## Contents

<table>
<thead>
<tr>
<th>Summary</th>
<th>iii</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>v</td>
</tr>
<tr>
<td>List of Tables</td>
<td>vii</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>viii</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Background and motivation</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Scope of the thesis</td>
<td>4</td>
</tr>
<tr>
<td>2 Theory</td>
<td>5</td>
</tr>
<tr>
<td>2.1 CO$_2$ capture</td>
<td>5</td>
</tr>
<tr>
<td>2.1.1 Basic systems for CO$_2$ capture</td>
<td>5</td>
</tr>
<tr>
<td>2.1.2 Technologies for CO$_2$ capture</td>
<td>6</td>
</tr>
<tr>
<td>2.2 Membranes for gas separation</td>
<td>8</td>
</tr>
<tr>
<td>2.2.1 Polymer chemistry</td>
<td>9</td>
</tr>
<tr>
<td>2.2.2 Transport theory</td>
<td>14</td>
</tr>
<tr>
<td>2.2.3 Asymmetric and composite membranes</td>
<td>18</td>
</tr>
<tr>
<td>2.2.4 Robeson’s upper bounds</td>
<td>20</td>
</tr>
<tr>
<td>2.2.5 Mixed matrix membranes</td>
<td>21</td>
</tr>
<tr>
<td>2.3 Ionic liquids</td>
<td>22</td>
</tr>
<tr>
<td>2.3.1 CO$_2$ capture by imidazolium-based ionic liquids</td>
<td>23</td>
</tr>
<tr>
<td>3 Experimental</td>
<td>25</td>
</tr>
<tr>
<td>3.1 Materials</td>
<td>25</td>
</tr>
<tr>
<td>3.2 Membrane preparation</td>
<td>26</td>
</tr>
<tr>
<td>3.2.1 Flat-sheet composite membranes</td>
<td>26</td>
</tr>
<tr>
<td>3.2.2 Preparation of self-supporting membranes</td>
<td>27</td>
</tr>
<tr>
<td>3.3 Membrane characterisation</td>
<td>28</td>
</tr>
<tr>
<td>3.3.1 Permeance measurements</td>
<td>28</td>
</tr>
<tr>
<td>3.3.2 Scanning electron microscopy (SEM)</td>
<td>28</td>
</tr>
<tr>
<td>3.3.3 Thermogravimetric analysis (TGA)</td>
<td>28</td>
</tr>
</tbody>
</table>
### CONTENTS

3.3.4 Differential scanning calorimetry (DSC) .......................... 30  
3.3.5 Fourier transform infrared (FTIR) spectroscopy ................. 30

4 Results and discussion 31  
4.1 Preparation of thin-film composite membranes ...................... 31  
4.1.1 Selection of solvent ........................................... 31  
4.1.2 Effect of Pebax® concentration ................................ 32  
4.1.3 Choice of membrane support ................................... 34  
4.1.4 Choice of coating method ...................................... 35  
4.1.5 Gutter layer .................................................... 36  
4.1.6 Permeation properties ......................................... 38  
4.2 Characterisation of Pebax®/ionic liquid blend membranes ........ 39  
4.2.1 Thermogravimetric analysis (TGA) ............................ 39  
4.2.2 Differential scanning calorimetry (DSC) ....................... 43  
4.2.3 Fourier transform infrared spectroscopy ........................ 46

5 Conclusion and further work 49  
5.1 Conclusion ......................................................... 49  
5.2 Recommendations for further work ................................ 50

Bibliography 51

Appendix A Risk assessment 61

Appendix B $^1$H NMR and ESI-MS for confirmation of TSIL structures 63

Appendix C Flowsheet of single-gas permeation setup 65
Summary

The aim of this thesis has been to optimise the method for preparation of thin-film composite membranes for CO\textsubscript{2} separation where the selective layer is a blend of Pebax\textsuperscript{®}2533 and a task-specific ionic liquid functionalised with amine groups. Pebax\textsuperscript{®}2533 is a poly(ether-block-amide) copolymer exhibiting selectivity of CO\textsubscript{2} over other gases such as N\textsubscript{2}, CH\textsubscript{4} and H\textsubscript{2}.

CO\textsubscript{2} is generally more soluble in ionic liquids than the mentioned gases. It is believed that the presence of the task-specific ionic liquid in the membrane will provide facilitated transport of CO\textsubscript{2} across the membrane due to the reversible chemical reaction between the amine group and CO\textsubscript{2}, and thus increase both the selectivity and the permeability of CO\textsubscript{2} in the membrane. The task-specific ionic liquids chosen in this regard were triethylene tetramine trifluoroacetate ([TETA][Tfa]) and triethylene tetramine lactate ([TETA] L).

In the optimisation, different factors affecting the composite membrane have been assessed, such as the solvent and polymer concentration of the coating solution, choice of porous support, coating method and presence of gutter layer. It was concluded that the many defects in both the investigated porous supports may have affected the membrane performance to such an extent that a better support should be investigated. Defects in the polymer coating layers may also be present. Because of these defects, and since the composite membranes were prepared only with Pebax\textsuperscript{®}, no usable permeation results have been obtained that can demonstrate the effect of the task-specific ionic liquids in the membrane.

When disregarding the porous support, the best composite membranes were obtained by dip-coating a solution of 0.2 wt\% Pebax\textsuperscript{®} in ethanol twice with an immersion time of 5 seconds. This resulted in a coating layer thickness of approx. 300 nm with no pore intrusion. A gutter layer of PTMSP was applied between the support and the Pebax\textsuperscript{®} layer to reduce the presence of defects.

In addition to optimising the membrane preparation, self-supporting Pebax\textsuperscript{®}/ionic liquid blend membranes have been prepared with the task-specific ionic liquids [TETA][Tfa] and [TETA] L and the conventional ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([bmim][Tf\textsubscript{2}N]). The membranes have been characterised with thermogravimetric analysis, differential scan-
ning calorimetry and Fourier transform infrared spectroscopy.
## List of Figures

2.1 CO\textsubscript{2} capture schemes ........................................ 6
2.2 Typical flow sheet of a gas absorption process using amines ....... 7
2.3 The reaction of MEA with CO\textsubscript{2} ................................. 8
2.4 Principle of a membrane .................................................. 8
2.5 Schematic drawings of some usual polymer structures .......... 10
2.6 Temperature variation of the tensile modulus of an amorphous poly-
mer ................................................................. 11
2.7 Specific and free volume of a polymer as a function of temperature.. 12
2.8 General structure of the poly(ether-block-amide) copolymer ........ 12
2.9 Chemical structure of poly(1-trimethylsilyl-1-propyne) .............. 13
2.10 Illustration of the solution-diffusion mechanism for transport in
dense membranes .................................................... 14
2.11 Illustration of the dual-sorption model for a glassy polymer ......... 16
2.12 Mechanism of carrier-facilitated transport ............................. 17
2.13 Effect of carrier on membrane flux .................................... 17
2.14 Structure of a composite membrane .................................. 18
2.15 A coated composite membrane with an illustration of the resistances
in the system ........................................................... 19
2.16 Robeson’s upper bound correlations for CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} .... 21
2.17 Schematic drawing of a mixed matrix membrane: Inorganic particles
dispersed in a polymer .............................................. 21
2.18 Common cations used in ionic liquids ................................ 22
2.19 Common anions used in ionic liquids ................................ 22
2.20 Proposed reaction between a task-specific ionic liquid and CO\textsubscript{2} ... 23

3.1 Chemical structures of [TETA]L, [TETA][Tfa] and [bmim][Tf\textsubscript{2}N] ... 26
3.2 Illustration of how the membrane support was fixed to the glass
plate before dip-coating ........................................... 27
3.3 Schematic drawing of a scanning electron microscope ............ 29
3.4 Q500 thermogravimetric analyser delivered by TA Instruments ... 29
3.5 Components in an infrared spectrometer ............................. 30
LIST OF FIGURES

4.1 Variation in coating layer thickness as a function of Pebax® concentration .................................................. 32
4.2 Cross-section SEM pictures showing the effect of Pebax® concentration on the coating layer thickness ....................... 33
4.3 SEM images showing the surface of the uncoated PSf support. ................................................................. 34
4.4 SEM image of the surface of the fluoro polymer support .......... 35
4.5 SEM images showing the effect of coating method on pore penetration .................................................. 36
4.6 SEM images of membranes with gutter layer. .............................................................................. 37
4.7 TGA thermograms of Pebax®2533, the ionic liquid [bmim][Tf$_2$N] and the task-specific ionic liquids [TETA] L and [TETA][Tfa]. ................................................................. 40
4.8 TGA thermogram of the pure Pebax membrane, pure [TETA][Tfa] and the blend membrane containing 30 wt% [TETA][Tfa] ................................................................. 41
4.9 TGA thermogram of the pure Pebax membrane, pure [TETA] L and the blend membrane containing 30 wt% [TETA] L ........................................................................ 42
4.10 TGA thermogram of pure Pebax®2533, pure [bmim][Tf$_2$N] and a blend membrane containing 30 wt% [bmim][Tf$_2$N] ........................................................................ 43
4.11 DSC thermograms of pure Pebax®, pure [TETA][Tfa] and Pebax®/[TETA][Tfa] blend membranes .................................................. 44
4.12 DSC thermograms of pure Pebax®, pure [TETA] L and Pebax®/[TETA] L blend membranes .................................................. 45
4.13 DSC thermograms of pure Pebax®, pure [bmim][Tf$_2$N] and Pebax®/[bmim][Tf$_2$N] blend membranes .................................................. 46
4.14 FTIR spectra of pure Pebax®, pure [TETA][Tfa] and blend membranes containing 10, 20 and 30% [TETA] L ........................................................................ 47
## List of Tables

2.1 Physical properties of some Pebax® grades .......................... 13

4.1 Permeation properties of Pebax®-coated composite membranes with a PTMSP gutter layer ................................................................. 39
Nomenclature

Greek symbols
\[ \alpha_{i/j} \quad \text{Ideal selectivity of gas } i \text{ over gas } j \, (-) \]
\[ \eta \quad \text{Dynamic viscosity (Pa s)} \]
\[ \rho \quad \text{Density (kg m}^{-3}) \]

Latin symbols
\[ A \quad \text{Membrane area (cm}^2) \]
\[ D \quad \text{Diffusivity (m}^2\text{s}^{-1}) \]
\[ E \quad \text{Tensile modulus (N m}^{-2}) \]
\[ h_{\infty} \quad \text{Equilibrium thickness of coating layer (m)} \]
\[ J \quad \text{Flux} \]
\[ L \quad \text{Membrane thickness (cm)} \]
\[ l \quad \text{Membrane thickness (m)} \]
\[ P \quad \text{Permeability (m}^3\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-1}\text{m}^{-1}) \]
\[ p_1 \quad \text{Pressure on feed side (Pa)} \]
\[ p_2 \quad \text{Pressure on permeate side (Pa)} \]
\[ R \quad \text{Gas constant (5 0.278 cmHg cm}^3\text{cm}^{-3}(\text{STP})\text{K}^{-1}) \]
\[ S \quad \text{Solubility (m}^3\text{m}^{-3}\text{Pa}^{-1}) \]
\[ T_g \quad \text{Glass transition temperature (°C)} \]
\[ V \quad \text{Downstream volume of permeation setup (cm}^{-3}) \]
NOMENCLATURE

$v$ Coating velocity

**Abbreviations**

[bmim][Tf$_2$N] 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide

[TETA] L Triethylene tetramine lactate

[TETA][Tfa] Triethylene tetramine trifluoroacetate

gpu Gas permeation unit ($10^{-6} \text{cm}^3(\text{STP}) \text{ cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$)

IL Ionic liquid

PA Polyamide

PDMS Polydimethylsiloxane

PE Polyether

PTMSP Poly(1-trimethylsilyl-1-propyne)

RTIL Room-temperature ionic liquid

TSIL Task-specific ionic liquid
Chapter 1

Introduction

1.1 Background and motivation

As a result of the improved economical growth in the world during the past decades, the anthropogenic greenhouse gas emissions to the atmosphere are increasing. CO\(_2\) is the most important gas in this context, since it is a product of fossil fuel combustion. Together with reducing the energy consumption and turning to sustainable energy sources, an acknowledged means of reducing the emissions is CO\(_2\) capture and storage [1]. CO\(_2\) capture is also important in gas sweetening processes, where the CO\(_2\) is removed from the main constituent methane in order for the gas to meet pipeline standards [2].

