STUDY ON INCORPORATION OF GRAPHENE OXIDE (GO) IN POLYVINYL CHLORIDE (PVC) MIXED MATRIX MEMBRANE (MMM) TO ENHANCE CO_2/CH_4 SEPARATION

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We hereby declare that We have checked this thesis and, in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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The ingredients of success are hard work, determination and confidence in carrying out a task. This journey has been a challenging yet amazing one. Surely, it has moulded me into a better individual, as the saying goes, 'Life's all about leaving a legacy behind'.

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ABSTRAK

Metana, CH_4 berperanan unik sebagai gas rumah hijau dan sebagai komponen gas asli di mana pengurangan pelepasan CH_4 boleh memberi manfaat ekonomi, alam sekitar dan operasi yang besar. Teknologi membran adalah dinamik dan berkembang pesat dalam bidang pemisahan gas. Dalam proses pemisahan gas berasaskan membran, komponen dipisahkan dari campuran oleh perbezaan penepuan melalui membran. Campuran matriks membran (MMMs) terdiri daripada suatu fasa berterusan polimer dan fasa pengisi tersebar, mendorong ramai penyelidik untuk mencapai lebih tinggi kadar resapan gas dan selectivity. Polivinil klorida (PVC) adalah polimer yang fleksibel dan tahan lasak dengan baik mekanikal dan kimia kestabilan, termasuk segmen-segmen yang keras, yang membawa kepada gerakan segmen rendah dan kadar resapan yang rendah. Grafit oksida (GO) juga digunakan sebagai bahan tambahan dalam membran fabrikasi bagi meningkatkan ciri-ciri membran. Dalam kajian ini pemisahan gas menggunakan membran matriks campuran, gas CO_2 dan CH_4 digunakan. Objektif kajian ini adalah untuk menghasilkan MMMs PVC/GO, serta kajian menapis dan pengoptimuman parameter dengan menggunakan FFD, dan menggolongkan MMMs yang dihasilkan. Pembangunan daripada MMMs PVC/GO adalah berdasarkan 5 faktor, iaitu nisbah berat PVC, nisbah berat GO, tekanan (bar), jenis-jenis pelarut yang digunakan iaitu N, N-Dimetilmetanamida (DMF) dan N-metil-2-pyrrolidona (NMP), dan masa untuk MMMs rendam dalam pembekuan mandian (s) dengan menggunakan Reka bentuk kebolehupayaan pecahan 25. Membran PVC/GO dihasilkan dengan NMP atau elaun sebagai pelarut yang menurut diberi nisbah berat (wt.%) 20 % dan 15 % untuk PVC manakala, 2 % dan 4 % untuk pergi melalui songsangan fasa kering/basah, di mana rendaman membran mengikut masa 300 s atau 600 s, dan juga tekanan semasa gas permeasi 1 bar atau 3 bar. Kajian prestasi dijalankan dengan MMMs dihasilkan dengan alat permeasi gas tersebut menggunakan gas CO_2 dan CH_4. Berdasarkan ujian saringan, larian itu yang terdiri daripada faktor-faktor PVC 20 %, GO 4 %, 1 bar tekanan semasa gas tembusan, pelarut NMP dan rendaman selama 300 s, rancangan untuk mempunyai selektiviti tertinggi pada 26.09 yang terletak di atas garis batas dalam Robeson di Plot Ikatan Atas. Faktor Reka Bentuk Pecahan (FFD) telah digunakan untuk mengkaji minima dipengaruhi faktor semasa penyediaan MMMs. Faktor-faktor yang dikeluarkan adalah membran masa yang rendaman dalam air mandian (s), dan juga tekanan gas semasa ujian permeasi gas. Pengoptimuman yang menggunakan pusat komposit reka bentuk (CCD) dijalankan dan menunjukkan peningkatan dalam margin kesilapan di mana faktor-faktor 3 yang terbaik dengan sumbangan tertinggi kesan daripada pemeriksaan menunjukkan kesilapan kurang daripada 5 %, menunjukkan model yang Reka bentuk ujikaji yang boleh digunakan untuk ramalan selektiviti mana-mana syarat dalam skop kajian. Faktor-faktor yang digunakan untuk pengoptimuman larian adalah nisbah berat (wt.%) PVC dan pergi serta jenis pelarut (DMF atau NMP). Pengoptimuman ujian menunjukkan bahawa larian dengan selektiviti yang tertinggi di 50.94, dengan faktor PVC 20 %, pergi 4 % dan pelarut NMP. MMMs yang dihasilkan disifatkan menggunakan Mikroskop Elektron Pengimbas – Tenaga Pengasingan X-ray (SEM-EDX), Jelmaan Fourier Spektroskopi Inframerah (FTIR) dan Mikroskop Kuasa Atom (AFM). SEM yang menunjukkan MMMs yang mempunyai ketebalan 223 µm. EDX menunjukkan kewujudan unsur-unsur karbon (C), oksigen (O), dan klorin (Cl), di mana kedua-dua unsur yang boleh ditemui di PVC membuktikan kewujudan kumpulan fungsian PVC menurut dengan panjang gelombang yang berkuat masing-masing. AFM menunjukkan jurang min akar (RMS) untuk menjadi 97.86 nm iaitu di bawah 100 nm, di mana permukaan dianggap licin.

