EFFECT OF DIFFER DEVELOPMENT OF
POLYETHERSULFON ES (MMMs) FOR O_2/N_2

MOHD KHAIRUL ANUAR BIN MAMAT

A thesis submitted in fulfillment
of the requirements for the award of the Degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

JULY 2012

ABSTRACT

Mixed matrix membrane (MMM) is a new class of membrane materials that offers the significant potential in advancing the current membrane-based separation technology. As an attractive material that demonstrates outstanding separation properties, MMM has been the subject of worldwide academic studies conducted by many researchers especially those related to membrane technology. In this study, MMMs were prepared from polyethersulfone (PES) containing embedded with two different inorganic fillers such as zeolite 4A and carbon molecular sieve. The effect of different inorganic filler was studied in order to identify the suitable types of inorganic filler and the performance of MMM membranes. The polymer solution contains Polyethersulfone (PES) as the polymer, N-Methyl Pyrrolidone (NMP) as the solvent and distilled water (H_2O) as the non-solvent. The zeolite concentration valued 25 wt % was applied. To increase the compatibility of zeolite with the polymer, 3-Aminopropyl-Trimethoxysilane (APTMOS) was used to treat the zeolite prior to dope formulation to modify the zeolite surface. For both membranes, the dry/wet phase inversion method was used to produce the asymmetric flat sheet membrane. The prepared membrane was coated with silicone and N-Hexane to decrease the surface defect of the membrane. In order to determine the membrane performance, the membranes were tested using O_2 and N_2 as the test gases using permeability test rig. The surface and cross section image of the prepared membrane was identified by using Scanning Electron Microscope (SEM). The results show that the MMMs with CMS had the highest selectivity of 3.61 while the zeolite MMMs selectivity is 1.44 and the optimum pressure was found at 3 bar. As a conclusion the CMS particles discussed in this paper seemingly offer several advantages over zeolites as possible molecular sieving entities for incorporation into mixed matrix membranes.

ABSTRAK

Membran matriks campuran (MMM) adalah kelas baru bahan membran yang menawarkan potensi yang besar dalam memajukan pemisahan membran berasaskan teknologi semasa. Sebagai bahan yang menarik yang menunjukkan pemisahan yang cemerlang, MMM telah menjadi subjek kajian di seluruh dunia akademik yang dijalankan oleh ramai para penyelidik terutama yang berkaitan dengan teknologi membran. Dalam kajian ini, MMMs telah disediakan dari polietersulfon (PSB) yang mengandungi mengandungi dua pengisi yang berbeza tak organik seperti 4A zeolit dan karbon molekul ayak. Kesan pengisi bukan organik yang berbeza telah dikaji untuk mengenal pasti kesesuaian jenis pengisi bukan organik dan prestasi membran MMM. Penyelesaian polimer mengandungi polietersulfon (PSB) sebagai polimer, N-Methyl Pyrrolidone (NMP) sebagai pelarut dan air suling (H_2O) sebagai bukan-pelarut. Kepekatan yang zeolite bernilai 25% berat telah digunakan. Untuk meningkatkan kesesuaian zeolit dengan polimer, yang-Trimethoxysilane 3-Aminopropyl (APTMOS) telah digunakan untuk merawat zeolite sebelum kepada pembentukan narkose untuk mengubah suai permukaan zeolite. Bagi kedua-dua membran, kaedah fasa balikan kering / basah telah digunakan untuk menghasilkan membran kunci rata asimetri. Membran bersedia telah disalut dengan silikon dan N-Heksana untuk mengurangkan kecacatan permukaan membran. Untuk menentukan prestasi membran, membran telah diuji dengan menggunakan O_2 dan N_2 sebagai gas ujian menggunakan pelantar ujian kebolehtelapan. Imej permukaan dan keratan rentas membran yang disediakan telah dikenal pasti dengan menggunakan Mikroskop Imbasan Elektron (SEM). Hasil kajian menunjukkan bahawa MMMs dengan CMS mempunyai kepilihan tertinggi 3,61 manakala selektiviti MMMs zeolit adalah 1,44 dan tekanan yang optimum telah dijumpai pada 3 bar. Sebagai kesimpulan zarah CMS yang dibincangkan dalam kertas ini seolah-olah menawarkan beberapa kelebihan lebih zeolit sebagai entiti mungkin pengayakan molekul untuk dimasukkan ke dalam membran matriks bercampur.