Currently, the prevalent process for CO\(_2\) capture is absorption with amine-based solvents. Although being a rather simple and highly effective removal process, there are also some drawbacks related to amine absorption. These include high equipment costs and problems with corrosion, as well as a considerable energy consumption, which may significantly reduce the benefit of capturing the gas [3].

During the last decades, membrane technology has shown good potential for gas separation applications, having a range of advantages including low energy consumption, low capital cost, easy scale-up and no requirement of additives [4]. Membranes can now be used in a range of gas separation processes, including separation of nitrogen from air, natural gas sweetening, hydrogen recovery from ammonia plants and air drying. The development of membranes for CO\(_2\) separation in both pre- and postcombustion processes are high on the agenda for researchers worldwide as a means against climate change [2]. There is, however, a need to improve the separation performance in order for membranes to become more attractive.

In the recent years, membranes in combination with ionic liquids have shown promising results. Room-temperature ionic liquids (RTILs) are organic salts with melting points below room temperature, and have many advantages such as negligible
vapour pressure, nonflammability and high temperature stability [5, 6, 7]. These properties make ionic liquids a more environmentally friendly alternative to conventional organic solvents. The solubility of CO\textsubscript{2} in ionic liquids is high compared to other light gases, which arises from the interaction between the quadropole moment of CO\textsubscript{2} and the charge of the ionic liquid.

Ionic liquids based on the imidazolium cation have been the focus of much research due to their high CO\textsubscript{2} solubilities, which are caused by the interaction between the quadropole moment of CO\textsubscript{2} and the charge of the ionic liquid [8, 9, 10]. Many research projects have studied different approaches to increase the CO\textsubscript{2} solubility and selectivity in these ionic liquids, and to improve the morphology of membranes with ILs incorporated.

'Task-specific' ionic liquids (TSILs) take advantage of functional groups to improve the CO\textsubscript{2} solubility. By combining the ionic liquid with amines it is possible to change the nature of the absorption; whereas normal ionic liquids interact with CO\textsubscript{2} in a physical way, amines react chemically with the gas, offering a facilitation effect [13]. Bates et al. [14] synthesised a TSIL with an primary amine moiety for selective reaction with CO\textsubscript{2} and found a TSIL/CO\textsubscript{2} molar ratio of 2:1, superior compared to a normal IL and comparable to conventional primary amines. Camper et al. [15] on the other hand, mixed amines and normal ILs consisting of Tf\textsubscript{2}N anion and found that the performance was better than TSILs. This method requires few preparation steps compared to TSILs and reduces problems with increase in viscosity when amine groups are covalently bonded to the IL.

Ren and coworkers [16] synthesised polyamine-based TSILs through the neutralisation of polyamines and organic acids. The two most efficient TSILs, triethylene tetramine lactate ([TETA]L) and triethylene tetramine trifluoroacetate ([TETA][Tfa]) reached CO\textsubscript{2} mole ratios of about 0.9 at 110 °C. As they were based on triethylene tetramine, having four amino groups, these TSILs had the highest number of free amino groups available for reaction with CO\textsubscript{2}.

The diffusion rate in liquid media is generally higher than in polymers [17, 18]. A common application of ionic liquids in membrane technology is in the form of supported liquid membranes (SLMs), in which a porous membrane support is impregnated with the liquid, which acts as a highly selective carrier phase [19, 13]. Due to the nonvolatility and the relatively high viscosity of many ILs, problems concerning evaporation of solvent from the SLMs are reduced [12, 20]. Membrane contactors is another application where these properties are advantageous. However, in both SLMs and membrane contactors, the liquid may still be replaced by a sufficient pressure difference across the membrane, thus limiting the areas of application [21].

Problems with displacement of the liquid can be solved by immobilisation of the ionic liquid. The challenge is to make a membrane that is permeable, selective, durable, pressure-resistant and easy to prepare. Noble and coworkers have tried different approaches for liquid immobilisation. By using ionic liquids with polymerisable groups, they prepared dense poly(RTIL) films that could be used as gas
separation membranes [22]. Physically gelled IL membranes also showed promising results, maintaining the good transport properties of ionic liquids while becoming more mechanically stable [23]. Different types of composite membranes have also been tested, such as incorporating ionic liquids in poly(RTIL)s [24, 25] and by using the ionic liquid to minimise the gaps between zeolites incorporated in a poly(RTIL) matrix [26, 27].

Kanehashi et al. [28] included the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([bmim][Tf$_2$N] ) in glassy fluorine-containing polyimide membranes. The membranes had good CO$_2$ selectivities over H$_2$ and O$_2$, and the gas permeability increased with increasing IL content in the range 51–81%.

Poly(ether-block-amide) with the commercial name Pebax® is a family of multiblock copolymers with considerable potential in CO$_2$ removal processes. The polymer consists of phase-separated blocks of soft polyether (PE) and hard polyamide (PA), of which the PE domains are responsible for the gas permeation.

Due to the interaction between the quadropolar moment of CO$_2$ and the polar polyether, the copolymer exhibits high selectivities for CO$_2$ over nonpolar gases such as H$_2$ and N$_2$ [29, 30]. Pebax® exists in several grades with different PE/PA ratios. Pebax®2533, containing 80 wt % of the polyether PEO, has the highest gas solubility among several tested Pebax® grades, which has been ascribed to its high PE content [29, 31]. With CO$_2$ selectivities of 28.2, 5.5 and 8.3 for separation from N$_2$, H$_2$ and CH$_4$, respectively, it is a promising material especially for separation from nitrogen [31].

Several attempts have been made to improve the inherently good separation properties of Pebax® membranes. By successfully incorporating ZIF-7 nanofillers in Pebax®1657, Li and coworkers [32] prepared thin-film composite membranes for CO$_2$ separation from N$_2$ and CH$_4$. These mixed matrix membranes exhibited both higher permeability and selectivities compared to the pure polymer. Yu et al.[33] increased the permeability of CO$_2$ by 28% by incorporating 5% single-walled carbon nanotubes in Pebax®1657. Thin-film composite materials consisting of a blend of polyethylene glycol (PEG) and Pebax®1657 were prepared by Car et al. [34]. The membranes exhibited an enhanced gas flux compared to the pure Pebax® membranes, which was ascribed to both a plasticising effect and enhanced CO$_2$ sorption due to the ethylene oxide groups of PEG.

Some researchers have also tried to add ionic liquids to Pebax®polymers. Bernardo et al. [31] prepared polymeric gel membranes from two Pebax® grades and the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate. Pebax®1657 showed good compatibility with the ionic liquid, and resulted in higher permeabilities of all the tested gases, whereas the CO$_2$ selectivity decreased somehow for all gas pairs.

In this thesis, the aim is to optimise the preparation method of thin-film composite membranes where the selective layer will consist of Pebax® and a task-specific ionic
liquid. It is believed that the advantageous properties of task-specific ionic liquids and the CO$_2$-selective block copolymer Pebax®2533 may be combined to give a membrane with facilitation that exhibits a high CO$_2$ selectivity and permeability.

1.2 Scope of the thesis
Chapter 2

Theory

This chapter introduces the most relevant theory behind the topics covered in this master thesis. Firstly, the basics of CO$_2$ capture will be presented, followed by theory about gas separation membranes, ionic liquids and Pebax® polymers.

2.1 CO$_2$ capture

Together with reducing the energy intensity and reducing the carbon intensity, carbon capture and storage (CCS) is considered as a main option for reducing the emissions of CO$_2$ to the atmosphere [1]. The capture is the most energy-demanding part of the CCS process, and much effort is put into the development of more efficient technologies. Whereas it is possible to capture the gas from a great range of sources, capture from large point sources such as fossil fuel power plants, fuel processing plants and other industrial plants holds the greatest potential for significant mitigation [35]. These technologies will be further explained in the next sections.

2.1.1 Basic systems for CO$_2$ capture

The capture of CO$_2$ from fossil fuels or biomass can be divided into three [1], as illustrated in Figure 2.1. In post-combustion capture, the CO$_2$ produced from combustion of fossil fuels in air, is separated from the flue gas stream containing mostly nitrogen and carbon dioxide. Such flue gas streams are usually very large in volume and at ambient pressures.

In oxy-fuel combustion, the combustion of the fuel occurs in an oxygen atmosphere, leaving CO$_2$ and water vapour as the main combustion products, together with
excess oxygen required for complete combustion. Compared to air combustion, no inert \( \text{N}_2 \) is present, which results in a much smaller flue gas volume. Cooling of the gas stream causes the water vapour to condense, giving a very pure \( \text{CO}_2 \) stream that can be compressed for subsequent storage.

The \( \text{CO}_2 \) can also be captured before combustion of the fuel. Pre-combustion capture is normally carried out by adding steam to the fossil fuel to produce \( \text{CO} \) and \( \text{H}_2 \), followed by the water gas shift reaction:

\[
\begin{align*}
\text{C}_x\text{H}_y + x\text{H}_2\text{O} & \rightleftharpoons x\text{CO} + (x + 0.5y)\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2
\end{align*}
\]

The carbon dioxide can then be removed from the mixture of \( \text{H}_2 \) and \( \text{CO}_2 \).

There are also a number of other important processes that produce \( \text{CO}_2 \)-containing streams where separation may be employed [1]. In natural gas sweetening, \( \text{CO}_2 \) is one of the impurities that is removed from the natural gas in order for the gas to comply with the pipeline specifications. The calcination of limestone in cement processes produces flue gas streams containing around 15-30\% \( \text{CO}_2 \), making this industry a suitable candidate for CCS. Also, the ammonia industry has potential for \( \text{CO}_2 \) capture. Steam reforming and the water gas shift reaction are common steps in many ammonia-producing processes, and the produced carbon dioxide may thus be captured.

### 2.1.2 Technologies for \( \text{CO}_2 \) capture

Currently, the prevalent method for removing \( \text{CO}_2 \) from gas streams is absorption. The absorption liquid may be a physical or a chemical solvent, the difference being...
2.1. \( \text{CO}_2 \) CAPTURE

the way the gas is absorbed [37]. With physical solvents there are only physical interactions between the solvent and gas, while chemical solvents capture \( \text{CO}_2 \) through reversible chemical reactions. The gas solution of physical solvents follows Henry’s law, which says that more gas is being absorbed as the partial pressure is raised. Therefore, the partial pressure of the gas should be high for physical solvents to be effective. Due to the chemical reaction, chemical solvents can usually be applied at lower partial pressures than physical solvents [37].

