Composite Membranes for Gas Separation

Thèse

Kazem Shahidi

Doctorat en génie chimique
Philosophiæ doctor (Ph. D.)

Québec, Canada

© Kazem Shahidi, 2018
Résumé

Dans ce travail, une méthode efficace est présentée pour la production de membranes composites planes à haute performance pour la séparation de gaz en utilisant une quantité limitée de solvant. En particulier, une série de polydiméthylsiloxane/polyéthylène de basse densité (PDMS/LDPE) a été produite en apposant une couche de PDMS active sur un support de LDPE microporeux produit par extrusion continue et lixiviation de sel et immersion dans l'eau chaude. La méthode proposée est simple et de faible coût car elle est basée sur des matériaux peu dispendieux (LDPE et PDMS) et utilise peu de solvant écologique (eau). En vue d'améliorer la performance et les propriétés des membranes composites, des particules de silice fumée traitée avec le triméthylsiloxy (TFS) ont été incorporées dans la couche de PDMS pour produire des membranes nano-composites PDMS-TFS/LDPE.

Les membranes ont ensuite été caractérisées en termes de morphologie, de porosité et de distribution de tailles de pores, ainsi que les propriétés thermiques, mécaniques, de sorption et de perméation. Comme les caractéristiques de la membrane dépendent des conditions de mise en œuvre, la production des membranes composites a été optimisée en fonction de différents revêtements, de la concentration en nanoparticules et de la concentration de la couche de revêtement.

Les performances membranaires (perméabilité et sélectivité) ont été étudiées pour différentes conditions opératoires (température et pression) et les résultats ont montré que la membrane nano-composite PDMS-TFS10%/LDPE est appropriée pour différentes applications industrielles dans la séparation d'hydrocarbures supérieurs.
Abstract

In this work, an efficient method with a limited amount of solvent use is presented to produce high-performance flat sheet composite membranes for gas separation. In particular, a series of polydimethylsiloxane/low-density polyethylene (PDMS/LDPE) membranes were produced by coating an active PDMS layer on a microporous LDPE support via continuous extrusion and salt leaching using immersion in hot water. The proposed method is simple and cost-effective since it is based on inexpensive materials (LDPE and PDMS) and uses a low amount of an environmentally friendly solvent (water). To improve the composite membranes performance and properties, trimethylsiloxy grafted fumed silica (TFS) particles were incorporated into the PDMS layer to produce PDMS-TFS/LDPE nano-composite membranes.

The membranes were then characterized in terms of morphology, porosity and pore size distribution, as well as thermal, mechanical, sorption and permeation properties. Since the membrane properties depend on the processing conditions, the composite membranes production was optimized for a different number of coatings, nano-particles loading and coating concentration.

Membrane performance (permeability and selectivity) was studied under different operating conditions (temperature and pressure), and the results showed that the PDMS-TFS10%/LDPE nano-composite membrane is highly suitable for different industrial applications of higher hydrocarbon separations.
Table of Contents

Résumé ......................................................................................................................... ii
Abstract ......................................................................................................................... iii
Table of Contents .......................................................................................................... iv
List of Tables ................................................................................................................. viii
List of Figures ............................................................................................................... ix
Abbreviations ............................................................................................................... xii
Symbols ....................................................................................................................... xiv
Acknowledgments ....................................................................................................... xvi
Forewords ..................................................................................................................... xvii
Chapter 1 ..................................................................................................................... 1
  1.1 Overview ............................................................................................................. 1
  1.2 Introduction ........................................................................................................ 1
    1.2.1 Membranes Structures and Mechanisms for Gas Separation .................... 2
    1.2.2 Membranes Materials and Modules for Gas Separation ......................... 5
  1.3 Vapor/gas separation ......................................................................................... 8
    1.3.1 VOC separation ......................................................................................... 8
  1.4 Polymer membranes for VOC separation ....................................................... 9
    1.4.1 Glassy and rubbery polymers .................................................................. 10
    1.4.2 Composite membranes preparation ....................................................... 11
  1.5 Literature review ............................................................................................. 12
    1.5.1 Influence of synthesis conditions on separation properties .................... 14
      1.5.1.1 Substrate characteristics ................................................................ 14
      1.5.1.2 Coating condition ........................................................................... 16
    1.5.2 Effect of operating conditions on gas separation properties ................. 21
    1.5.3 Membrane system design parameters ................................................. 24
      1.5.3.1 Module configuration ..................................................................... 25
  1.6 Composite membrane characterization ......................................................... 27
    1.6.1 Mechanical and thermal properties ....................................................... 27
    1.6.2 Morphology ............................................................................................ 29
  1.7 Thesis objectives and organization .................................................................. 32
Chapter 2 ..................................................................................................................... 34
3.3.3 Membrane characterization ......................................................... 68
  3.3.3.1 Scanning electron microcopy (SEM)........................................... 68
  3.3.3.2 Thermogravimetric analysis (TGA)............................................. 69
  3.3.3.3 Sorption and permeation measurement..................................... 69
3.4 Results and Discussion .................................................................. 69
  3.4.1 Morphology .............................................................................. 69
  3.4.2 TGA .......................................................................................... 72
  3.4.3 Sorption and permeation ............................................................. 73
    3.4.3.1 Effect of transmembrane pressure ........................................ 73
    3.4.3.1 Effect of temperature .............................................................. 77
3.5 Conclusion ................................................................................. 82
Acknowledgment .................................................................................. 83
Chapter 4 .......................................................................................... 84
Résumé ............................................................................................... 85
Abstract ............................................................................................. 86
4.1 Introduction .................................................................................. 87
4.2 Experimental ................................................................................ 88
  4.2.1 Material ..................................................................................... 88
  4.2.2 Nanocomposite membrane preparation ...................................... 89
  4.2.3 Membrane characterization .......................................................... 89
    4.2.3.1 Scanning electron microcopy (SEM) ...................................... 89
    4.2.3.1 Fourier-transform infrared spectroscopy (FTIR) ................... 90
    4.2.3.2 Thermogravimetric analysis (TGA) ....................................... 90
    4.2.3.1 Mechanical properties ......................................................... 90
    4.2.3.1 Gas transport measurements ............................................... 90
4.3 Results and Discussion .................................................................. 91
  4.3.1 Morphology .............................................................................. 91
  4.3.2 FTIR ........................................................................................ 92
  4.3.3 TGA ........................................................................................ 93
  4.3.4 DMTA ..................................................................................... 96
  4.3.5 Gas Transport ........................................................................... 100
    4.3.5.1 Effect of TFS loading ......................................................... 100
    4.3.5.2 Effect of operation conditions ............................................. 103
4.4 Conclusion .................................................................................. 105
List of Tables

Table 1.1. Overview of PDMS composite membranes for gas separation ........................................ 12
Table 1.2. Overview of polyolefin membranes for gas separation ..................................................... 14
Table 1.3. Dimensions of different PAN hollow fibers [19] ................................................................ 15
Table 1.4. Gas transport properties of uncoated PAN membranes [19] ................................................ 16
Table 1.5. Gas transport properties of PAN-PDMS composite membranes coated with 3 wt.% PDMS in hexane [19] ........................................................................................................ 16
Table 1.6. Coating parameters of PDMS composite membrane for gas separation ...................... 17
Table 1.7. Permeation data of pure and ternary gas mixture through PDMS composite membrane [21] ........................................................................................................................................ 22
Table 1.8. Gas permeance for PDMS coated PES at different operating parameters for binary \( \text{H}_2\text{S}/\text{CH}_4 \) feed gas [22] .................................................................................................................. 24
Table 2.1. Values of \( T_c, S^\infty, n, k_d \) and infinite dilution solubility selectivity of \( \text{C}_3\text{H}_8 \) with respect to the other gases at 27 °C ........................................................................................................ 53
Table 2.2. Infinite dilution gas permeability \((P_d), m \text{ and } \text{C}_3\text{H}_8/\text{gas ideal selectivity at } \Delta p = 0 \text{ and } 27 \degree \text{C for this study and the results of Merkel et al. obtained at } 35 \degree \text{C [69]} \) .... 56
Table 2.3. Values of \( \delta, V_c, D_0, q \) and ideal diffusivity selectivity of \( \text{C}_3\text{H}_8/\text{gas at } \Delta p = 0 \text{ and } 27 \degree \text{C} \) .................................................................................................................................................. 58
Table 3.1. EDS counts of the different positions presented in Figure 3.2 (from the surface to the support) ........................................................................................................................................ 71
Table 3.2. Activation energies and pre-exponential factors for the permeation and diffusion data, as well as the enthalpy of sorption for \( \text{CH}_4, \text{CO}_2 \) and \( \text{C}_3\text{H}_8 \) ......................................................................................... 80
Table 3.3. \( \Delta H_s, E_d \) and \( E_p \) values reported by Clarizia et al.[86] and Prabhakar et al. [66] for \( \text{CH}_4 \) and \( \text{C}_3\text{H}_8 \) ........................................................................................................................................ 80
Table 4.1. DMTA results for the PDMS-TSF/LDPE nano-composite membranes ......................... 98
Table 4.2. Infinite dilution gas permeability \((P_d), m \text{ and } \text{C}_3\text{H}_8/\text{CH}_4 \) ideal selectivity at \( \Delta p = 0 \) and 27 °C for PDMS-TFS10%/LDPE and PDMS/LDPE [83] ........................................................................ 104
List of Figures

Figure 1.1. Schematic of a membrane gas separation [1]...................................................... 2
Figure 1.2. Different possible transport mechanisms for membrane gas separation [3] .... 3
Figure 1.3. (a) Asymmetric membrane structure, (b) Asymmetric polyacrylonitrile membrane and (c) Asymmetric polysulfone membranes manufactured by GE-OsmoInc [4]................................................................................................................................. 4
Figure 1.4. (a) Composite membrane structure and (b) polyamide membranes manufactured by GE-OsmoInc. and (c) Dow-FilmTec [4]. .................................................................................. 5
Figure 1.5. Classification of membrane materials [5]. ........................................................ 6
Figure 1.6. Classification of membrane modules [5]. ........................................................... 6
Figure 1.7. Spiral wound module [6]. .................................................................................. 7
Figure 1.8. Hollow fiber module [6]. .................................................................................... 7
Figure 1.9. Different methods for VOCs separation [16]. .................................................... 9
Figure 1.10. Gas permeation as a function of gas molar volume for a glassy (PEI) and a rubbery polymer [17]. .................................................................................................................. 10
Figure 1.11. Pore size distribution for the PAN substrates [19]. .......................................... 15
Figure 1.12. The effect of coating solution concentration on permeability and selectivity (a). The effect of sequential film casting and dip-coating on permeability and selectivity (b) [20]................................................................................................................................. 20
Figure 1.13. Different configurations of membrane modules: (a) shell side feed, counter-current flow; (b) shell side feed, co-current flow; (c) shell side feed, counter-/co-current flow (permeate withdrawal from both ends of the fiber bores); and (d) bore side feed, counter-current flow [36] ........................................................................................................ 26
Figure 1.14. Productivity and recovery of CO₂/N₂ as a function of CO₂/N₂ concentration in permeate. Module configurations: (○) counter-current flow; (♦) co-current flow; (□) combination of counter-current and co-current flows [36]. ........................................................................... 27
Figure 1.15. (a) TGA and (b) stress-strain curves of PAN/PEI and PAN/PEI–PDMS-X% [37]................................................................................................................................. 29
Figure 1.16. Schematic representation of the interfacial interaction in PDMS–APTMS/PES composite membrane [38]. ................................................................................................. 30
Figure 1.17. (a) The cross-section scanning electron microscopy (SEM) image of the PDMS–APTMS-0.06/PES composite membrane for pervaporation experiments. (b) The cross-section SEM image of the PDMS–APTMS-0.06/PES composite membrane for EDS measurements. The five light spots shown in the PDMS active layer indicate the five EDS measurement points (spectrum) numbered from the interface to the surface. (c) Si content along the longitudinal direction of the PDMS–APTMS-0.06/PES active layer measured by EDS [38]. ................................................................. 31
Figure 1.18. PDMS polymer resin and the cross-linking agent............................................ 32
Figure 2.1. Schematic representation of the melt extrusion, sheet drawing, active layer coating and salt leaching steps for the production of FSCM ................................................. 42
Figure 2.2. SEM images of: (a) the salt particles at different magnification and (b) the initial particle size distribution of the salt. ........................................................................ 44
Figure 2.3. Typical SEM images at different magnifications of the LDPE support: (a) before and (b) after salt leaching, (c) the particle size distribution of the salt inside LDPE and (d) the pore size distribution of the microporous LDPE substrate. ......................... 45
Figure 2.4. Cross-sectional SEM images of a PDMS/LDPE FSCM ................................... 46
Figure 2.5. TGA results for neat LDPE pellet before extrusion, initial salt particle (SodaLO), LDPE substrate before and after leaching, and PDMS/LDPE composite membrane. 48
Figure 2.6. FTIR-ATR spectra of the LDPE support and the FSCM ................................. 49
Figure 2.7. Sorption isotherms of the different gases in FSCM at 27 °C ............................ 52
Figure 2.8. (a) Solubility of the gases in FSCM as a function of pressure at 27 °C and (b) infinite dilution solubility as a function of $T_c$ ................................................................. 53
Figure 2.9. Permeability through the FSCM as a function of the pressure difference at 27 °C ......................................................................................................................................... 55
Figure 2.10. (a) Diffusivity as a function of pressure difference at 27 °C and (b) infinite dilution diffusion coefficient $D_0$ as a function of $V_c$ ................................................................. 57
Figure 2.11. $C_3H_8$/gas overall (a) solubility and diffusivity, and (b) selectivity of the FSCM as a function of the upstream pressure ........................................................................... 59
Figure 3.1. Schematic representation of a MCPM structure and its electrical circuit analog. ...................................................................................................................................... 67
Figure 3.2. Typical cross-section morphology of a PDMS/LDPE MCPM ........................ 70
Figure 3.3. EDS spectra of the different positions as presented in Figure 3.2 (from the surface to the support). ........................................................................................................... 72
Figure 3.4. TGA-DTG curves for the neat PDMS and LDPE, as well as the PDMS/LDPE MCPM. ......................................................................................................................... 73
Figure 3.5. Sorption isotherm in the MCPM at 35°C .......................................................... 75
Figure 3.6. (a) Solubility, (b) permeability, and (c) diffusivity of the components in the MCPM as a function of pressure at 35°C ............................................................................... 77
Figure 3.7. Transport properties through the MCPM as a function of temperature for the different gas (CH$_4$, CO$_2$ and C$_3$H$_8$): (a) solubility, (b) permeability, and (c) diffusivity ................................. 79
Figure 3.8. Effect of feed temperature on the ideal selectivity of the MCPM for C$_3$H$_8$ over CO$_2$ and CH$_4$ ................................................................................................................. 81
Figure 3.9. The permeability–permselectivity diagram for C$_3$H$_8$/CH$_4$ (Adapted from Alentiev et al. [88]) ......................................................................................................................... 82
Figure 4.1. PDMS-treated and untreated trimethylsiloxy fumed silica ................................ 88
Figure 4.2. SEM images of PDMS-TFS/LDPE and TFS particle at different magnification. ........................................................................................................................................ 91
Figure 4.3. FTIR spectra for PDMS-TFS, neat PDMS and TFS particles. ......................... 93
Figure 4.4. TGA-DTG curves for the neat TFS, PDMS and LDPE, as well as the PDMS-
TFS/LDPE membranes. ........................................................................................................ 95
Figure 4.5. Storage modulus (a) and loss modulus (b) for the PDMS-TFS/LDPE nano-
composite membranes. ......................................................................................................... 97
Figure 4.6. Damping factor (tan δ) as a function of temperature for the PDMS-TFS/LDPE
nano-composite membranes. .............................................................................................. 98
Figure 4.7. Gas permeability as a function of TFS loading at 27 °C and 80 psig. The lines
are predictions from the Maxwell model (Equation 4.1).................................................... 101
Figure 4.8. Relative solubility (\(S_r\)), permeability (\(P_r\)) and diffusivity (\(D_r\)) coefficients as a
function of TFS loading at 27 °C and 80 psig. The lines represent the Maxwell model
(Equation 4.5). .................................................................................................................... 102
Figure 4.9. Effect of operation conditions on the permeability and ideal selectivity of
PDMS-TFS10%/LDPE membrane. The lines are regressions using Equations (4.6) and
(4.7) with the parameters of Table 4.2............................................................................... 104
Figure 4.10. The permeability-permselectivity diagram for \(\text{C}_3\text{H}_8/\text{CH}_4\) (Adapted from [88]).
............................................................................................................................................. 105
Figure 5.1. The permeability-selectivity diagram for \(\text{C}_3\text{H}_8/\text{CH}_4\) (Reprinted from [88])... 109
Figure A.1. Schematic representation of the sorption experimental set-up............. 121
Figure A.2. Typical pressure-decay data curve. ................................................................. 122
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>APTEOS</td>
<td>Aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>APTMS</td>
<td>Aminopropyltrimethoxysilane</td>
</tr>
<tr>
<td>ASTM</td>
<td>American society for testing and materials</td>
</tr>
<tr>
<td>ATR-IR</td>
<td>Attenuated total reflection-infrared</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>CERMA</td>
<td>Centre de recherche sur les matériaux avancés</td>
</tr>
<tr>
<td>CP</td>
<td>Constant pressure</td>
</tr>
<tr>
<td>CREPEC</td>
<td>Research Center for High Performance Polymer and Composite Systems</td>
</tr>
<tr>
<td>CV</td>
<td>Constant volume</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analyzer</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>FH</td>
<td>Flory-Huggins</td>
</tr>
<tr>
<td>FR</td>
<td>Flory-Rehner</td>
</tr>
<tr>
<td>FSCM</td>
<td>Flat sheet composite membrane</td>
</tr>
<tr>
<td>FRQNT</td>
<td>Fonds de recherche du Québec – Nature et Technologies</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HFM</td>
<td>Hollow fiber membrane</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LLDPE</td>
<td>Linear low-density polyethylene</td>
</tr>
<tr>
<td>MCPM</td>
<td>Multilayer composite polymer membrane</td>
</tr>
<tr>
<td>MS</td>
<td>Microporous substrate</td>
</tr>
<tr>
<td>NIH</td>
<td>National institute of health</td>
</tr>
<tr>
<td>NSERC</td>
<td>National Science and Engineering Research Council of Canada</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
</tbody>
</table>
PE Polyethylene
PEBAX Polyether block amide
PES Polyethersulfone
PP Polypropylene
PS Polysulfone
PTMOS Phenyltrimethoxysilane
PVDF Polyvinylidene fluoride
SEM Scanning electron microscopy
SL Selective layer
STP Standard temperature and pressure
TEOS Tetraethylorthosilicate
TFC Thin film composite
TGA Thermogravimetric analysis
VOC Volatile organic compound
VTMOS Vinyltrimethoxysilane
Symbols

\( a \) Gas activity

\( A \) Membrane area

\( C \) Gas concentration in the polymer

\( E' \) Storage modulus

\( E'' \) Loss modulus

\( E_p \) Activation energy of permeation

\( E_d \) Activation energy of diffusion

\( dV/dt \) Volumetric displacement rate of the soap film in the bubble flowmeter

\( D \) Diffusion coefficient

\( \text{GPU} \) Gas permeance unit

\( k_d \) Henry’s law constant

\( l \) Membrane thickness

\( \text{LDPE} \) Low density polyethylene

\( \text{LPG} \) Liquefied petroleum gas

\( N \) Gas flux

\( m, n \text{ and } q \) Slope

\( p \) Pressure

\( P \) Permeability

\( \text{PEI} \) Polyetherimide

\( \text{PDMS} \) Polydimethylsiloxane

\( \text{POMS} \) Polyoctylmethylsiloxane

\( \text{PO}, \varepsilon \) Porosity

\( R \) Universal gas constant

\( R_{\text{tot}} \) Total mass transfer resistance

\( S \) Solubility
\( S^\infty \)  
Infinite dilution solubility

\( T \)  
Temperature

\( T_{\alpha} \)  
Relaxation temperature

\( \tan \delta \)  
Damping factor

TFS  
Trimethylsiloxy fumed silica

\( V \)  
Volume

\( \overline{V}_2 \)  
Gas partial molar volume in the polymer

\( V_2 \)  
Gas molar volume in the polymer

\( x \)  
Diffusion direction

\( \alpha \)  
Ideal selectivity

\( \omega \)  
Gas mass fraction in the polymer

\( \rho \)  
Density

\( \phi_2 \)  
Gas volume fraction in the polymer

\( \phi_f \)  
Filler volume fraction

\( \overline{\chi} \)  
Concentration-averaged interaction parameter

\( \Delta H_s \)  
Enthalpy of sorption

\( \Delta H_{\text{cond}} \)  
Enthalpy of condensation

\( \Delta H_{\text{mix}} \)  
Enthalpy of mixing
Acknowledgments

Firstly, I wish to offer my deepest appreciation to my supervisor Professor Denis Rodrigue, for his availability, advice and insight in different aspects of this project. I thank him for giving me the opportunity to continue this doctorate.

