เยื่อเลือกผ่านนาโนคอมพอสิตที่มีกราฟีนออกไซด์สำหรับการแยกแก๊สคาร์บอนไดออกไซด์และมีเทน

นางสาวนาเดีย นรฮีม

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Nanocomposite membranes incorporated with graphene oxide for CO_2/CH_4 separation

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นาเดีย นรฮีม : เยื่อเลือกผ่านนาโนคอมพอสิตที่มีกราฟีนออกไซด์สำหรับการแยกแก๊สคาร์บอนไดออกไซด์และมีเทน (Nanocomposite membranes incorporated with graphene oxide for CO_2/CH_4 separation) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร. ชลิดา คล้ายโสม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. ขจรศักดิ์ เฟื่องนวกิจ, 78 หน้า.

แก๊สชีวภาพถือเป็นพลังงานทางเลือก ที่เกิดจากการย่อยสลายของสารอินทรีย์ โดยทั่วไปแล้วแก๊สชีวภาพประกอบไปด้วย มีเทน คาร์บอนไดออกไซด์ ไฮโดรเจนซัลไฟด์ และน้ำในปริมาณเล็กน้อย ในปัจจุบันการปรับปรุงแก๊สชีวภาพถูกนำมาใช้เพื่อเพิ่มค่าความร้อนที่ได้จากการเผาไหม้และเพิ่มคุณภาพของแก๊สชีวภาพให้ได้มาตรฐาน ด้วยการกำจัดแก๊สคาร์บอนไดออกไซด์ เยื่อเลือกผ่านชนิดเยื่อแผ่นคอมพอสิตของพอลิเมอร์ผสมระหว่างพอลิเอทิลีนไกลคอล 400 และ พีแบค 1657 กับการผสมกราฟีนออกไซด์ และกราฟีนออกไซด์ที่ผ่านการปรับปรุงโครงสร้างด้วยหมู่เอมีน ถูกพัฒนาขึ้นสำหรับการแยกคาร์บอนไดออกไซด์ออกจากมีเทน งานวิจัยนี้ศึกษาผลของการใส่สารเติมแต่ง ที่ประกอบไปด้วย กราฟีนออกไซด์ กราฟีนออกไซด์ที่ผ่านการปรับปรุงโครงสร้างด้วยหมู่เอมีน และพอลิเอทิลีนไกลคอล 400 ต่อประสิทธิภาพของการแยกแก๊ส เยื่อแผ่นคอมพอสิตที่ประกอบไปด้วยร้อยละ 0.25 ของกราฟีนออกไซด์โดยน้ำหนักในพีแบค 1657 แสดงค่าการแยกที่ดีขึ้น เมื่อเปรียบเทียบกับเยื่อแผ่นคอมพอสิตพีแบค 1657 ค่าการแยกเพิ่มขึ้นจาก 12.18 เป็น 42.33 แต่อย่างไรก็ตามเมื่อผสมกราฟีนออกไซด์เข้าไป ทำให้การผ่านของแก๊สคาร์บอนไดออกไซด์ลดลง การเติมสารพอลิเอทิลีนไกลคอล 400 ในเนื้อพอลิเมอร์พีแบค 1657 ช่วยเพิ่มค่าการผ่านของแก๊สคาร์บอนไดออกไซด์ และพบว่าเยื่อแผ่นคอมพอสิตที่ผสมพอลิเอทิลีนไกลคอล 400 ร้อยละ 50 โดยน้ำหนัก และร้อยละ 0.25 ของกราฟีนออกไซด์โดยน้ำหนักเทียบกับเนื้อพอลิเมอร์รวม ให้ค่าการแยกคาร์บอนไดออกไซด์ออกจากแก๊สผสมที่ดีขึ้น เมื่อเทียบกับเยื่อเลือกผ่านที่ยังไม่ผ่านการปรับปรุง ค่าการแยกเพิ่มขึ้นไปถึง 42.81 และค่าการผ่านของแก๊สคาร์บอนไดออกไซด์ อยู่ที่ 13.07 GPU จากผลการทดสอบสามารถสรุปได้ว่า กราฟีนออกไซด์เป็นตัวหลักที่ส่งผลต่อค่าการแยก เนื่องจากกราฟีนออกไซด์ทำให้ระหว่างผิวหน้าของเนื้อพอลิเมอร์กับกราฟีนออกไซด์มีความแข็งแรงขึ้น และสามารถขัดขวางการเดินทางของ CH_4 เพิ่มระยะทางให้แก๊สที่ผ่านเข้ามาในแผ่นเยื่อคอมพอสิต ซึ่งช่วยให้เกิดการแยกระหว่าง CO_2 และ CH_4 ได้ดีขึ้น ในขณะที่พอลิเอทิลีนไกลคอล 400 ให้ค่าการผ่านของแก๊สคาร์บอนไดออกไซด์ที่เพิ่มขึ้น เนื่องจากพอลิเอทิลีนไกลคอล 400 ทำให้สายโซ่พีแบค 1657 มีความหลวมมากขึ้น

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ปีการศึกษา 2560 ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

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NADIA NORAHIM: Nanocomposite membranes incorporated with graphene oxide for CO_2/CH_4 separation. ADVISOR: CHALIDA KLAYSOM, Ph.D., CO-ADVISOR: KAJORNSAK FAUNGNAWAKIJ, D.Eng., 78 pp.

Biogas is an alternative energy produced by anaerobic digestion of organic matter. Generally, raw biogas consists of methane (CH_4), carbon dioxide (CO_2), few amount of hydrogen sulfide (H_2S) and traces of water vapor. Nowadays, upgrading raw biogas is required in order to achieve higher calorific value and meet fuel standard by removal of CO_2. In this study, composite membranes of PEG 400/Pebax 1657 blended polymer with graphene oxide (GO) and amine functionalized graphene oxide (Fn-GO) were successfully developed for CO_2/CH_4 gas separation. The effects of graphene oxide, amine functionalized graphene oxide and PEG 400 additions on CO_2/CH_4 separation performance were studied in this research. The membrane containing 0.25 wt.% GO in Pebax 1657 showed a better separation factor compared to pristine Pebax 1657 composite membrane by increasing from 12.18 to 42.33. However, CO_2 permeance dropped when GO was incorporated in Pebax matrix. PEG 400 was added in Peabax 1657 matrix to increase CO_2 permeance and it was found that the composite membrane containing 50 wt.% PEG 400 in polymer matrix with 0.25 wt.% GO showed the good CO_2/CH_4 separation factor up to 42.81 and also CO_2 permeance of 13.07 GPU. With the obtained results, it could be concluded that GO mainly influenced separation factor because GO generated a rigidified interface between the polymer and fillers Moreover, GO also block the pathway for CH_4 through membrane resulting to an increased diffusion distance and enhance the separation between CO_2 and CH_4. Whereas PEG 400 provided a higher CO_2 permeance due to a loose chain of Pebax 1657 matrix.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEWS

1.1 Introduction

Nowadays, biogas has been considered as cheap and clean alternative energy since biogas usually refers to a mixture of different gases generated by an anaerobic digestion of organic matter. The raw materials used to produce biogas originate from many sources such as sewage plants, landfills, industrial wastes, and agricultural production [1].

Biogas generally consists of 55-70% methane, 30-45% carbon dioxide, and small amount of hydrogen sulfide and water. The presence of CO_2 leads to reduce quality of fuel and make it uneconomical. The upgrading raw biogas is thus required in order to achieve higher calorific value and meet fuel standard by removing of CO_2. Many separation and purification techniques have been utilized for CO_2 removal in biogas industries such as pressure swing adsorption, absorption, cryogenic method, and gas separation membrane [2]. At this time, membrane technology provides several advantages over aforementioned technologies including high energy efficiency, easy up scaling, continuous operation and low ecological footprint.

Table 1.1 Comparison of technologies in biogas upgrading

Technologies	Advantages	Disadvantages
Pressure swing adsorption	i) No chemical involved ii) Relatively high methane purity yield	i) High pressure operation ii) High energy cost
Chemical absorption	i) Relatively high methane purity yield	i) Chemical involved

	ii) Low pressure operation	ii) High cost of chemicals and energy
Water scrubber	i) High methane purity yield ii) No chemical involved	i) High pressure operation ii) High energy cost
Membrane	i) Ease of operation ii) Environmental friendly process iii) High energy efficiency	i) High cost of membrane purchase ii) Low methane yield

1.2 Background

1.2.1 Molecule transport theory in membrane

Gas separation membrane is defined as selective barrier to separate one or more gases from a feed mixture based on the principle that some gases permeate through membrane more rapidly than others. For gas separation membrane, especially CO_2/CH_4 gas separation, the gas molecules are transported through dense membranes via solution-diffusion mechanism. Considering solution-diffusion model, the selectivity is controlled by molecular structure of polymer that permits specific gas molecules to pass through membranes based on their solubility and diffusibility [3].

1.2.2 Trade-off between permeability and selectivity

Polymeric membranes gain an attention from many researchers nowadays owing to low cost, easy fabrication, and good mechanical stability. However, polymeric membranes demonstrate either low permeability or low selectivity that brings into an inverse relationship between the permeability and selectivity. In 1991, Robeson first proposed the relationship between separation factor and permeability from several experimental data, leading to determination of an upper limit value. Besides, Robeson’s upper bound was revisited in 2008 as Figure 1.1 [4].

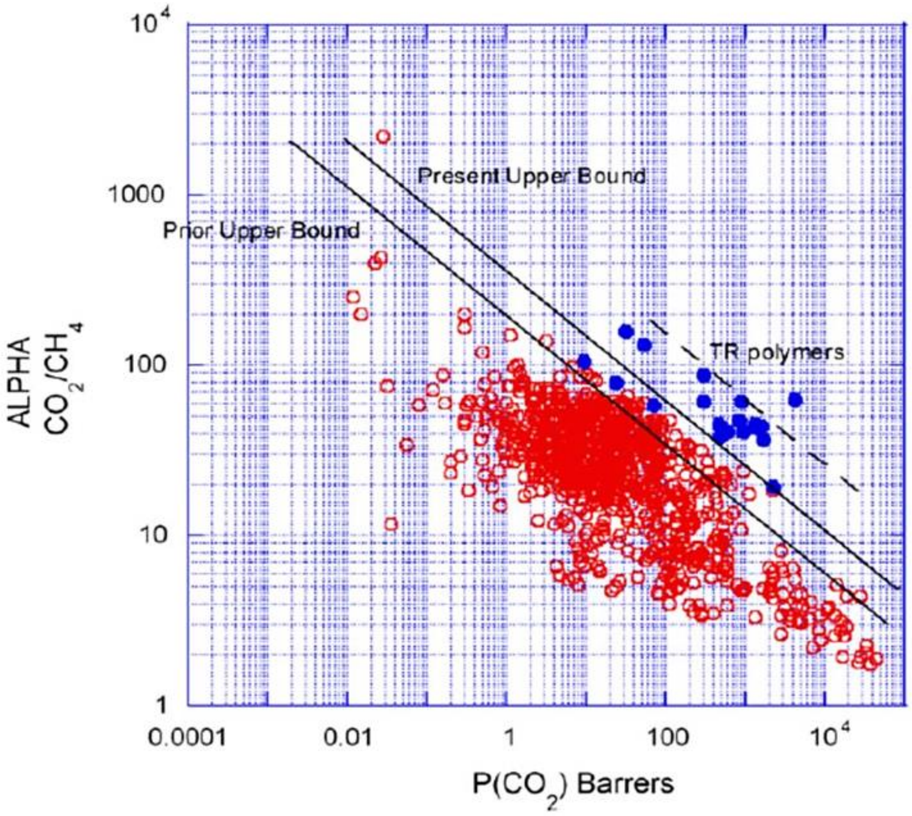


Figure 1.1 Robeson's upper bound for CO_2/CH_4 separation [4].

Robeson’s upper bound is a useful guideline to compare the performance of different membranes for gas separation. Currently, many researchers are working to improve membrane performance by developing new emerging materials or developing the existing membranes with new features.

1.3 Literature reviews

In this section, the past studies of CO_2/CH_4 membrane have been reviewed in term of type of membrane including polymeric membrane, mixed matrix membrane, composite membrane, and thin film nanocomposite membrane.

1.3.1 Types of membranes for CO_2/CH_4 gas separation

- **Polymeric membrane**

Commonly, polymeric membranes can be classified into two classes; rubbery and glassy materials. The rubbery polymer exhibits soft and elastic structure due to segments of polymer backbone that can rotate freely around their axis. On the other hand, glassy polymer provides a rigid and tough structure since segments of polymer is not able to rotate around polymer backbone. Based on the aforementioned statements, the rubbery polymer separate gas species based on condensability, while the glassy polymer separates gas species based on the difference in sizes or kinetic diameters of gas components [5].

There are many different polymer families that have been studied for gas separation membranes such as polysulfone, polyimide, polyetherimide, and poly (ether-block-amide). Table 1.2 shows the membrane performance of different neat polymers that have been studied in past researches.

Table 1.2 Past researches of polymeric membrane for CO_2/CH_2 gas separation

Material	Testing conditions			Performance		Ref.
	T (°C)	P (bar)	CO_2:CH_4 composition	P_{CO2} (Barrer)	Selectivity CO_2/CH_4	
Polyetherimide	25	10	Single gas	2.37	25.8	[6]
Polyimide (Matrimid 9725)	35	9	50:50	4	31	[7]
Polyimide (Matrimid 9725)	25	10	Single gas	6.2	31	[8]
Polyimide	35	9	50:50	4	30	[9]

(Matrimid 9725)						
Polysulfone	35	1	50:50	5.2	23	[10]
Polyimide (Matrimid 5218)	35	1	50:50	8.5	28	
Polyimide (Matrimid 5218)	30	2	30:70	8	28	[11]
Poly(ether-block-amide) (Pebax 1657)	25	2	30:70	500	18	[12]
Poly(ether-block-amide) (Pebax 1657) (Humidified condition)	25	1	Single gas	500	20	[13]

Among polymeric membranes in Table 1.2, poly (ether-block-amide) shows an outstanding performance in term of permeability while polyetherimide shows the poorest CO_2 permeability. On the other hand, polyimide possesses the highest selectivity but quite low permeability and the poly (ether-block-amide) exhibits the lowest value of selectivity comparing to other polymers. Even though polyimide shows better performance than polyetherimide and Pebax 1657, but with the problem to access and purchase this material leading to poly(ether-block-amide) or Pebax 1657 was selected as selective layer in this study due to its good separation property, excellent mechanical and thermal stability, and easy processibility.

