



UNIVERSITI PUTRA MALAYSIA

***PREPARATION AND CHARACTERIZATION OF POLYSULFONE
MEMBRANES FOR SEPARATION OF CARBON DIOXIDE AND
METHANE***

POURYA MORADIHAMEDANI

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METHANE**

By

POURYA MORADIHAMEDANI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of
Doctor of Philosophy**

July 2014

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Abstract of thesis presented to the notes of Universiti Putra Malaysia for the degree of
Doctor of Philosophy

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July 2014

Chairman : Nor Azowa Ibrahim, PhD

Faculty : Science

A wide variety of applications are available for gas separation, including physical and chemical adsorption. Currently, membrane processes are considered as promising technology for gas separation because of its simplicity, i.e. no absorbent, which has to be regenerated, low capital cost, less space requirement, environmental friendliness, and low energy consumption. There are several applications for gas separation membranes such as hydrogen/carbon dioxide separation, oxygen/nitrogen separation, carbon dioxide/methane separation, natural gas separation, vapor/vapor separation, and dehydration of air. Since, CO₂ possesses the most greenhouse effect, CO₂ removal is more attractive among other gas separation processes by polymeric membrane. Furthermore, CO₂ removal can be taken into account for natural gas upgrading and enhanced oil recovery.

In this study, flat sheet membranes were prepared by wet/wet phase inversion technique. The membranes were prepared by contacting wet polymer film with two non-solvent baths in the series. The first coagulation bath which was containing different alcohols such as ethanol, propanol and isopropanol was employed to obtain a concentrated layer of polymer at the interface. This step makes the ultra-thin surface layer. The purpose of second bath (distillate water) is the actual coagulation and formation of the final film. In order to investigate the morphology of the membranes and evaluate nanoparticles distribution and agglomeration in polymer matrix, cross section micrographs were taken with scanning electron microscopy. Variations in surface roughness parameters of prepared membranes were studied by atomic force microscopy. The chemical interaction concerning polysulfone as base polymer and other fillers was evaluated by Fourier transform-infrared spectroscopy. Energy dispersive X-ray analysis was also conducted to confirm dispersion of nanoparticles on the surface layer of prepared membrane. Thermal gravimetric analysis was conducted for identification of any variations in thermal properties of

membranes before and after cross-linking with a heating rate of 10 °C/min from room temperature up to 700 °C.

In this research five different membranes have been prepared and characterized for CO₂/CH₄ separation including polysulfone/polyvinylpyrrolidone (PSf/PVP) blend membranes, symmetric and asymmetric pure PSf membranes, PSf/zinc oxide (ZnO) nanoparticle mixed matrix membranes, PSf/titanium dioxide (TiO₂) mixed matrix membranes and novel PSf/chitosan composite membrane. Since, pure PSf membranes have numerous macro-voids at its structure, both CO₂ and CH₄ molecules can pass through the membrane easily. Nonporous fillers (ZnO and TiO₂) can improve the separation properties of the resultant mixed matrix membranes by decreasing the diffusion of larger molecules. Moreover, the hydroxyl functional groups on the surface of these nanomaterials (polar surface, which is resulted from ZnO and TiO₂ interactions with water molecules) may interact with CO₂ by hydrogen bonding and thus improve the penetrant solubility in the resulting mixed matrix membranes. In the case of polysulfone chitosan composite membrane, since pure PSf membrane has very thin active layer which is not able to separate CO₂ from CH₄, chitosan was applied as a top layer. Chitosan was able to improve the membrane performance because of its OH functional groups which interact with CO₂ and improve CO₂ permeability through the membrane. Also, the SEM photographs demonstrated a dense top layer of chitosan formed in PSf/chitosan composite membrane improving the resistance of membrane against larger molecules (CH₄) and enhance the separation performance of membrane.

Accordingly, PSf/PVP 10 wt.%, PSf/TiO₂ 3 wt.% and PSf/Chitosan 30µm were able to separate CO₂ from CH₄ completely. Furthermore, PSf/PVP 10wt.% which has 70 GPU CO₂ permeability at 3 bar feed pressure has the highest performance (high gas permeance and selectivity) among the prepared membranes.