In the absorption process, the \( \text{CO}_2 \)-containing gas stream is contacted with the solvent in a absorption column. The solvent which now contains the captured \( \text{CO}_2 \) is passed to a stripper section for regeneration. Depending on the type of solvent and process conditions, the \( \text{CO}_2 \) is released from the solvent either by increasing the temperature or by reducing the pressure. The \( \text{CO}_2 \) can then be compressed and stored, while the regenerated solvent is sent back to the absorption column.

Chemical absorption with aqueous alkanolamine solutions is a widely employed process due to its very high \( \text{CO}_2 \) removal efficiency. An overview of a typical post-combustion absorption process is shown in Figure 2.2. Although being a rather simple process with high efficiency, a major disadvantage with this process is the large energy requirements in the stripping section, significantly reducing the overall efficiency of for instance coal-fired power plants.

![Typical flow sheet of a gas absorption process using amines](image_url)

**Figure 2.2:** Typical flow sheet of a gas absorption process using amines

The reaction scheme for the absorption of \( \text{CO}_2 \) with the primary amine monoethanolamine (MEA) is shown in Figure 2.3. The reaction stoichiometry is 2:1, meaning that two amine molecules react with one \( \text{CO}_2 \) molecule to form a carbamate salt.

\( \text{CO}_2 \) can also be captured in other processes. In adsorption the gas is adsorbed on the surface of a microporous solid. Weak attractive forces are present between the
support and the adsorbate, so the adsorbate can usually be released by decreasing the pressure or increasing the temperature, similar to the stripping section in absorption processes.

Another promising technology for CO\textsubscript{2} capture is membrane processes, in which gases are selectively transported through a membrane. Important concepts regarding membranes will be presented in the following section. As will be explained later, the driving force for gas separation membrane processes is the difference in partial pressure across the membrane. Therefore, membrane technology is most promising in cases where the pressure and/or the CO\textsubscript{2} concentration is high.

## 2.2 Membranes for gas separation

A membrane can be defined as a semipermeable barrier between two phases. Figure 2.4 illustrates the principle of a gas separation membrane. A gas mixture enters the feed side. Depending on the membrane properties, some of the gas components go through the membrane to the permeate side, while the rest is retained on the feed side of the membrane.

The separation of the gas components occurs on the basis of membrane properties, gas properties and process conditions. This makes it possible to customise membrane systems to specific applications. Important terms in this context are permeability and selectivity. The permeability describes how efficient the transport across the membrane is. It is commonly reported with the non-SI unit Barrer, corresponding to \(10^{-10}\text{ cm}^3\text{ (STP)}\cdot\text{cm/cm}^2\cdot\text{s}\cdot\text{cmHg}\). The selectivity describes the
2.2. MEMBRANES FOR GAS SEPARATION

extent of transport of the different components in a gas mixture. Equation 2.1 expresses the selectivity as the separation factor $\alpha$:

\[
\alpha = \frac{y_A / x_A}{y_B / x_B}
\]

(2.1)

where $y_A$ and $y_B$ are the concentrations of components A and B in the permeate, respectively, and $x_A$ and $x_B$ are the concentrations of components A and B in the feed.

Most gas separation membranes are made of dense polymers, through which the transport is governed by the solution-diffusion mechanism. The transport equation for such membranes under ideal conditions (ideal sorption and diffusion behaviour) is given by:

\[
J = \frac{P}{l} (p_1 - p_2)
\]

(2.2)

where $J$ is the flux, $P$ is the permeability, $l$ is the membrane thickness and $p_1$ and $p_2$ are the feed and permeate pressures, respectively. From equation 2.2 it follows that the driving force is the difference in partial pressure across the membrane. Thus, the highest flux is achieved with a high pressure difference and a thin membrane. The permeability coefficient and the solution-diffusion mechanism is discussed in more detail in section 2.2.2.1. But first, an introduction to the chemistry regarding polymers is provided.

2.2.1 Polymer chemistry

The majority of membranes used in industry today are made of polymers. These materials consist of small units, monomers, that are linked together to form a solid high-molecular weight polymer. Polymers exhibit a range of different properties, most of which may be ascribed to the structure of the polymer. The most important factors are presented in this section, with all theory retrieved from ref. [4].

2.2.1.1 Homopolymers, copolymers and crosslinked polymers

A polymer consists of one or several repeating units, often with sidegroups. When only one repeating unit makes up the polymer chain, it is called a homopolymer. On the other hand, a copolymer consists of more repeating units. There are three ways to distinguish copolymers, as illustrated in Figure 2.5a. A random copolymer has a completely irregular order of the repeating units, block copolymers consist of blocks of the repeating units linked together, while a graft copolymer has a branched structure where one repeating unit makes up the main chain and another
Different types of copolymers

(a)

Crosslinking occurs by connecting polymer chains to form a network-like structure, usually by covalent bonding. This changes the properties of the original chain, for instance making it insoluble. A schematic drawing of a crosslinked polymer is shown in Figure 2.5b.

2.2.1.2 Amorphous and crystalline polymers

Properties such as mechanical strength and permeability are affected by the crystallinity of the polymer. Crystalline areas may arise when the structure of the polymer is regular, for instance if all the side groups are placed on the same side of the main chain, which allows efficient packing of the chains into a crystalline structure. However, if the orientation of the side groups on the main chain is more random, the chain is branched or the side groups are bulky, efficient packing is hindered and the material becomes amorphous. Other factors increasing the crystallinity is the presence of secondary intermolecular forces, such as hydrogen bonds.

Crystalline polymers have a higher mechanical strength and are more thermally and chemically resistant than amorphous polymers. However, the permeability of such polymers is low, making them less suitable for dense membranes. Many polymers are semicrystalline, which means that they consist of both amorphous and crystalline domains. The relative amounts of these domains hence determine the overall properties of the polymer.

2.2.1.3 Chain flexibility

The flexibility of the chain greatly affects the polymer properties, and is mainly dependent on the nature of the main chain and the nature of the side groups of the polymer. If the main chain consists only of single C-C bonds, it is highly flexible and chain rotation is possible. However, the presence of unsaturated bonds may
2.2. MEMBRANES FOR GAS SEPARATION

significantly reduce the rotational flexibility of the main chain. This is also the
case if the chain consists of larger units such as aromatic and heterocyclic groups.
On the other hand, atoms such as N and O linked to carbon atoms will increase
the chain flexibility.

The side groups also affect the flexibility. The steric hindrance provided by bulky
side groups significantly reduces the rotational freedom around the main chain,
leading to rigid materials. The chain flexibility is closely related to the state of the
polymer, and will be explained in the next section.

2.2.1.4 The state of the polymer

The state of a polymer is one of the most important factors when choosing polymers
for dense membranes, and the glass transition temperature ($T_g$) is a very important
term in this respect. The glass transition temperature is dependent on the polymer
structure and thus related to the chain mobility. The bigger and bulkier side groups
of the polymer, the more rigid the chain becomes and more energy must be added
to allow segmental motion, which implies a high $T_g$. If the side groups are small
and rather linear, segmental motion may occur readily without a significant energy
input, and the glass transition temperature is thus low.

Above the glass transition temperature the polymer is in its rubbery state, where
the chains are flexible and rotation is possible, while (and thus a larger free volume)
below $T_g$ it is in the glassy state, where rotation is restricted and the chains are
more rigid. This is illustrated in Figure 2.6, which shows the tensile modulus ($E$)
of an amorphous polymer as a function of temperature.

\[ \text{Figure 2.6: Temperature variation of the tensile modulus of an amorphous polymer. Adapted from [4]} \]

The concept of free volume, which can be explained by the space unoccupied by
the polymer itself, is useful for understanding the glass transition. Below $T_g$ this
free volume is independent of temperature, but above $T_g$ the free volume increases
with temperature. The relationship between the state of a polymer and its specific and free volumes is shown in Figure 2.7.

![Figure 2.7: Specific and free volume of a polymer as a function of temperature. Adapted from [39]](image)

2.2.1.5 Thermoplastic elastomers and Pebax® copolymers

Thermoplastic elastomers consist of blocks of polymers that are immiscible with each other, leading to separated microphases. This often means that one block is a dispersed phase in the other, continuous phase. If the elastomer consists of one crystalline polymer, this is usually the dispersed phase and acts as physical thermoreversible crosslinks, meaning that heating above the $T_g$ of the crystalline phase makes the elastomer soft. The properties of such thermoplastic elastomers are dependent on the ratio of the blocks.

Pebax® is the trade name of a series of poly(ether-block-amide) copolymers. They belong to the thermoplastic elastomers due to the phase-separated microphases consisting of polyether (PE) and polyamide (PA) segments [40]. The PE phase provides high permeability due to the high chain mobility, while the hard semi-crystalline PA segments provide the mechanical strength. Several grades of Pebax® exist, of which the properties are determined by the ratio of the constituent blocks. The general structure of Pebax® is shown in Figure 2.8.

![Figure 2.8: General structure of the poly(ether-block-amide) copolymer.](image)
2.2. MEMBRANES FOR GAS SEPARATION

Table 2.1 summarises the physical properties of some Pebax® grades. [29]

<table>
<thead>
<tr>
<th>Name</th>
<th>PE content (wt %)</th>
<th>Density (g/cm³)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$(PE) (°C)</th>
<th>$T_m$(PA) (°C)</th>
<th>Crystallinity in PA block (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pebax® 2533</td>
<td>80</td>
<td>1.01</td>
<td>-77</td>
<td>9</td>
<td>126</td>
<td>14</td>
</tr>
<tr>
<td>Pebax® 4033</td>
<td>53</td>
<td>1.01</td>
<td>-78</td>
<td>-1</td>
<td>159</td>
<td>32</td>
</tr>
<tr>
<td>Pebax® 5533</td>
<td>30</td>
<td>1.01</td>
<td>Not detectable</td>
<td>20</td>
<td>160</td>
<td>30</td>
</tr>
<tr>
<td>Pebax® 1074</td>
<td>55</td>
<td>1.09</td>
<td>-55</td>
<td>11</td>
<td>156</td>
<td>40</td>
</tr>
<tr>
<td>Pebax® 4011</td>
<td>57</td>
<td>1.14</td>
<td>-53</td>
<td>13</td>
<td>201</td>
<td>51</td>
</tr>
</tbody>
</table>

As can be seen from Table 2.1, Pebax®2533 has the highest PE content. It consists of poly(tetramethylene oxide) (PTMO) as the PE phase, interspaced by rigid Nylon 12 as the PA phase. The high PE content is the reason why Pebax®2533 exhibits the highest gas solubility among the mentioned Pebax® grades [29].

2.2.1.6 Poly(1-trimethylsilyl-1-propyne) - a high free-volume polymer

Poly(1-trimethylsilyl-1-propyne) (PTMSP) exhibits gas permeabilities in the range of $10^3 - 10^4$ Barrer, the highest permeability of any known polymer [4, 41]. The chemical structure of the polymer is shown in Figure 2.9. From this it can be seen that the polymer has a double bond in the main chain and a very bulky side group. These factors cause the material to be highly rigid, effectively preventing segmental motion in the polymer, which is indicative of a high glass transition temperature.