I would like to thank the thesis committee, Professors Larachi and Kaliaguine, as well as Dr. Mahi Hassanabadi for evaluating this dissertation.

I also would like to acknowledge the financial support of the National Science and Engineering Research Council of Canada (NSERC) and the Fonds de recherche du Québec – Nature et Technologies (FRQNT).

The technical support of Mr. Yann Giroux, the Centre de recherche sur les matériaux avancés de l’Université Laval (CERMA) and the Research Center for High Performance Polymer and Composite Systems (CREPEC) were much appreciated.

Many thanks to Nova Chemicals (Canada), Wacker Silicones Corporation (USA), Tate & Lyle (USA) and Cabot Corporation Product (USA) for providing LDPE, PDMS package, extra fine NaCl and TFS particles, respectively.

Last, but not least, I want to thank my family for encouragement and support.
Forewords

The first chapter of this thesis is an introduction to composite polymer membranes for gas separation. A brief literature review on the key parameters controlling the membrane performance is presented.

Chapters 2-4 present experimental results in the form of published or submitted journal papers. My contributions in these articles was performing the experimental works, collecting and analyzing the data and writing the first draft of the manuscripts.

In chapter 2, polydimethylsiloxane/low-density polyethylene (PDMS/LDPE) composite membranes were produced by coating an active PDMS layer on a microporous LDPE support via continuous extrusion and salt leaching using immersion in hot water. The membranes were then characterized in terms of morphology, porosity and pore size distribution, as well as thermal and permeation properties. The paper is published as:


Chapter 3 presents the preparation of PDMS/LDPE membranes by combining sequential coating with melt-extrusion/salt leaching techniques. The sequential coating at low concentration coating solution formed a penetrated PDMS layer into the microporous LDPE substrate surface layer leading to improved interfacial adhesion. Also, the thermal properties and the membrane performance at high temperature were improved. The paper is accepted for publication as:


In the fourth chapter, the effect of trimethylsiloxy grafted fumed silica (TFS) on the mechanical and permeation properties of PDMS-TFS/LDPE nano-composite membranes was examined. The results showed improvement in mechanical properties by incorporation
of TFS. Gas permeation at different particles loadings, pressure and temperature indicated that the performance of the PDMS-TFS10%/LDPE nano-composite membrane was more stable under different operating conditions. This paper is currently under revision as:

*Kazem Shahidi* and *Denis Rodrigue*, *Gas transport and mechanical properties of PDMS-TFS/LDPE nanocomposite membranes*, *Journal of Polymer Research. Volume 25(8), page 179 (2018).*

Finally, the fifth chapter provides overall conclusions regarding the work done along with some recommendations for future work.
Chapter 1

Introduction

1.1 Overview

Composite membranes with a thin rubbery selective layer are permeable membranes mainly used for gas and liquid separation systems. The use of composites has gained significant attention, as they can be designed and commissioned on an industrial scale. These types of membranes are used as flat sheet membranes converted into spirally wound modules in industrial applications or as hollow fiber. Gas streams with very high vapor contents are the preferred applications. The parameters affecting gas separation performance were studied for Polydimethylsiloxane (PDMS) composite membrane systems according to literature review. Three types of parameters are known to influence the gas separation performance, synthesis parameters, operating parameters and membrane system design parameters. Synthesis parameters are divided into two groups: substrate properties such as porosity and pore size of the support, coating conditions such as solution concentration and method. Operating parameters consist of pressure, temperature and feed concentration. Besides synthesis and operating parameters, design parameters such as flow distribution, number of stages and module configuration can affect the gas separation performance of the composite membranes.

1.2 Introduction

Several types of membrane processes have been developed based on different separation principles covering a wide range of particles and molecules. Membranes are used in several industries and various applications like water treatment, separation of proteins and cells in the pharmaceutical industry, gas separation and seawater desalination [1-3].

A membrane is a physical barrier made of a semi-permeable material allowing some components to pass through while holding others back. The permeate is the portion of the feed that passes through the membrane and the concentrate or retentate is the portion of the
feed rejected by the membrane (Figure 1.1). The membrane performances are given in terms of selectivity and flow through the membrane, called the flux. The driving force across the membrane can be the difference in concentration, pressure, temperature or electrochemical potential [4, 5].

![Figure 1.1. Schematic of a membrane gas separation [1].](image)

### 1.2.1 Membranes Structures and Mechanisms for Gas Separation

There are different gas transport mechanisms through membranes as described in Figure 1.2. In porous membranes, the selectivity is mainly controlled by the pore sizes. These types of membranes are used in microfiltration and ultrafiltration. Non-porous membranes are normally used in gas separation and pervaporation. In these membranes, the molecules first dissolve into the membrane and then diffuse across. The separation is based on how the different compounds dissolve and diffuse through the membrane as some molecules will diffuse faster than others [2]. In carrier transport membranes, a specific carrier molecule facilitates the transport of a particular molecule through the membrane. This kind of transport occurs for example in the lipid bilayer of a cell. The carrier-mediated transport is very selective and can be used to remove components like gases and liquids, as well as ionic or non-ionic components.
Membrane materials are usually made as thin as possible to increase the permeability (reduce mass transfer resistance), which is the ability of a chemical to pass through a material. But this makes the membrane very fragile. To overcome this problem, the membranes are made of an asymmetric structure where the thin selective nonporous layer is coated/grafted/formed on a thicker porous layer of the same material. This porous layer provides stability and allows a free flow of the compounds that permeate through the selective layer (Figure 1.3) [4].
The disadvantage of this membrane structure is that a single type of usually expensive material is used. This problem can be solved by making a “composite” membrane; i.e. adding a thin selective layer based on another low cost polymer to produce an asymmetric membrane as shown in Figure 1.4 [4].
1.2.2 Membranes Materials and Modules for Gas Separation

In principle, all types of materials can be used as membranes. However, material selection depends on cost, the separation to perform, the membrane structure and the operating conditions. Membrane materials are normally divided into polymeric and inorganic as shown in Figure 1.5 [5].

The most commonly used membrane materials are organic polymers for which a large number of different polymers is available. Some of the advantages of polymers are flexibility, permeability and ability to be formed into a variety of structures. On the other hand, polymers are generally not thermally stable, which can be a problem for some high temperature separations.
Inorganic membranes are however becoming more important. They are more chemically and thermally stable than polymers, but have limited use mainly due to their high costs and fragility. So hybrid membranes can be a compromise by combining both polymer and inorganic materials.

![Figure 1.5. Classification of membrane materials [5].](image)

Based on the membrane structure required for a given separation and material selection, the next step is to decide which type of membrane module to use (Figure 1.6).

![Figure 1.6. Classification of membrane modules [5].](image)

The choice of module design depends on factors including economics, difficulty of separation, units number and size, ease of operation and practical issues such as maintenance and cleaning requirements. The basic principle for each module design is to get the highest possible membrane surface area per unit volume. The two main industrial
membrane structures are the spiral wound module (Figure 1.7) and the hollow fiber module (Figure 1.8).

Figure 1.7. Spiral wound module [6].

Figure 1.8. Hollow fiber module [6].
1.3 Vapor/gas separation

The recovery of vapour in a gas stream can be designed based on customer requirements. The polishing of the retentate based on stringent downstream regulations can be performed by absorption, adsorption, catalytic conversion or thermal combustion. The strategy of membrane separation is influenced by the application:

• Efficient separation of a valuable component,

• Achievement of the stipulated downstream gas specification requirements,

• A combination of both.

Vapor/gas separation membranes can be used in volatile organic compounds (VOCs) removal, gas liquids (LPG) recovery from flare or vent lines, gas pipeline dew point control, engine or turbine fuel gas conditioning, vapor recovery from storage tank losses, biogas treatment, etc [7]–[15].

1.3.1 VOC separation

Volatile organic compounds (VOCs), with less than 12 carbon atoms, are a class of compounds in which hydrogen is attached to the organic carbon. Numerous wastes from various chemical processes in the petrochemical and refinery industries have VOCs. Furthermore, VOCs are produced by handling, storage and distribution of solvents and gasoline products.

VOCs, except for CH$_4$ which are called non-methane VOCs (nmVOCs), evaporate from crude oil. Storage, loading and unloading of oil offshore are known to release high non-methane VOCs amounts.

Two conventional methods can be used to separate VOCs: “active” and “passive” VOCs separation processes. In “active” processes, there is a compression step followed by adsorption and/or absorption, condensation. For “passive” one, a vapor-balanced loading/unloading with VOCs as blanket gas is used for storage vessels.

Membrane separation offers the possibility to increase the separation performance via absorption or condensation. The ease of operation, process simplicity, and long membrane
lifetime, as well as low investment and operating costs are the main advantages of membrane technology. But other factors must be accounted for as active technologies also have their advantages and disadvantages such as performance, safety, operating cost and facility space. Membrane processes provide an alternative solution to the other VOCs separations. Although the best selection is strongly related to site conditions, the main stream profiles for VOCs separation by carbon adsorption, membrane, and condensation are depicted in Figure 1.9 [16].

![Figure 1.9. Different methods for VOCs separation [16].](image)

### 1.4 Polymer membranes for VOC separation

For VOCs separation by membrane, usually thin film composite (TFC) membranes are used. These membranes consist of 3 layers: I) nonwoven layer to give mechanical strength, II) a microporous layer, and III) a thin dense layer made from a rubbery polymer. Commonly, the selective layer is PDMS because of its high permeability and good selectivity for VOCs separation. For separations needing higher selectivity, polyoctylmethylsiloxane (POMS) can be a good alternative because of its high selectivity and low permeability. The advantage of using POMS, besides high permeability and moderate selectivity, is the preferential permeability of VOC. The high VOC's permeability is favorable to prevent condensation on the membrane surface.
1.4.1 Glassy and rubbery polymers

The gas permeation is very different in rubbery and glassy membranes as shown Figure 10. In glassy polymers, the gas permeation decreases with increasing molecular size, and small components penetrate more easily due to the rigid nature of the polymer chains. When used to separate VOCs from N$_2$, amorphous glassy membranes favorably permeate N$_2$.

In rubbery polymers, the gas permeation increases with molecule size due to the high solubility of rubbery membrane, and large component penetrates more easily. When used to separate VOCs from N$_2$, rubbery membranes favorably permeate VOCs.

![Figure 1.10. Gas permeation as a function of gas molar volume for a glassy (PEI) and a rubbery polymer [17].](image)

However, the separation of vapor/permanent gas can be performed with both rubbery and glassy membranes. As most industrial plants use rubbery membranes, mainly PDMS, this material is preferred for the following reasons:
• PDMS tends to have much higher permeability than glassy membrane,

• The vapor/permanent gas selectivity of glassy polymers is mainly dependent on VOC partial pressure,

• PDMS provides better selective purge capability.

1.4.2 Composite membranes preparation

Thin film composite membranes (TFC) are usually made by coating a permselective layer on a porous structure through phase inversion or non-solvent induced phase separation processes. A good network forms during the phase inversion process, induced either by thermal cooling of a polymer solution or by introduction a non-solvent. In these manufacturing processes, large amounts of harmful, expensive, and flammable organic solvents are used which should be removed after TFC production through numerous washing steps, making the approach unfriendly and not economical. These methods also have low production rate due to the slow liquid-liquid phase separation.

Although only a few solvent-free approaches for porous TFC membrane were reported in the scientific literature, it is important to use solvent-free approaches for their preparation. The most applicable solvent-free procedures are stretching and melt-spinning techniques which are based on the melt-extrusion of neat semi-crystalline polymers to create precursors, followed by axial stretching to form a porous network. This method is only possible for semi-crystalline polymers and involves mechanical stretching, followed by various thermal post-treatments to develop crystallinity and prevent membrane shrinkage. Some work on the preparation of open-cell foams containing polymer/filler TFC using leachable salts with low density polyethylene (LDPE), polypropylene (PP), polysulfone (PSf), polymethylmetacrylate (PMMA), polystyrene (PS), and polyurethane rigid foams (PUR/PUF) are available. For example, Mosadegh et al. [18] proposed a hybrid process combining continuous template-leaching techniques with melt-extrusion. Besides producing a porous polymer structure, this approach offers an effective roughness of the polymer surface and high porosity. The method, compared to other methods discussed earlier, is simple, cheap and environmental friendly without post-treatment.
1.5 Literature review

From the discussion above, PDMS composite membranes are good candidates for gas separation. Several polymers have been used as support for PDMS such as polyvinylidene fluoride (PVDF), polysulfone (PSf), polyethersulfone (PES), polyetherimides (PEI), polyacrylonitrile (PAN) and cellulose acetate (CA) (Table 1.1). All of them were prepared by the standard phase inversion method. Table 1.1 summarizes the pure and mixed gas permeation rates through different PDMS composite membranes.

Table 1.1. Overview of PDMS composite membranes for gas separation.

<table>
<thead>
<tr>
<th>Membrane support &amp; module</th>
<th>Gas pairs &amp; test conditions</th>
<th>Permeability (Barrer)</th>
<th>Permeance (GPU)</th>
<th>Selectivity (-)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN-hollow fiber</td>
<td>CO₂/N₂-pure</td>
<td>CO₂=3800</td>
<td></td>
<td>9.5</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>CH₄/N₂-pure</td>
<td>CH₄=1200</td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>PES-flat sheet</td>
<td>CO₂/N₂-pure</td>
<td>CO₂=25</td>
<td></td>
<td>45.5</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>CO₂/CH₄-pure</td>
<td></td>
<td></td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>PES-flat sheet</td>
<td>C₃H₈/H₂-pure</td>
<td>C₃H₈=28000</td>
<td></td>
<td>22.1</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>C₃H₈/CH₄-pure</td>
<td></td>
<td></td>
<td>14.7</td>
<td></td>
</tr>
<tr>
<td>PES-hollow fiber</td>
<td>H₂S/CH₄-mixed</td>
<td>H₂S=28.86</td>
<td></td>
<td>10.9</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>CO₂/CH₄-mixed</td>
<td>CO₂=118.07</td>
<td></td>
<td>43.87</td>
<td></td>
</tr>
<tr>
<td>CA-flat sheet</td>
<td>C₃H₈/H₂-pure</td>
<td></td>
<td></td>
<td>82</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>C₃H₈/CH₄-pure</td>
<td>C₃H₈=23000</td>
<td></td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₃H₈/CO₂-pure</td>
<td></td>
<td></td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>PVDF-flat sheet</td>
<td>C₃H₈/N₂-mixed</td>
<td>C₃H₈=17690</td>
<td></td>
<td>19.17</td>
<td>[24]</td>
</tr>
<tr>
<td>PEI-hollow fiber</td>
<td>C₂H₄/N₂-pure</td>
<td></td>
<td></td>
<td>2.3</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>C₃H₆/N₂-pure</td>
<td></td>
<td></td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₄/N₂-pure</td>
<td></td>
<td></td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>PS-flat sheet</td>
<td>C₂H₆/N₂-pure</td>
<td></td>
<td></td>
<td>7.3</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>C₃H₆/N₂-pure</td>
<td></td>
<td></td>
<td>16.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₃H₈/H₂-pure</td>
<td></td>
<td></td>
<td>16.8</td>
<td></td>
</tr>
</tbody>
</table>
Due to excellent bonding between PDMS and polyolefin porous substrates, PDMS/polyolefin composite membranes are suitable candidates for VOC separation. Few studies used dense polyolefin membranes such as linear low density polyethylene (LLDPE), polyethylene (PE), low-density polyethylene (LDPE) and polypropylene (PP) for gas separations (Table 1.2), because of their low permeability and selectivity. However, most commercial membrane contactors are made from porous polyolefin membranes. Liqui-Cel membrane contactors are gas transfer devices used in several gas separation industries for more than 20 years [25]. Majumdar et al. [13] investigated the removal of VOC from N\textsubscript{2} via vapor permeation using microporous PP hollow fibers having an ultrathin PDMS skin (1-2 \(\mu\)m) on the outside surface. The VOC concentration in the gas stream was 14% of methanol, 2.5% toluene and 4% ethyl acetate. They reported a high removal (up to 98%) of solvent vapors from the solvent-contaminated N\textsubscript{2} streams even for very high VOC concentrations (up to 18%) in the gas streams.
Table 1.2. Overview of polyolefin membranes for gas separation.

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Gas pairs &amp; test condition</th>
<th>Permeability (Barrer)</th>
<th>Selectivity (M)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE</td>
<td>CO₂/N₂-Pure</td>
<td>CO₂=12</td>
<td>12</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>CO₂/C₃H₈-Mixed</td>
<td></td>
<td>5</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>CO₂/C₂H₆-Mixed</td>
<td>CO₂=3</td>
<td>1.5</td>
<td>[27]</td>
</tr>
<tr>
<td>PE</td>
<td>CO₂/N₂-Pure</td>
<td>CO₂=30</td>
<td>10</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>CO₂/H₂-Pure</td>
<td></td>
<td>1.5</td>
<td>[28]</td>
</tr>
<tr>
<td>LDPE</td>
<td>O₂/N₂-Pure</td>
<td>O₂=3</td>
<td>1.4</td>
<td>[29]</td>
</tr>
<tr>
<td>PP</td>
<td>CO₂/N₂-Pure</td>
<td>CO₂=0.53</td>
<td>13.25</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>O₂/N₂-Pure</td>
<td>O₂=0.15</td>
<td>3.75</td>
<td>[30]</td>
</tr>
</tbody>
</table>

Three types of parameters are known to influence gas separation performance: synthesis, operation and membrane system design. They are discussed in the next section.

1.5.1 Influence of synthesis conditions on separation properties

The composite membrane permeability coefficient is highly influenced by the polymer intrusion into the pores of the support which increases the gas transport resistance.

1.5.1.1 Substrate characteristics

It is important to identify how the substrate structure affects the permeability. The effect of the substrate on gas/vapor purification has not been considered much in permeation models. In the resistance-in-series model, a constant value is considered for the substrate resistance. The low tortuosity and high porosity of the support make it an appropriate candidate for composite membranes. Li et al. coated PDMS on four PAN supports with various characteristics as reported in Table 1.3 [19].
Table 1.3. Dimensions of different PAN hollow fibers [19].

<table>
<thead>
<tr>
<th></th>
<th>PAN-A</th>
<th>PAN-AF</th>
<th>PAN-B</th>
<th>PAN-BF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner diameter (µm)</td>
<td>440</td>
<td>440</td>
<td>340</td>
<td>340</td>
</tr>
<tr>
<td>Outer diameter (µm)</td>
<td>720</td>
<td>720</td>
<td>540</td>
<td>540</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>140</td>
<td>140</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

As displayed in Figure 1.11, the mean pore size increases in the following order:

PAN-B < PAN-A < PAN-BF < PAN-AF

PAN-A has larger pores and higher porosity than PAN-B. PAN-A, but PAN-B fibers have smaller pores and lower porosities than the corresponding PAN-AF and PAN-BF.

![Pore size distribution for the PAN substrates](image)

Figure 1.11. Pore size distribution for the PAN substrates [19].

