POLYSULFONE/GRAPHENE OXIDE MIXED MATRIX HOLLOW FIBER MEMBRANE FOR CARBON DIOXIDE REMOVAL

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To My Beloved Family and Friends

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ABSTRACT

The multiple benefits of membrane technology have promised the feasible application in large scale for carbon dioxide (CO_2) removal. Mixed matrix membrane (MMM) is an organic polymeric phase that is dispersed with inorganic fillers. MMM has become a promising type of membrane for CO_2 removal as it combines high processability of polymeric materials with superior gas separation properties of inorganic materials. In this study, an asymmetric mixed matrix hollow fiber membrane (MMHFM) was prepared by incorporating graphene oxide (GO) into polysulfone (PSf) polymer matrix for CO_2 removal. Graphite was used as a filler precursor and was subjected to surface modification by oxidation process to produce graphene oxide (GO). Different loading of as-synthesized GO in the range between 0.05 to 1.0 wt.% was physically mixed with PSf polymer for dope preparation. The asymmetric MMHFM were spun via dry-wet technique. The transmission electron microscopy and atomic force microscopy analysis have confirmed that the synthesized GO was in the nanosheets form structure. The addition of GO was found to change the formation of MMHFM substructure layer as well as the thickness of MMHFM dense selective layer. The active functional groups of GO have facilitated the uniform filler dispersion within the PSf polymer matrix. GO loading of 0.25 wt.% was found to be the optimum loading to enhance the overall membrane properties and gas separation performance with CO_2 permeance of 74.47 GPU. Both CO_2/N_2 and CO_2/CH_4 selectivity of MMHFM were enhanced by 310% and 211%, respectively, as compared to that of the neat PSf membrane. The well dispersed GO improves the CO_2 separation by fully utilized its π-π conjugated bond and creates a path for small molecule gas (CO_2) by restricting larger molecule gases (N_2 and CH_4) to pass through the membrane. However, the excessive of GO loading with more than 0.25 wt.% would lead to agglomeration and restacking problem, and this condition could deteriorate the MMHFM gas separation properties.

ABSTRAK

Kepelbagaian manfaat teknologi membran menjanjikan keboleh-upayaan aplikasi untuk menyingkirkan karbon dioksida (CO_2) dalam skala yang besar. Membran campuran matriks (MMM) ialah fasa polimer organik yang diserakkan dengan bahan pengisi bukan organik. MMM telah menjadi membran yang menjanjikan keberkesanan untuk penyingkiran CO_2 kerana ia menggabungkan kebolehprosesan bahan polimer yang tinggi dengan bahan bukan organik yang bersifat unggul dalam pemisahan gas. Dalam kajian ini, membran gentian geronggang campuran matriks asimatri (MMHFM) telah disediakan dengan menggabungkan grafin oksida (GO) ke dalam matrik polimer polisulfon (PSf) untuk menyingkirkan CO_2. Grafit digunakan sebagai bahan pengisi utama dan menjalani pengubahsuaian permukaan melalui proses pengoksidaan untuk menghasilkan GO. Muatan GO yang telah disintesiskan yang berbeza dalam julat 0.05 hingga 1.0 berat% dicampurkan secara fizikal dengan polimer PSf bagi penyediaan larutan cecair. MMHFM asimatri telah dipintalkan melalui teknik kering basah. Analisis mikroskop penghantaran elektron dan mikroskop daya atom mengesahkan struktur GO yang telah disintesiskan adalah dalam bentuk kepingan nano. Penambahan GO didapati telah mengubah pembentukan lapisan sub-struktur MMHFM serta ketebalan lapisan terpilih padat bagi MMHFM. Kumpulan berfungsi aktif GO membantu penyerakan yang sekata dalam matrik polimer PSf. Muatan GO sebanyak 0.25 berat% didapati menjadi muatan optimum untuk meningkatkan ciri-ciri membran secara keseluruhan dan juga meningkatkan prestasi pemisahan gas dengan nilai penelapan CO_2 sebanyak 74.47 GPU. Kedua-dua kememilihan gas CO_2/N_2 dan CO_2/CH_4 bagi MMHFM meningkat masing-masing sebanyak 310% dan 211%, berbanding matrik polimer PSf yang asli. GO yang diserakkan dengan baik menambah baik pemisahan CO_2 dengan menggunakan sepenuhnya ikatan konjugurasi π-π serta mewujudkan laluan gas bermolekul kecil (CO_2) dengan menghalang gas bermolekul besar (N_2 dan CH_4) melepasi membran. Walaubagaimanapun, muatan GO yang berlebihan yang lebih daripada 0.25 berat% akan menyebabkan masalah pembentukan gumpalan dan pelekatan semula yang mana situasi ini akan mengakibatkan kemerosotan sifat pemisahan gas MMHFM.

