

STUDY ON PRODUCTION OF PEG-PVDF MEMBRANE FOR GAS SEPARATION

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ABSTRACT

Membranes are also now playing a special role in the field of alternative energy, as one of the fundamental parts of gas product purification through the membrane gas separation process technology. In this sense, membrane technology has a potential contribution for a green chemistry locally, safely, simply, efficiently, and as much as an environmentally friendly manner. The separation of gas mixtures with membranes has emerged from being a laboratory curiosity to becoming a rapidly growing, commercially viable alternative to traditional methods of gas separation. The objective of this research is to develop a high performance of polyethylene glycol (PEG) membrane as an additive to the co-polymer polyvinyl difluoride (PVDF) membrane for gas separation mixture. In the study of separation of CO_2/N_2 using polymeric membrane system, the best balance for selectivity and permeability of the gas separation membrane is the main part that highly considered as achieving better membrane performance. The co-polymer polyvinyl difluoride (PVDF) membrane used was fabricated using 2-10% wt of polyethylene glycol (PEG) polymer and the rest % wt of ethanol. Coating the PVDF membrane will take the 4-6 hours for it to be totally dried based on the correct percentage of the PEG and ethanol as the solvent. The developed membrane is then tested to determine its performance. Proceed to the gas permeation test, CO_2 gas is feed and the permeation flux through the prepared membrane was measured at different pressures. The gas permeation experiment is repeated with N_2 gas. The results of this work served as a mean in determining the most balance selectivity and permeability to be used for gas separation processes.

ABSTRAK

Membran yang juga kini memainkan peranan khas dalam bidang tenaga alternatif, sebagai salah satu daripada bahagian-bahagian asas penulenan produk gas melalui proses teknologi pemisahan gas membran. Dalam pengertian ini, teknologi membran mempunyai potensi sumbangan untuk mesra alam di negara ini, dengan selamat, mudah, cekap, dan sebanyak sebagai cara yang terbaik. Pemisahan campuran gas dengan membran telah muncul daripada rasa ingin tahu saintis untuk menjadi yang pesat berkembang, alternatif yang berdaya maju secara komersial dengan kaedah tradisional pemisahan gas. Objektif kajian ini adalah untuk membangunkan prestasi yang tinggi membran (PEG) polietilena glikol sebagai tambahan kepada membran bersama-polimer polivinil difluoride (PVDF) untuk campuran pemisahan gas. Dalam kajian pengasingan CO_2/N_2 menggunakan sistem membran polimer, baki yang terbaik untuk pemilihan dan kebolehtelapan membran pemisahan gas adalah bahagian utama yang sangat dianggap sebagai mencapai prestasi membran yang lebih baik. Difluoride bersama polimer polivinil (PVDF) membran yang digunakan telah dibuat menggunakan 2-10% berat polietilena glikol (PEG) polimer dan berat rehat% etanol. Salutan membran PVDF akan mengambil 4-6 jam untuk benar-benar kering berdasarkan peratusan yang betul PEG dan etanol sebagai pelarut. Membran maju kemudiannya diuji untuk menentukan prestasi. Meneruskan ujian penyerapan gas, gas CO_2 makanan dan fluks penyerapan melalui membran yang disediakan telah diukur pada tekanan yang berlainan. Penyerapan gas eksperimen diulangi dengan gas N_2 . Hasil kerja ini berkhidmat sebagai langkah optimum dalam menentukan baki selektiviti dan ketelapan yang akan digunakan untuk proses pemisahan gas.

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LIST OF ABBREVIATIONS

mm	-	millimeter
ft	-	Feet
m	-	meter
Sm ³ /hr	-	Centimeter cubic per hour
UMP	-	Universiti Malaysia Pahang
U.S.	-	United State
°C	-	Degree of Celcius
°F	-	Degree of Farad
ppm	-	part per million
GPU	-	Gas permeation unit
PVDF	-	Polyvinil difluoride
PEG	-	Polyethylene glycol
TFC	-	Thin film composite

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CHAPTER 1

INTRODUCTION

1.1 Research background

Membrane technology has gained a huge significance competing with long conventional technologies for gas separation, water desalination, food processing and emerging as a unique solution in medical applications such as artificial kidney. Figuring out the fields to which membranes are already helping as important tools, the chemical industry is certainly one of the most fascinating. Reason for that is the opportunity of recovering valuable products as well as treating waste matters and minimizing environmental problems, which are usually claimed to be caused by the chemical industry. Membranes are also now playing a special role in the field of alternative energy, as one of the elemental parts of product purification through the membrane gas separation process technology. In this sense, membrane technology has a likely contribution for a green chemistry locally, safely, simply, efficiently, and as much as an environmentally friendly mode. The separation of gas mixtures with membranes has appeared from being laboratory inquisitiveness to becoming a rapidly growing, commercially practicable alternative to traditional methods of gas separation. Membrane gas separation has become one of the most significant new unit operations to emerge in the chemical industry.

