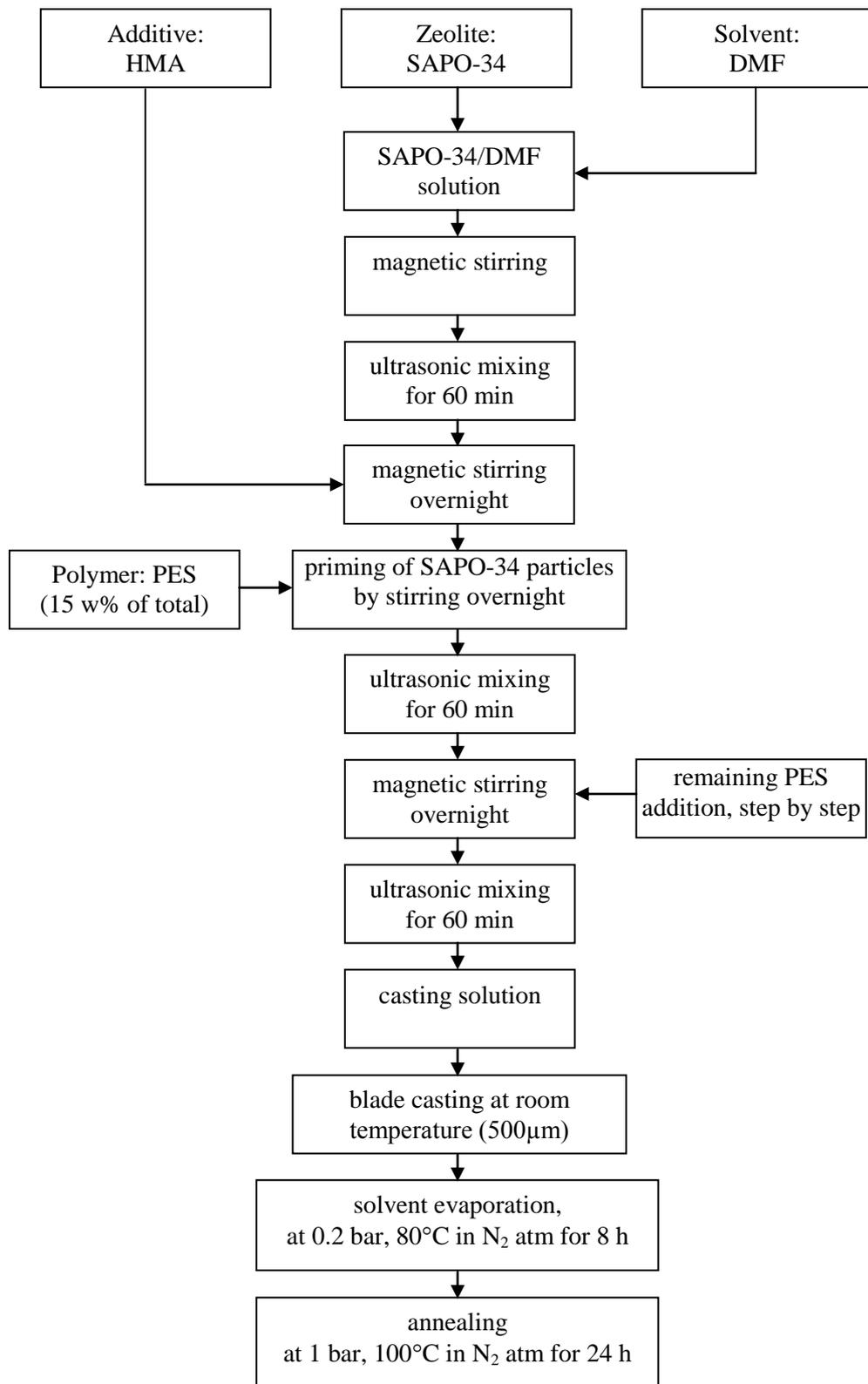


Figure 3.2 Flowchart of the preparation methodology of PES/HMA/SAPO-34 MMMs.

3.3 Membrane Characterization

Membranes were characterized with differential scanning calorimetry (Shimadzu DSC60) to determine the glass transition temperatures (T_g). For DSC analysis, small sections of membrane film were cut, weighed, and placed into aluminum DSC pans. Samples were heated from 30°C to 250°C at a rate of 10°C/min in N₂ atmosphere, and then was cooled down to 30°C. The first cycle was carried out to remove the thermal history. The sample was heated again to 250°C with the same procedure for the second scan. The second scan thermogram was used to determine the glass transition temperature of the membrane.

Membranes were also analyzed by a thermal gravimetric analyzer (Shimadzu DTG-60H) to determine the amount of residual solvent. The samples were heated at a rate of 10°C/min in N₂ atmosphere. The nitrogen flow rate was 75 ml/min.

In addition to thermal characterization, membranes were characterized with scanning electron microscopy (FEI Quanta-400 F) to determine the morphology. The membranes were fractured in liquid N₂ and mounted vertically on a circular aluminum sample holder with double-sided adhesive, electrically conductive carbon tape to view the cross-sections of the films. The samples were then coated with gold/palladium to provide a conductive coating that enhances the images under SEM.

The sorption studies of the membranes were conducted by the gravimetric system (IGA, Hiden Isochema, UK) which is situated at Chemical Engineering Department in ITU, Istanbul. The gravimetric method is based on measurement of the weight gained by an initially degassed sample when exposed to a gas. This weight gain was measured with the small stepwise pressure change, i.e. 100 mbar at the range of 0-10 bar, for CO₂ and CH₄.

3.4 Gas Permeability Measurements

3.4.1 Experimental Set-up

A schematic of the experimental set-up used to carry out both single gas and binary gas mixture permeation experiments is shown in Figure 3.3. It was previously designed, used

by our research group [31] and modified in this study for better temperature control. The set-up consists of a membrane cell, a pressure transducer, a gas tank, a vacuum pump, a temperature controller and a gas analyzer for binary gas permeation experiments. The set-up was all wrapped with a heating tape (Cole Parmer, Barnstead/Thermolyne) equipped with J-type thermometer and PID controller to control the temperature.

The membrane cell was a stainless steel Millipore filter holder (Millipore, part no. XX45 047 00) with a double-Viton O-ring seal. The effective membrane area was 9.6 cm^2 . The dead volume of the set-up, which is the volume occupied by the permeate gas from permeate side of the membrane cell to the pressure transducer and gas chromatograph, was measured as 22 cm^3 [31].

A pressure transducer (MKS Baratron, 0-100 Torr) with a sensitivity of 0.01 Torr was used to monitor the pressure increase at the permeate side of the permeation cell. The feed and permeate gas streams were analyzed by an online gas chromatograph (GC, Varian CP-3800) equipped with a Chromosorp 102 column (80-100 mesh) and a thermal conductivity detector (TCD). The GC was connected to the permeate section of the permeation cell and the vacuum pump through the six-port injection valve. The sample loop of GC has a total volume of $100 \text{ }\mu\text{l}$ (0.1 cm^3). The operation and operating conditions of GC were explained in detail previously [31].

3.4.2 Experimental Procedure

The gas permeation experiments were conducted at 35°C with a feed pressure of 3.0 bar. Measurements were performed by constant volume variable pressure technique. The membranes were evaluated by their single gas performances of H_2 , CO_2 , and CH_4 as well as by their separation performances of CO_2/CH_4 binary gas mixtures. The gases were purchased from local companies (Oksan) and their purities were higher than 99%.

For single gas experiments, the penetrant gas was sent to the feed tank. Since this is a dead-end system with no outlet for the feed except through the membrane, the pressure rise at the permeate side of the membrane was monitored to calculate the permeability. The permeability of each gas through a membrane was measured at least twice.

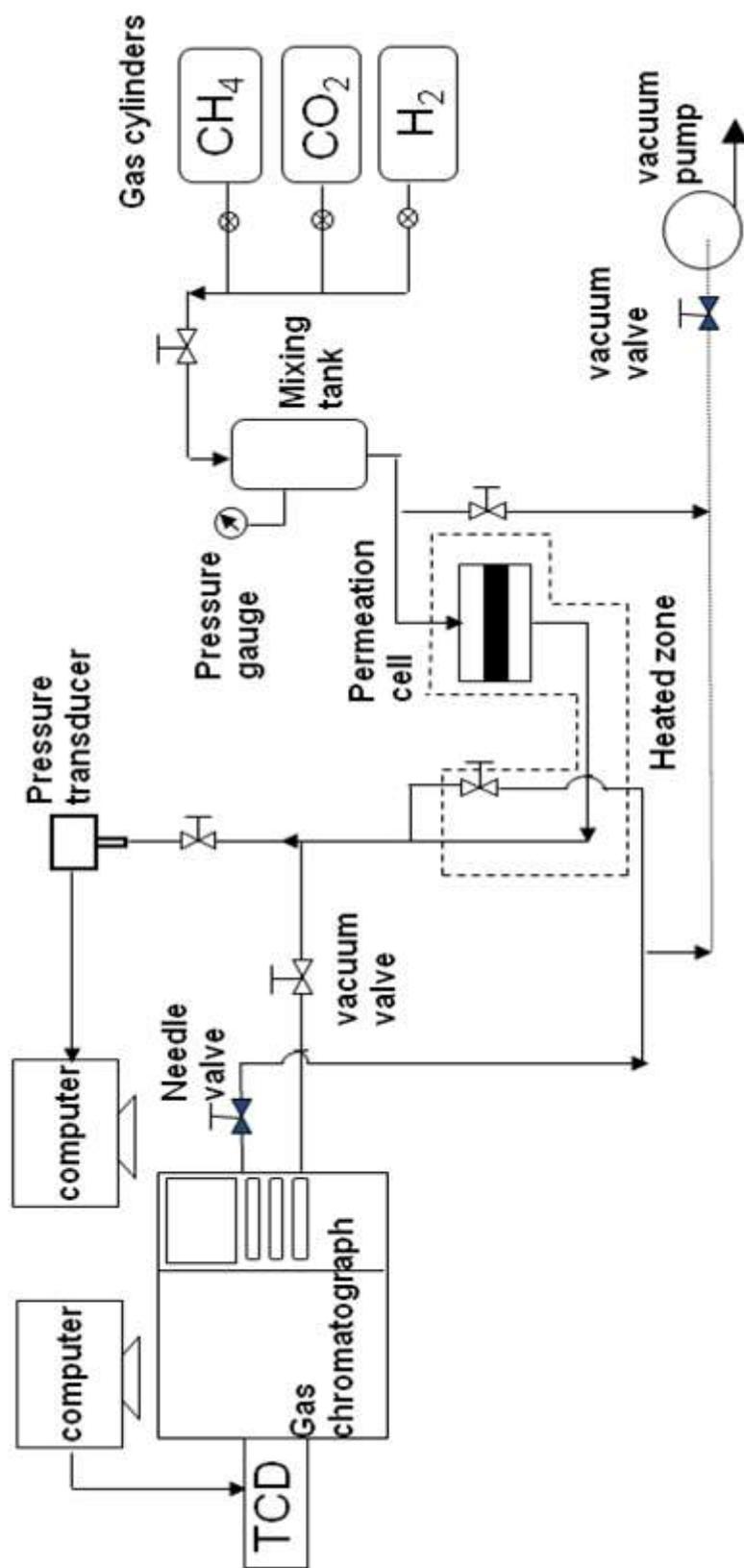


Figure 3.3 Schematic representation of the gas permeation set-up.

For separation of binary gas mixtures, first, a binary gas mixture with desired feed compositions was prepared in the feed tank by using the pressure gauge at the inlet. To obtain the desired proportion, one of the gases was fed to the tank up to the corresponding pressure and then the other was sent to final pressure. The feed composition was changed between 5 and 70% (mol/mol) CO₂. Then, this mixture was fed to the membrane cell, while the permeate side was held at vacuum (1.32×10^{-5} bar). The pressure rise at the permeate side of the membrane was monitored to calculate the permeability of the mixture. After the permeation finished, the permeate gas stream was analyzed online by GC followed with the analysis of the feed gas stream. Both the analysis of the feed and permeate side gas stream was held through a six-port injection valve of which operation procedure was explained in detail previously [31]. For both feed and permeate side gas stream composition analysis, at least three runs were carried out in order to confirm the compositions. Between each run, the sample loop of GC was degassed. During the analysis, the presence of air in the sample loop, even if it was a trace amount, may result in a difficulty in the determination of the compositions. Particularly, when the composition of one component in the permeate side may be very low that it may have a similar composition value with that small amount of air, the composition of this component could not be determined accurately due to the presence of air in the sample loop. To avoid this problem, the duration of degassing of the loop at the beginning of all analysis was increased. On the other hand, the presence of air only causes a problem when the composition of one of the components, here CH₄, is so low in the permeate side, namely lower than 2%.

For the quantitative analysis of feed and permeate gas mixtures, GC was calibrated with the CO₂, and CH₄ gases, separately. For each gas, a calibration curve was constructed by relating the chromatographic peak area to the measured amount of a gas, under fixed operating conditions of GC, which was stated before in detail [31]. The amount of each gas in the binary gas mixtures was determined from the chromatogram since for each single gas area corresponding to a known amount was previously determined. The calibration curves for GC were given in Appendix A. Permeate and feed gas stream compositions were used to calculate the separation selectivity of the membrane.

Before each permeation measurement, both sides of the membrane were evacuated to 1.32×10^{-5} bar by a 2-stage mechanical vacuum pump (Model E2M5, Edwards High Vacuum Pump) until the membrane was free of any residual gas from the previous permeation test.

3.4.3 Permeability and Selectivity Calculations

Since the selectivity and permeability calculations for single gas permeation experiments were interpreted by our research group in detail [31], it will not be explained here any further. Briefly, the algorithm used for single gas permeability calculation is given in Appendix B.

For binary gas permeation experiments, evaluation of the permeability was also explained before [31]. The same calculation methodology was used here. However, as a difference, for the calculation of separation selectivity, six different methods were used. The difference of using six different methods arose from low permeate composition of slow gas, CH₄, depending on feed composition of the mixture. For instance, in the case of high CO₂ feed concentration, the CO₂ permeate concentration gets higher than 97% whereas the CH₄ permeate concentration gets smaller than 2%. In such cases, the analysis of gas mixtures with GC may lead to difficulties because of low sensitivity of TCD of GC in He carrier gas. High concentration of CO₂ in the permeate may limit the accuracy of CH₄ concentration measurements because of the limitations in detection sensitivity. Moreover, as stated before, the presence of even low amounts of air in the permeate side introduced by the system leak may result in difficulties when measuring the CH₄ permeate concentration. These limitations may then affect the separation selectivity calculations. Therefore, besides using the feed and permeate compositions obtained as GC outputs, the separation selectivities of the membranes are also calculated with a different method. In this method, first, the measured permeate and feed side compositions of CH₄ obtained as GC outputs are used and the CO₂ compositions are calculated as $(1 - y_{\text{CH}_4})$. Then, the measured compositions of CO₂ obtained as GC outputs are taken as data, and the CH₄ compositions are calculated similarly. In addition to the selectivity calculations, the permeabilities are calculated using these composition values. As an example, the calculation of both the permeability of each component in the binary gas mixture and the separation selectivity using these six different methods are shown in Appendix C.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Material Selection

4.1.1 Polymer Selection

High gas flux and gas pair selectivity are the most important criteria for selecting polymeric materials for gas separation. Other factors affecting the selection of polymer may include chemical resistance, good mechanical strength, thermal stability, manufacturing reproducibility, and economical aspects [3, 85]. In this study, polyethersulfone (PES) was selected as the polymer matrix. PES is a well-known high performance engineering thermoplastic that has good mechanical and film forming properties as well as excellent thermal and chemical stability [86-89]. Furthermore, it is a glassy polymer with a high glass transition temperature of 220°C, indicating that it retains its integrity at elevated temperatures. PES exhibits high selectivity coefficients and acceptable permeability values for the separation of gas mixtures. Namely, it has CO₂ and CH₄ permeabilities of 3.38 and 0.112 Barrer [19], respectively, and CO₂/CH₄ selectivities of about 30 [19, 54] which are higher than the selectivities of commonly used polymeric membranes such as polycarbonate and polysulfone [86]. Moreover, unlike other glassy polymeric materials, the plasticization pressure of PES is sufficiently high. It is not plasticized up to about 25 bar in pure CO₂ [90, 91]. Therefore, PES is an excellent candidate as the polymer matrix.

4.1.2 Filler Selection

The pore size of the zeolite and the affinity of the permeating molecules toward the zeolite material are two significant properties determining the filler selection. The zeolite

used in this research is SAPO-34. It is an aluminosilicate material and has a chabazite structure with eight-ring windows and pore size of 0.38 nm [92], which is the same kinetic diameter as CH₄ (0.38 nm) and larger than CO₂ (0.33 nm) [8]. Hence, CO₂ is expected to permeate through the SAPO-34 pores, whereas CH₄ molecules are restricted. Moreover, adsorption isotherms of 1-2 μm sized SAPO-34 powder for both CO₂ and CH₄, obtained from IGA analysis was reported in Figure 4.1. Our data showed that CO₂ adsorbed more strongly than CH₄ on SAPO-34 crystals. The difference between the amounts of CO₂ and CH₄ adsorbed were higher in comparison with the difference of amounts adsorbed on zeolite 4A crystals [17, 93], most frequently used zeolite in mixed matrix membrane preparation. As a consequence, SAPO-34 is a good choice for CO₂/CH₄ separation and MMMs prepared with this zeolite are expected to have high CO₂/CH₄ selectivities due to a combination of differences in diffusivity and competitive adsorption. Moreover, the number of the studies using SAPO-34 as filler for the preparation of mixed matrix membranes is very limited, although there are many studies on SAPO-34 based zeolitic membranes [94, 95].

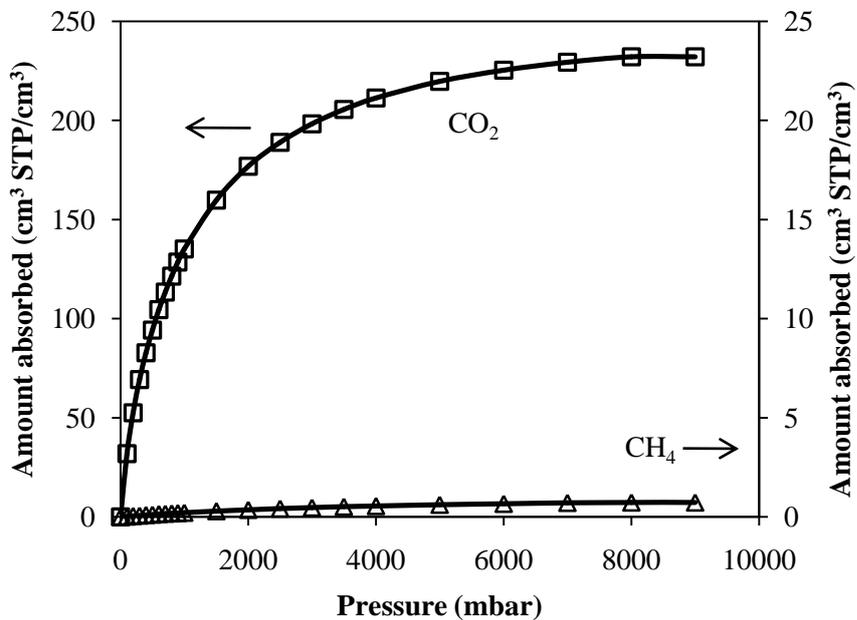


Figure 4.1 Adsorption isotherms for CO₂ and CH₄ at 35°C on SAPO-34 powder.

Moreover, the adsorption isotherms of the pure PES membrane, and PES/SAPO-34(20%) MMM for CO₂ and CH₄, obtained from IGA, was reported in Figure 4.2 and 4.3. Our data showed that the amount of CO₂ and CH₄ adsorbed increased with increasing pressure for both type of membranes. In addition, the amount of the sorbed CO₂ and CH₄ is greater for PES/SAPO-34 (20%) MMM than pure PES membrane.

4.1.3 LMWA Selection

Main criteria for the selection of suitable low molecular weight additive (LMWA) for a mixed matrix membrane formulation is that, it must have multifunctional groups capable of interacting with both polymer and filler [25]. Based on a screening of different types of LMWAs carried out by our research group [96], in this study, 2-hydroxy 5-methyl aniline (HMA) was selected as a LMWA. HMA has amine and hydroxyl groups, which may interact physically with both polymer and zeolite [20], thereby resulting in improving the separation properties of the membrane. Moreover, HMA is highly soluble in DMF, which is an advantage for membrane preparation. In addition, it has a high melting point, which enables to produce stable membranes, avoiding the evaporation of the compound during membrane annealing.

