PREPARATION AND CHARACTERIZATION OF MIXED MATRIX COMPOSITE MEMBRANE BASED ON PEBAX/AMINATED GRAPHENE OXIDE FOR GAS SEPARATION

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ABSTRACT

Mixed matrix composite membrane has attracted many researchers to develop due to the excellent ability in gas separation. Amine functionalized graphene oxide were used as nanofillers by incorporated amine functional group with graphene oxide. The PEBAX/AGO membrane were fabricated on the top of supporting layer of PSF. In this study, the gas separation performance were investigated by varying the AGO loadings (0.0, 0.25, 0.5and 0.75 (w/w%)) for CO_2 gas separation. The synthesis GO and AGO were characterized using FTIR to study the structure before being embedded into PEBAX based membrane. Then, the fabricated membrane were characterized using SEM and FTIR. The selectivity and permeability of PEBAX/AGO-0.5 showed the optimum condition with CO2 permeability 67.1 Barrer followed by PEBAX/AGO-0.25 with 64.3 Barrer. The result indicated that the permeability increase when AGO loading increased. Additionally, it is found that the additions of nanofillers lead to a significant enhancement in gas permeability especially in amine functionalized GO.

ABSTRAK

Membran komposit campuran telah menarik minat para penyelidik untuk memajukan penyelidikan kerana kebolehan membran komposit campuran yang bagus dalam proses pemisahan gas. Grafin oksida berfungsi amina digunakan sebagai isian-nano dengan mengintergrasi fungsian amin ke dalam struktur grafin oksida. Sintesis membran PEBAX/AGO dihasilkan dengan PSF sebagai lapisan sokongan. Dalam kajian ini, prestasi pemisahan gas dikaji dengan menggunakan muatan yang berbeza AGO (0, 0.25, 0.5 dan 0.75 (w/w)) untuk pemisahan gas CO_2. Sintesis GO dan AGO akan di cirikan menggunakan kaedah FTIR untuk mengkaji struktur sebelum ditanam ke PEBAX membrane. Membran yang telah difabrikasi akan dicirikan mengunakan SEM dan FTIR. Keputusan terhadap selektiviti dan permeasi PEBAX/AGO-0.5 menunjukkan keadaan optimum dengan keputusan 67.1 Barrer, diikuti dengan PEBAX/AGO-0.25 dengan 64.3 Barrer. Keputusan ini menunjukkan bahawa permeasi meningkat apabila kandungan AGO juga meningkat. Tambahan pula, jangkaan kajian menjangkakan penambahan isian-nano dapat meningkatkan dan menambahbaik permeasi pemisahan gas terutamanya apabila dia mengunakan GO yang mempunya fungsi amin

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LIST OF ABBREVIATIONS

EDX	-	Energy dispersion X-ray spectrometer
MMC	-	Mixed matrix composite
MMM	-	Mixed-matrix membrane
MOF	-	Metal-organic framework
NG	-	Natural gas
PSf	-	Polysulfone
SEM	-	Scanning electron microscopy
XRD	-	X-ray diffraction
ZIF	-	Zeolitic imidazole framework

LIST OF SYMBOLS

Å	-	Angstroms
A	-	Membrane effective area
b	-	Langmuir's affinity constant
C	-	Total sorption capacity
CD	-	Henry's sorption parameter
CH	-	Saturation sorption concentration
d	-	Distance of atoms in crystal lattice at different plane
DD	-	Gas diffusivity on Henry site
DH	-	Gas diffusivity on Langmuir site
Di	-	Diffusivity coefficient of gas i
K	-	Combination of sorption parameters
KD	-	Henry's law constant
Pi	-	Permeability of gas i
Si	-	Solubility coefficient of gas i
α	-	Gas pair selectivity
Δp	-	Transmembrane pressure difference
θ	-	Diffraction angle
λ	-	Wavelength of x-ray radiation

CHAPTER 1

INTRODUCTION

1.1 Background of Research

In past decades, carbon dioxide becomes one of the major greenhouse gases due to high concentration in surrounding. Increasing in global warming created awareness as people began to acknowledge the consequences of CO_2 contribution to environment. The consequences began to affect people daily life as world climate pattern slowly change over the time and also causing damage in natural ecosystem (Powell and Qiao, 2006). CO_2 emissions toward surrounding due to activities such as natural gas exploration, coal mining and deforestation, particularly, due to huge consumption of fossil fuel. In order to minimized and control CO_2 emission that has become a significant global issue, many studies has been conducted with purposes in minimizing the greenhouse effect and global warming.