ABSTRACT

Methane, CH_4 unique role as a greenhouse gas and as the primary component of natural gas means that reducing CH_4 emissions can yield significant economic, environmental and operational benefits. Membranes is a dynamic and rapidly growing in the field of separation of gas. In membrane-based gas separation process, components are separated from their mixtures by differential permeation through membranes. Mixed matrix membranes (MMMs) comprise of a continuous polymer phase and a dispersed filler phase, are pursued by many researchers to achieve higher gas permeability and selectivity. Polyvinyl chloride (PVC) is a flexible and durable polymer with good mechanical and chemical stability, including hard segments, which leads to low polymeric chain segmental motion and low permeability. Graphene oxide (GO) was also employed as an additive in membrane fabrication in order to improve the membrane characteristics. In this study of gas separation using mixed matrix membrane, gases such as CO_2 and CH_4 are used. The objectives of this research were to synthesize MMMs PVC/GO, to screen and optimize parameters using FFD, and characterize the produced MMMs. The development of MMMs PVC/GO was based on 5 factors, which were the weight ratio of PVC of ratios 20 % and 15 %, weight ratio of GO of ratios 2 % and 4 %, pressure (bar) during single gas permeation of 1 bar or 3 bar, types of solvent used which were N, N-Dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP), and time for casted MMMs immersed in coagulation bath (s) at 300 s or 600 s, via dry/wet phase inversion method using DoE of 2^5 fractional factorial design. Performance study is carried out with produced MMMs with the gas permeation device, using CO_2 and CH_4 gas. Based on the screening tests, the run which was made up of factors PVC 20 %, GO 4 %, 1 bar of pressure during gas permeation, NMP solvent, and immersion time of 300 s, shows to have the highest selectivity at 26.09 which is above the upper bound lines in the Robeson's Upper bound plot. Fractional Factorial Design (FFD) was applied to reduce the number of influenced factors during MMMs preparation. Factors removed were the time membrane immersed in water bath (s), and also gas pressure during gas permeation test. Optimization using Central Composite Design (CCD) via Design Expert was carried out and showed an improvement in error margin where the best 3 factors with the highest effect contribution from screening indicated errors less than 5 %, indicating the model of the experimental design can be used for selectivity prediction of any condition in the scope of study. Factors used for optimization runs were the weight ratios (wt.%) of PVC and GO, and type of solvents (DMF or NMP). Optimization tests shows that the run with the highest selectivity at 50.94, with factors of PVC 20 %, GO 4 % and NMP solvent. The produced MMMs are characterized using Scanning Electron Microscope – Energy Dispersive X-ray (SEM – EDX), Fourier Transform Infrared Spectroscopy FTIR, and Atomic Force Microscope (AFM). SEM showed the MMMs had a thickness of 223 µm. EDX showed the presence of elements carbon (C), oxygen (O), and chlorine (Cl), where both elements can be found in PVC and GO, proving its presence. FTIR shows the presence of the functional groups of PVC and GO according to its respective wavelength. AFM shows the root mean square (RMS) to be 97.86 nm which is below 100 nm, where the surface is considered as smooth.