Abstrak tesis dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENYEDIAAN DAN PENGKELASAN MEMBRAN POLISULFON BAGI PEMISAHAN KARBON DIOKSIDA DAN METANA

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Pelbagai aplikasi yang meluas terdapat bagi pemisahan gas, termasuklah penjerapan fizikal dan kimia. Kini, proses membran telah dikenalpasti sebagai satu teknologi yang menyakinkan bagi pemisahan gas disebabkan keringkasannya, i.e. tiada penyerap yang mana perlu dijana semula, kos modal yang rendah, keperluan ruang yang sedikit, mesra alam dan penggunaan tenaga yang rendah. Terdapat beberapa aplikasi bagi pemisahan gas membran seperti pemisahan hidrogen, pemisahan oksigen/nitrogen, pemisahan karbon dioksida/metana, pemisahan gas asli, pemisahan wap/wap dan dehidrasi udara. Oleh kerana CO₂ adalah memberi kesan kepada rumah hijau yang paling signifikan, mengeluarkannya adalah sangat penting berbanding kepada proses pemisahan gas yang lain dengan membran polimerik. Tambahan lagi, pembuangan CO₂ boleh diambil kira bagi penambahsuaian gas asli dan menambah pemulihan minyak. Dalam kajian ini, membran kepingan rata telah disediakan dengan teknik inversi fasa basah/basah, di mana membran telah disediakan dengan menyentuh filem polimer basah dengan dua rendaman tanpa pelarut dalam turutan. Bagi rendaman penggumpalan yang pertama, yang mengandungi pelbagai alkohol seperti ethanol, propanol dan isopropanol telah digunakan untuk mendapatkan kepingan polimer pekat yang sangat nipis pada permukaan. Tujuan bagi rendaman kedua (air suling) sebenarnya adalah penggumpalan dan pembentukan filem yang terakhir. Bagi kajian morfologi membran dan taburan nano partikel serta penggumpalan dalam matrik polimer, mikrograf keratan rentas telah diambil dengan mengimbas menggunakan elektron mikroskop. Variasi dalam parameter kekasaran permukaan bagi membran tersedia telah dikaji dengan mikroskopi tenaga atomik. Interaksi kimia antara polisulfon sebagai polimer asas dan pengisi yang lain telah dinilai dengan spektroskopi infra merah pengubah Fourier. Analisis tenaga menyebarkan X-ray telah dijalankan bagi mengesahkan penyebaran bagi partikel nano ke atas permukaan lapisan membran yang telah disediakan. Analisis terma gravimetrik telah dijalankan bagi mengenalpasti sebarang variasi dalam sifat thermal membran sebelum dan selepas rangkaian terbenluk dengan kadar pemanasan bagi 10 °C/min daripada suhu bilik kepada 700 °C.

Dalam kajian ini, lima membran berbeza telah disediakan dan dikelaskan kepada pemisahan kepada CO₂/CH₄ termasuklah campuran membran Polisulfon/polivinilpirrolidon (PSf/PVP), simetri dan assimetri tulen membran PSf, campuran nano partikel matriks membran PSf/zink oksida (ZnO), PSf/titanium dioksida (TiO₂) bercampur membran matrik dan novel komposit membran PSf/chitosan. Oleh kerana, membran PSf tulen mempunyai banyak lubang makro pada struktur, kedua-dua CO₂ dan molekul CH₄ boleh melalui membran dengan mudah. Pengisi tidak telap (ZnO dan TiO₂) boleh meningkatkan sifat-sifat pemisahan membran paduan matriks bercampur dengan mengurangkan resapan molekul yang lebih besar. Selain itu, kumpulan hidroksil berfungsi pada permukaan nanobahan ini (permukaan kutub, yang menyebabkan dari ZnO dan TiO₂ interaksi dengan molekul air) juga berinteraksi secara ikatan hidrogen dengan gas CO₂ dan dengan itu meningkatkan kelarutan bahan penusuk dalam membran matriks campuran. Bagi kes polysulfon kitosan membran komposit, oleh kerana membran PSf tulen mempunyai lapisan aktif yang sangat nipis maka tidak dapat memisahkan CO₂ daripada CH₄, oleh itu kitosan telah digunakan sebagai lapisan atas. Chitosan dapat meningkatkan prestasi membran kerana kumpulan berfungsi OH berinteraksi dengan gas CO₂ dan meningkatkan ketelapan CO₂ melalui membran. Selain itu, gambar-gambar SEM menunjukkan lapisan tebal kitosan ditubuhkan pada PSf/membran komposit kitosan meningkatkan rintangan membran terhadap molekul yang lebih besar (CH₄) dan meningkatkan prestasi pemisahan membran.