As reported in Table 1.4, the permeability of all three gases increases as:

PAN-B < PAN-A < PAN-BF < PAN-AF
which closely follows the same order as the mean effective pore sizes of the supports.

Table 1.4. Gas transport properties of uncoated PAN membranes [19].

<table>
<thead>
<tr>
<th>Fiber</th>
<th>$P_{O_2}$ (GPU)</th>
<th>$P_{N_2}$ (GPU)</th>
<th>$P_{CO_2}$ (GPU)</th>
<th>$P_{O_2}/P_{N_2}$</th>
<th>$P_{CO_2}/P_{N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN-A</td>
<td>13400±700</td>
<td>14400±600</td>
<td>11800±500</td>
<td>0.94</td>
<td>0.82</td>
</tr>
<tr>
<td>PAN-B</td>
<td>3700±200</td>
<td>3900±300</td>
<td>3400±200</td>
<td>0.95</td>
<td>0.86</td>
</tr>
<tr>
<td>PAN-AF</td>
<td>31000±2000</td>
<td>33000±2500</td>
<td>28000±2000</td>
<td>0.94</td>
<td>0.85</td>
</tr>
<tr>
<td>PAN-BF</td>
<td>25400±1500</td>
<td>27700±1700</td>
<td>22000±1500</td>
<td>0.92</td>
<td>0.87</td>
</tr>
</tbody>
</table>

For coated membrane (Table 1.5), the PAN-AF and PAN-BF selectivities are reduced, indicating defects in their selective layers. As the pore sizes of PAN-A and PAN-B are smaller than those of PAN-AF and PAN-BF, the intrusion of the polymer solution is more significant in PAN-AF and PAN-BF supports, producing some defects in the composite membranes. The porosity must be high enough to prevent further transport resistance against the penetrating permeants [19].

Table 1.5. Gas transport properties of PAN-PDMS composite membranes coated with 3 wt.% PDMS in hexane [19].

<table>
<thead>
<tr>
<th>Fiber</th>
<th>$P_{O_2}$ (GPU)</th>
<th>$P_{N_2}$ (GPU)</th>
<th>$P_{CO_2}$ (GPU)</th>
<th>$P_{O_2}/P_{N_2}$</th>
<th>$P_{CO_2}/P_{N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN-A</td>
<td>147±12</td>
<td>67±5</td>
<td>790±30</td>
<td>2.2</td>
<td>11.8</td>
</tr>
<tr>
<td>PAN-B</td>
<td>77±8</td>
<td>28±4</td>
<td>370±40</td>
<td>2.7</td>
<td>13.0</td>
</tr>
<tr>
<td>PAN-AF</td>
<td>258±20</td>
<td>216±10</td>
<td>710±80</td>
<td>1.2</td>
<td>3.3</td>
</tr>
<tr>
<td>PAN-BF</td>
<td>672±30</td>
<td>478±13</td>
<td>2000±200</td>
<td>1.4</td>
<td>4.2</td>
</tr>
</tbody>
</table>

1.5.1.2 Coating condition

The properties of PDMS composite membranes for gas/vapor recovery are strongly related to the casting conditions/formulations such as crosslinking agents (Vinyltrimethoxysilane (VTMOS), Phenyltrimethoxysilane (PTMOS), Tetraethylorthosilicate (TEOS), 3-
aminopropyltriethoxysilane (APTEOS)), coating technique, casting gap, dipping time, coating solvent, number of sequential coatings and coating concentration (Table 1.6).

Table 1.6. Coating parameters of PDMS composite membrane for gas separation.

<table>
<thead>
<tr>
<th>Coating parameters</th>
<th>Gas pairs &amp; test condition</th>
<th>Permeability (Barrer)</th>
<th>Permeance (GPU)</th>
<th>Selectivity (-)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosslinking agents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEOS</td>
<td>C₃H₈=5000</td>
<td></td>
<td>21.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VTMOS</td>
<td>C₃H₈/N₂-Pure</td>
<td></td>
<td>60.38</td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>PTMOS</td>
<td>C₃H₈=11000</td>
<td></td>
<td>46.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APTEOS</td>
<td>C₃H₈=13000</td>
<td></td>
<td>53.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coating technique</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pouring</td>
<td>H₂=7</td>
<td></td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film casting</td>
<td>H₂/CH₄-Pure</td>
<td></td>
<td>22</td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>Dip coating</td>
<td>H₂=9</td>
<td></td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting gap</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 µm</td>
<td>C₃H₆/N₂-Mixed</td>
<td></td>
<td>17</td>
<td></td>
<td>[32]</td>
</tr>
<tr>
<td>12.5 µm</td>
<td></td>
<td></td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipping time</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[33]</td>
</tr>
<tr>
<td>34 s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coating solvent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexane</td>
<td>CO₂/N₂-Pure</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>CO₂=1035</td>
<td></td>
<td>86.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>CO₂=812</td>
<td></td>
<td>81.20</td>
<td></td>
<td>[34]</td>
</tr>
<tr>
<td>Number of coatings</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[20]</td>
</tr>
<tr>
<td>Coating concentration</td>
<td>1%</td>
<td>CO₂=1766</td>
<td>12.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----</td>
<td>----------</td>
<td>------</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>CO₂=1075</td>
<td>13.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>CO₂=1073</td>
<td>12.8</td>
<td>[35]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4%</td>
<td>CO₂=728</td>
<td>13.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>CO₂=375</td>
<td>12.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Madaeni et al. [20] studied the effects of casting conditions including casting solution composition, casting approach, and number of casting on the PDMS composite membranes properties. The effect of PDMS concentration in the coating solution is presented in Figure 1.12a. They investigated dip-coatings and single film casting on a flat sheet support. In the film casting method, when the casting solution concentration increased, the CO₂ permeation decreased at first and slowly reached a constant value, while under dip-coating conditions, strong permeation reduction was initiated after incorporation of 5 wt.% PDMS. They also investigated the effect of five consecutive coating on the PDMS composite membranes properties (Figure 1.12a). As the number of casting and dip-coating increased, the CO₂ permeation decreased, but the reduction was slower for the dip-coating method compared with film casting. Dip-coating also exhibited a delay step before permeability reduction owing to the lower PDMS coated layer thickness. By casting, the CO₂ permeation was almost constant after double film casting, while triple dip-coating was needed to achieve constant permeation. By improving the number of coating, similar permeability was observed in both methods. Figure 1.12 presents the effect of consecutive coating on the
synthesized composite membranes selectivity. It can be seen that the selectivity increased by the formation of thicker layers during supplementary coating steps. By further coating, excellent sealing of the defect holes occurs and the unselective permeability from the pinholes decreases. By increasing the number of consecutive coating, the selectivity of composite membrane synthesized by casting was lower than dip-coating [20].
Figure 1.12. The effect of coating solution concentration on permeability and selectivity (a). The effect of sequential film casting and dip-coating on permeability and selectivity (b) [20].
1.5.2 Effect of operating conditions on gas separation properties

Pure gas permeation through rubbery membranes is related to the components and polymers, as well as the operating parameters. Moreover, for mixed gas, the separation performance of gas through membranes is also influenced by the presence of the other gases so deviation from the pure gas behavior is expected. So, the permeability data of pure gas tests is not always representative to estimate mixed gas permeability. This is due to the coupling effect (interactions) of gases making the separation behavior of gas mixtures different from those pure gases. For the pure test, the linear pressure dependency of permeability is as follows [21]:

\[
P = P_0 + m \Delta P
\]  \hspace{1cm} (1.1)

where \( P_0 \) is the permeability and \( m \) is the slope. The Arrhenius dependency of permeability with temperature is as follows:

\[
P = P_0 \exp \left( - \frac{E_p}{RT} \right)
\]  \hspace{1cm} (1.2)

where \( P_0 \) is the pre-exponential factor, \( E_p \) is the apparent activation energy of permeation [kJ/mol], \( R \) is the universal gas constant \((8.314 \times 10^{-3} \text{ kJ/mol K})\), and \( T \) is the absolute temperature (K). Sadrzadeh et al. [21] investigated the effect of operating conditions on the permeation of pure and ternary mixed gas \((\text{C}_3\text{H}_8, \text{CH}_4 \text{ and H}_2)\) through PDMS composite membranes and the results are reported in Table 1.7.
Table 1.7. Permeation data of pure and ternary gas mixture through PDMS composite membrane [21].

<table>
<thead>
<tr>
<th>Penetrant</th>
<th>Pure gas</th>
<th>Mixed gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m$ (Barrer/atm)</td>
<td>$E_p$ (kJ/mol)</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$-27.1 \pm 2.2$</td>
<td>$13.3 \pm 1.5$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>$-21.9 \pm 2.0$</td>
<td>$7.7 \pm 1.0$</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>$2534 \pm 25$</td>
<td>$-12.3 \pm 1.5$</td>
</tr>
</tbody>
</table>

The value of $m$ is mainly determined by the interaction between three factors: plasticization, hydrostatic pressure, and penetrant solubility. Plasticization refers to an increase in penetrant diffusivity resulting from increased polymer local segmental motions caused by the presence of penetrant molecules in the polymer matrix [21]. As transmembrane pressure and, therefore, penetrant concentration in the polymer increases, the tendency to plasticize the polymer matrix increases, particularly for strongly sorbing penetrants. On the other hand, the high transmembrane pressure acting on the polymer film can slightly compress the polymer matrix, thereby reducing the amount of free volume available for the penetrant transport and reducing the penetrant diffusion coefficient. In addition to these dual effects, which affect the penetrant diffusion coefficient, the penetrant solubility in rubbery polymers frequently increases with pressure, especially for organic vapor penetrants, leading to a corresponding increase in permeability. Hence, the permeability coefficients of low-sorbing penetrants, such as H$_2$, which do not plasticize the composite PDMS/PES membrane and, as indicated before, have pressure-independent solubility coefficients essentially, decrease very slightly with increasing pressure. This was confirmed by the negative $m$ values in Table 1.7. In contrast, the permeability coefficients of more soluble penetrants, such as C$_3$H$_8$, which induce significant plasticization and have solubility coefficients that also significantly increase with pressure, increase with increasing pressure. For these penetrants, $m$ is positive. So, for the lighter gases examined (H$_2$ and CH$_4$), the permeability coefficients increase with increasing temperature indicating that the activation energies of permeation ($E_p$) are positive. When the feed temperature increases, condensability or solubility of heavier gases such as C$_3$H$_8$ significantly
decreases, while the mobility or diffusivity of these gases slightly increases. On the other hand, the diffusivity of much smaller molecules, such as H₂, substantially increases with increasing temperature, while their solubility is very slightly affected by temperature. Thus, higher temperature decreases the C₃H₈ permeability, while increases those of H₂ and CH₄. As it can be seen, contrary to pure gas results, permeability values of C₃H₈ in the gas mixture slightly decrease with increasing transmembrane pressure, while those of H₂ and CH₄ increase. The permeability reduction of C₃H₈ may be due to the competitive sorption resulting in almost constant (or slightly increasing) solubility coefficient (the ratio of gas concentration in the polymer to its partial pressure) for each component. At the same time, the polymer swells, resulting in much higher diffusivity for smaller molecules such as H₂ and CH₄ compared to larger ones such as C₃H₈ due to competitive diffusion. The net result is an increase in the H₂ and CH₄ permeability with a decrease in the C₃H₈ permeability [20]. Mixed-gas permeation property of the PDMS/PES membranes was also determined as a function of temperature. Similar to pure gas results, C₃H₈ permeability was found to increase by decreasing the feed temperature. The increasing C₃H₈ permeability by reducing the feed temperature is attributed to the negative Ep (Table 1.7). The activation energy of permeation is the sum of the activation energy of diffusion, Ed, and the heat of sorption, ΔHs [20]. Because Ed is always positive in an activated diffusion process, the negative Ep for C₃H₈ is associated to a larger negative ΔHs value. On the other hand, the permanent feed gas components, H₂ and CH₄, exhibit slightly positive activation energy of permeation (10.9 and 6.2 kJ/mol, respectively), leading to lower permeabilities with decreasing the feed temperature [21].

Saedi et al. [22] performed four different tests on PDMS/PES composite membranes at various feed pressure composition and temperature for ternary H₂S/CO₂/CH₄ gases. The influence of the feed composition could be witnessed by matching the experiment numbers 2 and 4 from Table 1.8. As observed, by increasing the H₂S content in the feed, the permeability of all gases through membrane decreased except CH₄ in the binary feed mixture. The solubility of any component into the membrane is affected by other components in any mixtures. The presence of H₂S in the feed mixture increases plasticization and then reduces the interaction between the components and the membrane. Higher interaction between the membrane and the components is related to the higher
solubility term of the gas permeability. When the H₂S content increased, the plasticization phenomenon by H₂S increased. This plasticization allows higher polymer chain mobility and increase the free volume. This effect improves the CH₄ permeability and decreases the membrane selectivity [22].

Table 1.8. Gas permeance for PDMS coated PES at different operating parameters for binary H₂S/CH₄ feed gas [22].

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Feed composition</th>
<th>Feed pressure (bar)</th>
<th>Feed temperature (°C)</th>
<th>H₂S permeance (GPU)</th>
<th>CH₄ permeance (GPU)</th>
<th>H₂S/CH₄ selectivity (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂S: 1.68</td>
<td>10</td>
<td>25</td>
<td>32.8</td>
<td>2.97</td>
<td>11.04</td>
</tr>
<tr>
<td></td>
<td>CH₄: 98.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>H₂S: 1.68</td>
<td>30</td>
<td>25</td>
<td>16.38</td>
<td>3.15</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>CH₄: 98.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>H₂S: 1.68</td>
<td>30</td>
<td>35</td>
<td>12.71</td>
<td>3.21</td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td>CH₄: 98.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H₂S: 7.5</td>
<td>30</td>
<td>25</td>
<td>7.79</td>
<td>3.18</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td>CH₄: 92.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.5.3 Membrane system design parameters

Besides the synthesis and operating parameters, design parameters can also affect the gas separation performance of composite membranes. Optimization of the design parameters avoids energy loss in membrane systems. The most critical design parameters are:

- Flow distribution,
- Number of stages,
• Module configuration.

1.5.3.1 Module configuration

Several configurations are possible to use hollow fiber membrane (HFM) such as counter-current and co-current. Liu et al. [36] investigated the coating performance of a selective layer of polyether block amide (PEBAX) onto microporous PEI HFM and studied various configurations (Figure 1.13). A counter-current configuration was found to be more efficient than a co-current configuration. Moreover, taking into account the pressure buildup of permeate in the tube side, it is occasionally beneficial to remove the permeate from both ends of the HFM bores, which is a combination of the counter-current and co-current configurations. By itself, the performance of the PEBAX/PEI HFM was assessed for all three flow configurations for CO\textsubscript{2}/N\textsubscript{2} separation.

Permeate and residue flow rates produced per membrane area are two factors controlling the membrane productivity. The CO\textsubscript{2} recovery is also shown in Figure 1.14. Clearly, for both N\textsubscript{2} enriched residue and nitrogen-enriched permeate products, there is a trade-off between the product purity and product recovery. This trade-off was also observed for the recovery and permeate flow rate of CO\textsubscript{2}. Furthermore, for a high permeate flow rate, high CO\textsubscript{2} concentration on the permeate side is achieved, while the opposite result is obtained for N\textsubscript{2}. This means there is a slight reduction in CO\textsubscript{2} at a high residue flow rate along the flow path through the membrane module which is the driving force for CO\textsubscript{2} transportation through the HFM, leading to a high CO\textsubscript{2} permeation rate. Comparing the above three flow configurations, the counter-current configuration performs better than the co-current configuration in terms of product purity and recovery.
The separation performance is intermediate when the permeate is removed from both ends of the hollow fiber bores, for which the flow arrangement is equivalent to a combination of counter- and co-current flows. This is mostly due to the driving force variation available for transport in the three configurations in which the counter-current configuration has the maximum driving force across the membrane, causing the best recovery efficiency. Consequently, the counter-current configuration is the favored design in HFM separation processes.
Figure 1.14. Productivity and recovery of CO\textsubscript{2}/N\textsubscript{2} as a function of CO\textsubscript{2}/N\textsubscript{2} concentration in permeate. Module configurations: (○) counter-current flow; (□) co-current flow; (□) combination of counter-current and co-current flows [36].

1.6 Composite membrane characterization

A typical composite membrane, in addition to having excellent separation performance, must have high thermal, mechanical and morphological properties to be used in industrial applications. In this section, some typical approaches are presented.

1.6.1 Mechanical and thermal properties

A typical composite membrane needs high flux and selectivity, as well as excellent thermal and mechanical stabilities. Consequently, the permselective layer should be as thin as possible to get higher permeation. So both selective and non-selective layers, as well as interfacial properties, should be optimized to produce a suitable composite membrane with long-term stability. Thermal and mechanical stabilities have key roles in designing a composite membrane. The main techniques to assess these properties are tensile test and thermogravimetric analysis (TGA). Zhang et al. [37] studied the crosslinking of PEI and
PDMS as the permselective layer which was coated on a PAN microporous layer. The properties of the crosslinked composite membranes were studied by TGA (Figure 1.15). It was concluded that the whole composite membrane degraded in three stages. The first one, around 30-200 °C, was contributed by water evaporation. The second one, around 360-450 °C, was related to the branched chains degradation on PAN and PEI, and the last one, around 450-600 °C, was attributed to the pyrolysis of the polymer backbones. By introducing PDMS, a substantial weight loss was observed and increasing the PDMS content led to higher weight reduction. Such results showed that the presence of hydrophobic PDMS limited the water-absorbing ability of the composite membranes. The PAN/PEI showed a degradation temperature near 335 °C. In comparison to the addition of PDMS, higher decomposition temperature was observed up to 355 and 360 °C for PAN/PEI–PDMS-0.5% and PAN/PEI–PDMS-1.0%, respectively. This can be attributed to the restriction of PEI chains mobility after crosslinking with PDMS. PAN/PEI–PDMS-X% showed higher residues than PAN/PEI. For example, the residues of PAN/PEI was 18.5%, while for the 0.5% to 1.0% PDMS content, the residue increased from 23.4% to 28.5% [37].

The mechanical stability of the composite membranes was investigated by stress-strain curves as reported in Figure 1.15. The results showed that PAN/PEI with Young’s modulus of 700 MPa, have excellent mechanical stability along with a tensile strength of 36.1 MPa and an elongation at break of 23.2%.
1.6.2 Morphology

SEM can be used to monitor the morphology of the composite membranes and to study the interfacial quality. Wu et al. [38] investigated aminopropyltrimethoxysilane (APTMS), a bifunctional amino silane, to enhance the interfacial stability between the selective layer and microporous layer. APTMS acts as a crosslinking agent for polymer chains and also as a “sticker” anchoring top layer to the microporous substrate layer (Figure 1.16).
As observed, a dense selective layer with a homogeneous thickness was created (Figure 1.17(a)). No defects were observed at the interface between the selective layer and the microporous layer. To clarify the APTMS role in improving the interfacial adhesion, the Si loading was determined by energy dispersive spectroscopy (EDS). Five different points were investigated by EDS in Figure 1.17(b) and the relevant Si loading distribution is shown in Figure 1.17(c). In theory, the Si loading is 15.6% in APTMS and 37.9% in PDMS [38]. Consequently, the Si loading of the interfacial layer between PDMS and APTMS should be 15.6-37.9%. As it can be seen, the Si loading decreased from the surface (37.3%) to the interface (19.6%), an indication of the APTMS content from the surface to the interface. This enhancement due to APTMS loading led to an improvement of NH$_2$–CH$_2$–CH$_2$–CH$_2$–segments near the interface. This means that the APTMS molecules firstly uniformly dispersed in the PDMS-APTMS mixture and then were transported to the microporous layer during the crosslinking and membrane fabrication process. This
enhancement of APTMS comes from the various hydrophilic/hydrophobic property between both layers as PDMS is hydrophobic, while PES and APTMS are hydrophilic. As seen in Figure 1.17, this interfacial improvement leads to improved adhesion of the selective layer onto the microporous layer via better van der Waals forces and hydrogen bonds between the amino groups and the sulfone groups.

