FORMIC ACID CROSSLINKED CELLULOSE ACETATE DEFECT-FREE ASYMMETRIC MEMBRANE FOR GAS SEPARATION

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To my beloved parents, Mohamed bin Yat and Wan Fatimah binti Wan Ismail,
and my lovely sister, Fatin binti Mohamed
Thank you for your eternal love and never ending support.

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ABSTRACT

Cellulose acetate (CA) polymeric membrane has been used as gas separator; however, the modest selectivity and trade-off between permeability and selectivity have reduced the utilization of this polymer. Thus, the objectives of this study were to investigate the effect of polymer concentration and formic acid (FA) crosslinking agent loading on the formation of the membrane morphology and gas separation performance. The CA in tetrahydrofuran (THF) flat sheet asymmetric membrane was fabricated by dry/wet phase inversion process with two conditions of dope solution formulation: (1) varying the polymer concentration ranging from 13 to 16 wt.% and (2) manipulating FA:THF ratio between 0:100 to 10:90. The prepared membrane was analyzed by using viscometer, field emission scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis, and tensile testing machine. The membrane gas permeation performance was tested using pure gases of hydrogen (H_2), oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2) and methane (CH_4) by using soap bubble flow meter. The CA membrane produced possessed three layers consist of top skin layer, transition layer and porous support structure. The increase in polymer concentration had produced denser membrane with thicker skin layer and substructure, thus, significantly improved the selectivity. The optimum CA concentration obtained in this study was 15 wt.% that exhibited the highest selectivity for all gas pairs. Upon addition of FA, the membrane skin layer formation had further improved without severely sacrificed the gas permeability since the FA promotes the formation of more porous substructure. This was probably due to the crosslinking of the –OH group between CA and FA as confirmed by the FTIR. Moreover, all the gas pairs selectivities improved significantly as the FA loadings were increased. The highest selectivities obtained for H_2/N_2, O_2/N_2 and CO_2/CH_4 separation were 55.87, 6.83 and 48.64, respectively.

ABSTRAK

Membran polimer selulosa asetat (CA) telah banyak digunakan sebagai medium gas pemisah; namun, kememilihan yang sederhana dan keseimbangan pemisah antara kebolehtelapan dan kememilihan telah mengurangkan penggunaan polimer ini. Oleh itu, objektif kajian ini adalah untuk menyelidik kesan kepekatan polimer dan beban ejen rangkai silang asid formik (FA) terhadap morfologi membran dan prestasi pemisahan gas. Membran asimetrik CA dalam pelarut tetrahidrofuran (THF) telah dihasilkan melalui proses songsangan fasa kering/basah pada dua keadaan formulasi larutan dop iaitu: (1) kepekatan polimer dengan julat daripada 13 hingga 16% berat dan (2) memanipulasi nisbah FA:THF antara 0:100 kepada 10:90. Membran yang dihasilkan telah dianalisis dengan menggunakan meter likat, mikroskop imbasan elektron pancaran medan, spektroskopi inframerah transformasi Fourier (FTIR), analisis termogravimetri, dan mesin ujian ketegangan. Prestasi penyerapan gas bagi membran telah diuji dengan gas-gas asli hidrogen (H_2), oksigen (O_2), nitrogen (N_2), karbon dioksida (CO_2) dan metana (CH_4) dengan menggunakan meter aliran buih sabun. Membran CA yang terhasil mempunyai tiga lapisan iaitu lapisan kememilihan atas, lapisan peralihan dan struktur sokongan berliang. Peningkatan kepekatan polimer telah menghasilkan membran yang mempunyai lapisan kemilihan yang tebal serta substruktur yang lebih padat, jadi, kememilihan juga bertambah baik. Kepekatan optimum yang diperoleh dalam ujian ini adalah 15% berat yang memberikan kememilihan tertinggi bagi semua pasangan gas. Apabila FA bertambah, pembentukan lapisan kememilihan membran bertambah baik tanpa mengurangkan kebolehtelapan gas dengan ketara. Ini kerana kehadiran FA telah menggalakkan pembentukan substruktur yang lebih berliang. Ini berkemungkinan disebabkan oleh rangkaian silang pada kumpulan –OH antara CA dan FA seperti yang disahkan oleh FTIR. Tambahan pula, kememilihan untuk semua pasangan gas telah bertambah dengan nyata apabila kandungan FA meningkat. Kememilihan pasangan gas tertinggi yang diperoleh untuk H_2/N_2, O_2/N_2, dan CO_2/CH_4 adalah masing-masing 55.87, 6.83 dan 48.64.

