

Fabrication of a High-Performance Polyetherimide Membrane for Helium Separation

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Abstract—Helium market is continuously growing due to its essential uses in the electronic and healthcare sectors. Currently, helium is produced by cryogenic distillation but the process is uneconomical especially for low production volumes. On the other hand, polymeric membranes can provide a cost-effective solution for helium purification due to their low operating energy. However, the preparation of membranes involves the use of very toxic solvents such as chloroform. In this work, polyetherimide membranes were prepared using a less toxic solvent, *n*-methylpyrrolidone with a polymer-to-solvent ratio of 27 wt%. The developed membrane showed a superior helium permeability of 15.9 Barrer that surpassed the permeability of membranes made by chloroform.

Keywords—Helium separation, polyetherimide, dense membrane, gas permeability, solvent.

I. INTRODUCTION

HELIUM is one of the noble gases that have the properties of being odorless and inert. Helium also has an excellent thermal capacity and it is extensively used in the medical applications to cool down medical equipment such as magnetic resonance imaging (MRI) [1]. In addition, the gas is added to rockets to provide the force for displacing the fuel to the engine [2]. Moreover, helium has a lower density than air and that is why balloons are filled with helium so that the balloons fly up. Helium is also used in welding as a shield gas to prevent oxygen and water from entering the metal [3]. Furthermore, helium is used in the semi-conductors industry to protect silicon crystals from the reaction with oxygen and nitrogen.

The demand for helium is increasing and expected to rise by 3% annually [4]. The main source of helium is natural gas, which is produced from oil wells. Helium is separated from natural gas by cryogenic distillation where the gas is cooled down to an extreme temperature of $-185\text{ }^{\circ}\text{C}$. This process is energy intensive and requires special piping and equipment. Therefore, the process is considered economical only for large production of helium. Alternatively, the membrane system can provide an innovative solution for helium production, especially for low-volume production. This is because the system can operate at ambient temperature. Moreover, the system can operate continuously for many years without interruption due to the absence of mechanical parts. Furthermore, the system is compact and requires minimum time to install and operate.

The membranes can be classified based on the material to

metallic, ceramic, and polymeric. The metallic membranes have an infinite selectivity meaning that the produced gas can have a purity of 100%; however, the price of precious metals makes the membranes uneconomical. Furthermore, the metallic membranes are easily susceptible to corrosion due to the rapid reaction with sulfur and other impurities. Some examples of metallic membranes are platinum and palladium.

Ceramic membranes are well known for their excellent chemical and thermal stability. Nevertheless, it is difficult to reproduce the membrane due to the agglomeration of particles. In addition, some ceramic membranes require high temperature to operate and most of the sealants will fail at extreme temperatures. Silica, zeolite and mixed conductors are some materials for ceramic membranes.

Polymeric membranes, on the other hand, dominate the industry because of the competitive performance and low fabrication cost. They were commercialized in the 1980s for gas separation. The membranes have also good mechanical and chemical properties. Moreover, they can be operated at room temperature so they do not have a sealing issue. Polymeric membranes are generally made from cellulose acetate (CA), polysulfone (PSF) and polyimides (PI).

Polyetherimide (PEI) is a special type of thermoplastic that was engineered to overcome shaping limitation in PI. The production cost of PEI is considered low compared to other polymers making it an attractive material for the industry. General Electric developed PEI back in the 1980s under the name, Ultem®. Compared to other polymers, PEI exhibits an excellent chemical stability to resist aggressive solvents [19]. In addition, it has a high glass transition temperature of $217\text{ }^{\circ}\text{C}$ making it more thermally stable. PEI is heavily used in the fabrication of automobile lamps. Connectors, circuit boards, and switches are also made by PEI. In medical applications, sterilization equipment such as probes are made from PEI due to its high chemical and thermal stability. Moreover, PEI permeates gases and it has the highest gas selectivity between CA and PSF. This means that the separated gas will have a better purity. The material is selective to helium, hydrogen, oxygen and carbon dioxide.

The membrane preparation method plays an important role in determining the performance of the final membrane. Solvent selection is one of the key parameters in membrane preparation because it defines the physical structure [5]. Many researchers reported an enhancement in the membrane performance after alternating the solvent. They noticed a significant change in membrane morphology [6]. Usually, a thin, densified layer with a porous structure having uniform holes is preferred for gas separation. The thin layer is

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responsible mainly for determining the membrane performance. The thin layer should be fully dense and free from holes. The gas still passes through the thin layer by a mean of a solution-diffusion model [7]. The gas will first dissolve in the polymer and then diffuse through channels known as free volumes. Unlike physical pores, the shape and location of free volumes can change based on the gas and operating conditions. Selection of solvent will also affect the number of free volumes.