Figure 1.17. (a) The cross-section scanning electron microscopy (SEM) image of the PDMS–APTMS-0.06/PES composite membrane for pervaporation experiments. (b) The cross-section SEM image of the PDMS–APTMS-0.06/PES composite membrane for EDS measurements. The five light spots shown in the PDMS active layer indicate the five EDS measurement points (spectrum) numbered from the interface to the surface. (c) Si content along the longitudinal direction of the PDMS–APTMS-0.06/PES active layer measured by EDS [38].
1.7 Thesis objectives and organization

In this project, composite membranes were prepared by coating PDMS (commercial package of Dehesive resin (Figure 1.18), cross-linking agent and catalyst) on porous polyethylene (PE) substrates produced by a novel method which was patented in our research group. The idea is to determine the effect of synthesis parameters and operating conditions on the gas permeation and separation performance.

To do so, the work will be divided into three parts:

- Production of PDMS/LDPE composite membranes,
- Characterization of PDMS/LDPE composite membranes,
- Performance optimization of PDMS/LDPE composite membranes.

This dissertation consists of four main chapters:

In the first chapter, composite membranes and their applications were introduced. The parameters affecting the composite membranes performance were identified by a literature review and analytical methods to characterize the composite membranes.

The second chapter is devoted to describe in details the production and characterization of PDMS/LDPE composite membranes.
Chapter 3 studies the permeation and thermal properties of PDMS/LDPE composite membranes.

Chapter 4 optimizes the composite membranes performances under different operating conditions (pressure, temperature and gas composition) and processing formulations.

Finally, the fifth chapter provides overall conclusions regarding the work done with some recommendations for future work.
Chapter 2

Production of composite membranes by coupling coating and melt extrusion/salt leaching

Résumé

Ce travail présente une méthode simple et efficace pour produire une membrane composite plane (FSCM) avec une résistance minimale dans la couche de support. Le procédé est également peu coûteux et utilise une quantité limitée de solvant (eau). En particulier, une série de polydiméthylsiloxane/polyéthylène de basse densité (PDMS/LDPE) FSCM a été réalisée en enrobant une couche de PDMS active sur un support LDPE microporeux par extrusion continue et lixiviation de sel (68% NaCl) en immersion dans de l'eau chaude (50°C). Les membranes ont ensuite été caractérisées avant et après la lixiviation en termes de morphologie, de porosité et de distribution des tailles de pores, ainsi que de propriétés thermiques. Les résultats ont montré que la structure microporeuse est fortement corrélée au sel utilisé et à la quantité lessivée de la structure polymérique. Les FSCM résultantes ont été finalement utilisées pour la séparation en phase gazeuse de C₃H₈ du CO₂, CH₄, N₂ et H₂ en termes de perméabilité, de solubilité et de diffusivité. Les résultats montrent que pour une pression en amont de 120 psi, le FSCM est environ 6, 16, 23 et 53 fois plus perméable au C₃H₈ que le CO₂, CH₄, H₂ et N₂, confirmant les excellentes performances de séparation de ces membranes pour des applications industrielles.
Abstract

This work presents a simple and efficient method to produce a flat sheet composite membrane (FSCM) with minimum resistance in the support layer. The process is also low cost and uses a limited amount of solvent (water). In particular, a series of polydimethylsiloxane/low-density polyethylene (PDMS/LDPE) FSCM were produced by coating an active PDMS layer on a microporous LDPE support via continuous extrusion and salt leaching (68% wt. NaCl) using immersion in hot water (50°C). The membranes were then characterized before and after leaching in terms of morphology, porosity and pore size distribution, as well as thermal properties. The results showed that the microporous structure is highly correlated to the salt used and the amount leached out from the polymer structure. The resulting FSCM were finally used for gas separation of C$_3$H$_8$ from CO$_2$, CH$_4$, N$_2$, and H$_2$ in terms of permeability, solubility and diffusivity. The results show that for an upstream pressure of 120 psi, the FSCM is about 6, 16, 23, and 53 times more permeable to C$_3$H$_8$ than CO$_2$, CH$_4$, H$_2$, and N$_2$ respectively, confirming the outstanding separation performance of these membranes for industrial applications.

**Keywords:** Composite membrane; PDMS; LDPE; salt leaching; solubility; permeability; diffusivity.
2.1 Introduction

Composite membranes are usually fabricated by coating a permselective layer on a porous substrate which is prepared by phase inversion[39] or non-solvent induced phase separation[40] processes. These methodologies use large amounts of harmful, expensive, and flammable organic solvents which must be removed after the porous structure is created through numerous washing steps, making this approach not environmentally friendly and not economical (solvent recuperation and purification, health and safety hazards, etc.). These methods also have low production rates due to the slow kinetics of liquid-liquid phase separation[41]. For these reasons, solvent free technologies were developed.

Very few solvent free approaches for the fabrication of porous structures for membranes application can be found in the literature [42]–[44]. The most interesting ones are probably the stretching and melt-spinning techniques which are based on the melt-extrusion of neat semi-crystalline polymers to create the precursors, followed by axial stretching of these precursors to create a porous network. This method is only useful for semi-crystalline polymers, but following mechanical stretching, several thermal post-treatments are necessary to stabilize the crystalline structure and prevent membrane shrinkage [45]. Some development on the preparation of open-cell foams based on polymers/fillers compounds using leachable particles (salts) with low-density polyethylene (LDPE), polypropylene (PP), polysulfone, polymethylmethacrylate, polystyrene, and polyurethane rigid foams were presented [46]–[49]. Here, it is proposed to develop a hybrid continuous process to prepare flat sheet composite membranes (FSCM).

Various polymers have been used as a permselective layer for the fabrication of composite membranes. To remove hydrocarbons from other gasses, PDMS is the most commonly used polymer for the separation of higher hydrocarbons from other gases. Lately, several investigations were devoted to the separation of O2, N2, H2, CO2, CH4, and C2-C4 olefins and paraffins using PDMS membranes [13], [19], [24], [34], [50]–[52].

To the best of the authors knowledge, this paper is the first report disclosing the preparation of a FSCM by combining coating with melt-extrusion/salt leaching. In this work, a selective PDMS layer was coated on a LDPE microporous support to continuously produce
a FSCM. Then, the permeability and solubility of \( \text{C}_3\text{H}_8, \text{CO}_2, \text{CH}_4, \text{N}_2, \) and \( \text{H}_2 \) through the composite PDMS/LDPE membranes were determined at different feed pressures. According to the solution-diffusion theory, the concentration-averaged diffusion coefficient can also be determined. Finally, the ideal selectivity of \( \text{C}_3\text{H}_8 \) with respect to other gases was determined to show the efficiency of these membranes to remove hydrocarbons from light components.

### 2.2 Theory

Gas permeation in a PDMS film can be approximated by the solution-diffusion model via permeability \( (P) \) defined as:

\[
P = \frac{Nl}{p_2 - p_1}
\]  

(2.1)

where \( N \) is gas flux through a film with thickness \( l \) and a partial pressure difference \( (p_2 - p_1) \), \( p_1 \) is the downstream pressure and \( p_2 \) is the upstream pressure \( (p_2 > p_1) \). However, the diffusion can be modeled by Fick’s law as [53][54]:

\[
N = -\frac{D_{\text{loc}}}{(1 - \omega)} \left( \frac{dC}{dx} \right)
\]

(2.2)

where \( D_{\text{loc}} \) is the local diffusion coefficient, \( \omega \) is the gas mass fraction in the polymer and \( x \) is the diffusion direction. Integration of the expression yields:

\[
P = \frac{1}{p_2 - p_1} \int_{C_i}^{C_f} D_{\text{eff}} \, dC
\]

(2.3)

where \( C \) is the concentration in the polymer and \( D_{\text{eff}} \) is the effective diffusion coefficient \( (D_{\text{eff}} = D_{\text{loc}}/(1 - \omega)) \). If the diffusion coefficient is independent of concentration, the integration gives:

\[
P = \frac{C_f - C_i}{p_2 - p_1} D_{\text{eff}}
\]

(2.4)
But if the diffusion coefficient is a function of concentration, $D_{\text{eff}}$ is substituted by the averaged diffusivity ($\bar{D}$). Finally, when the downstream pressure (permeate side) is negligible compared to the upstream pressure (feed side), Equation (2.4) simplifies to:

$$P = SD$$

(2.5)

where $D$ is $D_{\text{eff}}$ or $\bar{D}$ and the solubility ($S$) should be evaluated at the feed conditions as:

$$S = \frac{C}{P}$$

(2.6)

The series resistance model can explain the component permeation through a composite membrane as[55]:

$$N_A = \left(p_2 - p_1\right) \left(\frac{i_{\text{MS}}}{P_{A}^{\text{MS}}} + \frac{i_{\text{SL}}}{P_{A}^{\text{SL}}} \right)^{-1}$$

(2.7)

where $N_A$ is the flux of component A at steady-state. The superscripts $MS$ and $SL$ are associated to the microporous substrate and permselective layer, respectively. The ideal selectivity may be written as the ratio of the component fluxes at a given a pressure as[55]:

$$\alpha_{A/B} = \frac{N_A}{N_B}$$

(2.8)

Therefore, the ideal selectivity of a gas for a composite membrane can be calculated as:

$$\alpha_{A/B} = \frac{i_{\text{MS}}}{P_{A}^{\text{MS}}} + \frac{i_{\text{SL}}}{P_{A}^{\text{SL}}}$$

(2.9)

From Equation (2.9), it can be concluded that the ideal selectivity of a gas for a composite membrane is based on the properties of both the substrate and the permselective layers. When the main resistance of a FSCM to component transport is in the selective layer (as in the present work), the terms $i_{\text{MS}}/P_{A}^{\text{MS}}$ and $i_{\text{MS}}/P_{B}^{\text{MS}}$ can be neglected to give:

$$\alpha_{A/B} = \frac{i_{\text{SL}}}{P_{A}^{\text{SL}}} = \frac{P_{A}^{\text{SL}}}{P_{B}^{\text{SL}}}$$

(2.10)
Equation (2.10) can also be expressed using Equation (2.5) to get a product of solubility selectivity and diffusivity selectivity as:

\[
\alpha_{A/B} = \left( \frac{S_A}{S_B} \right) \times \left( \frac{D_A}{D_B} \right)
\]  

(2.11)

In addition to parameters such as pressure, temperature, and composition, the solubility strongly depends on the gas condensability. In general, solubility increases with increasing condensability. Since gas condensability is related to the normal boiling point and critical temperature of a compound [56], the solubility selectivity increases with increasing condensability difference between both gases. Larger molecules having higher normal boiling point and higher condensability have higher solubility than smaller molecules. So diffusivity drops when molecular size increases and the diffusivity selectivity increases when the size difference between both molecules increases, with the smaller molecule having higher diffusivity [56]. Therefore, a trade-off generally occurs between diffusivity selectivity and solubility selectivity, with the overall selectivity being related to the order of magnitude of these two terms.

2.3 Experimental

2.3.1 Material

The polymer used for the support was low density polyethylene (LDPE) Novapol LA 0219-A (Nova Chemicals, Canada) with a density of 919 kg/m³ (ASTM D792) and a melt index of 2.3 g/10 min (ASTM D1238). NaCl with particles sizes of 5-55 µm and a density of 1981 kg/m³ (Soda-LO Extra Fine) was supplied by Tate & Lyle (USA).

The polydimethylsiloxane (PDMS, Dehesive 944, density 0.91 g/cm³ at 20°C) was supplied by Wacker Silicones Corporation (USA). This PDMS is reported to be suitable for coating polyethylene and polypropylene films according to the manufacturer's technical datasheet. Wacker also provided a cross-linker (V24, hydrogenpolysiloxane) and a catalyst (Catalyst OL). Toluene, as a solvent, was purchased from Anachemia (Canada) with a purity of 99.5%. All the gasses, with purity above 99.0%, were purchased from Praxair (Canada).
2.3.2 Membrane fabrication

The composite membranes were produced by combining a coating and a melt extrusion/salt leaching method (Figure 2.1). In this study, a LDPE flat support was made using a co-rotating twin-screw extruder (Leistritz ZSE 27) with a L/D ratio of 40. In the first step (melt extrusion), LDPE pellets were fed in the first zone of the extruder (main feeder) at a rate of 5 g/min, while NaCl particles were fed in the third zone of the extruder (side feeder) at a rate of 10.5 g/min to produce blends containing 68% wt. of salt [18]. The temperature profile in the extruder was controlled at 135 °C for zone 1, 140 °C for zones 2-8, and 145 °C for zone 9, 10 and the die (zone 11). The extruder was operated at a constant mass flow rate of 15.5 g/min and a screw speed of 60 rpm. A flat die with dimensions of 15 cm width and 250 µm gap opening was used to form the melt into a flat sheet. The material was then introduced in a calendar with a drawing speed of the take-up unit set at 16 cm/min. In the second step (coating), the PDMS coating solutions were prepared by dissolving an appropriate amount of PDMS polymer resin, cross-linking agent and catalyst (weight ratio of 10:1:1 (w/w/w)) in toluene to obtain a homogeneous 50% PDMS solution. The coating solution was poured onto the LDPE/NaCl sheet and cast with a roller to make a uniform layer. In the third step (salt leaching/solvent evaporation), the membranes were put in contact with the surface of a hot water bath (50 °C) to leach out the salt and evaporate the solvent of the coated layer. In the fourth step (curing), the membranes were kept for 48 h at room temperature to cure. In the last step, the membranes were placed in a vacuum oven for 2 h at 80 °C to complete PDMS cross-linking and remove the remaining solvent. For comparison, the LDPE porous support layer without coating was also produced.

The porosity of the substrate (PO) was determined as:

\[
PO(\%) = \left(1 - \frac{\rho_1}{\rho_2}\right) \times 100 \tag{2.12}
\]

where \(\rho_2\) and \(\rho_1\) are the densities of the neat LDPE and porous LDPE flat sheet calculated by the ratio of volume over weight.
2.3.3 Membrane characterization

2.3.3.1 Scanning electron microscopy (SEM)

The morphology of the membrane was examined via scanning electron microscopy (SEM) using a JEOL JSM-840A (JEOL, Japan). Samples were first immersed in liquid nitrogen (60 s) and then fractured to obtain well-defined cross-sections. Finally, pore size distributions were calculated by analyzing the SEM images using the Image-J V1.50i software (National Institutes of Health (NIH), USA).

2.3.3.2 Thermogravimetric analysis (TGA)

TGA analysis was performed using a TA Instruments (USA) model Q5000 IR for a temperatures range of 50 to 900 °C in a nitrogen atmosphere at a flow rate of 25 ml/min and a heating rate of 10 °C/min.

2.3.3.3 Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was performed using a Nicolet model 730 (Nicolet Instruments, USA) Fourier transform infrared analyzer in the reflectance mode (Golden-Gate accessories) between 500 and 3500 cm⁻¹ with a 0.5 cm⁻¹ resolution of 128 scans.
2.3.3.4 Sorption and permeation measurement

The pressure decay method was used to determine the gas sorption isotherms [57]. Pure gas permeation was measured using a constant volume/variable pressure method [58]. More details on the procedure are presented as supporting information (Appendix A).

2.4 Results and Discussion

2.4.1 Morphology

2.4.1.1 Morphology of the salt

As seen in Figure 2.2, SODA-LO contains NaCl and a small amount of an organic material introduced to prevent agglomeration [59]. The hollow salt particles have a structure composed of individual NaCl crystals linked together in each particle. Figure 2.2(b) presents the initial particle size distributions of the salt where the average is 32 microns with a standard deviation of 20 microns.
2.4.1.2 Morphology of the LDPE substrate

Typical SEM images of the LDPE microporous substrate before and after salt leaching are presented in Figure 2.3(b) shows that the support has a microporous structure and the resistance to gas permeation across this layer can be assumed to be negligible. Figure 2.3(c) reports the salt particle size distribution salt inside LDPE where the average is 5 microns with a standard deviation of 3 microns. It can be seen that the salt particles are smaller than before extrusion (Figure 2.2(b)). This size reduction is associated to the stresses (shear and elongation) involved in the extruder leading to particle dispersion and break-up. Figure 2.3(d) reports the pore size distribution of the microporous LDPE substrate. The pore size is in the range of 8-11 µm giving a porosity of 54% as calculated using Equation (2.12), but the porosity calculated by the volume of salt removed from the polymer is 47%. This 7%
difference can be associated to a large amount of void created around the salt particles during melt calendaring (Figure 2.3(a) high magnification) due to different coefficients of thermal expansion which is around $39.8 \times 10^{-6} \degree C^{-1}$ for the salt particles[60], and $3.20 \times 10^{-4} \degree C^{-1}$ for LDPE at room temperature [61]. As the LDPE/salt melt was cooled, the polymer matrix shrank more than the salt particles leading to interfacial voids. This is also the reason why the pore size after leaching (8-11 µm) is larger than the salt particle size in LDPE before leaching (3-4 µm).

Figure 2.3. Typical SEM images at different magnifications of the LDPE support: (a) before and (b) after salt leaching, (c) the particle size distribution of the salt inside LDPE and (d) the pore size distribution of the microporous LDPE substrate.
2.4.1.3 Morphology of the FSCM

Figure 2.4 presents a typical SEM image of the PDMS/LDPE FSCM. It can be seen that the LDPE microporous layer is not pore-penetrated and covered by a dense PDMS layer with a thickness of around 50 µm. A thick layer of the PDMS is formed due to the high concentration of PDMS solution (50%). The high concentration was chosen for three reasons; Firstly, to be sure that the selective layer covers any holes on the support surface with only one-time coating step. Second, to avoid penetration of the coating solution into the substrate pores to reduce the resistance of the LDPE microporous layer to component transport. Third, to improve the selectivity.

Figure 2.4. Cross-sectional SEM images of a PDMS/LDPE FSCM.
2.4.2 Formation of the porous structure

In the formation of the LDPE porous support, the salt particles were removed by leaching in water. The salt content (68% wt.) was selected as this value was optimized in our previous study [18]. Since the structure of the porous substrate highly depends on the amount of salt leached out from the polymer matrix, this value was determined by TGA.

Figure 2.5 presents the TGA curve for neat LDPE before extrusion, initial salt particles (Soda-LO), the LDPE substrate before and after leaching, as well as the FSCM. In the range of 220-320 °C, nearly 5 and 3% weight losses occurred for the salt and LDPE substrate before leaching due to the thermal degradation of the organic material coating Soda-LO. Above 800° C, a second loss was observed related to NaCl degradation. In the range of 360-485 °C, about 33, 82, 98, and 100%, weight losses were observed for the LDPE substrate before leaching, FSCM, LDPE substrate after leaching and neat LDPE before extrusion, respectively. These degradations steps are associated to the thermal degradation of LDPE. It can be approximated from Figure 5 that the salt loading is around 67% which is close to the expected value (68%) within experimental uncertainty. The TGA results combined with SEM (Figure 2.3(b) at high magnification) revealed that salt leaching was probably not complete, even after 160 min of continuous leaching and about 2% salt remains in the LDPE layer and FSCM after leaching. In the 485-580 °C range, nearly 16% weight loss occurred for FSCM due to the thermal degradation of PDMS [62].
Figure 2.5. TGA results for neat LDPE pellet before extrusion, initial salt particle (Soda-LO), LDPE substrate before and after leaching, and PDMS/LDPE composite membrane.
2.4.3 FTIR

Figure 2.6 presents the ATR-IR spectra of the LDPE support without coating and PDMS/LDPE FSCM. The strong adsorption bands of the LDPE support at 2916 cm\(^{-1}\) and 2847 cm\(^{-1}\) are associated to C–H stretching vibrations of –CH\(_3\), –CH\(_2\) and –CH groups[63]. These bands disappeared in the FSCM spectra indicating that the surface was completely covered by the PDMS layer [37]. A peak at 783 cm\(^{-1}\) is attributed to –CH\(_3\) rocking and –Si–C– stretching in –Si–CH\(_3\). The bands at 1004 cm\(^{-1}\), 1256 cm\(^{-1}\) and 2961 cm\(^{-1}\) are assigned to –Si–O stretching in –Si–OH, symmetric –CH\(_3\) deformation in –Si–CH\(_3\) and –CH\(_2\)– stretching in –Si–CH\(_2\)–, respectively. The multiple peaks between 650 cm\(^{-1}\) and 900 cm\(^{-1}\) are related to CH\(_3\) rocking and Si–C stretching. Finally, the peak at 1463 cm\(^{-1}\) is attributed to C–H bending deformation [62].

