PAPER • OPEN ACCESS

Synthesis of asymmetric polyetherimide membrane for CO_2/N_2 separation

To cite this article: A L Ahmad et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 206 012068

View the article online for updates and enhancements.

You may also like

- Production and characterization of polyetherimide mats by an electrospinning process
 Daniela Mitsuko Sato, Lília Müller Guerrini, Maurício Pinheiro de Oliveira et al.
- <u>Development of high temperature</u> <u>electrical conductive polymeric</u> <u>nanocomposite films for aerospace</u> <u>applications</u> Sajith Nair, Mohan Kumar Pitchan, Shantanu Bhowmik et al.
- <u>Development of Three Phase Composites</u> <u>Using Polyetherimide-Carbon Nanotubes</u> (Ba₆₋₈Sr₆₋₂)(Ti₆₋₉Zr₆₋₁)O₃ Ceramic Powder Cheng-Fu Yang and Chia-Ching Wu





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.144.86.134 on 05/05/2024 at 21:23

Synthesis of asymmetric polyetherimide membrane for CO₂/N₂ separation

A L Ahmad^{1,*}, Y O Salaudeen¹ and Z.A. Jawad²

¹School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus 14300, Nibong Tebal, Pulau Pinang, Malaysia.

²Faculty of Engineering and Science, Department of Chemical Engineering, Curtin University Malaysia, CDT 250, Miri 98009, Sarawak, Malaysia.

E-mail: chlatif@usm.my

Abstract. Large emission of carbon dioxide (CO₂) to the environment requires mitigation to avoid unbearable consequences on global climate change. The CO₂ emissions generated by fossil fuel combustion within the power and industrial sectors need to be quickly curbed. The gas emission can be abated using membrane technology; this is one of the most promising approaches for selective separation of CO₂/N₂. The purpose of the study is to synthesis an asymmetric polyetherimide (PEI) membrane and to establish its morphological characteristics for CO_2/N_2 separation. The PEI flat-sheet asymmetric membrane was fabricated using phase inversion with N-methyl-2-pyrrolidone (NMP) as solvent and water-isopropanol as a coagulant. Particularly, polymer concentration of 20, 25, and 30 wt. % were studied. In addition, the structure and morphology of the produced membrane were observed using scanning electron microscopy (SEM). Importantly, results showed that the membrane with high PEI concentration of 30 wt. % yield an optimal selectivity of 10.7 for CO₂/Nitrogen (N₂) separation at 1 bar and 25 °C for pure gas, aided by the membrane surface morphology. The dense skin present was as a result of non-solvent (water) while isopropanol generates a porous sponge structure. This appreciable separation performance makes the PEI asymmetric membrane an attractive alternative for CO₂/N₂ separation.

1. Introduction

The complications of global warming and climate change are today being generally discussed in terms of carbon dioxide (CO₂) emission by human activities [1]. Most of the world's primary energy requirement is supplied by fossil fuels, which results in rising emission of greenhouse gasses (GHGs) and related concerns over global warming and climate change [2]. In addition, different concentration of CO₂ in flue gasses depends on the fuel such as coal (12-15 mol-% CO₂), natural gas (3-4 mol-% CO₂), and oil refining (8-9 mol-% CO₂) which must be removed. Typically, CO₂ is the primary anthropogenic greenhouse gas, accounting for 77% of the human contribution to the greenhouse effect in the recent decade. Therefore, to remove CO₂ from the gas streams, various techniques have been improved such