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Abbreviations

CO_2 - Carbon Dioxide

H_2 - Hydrogen

MMMs - Mixed Matrix Membranes

AlO_4 - Aluminium Oxide

SiO_4 - Silicone Oxide

O_2 - Oxygen

N_2 - Nitrogen

NH2 - Amino Group

SEM - Scanning Electron Microscopic

GS - Gas Separation

H_2O - Water

PES - Polyethersulfone

NMP - 1-methyl-2-pyrrolidone

APTMOS - 3-Aminopropyl- Trimethoxysilane

UK - United Kingdom

GPU - Gas Permeation Unit

MW - Molecular Weight

Vt% - Weight percentage
C - Degree celcius

/V - Volume over volume total

TP - Standard Pressure and Temperature

arameters/Symbols

- Overall permeability

$_c$ - Permeability of the continuous polymer phase ($\frac{cm^3}{cmHg\ s\ cm^2}$)

$_d$ - Permeability of the dispersed zeolite phase ($\frac{cm^3}{cmHg\ s\ cm^2}$)

- Selectivity (Unitless)

- Flow rate of gas species (cm^3/s)

- Area of membrane (cm^2)

P - Pressure difference across membrane (cm Hg)

- Charge balancing cation

- cation valence

- Moles of water contained in the zeolitic voids

Å - Amstrong

m - Micrometer

m - Centimeter

% - Percentage

Kg - Kilogram

g - Gram

M_i - Molecular weight species i (g/mol)

η_i - Viscosity species i (µPa s)

σ_i - Collision diameter i (cm)

(P/*l*) - Pressure Normalized Flux (cm^3 (STP)/ cm^2. s. cmHg)

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays the cost of energy consumption and environment impact is great concern issue due to rapidly increasing of energy demand and green house gases impact on global climate mitigation. Compare to other membrane technologies like reverse osmosis and ultrafiltration, commercial gas separation using membrane is relatively new (Lonsdale, 1982). Gas separation membranes provide numerous of benefits over other gas separation technologies. This membrane technology has been applied commercially to separate individual components from mixtures of gases.

Polymeric materials have been extensively studied for gas separation (Koros *et al.,* 1993) there is a performance trade off between permeability and selectivity, which is evident for O_2/N_2 separation (Robeson *et al.,* 1991). For nearly a decade, incorporation of inorganic particles such as porous zeolites, carbon molecular sieves and nonporous silica into a polymer matrix has been conducted to advance the performance of gas separation membranes (Chung *et al.,* 2007) The goal in the development of ideal polymer/inorganic mixed matrix membranes (MMMs) is to improve both the permeability and selectivity, and overcome the limitation of the size sieving properties of the molecular sieving material [2].

In addition, membrane gas separation is a clean process and requires simple and inexpensive filtration. Among other membrane process, gas separation is also a foremost industrial process, which may perhaps engage enhancement of product streams, recovery of reactants, removal of impurities, and dehumidification of process streams.

Membrane separation processes have become one of the emerging technologies, which have undergone a rapid growth during the past few decades. Gas and liquid separation processes require a membrane with high permeability and selectivity (Ciobanu *et al.,* 2007). For this reason carbon molecular sieve and zeolites have been long known industrially and currently used as adsorbents in many adsorptive separations, their application in membrane processes is gaining increased research interest (Hennepe *et al.,*1987) Zeolite membranes have also been used for evaporation both industrially and in laboratory studies.

Incorporation of inorganic particles or fillers into polymeric materials has been examined for many applications. These applications use such fillers to enhance the mechanical properties of the original polymer matrix and more recently to improve the separation properties over those of the polymer material for liquid separations or evaporation. For example, inorganic fillers or fibers, such as metal or silica particles, have been integrated into polymers to increase the mechanical strength and toughness for industrial materials (Rong *et al.,* 2000) and for liquid separation (reverse osmosis, ion exchange, etc.) membranes (Solenberger *et al.,* 1982).