Figure 2.6. FTIR-ATR spectra of the LDPE support and the FSCM.
2.4.4 Solubility

The solubility of all tested gases as a function of pressure at 27 °C is represented in Figure 2.7. It can be seen that the sorption isotherms for all gases are linear (H₂, N₂, CH₄, and CO₂) or nearly linear (C₃H₈). The results show that the dissolved C₃H₈ in the FSCM is 26 and 6 times higher than CH₄ and CO₂ at 70 psi respectively, while the dissolved CO₂ in is 42 and 21 times higher than H₂ and N₂ at 290 psi, respectively. The concentration of low solubility gases such as N₂, H₂, CH₄ and CO₂ in rubbery polymers can be approximated by Henry’s law [56]:

\[ C = k_d p \]  
\[ (2.13) \]

where \( k_d \) [cm³(STP)/(cm³ psi)] is the Henry’s law constant and the values are reported in Table 2.1. The nonlinear behavior of C₃H₈ at high pressures is related to PDMS swelling due to the high concentration of dissolved C₃H₈ [64]-[68]. The concentration of high solubility gases in uncrosslinked rubbery polymers obeys the Flory-Huggins (FH) expression as [64]:

\[ \ln a = \ln \phi_2 + (1 - \phi_2) + \chi (1 - \phi_2)^2 \]  
\[ (2.14) \]

where \( a \) is the activity which can associated to a relative pressure, \( p/p_{sat} \) where \( p_{sat} \) is the saturation vapor pressure of the gas, \( \chi \) is the Flory-Huggins interaction parameter and \( \phi_2 \) is the volume fraction calculated as [69]:

\[ \phi_2 = \left[ 1 + \frac{22.414}{CV_2} \right]^{-1} \]  
\[ (2.15) \]

where \( V_2 \) is the partial molar volume and \( C \) is the equilibrium penetrant concentration in the polymer. The Flory-Rehner (FR) model is a modified FH equation for crosslinked rubbery polymers giving [64]:

\[ \ln a = \ln \phi_2 + (1 - \phi_2) + \chi (1 - \phi_2)^2 + V_2 \left( \frac{V_e}{V_0} \right) \times \left[ (1 - \phi_2)^{1/3} - \left( \frac{1 - \phi_2}{2} \right) \right] \]  
\[ (2.16) \]
where \( V_2 \) is the penetrant molar volume, \( \nu_e \) is the effective number of crosslinks, and \( V_0 \) is the volume of penetrant-free polymer. \( C_3H_8 \) saturation vapor pressure (145 psi), partial molar volume (80 cm\(^3\)/mol) and molar volume (76 cm\(^3\)/mol) were taken from the literature [69]. The average crosslink density \((\nu_e/V_0)\) was calculated by the following steps:

1- \( C_3H_8 \) sorption in uncrosslinked silicone oil was measured (67.5 cm\(^3\) gas/cm\(^3\) oil at 80 psi and 27°C). The FH interaction parameter (\( \chi \)) was calculated to be 0.387.

2- The volume fraction of \( C_3H_8 \) (\( \phi_2 \)) in the crosslinked polymer was then calculated at the same pressure and temperature to be 0.187.

3- Crosslink density \((\nu_e/V_0)\) was calculated by Equation (2.16) to be \(6.3 \times 10^{-4}\) mol/cm\(^3\).

The dash line in Figure 2.7 represents the model based on the FR theory using a concentration-averaged interaction parameter \( \bar{\chi} \) as [69]:

\[
\bar{\chi} = \frac{1}{\phi_{2,\text{max}}} \int_0^{\phi_{2,\text{max}}} \chi(\phi_2) \phi_2 \, d\phi_2
\]

which was found to be 0.315. Figure 2.7 shows that the FR model is better than Henry’s law at higher concentration.
The solubility parameters as a function of pressure for any gas can be determined from the sorption isotherms via Equation (2.6). As shown in Figure 2.8(a), the solubility of C$_3$H$_8$ increases with increasing pressure, while the sorption isotherms of the other gases are nearly constant. So a linear relation can be used as:

\[ S = S^\infty + np \]  

(2.18)

where \( n \) represents the pressure dependence of the solubility and \( S^\infty \) is the infinite dilution solubility given by:

\[ S^\infty = \lim_{p \to 0} \left( \frac{C}{p} \right) \]  

(2.19)

The values for both parameters are reported in Table 2.1. Without any interactions between the components and the membrane, the sorption isotherms are commonly related to the
condensability of the component (i.e. critical temperature, $T_c$) \cite{57}\cite{69}. To determine the solubility difference for each component, $S^\infty$ can be plotted as a function of $T_c$. Figure 2.8(b) shows that the logarithm of $S^\infty$ linearly increases with $T_c$.

Table 2.1. Values of $T_c$, $S^\infty$, $n$, $k_d$ and infinite dilution solubility selectivity of $C_3H_8$ with respect to the other gases at 27 °C.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$T_c$ (K)</th>
<th>$S^\infty$ (cm$^3$(STP)/cm$^3$ psi)</th>
<th>$n \times 10^3$</th>
<th>$k_d$ (cm$^3$(STP)/(cm$^3$ psi))</th>
<th>$S^\infty_{C3H8}/S^\infty_{gas}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>33</td>
<td>0.0037</td>
<td>0.0000</td>
<td>0.0037</td>
<td>92.5</td>
</tr>
<tr>
<td>$N_2$</td>
<td>126</td>
<td>0.0055</td>
<td>0.0011</td>
<td>0.0058</td>
<td>61.2</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>191</td>
<td>0.0289</td>
<td>0.0293</td>
<td>0.0349</td>
<td>11.7</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>304</td>
<td>0.1304</td>
<td>0.0491</td>
<td>0.1445</td>
<td>2.61</td>
</tr>
<tr>
<td>$C_3H_8$</td>
<td>370</td>
<td>0.3399</td>
<td>5.5877</td>
<td>0.5757</td>
<td>1.00</td>
</tr>
</tbody>
</table>

For the relatively low sorption gases such as $N_2$, $H_2$, $CH_4$, and $CO_2$, $n$ is close to zero indicating that the solubility of these components is fundamentally independent of pressure. On the other hand, for the highly soluble $C_3H_8$, a large value for $n$ is obtained indicating a stronger solubility dependence on pressure \cite{70}.

Figure 2.8. (a) Solubility of the gases in FSCM as a function of pressure at 27 °C and (b) infinite dilution solubility as a function of $T_c$. 

53
2.4.5 Permeability

Pure gas studies showed that permeability of more soluble permeants increases with increasing pressure, while that of less soluble ones remains constant or can even decrease with increasing pressure [21], [67], [68]. Figure 2.9 presents the effect of transmembrane pressure on H₂, N₂, CH₄, CO₂, and C₃H₈ permeabilities in the FSCM. It can be seen that the permeability coefficient increases in the following order:

N₂ < H₂ < CH₄ < CO₂ < C₃H₈

In general, a linear relation between permeability and pressure is observed which can be written as [65]:

\[ P = P_0 + m \Delta p \] (2.20)

The permeability of a component, determined at \( \Delta p = 0 \), is referred to as \( P_0 \), while \( m \) is the slope of the permeability vs. \( \Delta p \) curve. All the parameters for the tested gases and their relative values with respect to C₃H₈ (ideal selectivity at \( \Delta p = 0 \) \( (P_{0,C3H8}/P_{0,gas}) \)) are reported in Table 2.2. The value of the slope \( m \) can reveal three phenomena occurring in a membrane: plasticization, hydrostatic pressure and penetrant solubility [64], [66].

Plasticization is associated to increased diffusion as a result of increasing polymer segmental motion due to the presence of dissolved molecules between polymer chains [69][71]. For strong sorbing permeants such as C₃H₈ and CO₂, the solubility in rubbery polymers increases with pressure. As the upstream pressure and penetrant concentration in polymer increases, the tendency to plasticize the polymer matrix increases. In addition to these dual effects, which affect the diffusion coefficient, the permeability frequently increases with pressure.

Also, an increase of applied pressure on the membrane can slightly compress the polymer matrix, thereby reducing the amount of free volume available for molecular transport leading to lower diffusion coefficient [72]. Therefore, membrane compaction and solubility reduction with increasing pressure are two factors leading to lower permeability for low-sorbing molecules such as hydrogen. This can also be associated to negative \( m \) values (Table 2.2), while the value is positive for C₃H₈ and CO₂. Table 2.2 shows that the infinite dilution gas permeability and selectivity are in good agreement with the values reported by Merkel et al. for PDMS composite membranes [69] that means the support layer prepared
by new solvent free method did not induce significant transport resistance to gas permeation through PDMS composite membrane.

Figure 2.9. Permeability through the FSCM as a function of the pressure difference at 27 °C.

Figure 2.9. Permeability through the FSCM as a function of the pressure difference at 27 °C.
Table 2.2. Infinite dilution gas permeability \( (P_0) \), \( m \) and \( \text{C}_3\text{H}_8 \)/gas ideal selectivity at \( \Delta p = 0 \) and 27 °C for this study and the results of Merkel et al. obtained at 35 °C [69].

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Merkel et al. [69]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( P_0 ) (Barrer)</td>
<td>( m ) (Barrer/psi)</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>988</td>
<td>-0.70</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>421</td>
<td>-0.41</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>1360</td>
<td>-0.34</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>3322</td>
<td>1.43</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_8 )</td>
<td>3711</td>
<td>142</td>
</tr>
</tbody>
</table>

2.4.6 Diffusivity

Diffusivity in the FSCM at 27 °C was determined using Equation (2.5). As shown in Figure 2.10(a), the pressure dependence of the diffusion coefficient for all gases can be represented by a linear expression as:

\[
D = D_0 + q\Delta p
\]  \hspace{1cm} (2.21)

The diffusivity of each component at \( \Delta p = 0 \) is called \( D_0 \), while \( q \) is the slope of the diffusivity vs. \( \Delta p \) curve. The values reported in Table 2.3 for \( \text{H}_2 \), \( \text{N}_2 \), and \( \text{CH}_4 \) show that the diffusivity term slightly decreases with pressure due to the compression effect leading to negative \( q \) values. Furthermore, the solubility of these components is independent of pressure. Therefore, the permeation of these gases decreases slightly with pressure, while for \( \text{CO}_2 \) and \( \text{C}_3\text{H}_8 \), an increase in both permeability and diffusivity is observed with pressure. At low pressure, the diffusivity increases in the following order which is agreement with their decreasing kinetic diameter (\( \delta \)) (Table 2.3):

\( \text{C}_3\text{H}_8 < \text{CH}_4 < \text{N}_2 < \text{CO}_2 < \text{H}_2 \)

Figure 2.10(b) presents the \( D_0 \) values of each gas in the FSCM as a function of the critical volume of the gas \( (V_c) \) which varies over one order of magnitude. As observed, the diffusivity is a relatively weak function of the molecular size.
The relation between diffusivity and $V_c$ is commonly expressed by the following expression[73]:

$$D = \tau V_c^{-\eta}$$

(2.22)

where $\tau$ and $\eta$ are adjustable parameters. $\eta$ controls the decreasing level or rate of diffusivity with component size. Higher $\eta$ are associated to higher diffusivity selectivity in the FSCM, but membranes with high $\eta$ have diffusion strongly related to component size. According to the results of Figure 2.10(b), the value of $\eta$ for the FSCM is 2.073 which confirms that the components diffusivity is a relatively weak function of the molecular size.

Figure 2.10. (a) Diffusivity as a function of pressure difference at 27 °C and (b) infinite dilution diffusion coefficient $D_0$ as a function of $V_c$. 
Table 2.3. Values of $\delta$, $V_c$, $D_0$, $q$ and ideal diffusivity selectivity of $C_3H_8$/gas at $\Delta p = 0$ and 27 °C.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\delta$ (Å)</th>
<th>$V_c$ (cm$^3$/mol)</th>
<th>$D_0 \times 10^6$ (cm$^2$/s)</th>
<th>$q \times 10^8$ (cm$^2$/psi s)</th>
<th>$D_{0,C3H8}/D_{0,gas}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>2.89</td>
<td>64</td>
<td>139</td>
<td>-9.86</td>
<td>0.07</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.64</td>
<td>90</td>
<td>39</td>
<td>-4.22</td>
<td>0.24</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.80</td>
<td>99</td>
<td>24</td>
<td>-2.40</td>
<td>0.38</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.30</td>
<td>94</td>
<td>13</td>
<td>0.06</td>
<td>0.70</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>4.30</td>
<td>203</td>
<td>9</td>
<td>1.71</td>
<td>1.00</td>
</tr>
</tbody>
</table>

### 2.4.7 Ideal selectivity

For $C_3H_8$/gas pairs, the solubility selectivity, diffusivity selectivity, and ideal selectivity of the FSCM at $\Delta p = 0$ were reported in Tables 2.1, 2.2 and 2.3, respectively. Since $C_3H_8$ is substantially more soluble in PDMS than the other gases, the $C_3H_8$/gas solubility selectivity is higher than 1. As reported before, the solubility of $C_3H_8$ is higher at high pressure. Therefore, the $C_3H_8$ sorption increase is more significant than for the other gases and the $C_3H_8$/gas solubility selectivity increases with pressure (Figure 2.11(b)). But the $C_3H_8$/gas diffusivity selectivity is below unity indicating that the $C_3H_8$ diffusivity is smaller than for the other components. As observed, the diffusivity selectivity, like the solubility selectivity, also increases with pressure.

The $C_3H_8$/gas ideal selectivity for the FSCM as a function of pressure is presented in Figure 2.11(a). This increase was found to be related to the difference between the components condensability. At $p = 120$ psi, the FSCM is about 6, 16, 23, and 55 times more permeable to $C_3H_8$ than CO$_2$, CH$_4$, H$_2$, and N$_2$, respectively. According to Equation (2.11), the FSCM selectivity depends on the relative diffusion coefficients ($D_A$, $D_B$) of both components (A and B) in the FSCM and on the relative solubilities ($S_A$, $S_B$) of the components in the FSCM. Consequently, the FSCM favorably separate the larger, more condensable component ($C_3H_8$) over the smaller, less condensable components (H$_2$, N$_2$, CH$_4$, and CO$_2$). Therefore, it can be concluded that the FSCM can be a good candidate for the separation of higher hydrocarbons from light components.
2.5 Conclusion

In this work, a continuous processing technology was presented to prepare a composite membrane made from a porous polymer layer produced by melt extrusion/salt leaching and coated with a selective layer. The proposed method is simple and cost effective since it is based on inexpensive materials (LDPE and PDMS) and uses a lower amount of an environmentally friendly solvent (water). The results showed that the LDPE layer has an open cell microporous structure while the PDMS layer was compact. From the membranes produced, gas permeability, solubility, diffusivity, as well as selectivity where determined at 27 °C and different pressures for: C$_3$H$_8$, CO$_2$, CH$_4$, N$_2$, and H$_2$. C$_3$H$_8$ solubility was found to be much higher than the other gases due to its higher condensability. On the other hand, C$_3$H$_8$ diffusivity was smaller because its molecules (being larger) interact more strongly with the segments of the polymer chains compared to the other gases. However, the permeation of each component through the membrane is mainly controlled by solubility. Finally, it can be concluded that the high C$_3$H$_8$ permeability (20595 Barrer) for an upstream pressure of 110 psi with high selectivities (55, 23, 16 and 6 for N$_2$, H$_2$, CH$_4$, CO$_2$) are interesting for the gas separation of higher hydrocarbons from light components, especially for natural gas/biogas purification and the petrochemical industry.
Acknowledgment

The authors would like to acknowledge the financial support of the National Science and Engineering Research Council of Canada (NSERC) and the technical support of the Centre de recherche sur les matériaux avancés de l’Université Laval (CERMA). The technical help of Mr. Yann Giroux was also much appreciated.
Chapter 3

Permeability and Thermal Properties of PDMS/LDPE Multilayer Composite Membranes

Résumé

Ce travail rapporte la préparation et les propriétés de membranes polymères composites multicouches (MCPM) à base de polydiméthylsiloxane (PDMS)/polyéthylène de basse densité (LDPE) pour des applications de séparation de gaz. Les membranes ont été produites en combinant un recouvrement séquentiel avec des techniques de fusion-extrusion/lixiviation de sel. En particulier, les propriétés de sorption et de perméation du gaz à différentes pressions (40 à 90 psig) et température (27 à 55°C) sont rapportées avec des propriétés morphologiques et thermogravimétriques. Les résultats montrent qu'une couche de PDMS de 20 µm était capable de pénétrer dans le substrat de la couche superficielle de LDPE microporeux, ce qui conduisait à une meilleure adhérence interfaciale. Sur la base des différents gaz étudiés (CO₂, CH₄ et C₃H₈), la solubilité, perméabilité et diffusivité obtenues pour ces membranes sont considérées comme de bons candidats pour les séparations industrielles de gaz.
Abstract

This work reports on the preparation and properties of polydimethylsiloxane (PDMS)/low density polyethylene (LDPE) multilayer composite polymer membranes (MCPM) for gas separation applications. The membranes were produced by combining sequential coating with melt-extrusion/salt leaching techniques. In particular, the gas sorption and permeation properties at different pressure (40 to 90 psig) and temperature (27 to 55°C) are reported with morphology and thermogravimetric properties. The results show that a 20 µm PDMS layer was able to penetrate the microporous LDPE surface layer substrate leading to improved interfacial adhesion. Based on the different gases (CO$_2$, CH$_4$ and C$_3$H$_8$) solubility, permeability and diffusivity obtained, these membranes are seen as good candidates for industrial gas separations.

**KEYWORDS:** Composite membrane, PDMS, LDPE, Thermal properties.
3.1 Introduction

Generally, multilayer composite polymer membranes (MCPM), including a substrate, a gutter layer and a selective skin layer, are synthesized by deposition of a polymer solutions on a microporous substrate. This structure is necessary because the gutter layer reduces the substrate surface roughness and a thinner selective layer can be coated on a smooth surface [2], [74], [75]. Recently, MCPM have received a great deal of attention in various gas separation industries [76]. But in most industrial separation processes, such as natural gas production plants, the operating temperature is not constant due to temperature differences on a daily (day or night) or season (winter or summer) time scale. Therefore, it is necessary to determine the temperature effect on gas transport properties. However, only a limited amount of works investigated the membrane performances as a function of temperature [77]–[78], [79]. Since the thermal stability of polymer membranes is mostly function of the operating temperature [80]–[82], the permeation properties at different temperatures are highly important to understand their limits (failure).

In this study, a MCPM was synthesized using low density polyethylene (LDPE) as a mesoporous support, while polydimethylsiloxane (PDMS) was selected as the gutter and selective layers. LDPE was selected due to its excellent mechanical/chemical stability, good elasticity and crack resistance properties, while PDMS was selected because of its superior thermal properties and low temperature flexibility. So the combination of PDMS and LDPE could be complementary to prepare good MCPM for gas separation applications. The membrane preparation method is a combination of sequential coating with melt-extrusion/salt leaching which was introduced in the first part of our work [83]. In this second step, the MCPM were synthesized using different conditions to report on their morphology, thermal stability, and gas permeation properties at different pressure and temperature. The results show that the membranes produced in this study have better $C_3H_8/CH_4$ separation capacity in terms of permeability and selectivity compared with other polymer membranes reported in the literature. They also have more stable performances, especially at higher temperatures because of interfacial layer adhesion improvement.
3.2 Theory
A typical MCPM structure is presented in Figure 3.1. The system is composed of a coated active layer on a porous support substrate. But three different zones must be accounted for to completely understand the transport properties: the coating layer ($l_1$), the penetrated layer ($l_2$), and the porous substrate ($l_3$).

