

THIN FILM NANOCOMPOSITE MEMBRANE INCORPORATED WITH
POLYMETHYL METHACRYLATE GRAFTED MULTI-WALLED CARBON
NANOTUBES FOR GAS SEPARATION

WONG KAR CHUN

UNIVERSITI TEKNOLOGI MALAYSIA

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WONG KAR CHUN

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To my beloved mother and father

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ABSTRACT

Membrane technology is an appealing alternative to the conventional carbon dioxide (CO₂) separation processes due to its design simplicity, energy efficiency and environmentally benign approach. Nanocomposite membrane, especially the thin film nanocomposite (TFN) is a relatively new class of membrane which features good separation performance and practical processing. Yet, the challenge of achieving good dispersion of the nanosized fillers within the polymer matrix remains unsolved. This study investigated on the potential of TFN containing modified multi-walled carbon nanotubes (MWNTs) for gas separation. Mixed acid oxidation, micro-emulsion polymerization and ball milling have been employed to improve the dispersibility of MWNTs. The TFNs were fabricated via interfacial polymerization technique to allow control over the distribution of the fillers. The effects of modification, incorporation scheme and loading of MWNTs on the gas separation performance have been investigated. The results suggested that grafting MWNTs with polymethyl methacrylate (PMMA) allowed good dispersion of the fillers which can be further enhanced by the physical milling to suppress the formation of aggregates. TFN produced by incorporating the milled PMMA-MWNTs (m-PMMA-MWNTs) within the coating layer showed the best separation performance compared to other incorporation scheme. The performance enhancement of the TFN compared to the thin film composite counterpart was endowed by the addition of well-dispersed MWNTs that served as rapid diffusion channels and the formation defect-free skin. The optimum fillers loading is 0.25 g/L which gives TFN with CO₂ permeance of 53.5 gas permeation unit (12% increment), CO₂/nitrogen selectivity of 61.0 (1% increment) and CO₂/methane selectivity of 35.2 (54% increment). TFN embedded with m- PMMA-MWNTs could potentially be used for low pressure carbon capture and storage application with further development.

ABSTRAK

Teknologi membran merupakan alternatif yang menarik berbanding proses pemisahan karbon dioksida (CO₂) konvensional kerana rekabentuknya yang ringkas, mempunyai kecekapan tenaga dan pendekatannya yang mesra alam. Membran komposit nano, terutamanya membran filem nipis komposit nano (TFN) merupakan membran kelas baru yang bercirikan prestasi pemisahan yang bagus dan pemrosesan yang praktikal. Namun, kesukaran untuk mencapai serakan pengisi bersaiz nano dalam matriks polimer yang sekata masih dihadapi. Penyelidikan ini bertujuan untuk mengkaji potensi TFN yang mengandungi tiub-tiub nano karbon berbilang dinding (MWNTs) yang telah diubahsuai untuk pemisahan gas. Pengoksidaan campuran asid, pempolimeran emulsi mikro dan pengisaran menggunakan bebola besi dilaksanakan untuk meningkatkan serakan MWNTs. TFNs dihasilkan melalui teknik pempolimeran antara muka untuk mengawal pengagihan pengisi. Kesan pengubahsuaian, skema penambahan dan muatan MWNTs terhadap prestasi pemisahan gas telah dikaji. Hasil kajian menunjukkan bahawa pengolahan MWNTs dengan polimetil metakrilat (PMMA) membolehkan pengisi diserakkan dengan sekata, dimana serakan ini boleh diperhebatkan lagi dengan pengisaran secara fizikal untuk menghalang pembentukan agregat. TFN yang ditambah dengan PMMA-MWNTs yang telah dikisar (m-PMMA-MWNTs) ke dalam lapisan penyalut menunjukkan prestasi pemisahan yang terbaik berbanding skema penambahan yang lain. Peningkatan prestasi TFN berbanding komposit filem nipis adalah disebabkan oleh penyelerakan sekata MWNTs yang berfungsi sebagai saluran resapan pantas dan pembentukan lapisan permukaan yang sempurna. Muatan optimum pengisi adalah sebanyak 0.25 g/L, yang mana telah menghasilkan TFN yang mempunyai telapan CO₂ sebanyak 53.5 unit telapan gas (kenaikan 12%), kememilihan CO₂/nitrogen sebanyak 61.0 (kenaikan 1%) dan kememilihan CO₂/metana sebanyak 35.2 (kenaikan 54%). TFN yang mengandungi m-PMMA-MWNTs berpotensi untuk digunakan dalam aplikasi memerangkap dan menyimpan karbon bertekanan rendah melalui perkembangan yang selanjutnya.