![Chemical structure of poly(1-trimethylsilyl-1-propyne)](image)

Figure 2.9: Chemical structure of poly(1-trimethylsilyl-1-propyne) [4]

The polymer structure prevents efficient packing of the chains, which gives rise to a very high fractional free volume of 0.29 [42]. It is this property that is believed to cause the very high permeability of PTMSP. Compared to conventional glassy polymers, PTMSP has gas solubilities about ten times higher and diffusivities $10^3$-$10^6$ times higher. Since the transport in dense polymers follows the solution-diffusion model, it follows that the permeability of PTMSP is very high.
2.2.2 Transport theory

The way separation occurs in a gas separation membrane is dependent on the membrane type. For dense membranes the transport of species is based on a solution-diffusion mechanism, while for microporous membranes the transport can occur through several mechanisms; molecular sieving, Knudsen diffusion and selective surface diffusion [43]. An emerging field within membrane technology is facilitated liquid membranes, where an additional type of transport occurs due to the presence of a reactive carrier. In this section, theory regarding transport in dense membranes and facilitated transport is provided, while theory on transport in porous solids can be found elsewhere [39, 4]

2.2.2.1 Transport in dense membranes

Dense membranes for gas separation are mostly made of polymers. Transport in dense polymers is best explained by the solution-diffusion mechanism, and it is the differences in solubility and diffusivity of the gas components that determine the separation properties of the membrane. This can be utilised to separate molecules of similar size [39, 4]. The principle of the solution-diffusion mechanism is illustrated in Figure 2.10:

As the name indicates, the transport is a combination of two steps. First, the permeant is dissolved in the membrane material, and then the transport through the material occurs by molecular diffusion due to a concentration gradient. The permeability of a species can thus be written as the product of the solubility (S) and the diffusivity (D):

\[ P = S \times D \]
2.2. MEMBRANES FOR GAS SEPARATION

\[ P = S \times D \]  
\hspace{1cm} (2.3)

The ideal selectivity between two gases \((\alpha_{i/j})\) in a dense membrane can be expressed by the permeability ratio of the respective gases. This gives:

\[ \alpha_{i/j} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \times \frac{D_i}{D_j} \]  
\hspace{1cm} (2.4)

Thus, there are two selectivity contributions to the ideal selectivity; the solubility selectivity and the diffusivity selectivity. The solubility is a thermodynamic parameter describing the amount of penetrant absorbed by the polymer at equilibrium, while the diffusivity is a kinetic parameter describing how fast the penetrant diffuses through the membrane.

**Diffusivity**

Fick’s first law can be used to describe the diffusion of gases through membranes, as shown in equation 2.5:

\[ J = -D \frac{dc}{dx} \]  
\hspace{1cm} (2.5)

where \(J\) is the flux through the membrane, \(D\) is the diffusivity, \(dc\) is the concentration difference and \(dx\) is the membrane thickness. The diffusivity is the proportionality constant in Fick’s first law and describes the ease of transport through the surrounding environment (polymer) of the penetrant. This means that the size of the penetrant is an important factor. The geometry is also important, because linear molecules (such as \(\text{CO}_2\)) may more easily pass narrow openings than round molecules (such as \(\text{CH}_4\)). As a general rule, the diffusivity decreases as the penetrant size increases, but other behaviours may be observed for interacting systems [4].

The diffusivity of a component is also dependent on the free volume of the polymer. As mentioned in section 2.2.1, the free volume depends on the state of the polymer, i.e., whether it is glassy or rubbery. Rubbery polymers have higher free volumes and also higher diffusivity than glassy polymers. On the other hand, glassy polymers have lower free volumes. The ease of diffusion is thus more dependent on the size of the gas molecule, which lead to the higher selectivities normally exhibited by glassy polymers.

**Solubility**

The solubility is a measure of the amount of penetrant that is dissolved in the membrane at equilibrium. Whereas the diffusivity decreases with an increase in
CHAPTER 2. THEORY

penetrant size, the opposite is true for the solubility. The solubility is dependent on the ease of condensation, which increases as the molecular diameter increases. So for small molecules, the high permeability arises from the large diffusion coefficient, while the high permeability of larger molecules can be ascribed to the higher solubility.

In ideal systems, such as gases in elastomers, the solubility is low and follows Henry’s law, which means that the concentration of dissolved substance varies linearly with the applied pressure. In glassy polymers an additional model of sorption is used, in which the molecules are dissolved in the excess free volume. This sorption model has a typical Langmuir behaviour. The combination of the Henry’s law model and the Langmuir model is called the dual-sorption model and is shown in Figure 2.11.

![Figure 2.11: Illustration of the dual-sorption model for a glassy polymer, with Henry’s law sorption and Langmuir sorption contributing to the total gas sorption. Adapted from [39]](image)

2.2.2.2 Facilitated transport

Facilitated transport membranes take advantage of reactive carriers to enhance the selectivity and transport of specific components across the membrane [44]. The carrier forms a complex with the solute, and may be either fixed or mobile. Fixed carriers are bound to the polymer matrix of the membrane, which means that the transport of the solute occurs by a carrier-to-carrier jumping mechanism. On the other hand, mobile carriers are dissolved in a liquid so that the carrier-solute complex can diffuse through the membrane. Between the fixed and mobile carrier systems there are intermediate systems in which the carrier is dispersed in a swollen polymer or gel [4]. Only mobile carrier systems will be considered in this section. Such systems may exhibit higher fluxes due to the facilitated transport provided by the carrier.

Coupled transport is a special case of facilitated transport. Here, two different
components are transported in the opposite direction. Since the driving force for transport is based on the concentration gradient of only one of the species, the other species may therefore be transported against its concentration gradient. Figure 2.12 illustrates the difference between normal diffusive transport, facilitated transport and coupled facilitated transport.

![Figure 2.12: Mechanism of carrier-facilitated transport.][4]

A key point regarding facilitated transport is that the complexation reaction between carrier and solute must be reversible. If not, the enhanced effect of the carrier will stop when all the carriers have reacted. Also, the formed complex must have a stability that allows a certain facilitation but at the same time not be so stable that decomplexation is too slow.

When carriers are present the flux of solute is no longer directly proportional to the driving force for separation. There is a flux enhancement compared to a non-carrier system at all pressures, but the effect is more pronounced at lower pressures. This is illustrated in Figure 2.13, where the carrier has affinity to the oxygen.

![Figure 2.13: Effect of carrier on membrane flux in a system where the carrier reacts with oxygen. Adapted from [4]]

Two diffusion processes thus occur at the same time in carrier-mediated systems; normal Fickian diffusion of the uncomplexed component (A) through the liquid
film and facilitated diffusion of the solute-carrier complex (AC). This is illustrated in equation 2.6, where the subscripts 0 and \( l \) denote the feed and permeate side of the membrane, respectively.

\[
J_A = \frac{D_A}{l} (c_{A,0} - c_{A,l}) + \frac{D_{AC}}{l} (c_{AC,0} - c_{AC,l})
\]  

(2.6)

From equation 2.6 two limiting cases can be observed:

1. The Fickian diffusion is rate-determining, which means that the second term can be neglected, i.e., no facilitation occurs.
2. The diffusion of the complex is rate-determining. This occurs when the complexation rate is fast and diffusion of the free component is negligible.

These limiting cases can also be quantified with the second Damköhler number given by equation 2.7.

\[
Da_{II} = \frac{l^2}{D_A t_{0.5}}
\]  

(2.7)

where \( t_{0.5} \) is the time constant of the complexation reaction and the ratio \( D_A/l \) is the diffusion time constant. If \( Da_{II} \ll 1 \), the first limiting case occurs, while the second limiting case is characterised by \( Da_{II} \gg 1 \).

### 2.2.3 Asymmetric and composite membranes

Most membranes are prepared from polymer materials. A very common type of membrane used for many applications is the composite membrane, an asymmetric membrane where the different layers are made from different polymer materials. There is usually a porous support at the bottom which provides the necessary mechanical strength, while the dense toplayer is responsible for the separation properties. There may also be layers of different porosity in the support, as shown in Figure 2.14.

![Figure 2.14: Structure of a composite membrane](45)
Compared to the porous layer where the mass transfer is based on viscous or Knudsen flow [4, 39], there is a substantial resistance to mass transfer in the dense toplayer. This layer should therefore be very thin in order to achieve an efficient separation. Other requirements for an asymmetric membrane are [4]:

- The dense toplayer must be free of defects, which may be caused by dust particles, gas bubbles and support fabric imperfections [44]
- The porous support layer must be free of macrovoids
- The pore structure of the support must be open to minimise the mass transfer resistance

The absence of defects is crucial for the membrane performance in gas separation, as only a few defects may reduce the selectivity dramatically. It is often difficult to completely avoid defects, but one solution is to deposit a gutter layer between the support and the selective layer [44, 46]. This polymer should be highly permeable, and functions only to plug the pores and defects, so the resistance it exerts is low compared to the selective layer. This is illustrated in the left part of in Figure 2.15, while the right part shows the resistances in the system.

![Figure 2.15: A coated composite membrane with an illustration of the resistances in the system. Adapted from [4]](image)

When it comes to the transport properties of a composite membrane, the thickness of the total membrane product is often unknown. Therefore, it is more convenient to operate with the term permeance, defined by the ratio of permeability and membrane thickness as shown in equation 2.8 [47]. The permeance is often expressed with the gas permeation unit (gpu), defined as $10^{-6}$ cm$^3$(STP) cm$^{-2}$s$^{-1}$cmHg$^{-1}$.

$$
\text{Permeance} = \frac{\text{Permeability}}{\text{Thickness}}
$$

(2.8)
2.2.3.1 Preparation of composite membranes

The preparation of composite membranes is possible through several techniques, including dip-coating, spray-coating, spin coating, interfacial polymerisation, in-situ polymerisation, plasma polymerisation and grafting [4]. Since dip-coating is the only of these techniques employed in the thesis work, this is also the only technique that will be explained in this section. The reader is referred to ref. [4] and [39] for descriptions of the other techniques.

The simplicity of dip-coating makes it a very useful preparation method. The support membrane is immersed in a bath of diluted coating solution. After removal, a thin layer of polymer solution sticks to the support. The solvent evaporates and leaves a thin, dense polymer layer. The membrane can also be placed in an oven to enhance the solvent evaporation rate and in some cases to allow crosslinking to occur.

Several factors contribute to the equilibrium thickness \( h_\infty \) of the coating layer, as shown in equation 2.9: [48](as cited by [4])

\[
h_\infty = \frac{2}{3} \sqrt{\frac{\eta v}{\rho g}} \tag{2.9}
\]

where \( v \) is the coating velocity, \( \eta \) is the dynamic viscosity and \( \rho \) is the density. The resulting polymer layer is thus proportional to the volume fraction of the polymer in solution.

In order to make a defect-free layer, a polymer should be used which is in its rubbery state over the whole temperature range it is exposed to. Formation of defects is likely to occur if the polymer changes from rubbery to glassy during evaporation, due to the large forces present [4].