Gas transport inside polymer membranes can be expressed by a permeability coefficient ($P$) or the permeance ($P/l$) which are related to the total mass transfer resistance ($R_{tot}$) as:

$$\frac{N}{\Delta p} = \frac{P}{l} = \frac{1}{R_{tot} A}$$

where $N$ is the gas flux through the MCPM with total a thickness $l$ ($= l_1 + l_3$) under a pressure difference ($\Delta p$) between the downstream and upstream side of the membrane. The permeability coefficient is usually reported in units of Barrer [1 Barrer = $1 \times 10^{-10}$ cm$^3$ (STP) cm/cm$^2$ s cmHg] and $A$ is the membrane surface area (cm$^2$).

An analogy with an electrical circuit can be made by including four resistances (see Figure 1):

- the resistance of the coating layer ($R_1$),
- the resistance of the polymer in the porous substrate ($R_2$),
- the resistance of the pores filled with the coated polymer ($R_3$),
- the resistance of the pores in the porous substrate (usually negligible) ($R_4$).

These resistances can be expressed by:

$$R_1 = \frac{l_1}{P_1 A}$$

$$R_2 = \frac{l_2}{P_2 A (1 - \epsilon)}$$

$$R_3 = \frac{l_2}{P_3 A \epsilon}$$
where \( \varepsilon \) is the porosity of the porous substrate, while \( P_1 \) and \( P_2 \) are the intrinsic permeability coefficients of the top layer and the polymer in the porous substrate, respectively. The total resistance is given by:

\[
R_{tot} = R_1 + \left( R_2^{-1} + R_3^{-1} \right)^{-1}
\]  

Finally, combining Equations (1-5) gives:

\[
\frac{N}{\Delta \rho} = \left[ \frac{l_1}{P_1} + \frac{l_2}{P_1 \varepsilon + P_2 (1 - \varepsilon)} \right]^{-1}
\]  

The influence of the support layer on gas and vapor separation has often been neglected or overly simplified in permeation models, but the resistance-in-series model assumes a constant support layer resistance, which is determined by the gas permeation coefficient of the polymer in the porous substrate \( (P_2) \), the porous substrate porosity \( (\varepsilon) \), and the penetrated layer thickness \( (l_2) \) which is related to the pore size and the support layer surface tension.

The resistance-in-series model can explain the component \((A \text{ and } B)\) permeation through a multilayer membrane as:

\[
N_A = (p_2 - p_1) \left( \frac{l_{IL}}{P_{AL}} + \frac{l_{SL}}{P_{SL}} \right)^{-1}
\]  

\[
N_B = (p_2 - p_1) \left( \frac{l_{IL}}{P_{BL}} + \frac{l_{SL}}{P_{SL}} \right)^{-1}
\]  

where \( N_A \) and \( N_B \) are the steady-state flux of component \( A \) and \( B \), while superscripts \( IL \) and \( SL \) refer to the interface and permselective layers, respectively. The ideal selectivity may be written as the ratio of the component fluxes at a given pressure and temperature as:

\[
\alpha_{A/B} = \frac{N_A}{N_B}
\]  

Therefore, the ideal selectivity of a gas for a composite membrane can be calculated as:
From Equation (3.10), it can be concluded that the ideal selectivity of a gas for a MCPM is based on the properties of both the substrate and the permselective layers.

\[
\alpha_{A/B} = \frac{I_{B}^{IL} / P_{B}^{IL} + I_{B}^{SL} / P_{B}^{SL}}{I_{A}^{IL} / P_{A}^{IL} + I_{A}^{SL} / P_{A}^{SL}}
\]  

(3.10)

Figure 3.1. Schematic representation of a MCPM structure and its electrical circuit analog.

3.3 Experimental

3.3.1 Material

The polymer matrix was LDPE (Novapol LA 0219-A, 919 kg/m³) supplied by Nova Chemicals (Canada). To produce the porous structure, NaCl (Soda-LO Extra Fine, 1981 kg/m³) was purchased from Tate & Lyle (USA). For the active layer, a PDMS package (Dehesive 944, 910 kg/m³; V24, hydrogenpolysiloxane as crosslinker; Catalyst OL) was supplied by Wacker Silicones Corporation (USA). This type of silicone polymer was selected for coating polypropylene and polyethylene based on information provided by Wacker. Toluene, was purchased from Anachemia (Canada) with a purity of 99.5%. All the
gasses, with purity above 99.0%, were purchased from Praxair (Canada). More details for material specifications can be found in our previous study [83].

3.3.2 Membrane fabrication

The MCPP were produced by combining sequential coating with melt extrusion/salt leaching. The LDPE substrate was made using a co-rotating twin-screw extruder with the same temperature profile, flat die dimension and feeding/take-up speed (LDPE flowrate of 5 g/min, NaCl flow rate of 10.5 g/min, screw speed of 60 rpm and calendar speed of 16 cm/min) as in our previous study [83].

The PDMS coating was performed via two steps. In the first step, the solutions were prepared by mixing a suitable amount of PDMS polymer resin, cross-linking agent and catalyst (weight ratio of 10:1:1 (w/w/w)) in toluene to obtain homogeneous 20% wt. PDMS solutions. The coating solution was poured onto the LDPE/NaCl sheet and coated to cover any holes on the support surface. In the second step, the same PDMS coating solutions were cast with a roller to make a uniform layer. More details and information for salt leaching, solvent evaporation and curing was presented in our previous study [83].

To determine the porous support porosity (PO), the LDPE substrate was also produced without PDMS coating and the porosity was calculated by:

\[
PO(\%) = \left(1 - \frac{\rho_1}{\rho_2}\right) \times 100
\]  

(3.11)

where \(\rho_2\) and \(\rho_1\) are the densities of the neat LDPE and LDPE support, respectively. The measurements were done as the ratio of volume over weight.

3.3.3 Membrane characterization

3.3.3.1 Scanning electron microscopy (SEM)

A scanning electron microscope (SEM) equipped with energy dispersing spectroscopy (EDS) JSM-840A (JEOL, Japan) was used to monitor the samples morphology. The structure was exposed through cryogenic fractures and the cross-sections were coated with a thin Au/Pd layer. The average pore size was determined by analyzing the SEM images using the Image- J (V1.50i) software (National Institutes of Health, USA).
3.3.3.2 Thermogravimetric analysis (TGA)
TGA characterization was performed between 50 and 850°C using a model Q5000 IR (TA Instruments, USA) in a nitrogen environment (25 ml/min) and a heating rate of 10°C/min.

3.3.3.3 Sorption and permeation measurement
Pure gas permeation was measured using a constant volume based apparatus and sorption was calculated by the pressure decay method as described in our previous work [83].

Permeation and sorption measurements were operated between 40 and 90 psig of feed pressure and 27 to 55°C of feed temperature.

3.4 Results and Discussion

3.4.1 Morphology
Figure 3.2 presents a typical cross-section of the synthesized MCPM. It can be seen that the thickness of the PDMS dense layer is about 25 µm, while the LDPE substrate is microporous with an average pore size of 17±15 µm leading to a 52±2% porosity as calculated by Equation (11). LDPE and PDMS, due to their structural dissimilarity and large difference in surface energy, are not compatible with each other[84]. It is therefore appropriate to use low PDMS concentration for coating (low viscosity in step one) and excellent adhesion can be obtained between the selective layer (step two) and the support layer by partial penetration of the top layer into the substrate surface pores.
Figure 3.2. Typical cross-section morphology of a PDMS/LDPE MCPM.

Four different points in the cross-section (see Fig. 3.2) were selected to approximate the local composition from EDS measurement inside the PDMS layer, the interface layer and the LDPE microporous substrate, while their corresponding spectrum is presented in Figure 3.3. The highest peak from the first position is related to Si associated to the PDMS coating layer. The second highest peak at position 4 is related to C associated to the LDPE support. As reported in Table 3.1, the Si concentration decreased from the surface (1088) to the support (30) layer, indicating a reduction of Si concentration from the surface to the core. This Si concentration reduction is associated with an increase of C concentration from the support (640 counts) to the surface (158 counts). Very high Si counts at position 1 confirms
a 20 µm neat PDMS layer (R₁) coated on the surface. The sharp reduction of Si and O counts (related to PDMS) and the sharp increase of C counts (mostly related to LDPE) from position 1 to position 2 confirm that the interface of the PDMS layer (R₁) and penetrated layer (R₂+R₃) is between 20 and 30 µm from the top surface of the composite membrane. The Si and O counts at position 2 (421 and 40 counts respectively) confirms the penetration of the PDMS in the substrate. Figure 2 also indicates that the thickness of the gutter layer entering was around 20 µm. The white spots (Figure 3.2) in the pores of the LDPE substrate is associated to incomplete salt leaching which will be discussed in the TGA section. But EDS spectra do not show any NaCl traces because there was no salt between positions 1 to 4 (surface layer).

Table 3.1. EDS counts of the different positions presented in Figure 3.2 (from the surface to the support).

<table>
<thead>
<tr>
<th>Position</th>
<th>Approximate distance from surface (µm)</th>
<th>Si</th>
<th>O</th>
<th>C</th>
<th>Si/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>1088</td>
<td>113</td>
<td>158</td>
<td>6.89</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>421</td>
<td>40</td>
<td>597</td>
<td>0.71</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>78</td>
<td>20</td>
<td>564</td>
<td>0.14</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>30</td>
<td>10</td>
<td>640</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Figure 3.3. EDS spectra of the different positions as presented in Figure 3.2 (from the surface to the support).

3.4.2 TGA

Figure 3.4 presents the TGA analysis for the neat PDMS, LDPE and PDMS/LDPE MCPM. It can be seen that about 84% of the first MCPM weight loss in the 360-485°C range can be associated to the LDPE thermal degradation. The second MCPM weight loss in the 485-580°C range was around 14%. As observed in the neat PDMS DTG curve, the maximum PDMS degradation occurs at 526°C. Therefore, the second MCPM weight loss can be related to PDMS thermal degradation. It can be found from Figure 2 that leaching was not complete and some salt particles are still present inside LDPE pores. According to the TGA
results in our previous work, salt particles degrade above 800°C [83]. Therefore, the last weight loss (around 2%) is related to the remaining salt particles.

Figure 3.4. TGA-DTG curves for the neat PDMS and LDPE, as well as the PDMS/LDPE MCPM.

3.4.3 Sorption and permeation

3.4.3.1 Effect of transmembrane pressure

Henry’s law constant \( k_d \) \[[\text{cm}^3\text{(STP)}]/(\text{cm}^3 \text{ psi})]\) was used to predict the concentration \( C \) of low-sorbing components in PDMS/LDPE MCPM as [56]:

\[
C = k_d p
\]  

(3.12)

The condensability of CO\(_2\), CH\(_4\), and C\(_3\)H\(_8\) in the MCPM at 35°C is illustrated in Figure 3.5. The relation for both CH\(_4\) and CO\(_2\) is linear with \( k_d \) values of 0.03 and 0.11 cm\(^3\)(STP)/(cm\(^3\) psi).
psi), respectively. But C\textsubscript{3}H\textsubscript{8} does not follow Henry’s law which is in agreement with the literature [64]–[68]. The deviation from a linear relationship at high pressures is related to PDMS swelling due to the high C\textsubscript{3}H\textsubscript{8} concentration dissolved in the polymer matrix [64]–[68].

The concentration of dissolved C\textsubscript{3}H\textsubscript{8} in un-crosslinked MCPM can be calculated based on the Flory-Huggins (FH) equation [64]:

\[
\ln a = \ln \phi_2 + (1 - \phi_2) + \chi (1 - \phi_2)^2
\]

(3.13)

where the activity \(a\) is equal to the relative pressure \((p/p_{\text{sat}})\) with \(p_{\text{sat}}\) being the saturation vapor pressure, while \(\chi\) is the FH interaction parameter and \(\phi_2\) is the volume fraction of gas which is determined by [69]:

\[
\phi_2 = \left[1 + \frac{22.414}{C\bar{V}_2}\right]^{-1}
\]

(3.14)

where \(\bar{V}_2\) is the gas partial molar volume. For crosslinked MCPM, the Flory-Rehner (FR) equation can be used to determine the dissolved C\textsubscript{3}H\textsubscript{8} concentration via [64]:

\[
\ln a = \ln \phi_2 + (1 - \phi_2) + \chi (1 - \phi_2)^2 + V_2 \left(\frac{\nu_e}{V_0}\right) \times \left[(1-\phi_2)^{1/3} - \left(\frac{1-\phi_2}{2}\right)\right]
\]

(3.15)

where \(V_2\) is the penetrant molar volume, \(\nu_e\) is the effective number of crosslinks, and \(V_0\) is the penetrant-free polymer volume.

The crosslink density \((\nu_e/V_0)\) was determined as follows:

1- The solubility of C\textsubscript{3}H\textsubscript{8} in the un-crosslinked polymer was measured (50.3 cm\textsuperscript{3} gas/cm\textsuperscript{3} polymer at 80 psi and 35°C) and \(\chi\) was determined to be 0.342.

2- \(\phi_2\) in the crosslinked membrane was then estimated to be 0.145 at the same temperature and pressure.

3- Finally, \(\nu_e/V_0\) was determined using Equation (3.15) to be 9.7x10\textsuperscript{-4} mol/cm\textsuperscript{3}.
In Figure 3.5, the dash line represents a model based on the FR theory using the following empirical linear expression [69]:

\[ \chi = \chi_0 + \chi_1 (1 - \phi) \]  

(3.16)

where \( \chi_0 \) and \( \chi_1 \) are 0.3 and 0.05, respectively. As seen in Figure 3.5, it is not possible to calculate the \( \text{C}_3\text{H}_8 \) solubility at higher pressures by Henry's law, but the FR model does a better job.

![Sorption isotherm in the MCPM at 35°C](image)

Figure 3.5. Sorption isotherm in the MCPM at 35°C

The solubility coefficient of each component, \( S \) (cm\(^3\)(STP) gas/cm\(^3\) cmHg) was determined based on:

\[ S = \frac{C}{p} \]  

(3.17)
and the results are presented as a function of pressure in Figure 3.6(a). As observed, the sorption does not significantly increase with pressure, except for $C_3H_8$ which is more condensable at high pressure since sorption significantly increases with increasing gas condensability [57].

The MCPM gas permeability as a function of feed pressure at 35°C is reported in Figure 3.6(b). As observed, the $CH_4$ permeability slowly decreases with increasing feed pressure, while it increases for $C_3H_8$. It can be seen that CO$_2$ permeability is almost constant at different pressures because of a constant solubility and diffusivity coefficient for the conditions tested. By increasing the feed pressure (component concentration in the membrane), membrane plasticization, mainly for highly soluble penetrants such as $C_3H_8$, increases, leading to higher diffusion coefficient. Furthermore, sorption inside membranes usually increases with pressure, especially for $C_3H_8$, producing higher permeation. On the other hand, the $CH_4$ transport properties, which do not plasticize the PDMS/LDPE membrane, slowly decreases with pressure. This implies that high pressure can significantly modify the membrane volume and structure, leading to lower membrane free volume decreasing the $CH_4$ diffusion coefficient.

Diffusivity ($D$) was determined using the solution-diffusion mechanism as:

$$D = \frac{P}{S}$$  \hspace{1cm} (3.18)

The diffusion term can be expressed in terms of the pressure difference across the MCPM as reported in Figure 3.6(c).
Effect of temperature

The effect of temperature on sorption, permeation and diffusion coefficient is reported in Figure 3.7. Figure 3.7(a) shows that increasing temperature and gas condensability significantly decrease the \( \text{C}_3\text{H}_8 \) solubility, while slightly increasing mobility or diffusion (Fig. 3.7(c)). Therefore, increasing the temperature decreases the \( \text{C}_3\text{H}_8 \) permeation (Fig. 3.7(b)). As expected, the diffusion of smaller molecules such as \( \text{CH}_4 \) increases with temperature (Fig. 3.7(c)), while their solubility is very slightly influenced (Fig. 3.7(a)). So the \( \text{CH}_4 \) permeability increases with increasing temperature (Fig. 3.7(b)). Reduction of the \( \text{CO}_2 \) solubility and increasing \( \text{CO}_2 \) diffusivity at higher temperatures make the permeation almost constant at different temperatures (Fig 3.7).

The van’t Hoff-Arrhenius equation is often used to account for the temperature effect on solubility, permeation and diffusion as [65], [66], [68]:

---

Figure 3.6. (a) Solubility, (b) permeability, and (c) diffusivity of the components in the MCPM as a function of pressure at 35°C.
\[ S = S_0 \exp \left( -\frac{\Delta H_s}{RT} \right) \]  \hspace{1cm} (3.19)

\[ P = P_0 \exp \left( -\frac{E_p}{RT} \right) \]  \hspace{1cm} (3.20)

\[ D = D_0 \exp \left( -\frac{E_d}{RT} \right) \]  \hspace{1cm} (3.21)

where \( S_0, P_0, \) and \( D_0 \) are the pre-exponential factors, while \( \Delta H_s, E_d, \) and \( E_p \) are the enthalpy of sorption and the activation energies of diffusion and permeation, respectively. These parameters were computed using Eq. (3.19-3.21) and the results are reported in Table 3.2.

Gas solubility inside the membrane is considered to depend on two different phenomena (stages). The first one is component condensation from a gas/vapor phase to a liquid phase. The enthalpy change associated with component condensation is the enthalpy of condensation (\( \Delta H_{\text{cond}} \)). The second one is the mixing/interacting of the condensed components with the polymer matrix and the enthalpy change is the enthalpy of mixing (\( \Delta H_{\text{mix}} \)). So \( \Delta H_s \) is the sum of both steps as [66], [85]:

\[ \Delta H_s = \Delta H_{\text{cond}} + \Delta H_{\text{mix}} \]  \hspace{1cm} (3.22)

\( \Delta H_s \) is negative for CH\(_4\), CO\(_2\) and C\(_3\)H\(_8\) indicating that solubility decreases with temperature. For highly soluble components (like C\(_3\)H\(_8\)), \( \Delta H_s \) is much lower indicating important sorption reduction with increasing temperature due to the high \( \Delta H_{\text{cond}} \) contribution [85][5]. A temperature increase improves the mobility of gas molecules and polymer chains leading to higher diffusivity. Therefore, \( E_d \) is always positive for CH\(_4\), CO\(_2\) and C\(_3\)H\(_8\) (Table 2). In fact, the diffusivity of components with high \( E_d \) values is more affected by temperature. So the diffusivity of CH\(_4\) is more affected by temperature increase because of the small size of CH\(_4\) molecules. Based on the solution-diffusion mechanism (Eq. (3.18)), \( E_p \) is related to \( \Delta H_s \) and \( E_d \) via:

\[ E_p = E_d + \Delta H_s \]  \hspace{1cm} (3.23)
As observed for CH\textsubscript{4}, the permeability increases with temperature indicating that $E_p$ is positive (Table 3.2). The negative value of $E_p$ for C\textsubscript{3}H\textsubscript{8} is associated to a more negative $\Delta H_s$ value. On the other hand, CH\textsubscript{4} shows a positive $E_p$ because of its larger positive $E_d$.

Figure 3.7. Transport properties through the MCPM as a function of temperature for the different gas (CH\textsubscript{4}, CO\textsubscript{2} and C\textsubscript{3}H\textsubscript{8}): (a) solubility, (b) permeability, and (c) diffusivity.
Table 3.2. Activation energies and pre-exponential factors for the permeation and diffusion data, as well as the enthalpy of sorption for CH$_4$, CO$_2$ and C$_3$H$_8$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$P_0$</th>
<th>$E_p$</th>
<th>$S_0 \times 10^6$</th>
<th>$\Delta H_s$</th>
<th>$D_0 \times 10^6$</th>
<th>$E_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Barrer)</td>
<td>(kJ/mol)</td>
<td>(cm$^3$(STP)/cm$^3$ psi)</td>
<td>(kJ/mol)</td>
<td>(cm$^2$/s)</td>
<td>(kJ/mol)</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>15514</td>
<td>7.06</td>
<td>1730</td>
<td>-7.05</td>
<td>4637</td>
<td>14.1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>340</td>
<td>-4.99</td>
<td>323</td>
<td>-15.0</td>
<td>544</td>
<td>10.0</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>101</td>
<td>-12.2</td>
<td>57</td>
<td>-23.8</td>
<td>914</td>
<td>11.5</td>
</tr>
</tbody>
</table>

The permeation activation energy provides information about the temperature dependence of a penetrant through a polymer. Comparing our results (Table 3.2) with literature values (Table 3.3) shows that the CH$_4$ permeability coefficient through our MCPM is less affected by temperature, while the effect on C$_3$H$_8$ permeation is in the same range. This behavior shows that the performance stability of our MCPM for CH$_4$/C$_3$H$_8$ separation at higher temperatures is better than the other PDMS membranes.