4.2 Membrane Characterization

4.2.1 DSC Results

The glass transition temperatures of pure PES, PES/HMA (4, 10% w/w), PES/SAPO-34 (20% w/w), and PES/SAPO-34 (20% w/w)/HMA (4, 10% w/w) MMMs were determined with differential scanning calorimetry (DSC) according to the procedure described in Chapter 3. The second scan DSC thermograms of the membranes were given in Appendix D. T_g values of at least two samples, for every type of membrane were determined and reported in Table 4.1. As also given in the literature [83], the T_g of pure PES membrane is measured as 220°C. With HMA addition into the pure PES membrane, the T_g of the membrane was significantly lowered. The higher the HMA loading, the lower the T_g of the membrane. The additives that have very low glass transition temperatures diluted the PES matrix, and decreased the glass transition temperature of the membranes [25]. The

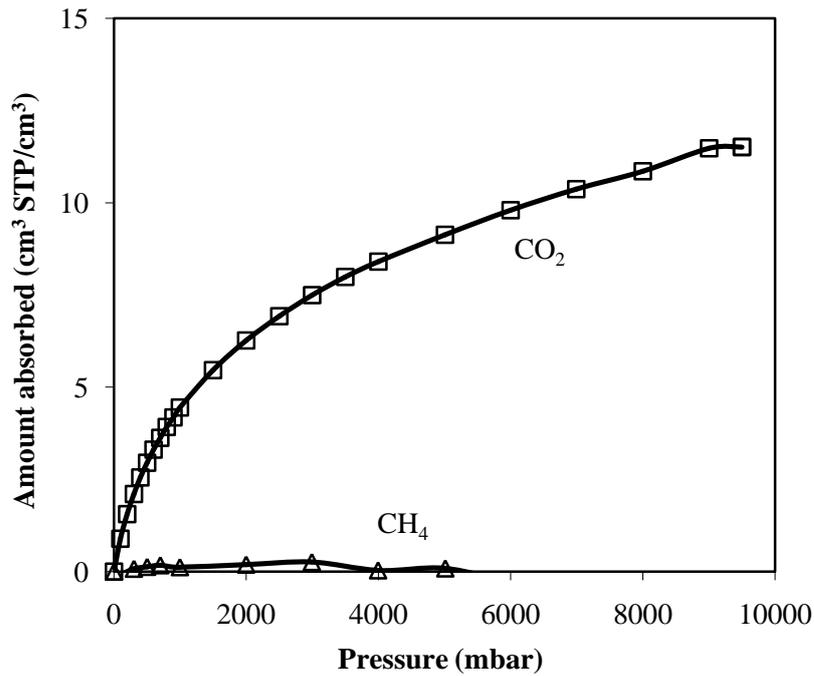


Figure 4.2 Adsorption isotherms for CO₂ and CH₄ at room temperature for pure PES membrane.

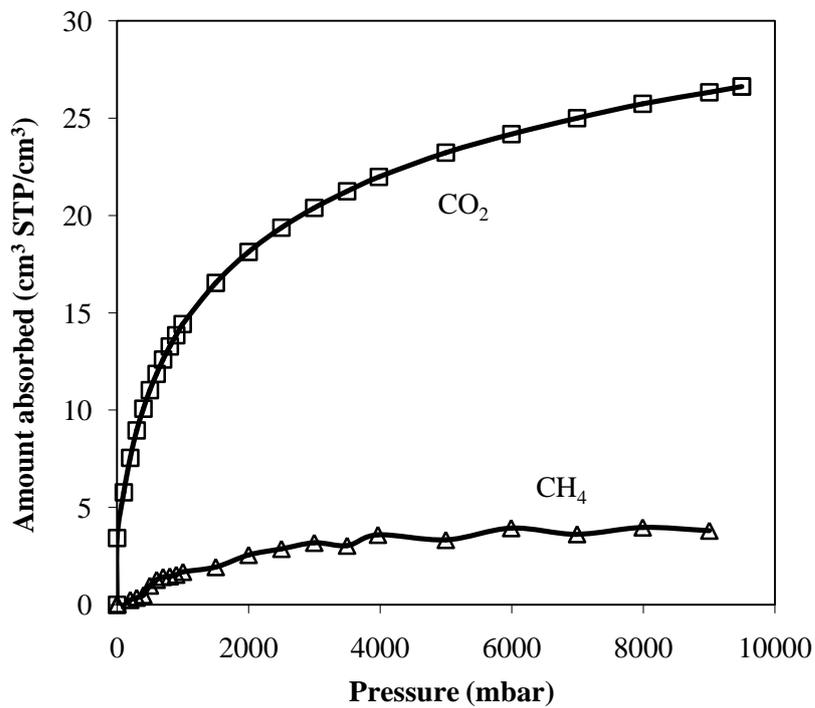


Figure 4.3 Adsorption isotherms for CO₂ and CH₄ at room temperature for PES/SAPO-34 (20%) MMM.

Table 4.1 Glass transition temperatures of different type of membranes used in this work.

Membrane Type	HMA Composition (%w/w)	SAPO-34 Composition (%w/w)	T _g (°C)
Pure PES	-	-	220
PES/HMA	4	-	205
	10	-	190
PES/SAPO-34	-	20	220
PES/SAPO-34/HMA	4	20	208
	10	20	196

effect of HMA on the T_g of PES membrane is similar to the effect of different LMWAs on glassy polymers [18, 22-25]. Like the other additives reported [20, 22-25, 62, 97-102], HMA acted as an antiplasticizer in the PES membrane matrix. On the other hand, the T_g of the membrane did not change with SAPO-34 zeolite addition in the absence of HMA, suggesting that there is no significant interaction between PES chains and SAPO-34 particles. A similar conclusion was also reached previously for PC/4A [31] and PES/4A MMMs [32]. The T_g of PES/HMA/SAPO-34 MMMs is lower than the T_g of PES/SAPO-34 MMM but higher than PES/HMA membrane. The increment in the T_g of PES/HMA membrane with the incorporation of SAPO-34 may be attributed to an interaction between the polymer matrix and SAPO-34 particles [31]. Therefore, it can be claimed that PES and SAPO-34 particles is likely to interact only in the presence of HMA, and HMA is necessary for SAPO-34 to affect the PES matrix [31]. Moreover, the T_g increment with the incorporation of SAPO-34 to the PES/HMA membrane is higher for the membranes containing higher amount of HMA. The T_g increment with increasing HMA amount can be correlated with the degree of interaction between the polymer chain and SAPO-34 crystals. Similar findings were reported for PC/4A/pNA MMM when pNA amount was increased from 1% to 5% [31]. Therefore, it can be concluded that addition of a suitable LMWA to the formulation of a mixed matrix membrane strongly affects its final structure.

4.2.2 TGA Results

For a dense membrane obtained by evaporation of the solvent, the amount of residual solvent in the membrane can have quite different effects on the final properties of the membrane [103]. The residual solvent may act as a plasticizer or an antiplasticizer, upon the gas separation properties of polymeric membranes, thereby altering the gas separation properties of the membranes [17, 103-105]. Therefore, in order to investigate whether or not any solvent remained in the membrane, the membranes were characterized with thermal gravimetric analyzer. Thermogravimetric analysis was performed with a heating rate of 10°C/min in the temperature range from 30 to 300°C in N₂ atmosphere. The weight losses of all membranes used are shown in Table 4.2. Also the thermograms for all membranes are given in Appendix E.

Table 4.2 The weight losses of different type of membranes used in this work.

Membrane Type	Weight Loss Up to 150°C (%)	Weight Loss After 150°C (%)	Total Weight Loss (%)
Pure PES	0.8	2.5	3.5
PES/HMA (4%)	0.7	5.5	6.3
PES/HMA (10%)	0.6	8.3	8.9
PES/SAPO-34(20%)	4.6	2.9	7.5
PES/SAPO-34(20%)/ HMA (4%)	4.1	4.6	8.7
PES/SAPO-34(20%)/ HMA (10%)	4.2	6.9	11.3

Nearly all weight loss of pure PES membrane is after 150°C which may be due to solvent loss or decomposition of the polymer. For PES/HMA membranes, similar trend is observed, but this time the weight loss is greater because of the possible decomposition of HMA in addition to the decomposition of polymer after 150°C. As shown in Figure 4.4, pure HMA powder starts to decompose after about 150°C. Therefore, significant portion of weight loss of HMA containing membranes after 150°C may be due to the decomposition of HMA. The membranes containing SAPO-34 molecules lost

approximately 4% of their weight up to 150°C which may arise from the loss of solvent and other impurities trapped in the membrane matrix due to the presence of SAPO-34 molecules. On the other hand, the amount of the weight losses after 150°C in the samples containing SAPO-34 molecules change according to membrane type. These weight losses may be attributed to solvent loss since DMF has a boiling point of 153°C. In addition to solvent loss, decomposition of HMA may contribute to these weight losses.

As stated in section 3.2, SAPO-34 was added with a loading of 20% (w/w) on solvent free basis according to the polymer loading. In order to determine the fraction of zeolite in the final membrane, the samples are burned off by heating the films up to 900°C. The result for PES/SAPO-34(20%) MMM is given in Figure 4.5. As can be seen, the weight loss due to the existence of the polymer is about 80%, which means that the fraction of SAPO-34 in the membrane determined by TGA is in good agreement with the fraction of SAPO-34 added into the membrane solution during membrane formulation.

4.2.3 SEM Results

The membranes were characterized with scanning electron microscopy (SEM) to determine the membrane morphology and to examine the polymer-zeolite interface. SEM is a commonly used tool for researchers investigating the interfacial phenomena in mixed matrix membranes. As mentioned earlier, the studies up to now usually observe larger voids, and these voids may reduce the selectivity and increase the permeability due to the increased transport through the interfacial voids. Although SEM analysis could not resolve Angstrom-sized voids which are believed to exist in some samples, larger voids between the polymer and zeolite can be recognized using the SEM.

Figure 4.6 shows the SEM images of pure PES membrane and PES/HMA membranes with HMA concentration of 4% and 10%. The cross-section views show smooth and clean morphology. The membranes have dense structures, and no pores were observed at these magnifications. Moreover, the images of both types of membranes are similar to each other which indicate that the homogeneous structure of membrane still exists with the addition of HMA into PES polymer matrix.

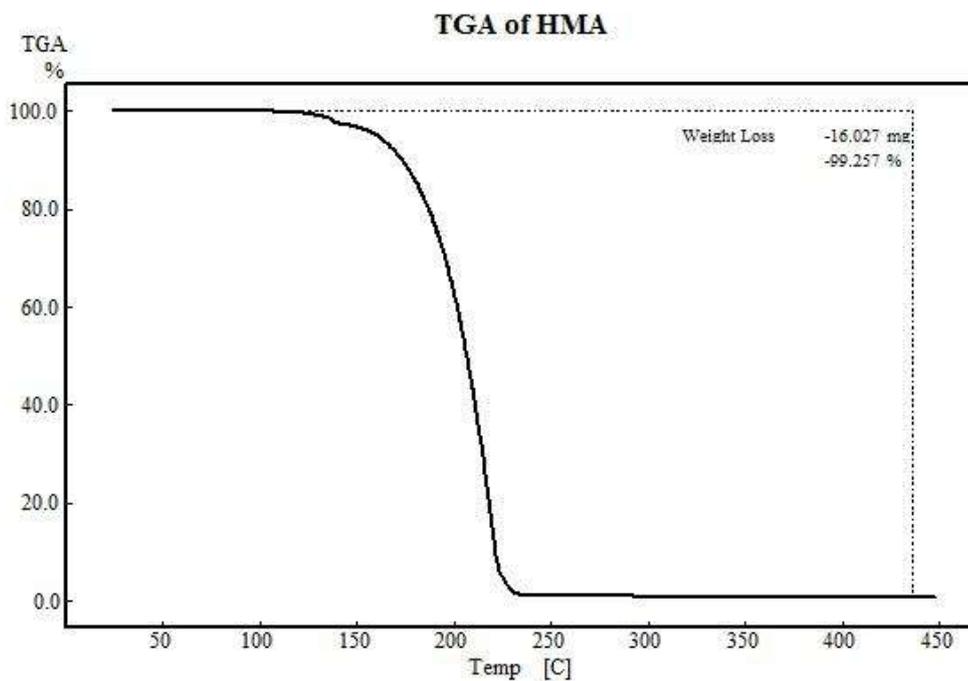


Figure 4.4 TGA graph of HMA.

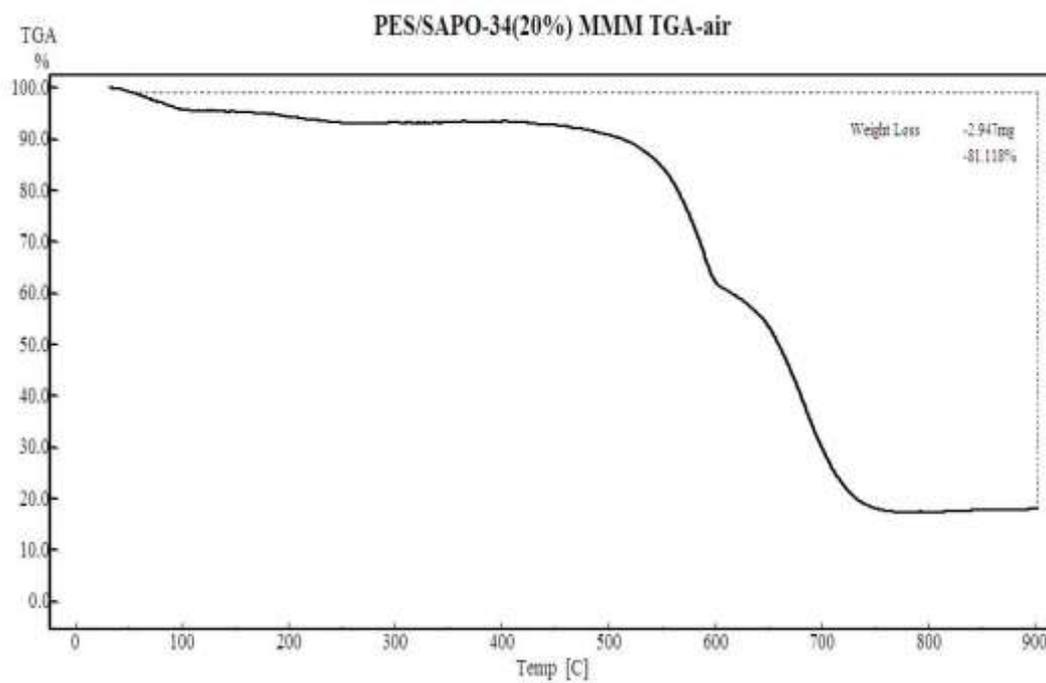


Figure 4.5 TGA graph of PES/SAPO-34(20%) MMM.

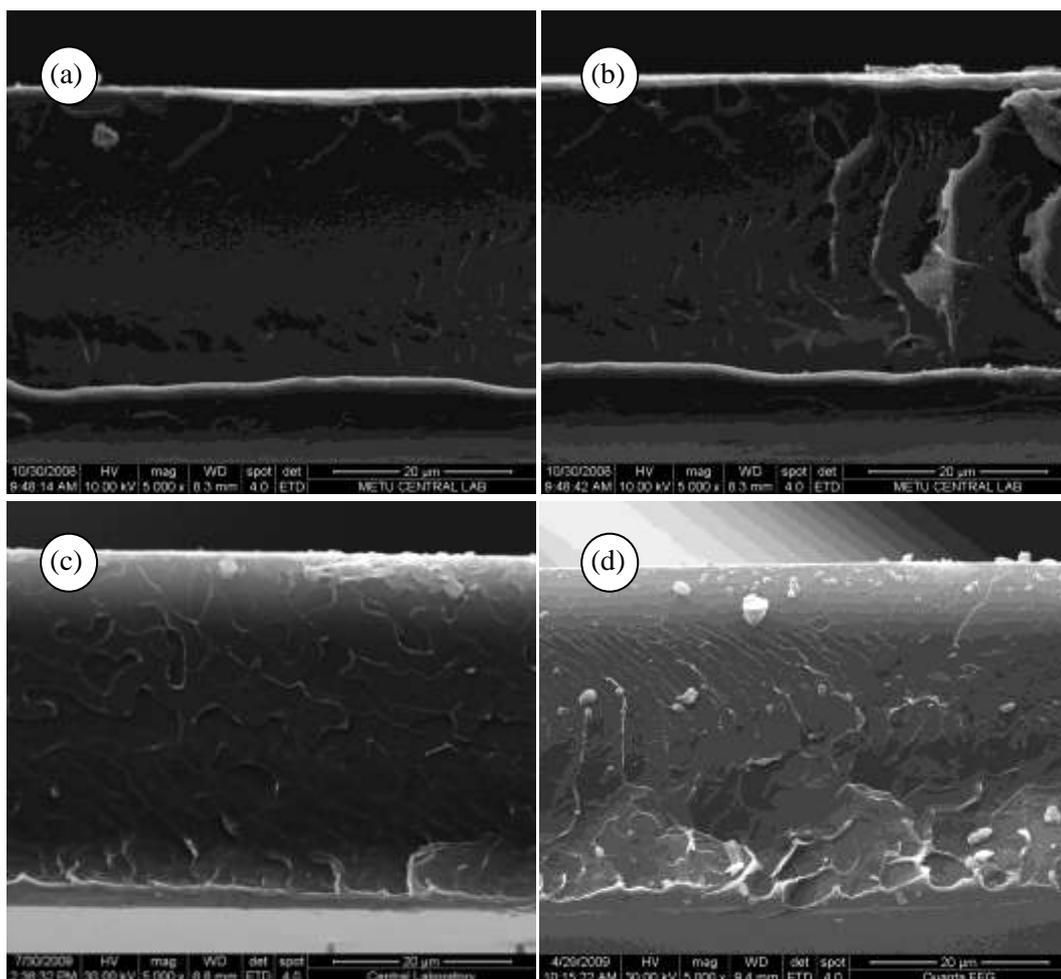


Figure 4.6 SEM images of the cross-section of pure PES (a, b), PES/HMA (4%) (c), and PES/HMA (10%) (d) membranes, respectively.

Figure 4.7 shows the SEM images of PES/SAPO-34 MMM. Unlike pure PES and PES/HMA membranes, the images show heterogeneous structures, where the cubic particles are SAPO-34 crystals, and the continuous phase is PES matrix. The SAPO-34 crystals have a narrow particle size distribution changing between 1-2 μm . They are homogeneously distributed throughout the PES matrix without forming agglomerates. However, SEM images at high magnifications reveal that some of the interfacial region around some zeolite particles appears to form voids. This morphology may possibly be resulted from poor compatibility between the zeolite particles and the polymer matrix [13, 16, 19, 20, 44, 55, 57], as well as from freeze fracturing during sample preparation [43].

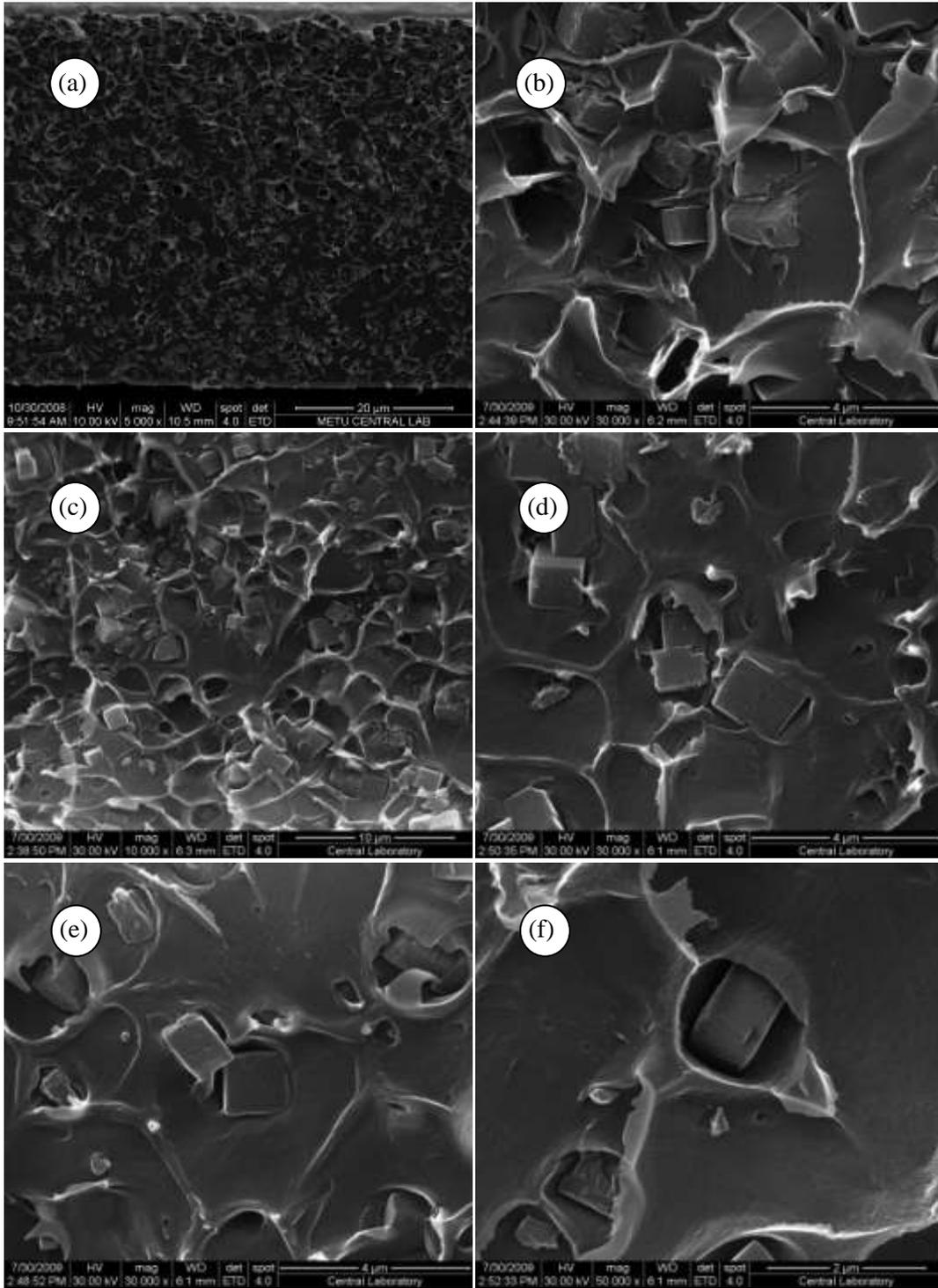


Figure 4.7 SEM images of cross-section at low magnification (a, and c), and cross-section at high magnification (b, d, e, and f) of PES/SAPO-34 (20%) MMMs.