Oleh itu, PSf/PVP 10 wt.%, PSf/TiO₂ 3 wt.% dan PSf/Chitosan 30µm mampu untuk memisahkan sepenuhnya CO₂ daripada CH₄. Tambahan lagi, PSf/PVP 10wt.% yang mempunyai 70 GPU CO₂ kebolehtelapan pada 3 bar kawalan tekanan pada prestasi yang tertinggi (gas yang tinggi telapan dan pemilihan) dikalangan membran tersedia.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of Supervisory committee were as follows:

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LIST OF ABBREVIATIONS

PSf	Polysulfone
PVP	Polyvinylpyrrolidone
PDMS	Polydimethylsiloxane
PVA	Polyvinyl alcohol
PES	Polyethersulfone
PA	Polyamide
PAN	Polyacrylonitrile
PI	Polyimide
CA	Cellulose acetate
NMP	1-methyl-2-pyrrolidone
DMAc	N-N-dimethyl-acetamide
DMF	Dimethylformamide
THF	Tetrahydrofuran
EtOH	Ethanol
PrOH	Propanol
IPA	Isopropyl alcohol
BuOH	Butanol
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
AFM	Atomic force microscopy
FT-IR	Fourier transform-infrared spectroscopy
DSC	Differential scanning calorimetry
TGA	Thermal gravimetric analysis
EDX	Energy dispersive X-ray
MMMs	Mixed matrix membranes
M _n	Number average molecular weight
MOFs	Metal organic frameworks
ZIF-90	Zeolitic imidazolate framework-90
CMS	Carbon molecular sieves
PBI	Polybenzimidazole
PAI	Poly amide-imide

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Membrane process technology has a promising future in the petrochemical, refining, and natural gas industries. One important part of separation is the purification of CH₄ from CO₂. There are more than 20 trillion standard cubic feet of natural gas produced in the USA yearly, and nearly 20% of that gas requires major treatment. CO₂ separation is a significant industrial procedure because around 70% of natural gas containing CO₂. Present pipeline specifications of US command that CO₂ content be less than 2%. In higher contents, it leads to corrosion of pipeline and reduces the natural gas calorific value. Conventional techniques for CO₂ separation are based on reversible absorption, such as amine scrubbing, but these methods are high energy demanding and cause environmental concerns. The advantages of gas separation by membrane technology over traditional methods include ease of function, low-energy required, and environmental friendliness. Table 1-1 presents established applications in the field of gas separation by membrane technology (Baker., 2011). However, low gas permeance and selectivity of present commercial polymeric membranes are important concern of this technology to process large volumes of gas. Any improvement in membrane separation efficiency could lead to important financial savings and further applications of membrane systems in gas separation. Even with decades of research on this subject, today there are less than 10 various types of polymers applied for commercial gas separation.

With the intention of being commercially competitive, new membrane materials must provide considerable improvements in CO₂ permeance and CO₂/CH₄ selectivity compared to existing techniques. Sophisticated membranes must have brilliant thermal and chemical stability, resistance to aging and plasticization (for polymeric membranes), low capital cost, and ease of scale-up and less space requirement. Current membrane systems for CO₂/CH₄ separation can be divided into three categories: polymeric, composite and mixed matrix membranes.. Polymeric membranes include membranes composed of polymers and polymer blends. Composite membrane includes two different layers (support and surface layer) which each one prepared by different polymers. Support layer usually does not provide any resistance for gas as permeate. While, the surface layer is responsible for separation of gases and just allow to a specific molecule of gas to pass through itself. Mixed matrix membranes include organic–inorganic that consist of an inorganic phase integrated into a continuous polymer matrix (Baker., 2011).

Organic polymers are the most extensively used materials in preparation of membrane for gas separation. Polymers can be divided into two main categories; those functioning above their glass transition temperature (rubbery polymers) and those working below their glass transition temperature (glassy polymers). Glassy polymers are able to effectively separate molecules based on small differences in molecular dimensions. They are innately more size and shape selective than rubbery polymers and therefore better suited for CO₂ separation.

Table 1-1: Gas membrane applications and suppliers.