In literature, chloroform is mainly used for the preparation of PEI membranes for helium separation because of its strong dissolving power [6]. However, chloroform is a very toxic solvent and it can cause dizziness even if inhaled in small quantities. It is also reported that chloroform can cause kidney damage and even death if inhaled in high concentrations [8]. The objective of this study is to substitute chloroform with *n*-methylpyrrolidone (NMP) because the latter has lower toxicity than chloroform. Hazard statements of chloroform and NMP are given in Table I. There is also a possibility for chloroform to cause cancer after long-term exposure. On the other hand, NMP is a very strong solubilizing agent and that is why it is used as a paint stripper. In industry, NMP is utilized to absorb hydrogen sulfide from sour gas and to remove sulfur compounds from petroleum fractions. Moreover, NMP has a higher boiling point of 202 °C compared to chloroform which has a boiling point of only 61 °C [6]. In addition, NMP has a higher viscosity of 1.65 cP and the increase in boiling point along with viscosity may give the polymer solution better physical properties for easy casting.

In this paper, NMP has been selected as a solvent for the preparation of PEI membranes. The membranes were tested for separation of helium from nitrogen by determining the permeability and selectivity. The permeability is associated with the flow of the produced gas while the selectivity is related to the product gas purity. Helium separation from nitrogen was selected because, during the production of natural gas from petroleum reservoirs, the hydrocarbons (mainly methane) are liquefied leaving a stream enriched with nitrogen and helium [9]. Furthermore, the waste gas from pressurized vessels and coolants are also enriched with helium and nitrogen. The performance of the developed membranes in this study was compared to other researchers' work where chloroform was used as a solvent.

TABLE I
HAZARD STATEMENTS OF CHLOROFORM AND NMP [10]

Solvent	Hazard statements
Chloroform	<ul style="list-style-type: none"> • Harmful if inhaled. • Harmful if swallowed. • Suspected of causing cancer • May cause damage to kidney, heart, skin, eyes and central nervous system.
NMP	<ul style="list-style-type: none"> • Highly flammable liquid. • Harmful if swallowed. • May cause skin and eye irritation. • May damage fertility or the unborn child.

II. EXPERIMENTAL SETUP

PEI membranes were prepared using the widely used

method, the phase inversion. The technique consists of three steps: 1) dissolving the polymer in a solvent then mixing it to have a homogenous solution, 2) tape casting the solution to form a thin film, and 3) immersion of the film in a non-immiscible liquid to participate the polymer [11]. The first step involved the addition of PEI pellets (99.9%, Sigma Aldrich) to NMP with a concentration of 27 wt% of PEI in the solution. NMP was selected because the solvent has a strong dissolving power to most polymers. The solution was heated to 80 °C for 24 h with mixing. The second step was to pour the solution in a tape-casting machine to form a film of 300 μm in thickness. The last step was to immerse the film in a water bath to remove NMP and precipitate the polymer. The membrane was kept to dry for 24 h. Finally, the membranes were cut into discs with a diameter of 47 mm. This procedure was followed based on a previous study where PEI membranes were prepared for hydrogen separation and it was found that membranes with 27 wt% PEI had the best performance [12].

Before operation, the membranes were characterized by scanning electron microscope, SEM (JEOL JSM-IT300), to examine the surface and make sure it is free from defects. The samples were immersed in liquid nitrogen for five minutes then cut to prepare the cross-section areas. The samples were analyzed by x-ray diffraction (XRD, PANalytical Empyrean XE) to determine the purity and crystallinity of the membranes.

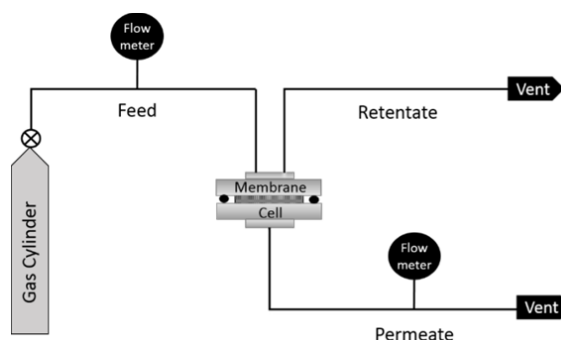


Fig. 1 Process flow diagram of the membrane-cell unit

The membranes were tested for helium permeation using a membrane-cell unit (Convergence Inspector Neptunus). The unit consists of a gas cylinder, mass-flow meters, and membrane housing as given in Fig. 1. Helium (99.999%, Kuwait Oxygen & Acetylene Company KOAC) was fed to the cell at a feed flow rate of 100 L/h. The temperature was set to 25 °C but the feed pressure was varied from 3 to 10 bar. The permeability, which describes the rate of gas flow through the polymer, was calculated by measuring the permeate flowrate as follows:

$$P \text{ (barrer)} = \frac{V_p l}{A \Delta P} \quad (1)$$

where V_p is the permeate volumetric flowrate (cm³/min), l is the membrane thickness (cm), A is the active membrane area