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LIST OF ABBREVIATIONS

AEAPTMS	-	N-β-aminoethyl-γ-aminopropyltrimethoxy silane
AFM	-	atomic force microscopy
APDEMS	-	3-aminopropyl diethoxymethyl silane
APDMES	-	γ-aminopropyldimethylethoxy silane
APTES	-	(3-aminopropyl)-triethoxy silane
BPAPC	-	bisphenol A polycarbonate
BPZ-PC	-	bisphenol Z polycarbonate
BTDA-DAPI	-	matrimid® 5218
CA	-	cellulose acetate
CG-MS	-	gas chromatography mass spectrometry
CMS	-	carbon molecular sieve
CNT	-	carbon nanotubes
CTA	-	cellulose triacetate
DAS	-	dynasylan Ameo silane
DMAc	-	*N*,*N*-dimethylacetamide
DSC	-	differential scanning calorimetry
EtOH	-	ethanol
FESEM	-	field emission scanning electron microscopy
FTIR	-	fourier transform infrared spectroscopy
GFNs	-	graphene family nanomaterials
GO	-	graphene oxide
GPU	-	gas permeation unit
HNT	-	halloysite nanotube
ID	-	inner diameter
MMHFM		mixed matrix hollow fiber membrane

MMM	-	mixed matrix membrane
MOF	-	metal organic framework
NG	-	natural gas
OD	-	outer diameter
P84	-	tetramethyl bisphenol A polycarbonate
PDMS	-	Polydimethylsiloxane
PEI	-	Polyetherimide
PES	-	polyethersulfone
PI	-	Polyimide
PIM	-	polymers of intrinsic microporosity
PO	-	poly(2,6-dimethylp-phenylene)oxide
P_{pl}	-	plasticization pressure
PSA	-	pressure swing absorption
PSf	-	Polysulfone
PU	-	Polyurethane
PVAc	-	polyvinyl acetate
PVC	-	polyvinyl chloride
PVDF	-	polyvinylidene fluoride
rGO	-	reduced graphene oxide
RO	-	reverse osmosis
TEM	-	transmission electron microscopy
TGA	-	thermogravimetric analysis
THF	-	tetrahydrofuran
TMBPA-PC	-	tetramethyl bisphenol A polycarbonate
XRD	-	X-ray diffractometer

LIST OF SYMBOLS

A	-	membrane surface area (cm^2)
Å	-	amstrong
CH_4	-	methane
ClO_2		chlorine dioxide
CO_2	-	carbon dioxide
cP	-	centipoise
D	-	outer diameter (cm)
H_2O_2	-	hydrogen peroxide
H_2SO_4	-	sulphuric acid
HCl	-	hydrochloric acid
HNO_3	-	fuming nitric acid
i	-	gas species
KBr	-	kalium bromide
$KClO_3$		potassium chlorate
$KMnO_4$	-	potassium permanganate
l	-	effective length (cm)
N_2	-	nitrogen
N_2O_4		nitrogen tetroxide
Na^+		sodium ion
$NaNO_3$		sodium nitrate
NO_2		nitrogen dioxide
NO_3^-		nitrate ion
P	-	permeability
Q	-	volumetric rate (cm^3/s)
T_d	-	decompose temperature

T_g	-	transition temperature
α	-	Selectivity
ΔP	-	pressure difference (cmHg)
λ	-	wavelength