Figure 4.8 shows the cross-sectional SEM images of PES/SAPO-34/HMA MMMs at a constant SAPO-34 loading of 20% with HMA loadings of 4 and 10% respectively. Similar to PES/SAPO-34(20%) MMMs, SAPO-34 crystals were uniformly distributed throughout PES matrix for all PES/SAPO-34/HMA MMMs independent from HMA loading. In addition, relative to PES/SAPO-34 (20%) MMMs, the interfacial voids were reduced to some extent. In addition, with the increase in HMA loading from 4% to 10%, the voids were eliminated further. Thus, the incorporation of LMWAs can enhance the compatibility between zeolite and polymer [31].

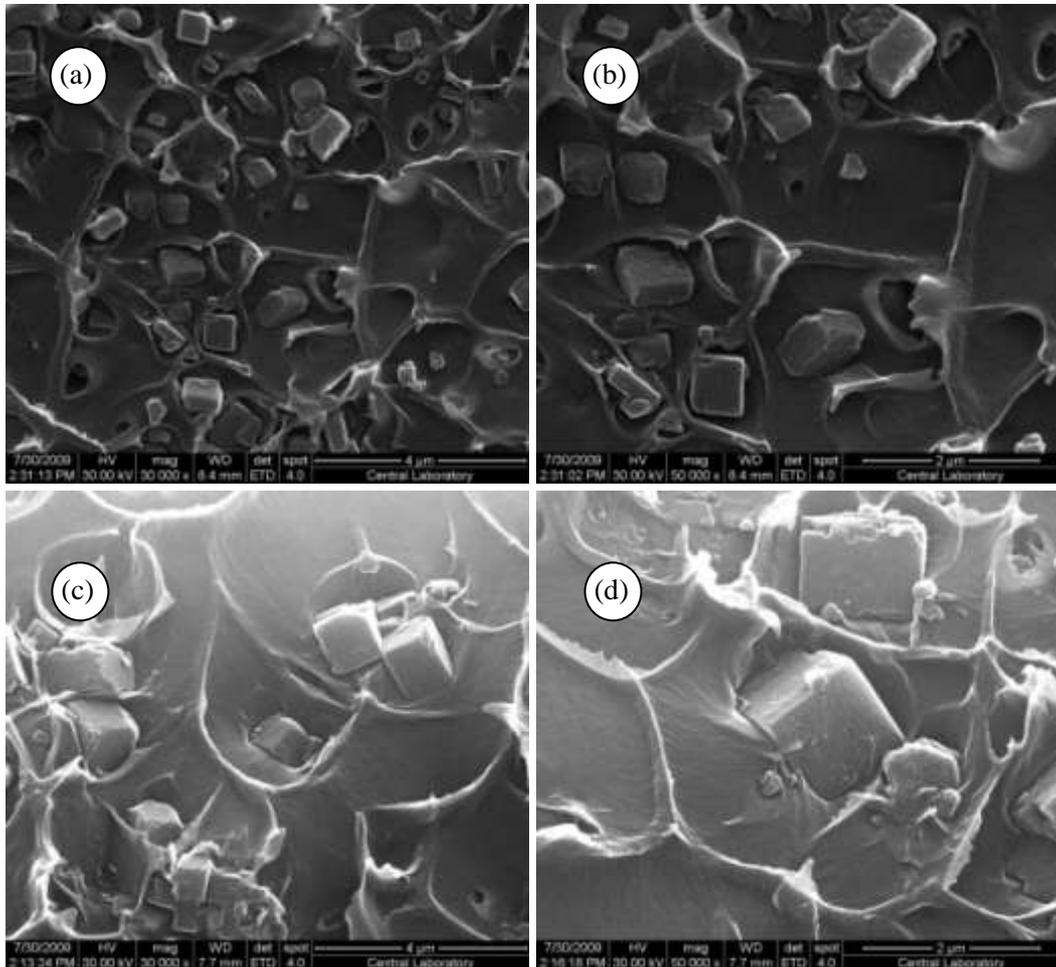


Figure 4.8 SEM images of cross-section at low magnification (a and c), and cross-section at high magnification (b, and d) of PES/SAPO-34/HMA MMMs at constant SAPO-34 loading of 20%, and HMA loading of 4% and 10%, respectively.

4.3 Single Gas Permeation Results

The permeabilities of single gases were measured by using a constant volume-variable pressure technique at 35°C. The feed side pressure was kept at 3.0 bar and the permeate side was initially at vacuum, 0.01 Torr (1.33×10^{-5} bar). The pressure rise at the permeate side with time was recorded. As stated before, the evaluation of the data and the calculation steps were explained earlier [31]. The algorithm for single gas permeability calculation is given in Appendix B. The same calculation methodology was used here.

The single gas permeabilities and ideal selectivities of all membranes used are given in Table 4.3. These results are the average values of at least two membranes for all types. For all the membranes, two parts of membrane from the same film were also tested. Hence, the reproducibility of membrane preparation was examined. In addition, the permeability of each gas through a given membrane was measured twice, in order to investigate the repeatability of permeability measurements. The reproducibility experiment results of the membranes were given in Appendix F. The relative standard deviation was found about 8.0% for CH₄, 5% for CO₂ and 4% for H₂. These results are similar to the standard deviations reported in the literature [25, 55], and confirm the reproducibility of the membrane preparation and testing methods.

The addition of HMA into the pure PES membrane resulted in decreasing permeabilities of all gases. When the amount of HMA increased, the permeabilities decreased further. The largest decreases were observed in CO₂ and CH₄ permeabilities which caused sharp increases in H₂/CO₂ and H₂/CH₄ selectivities. Nevertheless, CO₂/CH₄ selectivity remained nearly constant around the ideal selectivity of pure PES membrane demonstrating that addition of HMA mainly affected size selectivity. The similar trends were observed by Şen et al. with the incorporation of pNA into the pure PC membrane [31]. The effect of such additives on polymer matrix is explained by antiplasticization phenomena [97, 98] which leads to a reduction in free volume, restricts the movement of polymer chains, and increases stiffness, hence decreases the permeability [22-24, 62, 63, 97-102]. It may be speculated that the addition of HMA does not only leads to a reduction in free volume, but also results in a change of free volume distribution in the membrane which may explain observed increases in size selectivities. Therefore, it can be concluded that HMA, like other LMWAs reported [20, 22-25, 62, 63, 97-102], antiplasticized the PES matrix.

Table 4.3 Single gas permeability and ideal selectivity results of PES, PES/HMA, PES/SAPO-34, and PES/SAPO-34/HMA MMMs.

% weight of SAPO-34	% weight of HMA	Permeability (Barrer)			Ideal Selectivity		
		H ₂	CO ₂	CH ₄	H ₂ /CO ₂	H ₂ /CH ₄	CO ₂ /CH ₄
0	0	8.94	4.45	0.134	2.01	66.7	33.2
0	4	5.72	1.99	0.058	2.87	98.6	34.3
0	10	3.38	0.84	0.026	4.02	130.0	32.3
20	0	12.92	5.77	0.156	2.24	82.8	37.0
20	4	7.26	2.07	0.051	3.51	142.4	40.6
20	10	5.30	1.34	0.030	3.96	176.7	44.7

Interestingly, SAPO-34 addition improved both the permeabilities of all gases and the selectivities with respect to pure PES membrane. The highest increase was observed in H₂ permeability. However, in many studies [19, 21, 44, 50, 54, 82], the opposite trend had been shown in terms of permeabilities of the same gases; the addition of zeolite brings about decreasing permeabilities which is usually explained with either the pore blockage of the zeolites by the polymer chains [19, 44] or rigidified polymer region [44, 82]. This shows the effect of membrane preparation conditions to the separation properties of the membranes, even the same polymer was used as polymer matrix. On the other hand, as stated in Chapter 2, increasing permeabilities is usually attributed to formation of voids which can be due to both weak polymer-sieve interaction and the stresses generated during solvent removal [18]. However, in our case, also the selectivities of all gas pairs increased, which may be an indication of a more complex morphology. Generally, improved selectivities have been reported with the addition of zeolites into the glassy polymer membranes [16, 18, 54]. Furthermore, Sürer et al. [55] observed increasing selectivities with zeolite addition which they ascribed to adsorption affinity of zeolites to CO₂ gas molecules. In our case, the increase in both selectivity and permeability results suggest that a fraction of the zeolites are well-adhered to the polymer matrix while a

fraction may exhibit a “leaky” interface [81]. Moreover, both the molecular sieving effect of SAPO-34 molecules and high adsorption capacity of CO₂ on SAPO-34 molecules may contribute to the increased separation performance of PES/SAPO-34 MMMs relative to pure PES membranes. In other words, the enhancement in the membrane separation performances can be related with the complex heterogeneous morphology of the membranes. On the other hand, SEM micrographs pointed to the existence of a “leaky” interface as well as well-adhered zeolites. From DSC characterization, as concluded earlier, the same T_g value of PES/SAPO-34 MMM as pure PES membrane may be due to absence of a significant interaction between PES chains and SAPO-34 particles. It can be concluded that the addition of SAPO-34 into the pure PES polymer improved the membrane separation properties.

Table 4.3 also shows the separation performance of PES/SAPO-34/HMA MMMs. The permeabilities of all gases through PES/SAPO-34/HMA MMMs were lower than those through pure PES membrane. As the HMA concentration was increased at constant zeolite content, the extent of decrease in the permeabilities increased. The changes in the permeabilities can be correlated with the kinetic diameter of the permeating gas. The largest decrease was in the permeability of CH₄, and the lowest decrease was in the permeability of H₂, which resulted in a subsequent improvement in the selectivity of H₂/CH₄. In addition, the selectivities of H₂/CO₂ and CO₂/CH₄ increased when compared with those for pure PES membrane. The selectivities of all gas pairs were improved with addition of both SAPO-34 and HMA molecules into the pure PES membrane matrix, and as the HMA loading increased from 4% to 10% at a constant zeolite content, the extent of the enhancement in the selectivities increased. Similar selectivity improvements for different MMMs have been reported with addition of zeolite and LMWA to the pure polymer matrix [20, 21]. The enhancement was generally attributed to the complex membrane morphology which enables an improvement in the adhesion between the polymer and zeolite with HMA addition, and the decrease in the permeabilities of all gases may be due to this improved adhesion. Therefore, it can be concluded that the incorporation of zeolite and LMWA together to the membrane matrix created a synergy and has a higher contribution to the membrane performance than their individual addition to the membrane matrix [21]. The PES/SAPO-34/HMA MMMs worked better among the other types of membranes in terms of separation performance of the membranes. The separation performances of used membranes were shown in Figure 4.9 with reference to

the upper bound lines for H_2/CH_4 . Performance improvement was especially remarkable with the incorporation of zeolite and LMWA together to the pure PES membrane. Similar trend was observed with the addition of zeolite 4A and pNA to the pure PC membrane [31]. Although the performance values for PES/SAPO-34/HMA MMMs were still under the Robeson's upper bound for H_2/CH_4 , they show a better trade-off between permeability and selectivity than the pure PES membrane, indicating the potential of mixed matrix membranes.

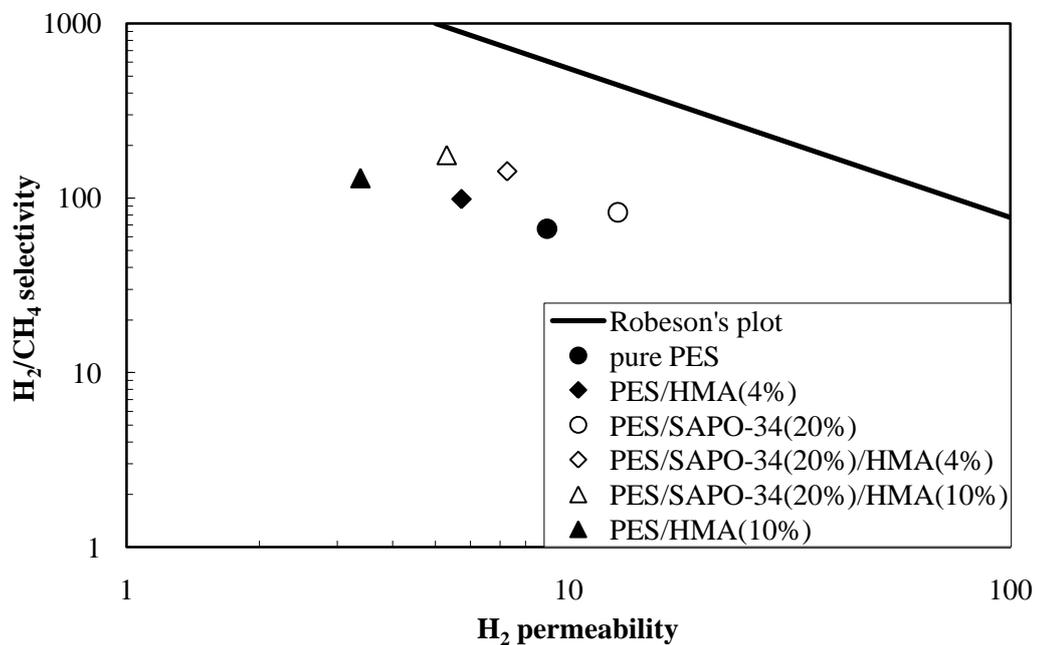


Figure 4.9 H_2/CH_4 selectivity and H_2 permeability of used membranes on a Robeson's upper bound trade-off curve.

4.4 Binary Gas Permeation Results

The research on the performance of homogeneous and mixed matrix membranes dealing with the separation of gas mixtures is limited, although it is well accepted that the presence of a more than one gaseous component and composition variations of gas

mixtures may affect the separation performance of the membranes. Therefore, in this study, separation of binary gas mixtures was also investigated. The effect of feed composition on the performance of MMMs was examined. All types of membranes used in single gas permeation tests, namely pure PES, PES/HMA (4%), PES/SAPO-34(20%), PES/SAPO-34(20%)/HMA (4%), and PES/SAPO-34(20%)/HMA (10%) were also used for the separation of binary gas mixtures. The performance of these membranes was investigated systematically for the separation of CO₂/CH₄ gas mixtures. A feed composition range of CO₂ as wide as possible was studied. Since high CO₂ feed concentration results in very high CO₂ permeate concentration, thereby limiting the accuracy of CH₄ concentration measurements because of the limitations in detection sensitivity, studied CO₂ concentration range was limited with an upper value.

The binary gas permeation experiments were conducted at the same set-up where single gas permeation experiments were held. The operating conditions are the same as single gas permeation experiments; the feed side pressure was kept at 3.0 bar and the permeate side was initially at vacuum, 0.01 Torr (1.33×10^{-5} bar). As explained before, the pressure rise at the permeate side of the membrane was monitored to calculate the permeability of the mixture. After the permeation, the permeated gas was analyzed by an online GC. The feed gas stream was analyzed twice, before and after the permeation in order to be sure that the feed side gas compositions remained constant throughout the permeation. During both permeate and feed side composition analysis, at least three runs were performed in order to obtain reliable results and the average values of these runs were reported as the permeate and feed side composition value. Permeate and feed gas stream compositions were used to calculate the separation selectivity of the membrane.

The calculation steps and the evaluation of the binary gas permeability were explained earlier [31]. The same calculation methodology was used here. However, as a difference, for the calculation of separation selectivity, six different methods were used, and six different separation selectivity values were obtained. The necessity for these methods arose due to low CH₄ composition at the permeate side. When the CH₄ composition is below 2%, the analysis of permeate gas mixtures with GC becomes difficult because of the limitations in detection sensitivity of TCD of GC in He carrier gas. These limitations may then affect the separation selectivity calculations. Therefore, in such cases, the evaluation of the separation selectivities using six different methods may be helpful. This

is explained in Appendix C in detail. Also, the calculation of both the permeability of each component in the binary gas mixture and the separation selectivity is shown in Appendix C. In addition, the permeate and feed gas stream compositions measured by gas chromatograph for all types of membranes used were given in Appendix G with the separation selectivities calculated using with these composition values. The separation selectivities reported in the following sections are the average values of these six different separation selectivities, and all separation selectivities, calculated by six different methods show the same trends as a function of feed composition for all of the membranes investigated, although their absolute values may vary slightly.

4.4.1 Binary Gas Permeation of Dense Homogeneous PES Membranes

The effect of CO₂ feed gas composition on the separation performance of dense homogenous PES membranes was investigated by changing CO₂ feed gas composition between 10 and 60% (mol/mol). Table 4.4 and Figure 4.10 (a) show the CO₂/CH₄ binary gas permeabilities and separation selectivities of pure PES membranes. The mixture permeabilities were always between the permeabilities of pure CO₂ and CH₄. As the composition of CO₂ in the feed gas mixture was increased, the mixture permeability increased owing to the increased partial pressure of CO₂. On the other hand, the separation selectivities of the membranes remained nearly constant slightly below the ideal selectivity of the membrane which may be caused by concentration polarization. The composition independency of the selectivities of dense homogeneous polymeric membranes was previously reported [31, 32] which was attributed to absence of the gas phase non-idealities and competition in sorption and diffusion among CO₂ and CH₄ in the membrane matrix because of the gas-membrane matrix and gas-gas-membrane matrix interactions. However, some researchers reported increasing separation selectivities with increasing CO₂ feed composition for different polymeric membranes [26, 79, 80]. Although they all prepared dense homogeneous polymeric membranes with solvent evaporation similar to our case, the variation of the operation conditions may cause different trends in separation selectivity with composition changes. For instance, Sridhar et al. [79] reported increasing separation selectivities for pure PC membranes at 30°C with a feed pressure of 20 bar. They explained increasing selectivities with greater sorption of CO₂ in the polymer matrix through plasticization/swelling. On the other hand, Şen et al. [31] observed no change with increasing CO₂ feed composition for the

polymeric membrane prepared using the same polymer at room temperature with a feed pressure of 3 bar. These studies show that not only the type of polymer matrix but also the operation conditions affecting the membrane structure and transport mechanism play an important role on the separation performances of dense homogeneous polymer membranes with the feed gas composition changes.

4.4.2 Binary Gas Permeation of PES/HMA Membranes

The effect of CO₂ feed gas composition on the separation performance of PES/HMA membranes were investigated with CO₂/CH₄ binary gas mixture by changing CO₂ feed gas composition between 5 and 70 % (mol/mol). Table 4.5 and Figure 4.10 (b) show the CO₂/CH₄ binary gas permeabilities and separation selectivities of PES/HMA membranes. Similar with the trend in the permeability of pure PES membrane, the mixture permeabilities increased with increasing concentration of CO₂ in the feed, while the CO₂/CH₄ separation selectivities of the membranes remained nearly constant, but unlike pure PES membranes, this time they were around the ideal selectivity of the membrane. These observations are similar to that reported by Şen et al. investigating the effect of CO₂ feed concentration on PC/pNA membranes [31]. The independent behavior of the selectivities of PES/HMA membranes on feed gas composition may point to the non-interactive nature of gas permeation through these membranes [31]. This means that, similar for pure PES membranes, due to the absence of gas-membrane matrix and gas-gas-membrane matrix interactions through these membranes, the separation selectivities did not change with CO₂ feed concentration [31, 32, 46]. Moreover, the permeabilities of both CO₂ and CH₄ in the mixture did not change with CO₂ concentration in the feed. From the point of view of single gas permeation and T_g measurement results, addition of HMA strongly changed the structure and performance properties of the PES membranes due to its antiplasticization effect on PES membrane matrix. However, the composition independency of selectivities for PES/HMA membranes may be explained with the dense homogeneous morphology of these membranes. They may act as a newly developed pure polymer membranes for binary gas mixture separations [31].