As mentioned above, it is possible to apply a gutter layer between the support and the selective layer. Another option is to make the hydrodynamic radius of the polymer larger, either by using polymers with a higher molecular weight or by using a good solvent. It is also possible to use a solvent that does not wet the surface of the support. In this way, no or little polymer solution will penetrate the pores. [4]

2.2.4 Robeson’s upper bounds

Generally, there is a compromise between high permeability and high selectivity for polymeric membranes. This means that a highly permeable polymer usually has a relatively low selectivity, and vice versa, which is a major obstacle for the industrial application of membranes. Robeson presented his upper bounds which showed the relationship between the permeability and separation factor for a range of reported gas separation membranes[49, 50]. Upper bound correlations for CO\(_2\) and other
gases are shown in Figure 2.16. Figure 2.16a shows two upper bounds; the prior upper bound as presented in 1991, and the updated upper bound as presented in 2008. The focus of many research projects is to cross the upper bounds in order for membrane technology to become an even more competitive technology.

![Figure 2.16: Robeson’s upper bound correlations for two gas pairs. Adapted from [50].](image)

2.2.5 Mixed matrix membranes

Mixed matrix membranes (MMM), which consist of both polymeric and inorganic elements, is a promising candidate for crossing the upper bound described in the previous section [51]. The usual conformation is inorganic particles dispersed in a bulk polymeric phase, as illustrated in Figure 2.17. The inorganic phase may consist of size-sieving particles such as zeolites and carbon molecular sieves or nano-size particles, which all have very good chemical and thermal stabilities and transport properties, but are expensive and difficult to process without defects. Thus, MMMs aim to combine the beneficial properties of both phases; the good mechanical properties and easy preparation of polymers and the excellent separation properties of the inorganic particles.

![Figure 2.17: Schematic drawing of a mixed matrix membrane: Inorganic particles dispersed in a polymer.](image)
2.3 Ionic liquids

Ionic liquids (ILs) are organic salts that have melting points below 150 °C [5], while room-temperature ionic liquids (RTILs) are liquids at and below room temperature. The low melting points of ionic liquids arise from their large degree of asymmetry, which effectively hinders packing and crystallisation [6]. This is illustrated in Figure 2.18 and 2.19, which show the bulky structure of some of the most common cations and anions that are used to form ionic liquids.

Ionic liquids are essentially nonvolatile and are in many cases stable over a large temperature range [5]. This is especially beneficial for solvent applications, as many processes employing conventional organic solvents are associated with large losses due to evaporation.

A wide range of choices of anions and cations exist. Through careful selection of the cation-anion pair and their substituents it is possible to tune many of the properties of ionic liquids, such as the density, viscosity, hydrophilicity and solubility [52, 6]. Many ionic liquids have high CO$_2$ solubility selectivities with respect to gases such as N$_2$ and CH$_4$, which is due to the interaction between the quadrupole moment of CO$_2$ and the electrostatic forces in the ionic liquid [53].

For reasons such as easy preparation and attractive properties, ionic liquids based on the imidazolium anion are the most studied for CO$_2$ separation. Thus, they will be the main focus of this section.

![Phosphonium, imidazolium, ammonium, and pyridinium cations](image)

**Figure 2.18:** Common cations used in ionic liquids [7]

![Tetrafluoroborate, hexafluorophosphate, trflate, bis(triflimide), dicyanamide, and tetracyanoborate anions](image)

**Figure 2.19:** Common anions used in ionic liquids [52]
2.3. IONIC LIQUIDS

2.3.1 CO₂ capture by imidazolium-based ionic liquids

The solvation of CO₂ in ionic liquids is mainly caused by physical interactions [8]. This means that the gas solubility follows Henry’s law, which says that the amount of gas dissolved in a liquid is directly proportional to the partial pressure of the gas above the liquid [54]. As a general rule the solubility of a gas decreases with increasing temperature, and this is also the case for many ionic liquids [55]. This means that normal ionic liquids are most efficient under high pressure and low temperature. For this reason, application of ionic liquids in gas sweetening processes where the pressure is high seems the most promising. Selectivity of processes employing ionic liquids is mainly based on the difference in solubility of the various gas species.

It is, however, possible to change the nature of the gas absorption from physical to chemical, by introducing groups that are capable of reacting chemically with CO₂ [52]. One example of such a functional group is the amine group. As was shown in Figure 2.3, a primary amine reacts with CO₂ and forms a carbamate salt. Amines and other chemical solvents can also be the mechanism in so-called task-specific ionic liquids. Bates et al. [14] synthesised an ionic liquid with a primary amine attached to an imidazolium cation, and found that the capacity of this TSIL approached that of primary amines, namely 0.5 moles of CO₂ absorbed per mole of TSIL. This led to a proposed reaction involving a carbamate species. A generalised version of this reaction is shown in Figure 2.20:

![Figure 2.20: Proposed reaction between a task-specific ionic liquid and CO₂](image)

Whereas the selectivity in normal ionic liquids separations is mainly based on differences in gas solubilities, the chemical affinity of the task-specific ionic liquid towards CO₂ gives rise to an additional selectivity. This, in combination with the possible employment at lower pressures, makes TSILs very promising also for separations at lower pressures, for instance in post-combustion capture.

As mentioned, the solubility properties of ionic liquids can be tuned by choosing the appropriate cation-anion pair. It has been shown that the choice of anion affects the CO₂ solubility more than is the case with the cation [9, 56].

Regular solution theory (RST) can be used to describe the behaviour of gases in regular ionic liquids [57, 58, 55]. The simplified RST model shown in equation 2.10 has shown to give a good estimate of the solubility of gases in 1-alkyl-3-methylimidazolium (Rmim)-based ILs at low pressures and near-ambient temperatures [59, 8].
\[ \ln(H_{2.1}(\text{atm})) = \alpha + \frac{\beta^*}{V_{1}^{4/3}} \] (2.10)

where \(H_{2.1}\) is the Henry constant of gas in ionic liquid and \(\alpha\) and \(\beta^*\) are experimentally determined constants and only dependent on the gas and temperature. Equation 2.10 gives that ionic liquids with a small molar volume have higher solubilities. It must be noted that this is on bulk basis. On a per anion-cation basis, ionic liquids consisting of the Tf\(_2\)N anion have higher solubilities. This effect is attributed to the large size of the anion, offering more interaction sites [56].
Chapter 3

Experimental

In this chapter, the experimental basis for the thesis will be presented. An important part of the thesis has been to optimise the preparation method for the thin-film composite membrane. The most important features in this respect have been the thickness of the coating layer and defects affecting the flux and selectivity of the membrane.

In addition to optimising the membrane preparation, different methods have been employed to characterise the membranes. These include permeation measurements, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier transform infra-red (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The composite membranes were used in the permeation measurements, while self-supported Pebax®-based membranes were used for the other characterisations.

3.1 Materials

Pebax® grade 2533 was delivered by Arkema in the form of pellets, and will hereby be referred to only as Pebax®. The ethanol that was used as solvent had a purity of 96% and was delivered by SOMEONE. Butanol and iso-propanol!! PTMSP was delivered by Fluorochem, and PDMS from Hydrogen, carbon dioxide, methane and nitrogen were used for the permeation tests and were all delivered by YARA.

The ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([bmim][Tf₂N]) (99 %) was delivered by IO-LI-TECH. The task-specific ionic liquids triethylene tetramine trifluoroacetate ([TETA][Tfa]) and triethylene tetramine lacate ([TETA]L) were prepared in the MEMFO group according to the procedure given by [16]. They were characterised with ¹H NMR spectroscopy and ESI-MS to confirm that the correct ionic liquids were synthesised. The characterisations were performed by Zhongde Dai and Lu Bai, respectively, both in the MEMFO
CHAPTER 3. EXPERIMENTAL

One of the support membranes used in the experimental work were made from polysulfone (PSf) on woven polypropylene (PP) with a molecular weight cut-off of 20,000. The other was a ETNA10PP composite fluoro polymer with a molecular cut-off of 10,000 delivered by Alpha Laval. The supports are hereby referred to as the PSf support and fluoro polymer support, respectively.

3.2 Membrane preparation

3.2.1 Flat-sheet composite membranes

Flat-sheet composite membranes were prepared by using different solution coating methods. Diluted Pebax® solutions were prepared by heating appropriate amounts of polymer and solvent under magnetic stirring and reflux at 80 °C for 6-8 hours or until the polymer was solved. A porous support membrane was coated with a dilute polymer solution, from which the solvent evaporated, leaving a thin layer of polymer on the support layer. After the first layer had dried, the procedure was repeated to reduce the occurrence of defects. Two coating techniques were tested:

- The support was fixed to a glass plate using aluminium tape. The support/tape edge was sealed with Araldite glue to avoid liquid entering the backside of the support, as illustrated in Figure 3.2. Then, the glass plate was immersed in the polymer solution for a certain amount of time, removed and left for evaporation.
- The support was fixed to a glass plate using aluminium tape. A cylindrical metal ring was glued to the support, forming a mould into which 5-10 mL of
the polymer solution was poured. After a short while (15 or 30 seconds), the polymer solution was poured out from the mould and left for evaporation.

**Figure 3.2:** Illustration of how the membrane support was fixed to the glass plate before dip-coating

Different factors were investigated in order to prepare membranes with the desired properties. The choice of solvent for the polymer solution was one such factor. An appropriate solvent must solve both the polymer and the ionic liquids, but not the porous support that the layer is to be deposited on. Three organic solvents (ethanol, isopropanol and butanol) were tested by adding Pebax®, the membrane supports and the ionic liquids to the solvents.

Polymer solution concentrations ranging from 4 wt% to 0.3 wt% were tested to find that resulting in the target layer thickness, which was decided to be around 300 nm. Membranes were coated according to one of the mentioned procedures, and the thickness of the membranes were found by studying the membrane cross-section with SEM.

A protective gutter layer of PDMS or PTMSP was applied to some of the membranes using two different methods. Dip-coating was performed as mentioned above with an immersion time of 5 seconds. The other method was a solution casting method, where an amount of 0.2 % PTMSP solution corresponding to a polymer layer of 1 µm was added the metal-ring mould, covered with a funnel and left for evaporation.

### 3.2.2 Preparation of self-supporting membranes

Self-supporting membranes were prepared by casting different polymer solutions on Teflon plates and leaving them for evaporation. The plates were covered with funnels to reduce the evaporation rate. The following membranes were prepared:
CHAPTER 3. EXPERIMENTAL

Pure Pebax®, Pebax® with 10, 20 and 30 wt% [TETA][Tfa], Pebax® with 30 wt% [TETA]L and Pebax® with 30 wt% [BMIM][Tf₂N].

3.3 Membrane characterisation

3.3.1 Permeance measurements

Permeance measurements of the composite membranes were carried out to check if proper coating layers were obtained. Two similar constant-volume variable-pressure rigs were tested with a feed pressure of 2 bar and with the single gases H₂, CH₄, N₂ and CO₂ in the mentioned order. The system was evacuated overnight before the first gas test was performed and at least 6 hours between each gas. The flowsheet of one of the permeation setups are presented in C. Equation 3.1 was used to calculate the permeance [33]:

\[
\frac{P}{l} = \frac{V}{ART(p_2 - p_1)} \left[ \left( \frac{dp}{dt} \right)_{ss} - \left( \frac{dp}{dt} \right)_{leak} \right]
\]  

(3.1)

where \(V\) is the downstream volume, \(L\) is the membrane thickness, \(A\) is the membrane area, \(R\) is the gas constant, \(T\) is the absolute temperature, respectively), and \(\frac{dp}{dt}_{ss}\) and \(\frac{dp}{dt}_{leak}\) are the steady-state rates of pressure rise in the downstream volume at a fixed upstream pressure and under vacuum, respectively.