Recently, polymer blends are fully studied in many researches and considered as an alternative method that has been developed to improve membrane performance and also to tackle any drawbacks of polymeric membranes. The advantages of each polymer are combined in order to achieve a suitable performance for gas separation. Some of polymer blends membranes in CO_2/CH_4 gas separation are summarized in Table 1.3.

Table 1.3 Past researches of polymer blends membrane for CO_2/CH_4 gas separation

Materials		Operating conditions			Performance		Ref.
Types of material	Material loading (wt.%)	T (°C)	P (bar)	CO_2:CH_4 composition	P_{CO2} (Barrer)	CO_2/CH_4 selectivity	
PSf-PEI	100-0	25	6	Single gas	5.4	9	[14]
	99-1	25	6	Single gas	5	10.7	
	98-2	25	6	Single gas	4.7	11	
	97-3	25	6	Single gas	4.4	11.5	
PES-PVA_c	100-0	N/A	10	Single gas	5.3*	1.55	[15]
	90-10	N/A	10	Single gas	5.7*	1.40	
	0-100	N/A	10	Single gas	11.4*	1.1	
Pebax 1657-PEG 400	100-0	N/A	N/A	Single gas	63	25.75	[16]
	80-20	N/A	N/A	Single gas	66	24.55	
	60-40	N/A	N/A	Single gas	78	23.60	
Pebax 1074-PEG 400	100-0	25	2	Single gas	64.8	20.2	[17]
	90-10	25	2	Single gas	105.6	20.3	
	80-20	25	2	Single gas	132.3	20.4	
	70-30	25	2	Single gas	151.3	20.6	
	60-40	25	2	Single gas	168.4	20.8	
Pebax 1657-PEG 400	100-0	25	2	Single gas	72.2	18.5	
	90-10	25	2	Single gas	114.6	18.6	
	80-20	25	2	Single gas	141.9	18.9	

	70-30	25	2	Single gas	156.9	19.1	
	60-40	25	2	Single gas	174.5	19.2	
Pebax 2533-PEG 400	100-0	25	2	Single gas	191.0	7.2	
	90-10	25	2	Single gas	247.7	7.2	
	80-20	25	2	Single gas	282.6	7.3	
	70-30	25	2	Single gas	302.2	7.4	
	60-40	25	2	Single gas	319.4	7.6	
Pebax 1074-PEG 1000	100-0	25	2	Single gas	64.8	20.2	
	90-10	25	2	Single gas	47.9	22.7	
	80-20	25	2	Single gas	228	24.7	
	70-30	25	2	Single gas	9.8	25.9	
	60-40	25	2	Single gas	6.3	27.1	
Pebax 1657-PEG 1000	100-0	25	2	Single gas	72.2	18.5	
	90-10	25	2	Single gas	51.0	21.1	
	80-20	25	2	Single gas	29.7	23.3	
	70-30	25	2	Single gas	15.2	24.5	
	60-40	25	2	Single gas	8.0	25.6	
Pebax 2533-PEG 1000	100-0	25	2	Single gas	191.1	7.2	
	90-10	25	2	Single gas	107.6	8.4	
	80-20	25	2	Single gas	64.4	9.5	
	70-30	25	2	Single gas	43.4	10.2	
	60-40	25	2	Single gas	13.7	10.9	

*1 gas permeation unit (GPU) = 10-6 cm3 (S.T.P)/ (s.cm2.cm Hg)

From Table 1.3, polsulfone was blended with polyetherimide and the experimental illustrated that increasing polyetherimide loading could be able to enhance the selectivity but reduced the CO_2 permeability.

In the recent time, polyethylene glycol (PEG) was the most common additive to polymeric membrane especially CO_2 gas separation due to the polar ether group in PEG trends to preferentially separate CO_2 gas in a gas mixture. From research study, the incorporation of different molecular weights of PEG provided different effects to Pebax matrices. The experimental results showed that increasing PEG 400 addition to Pebax was able to noticeably increase CO_2 permeability while CO_2/CH_4 selectivity slightly increased comparing to neat Pebax. On the other hand, Pebax with PEG 1000 incorporation provided opposite trend. Larger loading of PEG 1000 demonstrated higher selectivity but lower CO_2 permeability. A high molecular mass PEG caused non-uniform miscibility of the two polymers, leading to an irregular and convoluted blend membrane structure [17]. Nevertheless, other researches with the same matching of polymer blend for Pebax/PEG 400 showed some different performance. Those PEG 400 added to Pebax performed improved CO_2 permeability but reduced in CO_2/CH_2 selectivity due to the loose in polymer chain.

➢ Mixed matrix membranes (MMMs)

Mixed matrix membrane (MMM) is composed of inorganic fillers dispersing in polymer matrix, which acts as continuous phase. The mixed matrix membranes have been synthesized to improve the gas separation performance or eliminate any drawbacks of polymeric membranes. Besides, mixed matrix membranes are able to enhance the permeability, selectivity, thermal stability, and chemical stability of membranes. To achieve high separation performance, the selection of polymer and filler becomes crucial for mixed matrix membrane fabrication. Some of part researches on mixed matrix membranes for CO_2/CH_4 separation are concluded in Table 1.4

Table 1.4 The developments of mixed matrix membrane for CO_2/CH_4 gas separation

Materials			Operating condition			Performance		Ref.
Polymer	Filler	Filler content (wt.%)	T (°C)	P (bar)	$CO_2:CH_4$ composition	P_{CO2} (Barrer)	CO_2/CH_4 selectivity	
Polyetherimide (Ultem 1000)	No filler		25	10	Single gas	2.37	25.8	[6]
	GO	0.25	25	10	Single gas	2.738	40.9	
		0.50	25	10	Single gas	2.25	45	
		0.75	25	10	Single gas	1.926	58.4	
	GO-PEG	0.25	25	10	Single gas	0.786	56.4	
		0.50	25	10	Single gas	0.912	60.8	
		0.75	25	10	Single gas	1.197	74.8	
	$GO-NH_2$	0.25	25	10	Single gas	1.18	98.3	
		0.50	25	10	Single gas	1.92	137.1	
		0.75	25	10	Single gas	1.57	142.7	
Polyimide (Matrimid 9725)	No filler		35		50:50	4	31	[7]
	MCM-41	5	35	9	50:50	5	38	
		10	35	9	50:50	7	36	
		15	35	9	50:50	8	35.5	
		20	35	9	50:50	11	35	
		30	35	9	50:50	22	30	
	CSM-18.4	5	35	9	50:50	7	40.5	
		10	35	9	50:50	8	41	
		15	35	9	50:50	10	40	
		20	35	9	50:50	12	41	
		30	35	9	50:50	19	42	
	CSM-23.3	5	35	9	50:50	5	42.5	
		10	35	9	50:50	7	45	
		15	35	9	50:50	10	42.5	
		20	35	9	50:50	15	39	
		30	35	9	50:50	25	38	
Polyimide (Matrimid 9725)	No filler		25	10	Single gas	6.2	31	[8]
	MCM-41	5	25	10	Single gas	7	30.9	
		10	25	10	Single gas	7.8	30.8	

		15	25	10	Single gas	8.5	31	
		20	25	10	Single gas	9.4	31.1	
		25	25	10	Single gas	9.8	30	
		30	25	10	Single gas	10	28	
	SO$_3$H-MCM-41	5	25	10	Single gas	7.5	33	
		10	25	10	Single gas	7	36	
		15	25	10	Single gas	7.8	37	
		20	25	10	Single gas	8.5	38	
		25	25	10	Single gas	9.4	37.7	
		30	25	10	Single gas	10	37.5	
Polyimide (Matrimid 9725)	No filler		35	9	50:50	4	30	[9]
	MIL-125(Ti)	5	35	9	50:50	5	34	
		10	35	9	50:50	7	44	
		15	35	9	50:50	9	44	
		20	35	9	50:50	12	38	
		30	35	9	50:50	14	36	
	NH$_2$-MIL-125(Ti)	5	35	9	50:50	6	36	
		10	35	9	50:50	8	46	
		15	35	9	50:50	8.5	50	
		20	35	9	50:50	15	42	
		30	35	9	50:50	26	35	
Polysulfone	No filler		35	1	50:50	5.2	23	[10]
	NH$_2$-MIL-53(Al)	15	35	1	50:50	5	24	
		20	35	1	50:50	4.5	26	
		25	35	1	50:50	5.5	27.5	
	NH$_2$-MIL-101(Al)	8	35	1	50:50	5.5	24	
		15	35	1	50:50	7.2	25	
		25	35	1	50:50	8.5	28	
Polyimide (Matrimid 5218)	No filler		35	1	50:50	9	37.5	
	NH$_2$-MIL-53(Al)	15	35	1	50:50	8.2	38	
		20	35	1	50:50	8.6	43	
		25	35	1	50:50	8.7	35	
	NH$_2$-MIL-101(Al)	8	35	1	50:50	10.4	35	
		15	35	1	50:50	9.6	36	
	No filler		30	2	30:70	8	28	[11]

Polyimide (Matrimid 5218)	CNTs and GO	0/10	30	2	30:70	5	66	
		2/8	30	2	30:70	17	70	
		5/5	30	2	30:70	35	80	
		8/2	30	2	30:70	27	60	
		10/0	30	2	30:70	9	20	
Poly(ether-block-amide) (Pebax 1657)	No filler		25	2	30:70	500	18	[12]
	MCM-41	5	25	2	30:70	580	18.2	
		10	25	2	30:70	590	18	
		15	25	2	30:70	610	18.5	
		20	25	2	30:70	640	18	
	PEI-MCM-41	5	25	2	30:70	700	24	
		10	25	2	30:70	800	27.5	
		15	25	2	30:70	1040	30.5	
		20	25	2	30:70	1390	39	
Poly(ether-block-amide) (Pebax 1657)	No filler	10	25	1	Single gas	500	20	[13]
	GO	10	25	1	Single gas	250	23	
	PEG-GO	10	25	1	Single gas	720	25	
	PEI-GO	10	25	1	Single gas	1100	31	
	PEG-PEI-GO	10	25	1	Single gas	1310	44	
Poly(ether-block-amide) (Pebax 1657)	No filler		25	5	Single gas	55.8	18	[18]
	4A zeolite	5	25	5	Single gas	71.4 ± 5.1	32.2 ± 2.1	
		10	25	5	Single gas	97.0 ± 4.9	26.5 ± 1.9	
		20	25	5	Single gas	113.7 ± 5.5	17.6 ± 1.5	
		30	25	5	Single gas	155.8 ± 6.9	7.9 ± 0.5	
Poly(ether-block-amide) (Pebax 1657)	No filler		30	2.5	Single gas	88	19	[19]
	ZIF-7	5	30	2.5	Single gas	148	21	
		20	30	2.5	Single gas	110	23	
		35	30	2.5	Single gas	43	39	
Pebax 1657/ PEG 400 (50/50)	No filler		30	4	Single gas	120	23.1	[20]
	MWNT	2	30	4	Single gas	136	23.0	

	No filler		50	4	Single gas	191	20.2	
	MWNT	2	50	4	Single gas	221	20.1	

Over the past decades, there were many fillers that had been investigated for CO2/CH4 gas separation, including zeolites, metal organic frameworks (MOFs), spherical shape particles, and sheet-like particles.

Some of researches on CO_2/CH_4 gas separation membranes are summarized in the Table 1.2. Zeolite is a microporous crystalline compound that can accommodate variety of cations. 4A zeolites were incorporated in Pebax 1657 as mixed matrix membranes, and were found that increasing in 4A zeolite loading could increase permeability but decrease CO_2/CH_4 selectivity [18]. Since zeolites have been exposed difficulty to do functionalization of the pores. Thus, metal organic frameworks (MOFs) was introduced to solve those problems of zeolites. MOFs are mechanically less brittle and less stiff compared to zeolite. MIL-125(Ti), MIL-53(Al) and MIL-101(Al) are another type of MOF that show a good adhesion and excellent dispersion in polymer matrix. MIL-125(Ti), MIL-53(Al) and MIL-101(Al) were functionalized with amine to create H-bonds between the NH_2-group of fillers and polyimide. Addition of 15 wt. % NH_2-MIL-125(Ti) in polyimide matrix improved CO_2/CH_4 selectivity up to 50, compared to pure polyimide, with CO_2/CH_4 selectivity of only 30 [9]. In recent years, mesoporous silica spheres (MSSs) have been introduced as spherical-shape particles. MCM-41, CSM-18.4 and CSM-23.3 embedded in polyimide significantly increased both permeability and selectivity [7]. Somehow, the optimized loading played a significant role in membrane performances. Moreover, ZIF-7 had also been introduced to Pebax 1657 by varying filler addition from 5-35 wt.%. The pore size of ZIF-7 was about 0.30 nm and the pore gate of ZIF-7 was flexible then CO_2 could diffuse through the pore owing to rotation of the organic linker caused by the penetrant molecules [19]. The highest selectivity was obtained at 35 for 5 wt.% loading of ZIF-7 however, CO_2 permeability dramatically dropped [19].

The incorporation of MWNT to Pebax 1657/PEG 400 blended membrane had been introduced for CO_2/CH_4 gas separation [20]. The study revealed that increasing in

MWNT could be able to enhance the CO_2 permeability due to the interface voids of poor polymer/filler contact.

Also, the combination of CNTs and GO had been also studied. The optimal of CNTs and GO loading found to be at 5 wt. % of CNTs and 5 wt. % of GO leading to dramatically increase in selectivity [11]. Surprisingly, functionalized graphene oxide showed noticeable raise in selectivity when embedded in the polymer matrix. Graphene oxide obtains high thermal and mechanical properties. Besides, it is easy to do functionalization to graphene oxide. Some researchers have been studied on graphene oxide added into the polyetherimide and Pebax 1657 to improve membrane’s selectivity. Graphene oxide was functioned with PEG and NH_2 in order to enhance the selectivity. At the same loading of filler, NH_2-GO obtained the highest selectivity comparing to GO and PEI-GO due to the strong interface between filler and polymer matrix [13].