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LIST OF ABBREVIATIONS

APTES	-	aminopropyltriethoxysilane
ATR-FTIR	-	attenuated total reflectance Fourier transform infrared
BSA	-	bovine serum albumin
CA	-	cellulose acetate
CMS	-	carbon molecular sieve
CNT	-	carbon nanotube
CTAB	-	cetyltrimethylammonium bromide
CVD	-	chemical vapor deposition
DCB	-	1,2-dichlorobenzene
DGBAmE	-	diethylene glycol bis(3-aminopropyl) ether
DI	-	deionized
DNMDAm	-	3,3'-diamino-N-methyldipropylamine
DWNT	-	double-walled carbon nanotube
FCM	-	fixed carrier membrane
FESEM	-	field emission scanning electron microscopy
FO	-	forward osmosis
FTM	-	facilitated transport mechanism
GPU	-	gas permeation unit
IEM	-	ion-exchange membrane
IP	-	interfacial polymerization
IPC	-	isophthaloyl chloride
KPS	-	potassium persulfate
LSM	-	liquid support membrane
MMA	-	methyl methacrylate
MMM	-	mixed matrix membrane
MOF	-	metal organic framework
MPD or PPD	-	phenylenediamine (meta or para)

MWCO	-	molecular weight cut-off
MWNT	-	multi-walled carbon nanotube
NF	-	nanofiltration
NMP	-	N-methyl-2-pyrrolidone
PA	-	polyamide
PC	-	polycarbonate
PDMS	-	polydimethylsiloxane
PEG	-	polyethylene glycol
PEO	-	polyethylene oxide
PES	-	polyethersulfone
PI	-	polyimide
PIP	-	piperazine
PMMA	-	polymethyl methacrylate
PS	-	polystyrene
PSf	-	polysulfone
PVA	-	polyvinyl alcohol
PVDF	-	polyvinylidene fluoride
PVP	-	polyvinylpyrrolidone
RO	-	reverse osmosis
SWNT	-	single-walled carbon nanotube
TEM	-	transmission electron microscopy
TEOA	-	triethanolamine
TETA	-	trimethylene tetramine
TFC	-	thin film composite
TFN	-	thin film nanocomposite
TGA	-	thermal gravimetric analysis
THF	-	tetrahydrofuran
TMC	-	trimesoyl chloride
UV-Vis	-	ultraviolet-visible

LIST OF SYMBOLS

Δp	-	transmembrane pressure (cmHg)
A	-	effective membrane area (cm ²)
C ₆₀	-	fullerene
CH ₄	-	methane
C _o	-	concentration of solute at feed side (ppm)
CO ₂	-	carbon dioxide
C _p	-	concentration of solute at permeate side (ppm)
D	-	diffusivity
H ₂	-	hydrogen
H ₂ SO ₄	-	sulfuric acid
HCl	-	hydrochloric acid
HNO ₃	-	nitric acid
ID	-	inner diameter
L	-	length
<i>l</i>	-	membrane thickness (cm)
m-	-	undergone milling process
N ₂	-	nitrogen
Na ₂ CO ₃	-	sodium carbonate
Na ₂ SO ₄	-	sodium sulfate
NaCl	-	sodium chloride
NaHCO ₃	-	sodium hydrogen carbonate
O-	-	undergone oxidation
O ₂	-	oxygen
OD	-	outer diameter
P	-	permeation rate
PMMA-	-	grafted with polymethyl methacrylate
Q	-	volumetric flow rate (cm ³ /s)

R	-	rejection of solute (%)
S	-	solubility
T _g	-	glass transition temperature
TiO ₂	-	titanium oxide