3.3.2 Scanning electron microscopy (SEM)

The thickness and surface of the composite membranes were studied using a Hitachi S3400 scanning electron microscope, located at the Department of Materials Science and Engineering at NTNU. Samples of the cross-section were necessary to study the thickness of the membrane, and were prepared by freeze-fracturing in liquid nitrogen. The surface samples did not require any special treatment. The samples were mounted in a sample holder and coated with a thin gold layer in order to make the samples electronically conductive.

A schematic of a scanning electron microscope is shown in Figure 3.3.

3.3.3 Thermogravimetric analysis (TGA)

The thermal stability of the different dense membranes and the ionic liquids were investigated with a Q500 thermogravimetric analyser delivered by TA instruments, as shown in Figure 3.4. The principle of thermogravimetry is to measure changes in the sample weight as a function of temperature under controlled conditions [61].
3.3. MEMBRANE CHARACTERISATION

Figure 3.3: Schematic drawing of a scanning electron microscope. [60]

Samples of 5-10 mg were placed in aluminium pans and heated 10°C/min from room temperature to 550°C. Nitrogen was used as the balance and sample gas, with flow rates of 10 and 90 mL/min, respectively.

The thermal stability is reported as the onset temperature of thermal decomposition, which is the intersection of the slopes before and after decomposition starts [62].

Figure 3.4: Q500 thermogravimetric analyser delivered by TA Instruments [63]
3.3.4 Differential scanning calorimetry (DSC)

Investigations of the thermal properties of the self-supporting membranes was done using a Q100 differential scanning calorimeter delivered by TA Instruments. The principle behind DSC is to measure the heat flow when heating or cooling the sample. A sample pan containing the sample and an empty reference pan are placed in the instrument, with thermocouples attached to both pans. The difference in heat flow between the sample pan and the reference pan is measured as the temperature of the samples is changed. The thermal properties of the sample can thus be determined because the properties of the reference pan are known.

Samples of 5-10 mg were run in two cycles, with -90°C as the minimum temperature and the maximum temperature being well below the decomposition temperature, as determined from the TGA. Nitrogen was used as the purge gas with a flow rate of 50 mL/min.

3.3.5 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy is frequently used for identification and quantification of bond structures in organic compounds [64]. It is based on the principle that particular bonded atoms have a characteristic vibrational frequency. When infrared radiation is sent through the sample, some radiation is transmitted and some is absorbed. The resulting spectrum consists of peaks at different wavenumbers that can be ascribed to the different bonds in the molecule. The peaks can thus be used to identify bonds in the tested compound, but the size of the peak can also give an indication of the amount. The basic components of an infrared spectrometer are shown in Figure 3.5.

![Figure 3.5: Components in an infrared spectrometer](image)

The spectroscopy experiments were carried out with a SOMETHING spectrometer at the Department of Chemistry at NTNU. The experiments were carried out on the ionic liquid [TETA][Tfa], a pure Pebax membrane and Pebax membranes containing 10, 20 and 30% [TETA][Tfa] in order to identify any differences in composition. First, the background spectrum was measured. Then, the sample was placed in the instrument and a spectrum of the sample was recorded. Since this spectrum also contains the background signals, the background spectrum was used to remove the background signals from the sample spectrum.
Chapter 4

Results and discussion

This chapter consists of two parts. The first part (section 4.1) focuses on how the different preparation parameters affected the resulting thin-film composite membrane. In the second part (section 4.2.1-4.2.3), the results from the characterisation experiments with the self-supporting Pebax®/IL blend membranes are presented.

4.1 Preparation of thin-film composite membranes

The preparation of the thin-film composite membranes has been an optimisation process and has thus been an major part of the project. Many parameters have been investigated in order to find the most suitable parameters for preparing usable composite membranes. These parameters include the choice of solvent, solution concentration, coating method, application of gutter layer and choice of gutter layer material. The resulting membranes have been tested, and permeation data is presented where reasonable results were obtained.

4.1.1 Selection of solvent

Three solvent candidates were investigated based on what has been done in the literature [66]. These solvents were ethanol, iso-propanol and butanol. Pebax® (4 wt%) was added to the solvents, and after an appropriate time of heating at 80 °C, the polymer was dissolved in all the solvents. The immersion of the polymer supports (PSf and fluoro polymer) did not result in solvation of the support for any of the solvents, while all the ionic liquids [TETA][Tfa], [TETA] L and [bmim][Tf2N] were dissolved. These results indicate that all three solvents are suitable candidates for the preparation of composite membranes.
However, the viscosity of the polymer solutions were different, as the ethanol-based solution had a much lower viscosity than the two others. According to equation 2.9, the coating layer thickness increases with increasing viscosity. Therefore, in order to achieve a very thin coating layer, also with more diluted solutions, ethanol was chosen as the solvent to make the Pebax\textsuperscript{R} solutions. Ethanol also have other benefits, such as being cheaper and less harmful to the environment.

### 4.1.2 Effect of Pebax\textsuperscript{R} concentration

Several concentrations were tested in order to obtain the desired coating thickness ($\sim$300 nm), ranging from 4 wt\% solutions to 0.3 wt\%. It was observed that the viscosity of the polymer solution decreased as the Pebax\textsuperscript{R} was lowered. SEM images of the cross-section of the composite membrane were taken to check the thickness of the coating layer resulting from the the various polymer concentrations. Some of these images are shown in Figure 4.2. Figure 4.1 shows the trend in coating layer thickness as a function of the Pebax\textsuperscript{R} concentration.

![Figure 4.1: Variation in coating layer thickness as a function of Pebax\textsuperscript{R} concentration](image)

The coating layer thickness decreased with decreasing polymer concentration, from 16 $\mu$m for the highest concentration to 320 nm for the 0.3 wt \% solution. Thus, the target thickness was obtained by dip-coating the support twice with a 0.3 wt\% Pebax solution.
Figure 4.2: Cross-section SEM pictures showing the effect of Pebax® concentration on the coating layer thickness.
4.1.3 Choice of membrane support

PSf and the fluoro membrane were used as supports for the composite membrane. Initially, the PSf support was used as delivered for membrane preparation, but very low permeance values resulted from this. This was believed to be due to pore blocking of a substance that is often applied on microfiltration membranes, so it was decided to wash the membrane thoroughly to remove this substance before applying the polymer layer. This was done by first leaving the membrane sheet in a tub with flowing warm water (approx. 50°C) for 1.5–2 hours, followed by 30 minutes in another tub under cold, flowing deionised water.

Washing the support did not lead to improved results. To investigate this issue further, SEM images were taken of the surface of an uncoated and a coated PSf support. The images are shown in Figure 4.3.

![SEM images showing the surface of the uncoated PSf support.](a) ![SEM images showing the surface of the coated PSf support.](b)

Figure 4.3: SEM images showing the surface of the uncoated PSf support.

The SEM images show that the surface of the PSf support membrane is covered with defects, which would greatly affect the membrane performance. As mentioned in section 2.2.3, the porous support must be free of macrovoids and have an open structure in order for the composite membrane to perform well. The presence of this many defects would reduce the selectivity of the coating layer drastically, or make pore penetration more likely to occur, which reduces the permeability. Therefore, it was decided to prepare membranes with the fluoro polymer support instead. The surface of this support is shown in Figure 4.4.

It can be seen that the surface has much fewer defects than the PSf support. For this reason, and since there was no other support available, it was decided to use the fluoro polymer in the succeeding experiments. However, since there are still some defects, measures are required in order to prevent the reduced membrane performance. As mentioned in section 2.2.3.1, a gutter layer can reduce the impact of defects. This will be further discussed in section 4.1.5, but first, the coating method will be discussed.
4.1. PREPARATION OF THIN-FILM COMPOSITE MEMBRANES

4.1.4 Choice of coating method

As mentioned in section 3.2.1, two methods were investigated for coating of the Pebax® layer. Both methods had its advantages and disadvantages. The dip-coating method is very simple but quite time-consuming, as the glue takes about three hours to dry before the coating can be performed. On the other hand, the method allows easy control of the layer thickness. The other method, where the polymer solution was poured into a metal ring mould and poured out after a certain amount of time, was less time consuming since no glue was used. However, in some cases it was difficult to make the double-sided adhesive tape stick to the metal ring, resulting in leakage of the polymer solution. It is also more difficult to control the thickness with this method.

Another problem that was experienced with the second coating method was penetration of Pebax solution into the pores of the support membrane. This was also observed for dip-coating when the immersion time was long, such as 15 seconds, but was reduced for immersion times of 5 seconds. Figure 4.5a shows the cross-section of a dipcoated membrane with 5 seconds immersion time. It can be seen that there is distinct layer on top of the support, so the polymer has not entered the support pores. This is, however, not the case when the latter method was used, as shown in Figure 4.5b, where polymer has entered the pores.

This increasing extent of pore penetration with the second method is probably due to both capillary forces and gravitational forces acting in the same direction. Since the resistance to mass transfer is much higher in dense media than in porous media, pore penetration of the selective polymer is undesirable as it will reduce the permeability significantly.

Despite being rather time-consuming, the dipcoating method resulted in the best
coating with less pore penetration, so it was decided to use this method for the further experiments.

4.1.5 Gutter layer

Application of a highly permeable polymer layer before applying the selective polymer coating could plug the pores without leading to significant reduction in performance. This layer must be thin, but no so thin that it yields at normal operation pressures. Two highly permeable polymers (PTMSP and PDMS) and two methods were investigated for this purpose.

The first method for applying the gutter layer was by dipcoating the membrane support in a PTMSP/PDMS solution for 5 seconds. After this, the Pebax® layer was applied with the same method. The following polymer solutions were used for application of the gutter layer: 1, 0.5 and 0.2 wt% PTMSP in toluene and 2 wt% PDMS in hexane.

None of the resulting membranes exhibited useful permeation values. In some cases the first or the two first gas runs gave quite reasonable numbers, but after this too high flux occurred, meaning that the membrane was broken. This was probably due to rupture of the gutter layer caused by a too thin layer, defects or an uneven layer. In most of the tests, the membrane permeance was extremely low, which may be caused by the polymer going too deep into the porous substructure of the support. Also, an uneven gutter layer may have allowed Pebax® to enter some of the defects and cause a very low permeation.

In order to get an indication of the reason for the bad results, membrane samples where only the gutter layer was applied were studied with scanning electron microscopy. Some of these images are displayed in Figure 4.6. On some of the images the coating layers appear to be quite smooth (4.6a, 4.6c and 4.6e), while on others
the layer is barely visible (4.6b and 4.6d). The thickness of the 0.5 % coating layer was in the range of 300 nm, which should be acceptable.

When it comes to the choice of polymer there were two arguments for choosing PTMSP over PDMS. The main reason is that it is much more permeable than PDMS and will thus exert less resistance to mass transfer. However, as the PDMS solution had to be disposed of after being in contact with the glue used to seal the
membrane to the glass plate, this would require a large amount of solution. This is not the case for the PTMSP, so reducing the waste is also a benefit in addition to the higher permeability.

In order to improve the smoothness of the gutter layer and enhance pore penetration, an additional coating method was tested. The cylindrical metal ring that was mentioned in the section about coating methods was again used to form a mould for solution casting. An amount of solution corresponding to a layer thickness of 1 µm was poured into the mould and the solution was left for evaporation overnight. The permeation properties of the gutter layer membrane were tested with hydrogen and nitrogen. The gas permeances were found to be 9756 and 4049 gpu, respectively, giving a $\text{H}_2/\text{N}_2$ selectivity of 2.40, which is in accordance the selectivity of 2.39 reported in the literature [41].