Table 4.4 Effect of feed composition on permeabilities and selectivities of CO₂/CH₄ binary gas mixture through pure PES membrane* (measured at 35°C, with a pressure difference of 3.0 bar).

	CO ₂ concentration in the feed (%mol/mol)									
	0	10	20	30	40	50	60	70	80	100
Permeability, Barrer	0.134	0.37	0.84	1.41	2.02	2.50	3.08	3.08	4.45	
α_{CO_2/CH_4}	-	23.7	30.1	31.0	24.9	27.5	27.1	-		

* CO₂/CH₄ ideal selectivity is 33.2

Table 4.5 Effect of feed composition on permeabilities and selectivities of CO₂/CH₄ binary gas mixture through PES/HMA (4%) membrane* (measured at 35°C, with a pressure difference of 3.0 bar).

	CO ₂ concentration in the feed (%mol/mol)											
	0	5	10	15	20	26	30	42	52	63	70	100
Permeability, Barrer	0.058	0.11	0.20	0.29	0.36	0.54	0.63	0.82	1.02	1.15	1.35	1.99
α_{CO_2/CH_4}	-	33.8	33.6	33.4	32.1	38.5	38.7	38.1	39.8	39.4	46.6	42.3

* CO₂/CH₄ ideal selectivity is 34.3

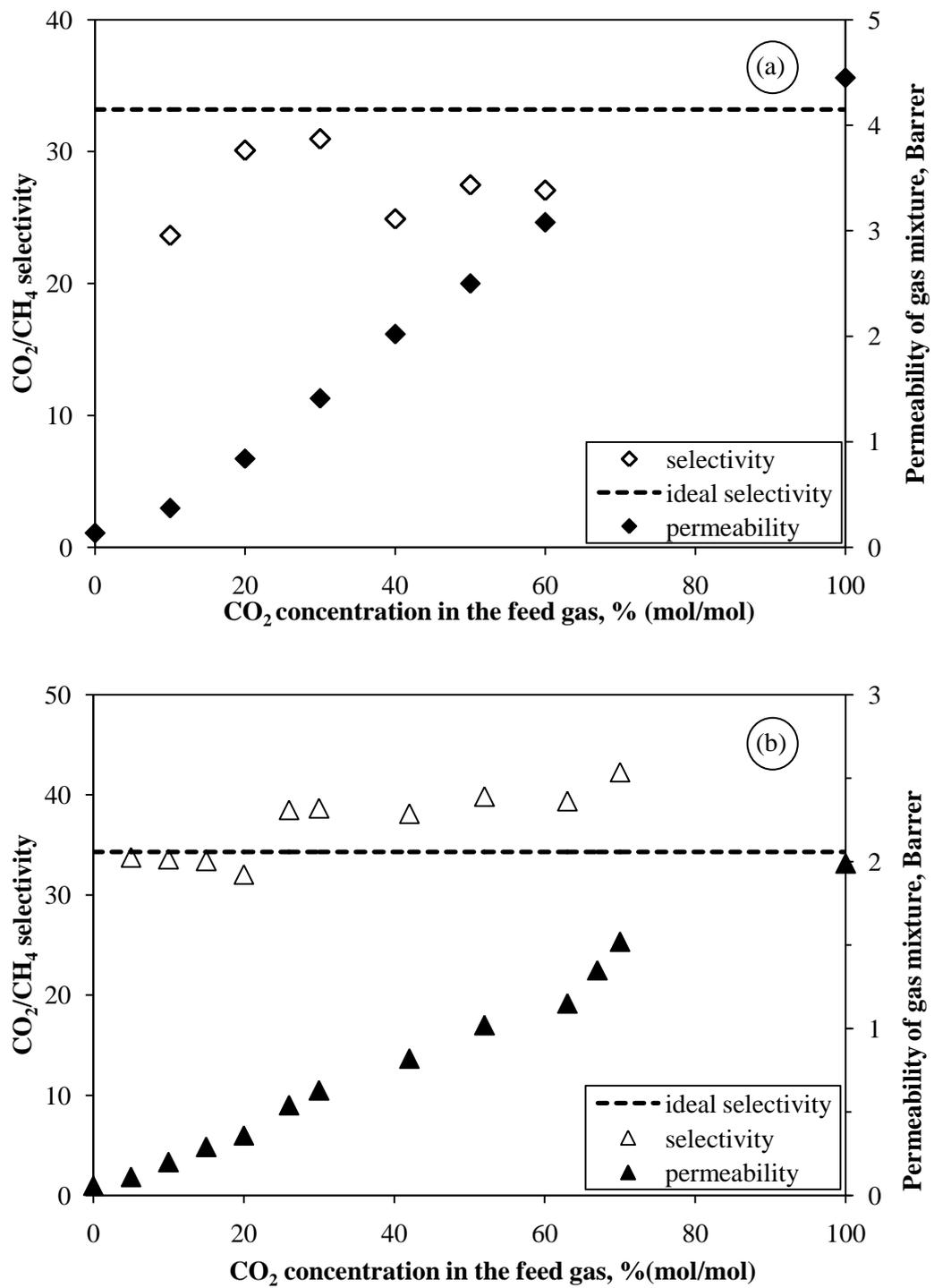


Figure 4.10 Effect of feed composition on permeability and selectivity for CO₂/CH₄ binary gas mixture through pure PES membrane (a), and PES/HMA membrane (b).

4.4.3 Binary Gas Permeation of PES/SAPO-34 MMMs

The effect of CO₂ composition in the feed on the separation performance of PES/SAPO-34 MMMs were investigated by changing CO₂ feed gas composition in CO₂/CH₄ mixture between 5 and 72 % (mol/mol). Table 4.6 and Figure 4.11 show the CO₂/CH₄ binary gas permeabilities and separation selectivities of PES/SAPO-34 MMMs, respectively.

As in the case of the permeabilities of pure PES and PES/HMA membrane, the mixture permeabilities increased with increasing concentration of CO₂ in the feed, while the CO₂/CH₄ separation selectivities of PES/SAPO-34 MMMs remained nearly constant, but slightly lower than the ideal selectivity of the membrane. The lower separation selectivity observation is not surprising since separation selectivities obtained for mixed gas tests are usually reported to be lower than ideal selectivities [64-66, 71, 72-79] due to several reasons such as the competition for sorption sites between the penetrants, plasticization phenomena, and concentration polarization [70, 71, 77], as explained in literature section in detail. The presence of less permeable gas, CH₄, may reduce the permeability of more permeable gas, CO₂. This then results in a lower separation selectivity compared to the ideal selectivity [64, 72]. However, the observation of composition independency of the separation selectivities is surprising. The separation selectivities would increase with increasing CO₂ feed concentration due to greater sorption of the gas in the membrane owing to the availability of more number of CO₂ molecules for interaction with the membrane and possible pore blockage effect by CO₂, inhibiting the permeation of CH₄. This is generally observed for SAPO-34 molecular sieve membranes in the mixed gas feed experiments [94, 95]. However, in the case of mixed matrix membrane, the absence of improvement in separation selectivities may be due to low sorption of CO₂ in the particles in the PES/SAPO-34 MMMs as compared to the SAPO-34 membranes. Jha and Way [82] observed similar behaviour in PPZ/SAPO-34 MMMs, and they proposed that the reason for low sorption of CO₂ in the zeolite particles when in the mixed matrix phase could be due to the low absorption of CO₂ in the polymer. Moreover, they even carried out CO₂/CH₄ binary gas experiments with different feed volume fraction of CO₂ at experimental conditions of higher pressure (4.3 bar) and low temperature (-15°C) to maximize the equilibrium sorption of CO₂ in the membranes. However, they could not obtain improved selectivities at these conditions which were still not favorable to restrict the transport of CH₄ through the pores of SAPO-34 particles by adsorption of CO₂.

Table 4.6 Effect of feed composition on permeabilities and selectivities of CO₂/CH₄ binary gas mixture through PES/SAPO-34(20%) MMM* (measured at 35°C, with a pressure difference of 3.0 bar).

	CO ₂ concentration in the feed (%mol/mol)							
	0	5	10	31	41	52	72	100
Permeability, Barrer	0.156	0.350	0.525	1.55	2.19	2.83	5.21	5.77
Selectivity, (CO ₂ /CH ₄)		33.2	33.6	31.1	31.1	34.3	37.7	

* CO₂/CH₄ ideal selectivity is 37.0

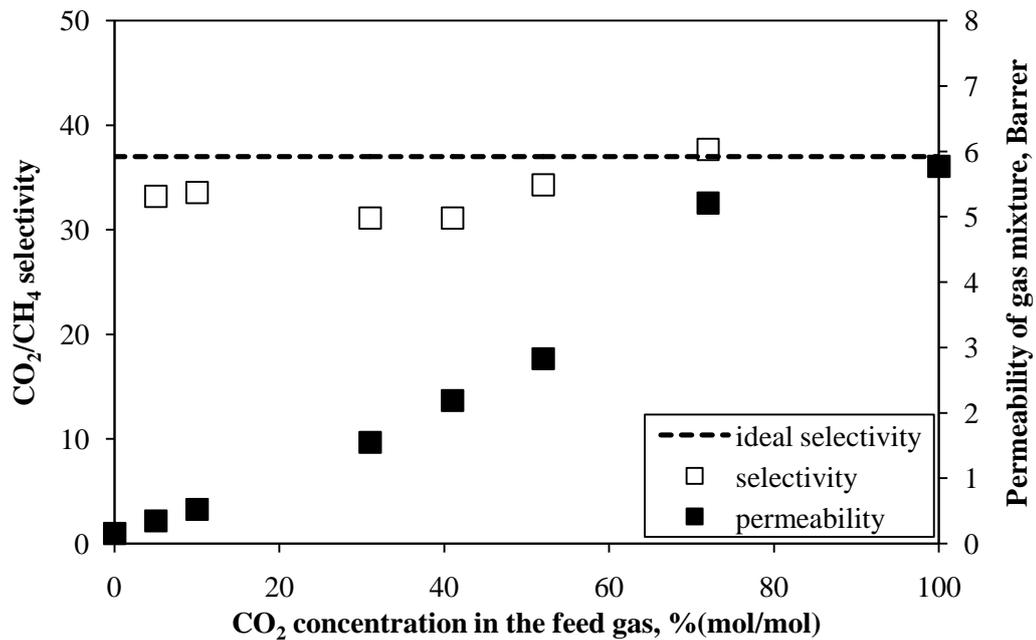


Figure 4.11 Effect of feed composition on the separation selectivity of CO₂/CH₄ through PES/SAPO-34 (20%) MMMs.

Another scenario can be related with the complex heterogeneous morphology of the PES/SAPO-34 MMMs. Due to both pore size and adsorption capacity, CO₂ permeation is favored through SAPO-34 molecules in the membrane matrix. However, changes in PES/SAPO-34 MMM performance are not only due to the intrinsic properties of zeolite particles, but also depend on the final morphology of the polymer-zeolite MMMs, including the polymer-zeolite interface morphology [31]. “Tailoring interfacial morphology is a difficult problem frequently encountered in composite materials, but it is especially challenging for membranes since small changes in interfacial morphology can lead to dramatic changes in transport properties” [17].

In fact, generally separation selectivities are reported to be concentration dependent in many studies with different type of membranes [27, 28, 30-32, 43, 70, 75, 79, 80, 106]. For instance, Battal et al. [32] reported strongly decreasing separation selectivities with increasing CO₂ feed composition for PES/4A MMMs due to self-inhibition of CO₂ as a consequence of saturation of the active sites of the zeolite at high CO₂ concentration. However, in our case, the composition independency of separation selectivities may be due to the absence of competition between CO₂ and CH₄ molecules for the sorption sites since there are sufficient active sites in the SAPO-34 crystals on the membrane. In other words, the interaction potential of CO₂ with the membrane matrix is not affected with CO₂ feed composition due to the sufficient sorption sites in the membrane matrix. Besides, since CH₄ molecules are already not able to use SAPO-34 molecules as a pathway due to its size, both CO₂ and CH₄ molecules behave as if they are permeating as a single gas.

As a consequence, the composition independency of the separation selectivities of PES/SAPO-34 MMMs is very promising especially for membrane development studies. Also absence of a strong decrease of selectivity with CO₂ composition increase is a sign of better performance and may increase possibility of industrial applications, especially for feeds with fluctuating compositions.

4.4.4 Binary Gas Permeation of PES/SAPO-34/HMA MMMs

Effect of feed gas composition on the separation performance of PES/SAPO-34/HMA MMMs were investigated with CO₂/CH₄ binary gas mixture for a feed gas composition changing between 10 and 60% (mol/mol) CO₂. Table 4.7, 4.8 and Figure 4.12 (a), (b) show the CO₂/CH₄ binary gas permeabilities and separation selectivities of PES/SAPO-34/HMA MMMs with HMA loading of 4 and 10% at a constant SAPO-34 loading of 20%, respectively.

Similarly with the trend of permeabilities of other types of membranes, the permeabilities of PES/SAPO-34/HMA MMMs increased with increasing CO₂ feed gas concentration. Moreover, the trend in the separation selectivities is similar with the trend of separation selectivities of other types of membranes. The separation selectivities did not change so much when compared with ideal selectivities. The inalterability of the separation selectivities with increasing CO₂ feed gas concentration is more prominent when HMA loading increased from 4% to 10% in the mixed matrix membrane. In addition to this, PES/SAPO-34/HMA MMMs with 10% loading of HMA concentration showed higher separation selectivities. As stated before for the composition independency of separation selectivities of the other types of the membranes, the composition independency of separation selectivities of these types of membranes may be due to the absence of competition between CO₂ and CH₄ molecules. SEM studies also revealed that for these membranes, the contact between SAPO-34 molecules and the polymer matrix was better due to the incorporation of HMA, relative to PES/SAPO-34 MMMs.

Table 4.7 Effect of feed composition on permeabilities and selectivities of CO₂/CH₄ binary gas mixture through PES/SAPO-34(20%)/HMA(4%) MMM* (measured at 35°C, with a pressure difference of 3.0 bar).

	CO ₂ concentration in the feed (%mol/mol)						
	0	10	30	41	51	60	100
Permeability, Barrer	0.051	0.183	0.65	0.94	1.13	1.41	2.07
α_{CO_2/CH_4}	34.9	30.1	49.1	40.9	39.3		

* CO₂/CH₄ ideal selectivity is 40.6

53

Table 4.8 Effect of feed composition on permeabilities and selectivities of CO₂/CH₄ binary gas mixture through PES/SAPO-34(20%)/HMA(10%) MMM* (measured at 35°C, with a pressure difference of 3.0 bar).

	CO ₂ concentration in the feed (%mol/mol)							
	0	11	20	31	40	50	60	100
Permeability, Barrer	0.030	0.13	0.23	0.41	0.57	0.72	0.85	1.34
α_{CO_2/CH_4}	36.0	36.9	38.7	46.3	44.7	43.0		

* CO₂/CH₄ ideal selectivity is 44.7

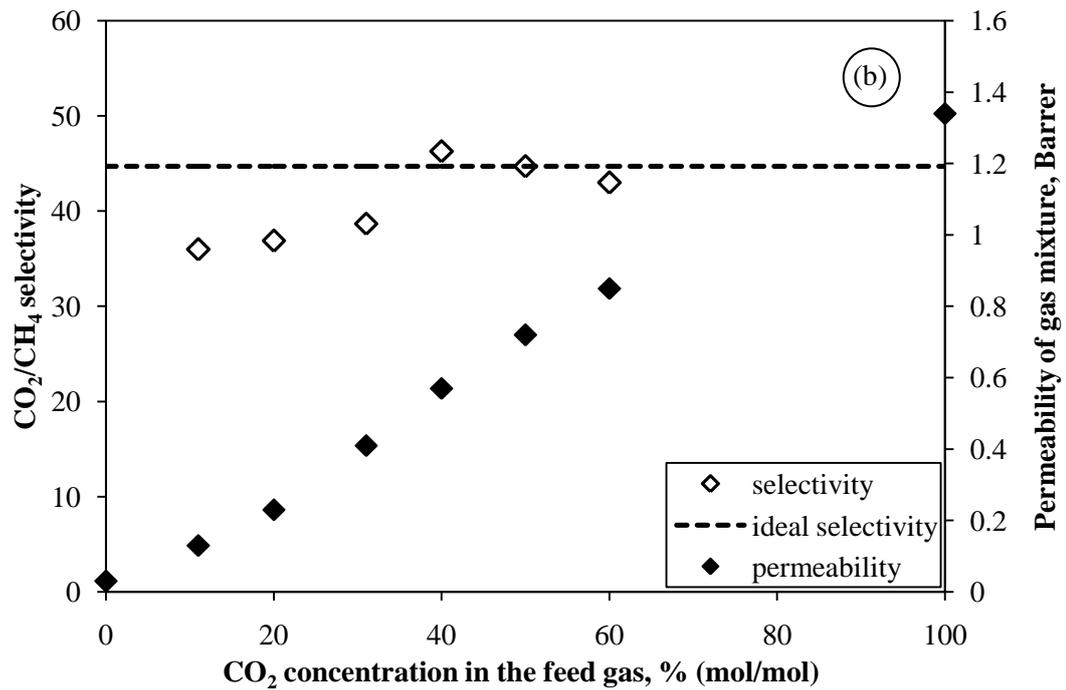
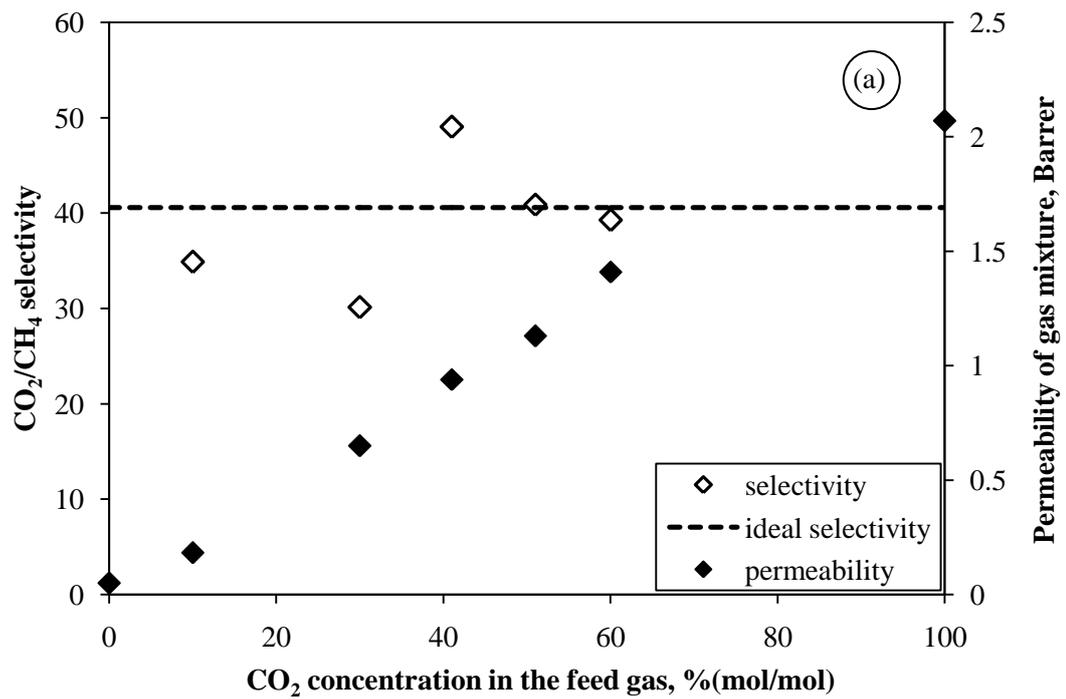


Figure 4.12 Effect of feed composition on permeability and selectivity for CO₂/CH₄ binary gas mixture through PES/SAPO-34(20%)/HMA (4%) MMM (a), and PES/SAPO-34(20%)/HMA (10%) MMM (b).

4.4.5 General Performance Comparison of Membranes

The CO₂/CH₄ binary gas measurement experiments showed that the mixture permeability of membranes depend strongly on feed composition. The mixture permeability of all types of membranes increased with an increase in CO₂ feed concentration due to increasing partial pressure of CO₂. Particularly, PES/SAPO-34 MMMs showed the highest mixture permeability with increasing CO₂ feed concentration.

