POLYETHERIMIDE/MULTIWALL CARBON NANOTUBE MIXED MATRIX HOLLOW FIBER MEMBRANE FOR GAS SEPARATION

NG BE CHEER

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Gas Engineering)

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

JULY 2020

ACKNOWLEDGEMENT

First and foremost, I would like to express my sincere gratitude to my sole supervisor **Prof. Datuk. Ts. Dr. Ahmad Fauzi Ismail** for the continuous guidance of my Ph.D study and research, for his patience, inspiration, enthusiasm, and immense knowledge.

I wish to express my deep appreciation and sincere gratitude to all my colleagues and students from **Advanced Membrane Technology Research Centre**, for creating lively knowledge-sharing environment. Their continuous support and help was endless.

ABSTRACT

Mixed matrix membrane (MMM) which incorporated with polymeric and inorganic materials has become an interest to engineers in the early twenty due to its potential in advancing the gas separation properties of the polymeric-based membrane. The main objective of this study is to establish an effective approach for mixing and dispersing carbon nanotube (CNT) into the matrix of polyetherimide (PEI) to obtain MMM with optimized gas separation performance efficiency. The changes in gas permeability and selectivity of the fabricated flatsheet MMM was correlated with three different functionalizations on CNT. It was found that aminopropyl-triethoxysilane treated CNT homogeneously dispersed CNT in the polymer solution and gave the best separation on CO_2 molecules. The result found that MMM exhibited CO_2/CH_4 selectivity of 30.59, which is significantly higher than the intrinsic value of PEI ever reported (common PEI CO_2/CH_4 selectivity = 29.66). Next, using the polymeric solution formulation with the optimum filler loading, hollow fiber (HF) MMM was tailored. The spinning parameters such as extrusion rate and air gap distance during dry phase inversion were optimized. It was found that the produced asymmetric membrane exhibited high permeance and selectivity. The average CO_2 permeance obtained was 67.72 GPU with CO_2/CH_4 selectivity of 58.89. Additionally, increasing the shear rate by a higher extrusion rate resulted in a membrane with higher selectivity. Moreover, the selectivity of all the MMM fabricated surpassed 80% of the recognized intrinsic value, implying that the membrane produced in the study can be considered as defect-free membrane. The best HF MMM was obtained by incorporating 0.5wt% CNT into dope containing 25wt% PEI and extruding the dope at 4 cm^3/min using air gap of 300 mm. The optimal HF MMM showed 28 times increment in permeance of pure gas CO_2 and 2 times higher selectivity of CO_2/CH_4, compared to that of neat PEI. A comparative study with other PEI MMM revealed that CNT with proper functionalization and fabrication technique indeed could impart a strong influence in improving the matrix properties for further in-depth development.