The above result may imply that an improved coating was achieved with this method. Therefore, the next step was to apply the selective layer by dipcoating and hopefully achieve a $\text{CO}_2$ selectivity corresponding to reported values for pure Pebax®. This will be discussed in the following section.

### 4.1.6 Permeation properties

As mentioned in the previous section, the promising permeance results of the PTMSP gutter layer implied that a proper coating technique of the gutter layer was achieved. Therefore, membranes were coated twice with a 0.2 % Pebax® solution, which according to the previous mentioned results would lead to a thickness of the selective coating layer of around 300 nm. As reported by Bernardo, Pebax®2533 exhibits a $\text{CO}_2/\text{N}_2$ ideal selectivity of 28.23, a $\text{CO}_2/\text{CH}_4$ selectivity of 8.29 and a $\text{CO}_2/\text{H}_2$ selectivity of 5.47 [31].

The permeation properties of the tested membrane samples are shown in Figure 4.1. Only the first sample exhibited selectivities in accordance with the literature values, but had very low permeance values. This is probably caused by a thicker Pebax® layer than was expected from using the mentioned dip-coating procedure. The other sample taken from a different part of the same membrane (sample 2) exhibited completely different properties, which was also the case for the two samples from another membrane prepared under the same conditions (sample 3 and 4). The reason for this deviating behaviour is most probably the presence of defects, either in the support or in the coating layers.

These results only emphasise the importance of a defect-free membrane. Although the fluoro support had significantly fewer defects than the PSf support, there are in most cases defects present that have crucial effects on the performance. Measures for eliminating the defects may work if the defects are small and few enough, but relying on this is not recommended in further work because of the high uncertainties involved.
4.2 CHARACTERISATION OF PEBAX®/IONIC LIQUID BLEND MEMBRANES

Table 4.1: Permeation properties of Pebax®-coated composite membranes with a PTMSP gutter layer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas</th>
<th>$P$(gpu)</th>
<th>$P_{CO2}/P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂</td>
<td>11.33</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>1.74</td>
<td>7.83</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>0.42</td>
<td>32.27</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>13.59</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>H₂</td>
<td>30.44</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>10.37</td>
<td>4.20</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>40.28</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>43.53</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>H₂</td>
<td>96.56</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>50.87</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>35.68</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>55.82</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>H₂</td>
<td>8.56</td>
<td>17.01</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>39.85</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>137.88</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>145.52</td>
<td>-</td>
</tr>
</tbody>
</table>

Although the work presented in this thesis did not lead to successful preparation of thin-film composite membranes, the preparation method has shown to be successful. In a similar project Zhongde Dai obtained reasonable permeation results when he used a polyacrylonitrile (PAN) support and dip-coating for application of both the gutter layer and the selective layer [67]. This may indicate that the main issue with the preparation of thin-film composite membranes has not been the method itself, but rather the porous support on to which the coatings were applied. However, since defects may also arise during coating of the polymer layers, further efforts with the coating procedure are necessary.

4.2 Characterisation of Pebax®/ionic liquid blend membranes

4.2.1 Thermogravimetric analysis (TGA)

This section contains the results from the thermogravimetric analyses of the different self-supporting membranes, but first data for the pure materials constituting the blend membranes will be provided. Figure 4.7 shows the TGA thermogram of pure Pebax and the three ionic liquids [TETA] L, [TETA][Tfa] and [bmim][Tf₂N].

As can be seen from the figure, [bmim][Tf₂N] has the highest thermal stability among the ionic liquids with an onset temperature of decomposition of approx.
400 °C. The task-specific ionic liquids have significantly lower thermal stability, and both start decomposing around 160 °C. The decomposition of [TETA][Tfa] occurs over a shorter temperature range than [TETA] L, which can be seen from the steeper curve of [TETA][Tfa]. The onset temperature of decomposition of Pebax® is around 340 °C.

These results indicate that the thermal stability of the Pebax®2533/IL blend membranes may be improved when [bmim][Tf$_2$N] is used as the ionic liquid, but that thermal stability of the blend membranes containing the task-specific ionic liquids [TETA][Tfa] and [TETA]L will be poorer.

4.2.1.1 Pebax®2533 and [TETA][Tfa]

Figure 4.8 shows the TGA thermograms of the pure Pebax membrane, pure [TETA][Tfa] and the blend membrane containing 30 wt% [TETA][Tfa]. As expected, the properties of the blend membrane lie somewhere between its constituents, and the curve shows two decomposition temperature ranges. The thermogram shows that approx. 30% of the sample weight is lost before the onset of Pebax® decomposition, which corresponds well with the amount of IL added to the Pebax® solution during preparation and indicates a homogeneous blend.
4.2. CHARACTERISATION OF PEBAX®/IONIC LIQUID BLEND MEMBRANES

4.2.1.2 Pebax®2533 and [TETA] L

The thermograms for pure Pebax®, pure [TETA] L and the blend membrane containing 30 wt% [TETA] L are shown in Figure 4.9. The curve shape of the blend membrane resembles that of the Pebax®/[TETA][Tfa] blend membrane, but the second decomposition starts at a higher Pebax® content of around 75 wt%. This indicates that the blend membrane contains a little less than 30 wt% [TETA] L, which may indicate that the blend is not homogeneous. Another possibility may be that the membrane actually contains less due to inaccuracies in the preparation.
4.2.1.3 Pebax\textsuperscript{®} 2533 and [bmim][Tf\textsubscript{2}N]

The thermograms from the thermogravimetric analyses of pure Pebax\textsuperscript{®} 2533, pure [bmim][Tf\textsubscript{2}N] and the blend membrane consisting of 30 wt\% IL are shown in Figure 4.10. The curve of the blend membrane exhibits two decompositions that can be attributed to each of the constituents of the blend. However, it appears that the IL content of the blend membrane is substantially lower than the 30 \% that were added to the Pebax\textsuperscript{®} solution. This is similar to the Pebax\textsuperscript{®}/[TETA] L blend membrane, where non-homogeneity of the blend was suggested to be the reason.

In contrast to the two aforementioned blend membranes, the thermal stability of the Pebax\textsuperscript{®}/[bmim][Tf\textsubscript{2}N] blend membrane is actually lower than is constituents. As previously mentioned, it was expected that the addition of [bmim][Tf\textsubscript{2}N] would increase the thermal stability of Pebax\textsuperscript{®}, but this does not seem to be the case. One reason for this behaviour may be that the presence of [bmim][Tf\textsubscript{2}N] causes structural changes in the Pebax\textsuperscript{®} structure, resulting in poorer thermal properties. Variations may also occur when different sample sizes are used in the TGA. If this was the case, a repeated experiment with a higher sample weight could yield other results.
4.2 CHARACTERISATION OF PEBAX®/IONIC LIQUID BLEND MEMBRANES

4.2.2 Differential scanning calorimetry (DSC)

The results from the DSC experiments are divided on basis of the three ionic liquids. Each part includes data on Pebax®, the pure ionic liquid and Pebax®/IL blend membranes. Note that although the minimum temperature of the DSC was set to -90 °C, it was not possible to reach this temperature for many of the experiments.

4.2.2.1 Pebax® and [TETA][Tfa]

Figure 4.11 shows the DSC curves for the two heating runs and the intermediate cooling run of pure Pebax®, pure [TETA][Tfa] and the blend membranes consisting of 10, 20 and 30 wt% [TETA][Tfa]. Two melting points can be observed for the Pebax®-containing samples when considering the second heating. The melting point around 15 °C can be ascribed to melting of the crystalline portions of the PTMO block, although being slightly higher than earlier reported values [29, 68, 69, 31]. It can also be seen that the melting point increases slightly with IL content.

The second melting point can be ascribed to the crystalline polyamide block in Pebax®, and is located at 140 °C for pure Pebax®. For the blend membranes this melting point is located somewhat lower, around 130 °C. These values are also a little higher than reported literature values.

There are some differences between the first and second heating traces. A rather wide trough can be observed on the heating trace of the membrane containing 30 % IL, but it has disappeared on the second heating trace. A possible explanation for this is the presence of a kinetically less stable crystal phase that recrystallises.
to a more stable phase between the heating cycles [31]. This is also a possible explanation for the disappearance of the melting point of Pebax® at approx. 65°C between the two heatings.

Glass transitions are second-order transitions that are characterised by a shift in the baseline [4]. The glass transition temperature of [TETA][Tfa] is observed to be just below -50°C. For Pebax® the glass transition temperature has been reported in the literature as -77°C [29]. It cannot be observed from the heating traces, but a small break in the curve is observable in the cooling trace just above -60°C. At first glance it may appear to belong to the IL glass transition, but since the break of the curve can also be seen on the pure Pebax® curve, it can probably be attributed to the glass transition of Pebax®.

A slight reduction of the melting point peak of the PE block can be observed when the ionic liquid content is increased. This is reasonable due to the lower amount of Pebax® in the blend.

![DSC thermograms of pure Pebax®, pure [TETA][Tfa] and Pebax®/[TETA][Tfa] blend membranes. The curves are shifted vertically for clarity.](image)

**Figure 4.11:** DSC thermograms of pure Pebax®, pure [TETA][Tfa] and Pebax®/[TETA][Tfa] blend membranes. The curves are shifted vertically for clarity.
4.2. CHARACTERISATION OF PEBAX®/IONIC LIQUID BLEND MEMBRANES

4.2.2.2 Pebax®2533 and [TETA] L

The DSC thermograms for the pure Pebax®, pure [TETA] L and the blend membrane containing 30% [TETA] L are shown in Figure 4.12. Similar to the previous discussion, a small increase in the melting point of the PE block of Pebax® can be observed with the addition of [TETA] L. Also, the additional melting point of the blend membrane located around 40 °C disappears before the second heating, which was ascribed to recrystallisation of a less stable crystal phase.

The melting point of the PA blocks in Pebax® cannot be seen in this figure. This is because the maximum temperature of the blend membrane test was chosen to be quite low based on the TGA results, which showed a 10% decomposition already at 100 °C.

The glass transition temperature of [TETA] L is just below -50°C, similar to [TETA][Tfa].

![DSC thermograms](image)

**Figure 4.12:** DSC thermograms of pure Pebax®, pure [TETA] L and Pebax®/[TETA] L blend membranes. The curves are shifted vertically for clarity.
4.2.2.3 Pebax®2533 and [bmim][Tf$_2$N]

DSC thermograms for the first and second heating run and the intermediate cooling run are shown in Figure 4.13. It shows similar results as for the two other ILs; a melting point disappearing between the two heatings, and a smaller size of the trough when 30 wt% IL is added.

The glass transition of [bmim][Tf$_2$N] cannot be observed, which may imply a glass transition temperature outside the DSC temperature range. This is supported by a reported glass transition temperature of -78°C [70].

![DSC thermograms](image)

**Figure 4.13:** DSC thermograms of pure Pebax®, pure [bmim][Tf$_2$N] and a blend membrane containing 30 wt% [bmim][Tf$_2$N]. The curves are shifted vertically for clarity.