CHAPTER 1

INTRODUCTION

1.1 Research Background

Carbon dioxide (CO_2) is a colourless and odourless gas that can be naturally found in the Earth's atmosphere, various water sources as well as in the deposition of petroleum and natural gas. CO_2 in real is a non-toxic gas. However, in high and uncontrolled concentration, it becomes acidic and harmful to the environment where it is fulfilled. CO_2 is also known as a greenhouse gas. The excessive CO_2 in Earth's atmosphere becomes a pollutant and results in climate change that directly or indirectly affect both human and environmental health (Singh *et al.,* 2015). It has very long lifetime in the atmosphere; 50% is about 30-95 years and 20% is about thousands of years to decay, which implies that its quantities will continuously concentrated in Earth's atmosphere without any degradation over time (Milan, 2018). Coal gasification, fossil fuel combustion and natural gas exploration by human are the source of CO_2 emission to atmosphere (Wu *et al.*, 2011). Apart from that, CO_2 existence in natural gas (NG) is another subject to be highlighted. CO_2 exists in NG as impurity that would decrease NG heating value and corrode the pipeline stream, which consequently increase the operational and maintenance cost (Zhang *et al.,* 2013). Thus, the procedure to filter CO_2 produced from those human activities before the emission to the atmosphere and its removal from natural gas are necessary.

The common conventional methods applied in industries to remove CO_2 gas are chemical absorption by solvents (e.g. amine scrubbing), chemical adsorption by sorbent (e.g. pressure swing adsorption (PSA)) and cryogenic separation (Basu *et al.*, 2010). Each process offers different separation mechanism with certain advantages and limitations. Chemical-based absorption requires absorbents to react with CO_2 where high energy consumption is needed for the regeneration. Furthermore, the adsorbents used in PSA are not suitable for large scale of CO_2 separation and relatively high energy consumption (high cost). Meanwhile cryogenic separation is only suitable for stream that contains high concentration of CO_2 and the process also requires high energy consumption for cooling. Moreover, the problems such as flooding, excessive loading, weeping, foaming and entrainment also frequently arise during the process. These bottlenecks have led to the exploration of new approach such as membrane separation technology to address aforementioned problems.

Membrane separation promises some advantages such as easy control and operation, easy to scale-up, small foot print, high reliability, environmentally friendly, reduced energy consumption as well as low capital and operating cost (Bernardo *et al.*, 2009; Li, 2008). Basically, membrane can be categorized to polymeric (organic) and non-polymeric (inorganic) membrane. Some polymeric membrane have already been commercially applied in industry which are made of polyimide (PI), polysulfone (PSf) and cellulose acetate (Scholes *et al.*, 2010). Meanwhile, non-polymeric membrane like zeolite membranes are proven to have excellent CO_2 separation performance due to their molecular sieve ability and adsorption affinity (Jha and Way, 2008). Inorganic membrane however is difficult to be produced at large scale due to its complication and long-time consumption of fabrication as compared to polymeric membrane. Moreover, both polymeric and non-polymeric membranes suffer trade-off of selectivity and permeability which means membranes with high permeability/permeance have low selectivity and vice-versa (Robeson, 1991).

Hence, the idea of combining both polymeric and inorganic compound was developed to overcome the aforementioned problems. Mixed matrix membrane (MMM) is the combination of polymeric membrane as continuous phase and

inorganic materials are normally present in particle size as dispersed phase. Graphene oxide (GO) is an emerging nanomaterial of graphene-based family which has the same carbon sheet structure as graphene and additional oxygenated functional groups attached on its planar sheet. It is interestingly found that the active functional groups such as epoxy, hydroxyl and carboxyl groups can help to enhance its good dispersion in polymer substrate, which in turn contribute to enhance gas separation performance (Kuila *et al.,* 2012; Yang *et al.,* 2013). When it is incorporated into the polymer matrix, GO acts as barrier to create tortuous path in the membrane to allow the gas with smaller molecules to effortlessly pass through the composite membranes meanwhile the gas molecules with larger size are hindered from passing through the membranes (Li *et al.,* 2015; Berean *et al.,* 2015). Also, the presence of GO in polymeric matrix was proven to induce improvement in the nanocomposite membrane thermal and mechanical stability (Ionita *et al.,* 2015) and demonstrated improvements for gas separation performance (Checchetto *et al.,* 2014) as compared with that of neat membrane. With the exceptional properties possessed by GO, the resultant MMM holds good potential to surpass the Robeson separation trade-off boundary by overcoming the polymeric membrane drawbacks.