Gas separation	Application	Suppliers
O ₂ /N ₂	Nitrogen generation Oxygen enrichment	A/G technology Permea Generon IMS Medal Aquilo Ube
H ₂ /Hydrocarbons	Refinery hydrogen	Air products Air liquid Praxair
H ₂ /CO	Syngas ratio adjustment	as above
H ₂ /N ₂	Ammonia purge gas	as above
CO ₂ /Hydrocarbons	Acid gas treating Enhanced oil recovery Landfill gas upgrading	Kvaerner Air products Ube
H ₂ S/Hydrocarbons	Sour gas treating	As above
H ₂ O/Hydrocarbons	Natural gas dehydration	Kvaerner Air products
H ₂ O/Air	Air dehydration	Air products Ube
Hydrocarbons/Air	Pollution control Hydrocarbon recovery	MTR, GMT, NKK
Hydro carbons from process streams	Organic solvent recovery Monomer recovery	MTR, GMT, SIHI

$$1 \text{ Barrer} = 1 \times 10^{-10} \left[\frac{\text{cm}^3 \text{ cm}}{\text{cm}^2 \text{ s cm hg}} \right] = 3.35 \times 10^{-10} \left[\frac{\text{mol}}{\text{m}^2 \text{ s Pa}} \right]$$

$$1 \text{ GPU} = 1 \times 10^{-6} \left[\frac{\text{cm}^3 \text{ cm}}{\text{cm}^2 \text{ s cm hg}} \right]$$

The easiest model applied to clarify and predict gas permeation through non-porous membranes is defined as the solution-diffusion model. Based on this mechanism, the permeants dissolve into the polymer matrix at the upstream face (high pressure), afterward diffuse through the polymer film and lastly desorb from the downstream side. Gases with a larger molecular diameter diffuse slower across the prepared membrane. It is further assumed that sorption and desorption at the interfaces is fast compared to the diffusion rate in the polymer. The gas phase on the high and low pressure side is in equilibrium with the polymer interface. The combination of Henry's law (solubility) and Fick's law (diffusion) leads to the equation

$$J = \frac{D S \Delta p}{l} \quad (1.1)$$

which can be simplified to

$$J = \frac{P \Delta p}{l} \quad (1.2)$$

where D is the diffusion coefficient of the gas in the polymer, S is the gas solubility, Δp is the pressure difference between the high and low pressure side, l is the membrane thickness and P is the permeability coefficient. As can be seen from (1) and (2) the permeability coefficient P is the product of D (a kinetic term) and S (a thermodynamic term).

$$P = D S \quad (1.3)$$

The selectivity of a polymer to gas A relative to another gas B can be expressed in terms of an ideal selectivity α_{AB} defined by the relation

$$\alpha_{AB} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \frac{S_A}{S_B} \quad (1.4)$$

1.2 Research approach

Today's industrial production and infrastructure in the world are based on fossil fuel use, which is related directly to the generation of energy. Thus, it is believed that the combustion of fossil fuels and other human activities are the reasons for the increased concentration of greenhouse gases all over the world. Carbon dioxide (CO_2) is one of the largest contributors to global warming. Therefore, its capture from different sources such as power stations, oil refineries and large cement works is very important. Another separation problem is the presence of CO_2 in natural gas, where it causes reduction of the heating value and waste of pipeline capacity. According to these problems which mentioned above, in this study we focused on preparation of polysulfone based membrane for separation of CO_2 from CH_4 .

Polysulfone (PSf) is selected for gas separation due to satisfactory gas permeance and acceptable selectivity. PSf is an amorphous thermoplastic polymer with glass transition temperature of 190°C . This is a flame retardant polymer, possesses high mechanical, thermal and oxidative stability and is soluble in common organic solvents. Preparation of PSf membranes by phase inversion is a well-known process.

Moreover, its relative low cost established PSf as the polymer in choice for fabrication of membranes. In this research, the solvents are different organic non-aqueous solutions such as NMP, DMAc, DMF, THF and CHCl_3 . Solvents were used to dissolve PSf beads and prepare casting solutions. Whereas, non-solvents are aqueous solutions such as distilled water, EtOH, PrOH, IPA and BuOH. The main role of non-solvent is phase inversion of wet film from liquid to solid. Accordingly, non-solvents act as coagulators.

In this study we investigated the performance and morphology of pure PSf membrane, PSf/polyvinylpyrrolidone (PVP) blend membrane, PSf/ZnO and PSf/TiO₂ mixed matrix membrane and PSf/chitosan composite membrane. Therefore, three different types of membrane were studied in this research such as: polymeric membrane, mixed matrix membrane and composite membrane. All prepared membranes in this research were applied for separation of CO₂ from CH₄. Different effective variables were investigated in this study such as: polymer concentration, thickness of membrane, type of solvent, type of coagulation bath, type of nanoparticles which were used for preparation of mixed matrix membranes, concentration of additive in blend membranes, thickness of active layer and concentration of coating solution in composite membranes. Moreover, the methods of membrane preparation were aimed to reach full separation of CO₂ from CH₄. This investigation has been motivated in improving the gas transport properties of polymeric membranes by a combination of nanoparticles such as ZnO and TiO₂. In this approach, using properties of both the organic and inorganic phase, a membrane with good permeability, selectivity, mechanical strength, and thermal, chemical stability and processibility can be prepared.