On the other hand, separation selectivities generally observed to be independent from feed composition. The CO₂/CH₄ binary gas experiments of pure PES membranes exhibited constant separation selectivity around 25 with different feed compositions of CO₂ but lower than the ideal selectivity of the membrane, with HMA incorporation to the pure PES membrane matrix, the separation selectivities again did not change with different feed compositions of CO₂, but in this case, they were around the ideal selectivity of the membrane. As SAPO-34 zeolite was added to the pure PES membrane matrix, the separation selectivities did not change with different feed compositions, but they were higher than the mixture selectivities of pure PES membrane. Moreover, the composition independency of these membranes eliminates the need of investigating at which feed gas composition the prepared membranes are best performing for practical applications. From this point of view, SAPO-34 crystals incorporated PES mixed matrix membranes are far better than the most used zeolite 4A incorporated PES mixed matrix membranes. When both SAPO-34 and HMA were added to the pure PES membrane, similar with the results of single gas permeation experiments, the separation selectivities increased when compared with other types of membranes, and when HMA loading increased from 4% to 10%, the selectivities increased further. Consequently, PES/SAPO-34/HMA MMMs with HMA loading of 10% and SAPO-34 loading of 20% demonstrated the highest separation selectivity among the used membranes.

CHAPTER 5

CONCLUSIONS

In this study, mixed matrix membranes were prepared by using polyethersulfone as a polymer matrix, and SAPO-34 crystals as filler with a multifunctional low molecular-weight additive, HMA to use for CO₂/CH₄ separation. The effect of CO₂ composition in the feed on the separation performances of different types of membranes was investigated in detail. The following conclusions were obtained:

1. Selective mixed matrix membranes with high performances using polyethersulfone as polymer matrix incorporated SAPO-34 crystals as filler with a multifunctional low molecular-weight additive, HMA, were obtained with a constant SAPO-34 concentration of 20% (w/w) and HMA concentration of 4% and 10% (w/w).
2. Using HMA as a multifunctional low molecular-weight additive did work to some extent for the elimination of voids that may be formed at the polymer-zeolite interface.
3. The ideal selectivities of membranes increased considerably but the permeabilities of the gases through the membranes decreased due to antiplasticization effect of HMA. With the incorporation of SAPO-34 crystals, the separation performance of the membranes improved. The best selectivity improvement was obtained with the incorporation of both HMA and SAPO-34 crystals to the PES membrane.
4. For all types of membranes used, the effect of feed composition did not appreciably affect the separation performance of the membranes, thus eliminating the need of investigating at which composition the membrane has the best separation performance especially for industrial applications. For about all types of membranes used, the separation selectivities stayed constant around the ideal selectivities of the membranes, which is an advantage for designing and evaluating a membrane separation system.

REFERENCES

- [1] Chenar, M.P., Soltanieh, M., Matsuura, T., Tabe-Mohammadi A., Khulbe, K.C., "The effect of water vapor on the performance of commercial polyphenylene oxide and Cardo-type polyimide hollow fiber membranes in CO₂/CH₄ separation applications" *Journal of Membrane Science*, 285, 2006, p. 265-271.
- [2] Baker, R.W., "Natural gas processing with membranes: An overview", *Ind. Eng. Chem. Res.*, 47, 2008, p. 2109-2121.
- [3] Xiao, Y., Low, B.T., Hosseini, S.S., Chung, T.S., Paul, D.R., "The strategies of molecular architecture and modification of polyimide-based membranes for CO₂ removal from natural gas-A review", *Progress in Polymer Science*, 34, 2009, p. 561-580.
- [4] Mohammadi, A., "A review of the applications of membrane separation technology in natural gas treatment", *Separation Science and Technology*, 34, 1999, p. 2095-2111.
- [5] Bernardo, P., Drioli, E., Golemme, G., "Membrane gas separation: A review/state of the art", *Ind. Eng. Chem. Res.*, 48, 2009, p. 4638-4663.
- [6] Feng, H., Zhang, H., Xu, L., "Polymeric membranes for natural gas conditioning", *Energy Sources, Part A*, 29, 2007, p. 1269-1278.
- [7] Vu, D.Q., "Formation and Characterization of Asymmetric Carbon Molecular Sieve and Mixed Matrix Membranes for Natural Gas Purification", PhD Thesis, The University of Texas at Austin, December 2001.
- [8] Mulder, M., "Basic Principles of Membrane Technology", Kluwer Academic Publishers, Second edition, 1997, Dordrecht.
- [9] Liu, C., Kulprathipanja, S., Hillock, A.M.W., Husain, S., Koros, W.J., "Chapter 30, Recent progress in Mixed Matrix Membranes", *Advanced Membrane Technology and Applications*, John Wiley & Sons, Inc 2008.
- [10] Robeson, L.M., "Correlation of separation factor versus permeability for polymeric membranes", *Journal of Membrane Science*, 62, 1991, p. 165-185.

- [11] Chung, T.S., Jiang, L.Y., Li, Y., Kulprathipanja, S., "Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation", *Prog. Polym. Sci.* 32, 2007, p. 483-507.
- [12] Ahn, J., Chung, W.J., Pinnau, I., Guiver, M.D., "Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation", *Journal of Membrane Science* 314, 2008, p. 123-133.
- [13] Moore, T.T., Koros, W.J., "Non-ideal effects in organic-inorganic materials for gas separation membranes", *Journal of Molecular Structure*, 739, 2005, p. 87-98.
- [14] Moore, T.T., Mahajan, R., Vu, D.Q., Koros, W.J., "Hybrid membrane materials comprising organic polymers with rigid dispersed phases", *AIChE Journal*, 50, 2004, p. 311-321.
- [15] Cornelius, C.J., Marand, E., "Hybrid silica-polyimide composite membranes: gas transport properties", *Journal of Membrane Science*, 202, 2002, p. 97-118.
- [16] Mahajan, R., Koros, W.J., "Mixed matrix membrane materials with glassy polymers. Part 1", *Polymer Engineering and Science*, 42, 2002, p. 1420-1431.
- [17] Moore, T.T., "Effects of Materials, Processing, And Operating Conditions On The Morphology And Gas Transport Properties Of Mixed Matrix Membranes", PhD Thesis, The University of Texas at Austin, December 2004.
- [18] Mahajan, R., Burns, R., Schaeffer, M., Koros, W.J., "Challenges in forming successful mixed matrix membranes with rigid polymeric materials", *Journal of Applied Polymer Science*, 86, 2002, p. 881-890.
- [19] Huang, Z., Li, Y., Wen, R., Teoh, M.M., Kulprathipanja, S., "Enhanced gas separation properties by using nanostructured PES-zeolite 4A mixed matrix membranes", *Journal of Applied Polymer Science*, 101, 2006, p. 3800-3805.
- [20] Yong, H.H., Park, H.C., Kang, Y.S., Won, J., Kim, W.N., "Zeolite-filled polyimide membrane containing 2,4,6-triaminopyrimidine", *Journal of Membrane Science*, 188, 2001, p. 151-163.
- [21] Şen, D., Kalıpçılar, H., Yılmaz, L., "Development of polycarbonate based zeolite 4A filled mixed matrix gas separation membranes", *Journal of Membrane Science*, 303, 2007, p. 194-203.

- [22] Ruiz-Treviño, F.A., Paul, D.R., “Modification of polysulfone gas separation membranes by additives”, *Journal of Applied Polymer Science*, 66, 1997, p. 1925-1941.
- [23] Ruiz-Treviño, F.A., Paul, D.R., “Gas permselectivity properties of high free volume polymers modified by a low molecular weight additive”, *Journal of Applied Polymer Science*, 68, 1998, p. 403-415.
- [24] Larocca, N.M., Pessan, L.A., “Effect of antiplasticization on the volumetric, gas sorption and transport properties of polyetherimide”, *Journal of Membrane Science*, 218, 2003, p. 69-92.
- [25] Şen, D., Kalıpçılar, H., Yılmaz, L., “Gas separation performance of Polycarbonate membranes modified with multifunctional low molecular-weight additives”, *Separation Science and Technology*, 41, 2006, p.1813-1828.
- [26] Dhingra, S.S., “Mixed gas transport study through polymeric membranes: A novel technique”, PhD Thesis, Virginia Polytechnic Institute and State University, June 1997.
- [27] Wu, F., Li, L., Xu, Z., Tan, S., Zhang, Z., “Transport study of pure and mixed gases through PDMS membrane”, *Chemical Engineering Journal*, 117, 2006, p. 51-59.
- [28] Ettouney, H., Majeed, U., “Permeability functions for pure and mixture gases in silicone rubber and polysulfone membranes: Dependence on pressure and composition”, *Journal of Membrane Science*, 135, 1997, p. 251-261.
- [29] Raharjo, R.D., Freeman, B.D., Paul, D.R., Sarti, G.C., Sanders, E.S., “Pure and mixed gas CH₄ and *n*-C₄H₁₀ permeability and diffusivity in poly(dimethylsiloxane)”, *Journal of Membrane Science*, 306, 2007, p. 75-92.
- [30] Yeom, C.K., Lee, S.H., Lee, J.M., “Study of transport of pure and mixed CO₂/N₂ gases through polymeric membranes”, *Journal of Applied Polymer Science*, 78, 2000, p. 179-189.
- [31] Şen, D., “Polycarbonate Based Zeolite 4A Filled Mixed Matrix Membranes: Preparation, Characterization, and Gas Separation Performances”, PhD Thesis, Middle East Technical University, February 2008.
- [32] Battal, T., Baç, N., Yılmaz, L., “Effect of feed composition on the performance of polymer-zeolite mixed matrix gas separation membranes”, *Separation Science and Technology*, 30, 1995, p. 2365-2384.

- [33] Moore, T.T., Damle, S., Wallace, D., Koros, W.J., "The Engineering Handbook", 2nd edition, CRC Press LLC, 2005.
- [34] Damle, S., "Membrane Based Separations of Carbon Dioxide and Phenol under Supercritical Conditions", PhD Thesis, The University of Texas at Austin, May 2004.
- [35] Nunes, S.P., Peinemann, V.K., "Gas separation with membranes", In Membrane Technology in the Chemical Industry. Weinheim, Germany: Wiley-VCH, 2006.
- [36] Javaid, A., "Membranes for solubility-based gas separation applications", Chemical Engineering Journal, 112, 2005, p. 219-226.
- [37] Pandey, P., Chauhan, R.S., "Membranes for gas separation", Prog. Polym. Sci., 26, 2001, p. 853-893.
- [38] Freeman, B.D., "Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes", Macromolecules, 32, 1999, p. 375-380.
- [39] Mahajan, R., "Formation, Characterization, and Modeling of Mixed Matrix Membrane Materials", PhD Thesis, The University of Texas at Austin, December 2000.
- [40] Seo, Y., Kim, S., Hong, S.U., "Highly selective polymeric membranes for gas separation", Polymer, 2006, 47, p. 4501-4504.
- [41] Zhang, Y., Musselman, I.H., Ferraris, J.P., Balkus, K.J., "Gas permeability properties of Matrimid membranes containing the metal-organic framework Cu-BPY-HFS", Journal of Membrane Science, 313, 2008, p. 170-181.
- [42] Suzuki, T., Yamada, Y., "Physical and gas transport properties of novel hyper-branched polyimide-silica hybrid membranes", Polymer Bulletin, 53, 2005, p. 139-146.
- [43] Perez, E.V., Balkus, K.J., Ferraris, J.P., Musselman, I.H., "Mixed-matrix membranes containing MOF-5 for gas separations", Journal of Membrane Science, 328, 2009, p. 165-173.
- [44] Li, Y., Chung, T., Cao, C., Kulprathipanja, S., "The effects of polymer chain rigidification, zeolite pore size and pore blockage on polyethersulfone (PES)-zeolite 4A mixed matrix membranes", Journal of Membrane Science, 260, 2005, p. 45-55.

- [45] Pechar, T.W., Kim, S., Vaughan, B., Marand, E., Baranauskos, V., Riffle, J., Jeong, H.K., Tsapatsis, M., "Preparation and characterization of poly(imide-siloxane) and zeolite L mixed matrix membrane", *Journal of Membrane Science*, 277, 2006, p. 210-218.
- [46] Zhang, Y., Balkus, K.J., Musselman, I.H., Ferraris, J.P., "Mixed-matrix membranes composed of Matrimid and mesoporous ZSM-5 nanoparticles", *Journal of Membrane Science*, 325, 2008, p. 28-39.
- [47] Ersolmaz, Ş.B.T., Şenorkyan, L., Kalaonra, N., Tatlier, M., Şenatalar A.E., "*n*-Pentane/*i*-pentane separation by using zeolite PDMS mixed matrix membranes", *Journal of Membrane Science*, 189, 2001, p. 59-67.
- [48] He, Z., Pinnau, I., Morisato, A., "Nanostructured poly(4-methyl-2-pentyne)/silica hybrid membranes for gas separation", *Desalination*, 146, 2002, p. 11-15.
- [49] Mahajan, R., Koros, W.J., "Factors controlling successful formation of mixed-matrix gas separation materials", *Industrial Engineering and Chemistry Research*, 39, 2000, p. 2692-2696.
- [50] Chung, T.S., Chan, S.S., Wang, R., Lu, Z., He, C., "Characterization of permeability and sorption in Matrimid/C₆₀ mixed matrix membranes", *Journal of Membrane Science*, 211, 2003, p. 91-99.
- [51] Wang, H., Holmberg, B.A., Yan, Y., "Homogeneous polymer-zeolite nanocomposite membranes by incorporating dispersible template-removed zeolite nanocrystals", *J.Mater. Chem.*, 12, 2002, p. 3640-3643.
- [52] Hosseini, S.S., Li, Y., Chung, T.S., Liu, Y., "Enhanced gas separation performance of nanocomposite membranes using MgO nanoparticles", *Journal of Membrane Science*, 302, 2007, p.207-217.
- [53] Anson, M., Marchese, J., Garis, E., Ochoa, N., Pagliero, C., "ABS copolymer-activated carbon mixed matrix membranes for CO₂/CH₄ separation", *Journal of Membrane Science*, 243, 2004, p. 19-28.
- [54] Li, Y., Chung, T.S., Kulprathipanja, S., "Novel Ag⁺-zeolite/polymer mixed matrix membranes with a high CO₂/CH₄ selectivity", *AIChE Journal*, 53, 2007, p. 610-616.
- [55] Süer, M.G., Baç, N., Yılmaz, L., "Gas permeation characteristics of polymer-zeolite mixed matrix membranes", *Journal of Membrane Science*, 91, 1994, p. 77-86.

- [56] Hillock, A.M.W., "Crosslinkable Polyimide Mixed Matrix Membranes for Natural Gas Purification", PhD Thesis, Georgia Institute of Technology, December 2005.
- [57] Mahajan, R., Koros, W.J., "Mixed matrix membrane materials with glassy polymers. Part 2", *Polymer Engineering and Science*, 42, 2002, p. 1432-1441.
- [58] Li, Y., Guan, H-M., Chung, T.S., Kulprathipanja, S., "Effects of novel silane modification of zeolite surface on polymer chain rigidification and partial pore blockage in polyethersulfone (PES)-zeolite A mixed matrix membranes", *Journal of Membrane Science*, 275, 2006, p. 17-28.
- [59] Pechar, T.W., Tsapatsis, M., Marand, E., Davis, R., "Preparation and characterization of a glassy fluorinated polyimide zeolite mixed matrix membrane", *Desalination*, 146, 2002, p. 3-9.
- [60] Hu, C.C., Liu, T.C., Lee, K.R., Ruaan, R.C., Lai, J.Y., "Zeolite-filled PMMA composite membranes: influence of coupling agent addition on gas separation properties", *Desalination*, 193, 2006, p. 14-24.
- [61] Ismail, A.F., Rahim, R.A., Rahman, W.A.W.A., "Characterization of polyethersulfone/Matrimid 5218 miscible blend mixed matrix membranes for O₂/N₂ gas separation", *Separation and Purification Technology*, 63, 2008, p. 200-206.
- [62] Robeson, L.M., "The effect of antiplasticization on secondary loss transitions and permeability of polymers", *Polymer Engineering and Science*, 9, 1969, p. 277-281.
- [63] Li, J., Tachihara, K., Nagai, K., Nakagawa, T., Wang, S., "Selective permeation of sour gases through polymeric membranes modified by sulfolanes. I. Study of selective permeation of CO₂ through modified polymeric membranes determined on different systems", *Journal of Applied Polymer Science*, 60, 1996, p. 1645-1654.
- [64] Costello L.M., Koros W.J., "Comparison of pure and mixed gas carbon dioxide and methane permeabilities in polycarbonate: effect of temperature", *Ind. Eng. Chem. Res.*, 32, 1993, p. 2277-2280.
- [65] Wang, R., Liu, S.L., Lin, T.T., Chung, T.S., "Characterization of hollow fiber membranes in a permeator using binary gas mixtures", *Chemical Engineering Science*, 57, 2002, p. 967-976.

- [66] Visser, T., Wessling, M., "Auto and mutual plasticization in single and mixed gas C₃ transport through Matrimid-based hollow fiber membranes", *Journal of Membrane Science*, 312, 2008, p. 84-96.
- [67] Jordan, S.M., Koros, W.J., "Permeability of pure and mixed gases in silicone rubber at elevated pressures", *Journal of Polymer Science: Part B: Polymer Physics*, 28, 1990, p. 795-809.
- [68] Sanders, E.S., Koros, W.J., "Sorption of CO₂, C₂H₄, N₂O and their binary mixtures in Poly(methyl methacrylate)", *Journal of Polymer Science: Polymer Physics Edition*, 24, 1986, p. 175-188.
- [69] Sada, E., Kumazawa, H., Wang, J.S., "Permeation of binary gas mixture through glassy polymer membranes with concentration-dependent diffusivities", *Journal of Polymer Science: Part B: Polymer Physics*, 30, 1992, p. 105-111.
- [70] Chern, R.T., Koros, W.J., Yui, B., Hoppenberg, H.B., Stannet, V.T., "Selective permeation of CO₂ and CH₄ through Kapton Polyimide: Effects of penetrant competition and gas phase non-ideality", *Journal of Polymer Science: Polymer Physics Edition*, 22, 1984, p. 1061-1084.
- [71] Tin, P.S., Chung, T.S., Liu, Y., Wang, R., Liu, S.L., Pramoda, K.P. "Effects of cross-linking modification on gas separation performance of Matrimid membranes", *Journal of Membrane Science*, 225, 2003, p. 77-90.
- [72] Sridhar, S., Suryamurali, R., Smitha, B., Aminabhavi, T.M., "Development of crosslinked poly(ether-block-amide) membrane for CO₂/CH₄ separation", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 297, 2007, p. 267-274.
- [73] Donohue, M.D., Minhas, B.S., Lee, S.Y., "Permeation behavior of carbon dioxide-methane mixtures in cellulose acetate membranes", *Journal of Membrane Science*, 42, 1989, p. 197-214.
- [74] Ismail, A.F., Lorna, W., "Penetrant-induced plasticization phenomenon in glassy polymers for gas separation membrane", *Separation and Purification Technology*, 27, 2002, p. 173-194.
- [75] Bos, A., Pünt, I.G.M., Wessling, M., Strathmann, H., "Plasticization-resistant glassy polyimide membranes for CO₂/CH₄ separations", *Separation and Purification Technology*, 14, 1998, p. 27-39.

- [76] Car, A., Stropnik, C., Yave, W., Peinemann, K-V., "Pebax/polyethylene glycol blend thin film composite membranes for CO₂ separation: Performance with mixed gases", *Separation and Purification Technology*, 62, 2008, p. 110-117.
- [77] He, G., Mi, Y., Yue, P.L., Chen, G., "Theoretical study on concentration polarization in gas separation membrane processes", *Journal of Membrane Science*, 153, 1999, p. 243-258.
- [78] Bhattacharya, S., Hwang, S.T., "Concentration polarization, separation factor, and pecclet number in membrane processes", *Journal of Membrane Science*, 132, 1997, p. 73-90.
- [79] Sridhar, S., Aminabhavi, T.M., Ramakrishna, M., "Separation of binary mixtures of carbon dioxide and methane through sulfonated polycarbonate membranes", *Journal of Applied Polymer Science*, 105, 2007, p. 1749-1756.
- [80] Sridhar, S., Smitha, B., Ramakrishna, M., Aminabhavi, T.M., "Modified poly (phenylene oxide) membranes for the separation of carbon dioxide from methane", *Journal of Membrane Science*, 280, 2006, p. 202-209.
- [81] Hillock, A.M.W., Miller, S.J., Koros, W.J., "Crosslinked mixed matrix membranes for the purification of natural gas: Effects of sieve surface modification", *Journal of Membrane Science*, 314, 2008, p.193-199.
- [82] Jha, P., Way, J.D., "Carbon dioxide selective mixed-matrix membranes formulation and characterization using rubbery substituted polyphosphazene", *Journal of Membrane Science*, 324, 2008, p. 151-161.
- [83] Radel Resins Design Guide, Solvay Advanced Polymers, L.L.C., 2004.
- [84] Kotiloğlu, C., "Development of Polyether Sulfone (PES)/ SAPO-34 Mixed Matrix Membranes for Natural Gas Treatment", Poster Presentation, Euromembrane 6-10 September 2009, Montpellier, France.
- [85] Sridhar, S., Smitha, B., Aminabhavi, T.M., "Separation of carbon dioxide from natural gas mixtures through polymeric membranes- A Review", *Separation & Purification Reviews*, 36, 2007, p. 113-174.
- [86] Chiou, J.S., Maeda, Y., Paul, D.R., "Gas permeation in Polyethersulfone", *J. App. Polym. Sci.*, 33, 1987, p. 1823-1828.