In gas separation technology, membrane has a wide range application include the permeation process through membrane. Permeation process becomes one of the fastest growing in the gas separation technology. The most widely used materials for gas separation are polymer. The limitation on the trade-off between permeability and selectivity influence the expanding application of membrane based gas separation in term of energy and capital cost *(Li et al., 2008).* The difference in permeability is resulted from diffusivity difference and from the physicochemical interactions between polymer matrixes.

To overcome the limitation in the membrane gas separation, mixed matrix membranes have been marked as an alternative approach to reach the higher selectivity. Mixed-matrix membranes (MMMs) are based on polymeric membranes filled with inorganic particles as a means to improve their gas separation performance (Duval *et al.*, 1994).

1.1 Problem Statement

There are a lot of gas separation technology develop in the recent year. One of them is by using membranes. The difficulties in the development of gas separation membranes are to achieve higher performance and higher selectivity. They are used the new alternative which is able to overcome the problem which are mixed matrix membranes (MMMs) (Aroon *et al.,* 2010). The previous research reported that in the development of Polyethersulfone MMMs, there are a lot of factors that affect the performance of gas separation such as weak contact of particles in the polymer matrix and poor distribution of dispersed phase in the continuous polymer matrix phase (Aroon *et al.,* 2010).There are some inorganic membranes, such as zeolites and carbon molecular sieves membrane that offer much higher permeability and selectivity. Therefore, it remains highly desirable to provide high performance PES membrane for O_2/N_2 separation. This study will focused on development MMMs using two different types of inorganic filler and comparing their separation performance.

1.2 Objectives of the Study

a) to develop PES MMM using phase inverse technique
b) to study the effect of different inorganic filler in development of PES MMMs
c) to identified the membrane morphology and performance

1.3 Scopes of the study

There are several scopes related to this research which are:

a) Preparation of two different types MMMs membrane which are:
    i. First, MMMs using Carbon Molecular Sieves as inorganic filler.
    ii. Second, MMMs using Zeolites 4A as inorganic filler.

b) Identified the effect of coating agent to the membrane performances.
c) Characterize the membranes morphology by using Scanning Electron Microscopy (SEM).

1.4 Rationale and Significance

The higher selectivity of membrane is the goal of membrane separation process (Baker, 2000). Thus, the different types of inorganic filler preparation of dope solution are important in the development of PES MMMs performance. The different dope solution will give the different result where the selectivity and the permeability of the membranes will be different. Therefore, this research must be done to find the effect of different inorganic filler and the performance of PES membrane. The better distribution of inorganic filler (zeolites and carbon molecular sieve) in the polymer solution will increase the selectivity of the gas separation. Actually, Carbon molecular sieves (CMS) can offer simultaneously high permeabilities and selectivities (Koros *et al.,* 1996). Their porous morphology and the presence of shape and size selective pores within this network enables very effective separation of gases compared to polymeric membranes. On the other hand, using these molecular sieves as dispersed entities in a mixed matrix membrane provides a very attractive alternative strategy (Zimmerman *et al.,*1998). Such an approach capitalizes on the superior separation properties of carbon membranes while potentially maintaining the superior processability typical of conventional membrane formation technology. In order to overcome the challenges, this research should be done on the development of PES MMMs performance, with different inorganic filler preparation of dope solution to have a higher potential to achieve high selectivity without decrease the permeability of gas.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Technology

Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components.

Membranes are being used to separate gases from their mixtures by the differential permeation of components through them. Polymeric membranes are the most popular membranes because of their high performance, easy synthesis, long life, good thermal stability, adequate mechanical strength and high resistance to gases and chemicals.

Membranes remain attractive opportunities for many gas separation industries natural gas processing, landfill gas recovery, olefin/paraffin separation, air separation, hydrogen recovery (Kesting *et. al,* 1993). Because of the economic competitiveness of the existing separation technologies and the present challenges of aggressive environments for membranes, many applications seek more robust membrane materials having higher selectivity's and permeability's. Not surprisingly, membrane materials development is an important research area to synthesize both higher performance and more durable membranes (Koros *et al.*, 1987).