Amine functionalized graphene oxide incorporated in polyetherimide demonstrated the significant rise of CO_2/CH_4 selectivity. 142.7 of CO_2/CH_4 selectivity was investigated for 0.75 wt. % of NH_2-GO in polyetherimide, however very low permeability was obtained in this condition [6]. For Pebax 1657, many types of functionalized graphene oxide were embedded into polymeric matrix. The effect of filler types and filler loading have been investigated. The humidified condition were applied in performance test operation due to the reversible reaction between CO_2 and amine groups. The reaction between CO_2 and amine group carrier can be described in the following mechanism;

First, CO_2 reacts with primary or secondary amines (RR’NH, where R is a functional group and R’ is a functional group or hydrogen) to form zwitterion as an intermediate.

$$CO_2 + RR'NH \leftrightarrow RR'NH{+}COO{-}$$

The zwitterion then is deprotonated by bases such as amine itself and H_2O to form the carbamate ion.

$$RR'NH^{+}COO^{-} + RR'NH \leftrightarrow RR'NCOO^{-} + RR'NH_2^{+}$$

$$RR'NH^{+}COO^{-} + H_2O \leftrightarrow RR'NCOO^{-} + H_3O^{+}$$

If the carbamate ion of the amine carrier is not stable, it will react with H_2O to form bicarbonate, HCO^{3-}

$$RR'NCOO^{-} + H_2O \leftrightarrow RR'NH + HCO_3^{-}$$

Additionally, a humidified condition may provide a better CO_2 facilitation than a dry condition. The presence of amino group leads to increase CO_2 hydration reaction in a humidified membrane. Therefore, CO_2 is facilitated in the forms of carbamate and bicarbonate. These carrier gas reaction products will diffuse due to their concentration gradient and pass off to next carrier agent under reversible reaction. Based on the literature studies, it has been found that compatibility between polymer and filler should be concerned in mixed matrix membrane synthesis. Therefore, the performance of membrane depends on type of materials used and filler loading.

➢ Composite membranes

Composite membranes is defined as membrane that selective layer and support layer are made of different materials. Commonly, dense or cross-linked polymer are formed on the microporous support membrane. Several composite membranes for CO_2/CH_4 gas separation are listed in the Table 1.5;

Table 1.5 The development of composite membrane for CO_2/CH_4 gas separation

Support layer	Selective layer				Operating condition			Performance		Ref.
	Polymer	Loading (wt.%)	Filler	Loading (wt.%)	T (°C)	P (bar)	CO_2:CH_4 composition	P_{CO2} (Barrer)	CO_2/CH_4 selectivity	
18 wt.% PES	Pebax 1657	1	No filler	N/A	N/A	2	Single gas	150	9.2	[21]
					N/A	2	10:90	260	7	
			ZIF-8	8	N/A	2	Single gas	464±21	13.8±0.4	
					N/A	2	10:90	491±25	9.1±0.2	
		4	No filler	N/A	N/A	2	Single gas	130	11	
					N/A	2	10:90	210	6.2	
			ZIF-8	8	N/A	2	Single gas	449±23	14.7±0.2	
					N/A	2	10:90	459±16	9.9±0.3	
15 wt.% PVC	Pebax 1657	3	No filler	N/A	25	5	Single gas	117	34.5	[22]
			TiO_2	1	25	5	Single gas	121	33.5	
				3	25	5	Single gas	137	35	
				5	25	5	Single gas	138	19	
			No filler	N/A	25	10	Single gas	128	42	
			TiO_2	1	25	10	Single gas	134	36	
				3	25	10	Single gas	147	43.5	
				5	25	10	Single gas	158	21.5	
			No filler	N/A	25	15	Single gas	129	37.5	
			TiO_2	1	25	15	Single gas	142	46	

				3	25	15	Single gas	151	50.5	
				5	25	15	Single gas	168	22	
			No filler	N/A	25	20	Single gas	146	35.5	
			TiO_2	1	25	20	Single gas	150	44	
				3	25	20	Single gas	161	53.5	
				5	25	20	Single gas	191	15.5	
20 wt.% PSF	PDMS	30	No filler and No selective layer		N/A	2	Single gas	*60	19	[23]
			With selective layer		N/A	2	Single gas	*48	32	

*GPU unit

From the Table 1.5, Pebax 1657 has been applied as selective layer in many research studies. There were many filler types used to mix with Pebax matrix. Comparing at the same Pebax concentration, the addition of ZIF-8 was able to enhance CO_2/CH_4 selectivity because ZIF-8 gains a high potential adsorbent for CO_2 due to an affinity for CO_2 [21]. In addition, TiO_2 has also been introduced into Pebax for composite membrane. The incorporation of TiO_2 in Pebax presented CO_2 permeability improvement. This was because TiO_2 disrupted the chain packing of polymer matrix, resulting in enhanced free volume fraction that promotes permeability of gas [22].

Not only Pebax has been utilized as selective layer for composite membrane, PDMS has also been studied. PDMS selective layer coated on support membrane exhibited higher selectivity comparing to pristine polysulfone since the complete phase transition and homogeneous crosslinking between PDMS and PSF [23].

- **Thin film nanocomposite membrane**

Thin film composite membrane is prepared by coating a very thin layer of aromatic polyamide (PA) onto polymeric supporting membrane. The thin film is normally prepared by an interfacial polymerization technique. The interfacial polymerization is the reaction at the interface of two immiscible solution containing two different monomers; the first monomer is polyfunctional amine dissolved in water solution and the second monomer is polyfunctional acid chloride dissolved in hydrocarbon solvent. Thin film composite membranes can be independently controlled and optimized to achieve desired selectivity and permeability while offering mechanical strength and compression resistance.

Table 1.6 The development of thin film composite membrane for gas separation

Materials		Testing conditions				Performance		Ref.
Substrate membrane	Thin film layer	Gas pair	Gas testing	T (°C)	P (bar)	P_{CO2} (GPU*)	Selectivity CO_2/CH_4	
Polysulfone	Polyamide	CO_2/CH_4	Single gas	N/A	10	CO_2 15.2 CH_4 1.05	14.4	[24]
		H_2S/CH_4	Single gas	N/A	10	H_2S 51.6 CH_4 1.05	49.1	
		O_2/N_2	Single gas	N/A	10	O_2 5.13 N_2 0.95	5.4	
Polysulfone	Milled PMMA grafted MWNTs polyamide	CO_2/N_2	Single gas	RT.	2	CO_2 70.54 N_2 1.05	67.18	[25]
		CO_2/CH_4	Single gas	RT.	2	CO_2 70.54 CH_4 2.43	29.03	

From Table 1.6, thin film of polyamide was developed on polysulfone substrate to separate pure CO_2, CH_4, H_2S, O_2 and N_2 gases. Polyamide thin film was synthesized via interfacial polymerization between m-phenylenediamine (MPD) and isophthaloyl chloride (IsoCl). The results were revealed that H_2S/CH_4 obtained the highest selectivity, while CO_2/CH_4 had only 14.4 of selectivity.

To increase membrane performance of thin film composite membrane, thin film of polyamide was modified by adding milled PMMA grafted MWNTS into thin film.

The permeability and CO_2/CH_4 selectivity were increased to 70.54 GPU and 29.03 respectively.

1.3.4 Membrane technology in industries

Membrane technologies have been deployed in many fields of industry. In gas separation especially CO_2 removal, membranes was recognized in natural gas and biogas industries.

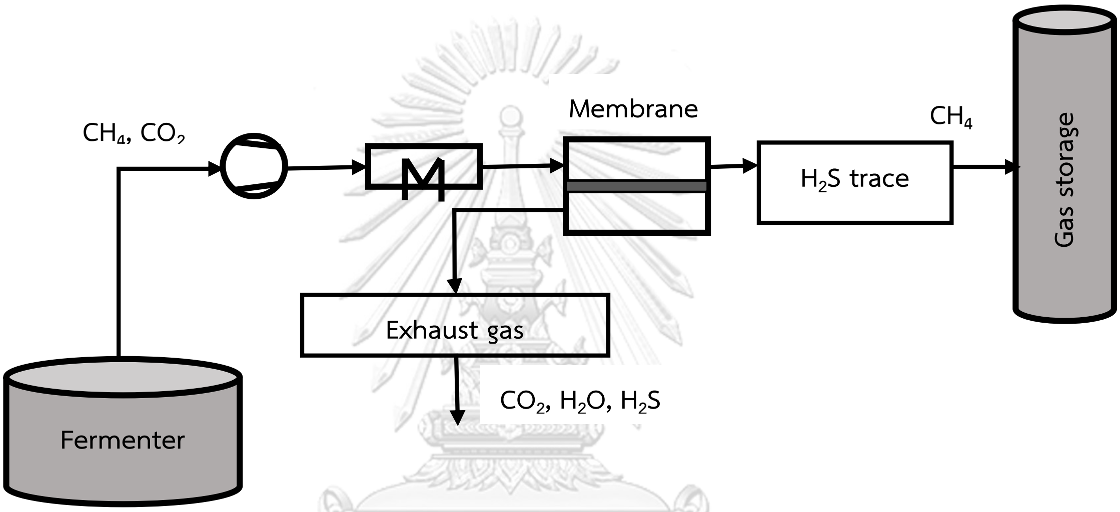


Figure 1.2 Basic flowsheet of membrane based biogas upgrading process [26].

Figure 1.2 represents the basic flowsheet of the membrane based biogas upgrading process. Firstly, the raw gas is compressed before entering to heat exchanger. The heat exchanger is used to control the gas temperature in the membrane system. Membrane is used to separate CO_2 from the gas mixture resulting to higher CH_4 purity obtained. A desulfurization unit is applied to reduce the H_2S level when the membrane system is not able to achieve H_2S level. Finally, the purified CH_4 enters the gas storage tank [26].

Many commercial membranes are available in the market with various materials to form membrane. Table 1.7 presents the company that produce gas separation membranes nowadays.

Table 1.7 Comparison of different membrane module designs to be applied to gas permeation [26]

Supplier	**Module type**	**Polymer**
Air Liquid Medal	Hollow fiber	Polyimide, polyaramide
Air Products	Hollow fiber	Polysulfone
Cameron former Natco Cynara	Hollow fiber	Cellulose acetate
GMT Membranetechnik	Envelope type	Poly(ethylene oxide)-poly(butylene therephthalate)
Evonik	Hollow fiber	Polyimide
IGS Generon Membrane Technology	Hollow fiber	Tretrabrome polycarbonate
Kvaerner Membrane Systems **	Spiral wound	Cellulose acetate
MTR Inc.	Spiral wound	Cellulose acetate
Parker	Hollow fiber	Polyphenylene oxide
Prazair ***	Hollow fiber	Polyimide
Sihi GKSS	Envelope type	Silicon rubber
UBE Membranes	Hollow fiber	Polyimide
UOP former Grace	Spiral wound	Cellulose acetate

The suppliers labelled with ** are no longer active in the field of gas permeation.

CHAPTER 2

SCOPES OF WORK

This project focused on the fabrication, characterization, and evaluation of developed membranes for biogas upgrading especially, CO_2/CH_4 gas separation.

2.1 Objectives

- To develop composite membranes of graphene oxide and functionalized graphene oxide fillers in PEG 400/Pebax 1657 blended on polyetherimide (PEI) support membrane.
- To investigate the effect of filler and polymer blend on physical, chemical and thermal properties of the developed membranes via various characterization methods.
- To evaluate the performance of membranes in term of permeance and separation factor for mixed gases of CO_2 and CH_4 testing.

2.2 Scopes of work

Composite membranes of PEG 400/Pebax 1657 blended with graphene oxide and functionalized graphene oxide additions on PEI support membrane were fabricated. Moreover, the effects of polymer blend, filler loading, and type of filler on the separation performance were investigated. The details of the material used and scopes of experiment are described as follows;

2.2.1 Membrane preparation

In this project, composite membrane consists of polytherimide support layer and PEG 400/Pebax 1657 blended selective layer. To improve membrane performance, graphene oxide and functionalized graphene oxide were embedded to the selective layer. The polyetherimide support layer was prepared via phase inversion while the selective layer was prepared by dip coating technique. The following parameters were investigated;

Table 2.1 The overview of membrane conditions in this research

Support layer	**Selective layer**			
	Type of polymer	**Polymer loading (wt.%)**	**Type of filler**	**Filler loading (wt.%)**
Polyetherimide (PEI)	Pebax 1657	100	Without filler	
			GO	0.25
				0.50
				0.75
				1.00
			Fn-GO	At optimal loading of GO in Pebax 1657
	PEG 400/Pebax 1657	25/75	Without filler	
		50/50	Without filler	
			GO	At optimal loading of GO in Pebax 1657
			Fn-GO	At optimal loading of GO in Pebax 1657

2.2.2 Membrane characterizations

All fabricated membranes were characterized by using various types of analytical equipment in order to identify and evaluate membrane properties and performances.

Physical characterization

- **Scanning Electron Microscope (SEM)**

The surface and cross-sectional morphologies of membranes were identified by using scanning electron microscope (SEM).

- **X-Ray Diffraction Analysis (XRD)**

The crystal structure and intermolecular distances between graphene oxide sheets were recorded on X-Ray Diffraction Analysis (XRD).

Chemical characterization

- **Attenuated Total Reflectance Fourier Transform Infared (ATR-FTIR)**

Chemical structures of membranes and fillers were measured by using ATR-FTIR technique.

Stability characterization

- **Thermal Gravimetric Analysis (TGA)**

Polymer blended membranes were tested for thermal stability analysis by using TGA.

2.2.3 Gas permeation test and separation analysis

To evaluate membrane performances, there are two key parameters need to be considered. First is permeance (P_i/l) which is the transport flux of gas species through membrane per unit driving force per unit membrane area (the ease of transport of each species). The permeance (P_i/l, GPU, and 1 GPU = 10^{-6} cm^3 (STP)/ (cm^2.s.cmHg)) of each gas was obtained by using the equation:

$$P_i/l = \frac{Q_i}{\Delta P_i \cdot A}$$

where Q_i is the volumetric flow rate of gas i (cm^3/s) at standard temperature and pressure (STP, ΔP_i is trans-membrane pressure difference of gas i (cmHg) between the feed side and permeate side pressure and A is the effective membrane area (cm^2).