Furthermore, CO_2 also portrayed a severe problem to the natural gas processing industry. High CO_2 concentration in gas can lower the heating value of product stream and corrode the pipeline of transportation system. Over the time, membrane technology dominating as a feasible alternative due to the simplicity of the design and fabrication process especially in scaling up process. In comparison with existing technology for sweetening process such as absorption and cryogenic separation, membrane separation possesses relative energy efficiency(Sanders *et al.*, 2013).

Membrane technology is a process of separation involving a certain species to pass through the membrane, meanwhile restricting others that depending on different type of membrane properties and material. Generally, membranes are grouped by according to the driving force and mode of ionic and molecular movement of the membrane. Two group of membranes known as dense and porous membrane. In short, membrane concept is that the difference species permeate at different specific

diffusion rate through membranes and also depending on solubility, diffusivity and porosity of the membrane (Lyu *et al.*, 2018).

In past few years, gas separation using polymeric membrane has experienced a major expansion during past few decades due to excellent ability in capturing greenhouse gas, natural gas sweetening process and hydrogen purification (Dong, Li and Chen, 2013). Intrinsic material properties become a key factor in determining the performance of polymeric membrane. Yet, the performance of the membrane rarely exceeds the permeability and selectivity trade-off even with many efforts been studied. Robeson upper bound becomes one of the main concerns in utilization of polymeric membrane. In contrast, inorganic membrane showed an outstanding gas separation performance compared with polymeric membrane. However, fabrication process of defect-free and continuous layers of inorganic membrane is difficult and the high cost becomes a concerned especially to produce in mass production (Li *et al.*, 2013).

As a result, current research being developed to overcome the "trade-of" constraint of polymer membranes. A new development known as mixed matrix membranes (MMMs) have been proposed by integrating high performance of inorganic fillers into polymeric membranes. MMMs structure based on solid-solid system comprised of inorganic disperse phase that being inserted into polymer matrix. MMMs purposely developed to have the potential to achieve higher selectivity, permeability, or both relative from existing polymeric membrane resulting from the integrating of inorganic particles with excellent separation characteristics (Zimmerman, Singh and Koros, 1997). For inorganic materials, porous and nonporous filler are major phase being utilized in MMMs fabrication. In short, if inorganic fillers are porous, typically it has the properties of molecular sieve, which separating gases by their size or shape and give higher permeability and selectivity of desired components. Compared with nonporous fillers, diffusion of larger molecules will decreased and matrix tortuous pattern will increase (Bastani, Esmaeili and Asadollahi, 2013). Although the development of MMMs has been improved with attractive separation properties, the critical problem is poor adhesion between the filler phase and the polymer continuous phase. As a result, the membranes have decreasing in selectivity (Chung *et al.*, 2007).

To utilized membrane technology in large-scale process such as sweetening gas process, a high permeance property in membrane is crucial. Permeability and the thickness of the membrane determine the permeance characteristics. Typically, membranes that have very thin selective layers at the range of 0.1-2 μm are the majority of being used in the industrial applications (Li *et al.*, 2013). Asymmetric or composite membranes can fabricate into such thin layer.

Composite membrane is a structure which selective layer is deposited on a highly porous and the tough support of the membrane is made from the low-cost polymer. Thus, the choice of polymer materials offers more compared with asymmetric membrane which the support and selective layer is the same. In particular gas separation process, there are several complications dealing with asymmetric mixed matrix membranes. In preparation of thin and defect free mixed matrix layer, the filler should have smaller size than film thickness, for example if the thin film have 1μm thickness, then filler size should be smaller than 50 nm (Basu *et al,*. 2011). However, only several reports and studied have being conducted on thin-film composite membrane with mixed-matrix selective layer (Li *et al.*, 2013).

1.2 Problem Statement

To date only polymeric membrane has been implemented for gas separation in large scale in industry due to the easy in fabrication and have high mechanical strength. However, the performance of polymeric membrane become to known due to the limitation in trade-off relationship between permeability and selectivity of the membrane. Robeson upper bound, low chemical and thermal stability and plasticization at higher pressure in the presence of strong adsorbing penetrants, in this case is CO_2, are among of disadvantages facing by polymeric membrane. Mixed matrix membranes (MMMs) have being developed to overcome the limitation of both polymeric and inorganic membrane.