Despite the progress and efforts made in the development of MMM, the application of GO as a nano-filler in PSf mixed matrix hollow fiber membrane (MMHFM) for CO_2 removal has not been reported. Most of previous studies related to GO as a filler were fabricated as a dense membrane (Wang *et al.,* 2015; Zhao *et al.,* 2015) and some of them were focused only on membrane characterization without studying their effect on gas separation performance (Ionita *et al.,* 2014). So, this study is the first attempt of making the asymmetric PSf MMHFM embedded with GO for CO_2 removal. The main objective of this study is to develop MMHFM by incorporating GO into PSf polymeric matrix, expecting to improve the characteristic of fabricated MMHFM especially for gas separation application.

1.2 Problem Statement

Selection of the inorganic phase fillers is an important factor in determining the properties of the resultant MMM. Various types of potential fillers such as zeolite, metal organic framework (MOF) and carbon nanotubes (CNT) have been commonly used as the nanofillers. These fillers are found to have excellent sieving characteristic which allows smaller penetrants to diffuse at higher rate compared to that of larger sized penetrants. Despite of having speciality in gas separation application, poor interaction between two phases of filler and polymer become the major problem to be solved in order to achieve the desired performance of the resulting MMM (Goh *et al.,* 2011). One of the strategies of improving the compatibility of filler in MMM is through the introduction of surface functional groups. In this aspect, the unique surface functionalities of graphene oxide (GO) seem to offer an attractive solution. GO is an emerging nanomaterial of graphene-based family which has the same carbon sheet structure as graphene and additional oxygenated functional groups attached on its planar sheet. It is interestingly found that, the oxidative functional groups attached on the GO surface, such as epoxy, hydroxyl and carboxyl groups can help to enhance its good dispersion in polymer substrate, which in turn contribute to enhance gas separation performance by improving the linkage-bridge between polymer and filler.

GO special properties offers several advantageous towards carbon dioxide (CO_2) separation, which the other carbon-based materials cannot provide it. GO is reported to have specific adsorption affinity to CO_2 molecules with the presence of polar groups such as hydroxide and carboxylic groups attached on its surface and edge planar sheets. Other than that, the π-π bond conjugated at GO chemical structure have strong interaction with CO_2 molecules that can facilitate the CO_2 sorption which in turns improved the membrane separation properties performance when it is incorporated into polymer matrix. However, commercialized GO with specific size and characteristic is considerably expensive and would certainly increase the cost production of GO/polymer membrane. Hence research to produce GO with economically feasible is worth and would be special interest to the material development. Various research has been conducted by previous researchers on

synthesizing GO in bulk, but somehow some of it are not eco-friendly. As example, Brodies' method applying potassium chlorate ($KClO_3$) and nitric acid (HNO_3) in the process of synthesizing GO, which will produce an explosive chlorine dioxide (ClO_2) gas and acid fog respectively throughout the procedure. Also, the use of sodium nitrate ($NaNO_3$) for the process of synthesizing GO by Hummers' method release toxic gas (i.e. nitrogen dioxide (NO_2) and nitrogen tetroxide (N_2O_4)) and produce the residual of sodium ion (Na^+) and nitrate ion (NO_3^-) which are difficult to be removed from the waste water formed from the process. An improved Hummers' method without the addition of those harmful chemical has been introduced and offers green approach to the environmental with maintaining the yield production of GO.

The incorporation of GO to form MMM in flat sheet has been attempted (Zhao *et al.,* 2015). However, as flat sheet configuration generally shows poor permeability, it is rarely attractive for industrial aspect. Asymmetric membrane configuration is more relevant for practical applications since it is more permeable and mechanically stable compared to dense membrane. Apart of that, hollow fiber membrane offers several advantages as it provides high surface/volume ratios (lower the cost production), which can reduce the equipment (footprint) overall dimensions and the overall cost operation. These membrane characteristics overcome the drawback of densed symmetric/flat sheet membrane. Moreover, the GO based asymmetric mixed matrix hollow fiber membrane (MMHFM) are still rarely reported since GO material is relatively new. Hence, it is necessary to investigate the common problems in its preparation such as filler size, filler loading and membrane preparation since it would affect membrane performance differently from that reported in dense flat sheet MMM. In this work, asymmetric MMHFM of PSf based polymer incorporated with GO was fabricated via the phase inversion dry-wet spinning technique for CO_2 separation. The morphological changes, mechanical and thermal properties as well as gas separation properties for different loading of GO were investigated in order to optimize the characteristic of fabricated MMHFM.