Second is separation factor used to determine separating capacity of membrane for 2 species. The separation factor can be calculated from more permeable gas species i and the less permeable gas species j in the permeate side divided by the ratio of the same gases i and j in the feed stream. Generally, separation factor depends on the membrane properties and the driving force which consist of pressure and concentration polarization phenomena.

$$\text{Separation factor (SF)} = \frac{x_{i,p}/x_{j,p}}{x_{i,f}/x_{j,f}}$$

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Materials

A commercial polyetherimide (PEI, MW 55000 g/mol) and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma Aldrich. Graphene oxide and functionalized graphene oxide were obtained from Kumamoto University, Japan. A non-woven backing support (Novatexx 2470) was purchased from Freudenberg Germany). Pebax 1657 was purchased from Akema Inc. Anhydrous ethanol (Ethanol, 99.5%) was purchased from Acros Organics All the reagents were of analytical grade.

3.2 Fabrication of membranes

In fact, membrane structure plays an important role for membrane application. Altered applications require different membrane morphologies in order to obtain optimal performance of membranes. The details of membrane preparation are described as follows;

3.2.1 Preparation of pristine polyetherimide support

In this study, 20 wt.% of polyetherimide was chosen to fabricate as support membrane

I. Weight amount of PEI was gradually added into NMP solvent.

II. The prepared solution was stirred at 80 °C until homogeneous solution was obtained.

III. Before casting, the solution was left at room temperature to cool down and remove bubble in the solution.

IV. The prepared solution was cast on a non-woven backing support by a casting knife with a fixed casting thickness of 250 μm. The cast membrane was left to atmosphere for 30 seconds before being immersed in a deionized water bath.

3.2.2 Preparation of composite membrane

In this study, composite membrane were fabricated via dip coating method. PEI support was prepared in the same method as mentioned previously.

Pebax 1657 composite membrane preparation (without filler)

I. Pebax 1657 granules were dissolved in a solvent of ethanol/water (70/30 wt.%) and stirred at 70 °C to get a 4 wt.% homogeneous solution.
II. Then the mixture was cooled down to room temperature.
III. The Pebax 1657 solution was poured into container for dip coating.
IV. 20 wt.% PEI support membranes were dipped into prepared solution for three times at dipping rate of 200 mm/s for 30 second of dwelling duration. Coated membranes were dried in an oven at 60 °C for one hour before dipping to second and third time respectively.
V. The prepared membranes were finally dried in the oven at 60 °C after completing 3 times dipping to remove residue solvent.

Pebax 1657 composite membrane preparation (with GO filler)

I. Pebax 1657 granules were dissolved in a solvent of ethanol/water (70/30 wt.%) and stirred at 70 °C to get a 4 wt.% homogeneous solution.
II. Then the mixture solution was cooled down to room temperature.
III. The GO supernatant in DI water (specific amount of GO) was mixed in Pebax 1657 solution and stirred at 30 °C to obtain homogeneous solution.
IV. The mixture solution was poured into container for dip coating.
V. 20 wt.% PEI support membranes were dipped into prepared solution for three times at dipping rate of 200 mm/s for 30 second of dwelling duration. Coated membranes were dried in an oven at 60 °C for an hour before dipping to second and third time respectively.
VI. The prepared membranes were finally dried in the oven at 60 °C after completing 3 times dipping to remove residue solvent

PEG 400/Pebax 1657 blended composite membrane preparation (without filler)

I. Pebax 1657 granules were added to the mixture of ethanol/water (70/30 wt.%) and stirred at 70°C to obtain homogeneous solution.
II. Then the mixture was cooled down.
III. After that, the specific amount of PEG 400 was added to Pebax 1657 solution and stirred at 30 °C until well mixing of solution was obtained
IV. The mixture solution was cooled down to room temperature.
V. Then, the PEG 400/Pebax 1657 solution was poured into container for dip coating.
VI. 20 wt.% PEI support membranes were dipped into prepared solution for three times at dipping rate of 200 mm/s for 3o second of dwelling duration. Coated membranes were dried in the oven at 60 °C for an hour before dipping to second and third time respectively.
VII. The prepared membranes were finally fried in the oven at 60 °C after completing 3 times dipping to remove residue solvent.

Combination of filler and polymer blend

Fillers (GO and Fn-GO) and polymer blend were mixed together with Pabax 1657 in selective layer. Each condition of membrane was prepared as following;

PEG 400/Pebax 1657 blended composite membrane preparation (with GO filler)

I. Pebax 1657 granules were added to the mixture of ethanol/water (70/30 wt.%) and stirred at 70°C to obtain homogeneous solution.
II. Then the solution was cooled down.
III. After that, the specific amount of PEG 400 was added to Pebax 1657 solution and stirred at 30 °C until well mixing of solution was obtained

IV. The GO supernatant in DI water (specific amount of GO) was mixed in PEG 400/Pebax 1657 blended solution and stirred at 30 °C to obtain homogeneous solution.

V. The mixture solution was cooled down to room temperature.

VI. Then, mixture solution was poured into container for dip coating.

VII. 20 wt.% PEI support membranes were dipped into prepared solution for three times at dipping rate of 200 mm/s for 3o second of dwelling duration. Coated membranes were dried in the oven at 60 °C for an hour before dipping to second and third time respectively.

VIII. The prepared membranes were finally fried in the oven at 60 °C after completing 3 times dipping to remove residue solvent

Pebax 1657 composite membrane preparation (with Fn-GO filler)

I. Pebax 1657 granules were dissolved in a solvent of ethanol/water (70/30 wt.%) and stirred at 70 °C to get a 4 wt.% homogeneous solution.

II. Then the solution was cooled down to room temperature.

III. The Fn-GO supernatant in DI water (specific amount of Fn-GO) was mixed in Pebax 1657 solution and stirred at 30 °C to obtain homogeneous solution.

IV. The mixture solution was poured into container for dip coating.

V. 20 wt.% PEI support membranes were dipped into prepared solution for three times at dipping rate of 200 mm/s for 30 second of dwelling duration. Coated membranes were dried in an oven at 60 °C for an hour before dipping to second and third time respectively.

VI. The prepared membranes were finally dried in the oven at 60 °C after completing 3 times dipping to remove residue solvent

PEG 400/Pebax 1657 blended composite membrane preparation (with Fn-GO filler)

I. Pebax 1657 granules were added to the mixture of ethanol/water (70/30 wt.%) and stirred at 70°C to obtain homogeneous solution.

II. Then the solution was cooled down.

III. After that, the specific amount of PEG 400 was added to Pebax 1657 solution and stirred at 30 °C until well mixing of solution was obtained.

IV. The Fn-GO supernatant in DI water (specific amount of Fn-GO) was mixed in PEG 400/Pebax 1657 blended solution and stirred at 30 °C to obtain homogeneous solution.

V. The mixture solution was cooled down to room temperature.

VI. Then, mixture solution was poured into container for dip coating.

VII. 20 wt.% PEI support membranes were dipped into prepared solution for three times at dipping rate of 200 mm/s for 3o second of dwelling duration. Coated membranes were dried in the oven at 60 °C for an hour before dipping to second and third time respectively.

VIII. The prepared membranes were finally fried in the oven at 60 °C after completing 3 times dipping to remove residue solvent

3.3 Membrane characterization

The morphology of filler and fabricated membranes were observed by Hitachi S-3400N scanning electron microscopy. The crystalline structure of fillers were investigated by X-ray diffraction (XRD) via Bruker D8 advance in the range of 3-90° at a scan rate of 2° /min. The average d-spacing of graphene oxide sheet was evaluated on the basis of Bragg’s law. Chemical structure of membranes and filler were recorded by using Nicolet 6700 model with scan range of 4000-400 cm^{-1}. In addition, thermal stability of membranes especially polymer blended was tested via thermal gravimetric analysis technique via Mettler Toledo TGA/DSC 1.

3.4 Membrane performance test

Figure 3.1 shows the schematic diagram of gas permeation apparatus. The inlet stream was varied under two conditions to evaluate membrane performances, consisting of mixed gas testing (CO_2/CH_4 = 52:48 %) and biogas testing. Total feed flow rate and the trans-membrane pressure were varied to find the optimal condition. The operating temperature was controlled at 35 °C. He was used as the carrier gas to carry gas to gas chromatography (GC). The composition of permeate and retentate was measured using gas chromatography (Shimadzu gc-14B).

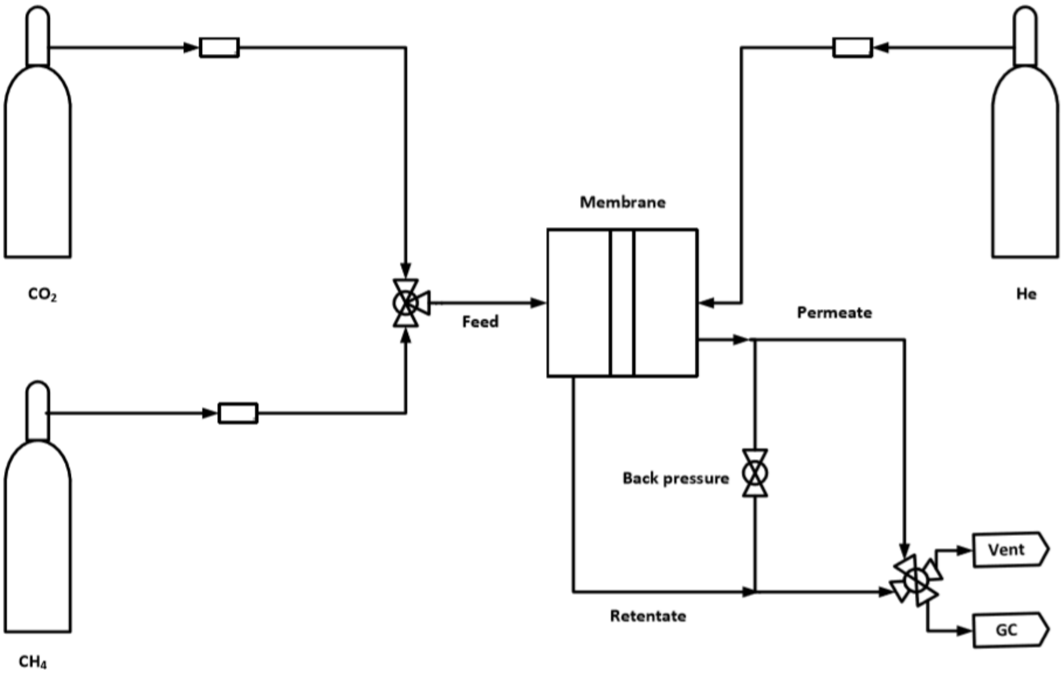


Figure 3.1 Schematic diagram of gas permeation for gas separation membrane

CHAPTER 4

RESULTS AND DISCUSSION

In this section, the suitable operating condition was discussed in the first part. The optimal operating condition was conducted with Pebax 1657 composite membrane. There were two parameters considered in this research including feed flowrate and trans-membrane pressure. Next, the effect of each additive on membrane performance was investigated. The effect of graphene oxide loading and PEG 400 addition was discussed individually. Lastly, the further improvement on membrane performance was carried out by combining the fillers and polymer blend. Finally, the investigation on effect of combined factors on membrane performance was discussed in the last part of this section.

4.1 Operating condition

For operating condition, there are two considered parameters have been taken into account to identify the optimal operation of membrane which consisting of feed flowrate and trans-membrane pressure. The effect of each parameter was discussed as follows;

4.1.1 Effect of feed flowrate

Firstly, feed flowrate was varied in order to find the optimal condition for membrane testing. The effect of feed flow rate was investigated in term of CO_2 permeance and separation factor. In this section, pristine Pebax 1657 composite membrane was carried out with the varying feed flowrate. The trans-membrane pressure was controlled at 3 bar and operating temperature was at 35°C.

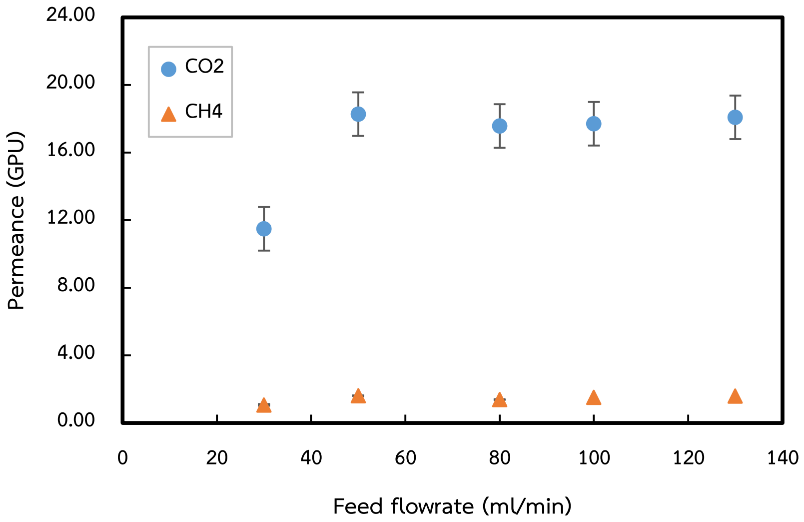


Figure 4.1 The effect of feed flowrate on CO_2 and CH_4 permeance (Trans-membrane pressure: 3 bar, Temperature: 35 °C)

The permeation performance of the membrane was tested using fixed mixed gas (CO_2:CH_4=52:48%) concentration in cross flow mode under dry condition at 35 °C. Figure 4.1 shows that feed flowrate of 30 ml/min provided the lowest CO_2 permeance while at other feed flowrates obtained higher CO_2 permeance noticeably. However, there was no significant difference of CO_2 permeance for feed flowrate from 50 ml/min to 130 ml/min.