1.2 Problem statement

The balance between the permeability and selectivity of a membrane material with respect to specific compositions of the gases, vapors, or liquids to be separated in specific applications such as natural gas purification or carbon dioxide, CO₂ management, require an extremely high degree of optimization. For this reason, multicomponent polymers are being developed.

However a polymeric membrane of a given specific materials need to be chosen correctly as to get the right balance of membrane permeability and selectivity to achieve the maximum enrichment of product purification. Besides, the separation performance influenced by feed, pressure or any other manipulated variables also highly need to be considered.

1.3 Research objective

The objective of this research is to prepare a polyethylene glycol (PEG) as an additive or selected layer to the co-polymer polyvinyl difluoride (PVDF) thin film composite membrane. In addition is further study on the right balance of membrane permeability and selectivity with respect to the specific materials as to allow the membrane to exhibit superior physical strength and chemical stability to achieve the maximum enrichment of gas separation process.

1.4 Scope of research

The research objectives will cover the following scopes:

- 1) The production of functional polymeric membrane by casting polyethylene glycol (PEG) as an additive to the co-polymer polyvinyl difluoride (PVDF) thin film composite membrane.
- 2) The study on physical, chemical and selectivity for the corresponding thin film composite, TFC membrane.
- 3) Test the performance of the thin film composite, TFC membrane in gas permeation experiment.

1.5 Rationale and significant

This research has two aspects of its importance; first is the development of the polymeric membrane based on the given specific materials and the second one is the achievement of highest performance membrane for gas separation. Using polymeric membrane as for the gas separation is one of the emerging technologies compared to the conventional separation technology. This is due to its beneficial features that make it attractive in industries. They are:

a) Less energy requirement

Since there is no phase change in membrane separation process, consequently, there is no latent heat involved. Thus, this will replace some unit operation which consumes heat such as distillation column or evaporation column.

b) No waste products

In membrane separation process, it does not create any waste from its operation except the unwanted components in feed. This will help to decrease the cost of operation to handle the waste.

c) Low operation cost

Membrane separation process need low operation cost based on type of materials and elements use in the process compare to the other types of unit operation.

d) Flexible

It is based on the type of modules used for the membrane separation process. If it is Hollow fibre, it can carry out the separation by 2 ways, either is inside-out or outside-in.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The aim of this chapter is to provide a comprehensive review on the preparation of a functional polymeric membrane for a gas separation process. In this section of literature review, the discussion is regarding to past research related to gas separation process by using polymeric membrane, polyethylene glycol (PEG) as an additive to co-polymer membrane polyvinyl difluoride (PVDF) membrane, and important applications of membrane in biogas purification. Significant approaches toward this aim consist of procedure to prepare the functional membrane by synergetic combination of different polymeric materials, study of clear structure of PEG-PVDF membrane and last but not least the evaluation of membrane performance by characterization and various testing.

2.2 Membrane

A membrane is mainly can be resemblance as a barrier, which separates two phases and limit the transportation of an assortment of chemicals in a selective manner. It is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two compartments. Membranes can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid can carry a positive or negative charge or be neutral or bipolar. Membrane transportation can be resulted by

convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may differ from as small as 100 micron to several mms (G. Srikanth, 2003).

A membrane is a selective semi permeable barrier that allows different gases, vapors, or liquids to move through it at different rates, explains Richard D. Noble, chemical engineering professor at the University of Colorado, Boulder. The membrane restricts the motion of molecules passing across it so that some molecules move more slowly than others or are excluded. A wide range of mechanisms are available for this restriction; for example, size variability of the molecules, affinity for the membrane material, and permeation driving forces--typically concentration or pressure difference. Each gas component in a feed mixture has a characteristic permeation rate through the membrane. The rate is determined by the ability of the component to dissolve in and diffuse through the membrane material (Benny D. Freeman, 2005).

In the field of chemical engineering, the most benefits of using membrane for transportation process is the exclusive separation principle based on the selectivity of the membrane. The separation process is unnecessary for any additives. Plus, the separation processes can be carried out isothermally at low temperatures compared to other thermal separation processes which working on at low energy consumption. Also, up scaling and downscaling of membrane processes as well as their integration into other separation or reaction processes are easy (Mathias Ulbricht, 2006).