4.2.3 Fourier transform infrared spectroscopy

FTIR spectroscopy was performed on the pure Pebax® membrane, three blend membranes containing 10, 20 and 30 % [TETA][Tfa] and pure [TETA][Tfa]. The
4.2. CHARACTERISATION OF PEBAX®/IONIC LIQUID BLEND MEMBRANES

characterisation resulted in the spectra shown in Figure 4.14. In the analysis, the spectra have been compared to the reported spectrum of pure Pebax®[71, 72] and the spectra of the individual compounds triethylene tetramine (TETA) [73] and trifluoroacetic acid [74].

![FTIR spectra of pure Pebax®, pure [TETA][Tfa] and blend membranes containing 10, 20 and 30% [TETA] L. The curves are shifted vertically for clarity](image)

**Figure 4.14:** FTIR spectra of pure Pebax®, pure [TETA][Tfa] and blend membranes containing 10, 20 and 30% [TETA] L. The curves are shifted vertically for clarity.

As can be seen from the figure, the presence and height of some of the peaks vary among the different samples, while others are similar. The rather small peak at around 3300 cm$^{-1}$ is rather similar for all samples and probably corresponds to N–H stretching, associated with the polyamide block of the polymer and the amine groups in ionic liquid. Further, there are two peaks around 2950-2850 cm$^{-1}$, which is within the characteristic absorption range of alkyl C–H stretch. The peaks are highest for pure Pebax® and lowest for pure [TETA][Tfa], which is reasonable due to the many C–H bonds in the polymer.

Moving to lower wavenumbers, a significant peak appears for [TETA][Tfa] at around 1670 cm$^{-1}$, which can be assigned to the carbonyl group of [TETA][Tfa]. The size of this peak is smaller for the blend membranes. The peak size of the 20 % blend membrane is, however, larger than the 30 % blend membrane, which may be caused by a nonhomogeneous blend. This is evident for most of the other peaks, too. There are also some smaller peaks present in this area for Pebax®, which can be assigned to the carbonyl groups in the polymer. For instance, the peak at around 1740 cm$^{-1}$ corresponds to stretching of the PA-CO-O-PE carbonyl group [71].
The peak of Pebax® at around 1640 cm$^{-1}$ indicates the presence of the H-N-C=O group [71, 72]. This is supported by the decreasing peak height with increasing amount of IL, and that the peak does not appear on the pure IL spectrum.

A double peak of [TETA][Tfa] appears in the range 1100-1200 cm$^{-1}$. The peak at 1200 cm$^{-1}$ is related to [TETA][Tfa], and may be attributed to the characteristic absorption range of the C–F bond, which is 1000-1400 cm$^{-1}$. The peak at 1100 cm$^{-1}$ is quite strong for all the samples, and should therefore correspond to a bond that is present in both compounds. In the literature, however, this peak has been assigned to C–O stretching of the polyether blocks [71, 72]. The stretching of the alkoxy C–O bond is also in the range 1050-1150 cm$^{-1}$, and may explain the presence of the peak for [TETA][Tfa].
Chapter 5

Conclusion and recommendations for further work

5.1 Conclusion

The method for preparation of thin-film Pebax®/ionic liquid blend composite membranes has been optimised in terms of the solvent and polymer concentration of the coating solution, choice of porous support, coating method and presence of gutter layer. Ethanol was found to be the preferred solvent because it solved both the Pebax® and the ionic liquids, in addition to being the least viscous and more environmentally friendly among the investigated solvents.

A coating layer thickness of approx. 300 nm was achieved by dip-coating the porous support twice in a 0.2 wt% Pebax® solution with an immersion time of 5 seconds. A selective layer of the highly permeable polymer poly(1-trimethylsilyl-1-propyne) (PTMSP) was applied between the support and the selective layer to reduce the influence of defects in the porous support.

No usable permeation results have been obtained. This is mainly believed to be caused by the presence of defects in the porous support, which would greatly affect the selectivity and permeability of the membrane, but it may also be caused by defects in the coating layers. Therefore, it has not been possible to assess the possible enhanced separation performance of the Pebax®/ionic liquid blend membranes compared to pure Pebax® membranes. Since better results have been obtained in a similar project using a different support, it is believed that changing the support could resolve this issue.

Self-supported membranes consisting of Pebax® and the ionic liquid [bmim][Tf$_2$N]
and the task-specific ionic liquids [TETA] L and [TETA][Tfa] have been prepared and characterised. Thermogravimetric analyses have been carried out to assess the thermal decomposition of the self-supported membranes and ionic liquids. It was found that [bmim][Tf$_2$N] had the highest thermal stability with an onset of thermal decomposition at 400°C, while the onset of decomposition of both [TETA][Tfa] and [TETA] L is approximately 160°C. The homogeneity of the Pebax®/IL blend seems to be best when [TETA][Tfa] is used.

The results from the differential scanning calorimetry experiments show that the size of the peaks corresponding to the different transitions vary with the amount of the constituents of the membrane. The glass transition temperature of both [TETA] L and [TETA][Tfa] were found to be approximately –50°C, while the glass transition of [bmim][Tf$_2$N] could not be observed in the given temperature range.

FTIR spectroscopy was carried out on the Pebax®/[TETA][Tfa] blend membranes, and the resulting spectra show behaviours that are in accordance with previously reported data.

### 5.2 Recommendations for further work

This work has revealed several aspects that could be considered in the further work. The preparation parameters may be further optimised in terms of defects and coating layer thickness. Different supports with fewer defects could be investigated, as well as factors affecting the occurrence of defects in the coating layers. The aim should be to reduce the layer thickness in order to further reduce the resistance to mass transfer and enhance the gas permeation.

When a proper coating method is developed the membrane performance should be tested in a mixed gas permeation set-up in order to assess the separation of CO$_2$ from other gases. The effect of the variation of process conditions such as pressure and temperature should be investigated, especially typical post-combustion conditions.

It would also be interesting to increase the IL content of the blend, as well as trying other Pebax® grades, for instance Pebax® 1657. Further, the blend membranes may be prepared with other liquids.
Bibliography


matrix composite membrane containing zif-7 nano-fillers,” Journal of Mem-

[33] B. Yu, H. Cong, Z. Li, J. Tang, and X. S. Zhao, “Pebax-1657 nanocom-
posite membranes incorporated with nanoparticles/colloids/carbon nanotubes
for CO₂/N₂ and CO₂/H₂ separation,” Journal of Applied Polymer Science,
vol. 130, no. 4, pp. 2867–2876, 2013.

[34] A. Car, C. Stropnik, W. Yave, and K.-V. Peinemann, “Pebax/polyethylene
glycol blend thin film composite membranes for CO₂ separation: performance
with mixed gases,” Separation and Purification Technology, vol. 62, no. 1,

dioxide capture and storage, ch. Capture of CO₂, pp. 105 – 178. UK: Cambridge

last accessed 13 May 2014.

[37] A. L. Kohl and R. Nielsen, Gas Purification. Houston: Gulf Publishing Com-

[38] J. F. Brennecke and B. E. Gurkan, “Ionic liquids for co2 capture and emission
3464, 2010.

third ed., 2012.

[40] J. P. Sheth, J. Xu, and G. L. Wilkes, “Solid state structure–property be-
havior of semicrystalline poly(ether-block-amide) pebax\textregistered thermo-

[41] K. Nagai, T. Masuda, T. Nakagawa, B. D. Freeman, and I. Pinnau, “Poly[1-
(trimethylsilyl)-1-propyne] and related polymers: synthesis, properties and

[42] L. Shao, J. Samseth, and M.-B. Hägg, “Crosslinking and stabilization of nan-
oparticle filled pmp nanocomposite membranes for gas separations,” Journal

[43] A. K. Pabby, S. S. Rizvi, and A. M. Sastre, eds., Handbook of membrane sep-
arations: Chemical, Pharmaceutical, Food, and Biotechnological applications.


[67] Z. Dai, K. N. Hval, and L. Deng, “Pebax®/tsil blend composite membrane for CO₂ separation,” in *MEMFO 20 years’ celebration seminar*, (Trondheim, Norway), Norwegian University of Science and Technology, May 2014.


Appendices
# Appendix A

## Risk assessment

<table>
<thead>
<tr>
<th>ID no.</th>
<th>Activity/process</th>
<th>Responsible person</th>
<th>Laws, regulations etc.</th>
<th>Existing documentation</th>
<th>Existing safety measures</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Membrane preparation, ethanol</td>
<td>Karoline</td>
<td></td>
<td>MSDS datasheets</td>
<td>Lab coat, goggles, gloves, emergency</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Polyacrylamide in ethanol solution</td>
<td>Karoline</td>
<td></td>
<td>MSDS datasheets</td>
<td>Lab coat, goggles, gloves, emergency</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Working with medium pressure rig</td>
<td>Karoline</td>
<td>operation manual</td>
<td></td>
<td>Safety valve, goggles</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Working with CH4 and H2, max. 5 bar (small leakage)</td>
<td>Karoline</td>
<td>MSDS datasheets</td>
<td>Safety valve, goggles</td>
<td>gas detector</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Big leakage of CH4 or H2</td>
<td>Karoline</td>
<td>MSDS datasheets</td>
<td>Safety valve, goggles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Working with ionic liquids</td>
<td>Karoline</td>
<td>Lab coat, gloves, emergency</td>
<td>MSDS datasheets</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Working with organic solvents</td>
<td>Karoline</td>
<td>Lab coat, gloves, emergency</td>
<td>MSDS datasheets</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Risk Assessment

**Unit:** Kjemisk prosessteknologi  
**Line manager:** Edv Bakkum  
**Date:** 15.01.2014  
**Participants in the identification process (including their function):** Karoline Nǿvik Hval (student) Zhuoqie Dai (PhD student) Gerd Flatberg (Engineer)  

### Signatures:

<table>
<thead>
<tr>
<th>ID no.</th>
<th>Activity from the identification process form</th>
<th>Potential undesirable incident/strain</th>
<th>Likelihood</th>
<th>Consequence</th>
<th>Risk value</th>
<th>Comment/status</th>
<th>Suggested measures</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Membrane preparation, ethanol</td>
<td>Spill</td>
<td>4</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>Polyimide polymer in ethanol solution</td>
<td>Spill</td>
<td>4</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>4A</td>
</tr>
<tr>
<td>3</td>
<td>Working with medium pressure gas</td>
<td>Rapid pressure release</td>
<td>1</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>4</td>
<td>Working with CH₄ and H₂, max 5 bar (small leakage)</td>
<td>Leakage</td>
<td>3</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>5</td>
<td>Big leakage of CH₄ or H₂</td>
<td></td>
<td>1</td>
<td>D</td>
<td>A</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>6</td>
<td>Working with ionic liquids</td>
<td>Spill</td>
<td>4</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>4A</td>
</tr>
<tr>
<td>7</td>
<td>Working with organic solvents</td>
<td>Spill</td>
<td>4</td>
<td>B</td>
<td>B</td>
<td>A</td>
<td>B</td>
</tr>
</tbody>
</table>
Appendix B

$^1$H NMR and ESI-MS for confirmation of TSIL structures

![Figure B.1: $^1$H NMR spectrum of [TETA] L](image)
APPENDIX B. $^1$H NMR AND ESI-MS FOR CONFIRMATION OF TSIL STRUCTURES

Figure B.2: $^1$H NMR spectrum of [TETA][Tfa]

Figure B.3: ESI mass spectrum of [TETA] L

Figure B.4: ESI mass spectrum of [TETA][Tfa]
Appendix C

Flowsheet of single-gas permeation setup

Figure C.1: Flowsheet of the single-gas permeation setup based on the constant volume-variable pressure principle.