ABSTRAK

Membran campuran matrik (MMM) yang digabungkan antara bahan polimer dan bahan bukan organik telah menjadi tumpuan para jurutera pada awal abad kedua puluh disebabkan potensinya untuk memperhebatkan ciri-ciri membran pemisahan gas yang berasaskan polimer. Tujuan utama kajian ini adalah untuk membangunkan satu pendekatan pencampuran dan penyerakkan tiub karbon nano (CNT) dalam matrik polieterimida (PEI) bagi memperolehi MMM yang mengoptimumkan kecekapan prestasi pemisahan gas. Perubahan-perubahan terhadap ketelapan dan kememilihan MMM kepingan rata yang telah direka bentuk telah dikaitkan dengan tiga kaedah fungsian yang berlainan ke atas CNT. Didapati bahawa CNT yang dirawati oleh aminopropil-trietoksisilana diserak secara sekata dalam larutan polimer dan memberikan pemisahan molekul CO_2 yang terbaik. Keputusan menunjukkan bahawa MMM mempamerkan kememilihan CO_2/CH_4 sebanyak 30.59 yang secara ketara lebih tinggi berbanding nilai intrinsik PEI yang pernah dilaporkan (kebiasaan kememilihan CO_2/CH_4 PEI = 29.66). Seterusnya, dengan menggunakan perumusan larutan polimer dengan muatan pengisi yang optimum, MMM gentian geronggong (HF) telah dihasilkan. Parameter pintalan seperti kadar penyemperitan dan jarak ruang udara ketika penyongsangan fasa kering dioptimumkan. Didapati bahawa membran asimitri yang terhasil mempamerkan telapan dan kememilihan yang tinggi. Purata telapan CO_2 purata yang didapati adalah sebanyak 67.72 GPU dengan kememilhan CO_2/CH_4 sebanyak 58.89. Selain itu, peningkatan kadar ricih melalui peningkatan kadar penyemperitan telah menghasilkan membran yang mempunyai kememilihan yang lebih tinggi. Tambahan pula, kememilihan semua hasilan MMM yang melangkaui 80% nilai intrinsik yang diakui, menunjukkan bahawa membran yang dihasilkan dalam kajian ini berada dalam lingkungan membran tidak berkecacatan. MMM HF yang terbaik telah diperolehi melalui penggabungan 0.5wt% CNT dalam larutan polimer yang mengandungi 25wt% PEI dan menyemperit larutan polimer pada 4cm^3/min dengan menggunakan jarak ruang udara sebanyak 300mm. MMM HF yang optimal menunjuk peningkatan 28 kali ganda pada telapan gas tulen CO_2 dan 2 kali ganda dalam kememilihan CO_2/CH_4, berbanding kepada PEI tulen. Kajian perbandingan dengan PEI MMM yang lain telah mendedahkan bahawa CNT dalam fungsian yang tepat dan teknik hasilan sesungguhnya memberi pengaruh yang kuat dalam meningkatkan sifat-sifat matrik dan harus dibangunkan secara mendalam.

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LIST OF ABBREVIATIONS

AFM	-	Atomic force microscope
ATR	-	Attenuated total reflection
BET	-	Brunauer, Emmet and Teller
CCVD	-	Catalytic chemical vapor deposition
CMS	-	Carbon molecular sieve
CNT	-	Carbon nanotube
CVD	-	Chemical Vapor decomposition
DSC	-	Differential scanning calorimetry
EtOH	-	Ethanol
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transformed infrared
Id/Ig	-	D-band to G-band ratio
MD	-	Molecular dynamic
MMM	-	Mixed matrix membrane
MWCNT	-	Multi-walled carbon nanotube
NMP	-	N-methyl-2-pyrrolidone
THF	-	Tetrahydrofuran
PEI	-	Polyetherimide
PSF	-	Polysulfone
*T*g	-	Glassy temperature
TEM	-	Transmission electron microscopy
TGA	-	Thermogravimetric analysis
UV	-	Ultra-violet

LIST OF SYMBOLS

A	-	Effective membrane area (cm^3)
C	-	Concentration (mol)
D	-	Diffusivity coefficient (cm^2/s)
Id/Ig	-	D-band to G-band ratio
J	-	Gas flux (cm^3 (STP)/cm^2.s)
l	-	Membrane thickness (cm)
m	-	Mass (g)
M	-	Molecular weight (mol/g)
p	-	Partial pressure (cmHg)
P	-	Permeability coefficient (cm^3 (STP).cm/cm^2.s.cmHg)
Q	-	Gas or liquid volumetric flow rate (cm^3/s)
S	-	Solubility (cm^3-gas/cm^3-polymer cmHg)
Tg	-	Glass transition temperature (°C)
l	-	Membrane thickness (m)
P	-	Permeance, GPU
Qi/j	-	Volumetric flow rate, cm^3/min
α	-	Selectivity
Δp	-	Pressure difference, cmHg