1.3 Objectives of Study

Based on the aforementioned problems, the current study is conducted to focus on the following objectives:

1. To synthesize and study the physico-chemical properties of GO nanosheets obtained from Hummers' method.
2. To investigate the influence of different GO loading on the fabricated asymmetric PSf MMHFM.
3. To evaluate and compare the pure gas separation performance of the fabricated asymmetric PSf MMHFM with different loading of GO in terms of their permeability and selectivity using carbon dioxide (CO_2), nitrogen (N_2) and methane (CH_4) gas.

1.4 Scopes of Study

In order to achieve the objective of this research, the following scopes are listed:

1. Synthesizing of GO from raw graphite via chemical oxidation process using Hummers' method.
2. Characterizing the synthesized GO using atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA).
3. Preparing dope solution containing PSf, *N*,*N*-dimethylacetamide, tetrahydrofuran, and ethanol with compositions of 30 wt.%, 35 wt.%, 30 wt.% and 5 wt.% respectively.
4. Incorporating GO into PSf dope solution with varies loading ranging from 0.05 wt.% to 1.0 wt.% (per total solid).
5. Fabricating asymmetric PSf/GO MMHFM through phase inversion technique via dry-wet spinning process (7 cm air gap, 1 cm^3/min dope

extrusion rate, 0.5 cm^3/min bore fluid flow rate, 4.8 Hz collection speed, and bore fluid composition DMAc/H_2O : 80/20).

6. Characterizing the fabricated asymmetric PSf/GO MMHFM through field emission scanning electron microscopy (FESEM), XRD, TGA, differential scanning calorimetry (DSC), and mechanical strength analysis.
7. Evaluating asymmetric PSf/GO MMHFM performance towards pure nitrogen (N_2), carbon dioxide (CO_2) and methane (CH_4) gas in term of its permeance and selectivity at 5 bar operating pressure and room temperature.

1.5 Significance of Study

Despite the progress and efforts made in the development of GO for composite materials, the application of GO as a nanofiller in PSf MMHFM for CO_2 removal has not been reported. In addition, this is the first attempt of making the asymmetric PSf membrane embedded with GO in hollow fiber configuration for CO_2 removal. GO appears to be a new filler and currently there is no massive study on it. It is well known that PSf is a glassy polymer which possesses high resistance towards plasticization effect and hence can be a good candidate for CO_2 removal applications. Apart of that, asymmetric membrane comprises of thin dense selective layer which is responsible for the separation and low resistance microporous/ macroporous substrate layer which is responsible for high permeation of gas. Besides, membrane in hollow fiber configuration offers more advantages compared to that of membrane in flat sheet configuration. The MMHFM is commercially attractive as it holds the potential to address the drawbacks encountered by the conventional membrane for practical industry application.

1.6 Limitation of Study

In many of their nanocomposite applications, GO has been modified to improve the surface chemistry for better dispersion in the matrix. However in this study, the as-synthesized GO was directly used as the nanofillers without further surface functionalization. The main objectives of this study are to investigate the roles of GO and the effects of different GO loadings to improve the physico-chemical properties and further enhance the gas separation performance.

Gas separation membrane is a pressure-driven process. Hence, pressure is one of important factors to be studied with. CO_2 separation for post-combustion activities usually operated at low pressure, meanwhile for natural gas processing high pressure is always required to separate desired gas. The delicate nature of hollow fiber membranes with their limited maximum allowable transmembrane pressure especially when fabricated for lab scale used discourage researchers to conduct their experimental work at high feed pressure. Moreover, the resistance of hollow fiber towards high pressure operation, however, can be sustained in the real footprint of membrane installation. Normally the operating system is fixed at one elevated pressure and temperature. Besides, this study is not focusing on the effect of different pressure on gas separation performance. These explained why only one operating pressure is applied (5 bar) in this experimental work.

Other than that, the investigation of MMHFM should be further tested on mixed gas so that the result of gas separation performance would be more reliable to be applied in real industry. However, other effects caused by mixed gas (i.e. coupling effect) will cause complexity to identify the ideal characteristic of fabricated MMHFM. Due to the constraints in dealing with complexity behaviour of mixed gas, the pure gas system was examined in this study. Other than that, pure single gas would have behaviour of an ideal gas, which is can be the best indicator for MMHFM separation performance characteristic. If the value of MMHFM permeation and separation characteristic are high for pure single gas, it is most likely the similar finding will also be obtained for mixed gas.

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