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LIST OF ABBREVIATIONS AND SYMBOLS

CA	-	Cellulose acetate
CAGR	-	Compound annual growth rate
CH_4	-	Methane
CO_2	-	Carbon dioxide
FA	-	Formic acid
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared spectroscopy
GPU	-	Gas permeation unit
H_2	-	Hydrogen
H_2S	-	Hydrogen sulfide
He	-	Helium
L–L	-	Liquid-liquid
N2	-	Nitrogen
PDMS	-	Polydimethylsiloxane
PEO	-	Poly(ethylene oxide)
PPG/PEG/PPGDA	-	Poly(propylene glycol) block poly(ethylene glycol) block poly(propylene glycol) diamine
PPO	-	Poly(2,6-dimethyl-phenylene oxide)
PSA	-	Pressure swing adsorption
PSF	-	Polysulfone
TGA	-	Thermogravimetric analysis
Ti	-	Titanium
α	-	Selectivity
°C	-	Degree Celsius
wt.%	-	Weight percent
vol%	-	Volume percent
ppm	-	Parts per million

CHAPTER 1

INTRODUCTION

1.1 Background

Gas separation process can be referred to any type of techniques used to separate gas mixture. Gas separation process has been contributing to our daily and commercial activities such as metal fabrication, metallurgy, petrochemicals, food processing, healthcare and many more by providing pure gases based on the specification of every sector. The global market for industrial gases was valued at $66.7 billion in 2014 and predicted to increase from $68.7 billion in 2015 to $80.9 billion in 2020 with compound annual growth rate (CAGR) of 3.3% from 2015 to 2020 (McWilliams, 2016b). Formerly, cryogenic distillation and absorption were the major processes for gas separation (Izumi *et al.*, 2002), however, the increasing quantity of the large scale production plant had opened the door for a new types of gas processing technologies.

One of the most significant unit operations for gas separation technology and has been rapidly growing for the last 15 years is membrane technology (Abedini and Nezhadmoghadam, 2010). According to McWilliams (2016a), the combined U.S. market for membranes used in gas and liquid separation applications was worth approximately $2.2 billion in 2013 and estimated to rise from nearly $2.4 billion in 2014 to about $3.5 billion by 2019, with compound annual growth rate (CAGR) of 7.9% during the five-year period from 2014 to 2019. Moreover, the global membranes market is projected to grow at a CAGR of 9.47% from 2015 to reach a value of USD 32.14 billion by 2020 (MarketsandMarkets, 2015). The increasing market size for membrane technology is due to its advantages including cost effectiveness, energy

efficient, require small footprint, low maintenance, and environmental friendly process over the other unit separations. The major contribution of membrane-based technology is as an efficient tool to the gas purification systems (Sridhar *et al.*, 2007). Membrane technology can be used either as a single process or complementing other conventional gas separation technologies.

Membrane has been developed using various organic and inorganic material including natural and synthetic polymer, carbon, ceramic and metals. The effectiveness of membrane material can be measured by its chemical resistant, mechanical and thermal stability, high permeability and selectivity and stability during operation. The selection of membrane material is highly related to the individual separation process application and the respective capital and operating cost (Scott, 1995c). Membrane material with high chemical and mechanical strength will have a longer operating lifetime reducing the capital cost while membrane with high selectivity require lower driving force thus lower the operating cost.