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Membrane-based separation has experienced rapid growth in the last decade. Several breakthroughs have been made in membrane-based separation processes to outperform the conventional technologies in many important industrial processes (Favvas *et al.*, 2017). Membrane process normally does not involve phase changes hence is more energy efficient compared to processes such as distillation. Membrane technology is also attractive with its operational continuity and simplicity. A membrane is generally defined as a thin layer of semipermeable barrier that only permits the passage of certain molecules while hindering other undesired molecules from crossing. The performance of membrane is of the major concern of a membrane process. A highly selective membrane allows efficient separation. Currently, membrane processes have been broadly applied in gas separation, water purification and energy generation (Han and Ho, 2018; Yin dan Deng, 2015)

Gas separation and purification are important chemical processes. Gas separation has been conventionally accomplished through cryogenic distillation, adsorption and absorption (Porcheron *et al.*, 2011; Sreedhar *et al.*, 2017). Despite their technological maturity, they still suffer from several disadvantages such as energy extensive and complicated operations. Gas separation based on membrane technology provides a green, economical and reliable mean for practical industrial applications. Particularly, the attractive features of membrane technology in terms of energy efficiency and simplicity compared to conventional methods have made it an attractive approach for a wide range of applications such as acidic gas removal, oxygen enrichment and methane gas purification (Liang *et al.*, 2019). For example, compared to amine absorption that has been commonly used in petrochemical industries, membrane process does not require chemical in its operation, hence the

operational cost of the process can be lower (Koros and Fleming, 1993). Issue such as solvent loss during operation can also be avoided. Furthermore, membrane is also a favourable option for platform operation owing to its compactness. The modular and minimum monitoring requirement also can meet the stringent offshore site-specific demands.

Tailoring membranes with better separation characteristics for specific industrial applications in important for its practicability and sustainability. The major requirement of a commercially attractive gas separation membranes are high permeability and selectivity as well as mechanically, chemically and thermally stable. For decades, polymeric membranes have been favourably used in gas separation due to the high throughout as well as ease of handling and processing compared to its inorganic counterpart (Brinkmann *et al.*,1993). Polymeric membranes can be further classified into glassy and rubbery polymer. In terms of their transport properties, rubbery polymers normally have higher diffusion coefficients but lower solubility coefficients compared to glassy polymers. Currently, many polymeric membranes have been successfully used in practical industrial processes such as air separation and purification (Dalane *et al.*, 2017). Polymeric membranes are well recognized with their high flexibility in term of the synthetic composition. The chemistry of polymers can be easily tailored during pre or post-fabrication processes. However, one of the drawbacks of polymeric membranes designed for gas separation is the trade-off between the permeability and selectivity as demonstrated by Robeson based on the upper bound curves (Robeson, 2008). As the result, the polymeric membranes usually exhibit lower gas selectivity compared to inorganic membranes.

Besides the Robeson's trade-off, polymeric membranes also suffer from poor chemical and thermal resistance particularly towards corrosive solvents. Aging and plasticization are also critical issues related to sustainability of polymeric membranes. Aging is a phenomenon where the polymer chains rearrange themselves over time to achieve a more stable configuration (Rowe *et al.*, 2009). Aging leads to the matrix densification and loss of membrane productivity. On the other hand, plasticization refers to the swelling of polymers upon their exposure to polarizable gases such as CO_2 at high pressure (Du *et al.*, 2011). The detrimental effects of plasticization are

related to the remarkable loss in the membrane selectivity. Mechanical strength of polymeric membranes is also another great concern for industrial applications as most processes require stable operation at high pressure.

In order to address the abovementioned issues, inorganic-organic composite membranes, which is more commonly known as mixed matrix membrane (MMM) has been developed. MMM is fabricated by dispersing inorganic particles into the polymer matrix (Wang *et al.*, 2018; Liang el al., 2017). These inorganic particles, which are normally in nano-sized, act as the filler to enhance some properties that cannot be attained by polymeric membrane alone. For instance, MMM has been evidenced to provide the high mechanical strength and ease processing of polymeric membranes, and also simultaneously render excellent separation performance owing to the presence of the inorganic fillers. MMM is also known as a straightforward approach to tackle the Robeson trade-off issue as the MMM combines the advantages of both polymer and inorganic entities. As a result, MMM has been the major focus of research and development of gas separation membranes.