The main advantages of membrane technology as compared with other unit operations in (bio) chemical engineering are related to this unique separation principle which is the transport selectivity of the membrane. Separations with membranes do not require additives, and they cabe performed isothermally at low temperatures compared to other thermal separation processes which is working on at low energy consumption. Also, upscaling and downscaling of membrane processes as well as their integration into other separation or reaction processes are easy.

2.1.1 Fundamentals of Membrane Technology

The growing significance of membrane and membrane process as efficient tools for laboratory and industrial scale mass separations is based on the several properties, characteristics off all membrane separation process, which make them superior to many conventional mass separation methods (Ghazali, 1997). An appreciable energy saving offered by membrane separation process regarding for replacing conventional technique process like distillation, cryogenic distillation, ion exchange and many more chemical treatment systems. Membrane separation system also offered greater flexibility in designing the systems itself while still produces high quality products. The application of the membrane itself (separation process) is part of in the daily life such as in chemical process. Chemical process, in general can be regarded, as a sequence of pretreatment step, a reaction step and a separation step, transforming the incoming raw materials (input) into the desired products (output) to fulfill the whole process. Engineering of chemical process is carried out in the framework of minimization of energy consumption and waste disposal.

Membrane come from Latin word that is membrane, membrane in a general definition is a selective layer between two phases. The membrane can be defined essentially as a barrier, which separate two phases and restricts transport of various substances in a selective manner. A membrane can be heterogeneous or homogenous, symmetric or asymmetric in structure, solid or liquid; can carry a positive or negative charge or be neutral or sometimes bipolar. A membrane separation system separates an influent stream into two effluent stream known as the permeate stream (low pressure side) and the retentate stream (high pressure side).The permeate is the portion of component has pass through the semi-permeable membrane whereas the retentate stream contains the component that have been rejected by the membrane.

In a membrane process, a membrane acts as a selective interphase between two bulk phases. By means of a driving force, some of the species from a multicomponent mixture are transported through the membrane into the other bulk phase while the membranes retain other components. Selective mass transport has occurred. Often a membrane, which has a sufficiently high selectivity, is accompanied by a low transmembrane flux and vice versa making highly selective membrane process too expensive. Membrane separation process enjoys numerous industrial applications such as environmentally benign and it also an appreciable energy savings technique.

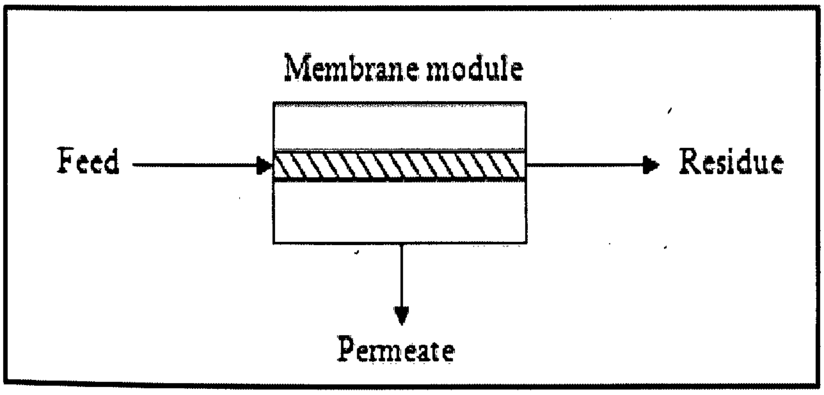

Figure 2.1: Schematic diagram of basic membrane for gas separation

Industrial process have a different mode of operation depends on the complexity of the process itself. The complexity of the process required the most advance separation tools. Membrane separation process may have different mode of operation, different structures used as separating barrier and different driving force used to transport the different chemical species but they actually posses several features in common which makes them very attractive as a separation tools.

Criteria for selecting membranes for a given application are complex, durability, mechanical integrity at the operating conditions, productivity and separation efficiency are important stipulation that must be balance in all cases (Koros, 1994). Of all these characteristics for a given membrane, selectivity or separation efficiency and permeation rate (productivity) is clearly the most basic. The higher the selectivity the more efficient the process, the lower driving force (pressure ratio) required to achieve a given separation and therefore, the lower the operating cost of the membrane system. The higher the flux the smaller the required membrane area and therefore the lower the capital cost of the membrane system (Koros, 2000).