Table 3.3. $\Delta H_s$, $E_d$ and $E_p$ values reported by Clarizia et al.[86] and Prabhakar et al. [66] for CH$_4$ and C$_3$H$_8$.

<table>
<thead>
<tr>
<th></th>
<th>$E_p$</th>
<th>$\Delta H_s$</th>
<th>$E_d$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kJ/mol)</td>
<td>(kJ/mol)</td>
<td>(kJ/mol)</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>9.7</td>
<td>-5.2</td>
<td>14.9</td>
<td>Clarizia et al.[86]</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>-13.3±1.3</td>
<td>-20±0.2</td>
<td>7±1.2</td>
<td>Prabhakar et al.[66]</td>
</tr>
</tbody>
</table>

Figure 3.8 presents the effect of temperature on the ideal selectivity of C$_3$H$_8$ over CO$_2$ and CH$_4$ (calculated using Eq. (3.9)). The ideal selectivity for C$_3$H$_8$/CO$_2$ slightly decreases with increasing feed temperature because C$_3$H$_8$ permeability decreases while CO$_2$ permeability remains almost constant. On the other hand, increasing the feed temperature substantially decreases the C$_3$H$_8$/CH$_4$ ideal selectivity because of CH$_4$ permeability improvement. The C$_3$H$_8$/CH$_4$ ideal selectivity of the PDMS membranes prepared by Stern et al. [87] is in the 9.0 - 5.3 range for temperatures between 35 and 55°C, while the ideal selectivity of our
membranes is higher being 12.2 at 35°C and 7.8 at 55°C. As a result, it can be concluded that PDMS/LDPE MCPM are appropriate candidates for the separation of higher hydrocarbons from lower ones and they can be used as a substrate/gutter layer for coating a thin layer of highly selective CO$_2$ polymer to produce less expensive membranes for biogas treatment.

![Figure 3.8. Effect of feed temperature on the ideal selectivity of the MCPM for C$_3$H$_8$ over CO$_2$ and CH$_4$.](image)

Finally, a Permeability-permselectivity diagram, as developed by Alentiev et al. [88], was used to compare the C$_3$H$_8$/CH$_4$ separation performance of our PDMS/LDPE MCPM with other polymer membranes (literature data) and the membrane produced in our previous work [83]. Figure 3.9 clearly shows that the separation performance of the composite membranes produced in this study is very good in terms of both permeability and selectivity.
Figure 3.9. The permeability-permselectivity diagram for C$_3$H$_8$/CH$_4$ (Adapted from Alentiev et al. [88]).

3.5 Conclusion

In this work, a simple and cost effective method was presented to produce a multilayer composite polymer membrane (MCPM) by sequential coating of PDMS on a porous LDPE substrate made by melt extrusion/salt leaching. The morphological results showed that about a 20 µm thick top layer penetrated into the microporous substrate pores increasing the adhesion between both layers. The PDMS/LDPE MCPM were shown to have higher permeation properties for higher hydrocarbon (C$_3$H$_8$) compared to lighter ones (CH$_4$). This result was related to the very high solubility of larger gas molecules in the PDMS coating combined with their lower relative diffusivity compared to smaller molecules. On the other hand, C$_3$H$_8$ permeation decreased and CH$_4$ permeability increased with increasing temperature. All the variations were related to the different activation
energies. The results also showed that the PDMS/LDPE MCPM permeation properties are more stable at higher temperature than for other PDMS membranes. Finally, the ideal selectivity for C\textsubscript{3}H\textsubscript{8}/CH\textsubscript{4} was in an acceptable range (7-15).

**Acknowledgment**

The authors would like to acknowledge the financial support of the Fonds de recherche du Québec – Nature et Technologies (FRQNT) and the technical support of the Research Center for High Performance Polymer and Composite Systems (CREPEC). The LDPE samples were supplied by Nova Chemicals (Canada). The technical help of Mr. Yann Giroux was also much appreciated.
Chapter 4

Gas transport and mechanical properties of PDMS-TFS/LDPE nanocomposite membranes

Résumé

Cette étude rapporte l'effet de la silice fumée modifiée au triméthylsiloxane (TFS) sur les propriétés de perméation gazeuse et mécaniques de membranes nanocomposites polymères. Les membranes ont été produites par recouvrement de polydiméthylsiloxane (PDMS) incorporé de TFS à différentes charges (5, 10 et 15% en poids) sur un substrat poreux de polyéthylène de basse densité (LDPE) qui a été formé par une technique de fusion-extrusion lixiviation de sel. Les membranes PDMS-TFS/LDPE ont été caractérisées par SEM, TGA et DMTA. Les résultats ont montré qu'une bonne affinité entre les particules de TFS traitées par PDMS et la matrice de PDMS a été obtenue, conduisant à des propriétés mécaniques et thermiques améliorées. La perméation de gaz (CH₄ et C₃H₈) à différentes pressions en amont (50 à 80 psig) et températures (27 à 55°C) a été étudiée. Les résultats ont montré que la sélectivité idéale C₃H₈/CH₄ (17,6) et la perméabilité du C₃H₈ (1,89×10⁴ Barrer) dans la membrane chargées de 10% TFS (PDMS-TFS10%/LDPE) étaient supérieures de 41% et 14% comparés aux membranes non-chargées (PDMS-TFS0%/LDPE), respectivement. Les résultats de perméation indiquent également que la stabilité des performances dans les conditions étudiées rend les membranes PDMS-TFS/LDPE intéressantes pour des applications industrielles.
Abstract

This study investigates the effect of trimethylsiloxy fumed silica (TFS) on the mechanical and gas permeation properties of polymer nano-composite membranes. The membranes were produced by coating TFS incorporated polydimethylsiloxane (PDMS) at different loadings (5, 10 and 15 wt.%) on a porous low density polyethylene (LDPE) substrate which was formed by a melt-extrusion/salt leaching technique. The PDMS-TFS/LDPE membranes were characterized by SEM, TGA and DMTA. The results showed that a good affinity between the PDMS treated TFS particles and PDMS matrix was obtained leading to improved mechanical and thermal properties. For gas permeation, CH₄ and C₃H₈ at different upstream pressure (50 to 80 psig) and temperature (27 to 55 °C) were investigated. The results showed that the C₃H₈/CH₄ ideal selectivity (17.6) and C₃H₈ permeability (1.89×10⁴ Barrer) through 10 wt.% TFS loaded membranes (PDMS-TFS10%/LDPE) were 41% and 14% higher than the neat membranes (PDMS-TFS0%/LDPE), respectively. The permeation results also indicate that the performance stability under the conditions investigated makes PDMS-TFS/LDPE membranes interesting for industrial applications.

Keywords: Nano-composite membrane; Trimethylsiloxy fumed silica; PDMS; LDPE; Mechanical properties.
4.1 Introduction

To meet industrial service requirements, reinforcing fillers have been extensively used to improve neat materials, especially the performance of polymer membranes. For example, the addition of silica into polymers significantly improves processability, reliability, durability, thermal and oxidative resistance, as well as gas separation [62], [89]-[92]. Untreated silica is however intrinsically hydrophilic due to a large quantity of Si–OH groups on its surface. Consequently, it is not compatible with hydrophobic polymer membranes like polydimethylsiloxane (PDMS). Very few investigations addressed the possibility to use pre-treated silica into silicone-based composite membranes to improve separation properties, especially for C$_3$H$_8$/light gases such as N$_2$, H$_2$, CO$_2$ and CH$_4$.

Beltran et al. [62] investigated PDMS membranes for propylene recovery from permanent gases like N$_2$ or air. Two types of chlorosilane were successfully grafted on the silica surface through silanization. PDMS membranes with 10 wt.% surface-modified SiO$_2$ showed 35% improvement in C$_3$H$_6$/N$_2$ selectivity. Both nano-composites had lower O$_2$ and N$_2$ permeability compared to the neat membrane, while higher C$_3$H$_6$ permeation was observed. Kim et al. [93] treated silica nano-particles with silane coupling agents to increase compatibility with PDMS. Mercapto-silane showed the best performance in terms of thermal stability and hydrophobicity. The C$_3$H$_6$ separation factor and permeability increased with increasing silica content. For instance, 20 wt.% silica into PDMS membranes increased the separation factor from 5.5 to 7.5 and C$_3$H$_6$ permeance from 32 to 40 GPU. Silica was shown to increase the C$_3$H$_6$ solubility and improved the separation factor while preserving the C$_3$H$_6$ permeability.
Here, hydrophobic PDMS-treated trimethylsiloxy fumed silica (TFS) is proposed to improve the compatibility towards PDMS (Figure 4.1). Also, a new synthesis method is presented to introduce the TFS nano-particles into a PDMS/low density polyethylene (LDPE) composite membrane produced by a combination of coating and melt-extrusion/salt leaching as reported in our previous work [83]. So the objective of the work is to determine the effect of TSF content on the gas permeation and thermal stability of nano-composite membranes.

![Chemical structure of TFS](image)

Untreated TFS  PDMS-treated TFS

Figure 4.1. PDMS-treated and untreated trimethylsiloxy fumed silica.

4.2 Experimental

4.2.1 Material

The LDPE (LA 0219-A, 919 kg/m³) was supplied by Nova Chemicals (Canada). NaCl (Soda-LO Extra Fine, 1981 kg/m³) was supplied from Tate & Lyle (USA). PDMS (Dehesive 944, 910 kg/m³; V24, hydrogenpolysiloxane as crosslinker; Catalyst OL) was supplied by Wacker Silicones Corporation (USA). Toluene with a purity of 99.5% was
purchased from Anachemia (Canada). PDMS-treated TFS particles (CAB-O-SIL® TS-720) was obtained from Cabot Corporation Product (USA) with a density of 2200 kg/m³. All the gases were purchased from Praxair (Canada) with a purity above 99.0%.

### 4.2.2 Nanocomposite membrane preparation

The PDMS-TFS/LDPE nanocomposite membranes were fabricated using coating combined with melt extrusion/salt leaching. The substrate was obtained by a co-rotating twin-screw extruder with a LDPE flowrate of 5 g/min and a NaCl flowrate of 10.5 g/min. The screw speed was set at 60 rpm and the calendar speed at 16 cm/min. The extruder temperature profile (135 °C for zone 1, 140 °C for zones 2-8, and 145 °C for zone 9, 10 and die) and flat die dimensions (15 cm width and 250 µm gap opening) were optimized in our previous work where more information can be found [83].

The coating solutions were prepared via multiple steps. Firstly, the TFS nano-particles were oven dried (80 °C for 24 h) to eliminate water. Then, they were cooled to room temperature and suspended in toluene. The solutions were vigorously stirred for 2 h and subsequently sonicated for 30 s to break down aggregation and enhance homogeneity. PDMS polymer resin (Dehesive) was added to the solutions and stirred for another 2 h. All the solutions contained 30 wt.% PDMS while TFS loading was varied as 5, 10 and 15 wt.%. The crosslinker and catalyst with a weight ratio of 1:1 were introduced in the polymer solution and stirred until a homogeneous mixture was obtained. Afterward, the coating solution was poured onto the LDPE/NaCl sheet and cast with a roller to make a uniform layer. For comparison, the neat PDMS solution was also coated to produce the PDMS-TFS0%/LDPE membrane. More details and information for salt leaching, solvent evaporation and curing was presented in our previous study [83].

### 4.2.3 Membrane characterization

#### 4.2.3.1 Scanning electron microscopy (SEM)

SEM was performed to analyze the nano-composite membranes morphology and determine the TSF dispersion and interfacial state. PDMS treated TFS nano-particles and PDMS-TFS/LDPE nano-composite membranes were oven dried at 80 °C for 24 h before taking SEM images at different magnifications on a Quanta 3D FEG (FEI, Netherland-2008). The
size of the TFS particles was characterized by analyzing the SEM images using the Image-J V1.50i software (National Institutes of Health (NIH), USA).

### 4.2.3.1 Fourier-transform infrared spectroscopy (FTIR)
FTIR spectra were collected on a Nicolet Magna 850 Fourier transform infrared analyzer (Thermo Scientific, USA) at room temperature. The nano-particles and membranes were totally dried in a vacuum oven before measurement to reduce the presence of water. The IR spectra were obtained in reflectance mode (attenuated total reflection, ATR) using GoldenGate (diamond IRE) accessories (Specac Ltd., UK). The spectral range covered was 650 to 3650 cm\(^{-1}\) with a 0.5 cm\(^{-1}\) resolution of 128 scans using Happ-Genzel apodization. Appropriate background corrections were also applied.

### 4.2.3.2 Thermogravimetric analysis (TGA)
Thermal degradation measurements were carried out using a thermogravimetric analyzer (TGA) model Q 5000 IR (TA Instruments, USA). The temperature was programmed from 50 to 900 °C at a heating rate of 10 °C/min in a nitrogen atmosphere (25 ml/min).

### 4.2.3.1 Mechanical properties
The tensile properties were measured using a dynamic mechanical thermal analyzer (DMTA) RSA3 (TA Instruments, USA). Rectangular samples with dimensions of 30 × 5 × 0.42 mm\(^3\) were analyzed. Dynamic ramps were performed by increasing the temperature from 35 to 85 °C at a rate of 5 °C/min with a deformation of 0.2% and a frequency of 1 Hz.

### 4.2.3.1 Gas transport measurements
Gas sorption and permeation was obtained using a constant volume based apparatus as described in our previous work [83]. The nano-composite membranes permeability \(P_{cp}\) containing impermeable nano-fillers can be modeled by Maxwell’s equation as [94]:

\[
P_{cp} = P_{np} \left( \frac{1 - \phi_f}{1 + \frac{\phi_f}{2}} \right)
\]

where \(P_{np}\) is the permeability of the neat polymer and \(\phi_f\) is the nano-filler volume fraction.
4.3 Results and Discussion

4.3.1 Morphology
The main issue related to nano-particles introduction in polymer matrices through physical blending is filler dispersion and presence of nonselective voids at the polymer-filler interface. The surface morphology of PDMS-TFS/LDPE nano-composite membranes and the structure of TFS particles were monitored via SEM and presented in Figure 4.2. The SEM images show no evidence of TSF-PDMS interfacial void/defect which can be associated to good adhesion between both components. In fact, gas separation improvements in any kind of nano-composite membranes may be succeeded by tailoring the interaction between the polymer chains and nano-particles. It must be pointed out that nano-particles have a higher tendency to aggregate in polymer matrices, especially as loading increases. This can be observed around 15 wt.% TFS in our case limiting the nano-composite membrane performances short of expectation through the formation of non-selective defects (gaps, voids, etc.). The results of the image analysis on Figure 4.2 reported 52±22 nm, 46±10 nm and 69±21 nm for the average particle size of TFS 5, 10 and 15%, respectively.

Figure 4.2. SEM images of PDMS-TFS/LDPE and TFS particle at different magnification.
4.3.2 FTIR

Figure 4.3 presents the FTIR spectra of the different materials. It can be seen that the neat PDMS spectrum is similar to that of the PDMS-TFS. TFS shows a strong peak at 1041 cm\(^{-1}\) which is related to Si–O bonds [95]. The multi-component peaks ranging from 650 to 900 cm\(^{-1}\) correspond to –CH\(_3\) rocking and the Si–C stretching. The –CH\(_3\) deformation vibration was observed at 1400-1460 cm\(^{-1}\) and between 1250-1260 cm\(^{-1}\). The other peaks at 1258 and 2960 cm\(^{-1}\) are associated to CH\(_3\) vibrations. A common peak at 1455 cm\(^{-1}\) and a weak peak at 2960 cm\(^{-1}\) are respectively associated to C–H bending and –CH\(_2\)– stretching in –Si–CH\(_2\)–. It is particularly noteworthy that PDMS has double peaks at 1005 cm\(^{-1}\) and 1060 cm\(^{-1}\) which are respectively assigned to Si–O–Si asymmetric stretching vibration and Si–O–Si asymmetric deformation vibration. As siloxane chains become branched or longer, the Si–O–Si stretching vibration peak becomes broader. Figure 4.3 also shows that by incorporating TFS into PDMS, the peaks in the 1060-1005 cm\(^{-1}\) region merged together to form a broad band.
4.3.3 TGA

Figure 4.4 presents the TGA curve of neat TFS, PDMS and LDPE, as well as the PDMS-TFS/LDPE nano-composite membranes. A limited weight loss (12%) was observed for neat TFS up to 900 °C indicating that these nano-particles have excellent thermal stability. The decomposition of PDMS-TFS/LDPE nano-composite membranes was more gradual as TFS content increased. These results clearly show that the thermal stability of the host polymer matrix was highly improved with TFS addition and these results are similar to those reported by Nisola et al. [96] for silica filled PDMS films.
As seen in the DTG curves (Figure 4.4), the final degradation temperature and peak decomposition temperatures (845, 860 and 855 °C) were shifted to higher temperature with increasing filler content. Hence, it can be concluded that the thermal stability of the PDMS-TFS/LDPE membranes was improved by the presence of TFS nano-particles. Moreover, similar to the neat LDPE and PDMS, the PDMS-TFS/LDPE membranes exhibit two degradation steps in the 360-480 °C and 480-580 °C ranges associated to LDPE and PDMS, respectively.
Figure 4.4. TGA-DTG curves for the neat TFS, PDMS and LDPE, as well as the PDMS-TFS/LDPE membranes.
4.3.4 DMTA

To study the PDMS/TFS interaction and its effect on the membranes mechanical properties, uniform nano-particles dispersion and polymer chains mobility, the dynamic thermomechanical properties of the membranes were investigated in terms of storage (elastic) modulus ($E'$), loss modulus ($E''$) and damping (loss) factor (tan $\delta$). The curves are presented in Figures 4.5 and 4.6 with the main results reported in Table 4.1.
Figure 4.5. Storage modulus (a) and loss modulus (b) for the PDMS-TFS/LDPE nano-composite membranes.
Figure 4.6. Damping factor (tan δ) as a function of temperature for the PDMS-TFS/LDPE nano-composite membranes.

Table 4.1. DMTA results for the PDMS-TFS/LDPE nano-composite membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>T_α (°C)_a</th>
<th>E' at 40 °C (MPa)</th>
<th>E'' at 40 °C (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS-TFS0%/LDPE</td>
<td>62.6</td>
<td>10.4</td>
<td>2.4</td>
</tr>
<tr>
<td>PDMS-TFS5%/LDPE</td>
<td>65.2</td>
<td>17.9</td>
<td>4.1</td>
</tr>
<tr>
<td>PDMS-TFS10%/LDPE</td>
<td>66.2</td>
<td>27.4</td>
<td>5.9</td>
</tr>
<tr>
<td>PDMS-TFS15%/LDPE</td>
<td>67.0</td>
<td>33.1</td>
<td>7.2</td>
</tr>
</tbody>
</table>

_a obtained from the tan δ peak

T_α (relaxation temperature) was assigned to the maximum peak of the tan δ vs. temperature curve as shown in Figure 4.6. The results show that nano-filler addition increased the T_α from 62.6 to 67.0 °C. This increase is related to TFS particles limiting the local segmental
motions of the PDMS polymer chains. Furthermore, the tan δ peak is broadened with increasing TFS loading. This broadening is associated to local membrane heterogeneity due to the nano-fillers presence which is also an indication of the interaction between the particles and the interfacial PDMS chains leading to a different distribution of local segmental motions [97]. Furthermore, the interaction between the polymer and nano-fillers becomes stronger with higher nano-fillers loading broadening the peak. This phenomenon is also associated to the compatibility between the PDMS segment on the treated TFS with the PDMS chains in the polymer matrix. The interfacial adhesion between the nano-particles, the polymer chains and polymer chain/nano-particles are all affecting the damping factor (tan δ), but the stronger the interfacial adhesion, the lower the damping factor. Hence, the tan δ order is: TFS0% > TFS5% ≈ TFS10% > TFS15%. It can be concluded that interfacial adhesion in the PDMS-TFS15%/LDPE is the lowest which may be related to particle aggregation as observed in the morphological results of Figure 4.2.