- [87] Guan, R., Zou, H., Lu, D., Gong, C., Liu, Y., "Polyethersulfone sulfonated by chlorosulfonic acid and its membrane characteristics", *European Polymer Journal*, 41, 2005, p. 1554-1560.
- [88] Jiang, D., Zhang, S-L., Yang, Y-H., Jiang, Z-H., Ma, R-T., "Effect of random copolymers of 2,2-Di(4-hydroxy Phenyl) and 4,4'-Dihydroxydiphenylsulfone on the morphology and mechanical properties of Polyethersulfone and Polycarbonate blends", *Journal of Macromolecular Science, Part B: Physics*, 47, 2008, p. 1-9.
- [89] Zhao, C., Yu, B., Qian, B., Wei, Q., Yang, K., Zhang, A., "BPA transfer rate increase using molecular imprinted polyethersulfone hollow fiber membrane", *Journal of Membrane Science*, 310, 2008, p. 38-43.
- [90] Kapantaidakis, G.C., Koops, G.H., Wessling, M., Kaldis, S.P., Sakellaropoulos, G.P., "CO₂ plasticization of Polyethersulfone/Polyimide gas-separation membranes", *AIChE Journal*, 49, 2003, p. 1702-1711.
- [91] Bos, A., Pünt, I.G.M., Wessling, M., Strathmann, H., "CO₂-induced plasticization phenomena in glassy polymers", *Journal of Membrane Science*, 155, 1999, p. 67-78.
- [92] Szostak, R., "Handbook of Molecular Sieves", Van Nostrand Reinhold, New York, 1992.
- [93] Harper R.J., Stifel R., Anderson R.B., "Adsorption of gases on 4A synthetic zeolite", *Canadian Journal of Chemistry*, 47, 1969, p. 4661-4670.
- [94] Krishna, R., Li, S., Baten, J.M., Falconer, J.L., Noble, R.D., "Investigation of slowing-down and speeding-up effects in binary mixture permeation across SAPO-34 and MFI membranes", *Separation and Purification Technology*, 60, 2008, p. 230-236.
- [95] Li, S., Alvarado, G., Noble, R.D., Falconer, J.L., "Effects of impurities on CO₂/CH₄ separations through SAPO-34 membranes", *Journal of Membrane Science*, 251, 2005, p. 59-66.
- [96] Karatay, E., "Synthesis and Characterization of SAPO-34 for Membrane Applications in Natural Gas Treatment", MSc Thesis, Middle East Technical University, August 2009.
- [97] Jackson, W.J., Caldwell, J.R., "Antiplasticization. II. Characteristics of antiplasticizers", *Journal of Applied Polymer Science*, 11, 1967, p. 211-226.

- [98] Jackson, W.J., Caldwell, J.R., “Antiplasticization. III. Characteristics of antiplasticizers”, *Journal of Applied Polymer Science*, 11, 1967, p. 227-244.
- [99] Vrentas, J.S., Duda, J.L., Ling, H-C., “Antiplasticization and volumetric behavior in glassy polymers”, *Macromolecules*, 21, 1988, p. 1470-1475.
- [100] Maeda, Y., Paul, D.R., “Effect of antiplasticization on gas sorption and transport. III. Free volume interpretation”, *Journal of Polymer Science: Part B: Polymer Physics*, 25, 1987, p. 1005-1016.
- [101] Maeda, Y., Paul, D.R., “Effect of antiplasticization on gas sorption and transport. II. Poly(phenylene Oxide)”, *Journal of Polymer Science: Part B: Polymer Physics*, 25, 1987, p. 981-1003.
- [102] Maeda, Y., Paul, D. R., “Effect of antiplasticization on gas sorption and transport. I. Polysulfone”, *Journal of Polymer Science: Part B: Polymer Physics*, 25, 1987, p. 957-980.
- [103] Fu, Y-J., Hu, C-C., Qui, H-Z., Lee, K-R., Lai, J-Y., “Effects of residual solvent on gas separation properties of polyimide membranes”, *Separation and Purification Technology*, 62, 2008, p. 175-182.
- [104] Joly, C., Cerf, D.L., Chappey, C., Langevin, D., Muller, G., “Residual solvent effect on the permeation properties of fluorinated polyimide films”, *Separation and Purification Technology*, 16, 1999, p. 47-54.
- [105] Jansen, J.C., Macchione, M., Drioli, E., “On the unusual solvent retention and the effect on the gas transport in perfluorinated Hyflon AD membranes”, *Journal of Membrane Science*, 287, 2007, p. 132-137.
- [106] Kurdi, J., Kumar, A., “Performance of PEI/BMI semi-IPN membranes for separations of various binary gaseous mixtures”, *Separation and Purification Technology*, 53, 2007, p. 301-311.

APPENDIX A

CALIBRATION OF GC

To analyze both permeate and feed gas composition for CO₂/CH₄ binary gases, gas chromatograph was first calibrated for CO₂ and CH₄ gases. The calibration started with feeding each gas to the GC separately at several pressures, which were varied between 0-100 Torr, and both the pressures and the corresponding area under the peaks were recorded. For each gas, pressures versus area counts graphs were plotted as pure gas calibration curves. The slope of these curves and the areas corresponding to each gas component obtained from the chromatogram of the binary gas mixtures were used to calculate the partial pressures of the gases in the binary mixture. Pure gas calibration curves for CO₂ and CH₄, are given in Figures A.1 and A.2.

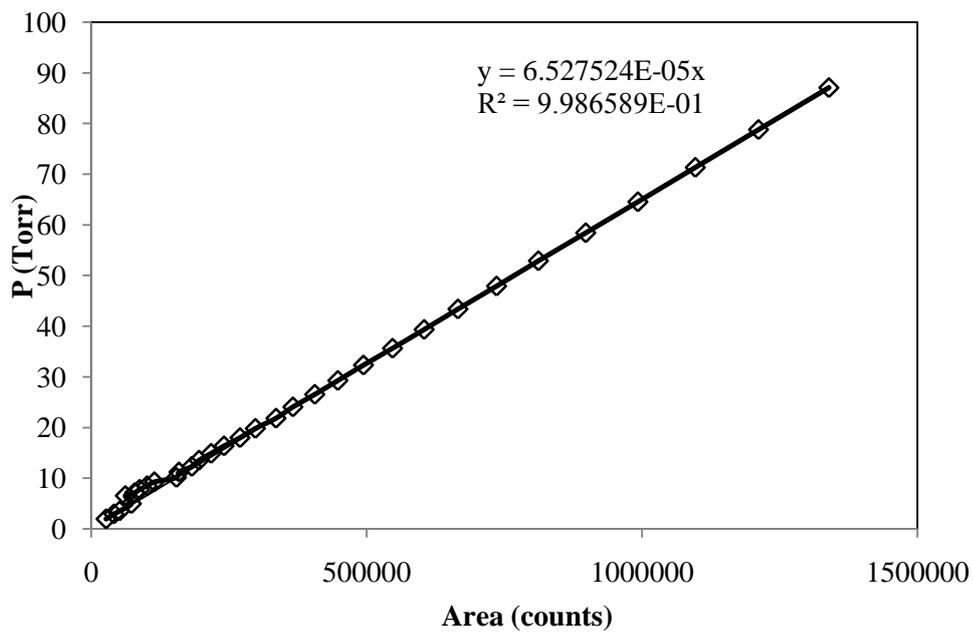


Figure A.1 Calibration plot of CO₂ for GC analysis.

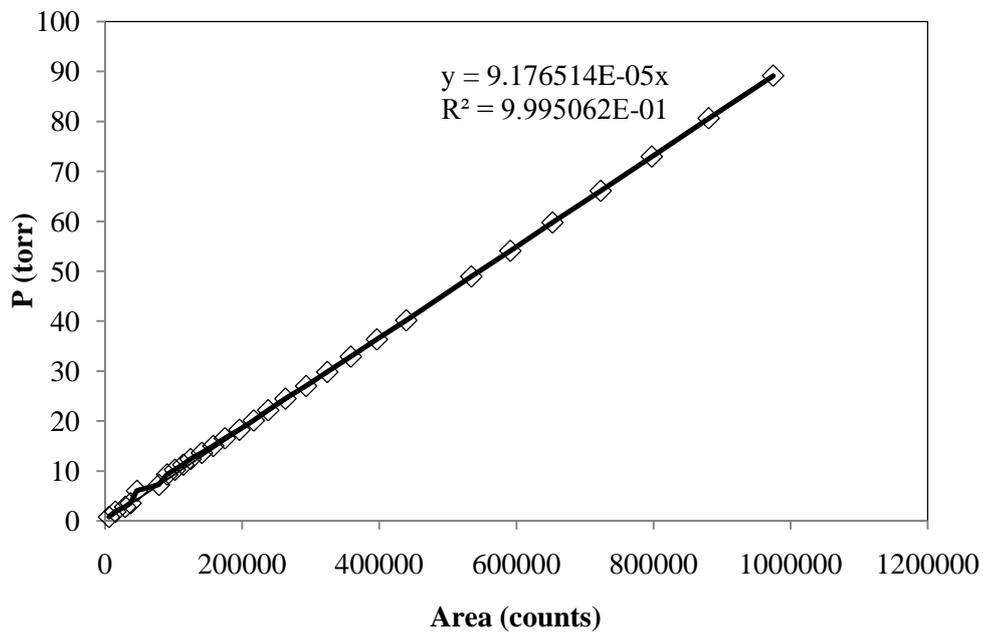


Figure A.2 Calibration plot of CH₄ for GC analysis.

APPENDIX B

CALCULATION OF SINGLE GAS PERMEABILITIES

Pressure change at the permeate side with respect to time data points were recorded with certain time intervals. This time intervals were changed with respect to gases used. For fast gases, H₂, and CO₂, this interval was 10 and 30 seconds respectively, for slow gas, CH₄, it was 100 seconds. From the slope of pressure versus time graphs permeabilities were calculated according to the algorithm given in Figure B.1.

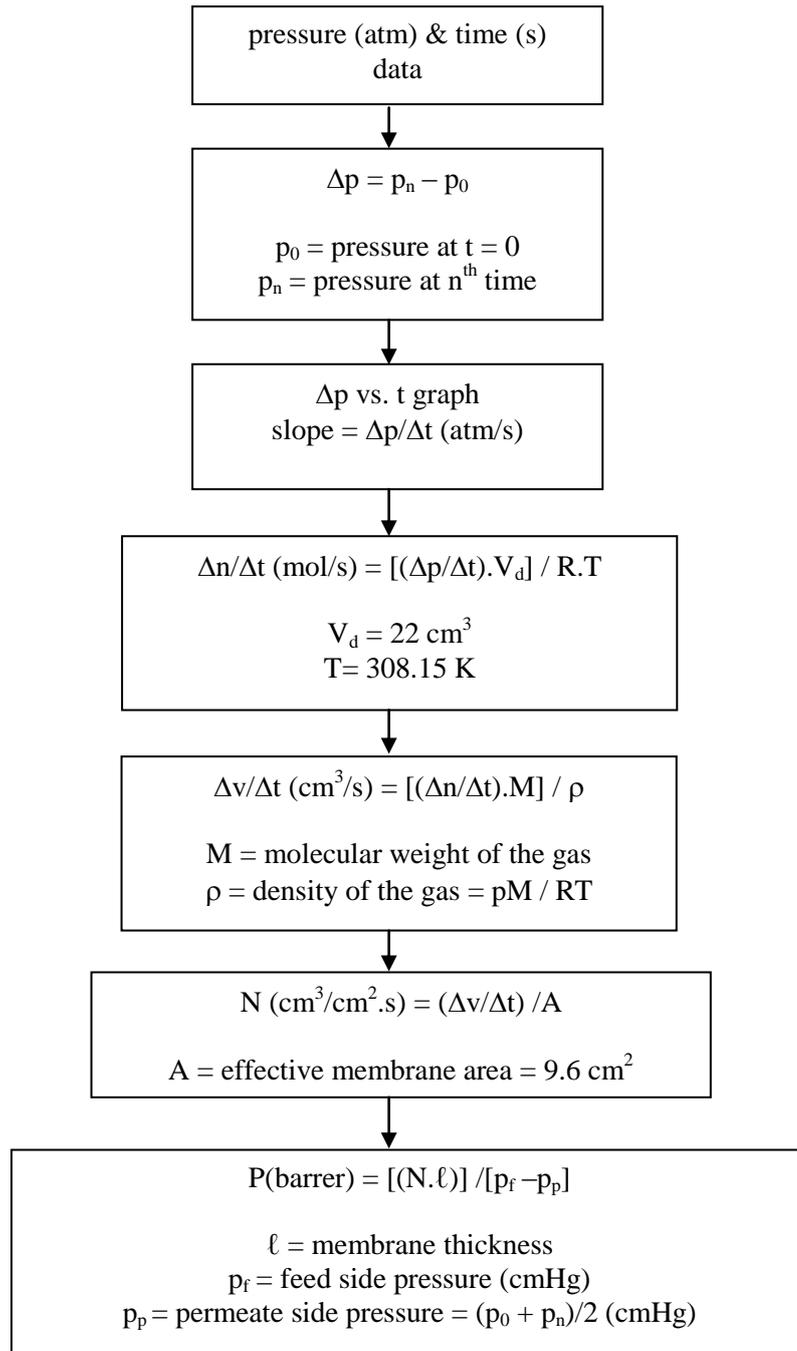


Figure B.1 Algorithm for single gas permeability calculation.

APPENDIX C

SAMPLE CALCULATION FOR THE DETERMINATION OF PERMEABILITIES AND SELECTIVITIES OF BINARY GAS MIXTURES OF CO₂/CH₄

Membrane: PES/SAPO-34 (20%)/HMA (10%) MMM

Membrane thickness: 47 μm

Feed composition: 50/50% (mol/mol) CO₂/CH₄

System temperature: 35°C

Feed pressure: 3bar

C.1 Feed side analysis

1st analysis, Feed pressure = 73.74 Torr

GC outputs:

Area counts for CO₂= 569499

Retention time for CO₂= 2.316 min.

Area counts for CH₄= 401308

Retention time for CH₄= 1.621 min.

By using the slope of the pure gas calibration curves, the partial pressures are calculated

Partial pressure of CO₂ = $P_{CO_2, feed} = 6.527524 \cdot 10^{-5} \cdot (\text{area counts of CO}_2)$

Partial pressure of CH₄ = $P_{CH_4, feed} = 9.176514 \cdot 10^{-5} \cdot (\text{area counts of CH}_4)$

$$P_{CO_2, feed} = 6.527524 \cdot 10^{-5} \cdot 569499 = 37.1742 \text{ Torr} \quad (\text{C.1})$$

$$P_{CH_4, feed} = 9.176514 \cdot 10^{-5} \cdot 401308 = 36.8261 \text{ Torr} \quad (\text{C.2})$$

$$x_{CO_2, feed} = \frac{P_{CO_2, feed}}{feed \text{ pressure}} = \frac{37.1742 \text{ Torr}}{73.74 \text{ Torr}} = 0.5041 \quad (\text{C.3})$$

$$x_{CH_4, feed} = \frac{P_{CH_4, feed}}{feed \text{ pressure}} = \frac{36.8261 \text{ Torr}}{73.74 \text{ Torr}} = 0.4994 \quad (\text{C.4})$$

The feed side analysis was carried out before and after the permeation in order to be sure that the feed composition was constant during the permeation. The results obtained after the permeation were given here. For the analysis, first of all, the permeate side was filled with the mixture, and a fraction of this mixture was sent to the GC. The other runs were carried out in the same way. At least 3 runs are carried out. The averages of these runs are used as a result. The results are given in Table C.1.

Table C.1 The results for feed side.

	1 st Analysis		2 nd Analysis		3 rd Analysis		Average	
Feed P (torr)	73.74		60.50		40.68			
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
Area Counts	569499	401308	467490	329407	314260	221432		
P _i	37.1742	36.8261	30.5155	30.2281	20.5134	20.3197		
x _i	0.5041	0.4994	0.5044	0.4996	0.5043	0.4995	0.5043	0.4995

C.2 Permeate side analysis

1st analysis, Permeate pressure = 55.68 Torr

GC outputs:

Area counts for CO₂= 835487

Retention time for CO₂= 2.308 min.

Area counts for CH₄= 14142

Retention time for CH₄= 1.629 min.

By using the slope of the pure gas calibration curves, the partial pressures are calculated separately;

$$P_{\text{CO}_2, \text{permeate}} = 6.527524 \times 10^{-5} * 835487 = 54.5366 \text{ Torr} \quad (\text{C.5})$$

$$P_{\text{CH}_4, \text{permeate}} = 9.176514 \times 10^{-5} * 14142 = 1.2977 \text{ Torr} \quad (\text{C.6})$$

$$y_{CO_2,permeate} = \frac{P_{CO_2,permeate}}{\text{permeate pressure}} = \frac{54.5366Torr}{55.68Torr} = 0.9795 \quad (C.7)$$

$$y_{CH_4,permeate} = \frac{P_{CH_4,permeate}}{\text{permeate pressure}} = \frac{1.2977Torr}{55.68Torr} = 0.0233 \quad (C.8)$$

At least 3 runs are carried out for permeate side analysis. The same calculation steps are used for the other analysis runs. The average values of these runs are used as a result. The results are given in Table C.2.

Table C.2 The results for permeate side.

	1 st Analysis		2 nd Analysis		3 rd Analysis		Average	
Feed P (torr)	55.68		46.06		38.42			
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
Area Counts	835487	14142	690928	11723	576249	9773		
Pi	54.5366	1.2977	45.1005	1.0758	37.6148	0.8968		
yi	0.9795	0.0233	0.9792	0.0234	0.9790	0.0233	0.9792	0.0233

Separation selectivity is the ratio of mol fractions of gases in the permeate and feed side.

$$\alpha_{ij} = ((y_i / y_j)_{permeate} / (x_i / x_j)_{feed}) \quad (C.9)$$

$$\alpha_{CO_2/CH_4} = [(0.9792 / 0.0233) / (0.5043 / 0.4995)] = 41.63 \quad (C.10)$$

C.3 Permeability Calculation of CO₂-CH₄ binary gas mixture

The permeability of each gas in binary gas mixture is calculated by using the pressure versus time data of binary gas mixture. The pressure vs. time graph of CO₂-CH₄ binary gas mixture through PES/SAPO-34 (20%)/HMA (10%) MMM is shown in Figure C.1. The slope of this graph, dp/dt, is split into individual dp/dt data for each gas.