Passive transport through membranes occurs as consequence of a driving force, a difference in chemical potential by a gradient across the membrane in, for examples concentration or pressure, or by an electrical field. The barrier structure of membranes can be classified according to their porous character. Active development is also concerned with the combination of nonporous or porous membranes with additional separation mechanisms, and the most important ones are electrochemical potentials and affinity interactions.

Most membrane processes are characterized by two key process parameters: flux (the rate of flow of fluid or gas through the membrane) and selectivity (the ability of the membrane to reject prevent the passage of one or more species in the feed suspension or solution). The selectivity is governed by the intrinsic nature of the membrane material, built into it by its method of manufacture, and measured by its permeability to the species in question. The flux is determined by the specific resistance of the membrane material (the volumetric or mass flow of fluid per unit of membrane area) under a given differential pressure across the membrane, so that the flux increases with the operating area of the membrane and with the applied pressure (Ken Sutherland, 2009).

2.2.1 Membrane Characteristic

The primal function of a membrane is to act as a selective barrier, allowing the passage of certain components and the retention of others from a determined mixture, implying the concentration of one or more components both in the permeate and in the retentate. Its selectivity is related to the dimensions of the molecule or particle of interest for separation and the pore size, as also the solute diffusivity in the matrix and the associated electric charges (Coutinho et al., 2009). The separation performance of a membrane is influenced by its chemical composition, temperature, pressure, feed flow and interactions between components in the feed flow and the membrane surface (Lin, et al., 1997).

The membranes can be classified as symmetrical or asymmetrical. This asymmetry is considered with respect to the internal structure of the membranes. Symmetrical membranes show uniform pore sizes in their cross-section whereas the pores of asymmetric membranes are usually larger the further they are from the filter surface. In general the most important characteristics of membranes are: thickness, pore diameter, solvent permeability and porosity. Other important parameters are: permeate flow rate, heat, chemical and mechanical resistance (Coutinho et al., 2009).

From the morphological point of view, membranes can be divided into two large categories: dense and porous. Membranes are considered to be dense when transport of the components involves a stage of dissolution and diffusion across the material constituting the membrane. On the other hand a membrane is denominated as porous when permeate transport occurs preferentially in the continuous fluid phase which fills the membrane pores (Habert et al., 2006).

2.2.2 Polymeric Membrane

The morphology of the membrane depends strongly on the conditions under which the phase separation is carried out (Boom et al., 1996). Adding the inorganic nanoparticles into polymeric materials to improve the filtration membrane properties has attracted broad attentions in the development of membrane science and technique. By adding proper inorganic nanoparticles in polymeric casting solution could suppress the formation and growth of macro voids, to increase the number of small pores and run-through pores, to improve the porosity, hydrophilicity and permeability with almost unchanged retention, and to enhance the mechanical and thermal stabilities and the anti-fouling performance (Yang et al., 2007).

The first condition to produce a polymeric membrane is to cast a polymer solution as an additive on a support. Then, the phase separation can be induced by means of contacting the polymer solution with a suitable non-solvent in the liquid or vapor phase (liquid induced phase separation or vapor induced phase separation). Diffusional exchange of solvent and non-solvent induces a thermodynamic instability in the polymer solution causing phase separation to occur into a polymer-rich phase and a polymer-lean phase. The polymer-rich phase forms the body of the membrane, whereas the polymer-lean phase will form the porosity inside the membrane (Amanda, 2009).

2.3 Membrane Application

The whole range of chemicals manufacturing activity (including makers of personal care and household consumable products), if taken together, is the largest end-user sector for membrane modules. The full range includes some very different industries, varying widely in nature and size, covering the production of:

- a) Gases, acids, alkalis, fertilisers and other bulk inorganic chemicals
- b) Bulk organic chemicals
- c) Man-made fibres
- d) Other agrichemicals
- e) Inks, paints and other coatings
- f) Soap, detergents, toiletries and perfumes
- g) Explosives, glues, essential oils and else
- h) Pharmaceuticals and medicinals
- i) Chemicals and other products made by biochemical means (but excluding fermented beverages)

The standard membrane processes which are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) are now reasonably commonplace in the bulk chemicals sector. Reverse osmosis, which began life as a device solely required to separate sodium chloride from water, is now being used to reject a wider range of solutes. Nanofiltration in turn is dealing with quite large inorganic ions. Ultrafiltration is becoming the pre-filter of choice ahead of reverse osmosis desalination plants, and membranes are being employed with great success in the microfiltration range, where until relatively recently, they could not have been considered. A prime example of the latter situation is the rapid spread of the microfiltration-based MBR (membrane bioreactor), combining a biological process with a membrane separation process (Ken Sutherland, 2009).