Most of the current commercial membranes are made from polymeric material (Baker and Low, 2014). Polymer is a molecule composed of repeated monomer subunit that plays an essential and ubiquitous role in everyday life. Polymer can be divided into two categories, which are natural and synthetic polymer. Several polymers has been selected as a commercially relevant polymer for membrane fabrication such as polysulfones (PSF), cellulose acetate (CA), poly(2,6-dimethyl-phenylene oxide) (PPO), aramids, polycarbonates and polyimides (Sanders *et al.*, 2013). However, most of the commercial polymeric membranes are having major drawback in which they are not able to economically produce gas with high purity in large scale operation as compared to cryogenic distillation and pressure swing adsorption (PSA) (Belaissaoui *et al.* 2014). Increasing both permeability and selectivity of gas production is critical issue in order to make membrane process more competitive and energy efficient.

Cellulose acetate (CA) is one of the first membrane materials that has been introduced to the industry. It is one of the world's oldest bio-based polymers that firstly invented in 1865 by Paul Schutzanberger via esterification (Erdmann *et al.*, 2014). The first CA commercialization was as a coating lacquer for airplanes in World War 1 and as a spun fiber for clothing materials (Edgar *et al.*, 2001). CA was first made into

membrane by Brown in 1910 (Shibata, 2004) and developed into asymmetric membrane for reverse osmosis by Loeb and Sourirajan in 1960 (Williams, 2003).

CA membrane has been used extensively covering many applications such as medical application, wastewater treatment and gas separation process. The first CA based gas separation membrane application was in 1982 by Separex for carbon dioxide/hydrogen (CO_2/H_2) gas separation and has been used in the largest plant for CO_2/natural gas separation developed by Pakistan UOP in 1995 (Bernardo and Clarizia, 2013). CA membrane has been dominating 80% of the market for natural gas processing (Scholes *et al.,* 2012). CA membrane has became one of the industrial comparison standards for membrane gas separation due to the wide acceptance from various industry. The usage of CA based gas separation membrane is commonly used for natural gas processing industry, air separation process and syngas process. Hence, for this study, the fabrication of formic acid (FA) crosslinked CA defect-free asymmetric membrane is focusing on the separation of CO_2/CH_4 for natural gas processing, O_2/N_2 for air separation process and H_2/N_2 for syngas process.

One of the desirable characteristic of high selectivity gas separation asymmetric membrane is the defect-free selective layer that avoid the nonselective pore flow where gas transport occurs by viscous or Knudsen mechanisms (Kurdi and Tremblay 1999). For defect-free membrane, ideally, the skin layer will be responsible for the selective separation and the porous substructure provides mechanical support (Pan *et al.,* 2009). Many attempts have been made in fabricating defect-free membrane ever since the development of defect-free high-flux asymmetric membrane developed by Loeb and Sourirajan in 1960. The production of defect-free asymmetric membrane reported can be achieved by manipulating dope formulation and preparation conditions. Until now, only a few of advanced polymers have been successfully fabricated into defect-free membranes (Xu *et al.*, 2014).

According to Xu *et al.*, (2014), sufficient viscosity is the first factor required to form a defect-free membrane skin layer. Sufficient viscosity is a viscosity that exhibits a significant degree of chain entanglement required for the proper formation of membrane skin layer and well-interconnected pores of the membrane substructure. (Hołda and Aernouts 2013). One of the key parameters to achieve a sufficient dope

viscosity is by manipulating the polymer concentration during dope preparation. Polymer concentration significantly affects the dope solution viscosity through the interaction between solvent, non-solvent and polymer.

Chemical crosslinking is one of the methods used for polymer modification for the fabrication of defect-free gas separation membrane. Chemical crosslinking plays role in restraining the polymer chain mobility by changing the backbone structure of interest (He *et al.*, 2016; Staudt-Bickel and Koros, 1999). The changes in polymer backbone structure through the incorporation of new covalent bond between the polymer chain has influenced the formation of membrane structure, thermal and mechanical stabilities as well as gas separation performance.