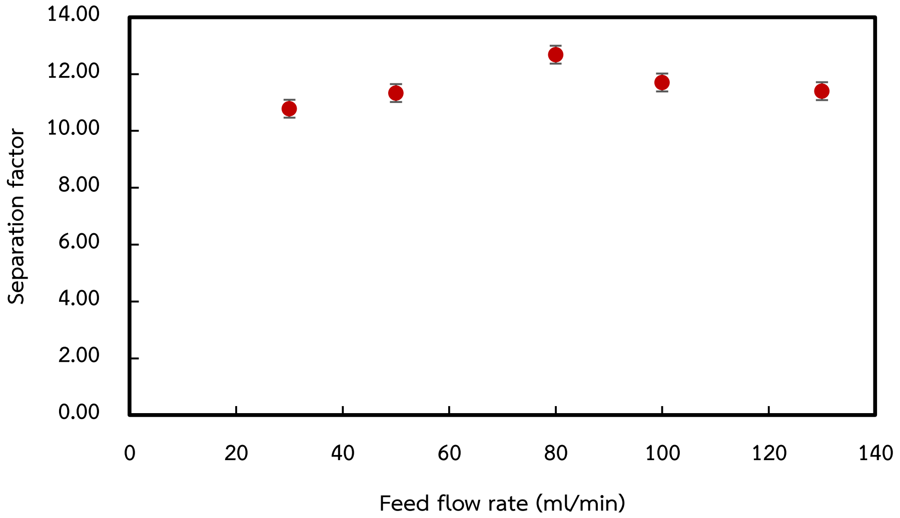


Figure 4.2 The effect of feed flowrate on CO_2/CH_4 separation factor (Trans-membrane pressure: 3 bar, Temperature: 35 °C)

Figure 4.2 clearly reveals that at 80 ml/min of feed flowrate provided the highest CO_2/CH_4 separation factor. When the feed flowrate increased, the boundary layer on membrane surface decreased, meaning that the concentration polarization was reduced. Therefore, more CO_2 component could diffuse through membrane easier. However, the highest separation factor was obtained at 80 ml/min. Moreover, the lower separation factor was investigated when increasing feed flowrate higher than 80 ml/min. The feed flowrate at 100 ml/min onwards showed separation factor decrement which implied that the residence time was dominant over concentration polarization in this feed flowrate range.

4.1.2 Effect of trans-membrane pressure

Trans-membrane membrane pressure was varied from 3 bar to 7 bar with constant temperature of 35°C and feed flowrate of 80 ml/min. The investigations of performance on pristine Pebax 1657 composite membrane are shown in the following graphs.

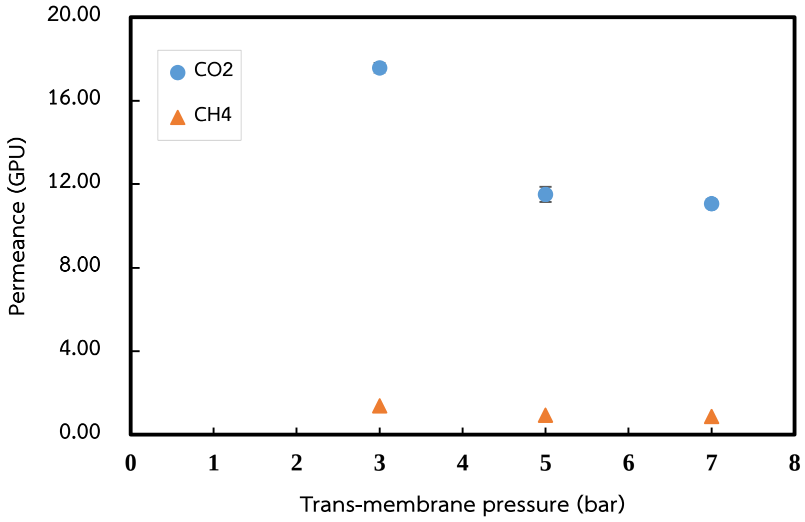


Figure 4.3 The effect of trans-membrane pressure on CO_2 and CH_4 permeance (Feed flowrate: 80 ml/min, Temperature: 35 °C)

The effect of trans-membrane pressure ranging from 3 bar to 7 bar on the separation performance of pristine Pebax 1657 composite membrane was studied. From Figure 4.3, CO_2 permeance decreased with increasing trans-membrane pressure. The mass transfer of gases through a membrane by solution-diffusion mechanism is commonly dependent to feed gas pressure. The decline of CO_2 permeance might be due to membrane compaction which led to a free volume reduction resulting in restraining the transport of the penetrating molecules [12].

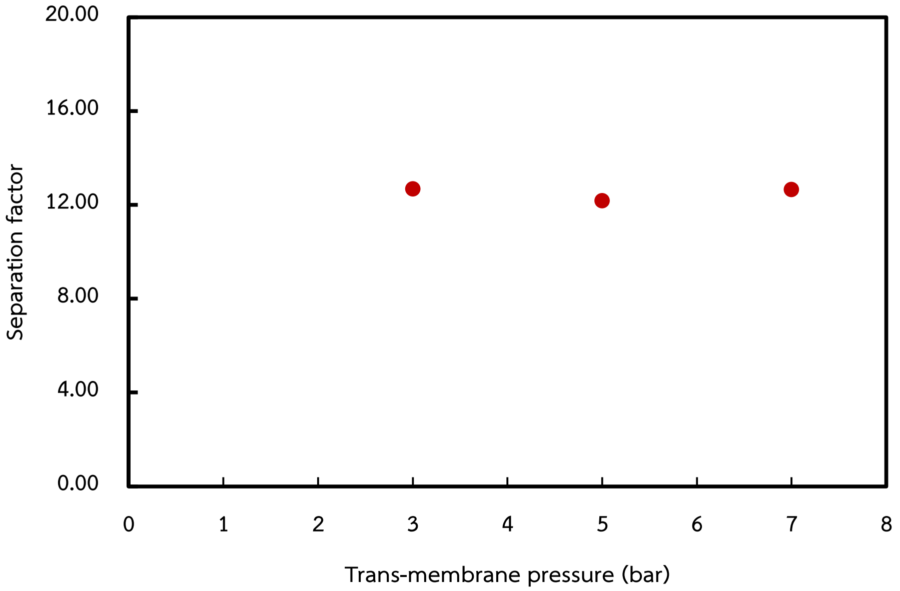


Figure 4.4 The effect of trans-membrane pressure on CO_2/CH_4 separation factor (Feed flowrate: 80 ml/min, Temperature: 35 °C)

Figure 4.4 shows that the CO_2/CH_4 separation factor at each trans-membrane pressure did not change significantly. The CO_2/CH_4 separation factor was about 12 at trans-membrane ranging from 3-7 bar. This no difference in separation factor could be explained by the ratio of CO_2 to CH_4 permeance is almost constant in each varied trans-membrane pressure.

In conclusion, the suitable testing condition for pristine Pebax 1657 composite membrane was found to be at 80 ml/min of feed flowrate and trans-membrane pressure at 3 bar. With this testing condition, the highest CO_2 permeance and CO_2/CH_4 separation factor was obtained.

4.2 Effect of graphene oxide filler loading on membrane properties and performances

4.2.1 Morphology and chemical structure

- **Scanning Electron Microscopy (SEM)**

The structures of the obtained membranes were examined by scanning electron microscope (SEM) as shown in Figure 4.5.

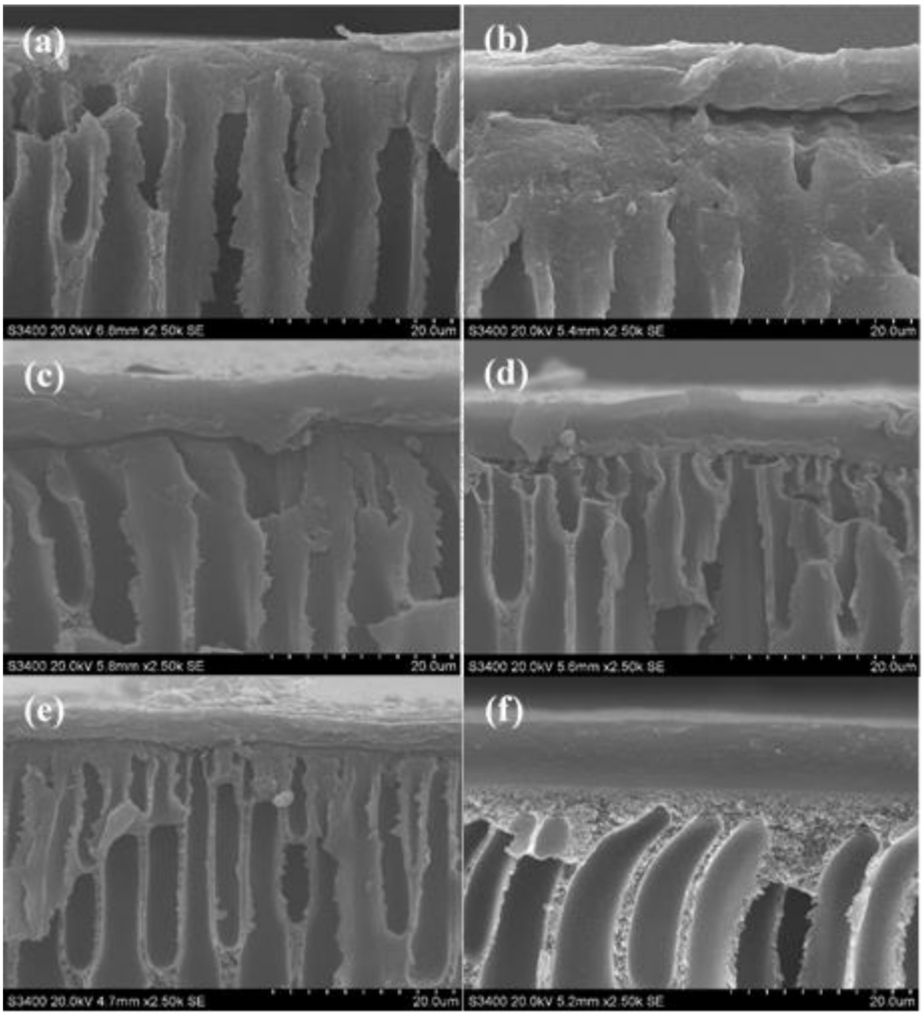


Figure 4.5 Comparison of cross-sectional SEM images of (a) bare PEI and Pebax coated on PEI with GO addition of (b) 0 wt.%, (c) 0.25 wt.%, (d) 0.50 wt.%, (e) 0.75 wt.% and (f) 1.0 wt.%

From SEM images, the structure of PEI support membrane presents a dense structure on the top and finger-like structure at the bottom. Different membranes prepared from different filler loadings showed a different thickness as shown in Figure 4.5.

The Pebax 1657 selective layer was coated on the top of PEI support membrane. Referring to SEM images for top layer, there is no significantly different for each membrane conditions since the tops layer of membranes are dense structure. Furthermore, the GO content is quite low and disperse homogeneously in polymer matrix. The top surface of membrane is shown in Figure 4.6.

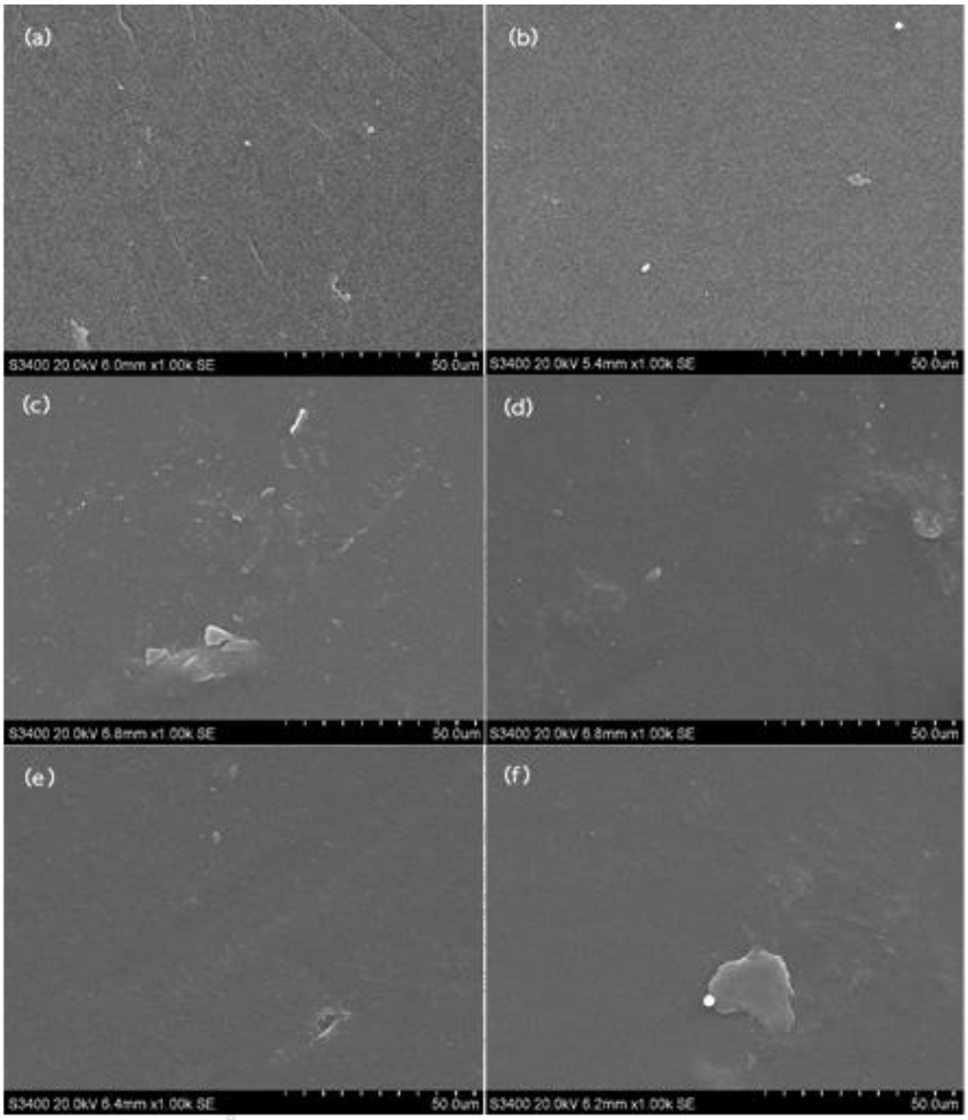


Figure 4.6 Comparison of top surface SEM images of (a) bare PEI and Pebax 1657 coated on PEI with GO addition of (b) 0 wt.%, (c) 0.25 wt.%, (d) 0.50 wt.%, (e) 0.75 wt.%, and (f) 1.0 wt.%.