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

as chemical and physical absorption, solid adsorption, cryogenic distillation, membrane separation [3]. Finding a proper separation technology for the removal of CO_2 from different gas streams will drastically lead to the reduction of emissions. Although CO₂ production contributes to global warming, it is also considered as a raw material in many industries. Global CO₂ consumption, for example, has reached approximately 20 million tons per year, which is strictly dedicated to the so-called merchant market, food, beverage, chemical and other industries [4]. Nevertheless, either for storage or for its utilization, CO_2 must be separated. At present, the most widely used CO_2 separation processes consist of reversible chemical and physical absorption. Membrane processes are not used very much; however, they are attractive because of their simplicity and energy efficiency [5]. Actually, there are not yet suitable technologies or technical solutions which can effectively fight against the CO₂ increase in the atmosphere. In the membrane cluster, it is deduced that membrane technology capable of operating under a wide variety of conditions that have a considerable impact on the separation and purification of CO_2 [6–8]. As known, membranes have become an established technology for CO_2 removal since 1981 [9]. However, in order to reduce the overall environmental impacts and cost of CO_2 capture, the priority is given to the technologies with improved CO_2 removal efficiency. In addition, membrane technology is one of the promising alternatives for CO_2 capture, which has been used in different processes such as membrane gas separation, membrane gas absorption, and facilitated transport membrane [10].

Currently, the commercially viable membranes used for CO_2 removal mostly are polymer based. Commercially available polyetherimide (PEI) has several important advantages as a membrane material. This polymer has good chemical and thermal stability. The studies on gas permeation of the PEI dense films reveal that PEI exhibits impressively high selectivity for many important gas pairs especially He and N_2 separation from other gasses with a separation factor of 16.6 [11]. Shamsabadi et al. [12] prepared flat sheet asymmetric polyetherimide membrane for the separation of H_2 from CH_4 with an ideal selectivity of 27.8. Meanwhile, Saedi et al. [13] fabricated flat sheet asymmetric polyethersulfone membrane for separation of CO₂ from CH₄ using PEI as a polymeric additive with a CO₂ permeance of 11.1 at 5 bars. Ren et al. [14] prepared the polyetherimide flat sheet membrane with N-methyl-2pyrrolidone (NMP)/non-solvent system, and they investigated the influence of the various non-solvents on the membrane morphology. Kurdi and Tremblay [15] produce defect-free asymmetric flat sheet membrane for separation of oxygen from nitrogen using LiNO₃ and isopropanol as dual bath coagulation method. Simons et al. [16] investigated CO_2 and CH_4 sorption and transport behavior using the PEI membrane with the CO_2 permeability of 1.4 at 5 bars. lower concentration of 10 and 15 wt. % of the polymer solution results in a porous membrane, which is not suitable for gas separation. This is due to loosely packed structure and weak mechanical strength [17]. In summary, the preparation of the polymer membranes with different concentrations is a method for optimizing the effect of the polymer concentration. Thus, in this research, asymmetric PEI membranes were synthesized with different concentration of the polymer solution by phase inversion method for CO_2/N_2 separation. Also, the performance test, the morphological characteristic of the membrane was investigated.

2. Experimental

2.1. Materials

Polyetherimide (PEI, Ultem®) was purchased from General Electric plastic (Malaysia) where figure1 represents the molecular structure of the used polyetherimide [15]. Table 1 shows the physical properties of the PEI. Also, Isopropanol, anhydrous 1-methyl-2-pyrrolidinone (NMP) (EMPLURA1, 99.5%, water < 0.1%) were supplied from Merck (Malaysia). In addition, the pure gasses including CO₂ (99.9%) and

IOP Publishing

IOP Conf. Series: Materials Science and Engineering 206 (2017) 012068 doi:10.1088/1757-899X/206/1/012068

 N_2 (99.9%) were supplied from Technical Gas Services (Malaysia), where these gasses were used in the permeation measurement experiments.



Figure 1. The molecular structure of used PEI where n represents the degree of polymerization.

Properties	Units	Values
Molecular weight	kg Kmol ⁻¹	30,000
Density	kg/m ³	1270
Water absorption	mg	20/41
After 24h/996h immersion in water of 23°C		
Melting point	°C	219
Glass transition temperature	°C	206
Thermal conductivity at 23°C	W/ (m.K)	0.22
Specific heat	kJ.kg ⁻¹ .K ⁻¹	2.0
Upper working temperature	°C	170-200
Elongation at break	%	15
Compressive strength	MPa	140
Tensile strength	MPa	85

Table 1. The Physical properties of PEI [12].