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Carbon dioxide (CO₂) is one of the major greenhouse gases that contributes to the global warming issue whereby the drastic increase of the globe temperature changes the world climate pattern and upset the health of our ecological system. This scenario will ultimately leads to the loss of crops production and natural biodiversity (Powell and Qiao, 2006). Anthropogenic activities such as biogas anaerobic digestion, coal gasification, fossil fuel combustion and natural gas exploration are the sources of emission of large amount of CO₂ into the atmosphere. Since it is anticipated that the global population will expand close to 10 billion inhabitants by year 2050 (Lalia *et al.*, 2013), increase in the world resources and energy demand is inevitable and will only bring about more greenhouse gases emission (Adewole *et al.*, 2013). Apart from the aforementioned impact of CO₂ at global scale, back to industrial application especially in natural gas processing, this gas presents a serious problem because it can lower the heating value of the gas stream. Additionally, CO₂ acidic nature decreases of the gas stream pH and causes corrosion to the pipelines which severely impairs the transportation system (Zhang *et al.*, 2013b). Therefore, recently, removal and emission mitigation of CO₂ have become hot research topics (Lindau *et al.*, 1995).

Thus far, chemical absorption, pressure swing adsorption and cryogenic separation are the most common techniques employed for the aforementioned objectives. Even though these technologies have reached developmental maturity, they are constantly plagued by problems such as flooding, foaming, entrainment, weeping and absorbents degradation. Additionally, their high capital and maintenance costs, great energy consumption and large plant size as well as complexity of operation units force investors and scientists to look for better alternatives. Membrane technology prevails as a viable option due to its design simplicity and modularity that ease scaling up process and membrane separation is relative energy efficient compared to conventional approaches (Sanders *et al.*, 2013).

In general, membranes can be categorized into organic or polymeric and inorganic membranes. Currently, polymeric membranes are the dominating materials used for gas separation because they are highly processable into different format and the raw materials are relatively cheap compared to inorganic membranes (Adewole *et al.*, 2013). Nevertheless, contemporary polymeric materials are insufficient to exploit the full potentials of membrane application in the industrial scale (Chung *et al.*, 2007). This is because development of the polymeric membranes is often bounded by the Robeson's tradeoff between selectivity and permeance. In view of such predicament, attempts to improve the polymeric membrane performance via material engineering such as heat and chemical treatment, polymers blending and incorporation of inorganic fillers have been made. Recent years, the scheme of mixed matrix membrane (MMM) has gained much attention and is being studied intensively (Kim *et al.*, 2007). Incorporation of inorganic fillers which are integrally superior in term of selectivity into the polymeric membrane can push the performance of the resulted MMM to greater heights (Bastani *et al.*, 2013). There are two types of fillers used for MMM fabrication which are porous filler such as zeolite, carbon molecular sieve (CMS), activate carbon, metal organic framework (MOF) and carbon nanotubes (CNTs) and non-porous fillers such as silica, titanium oxide (TiO₂) and fullerene (C₆₀) (Aroon *et al.*, 2010).

The invention of asymmetric membrane by Loeb and Sourirajan marks a significant breakthrough in membrane development because the scheme of fabricating a thin dense skin on top a porous substrate has successfully resolved the issue of low permeation of the dense polymeric membrane including MMM. In general, the skin of the asymmetric membrane is the main layer that performs gas separation function while the porous layer acts as the support for the fragile skin (Chung *et al.*, 2007). Since the skin is only approximately 0.2 μ m thick, resistance of mass transport across an asymmetric membrane is much lower compared to a dense membrane. In 1965, instead of fabricating an asymmetric membrane, Mogan has invented the interfacial polymerization (IP) technique for producing thin film composite (TFC) membrane. The resulted TFCs produced from this method are very similar to the asymmetric membranes but instead of a single-step fabrication approach, IP is a two-step process which enables each layer of the TFC to be controlled and optimized independently to suit targeted applications (Sorribas *et al.*, 2013). Therefore, membranes that are more versatile can be tailored via IP technique. Apart from that, IP exhibits self-termination property whereby at certain point of the reaction, the growing film restricts the supply of reactants to the interface which leads to formation of very thin (approximately 50nm thick) skin layer (Yu *et al.*, 2010)

Although much attention have been given on the scheme of synthesizing very thin organic-inorganic composite selective layer, only a handful of studies have actually been done (Chung *et al.*, 2007). This is especially true for incorporation of fillers into TFC (also known as thin film nanocomposite) because most of the past studies focus on dispersion of the nanotubes in polymer matrix via phase inversion technique (Wu *et al.*, 2013). Hence, there are still tremendous room of development and in-depth research on thin film nanocomposite (TFN) membrane that can be done. The main purpose of this study is to develop TFN membranes containing polymethyl methacrylate grafted multi-walled carbon nanotubes (PMMA-MWNTs) and to evaluate their performance for CO₂ capture.