The expansion of membrane separations into the microfiltration range is being driven by the market's wish for finer degrees of filtration of its products (or waste streams), to match its customers' demands for clearer final products or environmental regulators demands for less contaminating effluents. In whichever part of the bulk chemicals sector a need exists for fine filtration, in the 1 μ m region, then the chances are that it will now be met by a membrane separation process, assuming that the materials of construction can withstand the process conditions (Ken Sutherland, 2009).

In the somewhat more exotic processes, mainly involving gases or vapours, gas permeation is widely used for the separation of gas mixtures in both the chemical and petrochemical components, where gas recovery is an essential process. Higher temperature resistant membranes have an important role to play here, especially in petroleum refinery operations, for example in the recovery of hydrogen from cracker off gases, and for the separation of ethylene and aromatics. The separation and recovery of carbon dioxide, en route to its sequestration, as part of a greenhouse gas emission reduction programme, could well become a large membrane market. At present, the largest application for gas permeation is in the separation of air into its constituent gases, where locally situated air separation plants are most likely to be based on membrane separation (Ken Sutherland, 2009).

Pervaporation, the separation of two perfectly mixed liquids (usually where they cannot be separated by distillation, because they form an azeotropic, constant boiling mixture at a particular concentration ratio – most famously the azeotrope of ethanol and water), is easily achieved through a membrane, by virtue of the different diffusion rates of the two vapours. It is also used to treat rinse waters that have become contaminated by VOCs (volatile organic compounds, hazardous to human health), such as solvents, degreasers and petroleum-based mixtures. In either case, 99% contaminant removal can be achieved. Vapour permeation is used for the separation of a mixture of saturated vapours, and is often combined with distillation, to separate solvents from exhaust air streams, especially in degassing operations such as resin production (Ken Sutherland, 2009).

The dialysis processes (especially electro dialysis) are used for the selective extraction of ions from solution in water and/or their concentration in one liquid stream. The most important application of dialysis (blood processing for kidney action support) is not replicated in the chemicals sector, but electro dialysis, using ion exchange membranes, is finding increasing usage (Ken Sutherland, 2009).

2.3.1 Membrane in Gas Separation

Gas membranes are now widely used in variety of application areas, as shown in **Table 2.1**. 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 2.1: 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 ₂ O / Hydrocarbons	Natural gas dehydration
H ₂ S/ Hydrocarbons	Sour gas treating
He/ Hydrocarbons	Helium separation
He/ N ₂	Helium recovery
Hydrocarbons / Air	Hydrocarbons recovery, pollution control
H ₂ O/ Air	Air dehumification

(R.W. Spillman, 1989)

Gas separation membranes offer a number of benefits over other gas separation technologies, according to Benny D. Freeman, professor of chemical engineering at the University of Texas, Austin, “Conventional technologies such as the cryogenic distillation of air, condensation to Austin”. Conventional technologies such as the cryogenic distillation of air, condensation to remove condensable organic vapors from gas mixtures, and amine absorption to remove acid gases such as carbon dioxide from natural gas require a gas-to-liquid phase change in the gas mixture that is to be separated. The phase change adds a significant energy cost to the separation cost. Membrane gas separation, on the other hand, does not require a phase change.

In addition, gas separation membrane units are smaller than other types of plants, like amine stripping plants, and therefore have relatively small footprints. A small footprint is important in environments such as offshore gas-processing platforms. The lack of mechanical complexity in membrane systems is another advantage. Currently, gas separation membranes are most widely used in industry for:

- a) Hydrogen separation, for example, hydrogen/nitrogen separation in ammonia plants
- b) Hydrogen/hydrocarbon separations in petrochemical applications
- c) Separating nitrogen from air
- d) CO₂ and water removal from natural gas
- e) Organic vapor removal from air or nitrogen streams

At the moment, the most widely used membrane materials for gas separation are polymers. They are attractive as membranes because they can be processed into hollow fibers with high surface areas. The relatively low cost of manufacturing the fibers makes them of interest for large-scale industrial applications.