2.2. Preparation of asymmetric flat sheet membranes

PEI polymer was dried in a vacuum oven at 110 °C overnight in order to remove any trace of adsorbed humidity. The desired polymer solution (w/w) was prepared by dissolving a certain weight of PEI in a pre-determined weight of NMP in a closed glass jar. Table 2 shows the composition of the membranes prepared. A stirring speed of 400 rpm at 60 °C was used for efficient mixing for 24 h until a clear yellowish uniform viscous solution was achieved and left overnight. Then the solution was degassed for 30 min in order to remove the air bubbles from the solution. After the degassing process, the polymer solution was cast on a glass plate with a casting knife of 300 μ m by a motorized film applicator (Elcometer 4340, Dutech Instruments Malaysia). The cast film along with the glass plate was immediately immersed in a water–isopropanol (4:1) bath to accomplish the phase inversion for 5 min, followed by immersed the membrane in distilled water for 24 h. Then, the membrane was placed inbetween two dried glass filled with sheets of filter paper and dried for 24 h at room temperature. Finally, the PEI membrane was dried in an oven at 70±2 °C for 12 h for complete removing of the solvents and adsorbed humidity

(2)

IOP Conf. Series: Materials Science and Engineering 206 (2017) 012068 doi:10.1088/1757-899X/206/1/012068

Solution No	Dope		Dope
	composition		viscosity
	(wt. %)		_
	PEI	NMP	
PEI-1	20	80	2200
PEI-2	25	75	8150
PEI-3	30	70	19120

Table 2. The composition and	l viscosity of	polymer solution.
-------------------------------------	----------------	-------------------

2.3. Gas permeation test

A gas permeation experiment was performed using an assembled setup as shown in figure 2. A crossflow membrane cell made from stainless steel was used to perform the experiments. The cell consists of two detachable circular compartments clamped together by six screws. The upper part was connected to the feed and the retentate streams. The permeate streams were exhausted from the lower part. Circular membrane discs an effective permeation area of 7.0 cm² were used. The pressure-normalized fluxes of the fabricated flat sheet membranes were measured for pure CO₂ and N₂ at 25 °C and 1 bar. The feed gas was supplied to the shell side of the module. The standard permeate volumetric flow rate at atmospheric conditions was measured by a soap bubble flow meter. Each set of data represents an average of 6 replicates. Pressure-normalized flux, called permeance through the membranes was calculated using equation [1] [18]:

$$\left(\frac{p}{l}\right) = \frac{Q}{A\Delta P} \tag{1}$$

where Q is the measured volumetric flow rate (at standard pressure and temperature) of the permeated gas (cm³ (STP)/s), p is permeance, l is membrane skin layer thickness (cm), A is the effective membrane area (cm²) and ΔP is the pressure difference across the membrane (cmHg). The common unit of permeance is GPU where GPU is equal to 10^{-6} cm³ (STP)/cm² s cmHg [19]. Also, the ideal gas separation factor (α) can be calculated using equation (2)[20]:



Figure 2. Schematic diagram of gas permeation set up. 2.4. *Characterization of flat sheet polyetherimide membrane*

29th Symposium of Malaysian Chemical Engineers (SOMChE) 2016

IOP Conf. Series: Materials Science and Engineering 206 (2017) 012068 doi:10.1088/1757-899X/206/1/012068

The morphology of fabricated flat sheet membranes was investigated by scanning electron microscope (SEM) (TM 3000 Hitachi, High-Tech TOKYO) with an accelerating voltage of 25.0 kV. Prior to scanning, small pieces of the membrane samples were immersed into liquid nitrogen carefully for a minimum of 120 sec. Then, it fractured to obtain a clear cross section. After drying, the fractured fibers were placed on a disc for sputtering with a thin film of platinum before testing. Where, the SEM allows a clear magnification of the overall structure of the membranes; the top surface, the cross section, and the bottom surface can all be observed easily.