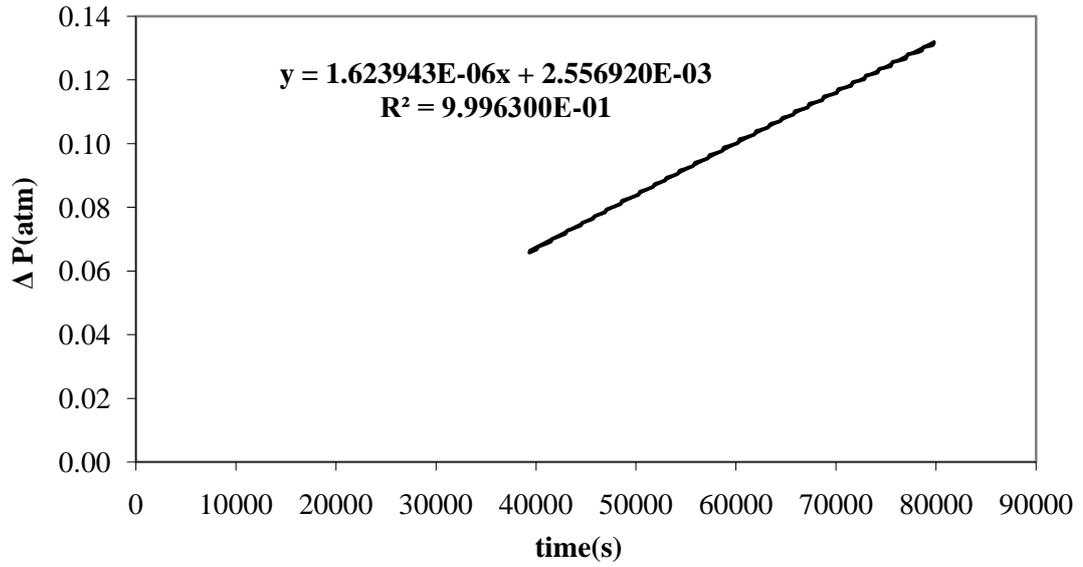


Figure C.1 Pressure difference vs. time graph for CO₂-CH₄ binary gas mixture through PES/SAPO-34 (20%)/HMA (10%) MMM.

$$\left(\frac{dp}{dt}\right)_{CO_2-CH_4} = 1.623943 \cdot 10^{-6} \text{ atm/s} \quad (C.11)$$

$$\left(\frac{dp}{dt}\right)_{CO_2} = \left(\frac{dp}{dt}\right)_{CO_2-CH_4} * y_{CO_2, permeate} = 1.590165 \cdot 10^{-6} \text{ atm/s} \quad (C.12)$$

$$\left(\frac{dp}{dt}\right)_{CH_4} = \left(\frac{dp}{dt}\right)_{CO_2-CH_4} * y_{CH_4, permeate} = 3.783787 \cdot 10^{-8} \text{ atm/s} \quad (C.13)$$

Partial pressures of each component in the feed and permeate side are also calculated;

$$P_{CO_2, feed} = P_{feed} * x_{CO_2, feed} = 2.92 \text{ atm} * 0.5043 * 76 \text{ cmHg/atm} = 111.9526 \text{ cmHg}$$

$$P_{CO_2, feed} = P_{feed} * x_{CO_2, feed} = 2.92 \text{ atm} * 0.4995 * 76 \text{ cmHg/atm} = 110.8870 \text{ cmHg}$$

$$P_{CO_2, permeate-average} = (P_{permeate, initial} + P_{permeate, final}) * y_{CO_2, permeate} / 2$$

$$P_{CO_2, permeate-average} = (50 \text{ Torr} + 100.2 \text{ Torr}) / 10 \text{ Torr/cmHg} * 0.9792 / 2 = 7.3533 \text{ cmHg}$$

$$P_{CH_4, permeate-average} = (50 \text{ Torr} + 100.2 \text{ Torr}) / 10 \text{ Torr/cmHg} * 0.0233 / 2 = 0.1750 \text{ cmHg}$$

After calculation of the individual dp/dt data for each gas and their partial pressures at the permeate and feed side, the permeability of each gas are calculated according to the algorithm used for single gas permeation experiments which were explained earlier [59].

At the last step permeability becomes,

$$P_{CO_2} (\text{Barrer}) = \left[\frac{J_{CO_2} * \delta}{P_{CO_2,feed} - P_{CO_2,permeate-avg}} \right] \quad (\text{C.14})$$

$$P_{CH_4} (\text{Barrer}) = \left[\frac{J_{CH_4} * \delta}{P_{CH_4,feed} - P_{CH_4,permeate-avg}} \right] \quad (\text{C.15})$$

$$P_{CO_2} = 1.45 \text{ Barrer} \quad (\text{C.16})$$

$$P_{CH_4} = 0.033 \text{ Barrer} \quad (\text{C.17})$$

The separation selectivity is also calculated with the ratios of the permeabilities.

$$\alpha_{CO_2/CH_4} = 1.45/0.033 = 43.94 \quad (\text{C.18})$$

C.4 Evaluation of the selectivity and permeability using CH₄ and CO₂ composition based method

As explained in Section C.2 (Appendix C), the separation selectivities are calculated from the ratio of permeate and feed side compositions of the binary gas mixtures. In the case of high CO₂ feed concentration, the CO₂ permeate concentration gets higher than 97% whereas the CH₄ permeate concentration gets smaller than 2%. In such cases, the analysis of gas mixtures with GC may lead to difficulties because of low sensitivity of TCD of GC in He carrier gas. High concentration of CO₂ in permeate may limit the accuracy of CH₄ concentration measurements because of the limitations in detection sensitivity. Moreover, the presence of even low amounts of air in the permeate side introduced by the system leak may result in difficulties when measuring the CH₄ permeate concentration. These limitations may then affect the separation selectivity calculations. Therefore, besides using the feed and permeate compositions obtained as GC outputs, the separation selectivities of the membranes are also calculated with a different method. In this method, first, the permeate and feed side compositions of CH₄ obtained as GC outputs are kept constant, and the CO₂ compositions are calculated as (1-y_{CH₄}). Then, the compositions of CO₂ obtained as GC outputs are kept constant, whereas the CH₄ compositions are calculated similarly. In addition to the selectivity calculations, the permeabilities are calculated using these composition values. For instance, for the same membrane mentioned, the selectivities and permeabilities are calculated as follows:

C.4.1 CH₄ composition based

In the first part, CH₄ permeate and feed compositions obtained as GC outputs are kept constant, and CO₂ feed and permeate compositions are calculated as (1-y_{CH₄}). The results are given in Table C.3.

Table C.3 Feed and permeate side compositions for constant CH₄ composition.

	Feed composition	Permeate composition
CH ₄	0.4995	0.0233
CO ₂	0.5005	0.9767

After the feed and permeate side compositions are calculated, the same calculation methodology is followed for both permeability and selectivity calculations.

Separation selectivity is the ratio of mol fractions of gases in the permeate and feed side.

$$\alpha_{CO_2/CH_4} = [(0.9767/0.0233)/(0.5005/0.4995)] = 41.83 \quad (C.19)$$

Permeabilities are calculated with the method explained in Section C.3.

$$P_{CO_2} = 1.46 \text{ Barrer} \quad (C.20)$$

$$P_{CH_4} = 0.033 \text{ Barrer} \quad (C.21)$$

The separation selectivity is also calculated with the ratios of the permeabilities.

$$\alpha_{CO_2/CH_4} = 1.46/0.033 = 44.24 \quad (C.22)$$

C.4.2 CO₂ composition based

In the second part, both CO₂ permeate and feed compositions determined before are kept constant, and CH₄ feed and permeate compositions are calculated as (1-y_{CO₂}). The results are given in Table C.4.

Table C.4 Feed and permeate side compositions for constant CO₂ composition.

	Feed composition	Permeate composition
CH ₄	0.4957	0.0208
CO ₂	0.5043	0.9792

Separation selectivity becomes;

$$\alpha_{CO_2/CH_4} = [(0.9792/0.0208)/(0.5043/0.4957)] = 46.27 \quad (C.23)$$

Permeabilities are calculated with the method explained in Section C.3.

$$P_{CO_2} = 1.45 \text{ Barrer} \quad (C.24)$$

$$P_{CH_4} = 0.029 \text{ Barrer} \quad (C.25)$$

The separation selectivity is also calculated with the ratios of the permeabilities.

$$\alpha_{CO_2/CH_4} = 1.45/0.029 = 50 \quad (C.26)$$

C.4.3 Separation Selectivities

The compositions and separation selectivities calculated using these compositions are shown in Table C.5.

Table C.5 Feed and permeate side compositions and separation selectivities calculated using compositions.

	Feed	Permeate	Feed	Permeate	Feed	Permeate
CH ₄	0.4995	0.0233	0.4995	0.0233	0.4957	0.0208
CO ₂	0.5043	0.9792	0.5005	0.9767	0.5043	0.9792
α_{CO_2/CH_4}	41.63		41.83		46.27	

The separation selectivities are also calculated as the ratio of the permeabilities. The results are shown in Table C.6.

Table C.6 Permeabilities of the gases and separation selectivities calculated using these permeabilities.

	Permeability	Permeability	Permeability
CH ₄	0.033	0.033	0.029
CO ₂	1.45	1.46	1.45
$\alpha_{\text{CO}_2/\text{CH}_4}$	43.94	44.24	50

As a result, the separation selectivities are calculated using six different methods. The averages of these values are reported as the separation selectivity value of a membrane. The separation selectivities of the membranes are given in Appendix F with feed and permeate compositions.

APPENDIX D

SAMPLE DSC THERMOGRAMS OF THE PREPARED MEMBRANES

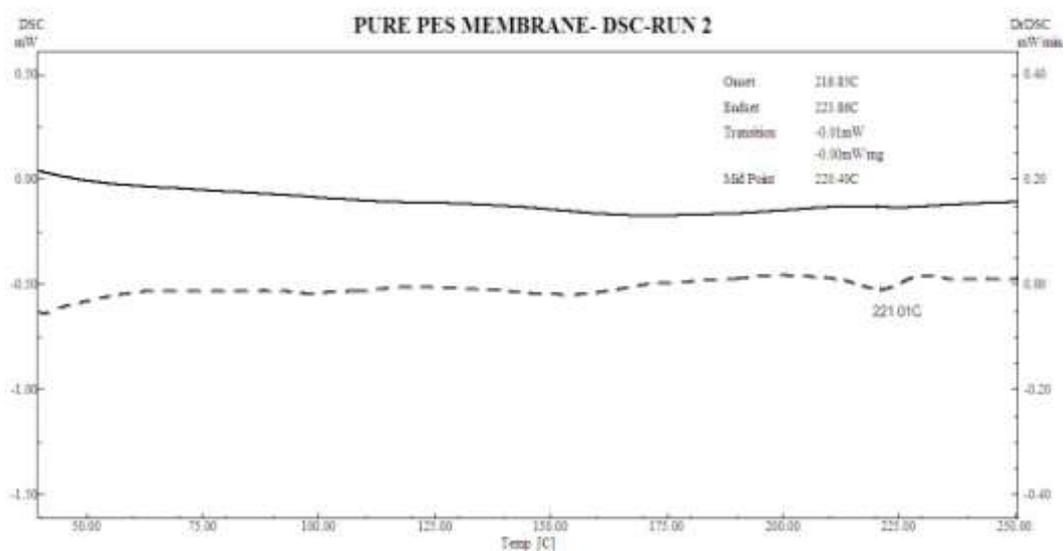


Figure D.1 The DSC graph of pure PES membrane (2nd scan).

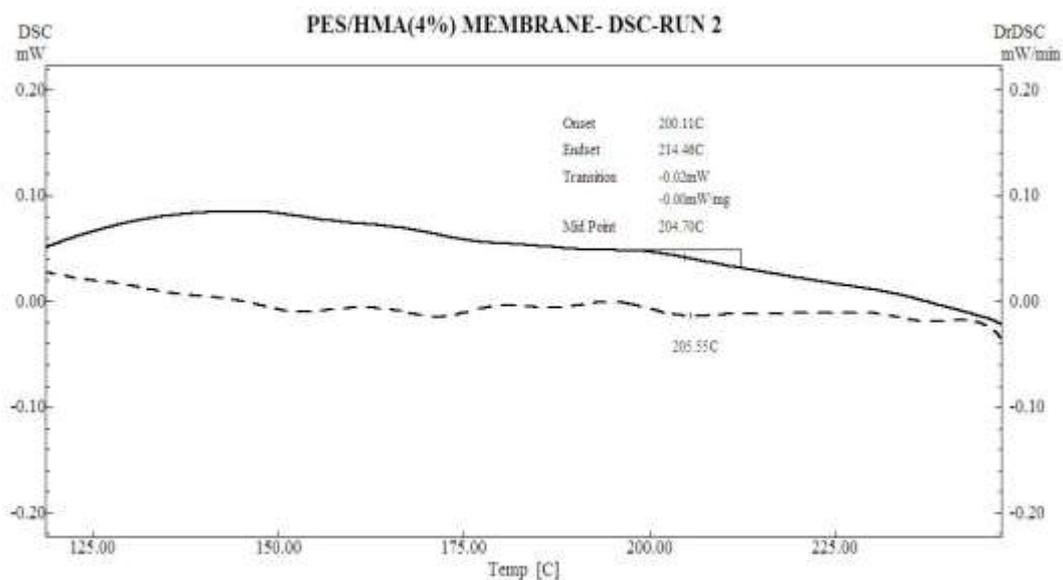


Figure D.2 The DSC graph of PES/HMA (4%) membrane (2nd scan).

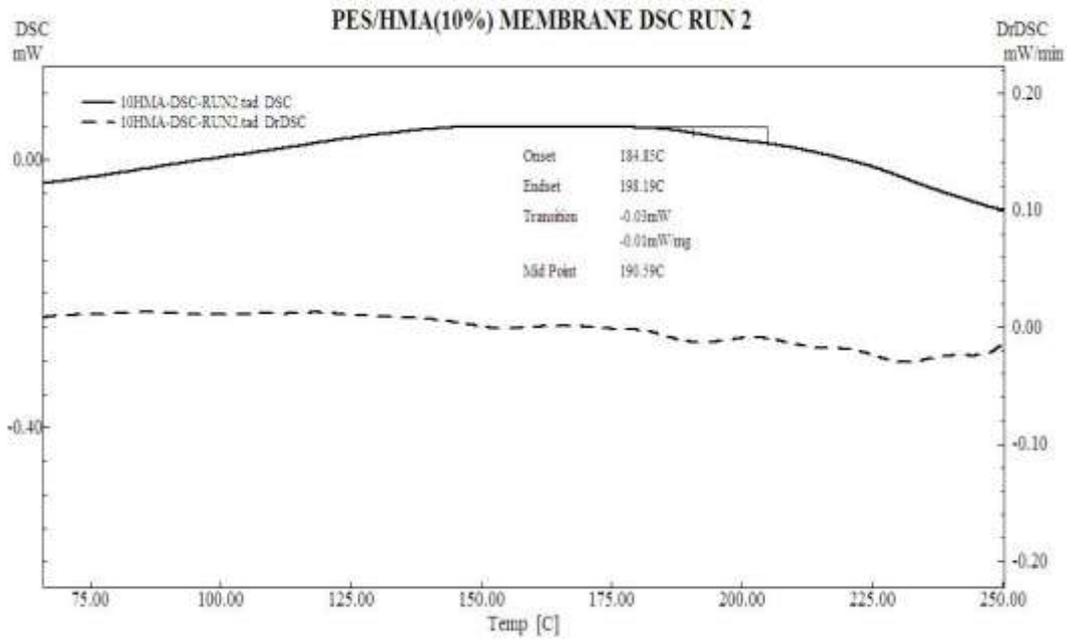


Figure D.3 The DSC graph of PES/HMA (10%) membrane (2nd scan).

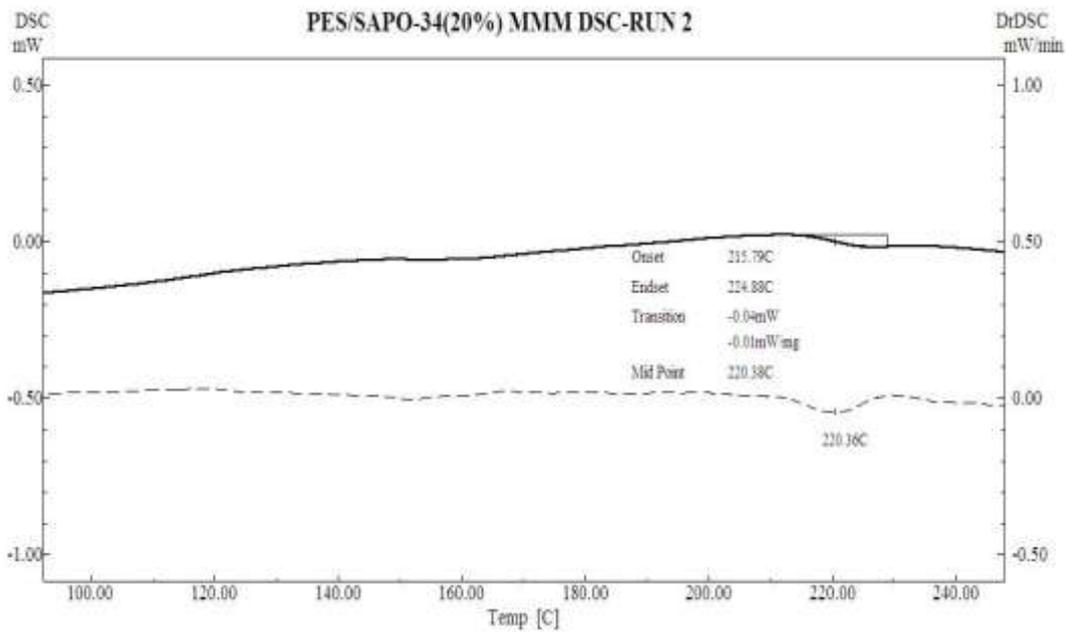


Figure D.4 The DSC graph of PES/SAPO-34 (20%) MMM (2nd scan).

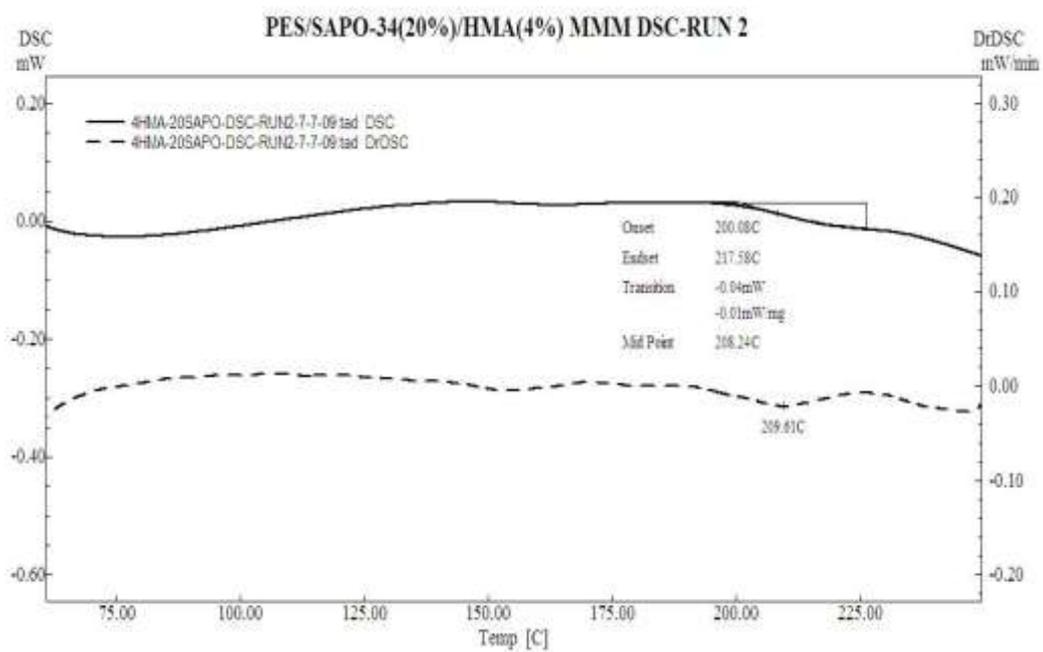


Figure D.5 The DSC graph of PES/SAPO-34 (20%)/HMA (4%) MMM (2nd scan).

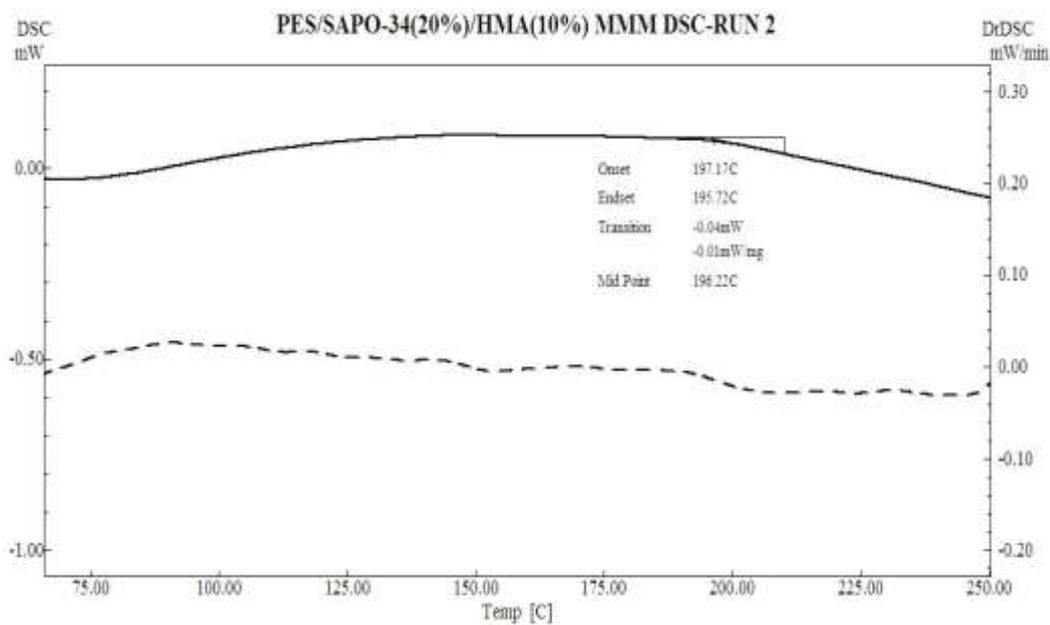


Figure D.6 The DSC graph of PES/SAPO-34 (20%)/HMA (10%) MMM (2nd scan).