The advancement in material sciences particularly in nanomaterial development have allowed a wide selection of nanomaterials to be selected for MMM fabrication. Currently, various classes of nanomaterials have been explored as the inorganic phase in MMMs. Some of the commonly used are silica Chen *et al.*, 2018), carbon nanotubes (CNTs) (Ismail *et al.*, 2009), zeolite, graphene oxide (GO) (Zhou *et al.*, 2017) and metal organic framework (MOF) (Li *et al.*,2014). Depending on the shape, size, dimension and unique features of these nanomaterials, they can impart some desired properties to the resultant MMMs. These nanomaterials can be incorporated directly during the membrane fabrication or introduced on the membrane surface through post-fabrication modification. These nanomaterials play different roles when they are used as nanofillers in MMM.

Among the mentioned inorganic fillers, CNT is one of the most studied nanomaterials due to its attractive properties for gas separation. Structurally, CNT consist of the rolling of graphene sheets into cylindrical form. The inner structure of CNT offers a frictionless channel for the fast transport of molecules (Wong *et*

al.,2019). Due to this special feature, CNT has been identified as a promising filler to enhance the permeability of the resultant MMM. The high theoretical mechanical strength of CNT is also another attractive feature of nanofiller. When incorporated into polymeric matrix, it has been evidenced that CNT can improve the Young's modules and tensile strength of the resultant MMM.

One of the main challenges to produce defect-free MMM is to improve the dispersibility of the inorganic fillers in the polymer dope during the fabrication of MMM (Li *et al.*,2005). The well dispersed fillers can render good compatibility with the polymer matrix. This feature is of great importance to reduce the likelihood of the formation of undesired voids at the filler-polymer interface. These voids have been associated with the deterioration of the MMM performance particularly in term of gas selectivity. Currently, one of the most applied strategies to tackle this issues is to introduce functional groups to the surface of the inorganic fillers. Various chemical and physical modifications have been well established to achieve the goal (Zhang *et al.,* 2019). Some of these modifications include oxidation using air and oxidizing reagents, aminations as well as polymer and surfactant wrapping. Depending on the nature of the reagents and the conditions of the modification reactions, different types of functional groups can be effectively introduced to the surface of the nanomaterials.

1.2 Problem Statement

Polymer membranes have been commercially used for a wide range of gas separation applications in both laboratories and industries. However, conventionally polymeric membranes suffer from the typical permeability-selectivity trade off where the increase of productivity is obtained with the expense of selectivity. In order to address this issue, MMM that consists of the dispersion of inorganic fillers within polymer matrix has been developed. CNTs has been recognized as one of the most promising fillers to enhance the performance of MMM due to its ability to improve the gas permeability rendered by the smooth and frictionless tubular structure.

Nevertheless, the main challenge in incorporating CNTs into polymer matrix is the poor dispersion issue related to the van der Waals forces that cause entanglements of the nanotubes. This phenomenon has consequently resulted in the formation of voids at the filler-polymer interface and unfavourably caused the loss of selectivity. Additionally, the mechanical strength and chemical stability are also found to deteriorated with the formation of these voids. In order to tackle this challenge, functionization of CNTs are performed. Acid oxidation, surfactant wrapping and silane functionalization are several effective approaches to simultaneously purify and introduce desired functional groups on the surface of CNTs, hence reduce agglomeration and improve the dispersion of CNT. In this study, the MWCNT treatment based on strong acid oxidation, non-covalent modification with Triton X100 and functionalization with 3-aminopropyltriethoxysilane (APTES) were attempted to compare their effectiveness to facilitate good dispersion for MMM fabrication.