➢ Attenuated Total Reflectance Fourier Transform Infared (ATR-FTIR)

To determine the chemical functions of membrane, ATR-TIR was used to confirm that there is a selective layer coated on the support membrane.

PEI consists of benzene ring, ether group, and tertiary amide group. The chemical structure of PEI is depicted in Figure 4.7.

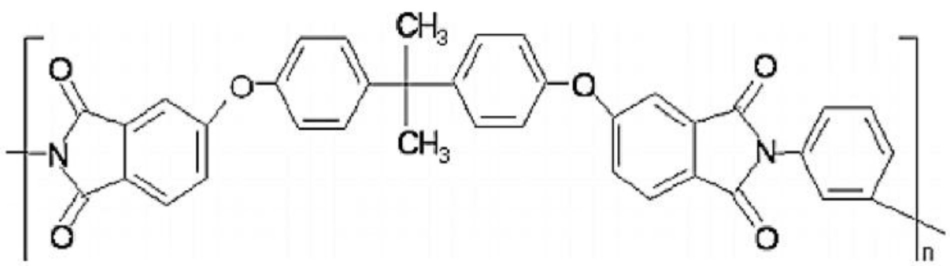
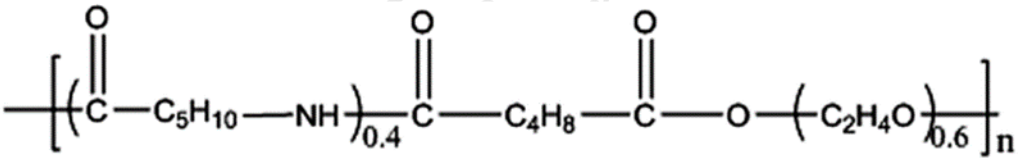


Figure 4.7 Chemical structure of PEI [27]

Pebax 1657 is the copolymer composed of rigid polyamide blocks and soft polyether blocks. The chemical structure of Pebax 1657 is shown in Figure 4.8.



$$-\left[\left(\overset{O}{\overset{\|}{C}}-C_5H_{10}-NH\right)_{0.4}\overset{O}{\overset{\|}{C}}-C_4H_8-\overset{O}{\overset{\|}{C}}-O-\left(C_2H_4O\right)_{0.6}\right]_n$$

Figure 4.8 Chemical structure of Pebax 1657 [28]

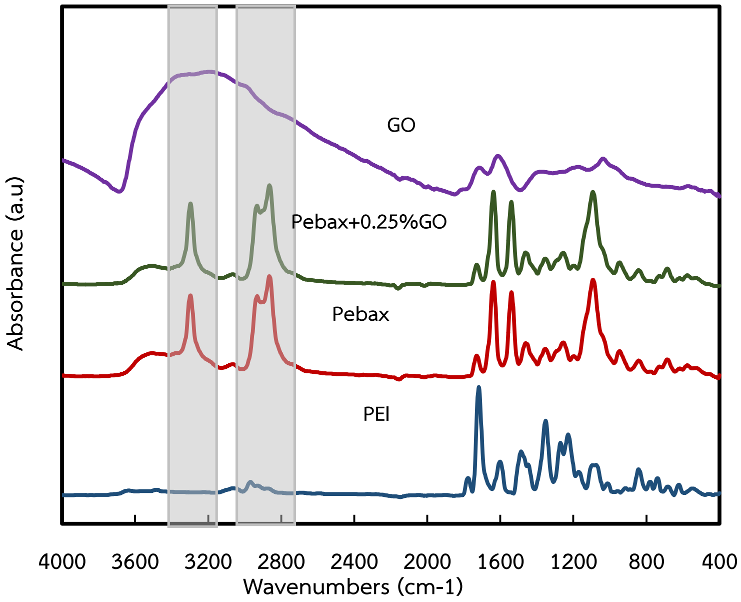


Figure 4.9 FTIR graph of filler and composite membrane

The obtained membranes and filler were analyzed the chemical structure of by using ATR-FTIR. For comparison, the FTIR spectra of PEI support with and without Pebax 1657 selective layer were studied. The results are shown in Figure 4.9. There is a peak at about 3300-3500 cm^{-1} in the spectrum of Pebax 1657 and Pebax 1657 with 0.25 wt.% of GO which is assigned to N-H stretch. The appearance of this peak could confirm that Pebax 1657 was successfully coated on top of PEI support because there is no N-H stretch in the range of 3300-3500 cm^{-1} region in the tertiary amide. Besides, the peak at about 2850-3000 cm^{-1} is assigned to the symmetrical stretching vibration of CH_3 in Pebax 1657.

4.2.2 Separation performance of graphene oxide in composite membrane

The operating condition applied to test for composite membranes incorporated with graphene oxide was controlled at 80 ml/min of feed flowrate, 5 bar of trans-membrane pressure, and 35°C. Even though at 3 bar of trans-membrane pressure was optimal for bare Pebax 1657 composite membrane, but it was not suitable to operate for composite membranes incorporated with graphene oxide conditions. Ttrans-membrane pressure of 5 bar was selected instead of 3 bar because there was nothing pass through membrane to permeate side due to not enough driving force.

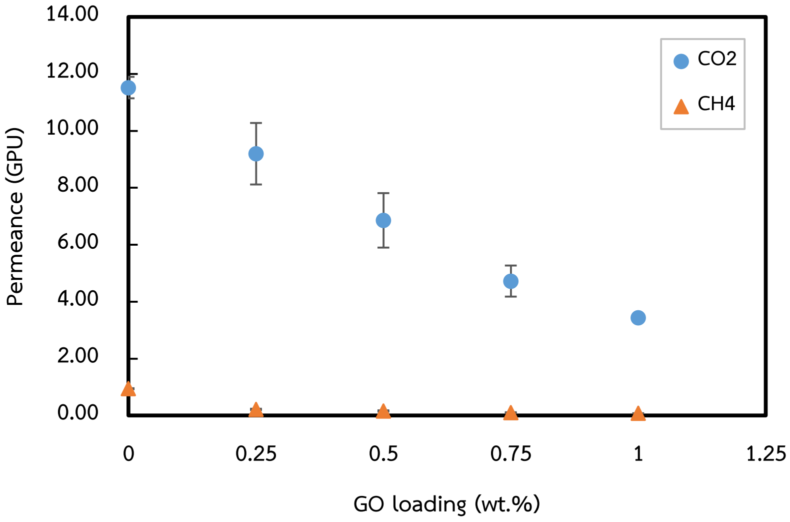


Figure 4.10 The effect of GO loading in Pebax 1657 composite membrane on gas permeance (Feed flowrate: 80 ml/min, Trans-membrane pressure: 5 bar, Temperature: 35 °C)

The performance of membrane by varying graphene oxide loading in Pebax 1657 matrix was investigated. The results revealed that the presence of graphene oxide in the polymer matrix decreased the CO_2 permeance as shown in Figure 4.10. The higher loading of GO restricted the mobility of Pebax chains and generated a rigidified interface between the polymer and filler [6].

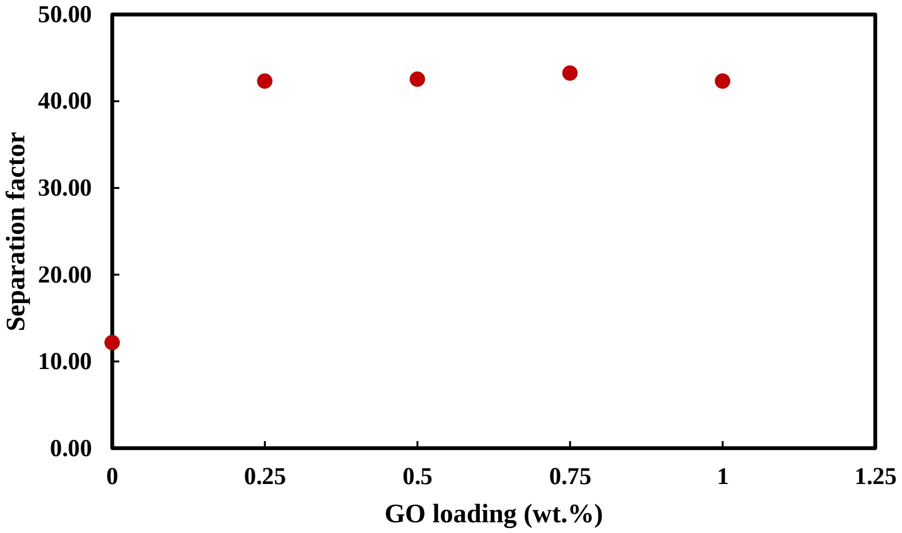


Figure 4.11 The effect of GO loading in Pebax 1657 composite membrane on CO_2/CH_4 separation factor (Feed flowrate: 80 ml/min, Trans-membrane pressure: 5 bar, Temperature: 35 °C)

In case of separation factor, the containing of GO provided the perceptibly increase in separation factor comparing to pristine Pebax 1657. From Figure 4.11, the separation factor increased from 12.18 to 42.33 when 0.25% GO was embedded in Pebax 1657. The addition of graphene oxide could increase the pathway of CO_2 through membrane due to affinity of GO to CO_2. Moreover, the addition of GO might increase or block the travel way of CH_4 leading to high separation factor as shown in Figure 4.12. However, the separation factor was constant even through GO loading was increased.

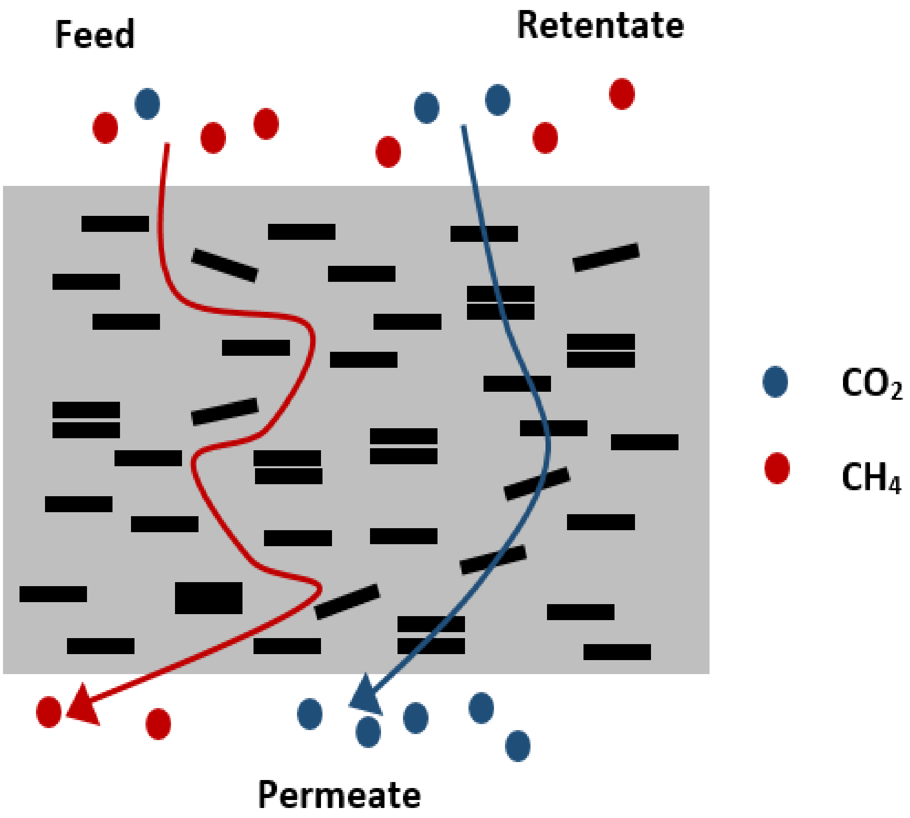


Figure 4.12 The schematic of gas pass through added GO membrane

In conclusion, incorporation of GO to polymer matrix membrane affected significantly to enhance CO_2/CH_4 separation factor. The CO_2/CH_4 separation factor was constant even though the GO content was increased. However, increasing of GO loading reduce CO_2 permeance. Thus, at 0.25 wt.% of GO loading was considered as the optimal loading due to the highest CO_2 permeance among GO loading condition.

4.3 Effect of PEG loading

4.3.1 Morphology and chemical structure

- **Scanning Electron Microscopy (SEM)**

The structures of polymer blended membranes were examined by scanning electron microscope (SEM) as shown in Figure 4.13.

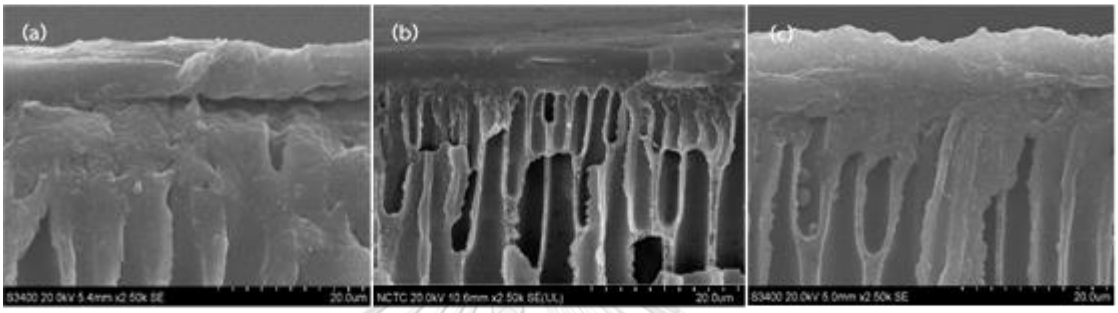


Figure 4.13 Comparison of cross-sectional SEM images of (a) pristine Pebax 1657, (b) PEG 400/Pebax 1657 (25/75 wt.%), and (c) PEG 400/Pebax 1657 (50/50 wt.%)

From SEM images, the structure of polymer blended membrane became thicker at the top of membrane when PEG loading increases. Different of membrane conditions showed a different thickness as shown in Figure 4.13.

➢ Thermal Gravimetric Analysis (TGA)

The thermal stability of polymer blended membranes was carried out via thermal gravimetric analysis (TGA) technique.