Membrane devices for gas or vapor separation usually operate under continuous steady-state conditions with three streams. The feed stream a high-pressure gas mixture passes along one side of the membrane. The molecules that permeate the membrane are swept using a gas on the other side of the membrane in the so-called permeate stream. The nonpermeating molecules that remain on the feed-stream side exit the membrane as the retentate stream. A pressure difference across the membrane drives the permeation process (Benny D. Freeman, 2005).

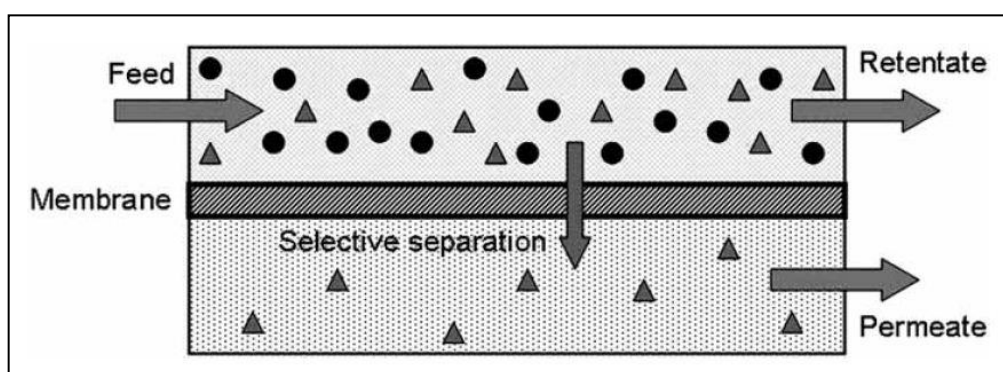


Figure 2.1: Schematic of membrane in gas separation

(Benny D. Freeman, 2005)

The economics of a gas separation membrane process is largely determined by the membrane's transport properties that is, its permeability and selectivity for a specific gas in a mixture. Ideally, membranes should exhibit high selectivity and high permeability. For most membranes, however, as selectivity increases, permeability decreases, and vice versa.

Alan R. Greenberg, professor of mechanical engineering at the University of Colorado, Boulder, points out that polymeric membranes used in gas separation applications often experience compaction that is, a decrease in membrane thickness over time. “Compaction and plasticization are simultaneous and competing effects in these applications,” he says. Plasticization usually leads to swelling and an increase in the

permeability of glassy polymers. Compaction, on the other hand, is due to mechanical deformation that is creep when a large pressure drop is applied across the membrane.

Compaction, he adds, has been reported to cause a significant decrease in the performance of a membrane over time. This is possibly a result of a decrease in the free volume of the membrane skin layer or an increase in the thickness of the skin. Increased skin thickness occurs if the porous sub layer of the membrane in the region adjacent to the skin compacts and becomes as dense as the skin.

2.4 Mechanism of Membrane Gas Separation

Knudson diffusion, molecular sieving, solution-diffusion separation, surface diffusion and capillary condensation, of which the first three are schematically was represented in **Figure 2.2**. Molecular sieving and solution diffusion are the main mechanisms for nearly all gas separating membranes. Knudson separation is based on gas molecules passing through membrane pores small enough to prevent bulk diffusion.

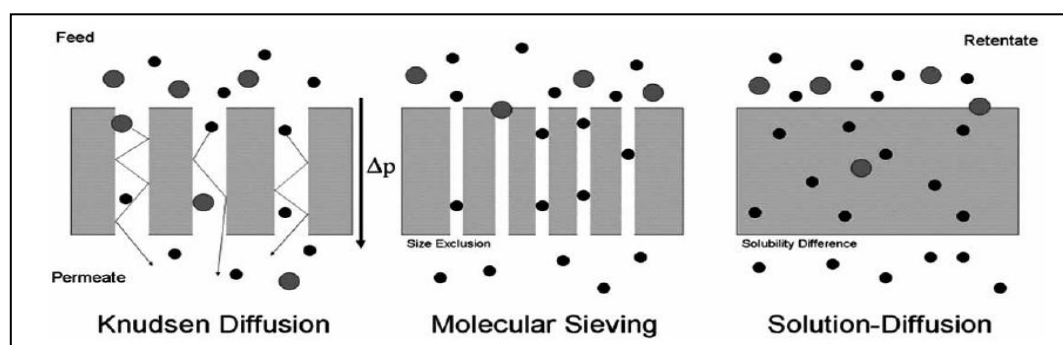


Figure 2.2: Schematic representation of three of the different possible mechanisms for membrane gas separation, Knudsen diffusion, molecular sieving and solution-diffusion.

(Benny D. Freeman, 2005)