3. Results and discussion

3.1. Effect of polymer concentration on the gas separation

SEM images taken of the surface in figure 3 of the membranes, one can see that when 30 wt. % polymer concentrations were used at the dope; the surface of the membrane was smooth with no clear pores. When 25 wt. % was used at dope, pinholes appeared sparsely on the membrane surface, while the use of 20 wt. % polymer concentrations at dope caused the appearance of a large amount of pinholes on the surface. The gas permeance and the selectivities for CO_2/N_2 of the membranes prepared by using 20, 25, and 30 wt. % are shown in table 3. By comparing the data depicted in Table 3, reveals that the flat sheet membranes of PEI-1 and PEI-2 prepared from a lower polymer concentration (20 and 25 wt. %) exhibit much higher permeability but poorer selectivity compared to PEI-3 which was prepared from higher polymer concentration of 30 wt. % [11]. Meanwhile, the CO₂ permeance in PEI-1 and PEI-2 was about 306 and 70 times respectively greater than PEI-3.

As it can be seen from figure 4a, (PEI-1) has a dense outer skin layer with a tiny finger-like layer beneath, these finger-like macrovoids developed to the sublayer in cavity shape and this is surrounded by traces of sponge-like structure. These irregular finger-like macrovoids responsible for the high permeation achieved in the result [12]. Meanwhile, the finger-like structure at the skin layer of the figure 4b (PEI-2) is short and open and the development of sponge-like structure started from the skin layer to the sublayer with obvious pores at this sublayer. The sponge-like structure at the skin layer was responsible for the reduction of the gas flux as presented in table 3 [17]. However, increasing the polymer concentration in the casting solution as in figure 4c (PEI-3) caused changes in thickness, overall membrane porosity and gas permeability. It was observed that the increase in the polymer concentration results in a dense selective layer, a sponge-like structure with obvious pores at the sublayer of the membrane. As shown in the cross-sectional image, the membrane prepared with higher polymer concentration exhibited no finger-like macro void and a less obvious porous substructure. This means, the volume fraction of polymer increases and consequently, a lower porosity is obtained [12]. As a result of fast phase separation at surface layer and slower phase separation at sublayer, an asymmetric membrane with dense and thick skin layer supported by a close cell sublayer was produced by dope of higher polymer concentration. During the immersion process, polymer concentration at the membrane surface which in contact with non-solvent increased due to non-solvent/ solvent exchange process. During rapid exchange process, a skin layer was produced near the membrane non-solvent interface. Therefore, increased of polymer content would expect to support higher polymer precipitation; hence, greater polymer stress was produced in the polymer matrix. As a result, smaller pores were formed at the membrane surface which drastically reduced the gas permeability.



Figure 3. Cross sectional SEM of membrane (a) PEI-1 (b) PEI-2 (c) PEI-3.

concentrations.				
Samples	CO ₂	N_2	CO_2/N_2	
	Permeance	Permeance	Selectivity	
	(GPU)	(GPU)		
PEI-1	1942.76	842.53	2.3	
PEI-2	443.75	158.7	2.8	
PEI-3	6.35	0.59	10.76	

Table 3. CO2 and N2 Permeance (GPU) and ideal selectivity at 1 bar for various polymer

(a)



PEI-3

Figure 4. The SEM images of top surface of the membrane cast (a) PEI-1 (b) PEI-2 (c) PEI-3.

3.2. Determination of critical concentration

As shown in figure 5, viscosity data implies a dramatic slope change in a range of polymer concentration between 20 wt. % and 30 wt. %. Thus, the intersection of the tangents at these two concentrations renders the critical concentration of about 23 wt. %, where a significant change in the degree of chain entanglement occurs [21,22]. Therefore, the membranes which are cast from solutions with polymer concentrations higher than 23 wt. % have a higher entangle conformation, tighter intermolecular chain displacement, and less defective outer skin layers than those are casted from the solution with the polymer lower than 23 wt. % [18]. On the other hand, membrane casted below this critical point has a loosely packed chain thus are able to move freely and allow the non-solvent to penetrate via diffusion mechanism to form microvoid on the membrane surface [17]. Thus, the results showed that the solution viscosity increased as the polymer concentration of the solution was increased.