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LIST OF SYMBOLS

%	Percentage
wt%	Weight Percentage
ºC	Degree Celcius
P	Pressure
Q	Volumetric Flow
A	Surface Area
P	Permeability
l	Membrane Thickness
α	Selectivity
Δ	Delta
Å	Angstrom

LIST OF ABBREVIATIONS

6FDA-DAM	(4,4'-hexafluoroisopropylidene) – (N-methyl-α-β-dehydroalanine)
AC	Activated Carbon
AFM	Atomic Force Microscope
AFGO	Amine-Functional Graphene Oxide
Ar	Argon
C	Carbon
C-C	Carbon to Carbon Bond
C-H	Carbon to Hydrogen Bond
C-Cl	Carbon to Chlorine Bond
C-F	Carbon to Fluorine Bond
C=O	Carbon to Oxygen Double Bond
CA	Cellulose Acetate
CCD	Central Composite Design
CCVD	Catalyst Chemical Vapour Deposition
CMS	Carbon Molecular Sieve
CN	Cellulose Nitrate
CNF	Carbon Nanofibre
CE	Cellulose Ester
CH_4	Methane
CO_2	Carbon Dioxide
CO	Carbon Monoxide
Cys	Cysteine
DAT	Diamine Toluene
DIPS	Diffusion-Induced Phase Separation
DMA	Dimethylacetamide
DMF	N, N-Dimethylformamide
DMS	Dimethylsulfide
DOE	Design of Experiment
EDX	Energy Dispersive X-ray

FS	Fumed Silica
FFD	Fractional Factorial Design
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GO	Graphene Oxide
HE	Helium
HF	Hollow Fiber
HFP	Hexafluoropropylene
HG	Mercury
H_2	Hydrogen
H_2S	Hydrogen Sulphide
HFP	Hexafluoropropylene
IMGO	Imidazole Functionalized Graphene Oxide
LS	Light Scattering
LT	Light Transmission
M-PVDF	Modified Polyvinyldifluoride
MF	Microfiltration
MMM	Mixed Matrix Membrane
MOF	Metal Organic Framework
MWCNT	Multiwalled Carbon Nanotubes
NF	Nanofiltration
NH_2	Amino
NIPS	Nonsolvent-Induced Phase Separation
NMP	N-Methyl-2-Pyrrolidone
N_2	Nitrogen
O_2	Oxygen
-OH	Hydroxyl Group
O-MMT	Organic Montmorillonite
PA	Polyamide
PAN	Polyacrylonitrile
PE	Polyethylene
PEST	Polyester
PCM	Phase Contrast Microscopy

PI	Polyimide
PP	Polypropylene
PDADMAC	Poly (Diallyldimethylammonium chloride)
PDMS	Polydimethylsiloxane
PEBAX	Poly (Ether-B-Amide)
PEG	Poly (Ethyleneglycol)
PEGMA	Poly (Ethyleneglycol) Methyl Ether Methacrylate
PEI	Polyethylenimine
PES	Polyethersulfone
PFMD	Perfluoromethyldecalin
PFMMD	Poly (Perfluoro 4-Methyl-2-Methylene-1,3-Dioxolane)
PNC	Porous nanocrystalline
POSS	Polyhedral Oligomeric Silsesquioxane
PPO	Polyphenylene Oxide
PPSU	Polyphenylsulfone
PS	Polysulfone
PVA	Polyvinylacetate
PVC	Polyvinylchloride
PVDF	Polyvinyldifluoride
PVP	Polyvinyl Pyrrolidone
Ra	Average Roughness
RIPS	Reaction-Induced Phase Separation
RMS	Root-mean-square
RSM	Response Surface Methodology
Rt	Peak to valley
S	Silicone
SAPO	Silico-alumino-phosphate
SAXS	Small Angle X-Ray Scattering
SWCNT	Single-walled Carbon Nanotubes
SIPS	Solution-Induced Phase Separation
SEM	Scanning Electron Microscope
SPEEK	Sulfonated Polyether Ether Ketone
TEM	Transmission Electron Microscopy

TEOA	Triethanolamine
TEPA	Tetraethylene pentamine
TFCM	Thin film composite membrane
THF	Tetrahydrofuran
TiNT	Titanium oxide nanotubes
TIPS	Thermally-Induced Phase Separation
TMC	Trimesoyl Chloride
TR	Thermally Rearranged
VIPS	Vapor-Induced Phase Separation
VMD	Vacuum Membrane Distillation
XRD	X-ray Diffraction
ZSM	Zeolite Socony Mobil

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