Recently, most mixed matrix membranes for CO_2 separation have several thicknesses that range from several dozen to several hundred micrometers. However,

in industrial sector, the demands on the membrane that have higher productivity become one of the objectives most researcher developed composite membrane (Wang *et al.*, 2017). As a result, mixed matrix composite (MMC) membrane are developed which consists of a thin separation layer and a support layer. At the separation layer, interphase void easier to form when there is a poor compatibility between polymer and filler. In fabrication of MMC membrane, one of the challenging factors is to avoid the formation of void in the separation layer. MMC membrane generally composed of two or three layers. The bottom layer is made from nonwoven fabric and the function is to provide the foundation support to other layer above it. The middle layer functions as a base for the top layer. Typically, this layer is a porous polymeric nature layer being made from a mechanically and thermally stable polymer such as polysulfone (PSf) or polyethersulfone (PES). Lastly, at the top layer is a thin film selective layer (Etxeberria-Benavides *et al.*, 2018)

The emerged of graphene oxide (GO) offers an opportunity as a new promising nanofillers in the selective layer of MMC membrane. Graphene-based materials have excellent mechanical strength, chemical ability, cost effective production and unique two-dimension structure consisting of a layer of bonded sp^2 carbon atoms arranges in hexagonal network structure (Zhu *et al.*, 2010). GO which is a derivative of graphene consists of oxygen functional groups on their basal planes and edges. In a previous work, GO was incorporated with PEBAX as the selective layer, supported by Psf porous membrane (Mohammed *et al.*, 2019). The GO was partially reduced prior to amination through GO thermal annealing method. The purpose partially reduction of GO (A-prGO) is to control the interlayer diameter of GO plates to par with dynamic diameter of the separated gases species. Besides, the aminated reduced graphene oxide (A-rGO) also been studied. The GO was fully reduced by heating during the amination process and characterized by the crystallinity and functional group studies. A porous Psf membrane supported the thin selective layer on-top through a dip-coating technique. This modification at the surface of GO with amines or amine-containing molecules via corresponding nucleophilic substitution reactions takes place easily. Zhao *et al.*, (2012) stated that, if polyamines covalently attach to GO layers, unreacted amine groups can react with CO_2 and have the potential in removing CO_2 in natural gas sweetening process. Additionally, studies have found that individual GO nanosheets is completely impermeable for gas separation due to high electron density

of the aromatic rings on the nanosheets (Nair and Wu, 2012). Currently, GO-polymer gas separation membranes have been fabricated via blending, interfacial polymerization or surface coating.

Although there have been several research breakthroughs regarding GO-polymer membrane, the main problem faced related to low gas permeability, which arises from the substantial resistance of microporous substrates (Kim *et al.*, 2014). On the other hand, the presence of oxygen-containing groups such as epoxy, hydroxyl, carboxyl and carbonyl group on the GO surface causing reducing agents react and create nano-sized pores. The reaction can be prevented by carried out the reaction with chemicals, either acids or bases (Rourke *et al.*, 2011).

In this work, amine functional group was incorporated with GO and used as nanofillers in PEBAX polymer matrix as selective layer of MMC membrane. The study of the fabricated membrane on the permeability and selectivity of also been conducted to identify the ideal AGO loading in membrane fabrication. Characterization on the structure and morphology of the membrane were identified using SEM and FTIR. The pure gas permeation properties of CO_2, CH_4 and N_2 at 25°C and pressure 4 bar.

1.3 Research Objective

Based on the problem statements, this study sets out with the following objectives:

(a) To study the effects and compatibility of amino functionalization and GO co-dispersion.

(b) To identify the effect of different nanofillers loading in fabrication of PEBAX/AGO properties and membranes performance.

1.4 Scope of Study

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

(a) Synthesizing GO from graphite via modified Hummer's method

(b) Functionalizing GO with amino groups under basic condition to obtain amino-functionalized GO (AGO) by using modified Bucherer's method.

(c) Characterize the chemical properties and crystallinity of modified nanofillers via Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscope (SEM) respectively.

(d) Preparing and fabricating PSf support membrane solution via phase inversion technique.

(e) Preparing dope solution suspension of PEBAX/AGO at 4wt% of PEBAX 1657 and different loading of AGO (0.25 wt%, 0.5 wt% and 0.75 wt%)

(f) Forming PEBAX solution with nanofillers atop of PSf support via dip coating method.

(g) Characterizing chemical properties, morphologies and surface roughness of MMM using FTIR and SEM.

(h) Evaluating the effects of nanofillers (AGO) incorporation loading on PEBAX formation and CO_2 separation performance using pure CO_2, N_2 and CH_4 feed stream gas.

1.5 Significance of Study

In this study, incorporation of amine group and graphene oxide into PEBAX polymer to fabricate membrane for gas separation is one of the new studies that become interest of research. Since GO have good affinity characteristics toward carbon

dioxide transportation, several modification and combination have been introduced to better gas separation technology. There are several studies regarding to aminated GO for gas separation. Therefore, this study is important in developing and exploring potential characteristics that provided by aminated graphene oxide in MMM for gas separation.

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