Figure 5. Dope viscosities at 30 °C versus polymer concentration.

4. Conclusion

PEI flat sheet membranes were fabricated via phase inversion process. Isopropanol and water were used as a non-solvent additive in the coagulation bath to improve the phase inversion rate and provide a dense skin-selective layer with a porous sponge-like structure at the sub-layer. In order to eliminate the sublayer porosity and minimize the gas permeance, the polymer concentration of the solution was increased. Permeation test was conducted for CO_2 and N_2 gas and the considerable separation factor was achieved at 30 wt. % polymer concentration. The critical point diagram reveals that there can only be less defective outer skin layer with a polymer higher than 23 wt. %. The SEM examination exhibits typical morphology for the asymmetric membrane.

References

- [1] Lahijani P, Zainal Z A, Mohammadi M and Mohamed A R 2015 *Renew. and Sustain. Energy Rev.* **41** 615–32
- [2] Leung D Y C, Caramanna G and Maroto-Valer M M 2014 *Renew. and Sustain. Energy Rev.* **39** 426–43
- [3] Songolzadeh M, Soleimani M, Ravanchi T M and Songolzadeh R 2014 Sci. World J. 2014 34
- [4] Kargari A and Takht Ravanchi M 2012 Greenh. Gases Capturing, Util. Reduct. 1 3–30
- [5] Abu-Zahra M R M, Feron P H M, Jansens P J and Goetheer E L V 2009 Int. J. Hydrogen Energy 34 3992–4004
- [6] Czyperek M, Zapp P, Bouwmeester H J M, Modigell M, Peinemann K V., Voigt I, Meulenberg W A, Singheiser L and Stöver D 2009 Energy Proceedia 1 303–10
- [7] Shao L, Low B T, Chung T-S and Greenberg A R 2009 J. Memb. Sci. 327 18–31
- [8] Baker R W, Lokhandwala K, Baker R W and Lokhandwala K 2008 J. Ind. Eng. Chem. 47 2109–21
- [9] Dortmundt D and Doshi K 1999 *Recent Developments in CO*₂ *Removal Membrane Technology Uop Llc p* 1–32
- [10] Brunetti A, Scura F, Barbieri G and Drioli E 2010 J. Memb. Sci. 359 115–25
- [11] Wang D, Li K and Teo W K 1998 J. Memb. Sci. 138 193–201
- [12] Shamsabadi A A, Kargari A, Babaheidari M B and Laki S 2013 J. Ind. Eng. Chem. 19 1680-8
- [13] Saedi S, Madaeni S S and Shamsabadi A A 2014 Chem. Eng. Res. Des. 92 2431-8
- [14] Ren J, Zhou J and Deng M 2010 Sep. Purif. Technol. 74 119–29
- [15] Kurdi J and Tremblay A Y 1999 J. Appl. Polym. Sci. 73 1471–82
- [16] Simons K, Nijmeijer K, Sala J G, van der Werf H, Benes N E, Dingemans T J and Wessling M 2010 J. Appl. Polym. Sci. 51 3907–17
- [17] Jamil A, Ching O P and Shariff A M 2016 ARPN J. Eng. Appl. Sci. 11 1687–91
- [18] Ismail A F and Yean L P 2003 Sep. Purif. Technol. 33 442–51
- [19] Powell C E and Qiao G G 2006 J. Memb. Sci. 279 1–49
- [20] Adewole J K, Ahmad A L, Ismail S and Leo C P 2013 Int. J. Greenh. Gas Control 17 46-65
- [21] Chung T-S and Kafchinski E R 1997 J. Appl. Polym. Sci. 65 1555-69
- [22] Chung T S, Teoh S K and Hu X 1997 J. Memb. Sci. 133 161–75

Acknowledgement

The author would like to acknowledge and thank the research grant 203.PJKIMIA.6071334 provided by Universiti Sains Malaysia that made this study successful.