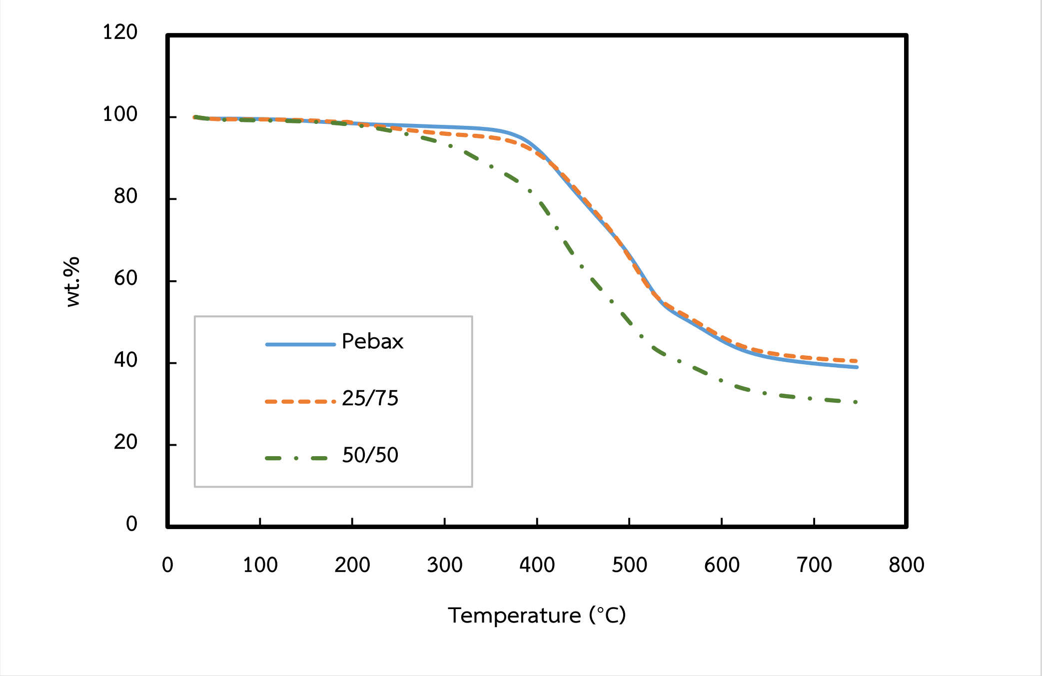


Figure 4.14 TGA weight loss versus temperature for varying PEG 400 loading (At nitrogen atmosphere, heating rate: 10°C/min)

From Figure 4.14, the graph represents the degradation of each membrane. PEG 400/Pebax 1657 (50/50 wt.%) started to degrade at 230 °C whereas PEG 400/Pebax 1657 (25/75 wt.%) degraded at 330 °C and pure Pebax 1657 degraded at 360 °C. t is obvious that at condition of PEG 400/Pebax 1657 (50/50 wt.%) could easily degrade at lower temperature than the other two membranes.

It shows that PEG 400/Pebax 1657 (50/50 wt.%) had the lowest thermal stability among these three membranes.

4.3.2 Separation performance of PEG 400 loading in composite membrane

The performance of membrane with varying PEG 400 content in Pebax 1657 was studied. There are three conditions of blending consist of neat Pebax 1657, PEG 400/Pebax 1657 (25/75 wt.%) and PEG 400/Pebax 1657 (50/50 wt.%).

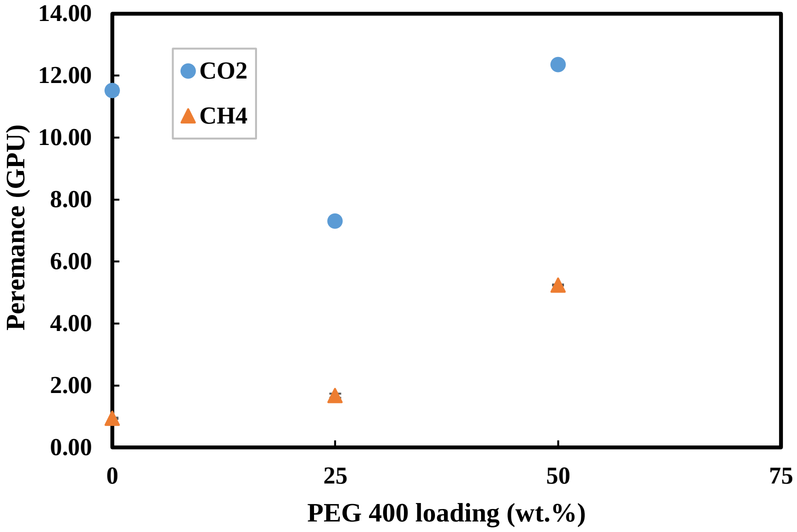


Figure 4.15 The effect of PEG 400 loading in Pebax 1657 composite membrane on gas permeance (Feed flowrate: 80 ml/min, Trans-membrane pressure: 5 bar, Temperature: 35 °C)

The effect of PEG 400 loading to Pebax 1657 composite membrane on gas permeance is reveled in Figure 4.15. The highest CO_2 permeance was obtained at PEG 400/Pebax 1657 (50/50 wt.%) due to the addition of low molecular weight PEG caused layer chain spacing. Even though, the addition of PEG enhanced EO groups to polymer matrix and caused more sorption of CO_2, but the solubility was less affected by loading of PEG compared to the diffusion coefficient [16]. From the graph, PEG 400/Pebax 1657 (25/75 wt.%) composite membrane displayed the lowest CO_2 permeance comparing to the pristine Pebax 1657 that might be caused by PEG 400/Pebax 1657 (25/75 wt.%) penetrated to PEI support layer. The penetration of PEG 400/Pebax 1657 (25/75 wt.%) to support layer might lead to thinner but denser selective layer resulting in CO_2 permeance reduction. The thin selective layer of PEG 400/Pebax 1657 (25/75 wt.%) is shown in Figure 4.12. Nevertheless, these obtained results contradict with other studies. Azizi and coworkers had been studied the effect of PEG 400 addition to Pebax 1657 and found that both CO_2 permeance and CO_2/CH_4 separation factor increased when PEG 400 content increased since PEG enhanced EO groups to polymer matrix and caused more sorption of CO_2 [17]. Furthermore, the effect of PEG 400 to Pebax 1657 was also investigated by Jazebizadeh and his friends. The results exhibited that PEG 400 added to Pebax 1657 performed improved CO_2 permeability but reduced in CO_2/CH_4 selectivity due to the loose in polymer chain [16]. In the research of Wang and his group, it was reported that the incoporation of PEG 400 to Pebax 1657 could decrease T_g value leading to increase chain mobility [20]. However, it is recommended if more investigations and characterizations can be taken into account to explain this phenomena.

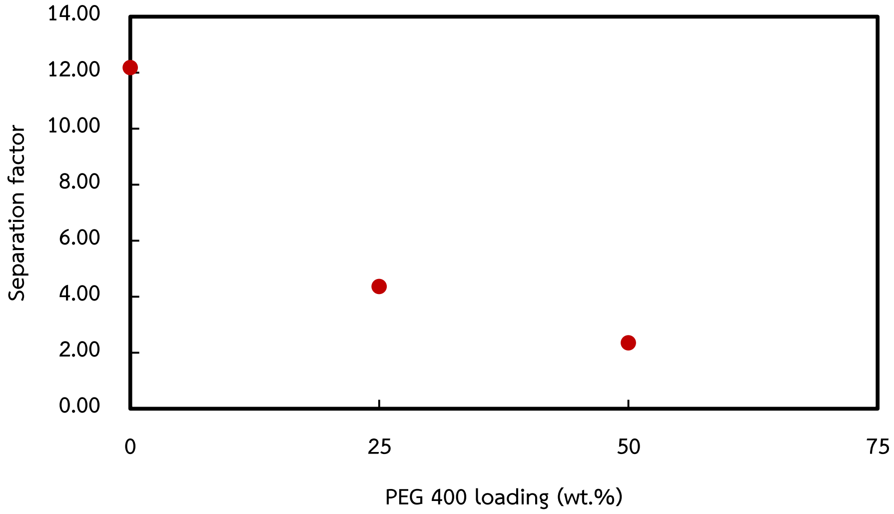


Figure 4.16 The effect of PEG 400 loading in Pebax composite membrane on CO_2/CH_4 separation factor (Feed flowrate: 80 ml/min, Trans-membrane pressure: 5 bar, Temperature: 35 °C)

From Figure 4.16, the separation factor of CO_2/CH_4 is reported. It is found that the increment of PEG 400 content up to 50% into Pebax 1657 might cause void in Pebax 1657 matrix, which both CO_2 and CH_4 could easily pass, resulting in CO_2/CH_4 separation factor decrement.

In conclusion, the addition of PEG 400 at 50 wt.% into Pebax 1657 leaded to increase CO_2 permeance. To improve the CO_2 permeance, thus PEG 400 at 50 wt.% was selected to further investigate for the next section (further improvement of composite membrane).

4.4 Further improvement of composite membrane

In this section, the combination of fillers and polymer blend was further investigated. With the advantage of each factor, the further investigation of combination would be studied.

4.4.1 Effect of chemical functionality of filler

- **Scanning Electron Microscopy (SEM)**

The size of fillers was measured by using SEM. Fig. 4.15 shows the particle size of GO and amine functionalized GO (Fn-GO). The particle size of unmodified GO was about 80.30 μm for horizontal plane but the thickness of the stack layer was around 21.30 μm This size was measured in the powder form of GO. The big size of GO was obtained because the method to prepare GO powder was required to manually grind after GO drying in an oven resulting to stack and accumulation of GO.

On the other hand, the morphology of GO was totally changed after functionalization with ethylenediamine (EDA). The particle size of functionalized GO become larger than the unmodified GO and it is about 106 μm. Besides, the morphology was changed from layer into accumulated

However, GO and Fn-GO supernatants in water were used instead of GO powder in this research in order to get smaller size of GO and Fn-GO particles and a homogeneous dispersion in the polymer matrix. The smaller size and a good dispersion of GO can be proved from SEM images of the composite membranes since cross-sectional and top surface of membranes showed a smooth morphology.

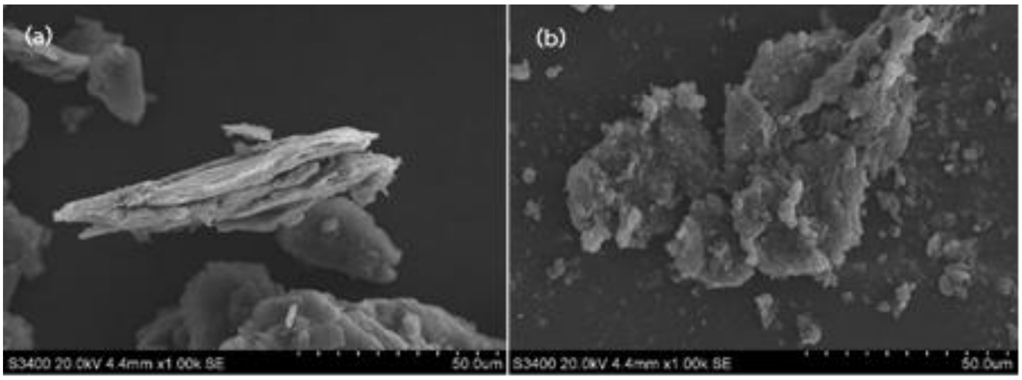


Figure 4.17 The SEM images of filler size and morphology of (a) GO and (b) Fn-GO

Furthermore, SEM-EDS was applied to identify the composition of C, O, N in GO and Fn-GO. The composition of each element is summarized in the Table 4.3.

Table 4.1 The composition of elements in GO and Fn-GO fillers

Filler	C (wt.%)	O (wt.%)	N (wt.%)	S (wt.%)	Cl (wt.%)
GO	57.92	36.54	-	4.87	0.66
Fn-GO	57.31	19.42	18.80	3.83	0.64

From Table 4.3, GO is composed of C, O, S, and Cl. The elements S and Cl were detected since there was small trace amount of, H_2SO_4, and HCl from GO preparation procedure via modified Hummer's method [29]. On the other hand, EDA functionalized GO obtained N element while graphene oxide does not. This implies that amine group was successfully grafted on the GO.

➢ X-Ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) analysis was used to examine the influence of amine function addition on GO structure. The XRD patterns are shown in Figure 4.18. The XRD pattern of GO had a strong peak at a 2θ of 9.94° and the spacing between graphene oxide sheet was 0.888 nm. This was comparable to previous reports [30, 31]. Compared to the pattern of GO, EDA functionalized GO showed a board peak in XRD pattern. The board peak indicated that the functionalized GO was in a disordered structure and poorly ordered along the different stacking directions.

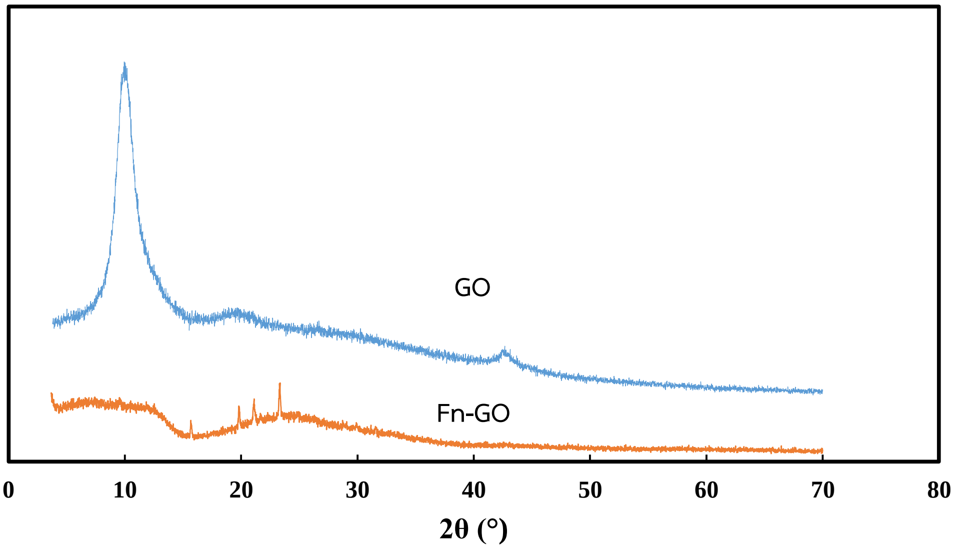


Figure 4. 18 XRD patterns of GO and Fn-GO

According to other researches, functionalized GO with EDA showed a different XRD pattern from this study. Xue et al., grafted EDA on GO via a physical sorption similar to our work [30].Their XRD patterns are reported as shown in Figure 4.19.