1.2 Problem Statement

According to Baker and Low (2014), despite the research on thousands of new materials, fewer than 10 membrane materials were commercialized and have been in use for decades. One of the reasons might be due to the reduce in membrane performance in terms of gas selectivity when tested with the industrial gas mixture. Other possibility is the membrane low mechanical strength that will results in membrane rupture when subjected to high pressure during an actual gas separation process. Higher material cost, complicated fabrication process and membrane performance affected by impurities are the other possibility that prevents the gas separation membrane from being commercialized. (Pabby *et al.*, 2015).

CA membrane has been used in gas separation for decade due to its unique properties of high carbon dioxide (CO_2) and hydrogen sulfide (H_2S) solubility within the CA polymer matrix that lead to high CO_2 and H_2S permeability (Ahmad *et al.*, 2014). Nevertheless, the number of plant that used this membrane has been decreasing due to the modest selectivity of CA membrane thus reducing CA membrane performance under mixed gas condition due to the competitive sorption and plasticization effect (Scholes *et al.*, 2012; Scholes *et al.*, 2009). In addition, the trade-off between the gas permeability and separation performance causing it to be replaced

by membrane that is more selective and permeable such as polysulfone, polyimides and polyethylene oxide.

Therefore, several methods have been implemented in order to produce CA membrane with high permeability and selectivity including polymer blending, mixed-matrix membrane, polymer modification, composite membrane, additive addition and many more. Thus, for this study, the effect of CA polymer concentration and formic acid (FA) crosslinking agent loading were investigated for the improvement of gas pair selectivity for CA flat sheet asymmetric membrane.

1.3 Research Objective

The general aim for this project is to develop defect-free CA based asymmetric membrane for high performance gas separation application. The specific objectives of this project are:

1. To investigate the effect of powder form cellulose acetate concentration on the formation of the membrane morphology, mechanical properties and gas separation performance.
2. To examine the effect of formic acid (crosslinking agent) loading on the membrane morphology, mechanical strength and gas separation performance.

1.4 Scope of Study

In order to achieve the objective of this research, the following scopes were outlined:

1. Preparing the polymer dope solution by varying CA concentration and FA loading.
2. Measuring the CA dope solution viscosity using viscometer.

3. Fabricating the flat sheet asymmetric membrane by dry/wet phase inversion technique.
4. Coating the prepared membranes (polymer concentration parameter only) using silicone rubber coating.
5. Observing the membrane morphology using field emission scanning electron microscopy (FESEM).
6. Characterising the membrane molecular crosslinking using Fourier transform infrared spectroscopy (FTIR).
7. Determining the membrane thermal properties using thermogravimetric analysis (TGA) for crosslinked CA membrane.
8. Measuring the membrane mechanical properties using tensile test.
9. Determining the membrane gas separation performance using soap bubble flow meter.

1.5 Significant of the Study

Cellulose acetate (CA) is a common polymer used as raw material for the fabrication of gas separation membrane. The usage of CA polymer in powder form has significantly reduce the amount of CA polymer required for the fabrication of CA membrane by 35% as compared to the CA polymer in pellet form. As the membrane separation becomes more important for various applications, this study proves that polymer crosslinking using formic acid (carboxylic acid) is an excellent alternative for the improvement of CA gas separation membrane. As there are limited studies have been conducted on the effect of crosslinking on the separation performance of membrane, this study provides a better understanding in fabrication of crosslinked CA asymmetric membrane with improved gas separation performance. The incorporation of formic acid (FA) improved the CA membrane structure formation and led to the improvement of gas separation. The use of FA as crosslinked agent was done in-situ during dope solution preparation, thus, does not require any other additional step or catalyst to induce the crosslinking reaction. The incorporation of FA induced the formation of defect-free membrane surface and does not require any additional skin layer coating for the improvement of gas separation. In addition, the usage of CA

biopolymer from renewable resources can reduce the dependent on non-renewable synthetic polymer.

1.6 Limitation of the Study

The limitations of this study are as follows:

1. Gas separation performance for all membrane samples were tested only using pure gases of hydrogen, oxygen, nitrogen, carbon dioxide and methane.
2. The maximum pressure for the gas separation performance testing is 10 bar due to the capability limitation of gas permeation system. Operating above 10 bar can cause leakage to the system.

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