1.2 Problem Statement

In this subsection, three problems that limits the development of gas separation membrane have been identified and highlighted as the subject of interest in this research. First, the trade-off between the selectivity and permeance of polymeric membrane which presents as a great barrier to the enhancement of membrane performance. Although much success to improve the separation properties of polymeric membranes have been achieved in past efforts via manipulation of the polymer structure, the performance is still trivial compared to the performance of inorganic membrane. On the other hand, fabrication of inorganic membrane is costly and often faced with difficulty to produce continuous, defect-free membrane which requires carefully handling due to its inherent brittleness. Nanocomposite membrane which comprises a continuous polymeric phase and an inorganic dispersed phase, also known as fillers, appears to be the way out of the aforementioned bottleneck. This class of material unites the goodness of both polymeric (ease of processing) and inorganic (superior selectivity and permeance) materials into a robust candidate which is easy to scale up for production.

The second problem is related to the incorporation of CNTs (filler of choice in this study) in the polymer matrix. Despite the advantages offered by this nanomaterial, past studies have witnessed the poor compatibility between CNTs fillers and polymer matrix as a major hiccup to the development of CNTs/polymer composite because the overall transport properties of MMM are critically dependent on the nanoscale interface morphology of the membrane (Chung *et al.*, 2007). Ideally, full contact of polymer matrix with the fillers surface without formation of defects is favorable for material transport. Yet, poor adhesion of polymer with CNTs often results in the presence of interface which is significantly differing from the bulk polymer. As such, surface modification of the fillers is necessary to improve the interfacial properties which could bring about the homogenous dispersion of CNTs throughout the polymer matrix.

Finally, the third issue concerns the thickness of mixed MMM fabricated via phase inversion technique. Thickness of membrane influence the mass transport of penetrant species through the matrix. Thin membrane is definitely more preferable than thick ones as it allows greater gas permeation rate. Ideally, the nanofillers are preferably to be deposited within the skin layer where the selective layer performs most of the separation function while the porous layer only acts as the support. This also allows cost and material saving as the usage of the costly inorganic fillers could be reduced. However, controlling the distribution of fillers within the membrane through a single-step fabrication approach is not a casual task (Aroon *et al.*, 2010). This feat is made possible by employing a two-steps fabrication method such as dip-coating, spin-coating and interfacial polymerization in which the skin and support layers can be manipulated discretely. In this study, IP techniques is adopted due to its relative simple procedure and capability to produce very thin selective skin through self-inhibition.

Furthermore, CNTs have rarely been explored as fillers to be incorporated into the active layer of interfacial polymerized thin film composite because it is challenging to achieve good dispersion of CNTs in the polyamide layer during synthesis which will ultimately reflects the performance of the membrane (Shen *et al.*, 2013). While IP technique is commonly adopted for fabrication of TFC and TFN membranes for liquid separation, relevant literature for the field of CO₂ separation is rather limited (Li *et al.*, 2013). Largely, incorporation of fillers was conducted within the skin and support layers. Yet, since the pristine MWNTs used in this study have length around 3-6 μm , in which is greater than the average thickness of the thin film that could be formed (0.15 μm) using the parameters of IP reported by Li *et al.* (2013), some of the randomly oriented nanotubes might protrude from the membrane surface if they were directly incorporated into the skin layer. In order to minimize the unfavorable CNT protrusion, the functionalized MWNTs were incorporated into the polydimethylsiloxane (PDMS) coating layer (sub-layer beneath the thin film) during the TFN fabrication. Mechanical ball-milling procedure have also been employed to shorten the nanotubes (Fonseca *et al.*, 2010) in hope to minimize protrusion. As such, it is of great interest in this research to investigate the potential performance of TFN gas separation membranes embedded

with modified CNTs as well as devising better CNTs incorporation techniques in order to optimize the output of this type of membrane

1.3 Objectives of Study

Based on the aforementioned issues, this study set out to investigate the potential of TFN embedded with modified MWNTs for gas separation with the following objectives:

- i. To investigate the effects of MWNTs modifications on the dispersibility of the fillers, surface morphologies and gas separation performance of resultant TFNs.
- ii. To identify the best fillers incorporation scheme based on the overall morphologies and gas separation performance of the resultant TFNs
- iii. To determine the optimum fillers loading to be embedded in the TFN based in the best incorporation scheme.