(12.6 cm²), and ΔP is the pressure difference between the feed and permeate sides (cmHg). Helium and nitrogen permeabilities were used to calculate the ideal selectivity (α):

$$\alpha_{He/N_2} = \frac{P_{He}}{P_{N_2}} \quad (2)$$

where P_{He} and P_{N_2} are the selectivities of helium and nitrogen, respectively. The selectivity generally represents the purity of the produced gas while the permeability represents the recovery or gas flow.

III. DISCUSSION AND RESULTS

SEM image of the cross-section surface is given in Fig. 2. As shown, the membrane consists of porous and dense structures. The porous layer is generated due to the evolution of the solvent from the polymer. The dense layer determines the gas selectivity and it has an average thickness of 2.8 μm . XRD data are given in Fig. 3 and only two peaks were detected at 21.3 and 23.8 ($2\theta^\circ$) indicating that the sample is purely PEI. Helium and nitrogen permeabilities of the developed PEI membranes are given in Table II. The highest helium permeability was 19.8 Barrer at a feed pressure of 5 bar. The corresponding helium-to-nitrogen selectivity was 80. The highest selectivity was 145 at 10 bar but the permeability decreased to 15.9 Barrer. It is known that in polymeric membranes there is a trade-off between permeability and selectivity meaning that high permeable membranes suffer from the low selectivity, and vice versa. This phenomenon is still unclear but most of the researchers relate this to the nature of polymers [13]. PEI is a glassy polymer meaning that the structure (in molecular level) is more crystallized. Glassy polymers are also known to be more selective but at the expense of the permeability. The high selectivity in glassy polymers is related to the high solubility of the gas inside the polymer. Furthermore, glassy polymers have less free volumes and this limits the gas diffusion and reduces the permeability.

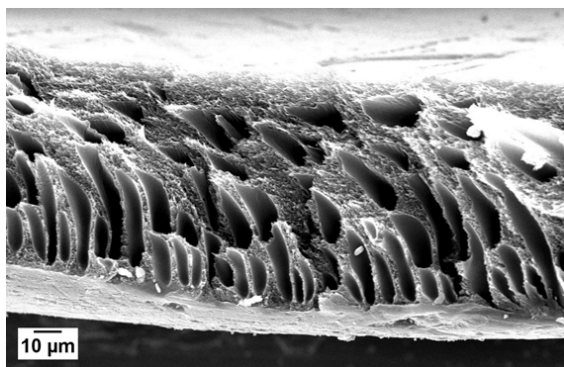


Fig. 2 SEM image of the cross-section surface of PEI membrane

The permeability data in this work were compared with other researchers' results as given in Table III. The developed membranes in this study had the highest helium permeability of 15.9 Barrer where the other researchers reported values

between 6.9 to 9.4 Barrer [14]-[17]. The high permeability can be related to the thin selective layer and uniform holes of the porous structure (Fig. 2). In this study, NMP was used as a solvent where other researchers used chloroform and dichloromethane [15]-[17]. The strong dissolving power of NMP may increase the interaction between the polymer and the solvent and this may facilitate polymer chain relaxation resulting in a thin densified layer. To confirm that, Hansen model was used to calculate the distance (d) between the polymer and solvent as:

$$d = \sqrt{[\delta_{d(s)} - \delta_{d(p)}]^2 + [\delta_{p(s)} - \delta_{p(p)}]^2 + [\delta_{h(s)} - \delta_{h(p)}]^2} \quad (1)$$