The loss modulus (energy dissipation) and the storage modulus (energy absorption) of the nano-composite membranes increase with nano-fillers content and their temperature variation are presented in Figure 4.5. The storage modulus at 40 °C increases from 10.4 MPa at 0% TFS to 33.1 MPa (218% relative improvement) at 15 wt.%. When the PDMS chains are attached to the nano-fillers surface, the polymer segments in the nano-composites bulk have some mechanical interlocking leading to improved interfacial stress transfer. The storage modulus curves show that nano-fillers addition induces an important reinforcing effect. As the membrane structure is reinforced with nano-fillers, the polymer segments close to the nano-particles are mechanically restrained. The trimethylsiloxy functionalized surfaces of the nano-fillers act as strong regions and sites of low stress concentration for the nano-composites. The samples also exhibit a decreasing trend with increasing temperature. The thermal energy (potential barrier) increases the local polymer chains rotational and translational mobility leading to lower storage and loss moduli with increasing temperature.

The results are in an excellent agreement with the data reported by Mora-Barrantes et al. [98] in overcoming the disadvantages of neat silica as a filler in elastomer composites.
Moreover, the trends observed are coherent with the morphology (Fig. 4.2) and TGA (Fig. 4.4) measurements.

**4.3.5 Gas Transport**

**4.3.5.1 Effect of TFS loading**

The effect of TFS loading on gas transport properties was studied. The permeability of highly soluble gas (C$_3$H$_8$) was improved, while the permeability of low-sorbing gases (CH$_4$) decreased with increasing TFS content (Figure 4.7). So the C$_3$H$_8$ permeability of all the nano-composite membranes was higher than for CH$_4$, as for the neat membrane. It is known that gas permeability through PDMS is mostly driven by the sorption step. Since PDMS has a highly flexible polymer backbone, it is unable to discriminate the molecules based on sizes [15]. So the nano-composite membranes gas transport properties can be controlled by two phenomena: I) as TFS loading increases, the transport pathway (tortuosity) could be disturbed by the impermeable nano-size TFS particles increasing the mass transfer resistance [93]; and II) the nano-sized TFS particles can disrupt the polymer chain packing density. So the nano-composite performances are a balance between these two factors. As seen in Figure 4.7, improved nano-composite performances with TFS addition can mainly be attributed to changes in both gas permeability so C$_3$H$_8$/CH$_4$ ideal selectivity (17.6) and C$_3$H$_8$ permeability (1.89×10$^4$ Barrer) through the PDMS-TFS10%/LDPE membrane were 41% and 14% higher than PDMS-TFS0%/LDPE, respectively.

Based on the Maxwell model (Equation 4.1), the gas permeability coefficients of nano-composite polymer membranes will decrease by increasing nano-filler loading. The reduction of CH$_4$ permeability coefficient (Figure 4.7) is in agreement with the Maxwell model. On the other hand, the C$_3$H$_8$ permeation does not follow the Maxwell model but increases with increasing TFS loading in the membranes. This phenomenon can be related to the fact that in the Maxwell model, the interaction between the particles and the penetrating gas (adsorption) is neglected while in our case, the PDMS treated TFS particles have a dominant feature on the gas permeability.
Figure 4.7. Gas permeability as a function of TFS loading at 27 °C and 80 psig. The lines are predictions from the Maxwell model (Equation 4.1).

To better determine the effect of TFS loading on CH₄ and C₃H₈ transport, relative values for solubility \( S_r \), permeability \( P_r \) and diffusivity \( D_r \) coefficients through the nano-composite membranes are presented in Figure 4.8 and calculated as:

\[
S_r = \frac{S_{cp}}{S_{np}} \tag{4.2}
\]

\[
P_r = \frac{P_{cp}}{P_{np}} \tag{4.3}
\]

\[
D_r = \frac{D_{cp}}{D_{np}} \tag{4.4}
\]

Solubility coefficients in the neat PDMS \( (S_{np}) \) were reported in our previous work at different pressure and temperature [83]. Based on the solution-diffusion transport mechanism \( (P = D \cdot S) \), the diffusion coefficients of the gases through the nano-composite membranes \( (D_{cp}) \) were calculated by the measured solubility coefficients of nano-composite membranes \( (S_{cp}) \).
As presented in Figure 4.8, CH$_4$ and C$_3$H$_8$ relative solubility coefficients increased with increasing TFS content in the PDMS-TFS/LDPE nano-composite membranes. The addition of TFS in the PDMS top layer increases the effective surface area of the nano-composite membranes improving the gas sorption on the membrane surface. On the other hand, the diffusivity of polymer membranes with TFS nano-particles decreased because of the nano-particles impermeability. The Maxwell model can be written for the relative diffusivity as [99]:

$$D_r = \left(\frac{1 - \phi_f}{\phi_f}\right)\left(\frac{1}{1 + \frac{\phi_f}{2}}\right)$$

As reported on Figure 4.8, the diffusion coefficients decrease with increasing TFS content in PDMS-TFS/LDPE membranes. This behavior is in agreement with the Maxwell theory for both CH$_4$ and C$_3$H$_8$. Therefore, it can be concluded that the dominant feature on the permeability of highly soluble gases like C$_3$H$_8$ through the nano-composite membranes is the higher solubility coefficient, while for low sorbing gases like CH$_4$, the reduction of their diffusion coefficients controls the permeation rate.

Figure 4.8. Relative solubility ($S_r$), permeability ($P_r$) and diffusivity ($D_r$) coefficients as a function of TFS loading at 27 °C and 80 psig. The lines represent the Maxwell model (Equation 4.5).
4.3.5.2 Effect of operation conditions

As presented in Figure 4.9, the \(\text{C}_3\text{H}_8\) permeability through PDMS-TFS10%/LDPE increased with increasing upstream pressure. On the other hand, the \(\text{CH}_4\) permeability decreased with increasing upstream pressure, which is in agreement with our previous observations on PDMS/LDPE membranes [83]. A linear relationship between permeability and pressure can be written as:

\[
P = P_0 + m \Delta p
\]

and the parameters \((P_0\) and \(m)\) are reported in Table 4.2. According to these results, the \(\text{CH}_4\) and \(\text{C}_3\text{H}_8\) permeability through PDMS-TFS10%/LDPE at \(\Delta p = 0\) \((P_0)\) decreased by 20% and increased by 80% respectively, compared with the PDMS/LDPE. These results led to a 125% improvement of the \(\text{C}_3\text{H}_8/\text{CH}_4\) ideal selectivity at \(\Delta p = 0\).

The effect of operation temperature (27 to 55 °C) at constant upstream pressure (80 psig) was studied for the PDMS-TFS10%/LDPE membrane. By increasing the temperature, \(\text{C}_3\text{H}_8\) permeability and \(\text{C}_3\text{H}_8/\text{CH}_4\) selectivity decreased (Figure 4.9) so the rate of \(\text{C}_3\text{H}_8\) recovery is higher at lower temperature. \(\text{CH}_4\) and \(\text{C}_3\text{H}_8\) permeation activation energy \((E_p)\) through the PDMS-TFS10%/LDPE membrane (-8.60 and 3.94 kJ/mol, respectively) was calculated from the van’t Hoff-Arrhenius equation:

\[
P = P_0 \exp \left( \frac{-E_p}{RT} \right)
\]

The \(E_p\) values for \(\text{CH}_4\) and \(\text{C}_3\text{H}_8\) in the PDMS/LDPE (-12.2 and 7.06 kJ/mol) was reported in our previous work [100], showing better performance stability of the PDMS-TFS10%/LDPE nano-composite membrane at higher temperature. Therefore, it can be concluded that treated TFS addition improved the PDMS/LDPE membranes performance at higher temperature and lower pressure, which are the most unfavorable operating conditions for \(\text{C}_3\text{H}_8/\text{CH}_4\) separation.
Figure 4.9. Effect of operation conditions on the permeability and ideal selectivity of PDMS-TFS10%/LDPE membrane. The lines are regressions using Equations (4.6) and (4.7) with the parameters of Table 4.2.

Table 4.2. Infinite dilution gas permeability ($P_0$), $m$ and $C_3H_8/CH_4$ ideal selectivity at $\Delta p = 0$ and 27 °C for PDMS-TFS10%/LDPE and PDMS/LDPE [83].

<table>
<thead>
<tr>
<th></th>
<th>This work (PDMS-TFS10%/LDPE)</th>
<th>Previous work (PDMS/LDPE) [83]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_0$</td>
<td>$m$</td>
</tr>
<tr>
<td></td>
<td>(Barrer)</td>
<td>(Barrer/psi)</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1090</td>
<td>-0.16</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>6700</td>
<td>134</td>
</tr>
</tbody>
</table>

One way to compare the $C_3H_8/CH_4$ separation performance of polymer membranes is via a permeability-permselectivity diagram as developed by Alentiev et al. [88]. Figure 4.10 clearly shows that the separation performance of the nano-composite membranes produced in this study are very good in terms of both permeability and selectivity compared to literature data. So it is believed that they are possible candidates for industrial applications in the field of $C_3H_8/CH_4$ separation.
4.4 Conclusion

In this work, PDMS-TFS/LDPE membranes were produced by coating different contents of PDMS-TFS nano-composites at 0, 5, 10 and 15 wt.% on a porous LDPE substrate formed by melt-extrusion/salt leaching techniques. The morphological results showed that the nano-particles tend to aggregates in the polymer matrix around 15 wt.% of TFS. TGA analysis indicated thermal stability improvement with TFS nano-particles addition. Improvements in the storage and loss moduli were observed from DMTA results revealing that the membrane structure was reinforced with TFS nano-fillers. Incorporating the PDMS treated TFS increased the permeation performance of the PDMS/LDPE membranes because the surface functional groups increased the sorption of penetrants on the TFS surface improving the membrane selectivity and permeability.

The results showed that the C$_3$H$_8$/CH$_4$ ideal selectivity and C$_3$H$_8$ permeability increased by 41 and 14% respectively, by adding 10 wt.% TFS nano-particles. The PDMS-TFS10%/LDPE was also shown to produce better separation performance at different
operating conditions making this material suitable for industrial applications like higher hydrocarbon separation associated to gas-liquid recovery, volatile organic compounds (VOC) removal, liquefied petroleum gas (LPG) recovery from flare or vent lines, gas pipeline dew point control, engine or turbine fuel gas conditioning, vapor recovery from storage tank losses, etc.

**Acknowledgment**

The authors would like to acknowledge Nova Chemicals (Canada), Wacker Silicones Corporation (USA), Tate & Lyle (USA) and Cabot Corporation Product (USA) for providing LDPE, PDMS package, extra fine NaCl and TFS particles, respectively.
Chapter 5

Conclusions and recommendations

5.1 General conclusions
In this work, a continuous process was presented to prepare a composite membrane made from a porous polymer layer produced by melt extrusion/salt leaching and coated with a selective layer. The proposed method is simple and cost effective since it is based on inexpensive materials (low density polyethylene (LDPE) and polydimethylsiloxane (PDMS)) and uses a low amount of an environmentally friendly solvent (water). The results showed that the LDPE support layer has an open cell microporous structure, while the PDMS active layer was compact.

Three type of composite membranes were prepared by changing the synthesis parameters:

1- PDMS/LDPE flat sheet composite membrane (FSCM) was produced by single stage coating with high coating solution concentration (50%).
2- PDMS/LDPE multilayer composite polymer membrane (MCPM) was formed by low solution concentration (20%) sequential (2 times) coatings.
3- By incorporating trimethysiloxy fumed silica (TFS), PDMS-TFS/LDPE nanocomposite membranes were synthesized by a one-step coating process using a medium concentration solution (30%) with different contents of PDMS-TFS nanocomposites (0, 5, 10 and 15 wt.%).

The morphological results showed that by decreasing the coating solution concentration from 50 to 20%, a 20 µm thick top layer penetrated into the microporous substrate pores increasing the adhesion between both layers. A second coating was required at low concentration to cover any holes on the top surface which were formed because of penetration (to produce a flat surface).

The thermal and mechanical properties of PDMS/LDPE composite membranes were improved with TFS nano-particles addition. TGA analysis reported thermal stability
improvement at high temperatures. Higher storage and loss moduli were observed from DMTA results revealing that the membrane structure was reinforced by the TFS nanofillers.

From the FSCM produced, gas permeability, solubility, diffusivity, as well as selectivity where determined at 27 °C and different pressures (50 to 400 psig) for several gases: C₃H₈, CO₂, CH₄, N₂, and H₂. C₃H₈ solubility was found to be much higher than the others due to its higher condensability. On the other hand, C₃H₈ diffusivity was lower because its molecules (being larger) interact more strongly with the segments of the polymer chains compared to the other gases. However, the permeation of each component through the membrane was mainly controlled by their solubility. The gas transport results showed that the high C₃H₈ permeability (20595 Barrer) for an upstream pressure of 110 psi with high selectivities (55, 23, 16 and 6 for N₂, H₂, CH₄ and CO₂) are interesting for the gas separation of higher hydrocarbons from light components, especially for natural gas/biogas purification and the petrochemical industry.

The PDMS/LDPE MCPM were shown to have more stable performance at higher temperatures than for other PDMS membranes because of interfacial layer adhesion improvement. On the other hand, C₃H₈ permeation decreased and CH₄ permeability increased with increasing temperature, but the C₃H₈/CH₄ ideal selectivity was in an acceptable range (7-15) even at higher temperatures.

Addition of PDMS treated TFS not only increased the thermal and mechanical properties, but also improved the permeation performance of the PDMS/LDPE membranes because the surface functional groups increased the penetrants sorption on the TFS surface to improve membrane selectivity and permeability. The results showed that the C₃H₈/CH₄ ideal selectivity and C₃H₈ permeability increased by 41 and 14% respectively, by adding 10 wt.% TFS nano-particles.

Permeability-permselectivity diagram which was developed by Alentiev et al. [88], used for comparing the C₃H₈/CH₄ separation performance of composite membranes was produced in this study with the other polymer membranes. Figure 5.1 clearly shows that the separation
The performance of the nano-composite membranes produced in this study are very good in terms of both permeability and selectivity compared to literature data.

The PDMS-TFS10%/LDPE was shown to have the best performance over a wide range of operating conditions making this material suitable for industrial applications like higher hydrocarbon separation associated to gas-liquid recovery, volatile organic compounds (VOC) removal, liquefied petroleum gas (LPG) recovery from flare or vent lines, gas pipeline dew point control, engine or turbine fuel gas conditioning, vapor recovery from storage tank losses, etc.

![Permeability-Selectivity Diagram](image)

**Figure 5.1.** The permeability-selectivity diagram for C$_3$H$_8$/CH$_4$ (Reprinted from [88]).
5.2 Recommendations for future work

Based on the results obtained from this work, there is still room for more improvement. A list of possible works is provided next based on the different aspects studied in terms of membrane processing and formulation.

In the field of substrate production, the following directions are suggested for future works:

- Utilization of different types of salts with different particles sizes and surface modifications.
  
  The salt which was used in this study contains NaCl and a small amount of an organic material introduced to prevent agglomeration. It is suggested to use other types of particles like starch.

- Use of other types of die to produce hollow fiber membrane.
  
  The flat die was coated in this study to produce FSCM. It is suggested to form the substrate with tubular die in order to produce hollow fiber membranes.

- Use of different grades of polyethylene such as linear low or high density and also different types of polymers such as polypropylene (PP).
  
  LDPE was used as a substrate layer of composite membranes in this study.

In the field of composite membrane production, the following directions are suggested for future works:

- Coating a thin permselective polymer layer (1-2 µm) on the PDMS layer to produce thin film multilayer composite membrane for different applications such as CO₂/CH₄.
  
  PDMS/LDPE MCPM can be used as substrate/gutter layer for coating a thin layer of highly selective CO₂ polymer to produce less expensive membranes for biogas treatment.

- Utilization of different types of fillers with different treatments.
  
  Non-permeable PDMS treated TFS incorporated into PDMS layer of composite membranes in this study. It is suggested to use mesoporous particles as fillers to enhance the performance of composite membranes.
In the field of gas separation tests and applications, the following directions are suggested for future works:

- Testing higher hydrocarbons separations such as C₄H₁₀.
  C₃H₆/gas separation was investigated in this study. It is suggested to test the performance of the composite membranes for C₄H₁₀/gas separation.

- Mixed gas tests at different compositions and operating conditions.
  All the permeation tests in this study were conducted with pure feed gas. It is suggested to test the performance of the composite membranes with mixed feed gas.
References


[27] S. A. Stern, G. R. Mauze, and H. L. Frisch, “Tests of a free-volume model for the permeation of gas mixtures through polymer membranes. CO$_2$-C$_2$H$_4$, CO$_2$-C$_3$H$_8$, and


[69] T. C. Merkel, V. I. Bondar, K. Nagai, B. D. Freeman, and I. Pinnau, “Gas sorption,


[95] R. M. Silverstein, F. X. Webster, and D. J. Kiemle, *Spectrometric identification of*


Sorption measurement

The pressure decay method was used to determine the gas sorption isotherms [1]. The setup (Figure A.1) is composed of a sample cell ($V_{SC}$) and a reservoir ($V_R$) chamber. Before testing, the equipment was evacuated (vacuum was made). During the sorption test, the pressure at a given temperature was recorded by two pressure transducers, one on each side of the sample. The setup was kept at isothermal conditions using an oven. To determine the sorption isotherm of a sample, the following procedure was applied:

1. To evacuate the setup, valves 4, 2 and 3 were opened while keeping valves 1 and 5 closed.
2. By closing valves 2 and 3, the sample cell was isolated from the system.
3. For a desired pressure, valve 1 was gradually opened to allow the gas to be injected into the reservoir chamber. When the pressure reached the set point, valve 1 was closed.
4. Valve 2 was then gradually opened to transfer the gas to the sample cell and be in contact with the sample.
5. After stabilization (steady state condition = constant pressure), the pressure data was send to the acquisition system (computer). A typical pressure-decay curve is provided in Figure A2.

The gas concentration (cm$^3$ STP/cm$^3$ polymer) inside the sample can be determined by [1]:

$$ C = \frac{22414 (n_i - n_f)}{V_p} $$

where $V_p$ (cm$^3$) is the volume of the sample inside $V_{SC}$, while $n_i$ and $n_f$ are the initial and the final total number of moles of the component inside $(V_R)$ and $(V_R + V_{SC})$, respectively.

3.3.5. Gas permeation set-up

Pure gas permeation was measured using a constant volume apparatus as described in our previous work [2]. A membrane was placed in the cell before degassing the whole apparatus. The permeation gas was then fed to the system and the downstream pressure increased until a steady-state condition was obtained. At steady-state, permeability was calculated as:

$$ P = \frac{22414 \frac{l}{A} \frac{V}{p_2 - p_1} \frac{dp}{dt}}{RT} $$

where 22414 is the number of cm$^3$(STP) of penetrant per mole, $A$ is the membrane area (cm$^2$), $l$ is the membrane thickness (cm), $p_2$ and $p_1$ are the upstream and downstream pressure (psi), respectively. $V$ is the downstream volume (cm$^3$), $R$ is the universal gas constant [8.3145 cm$^3$·cmHg/(mol·K)], $T$ is the absolute temperature (K) and $dp/dt$ is the permeation rate (psi/s). The permeabilities are reported with units of Barrer [1 Barrer = $1 \times 10^{-10}$ cm$^3$ (STP) cm/(cm$^2$ s cmHg)].
Figure A.1. Schematic representation of the sorption experimental set-up.
Figure A.2. Typical pressure-decay data curve.