To date, various nano-sized inorganic fillers have been explored to enhance the performance of MMMs for gas separation. CNT incorporated MMMs have also been fabricated for gas separation. Goh *et al.* prepared PEI-based MMM incorporated with surfactant modified CNT for O_2/N_2 separation (Goh *et al.*, 2012). The study focused on the fabrication of flat sheet membranes through phase inversion technique. Despite the improvement observed, the CNT incorporated MMM in hollow fiber configurations have not been attempted. In practical membrane-based gas separation processes, hollow fiber membranes are more favourable due to their higher larger surface area per volume compared to their flat sheet counterpart.

Currently, due to the ease in the lab-scale set up and preparation, most of the bench scale studies of MMM are still focused on flat sheet membrane fabrication. The optimization of the MMM hollow fiber spinning conditions have been scarcely reported. In fact, the spinning parameters such as air gap and dope extrusion rate (DER) can impart significant influence on the membrane morphology, hence the separation performances. Currently, there is no correlation studies have been performed to relate the air gap and DER with the gas separation performance of the

MMM hollow fiber membranes. Due to the importance of these two parameters during the spinning of hollow fibers, it is crucial to optimize them in order to maximize the performance of the MMM for gas separation.

In this study, hollow fiber MMMs consists of polyetherimide (PEI) and multiwalled carbon nanotubes (MWCNTs) were developed for gas separation application. The MWCNTs were pre-treated with acid oxidation and surfactant wrapping in order to improve the dispersion and establish better interaction with the polymer chain. Various characterizations have been conducted to study the physico-chemical properties of the MWCNTs and MWCNT/PEI MMM. Finally, the gas separation performance in terms of permeability and selectivity of the resultant MMMs were evaluated. The polymer fabrication parameters in terms of polymer concentration and MWCNT loading as well as the spinning conditions in terms of air gap and dope extrusion rate have been investigated to optimized the performance for gas separation.

1.3 Objectives of Study

The main goal of this study is to develop gas separation PES mixed-matrix hollow fiber membranes that are incorporated with MWCNTs that have been modified through acid treatment and surfactant wrapping. The objectives are:

i. To synthesize and modify MWCNTs using acid oxidation, surfactant wrapping and silane functionalization.
ii. To fabricate the PEI/MWCNTs MMMs containing MWCNT modified with different approaches through phase inversion technique.
iii. To study the effects of MWCNT modification on the physico-chemical properties and gas separation performance of the MMMs
iv. To optimize the MMM hollow fiber membrane spinning parameters in terms of air gap and DER.

1.4 Scopes of Study

In order to achieve the objectives stated above, the following scopes of study are identified:

i. Synthesis of MWCNT using catalytic chemical vapour deposition (CCVD) technique with ethylene as carbon source and cobalt-nickel as the catalyst substrate
ii. Oxidation of as-synthesized MWCNT using 3M of concentrated sulphuric acid under reflux condition
iii. Surface modification of MWCNT using non-ionic Triton X100 surfactant with concentration of 2.5 mg/ml at room temperature
iv. Functionalization of MWCNT using APTES as the silane agent
v. Characterization of as-synthesized and treated MWCNTs in terms of morphology, mechanical strength, presence of functional groups and dispersibility in aqueous solutions.
vi. Formulation of polymer dope consists of PEI, N-Methyl-2-pyrrolidone (NMP), Tetrahydrofuran (THF), Ethanol (EtOH) and functionalized multi wall carbon nanotubes (MWCNT)
vii. Fabrication of flat sheet membranes and hollow fiber PEI/MWCNT MMM through dry-wet spinning technique
viii. Characterization of hollow fiber PEI/MWCNT MMM in terms of morphology and mechanical strength
ix. Performance evaluation in terms of gas permeability and selectivity using CO_2 and CH_4
x. Study of the effects of MWCNT loadings (0-1.0wt%) on the properties and separation performance of the PEI/MWCNT MMM
xi. Optimization of the spinning condition in terms of air gap (10-500 mm) and dope extrusion rate (1.2-6 cm^3/min).

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