The effect of the inorganic dispersed phase on the mixed matrix membrane properties is related to its chemical structure, surface chemistry and the type of particles. The inorganic materials used for MMMs can be classified into porous and nonporous types. The effect of porous fillers on the mixed matrix membrane is different from nonporous inorganic fillers and can be related to their structure and their pore size. Generally, porous fillers act as molecular sieving agents in the polymer matrix and separate gas molecules by their shape or size. Due to their concise apertures, porous inorganic particles have usually high permeability and selectivity which is above the Robeson upper bound. Therefore when these highly selective porous fillers are added to the polymer matrix, they selectively allow the desired component to pass through the pores and thus a mixed matrix membrane, whose selectivity is higher than that of the neat polymeric membrane, can be obtained (Aroon et al., 2010).

In contrast, nonporous material fillers (ZnO and TiO₂) can improve the separation properties of the resultant mixed matrix membranes by decreasing the diffusion of larger molecules. Moreover, the hydroxyl functional groups on the surface of these nanomaterials (polar surface which is resulted from ZnO and TiO₂ interaction with water molecules) also interact with CO₂ and thus improve the penetrant solubility in the resulting mixed matrix membranes. In addition, nano-scale inorganic materials may disrupt the polymer chain packing and increase the free volume between polymer chains and thus increase gas diffusion (Aroon et al., 2010).

Customary polymeric membranes operated for CO₂ removal are prepared from a single polymer, such as cellulose acetate, cellulose triacetate or polyimide. These traditional membranes have a significant problem regarding to the trade-off relationship between permeability and selectivity suggested by Robeson (Cai et al., 2008), which signifies that a high permeability rate as well as high selectivity are hardly achieved at the same time (Cai et al., 2008). Luckily, the upper bound between permeability and selectivity might be improved by composite membranes, because they usually have both high permeability and selectivity (Kim et al., 2004). Composite membranes are usually considered as a type of polymeric membrane for gas separation which is fabricated from thin selective surface layers on the porous support layer. The combination of top and support layers reduces the thickness of the final prepared membrane without affecting the membrane mechanical strength (Madaeni et al., 2013). There are several factors which affect the composite membrane performance during the gas separation process including support top layer component, coating methods, and preparation conditions. In composite membrane, the porosity of support layer should be high to avoid additional mass transfer resistance against the permeate components. Moreover, the active layer should provide the selectivity for the desired gas (Madaeni et al., 2013). Since chitosan has OH functional group in its structure, can have interaction with CO₂ and improve the CO₂ permeability through the membrane. Chitosan which is the second most plentiful biopolymer in nature is a linear polymer primarily of glucosamine. This polymer is the N-deacetylated product of chitin, a natural polymer that can be extracted from outer shells of crustaceans which has been considered as one of the most promising materials due to its biodegradability, biocompatibility and non-toxicity (Tsai et al., 2006, Chen et al., 2007, Kumar et al., 2004, Padaki et al., 2012).

1.3 Objectives

Since pore size, thickness of top layer and thickness of membrane are the most important parameters for gas separation, in this study we aimed to prepare PSf based membranes with proper characteristics for gas separation. In this regards, PVP and two different nanoparticles such as ZnO and TiO₂ were added to the casting solution separately. Furthermore, chitosan was applied as a top layer for preparation of PSf composite membrane. The main objectives of this research are:

1. To prepare PSf/PVP blend membrane and study the effect of addition of PVP with different concentrations to the casting solution on membrane morphology and performance.
2. To fabricate high selective symmetric and asymmetric pure PSf membrane and investigate the influence of type of solvent and non-solvent (coagulation bath) on structure and gas separation properties of prepared membranes.
3. Preparation and characterization of novel polysulfone/zinc oxide (PSf/ZnO) mixed matrix membranes (MMMs) with different ZnO loadings for high selective CO₂/CH₄ separation.
4. To fabricate polysulfone (PSf)-based mixed matrix membranes (MMMs) with the incorporation of titanium dioxide (TiO₂) nanoparticles for separation of CO₂ from CH₄.
5. To study the influence of membrane preparation parameters on structural morphology and performance of polysulfone (PSf)/chitosan composite membrane for gas separation. Asymmetric PSf flat sheet membranes were composed by phase inversion method and used as supports. PSf composite membranes were fabricated

by coating chitosan as selective layer on the top surface of support by film casting and dip-coating techniques.



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