where δ_d , δ_p , and δ_h are the solubility parameters of dispersion component, dipolar intermolecular component, and hydrogen bond component, respectively. Hansen stated that the lower the distance, the more dissolving power the solvent will have [18]. The distance was calculated for various solvents and the data are given in Table IV. It is clear that PEI has a better solubility with chloroform compared to NMP because of the lower value of polymer-to-solvent distance to almost half. Despite that, the developed membranes by NMP have more permeability in comparison with chloroform membranes. Other possible parameters that can change the membrane permeability are the viscosity and boiling point. NMP has a higher viscosity and boiling point and this may alter the solvent exchange rate when immersed in water to form a thin layer with uniform holes. Also, NMP could interact faster with water and this may interpret the low thickness in NMP membranes. For membranes made from chloroform, the membranes are generally heated in an oven instead of immersing them in water because chloroform is insoluble in water. Nevertheless, the developed membranes have an average selectivity of 145 whereas Koros et al. [16] reported the highest selectivity of 184. The selectivity is strongly related to the thickness of the dense layer and generally, the higher the thickness, the higher the selectivity. Actually, the selectivity is controlled by two parameters; diffusion coefficient and solubility coefficient. The diffusion coefficient decreases with the increase in molecular size of the gas because it will take more time to pass through the polymer chain. On the other hand, the solubility coefficient depends on the gas condensability. In thick membranes, the gas transport is limited by the diffusion coefficient so, this will cause a drop in the permeability but the selectivity will increase because it will take more time for the unwanted gas molecules to pass through the membrane. Unfortunately, it is difficult to produce a membrane with maximum permeability and selectivity at the same time due to the trade-off phenomena, as mentioned before. The selectivity of the developed membranes of 145 is still acceptable for industrial application as the membranes can produce helium with a purity of 99.3 mol%. The purity can be further improved by using a second-stage membrane.

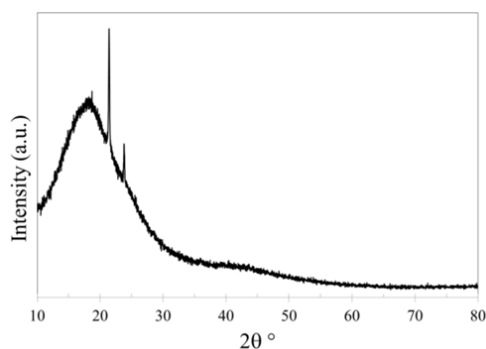


Fig. 3 XRD analysis of PEI membrane

TABLE II
HELIUM AND NITROGEN PERMEABILITY DATA OF PEI MEMBRANE AT 25 °C

Feed pressure (bar)	P_{He} (barrer)	P_{N_2} (barrer)	α_{He/N_2}
3	17.3	0.49	35
5	19.8	0.25	80
10	15.9	0.11	145

TABLE III
COMPARISON OF PERMEABILITY DATA OF PEI MEMBRANE WITH LITERATURE

Study	P_{He} (barrer)	P_{N_2} (barrer)	α_{He/N_2}	T (°C)	P (bar)	Ref
Takashi et al.	6.9	0.050	139	35	3	[14]
Hao et al.	8.8	0.054	163	35	3.5	[15]
Koros et al.	9.4	0.051	184	35	–	[16]
Barbari et al.	9.4	0.053	177	35	< 5	[17]
This work	15.9	0.250	145	25	10	–

TABLE IV
HANSEN SOLUBILITY PARAMETERS FOR VARIOUS SOLVENTS AND THE CALCULATED POLYMER-TO-SOLVENT DISTANCE [18]

Compound	δ_h (MPa) ^{1/2}	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	d (MPa) ^{1/2}
PEI	6.4	17.7	6.0	–
NMP	7.2	18.4	12.3	6.39
Chloroform	5.5	17.8	3.1	3.04

IV. CONCLUSION

Helium plays an important role in the medical and semi-conductor industries because of the high thermal capacity and chemical inertness. The gas is produced from oil wells and being separated by cryogenic distillation. This process requires high capital and operating costs due to the extremely low temperature. Instead, polymeric membranes can be utilized for helium separation with minimum energy. The membranes are usually made from CA, PSF, and PI. PEI is a special type of PI with ether group that gives it better chemical and mechanical properties. PEI has also better permeability and selectivity towards helium. However, PEI membranes are usually made from a very toxic solvent like chloroform because of its strong dissolving power. In this work, NMP was used for preparing PEI membranes instead of chloroform. NMP has lower toxicity than chloroform with a higher viscosity and boiling point. PEI membranes were prepared using the phase-inversion method in which the polymer was mixed with NMP then tape casted on a glass sheet. The solvent was removed by exchanging it with water. The

membranes were analyzed by SEM and XRD. The analyses revealed that the membranes were well prepared and were free from defects. The membranes were tested for helium separation from nitrogen. The membranes showed an excellent helium permeability of 15.9 Barrer with a selectivity of 145 at a feed pressure of 5 bar. Compared to other researchers' work, helium permeability was the highest to be reported. The high permeability was associated with the formation of a thin, selective layer while the reduction in selectivity was related to the trade-off between permeability and selectivity, which is common in polymeric membranes. Still, the selectivity of the developed membranes can produce helium of 99.3 mol% which is suitable for most applications.

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