APPENDIX E

SAMPLE TGA THERMOGRAMS OF THE PREPARED MEMBRANES

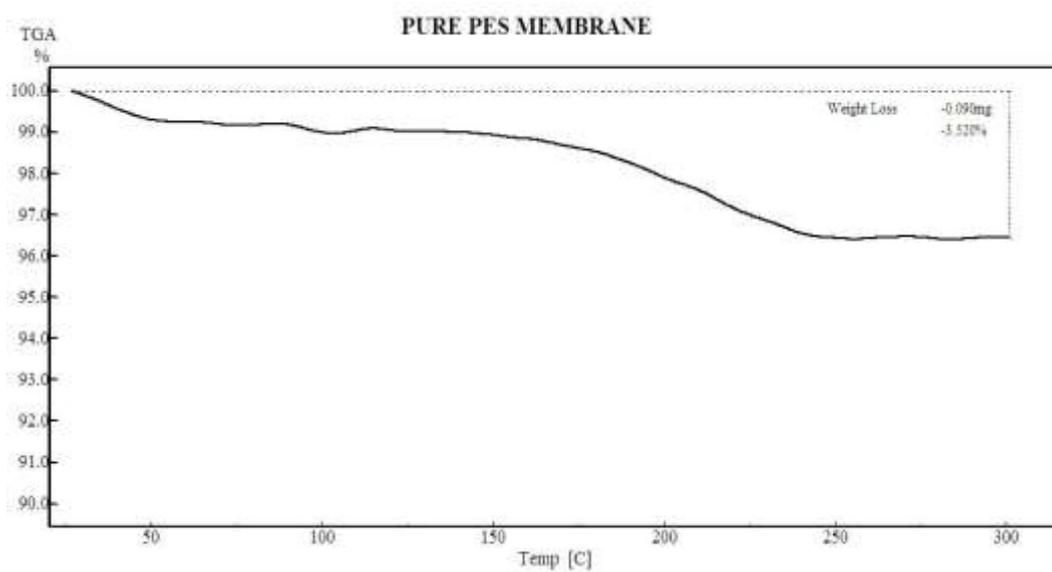


Figure E.1 The TGA graph of pure PES membrane.

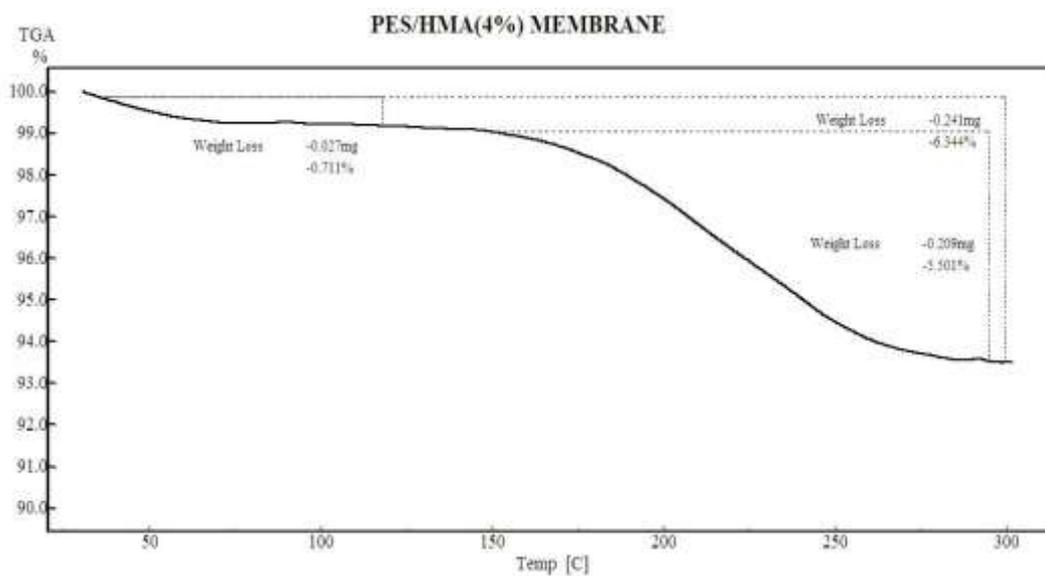


Figure E.2 The TGA graph of PES/HMA (4%) membrane.

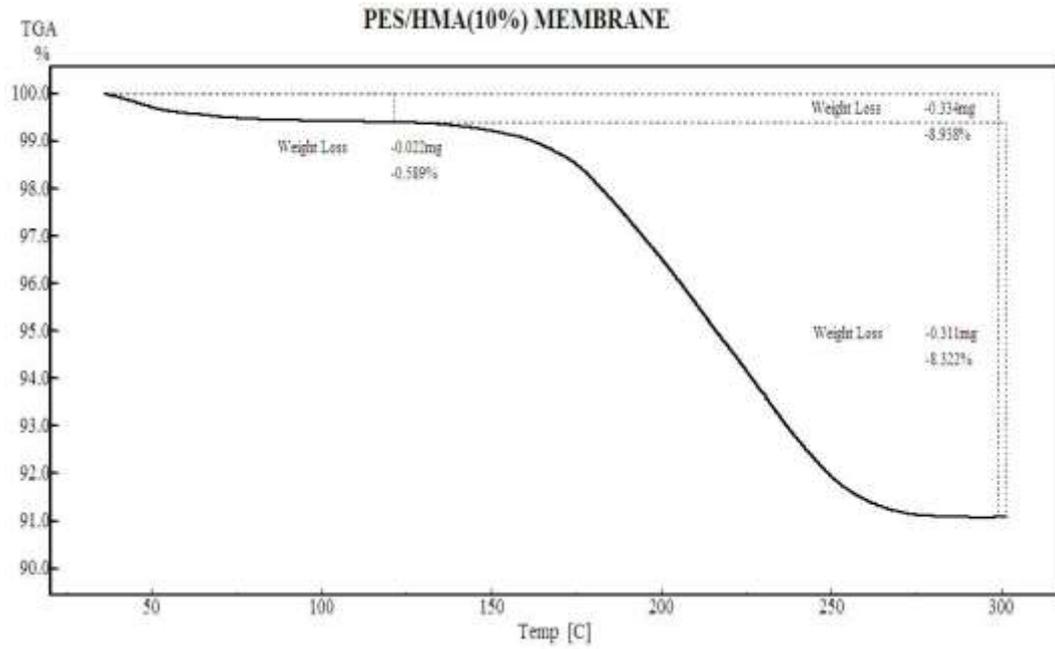


Figure E.3 The TGA graph of PES/HMA (10%) membrane.

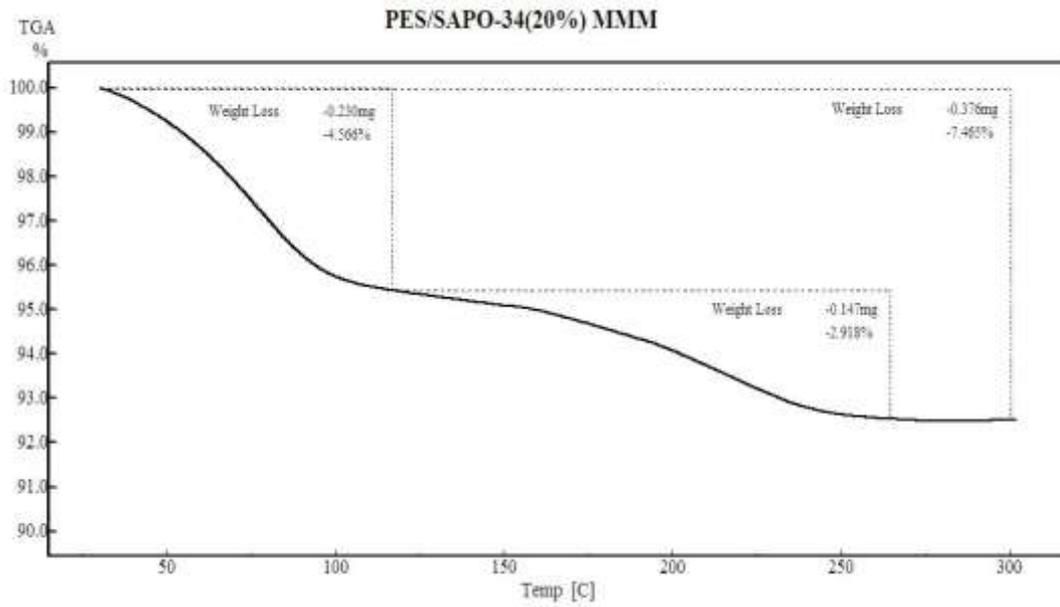


Figure E.4 The TGA graph of PES/SAPO-34 (20%) MMM.

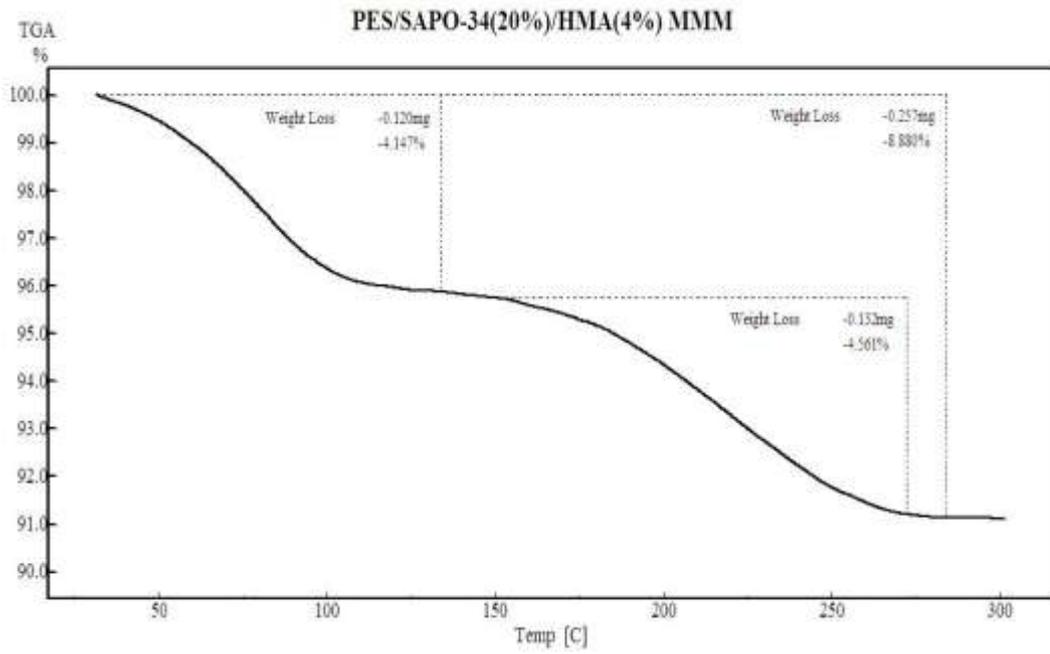


Figure E.5 The TGA graph of PES/SAPO-34 (20%)/HMA (4%) MMM.

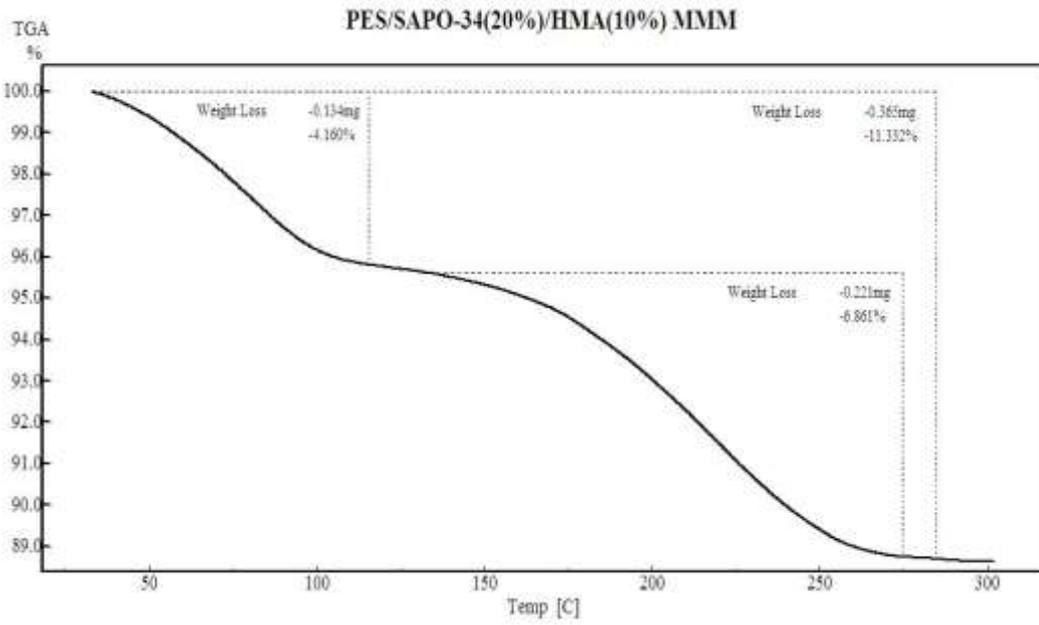


Figure E.6 The TGA graph of PES/SAPO-34 (20%)/HMA (10%) MMM.

APPENDIX F

REPRODUCIBILITY EXPERIMENTS FOR SINGLE GAS PERMEATION

Table F.1 Reproducibility data for pure PES membrane.

Membrane Code		Permeability (Barrer)							Ideal Selectivity			Thickness (μm)
		H ₂			CO ₂			CH ₄	H ₂ /CO ₂	H ₂ /CH ₄	CO ₂ /CH ₄	
		1 st	2 nd	Avg	1 st	2 nd	Avg	1.Run				
Pure PES	Part 1	8.91	8.96	8.94	4.09	4.15	4.12	-	2.17	-	36.14	50
	Part 2	-			4.52	4.62	4.57	0.134	-	-	34.10	
Pure PES	Part 1	-			4.10	4.18	4.14	0.137	-	-	30.22	45
	Part 2	-			4.93	5.03	4.98	0.131	-	-	38.02	

Table F.2 Reproducibility data for PES/HMA membrane.

Membrane Code		Permeability (Barrer)							Ideal Selectivity			Thickness (μm)
		H ₂			CO ₂			CH ₄	H ₂ /CO ₂	H ₂ /CH ₄	CO ₂ /CH ₄	
		1 st	2 nd	Avg	1 st	2 nd	Avg	1.Run				
PES/ HMA (4%)	Part 1	-			1.88	1.94	1.91	0.059	-	-	32.37	47
	Part 2	5.53	5.54	5.54	1.99	2.03	2.01	0.058	2.76	95.52	34.66	
PES/ HMA (4%)	Part 1	5.96	5.86	5.91	2.04	2.08	2.06	0.058	2.87	101.90	35.52	47
	Part 2	-			-			-	-	-	-	
PES/ HMA (10%)	Part 1	3.39	3.37	3.38	0.83	0.85	0.84	0.026	4.02	130	32.31	50
	Part 2	-			-			-	-	-	-	

Table F.3 Reproducibility data for PES/SAPO-34 MMM.

Membrane Code		Permeability (Barrer)							Ideal Selectivity			Thickness (μm)
		H ₂			CO ₂			CH ₄	H ₂ /CO ₂	H ₂ /CH ₄	CO ₂ /CH ₄	
		1 st	2 nd	Avg	1 st	2 nd	Avg	1.Run				
PES/SAPO-34 (20%)	Part 1	12.65	13.15	12.9	6.02	6.07	6.04	-	2.14	-	-	52
	Part 2	12.96	13.15	13.06	5.69	6.00	5.85	0.164	2.23	79.63	35.67	55
PES/SAPO-34 (20%)	Part 1	12.79	12.82	12.81	5.52	5.61	5.57	0.153	2.29	83.73	36.41	50
	Part 2	-			5.49	5.76	5.63	0.151	-	-	37.28	

Table F.4 Reproducibility data for PES/SAPO-34/HMA MMM.

Membrane Code		Permeability (Barrer)							Ideal Selectivity			Thickness (μm)
		H ₂			CO ₂			CH ₄	H ₂ /CO ₂	H ₂ /CH ₄	CO ₂ /CH ₄	
		1 st	2 nd	Avg	1 st	2 nd	Avg	1.Run				
PES/SAPO-34 (20%)/HMA (4%)	Part 1	7.26	7.26	7.26	2.07	2.07	2.07	0.051	3.51		40.6	55
	Part 2	-			-			-	-	-	-	
PES/SAPO-34 (20%)/HMA(10%)	Part 1	5.11	5.25	5.18	1.30	1.35	1.33	0.029	3.89	178.62	45.86	47
	Part 2	5.41	-	5.41	1.35	-	1.35	0.031	4.01	174.52	43.55	

APPENDIX G

THE COMPOSITIONS AND SEPARATION SELECTIVITIES OF USED MEMBRANES

The separation selectivities are given for pure PES, PES/HMA (4%), PES/SAPO-34 (20%), PES/SAPO-34 (20%)/HMA (4%), and PES/SAPO-34 (20%)/HMA (10%) MMMs in Table G.1, G.2, G.3, G.4, and G.5 respectively with the CO₂ and CH₄ composition values in the feed and permeate side. The separation selectivities are calculated with using the given permeate and feed side composition values.

Table G.1 Feed and permeate side compositions and separation selectivities of pure PES membrane.

CO ₂ conc.	10		20		30		40		51		60	
	F	P	F	P	F	P	F	P	F	P	F	P
CO ₂	0.0960	0.6843	0.2010	0.8774	0.3045	0.9310	0.4042	0.9444	0.5064	0.9685	0.5975	0.9783
CH ₄	0.9083	0.3207	0.8032	0.1288	0.7010	0.0755	0.5999	0.0602	0.4999	0.0385	0.4064	0.0267
α_{CO_2/CH_4}	20.19		27.22		28.39		23.28		24.83		22.40	

Table G.2 Feed and permeate side compositions and separation selectivities of PES/HMA (4%) membrane.

CO ₂ conc.	5		10		16		21		26		31		42		52		63		72			
	F	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P		
CO ₂	0.0499	0.5978	0.1033	0.7803	0.1626	0.8550	0.2083	0.8880	0.2640	0.9316	0.3129	0.9451	0.4245	0.9663	0.5203	0.9789	0.6273	0.9869	0.6766	0.9924	0.7247	0.9927
CH ₄	0.9534	0.4084	0.9006	0.2149	0.8409	0.1456	0.7963	0.1168	0.7426	0.0755	0.6932	0.0573	0.5793	0.0569	0.4826	0.0249	0.3797	0.0170	0.3313	0.0131	0.2781	0.0105
α_{CO_2/CH_4}	27.90		30.25		30.37		29.06		35.65		36.54		35.74		36.46		35.14		37.09		36.28	

Table G.3 Feed and permeate side compositions and separation selectivities of PES/SAPO-34 (20%) MMM.

CO ₂ conc.	5		10		31		42		52		72	
	F	P	F	P	F	P	F	P	F	P	F	P
CO ₂	0.0480	0.5985	0.1044	0.7832	0.3141	0.9308	0.4165	0.9610	0.5209	0.9768	0.7241	0.9921
CH ₄	0.9560	0.4064	0.9008	0.2225	0.6945	0.0703	0.5917	0.0460	0.4839	0.0297	0.2835	0.0124
α_{CO_2/CH_4}	29.33		30.37		29.28		29.68		30.55		31.32	

Table G.4 Feed and permeate side compositions and separation selectivities of PES/SAPO-34 (20%)/HMA (4%) MMM.

CO ₂ conc.	10		31		41		51		61	
	F	P	F	P	F	P	F	P	F	P
CO ₂	0.0994	0.7689	0.3124	0.9296	0.4147	0.9740	0.5145	0.9776	0.6078	0.9883
CH ₄	0.9055	0.2336	0.6926	0.0728	0.5884	0.0309	0.4896	0.0260	0.3948	0.0168
α_{CO_2/CH_4}	29.98		28.31		44.72		35.78		38.21	

Table G.5 Feed and permeate side compositions and separation selectivities of PES/SAPO-34 (20%)/HMA (10%) MMM.

CO ₂ conc.	10		19		31		41		50		60	
	F	P	F	P	F	P	F	P	F	P	F	P
CO ₂	0.1094	0.7942	0.1862	0.8861	0.3129	0.9445	0.4073	0.9713	0.5043	0.9792	0.6058	0.9903
CH ₄	0.8944	0.2081	0.8171	0.1164	0.6902	0.0372	0.5991	0.0342	0.4995	0.0233	0.4001	0.0137
8 CO ₂ /CH ₄	31.20		33.41		36.42		41.77		41.6		41.66	