1.4 Scope of Study

In order to achieve the objectives of this study, the following scopes of study have been identified.

- i. Oxidizing the MWNTs (O-MWNTs) using sulfuric acid (H_2SO_4)/nitric acid (HNO_3) (3 M each) mixed acid in volume ratio of 3:1 under reflux condition.
- ii. Grafting the MWNTs with PMMA (PMMA-MWNTs) via microemulsion polymerization using cetyltrimethylammonium bromide as surfactant to suspend the nanotubes and methyl methacrylate monomers in micelles and potassium persulfate as initiator of the polymerization process.
- iii. Ball-milling the functionalized MWNTs for 8 hrs to obtained milled oxidized (m-O-MWNTs) and milled PMMA grafted (m-PMMA-MWNTs) fillers.

- iv. Confirming the modification of MWNTs using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).
- v. Determining the purity of functionalized MWNTs using thermal gravimetric analysis (TGA)
- vi. Characterizing the functionalized MWNTs in term of structural morphology using transition electron microscopy (TEM)
- vii. Formulating polysulfone (PSf) polymer dope and casting of PSf flat sheet support layer via phase inversion technique.
- viii. Estimating the molecular cut-off (MWCO) of the PSf supports via solute rejection method using ultraviolet-visible spectroscopy (UV-Vis)
- ix. Performing interfacial polymerization atop the polydimethylsiloxane (PDMS) coated PSf supports to produce TFNs consisting modified MWNTs.
- x. Incorporating modified MWNTs into different layers (inter-coating layer and skin layer) of the TFNs.
- xi. Manipulating the loading of modified MWNTs in the TFN membranes in between 0.00 g/L and 1.00 g/L.
- xii. Confirming the formation of polyamide (PA) thin film layers using ATR-FTIR.
- xiii. Characterizing the surface and cross-sectional morphologies of the TFNs using field emission scanning electron microscopy (FESEM).
- xiv. Evaluating the separation performance of the TFN membranes in terms of permeance and selectivity using CO₂, nitrogen (N₂) and methane (CH₄) pure gas.

1.5 Significance of Study

Despite a rich amount of research works that have been conducted on thin film composite membrane, relative little studies have focused on gas separation and works that related to incorporation of CNTs nanoparticles into the interfacial polymerized thin selective layer of are even scarcer. Apart from that, studies related to the incorporation of nanofillers within the coating layer of gas separation membrane has never been reported. As such, it is the ultimate goal of this study to contribute to understanding of the gas separation performance of TFN membrane embedded with MWNTs. The outcome of this investigation could pave ways for more effective fabrication method and accelerate the development of CNTs/TFN membrane for gas separation.

1.6 Assumptions and Limitations of Study

In this study, the morphologies of support layers such as surface roughness, pore size and structure and surface charge are assumed to have minor effects on the formation of the thin polyamide layer. It is assumed that the carbon nanotubes used do not possess molecular sieving capability towards the tested gases because the diameter of MWNTs ($OD \times ID = 10 \pm 1 \text{ nm} \times 4.5 \pm 0.5 \text{ nm}$) is larger than the kinetic size of all the gas species ($\text{CO}_2 = 3.3 \text{ \AA}$, $\text{N}_2 = 3.6 \text{ \AA}$ and $\text{CH}_4 = 3.8 \text{ \AA}$). Pure gases of CO_2 , N_2 , and CH_4 are used for the permeation test and selectivity is calculated for ideal cases.

The length of milled MWNTs cannot be determined due to their thread-like structure and limited analytical tool. Due to time constrain, the fabrication method used to produce the flat sheet support was fixed to phase inversion technique while the thin film layer was produced by first immersing the support into the organic phase followed by reaction with the aqueous phase to produce single skin. The immersion duration, reaction duration and monomer concentration used in interfacial polymerization were also kept constant based on previous studies.

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