Membrane and membrane separation process have been developed and optimized more than two decades even for industrial applications (Bruschke, 1995). Separation of various mixtures, especially organic liquid is a very necessary unit operation in a chemical industry. A large number of conventional techniques are available such as adsorption, cryogenic process, distillation, solvent extraction and fractional crystallization. A new method that can exceed this conventional method is offered by the application of the membrane itself By using membrane, conventional separation process can be done in ambient temperature (Weber and Waren, 1986).

Lately, membrane separation process has been widely used to replace common separation process that used high technology and also high in capital cost. Membrane systems offer a low capital cost investment; ease of operation, low energy consumption and moreover is space efficiency. Membrane process offers a wide range of application ranging from industrial applications such as gas separations to dairy products. The demand and the driving force for the wide application of membrane itself offer the potential of this research to be done. Membrane separation process can be described as in **Table 2.1**.

Table 2.1: Membrane Separation Process

Membrane Process	Physical state Feed/Permeate	Driving Force	Separation Mechanism	Application (Separation of)
Microfiltration	Liquid/liquid	Pressure (10-100kpa)	Sieving	Suspended materials
Ultrafiltration	Liquid/liquid	Pressure (0.1-1Mpa)	Sieving	Macromolecular solution
Reverse Osmosis	Liquid/liquid	Pressure (1-10Mpa)	Solution-Diffusion	Microsolutes and salts from solutions
Dialysis	Liquid/liquid	Concentration Difference	Diffusion	Low molecular species from macromolecular solutions
Electro dialysis	Liquid/liquid	Electric Potential	Selective ion transport	Desalination of water or process streams
Gas Separation	Gas/gas	Pressure (0.1-10 Mpa)	Solution-Diffusion	Gases from gas mixtures
Pervaporation	Liquid/gas	Partial Pressure Difference (0-100 kpa)	Solution-Diffusion	Solvent and azeotropic mixture

(Waren, 1986)

2.2 Membrane application

Table 2.2: Classification of membranes and membrane processes for separations via passive transport

Membrane barrier structure	Trans-membrane gradient		
	Concentration	Pressure	Electrical field
Non-porous	Pervaporation (PV)	Gas separation (GS) Reverse Osmosis (RO)	Electrodialysis (ED)
Microporous pore $d_p \leq 2$ nm	Dialysis (D)	Nanofiltration (NF)	
Mesoporous pore $d_p = 2$-50 nm	Dialysis	Ultrafiltration (UF)	Electrodialysis
Macroporous pore $d_p =$ 50-500 nm		Microfiltration (MF)	

(Spillman *et al.*, 1989).

- D for blood detoxification and plasma separation ('medical devices')
- RO for the production of ultrapure water, including potable water ('water treatment')
- MF for particle removal, including sterile filtration (various industries)
- UF for many concentration, fractionation or purification processes (various industries including 'water treatment')
- GS for air separation or natural gas purification

2.3 Membrane in gas separation

In this century, membranes gas separation was emerged as a commercial process on a large scale. In this period, significant progress was made in every aspect of membrane technology, including improvements in membrane formation processes such as interfacial polymerization and multiplayer composite casting and coating, chemical and physical structures, configuration and applications. Gas membranes are now widely used in variety of application areas, as shown in **Table 2.3** (Spillman *et al.,*1989). This is because of its advantages in separation, low capital cost, low energy consumption, ease of operation, cost effectiveness even at low gas volumes and good weight and space efficiency.

Table 2.3: Membrane application in gas separation areas

Common on gas separation	Application
O_2/N_2	Oxygen enrichment, inert gas generation
H_2 /Hydrocarbons	Refinery hydrogen recovery
H_2/N_2	Ammonia Purge gas
H_2/CO	Syngas ratio adjustment
CO_2/ Hydrocarbons	Acid gas treatment, landfill gas upgrading
H_2O / Hydrocarbons	Natural gas dehydration
H_2S/ Hydrocarbons	Sour gas treating
He/ Hydrocarbons	Helium separation
He/ N_2	Helium recovery
Hydrocarbons / Air	Hydrocarbons recovery, pollution control
H_2O/ Air	Air dehumification

(Spillman *et al.,*1989).