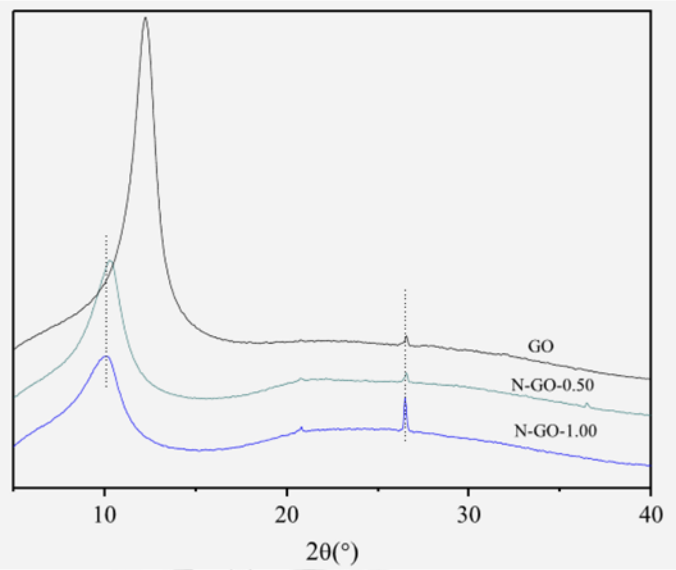


Figure 4.19 XRD patterns of GO and EDA functionalized GO (N-GO) [30]

The results was revealed that grafting of EDA into the layer of GO obtains a sharp peak shifting to the lower 2θ compared to the unmodified GO. Also, the increasing intensity at 2θ = 26.3° was investigated when EDA was added. With this observation, grafting EDA on GO was successfully done.

Besides, the XRD patterns of EDA functionalized GO was reported by Yan and coworkers [31]. The XRD patterns are depicted in Figure 4.20. Similar to the work from Xue et al., the functionalized GO displays a shift peak to the lower 2θ.

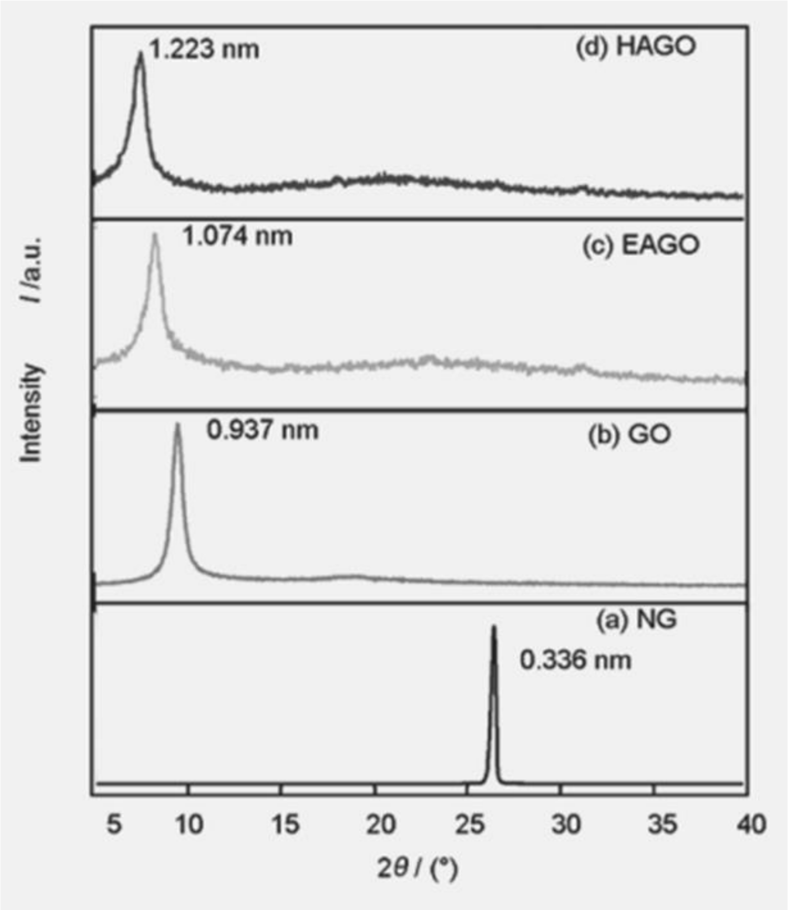


Figure 4.20 XRD pattern of GO and EDA functionalized GO (EAGO) [31]

- Attenuated Total Reflectance Fourier Transform Infared (ATR-FTIR)

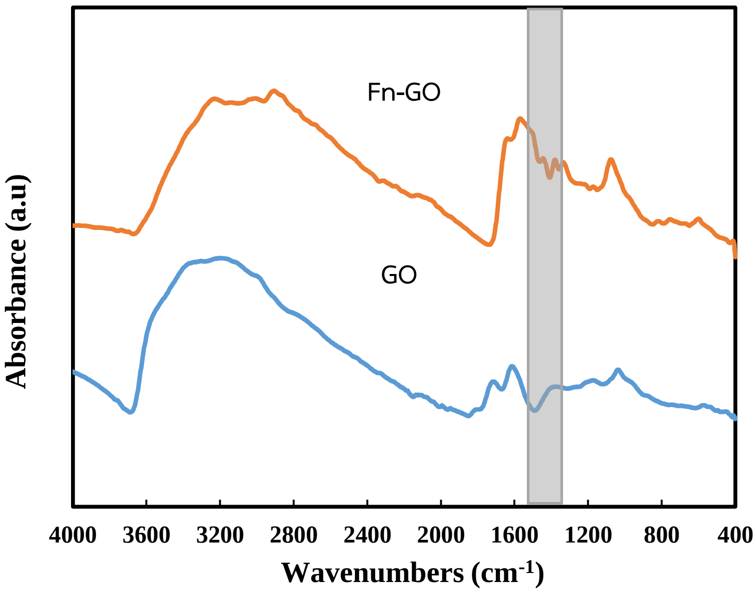


Figure 4.21 FTIR spectra of fillers

To confirm that amine group was assuredly attached on GO, the ATR-FTIR was applied to analyze. From Figure 4.22, it is revealed that the peak at about 1250-1360 cm-1 is assigned to C-N group which only contain in EDA functionalized GO as shown in Figure 4.22.

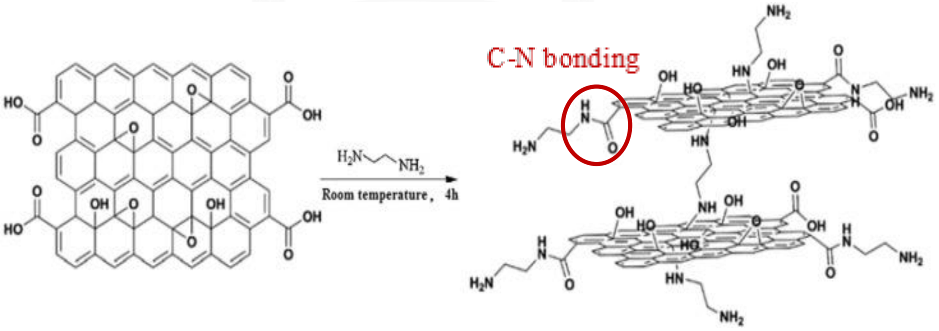


Figure 4.22 The comparison of chemical structure for GO and amine functionalized GO [30]

4.4.2 Separation performance of combined additives in composite membrane

In this section, PEG 400, GO and Fn-GO were embedded in the selective layer to study the effect of each factor to CO_2/CH_4 separation performance. Due to previous study, separation factor obtained no difference but CO_2 permeance obviously changed when GO loading increased. Thus, 0.25 wt.% GO was chosen as the optimal condition for GO loading in Pebax 1657 and 0.25% Fn-GO was developed to compare with unmodified GO condition.

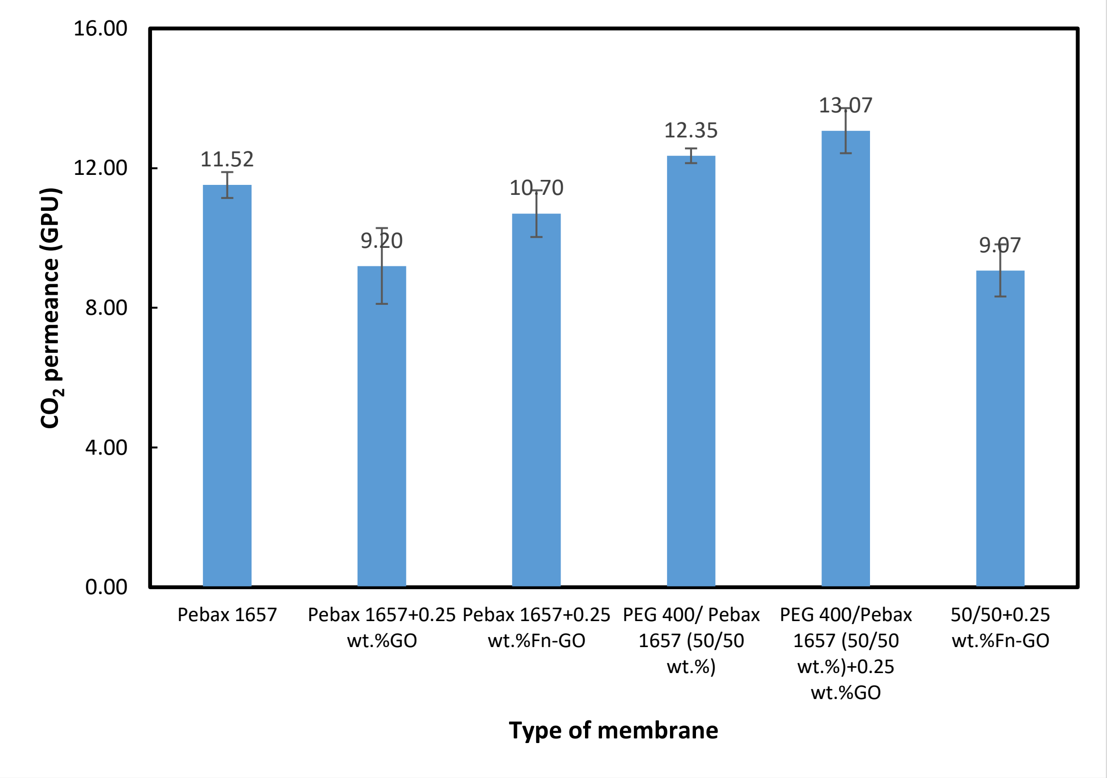


Figure 4.23 The comparison of different membrane conditions on CO_2 permeance (Feed flowrate: 80 ml/min, Trans-membrane pressure: 5 bar, Temperature: 35 °C)

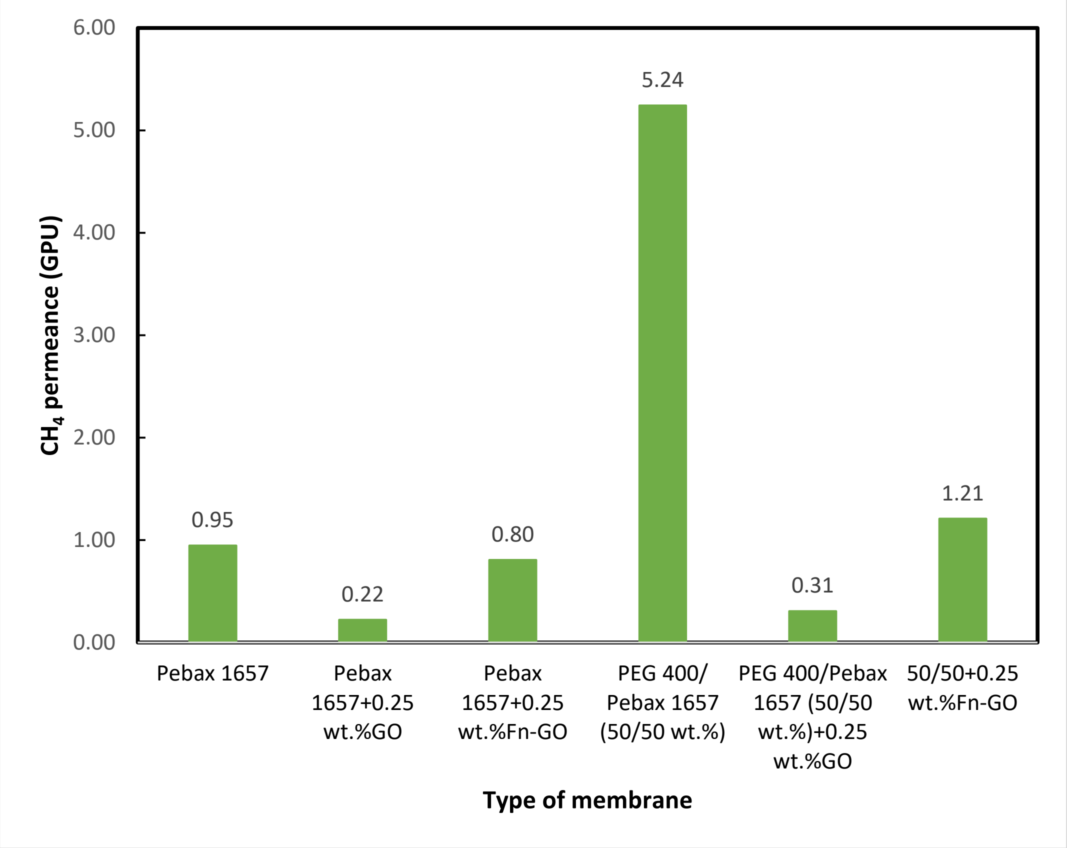


Figure 4.24 The comparison of different membrane conditions on CH_4 permeance (Feed flowrate: 80 ml/min, Trans-membrane pressure: 5 bar, Temperature: 35 °C)

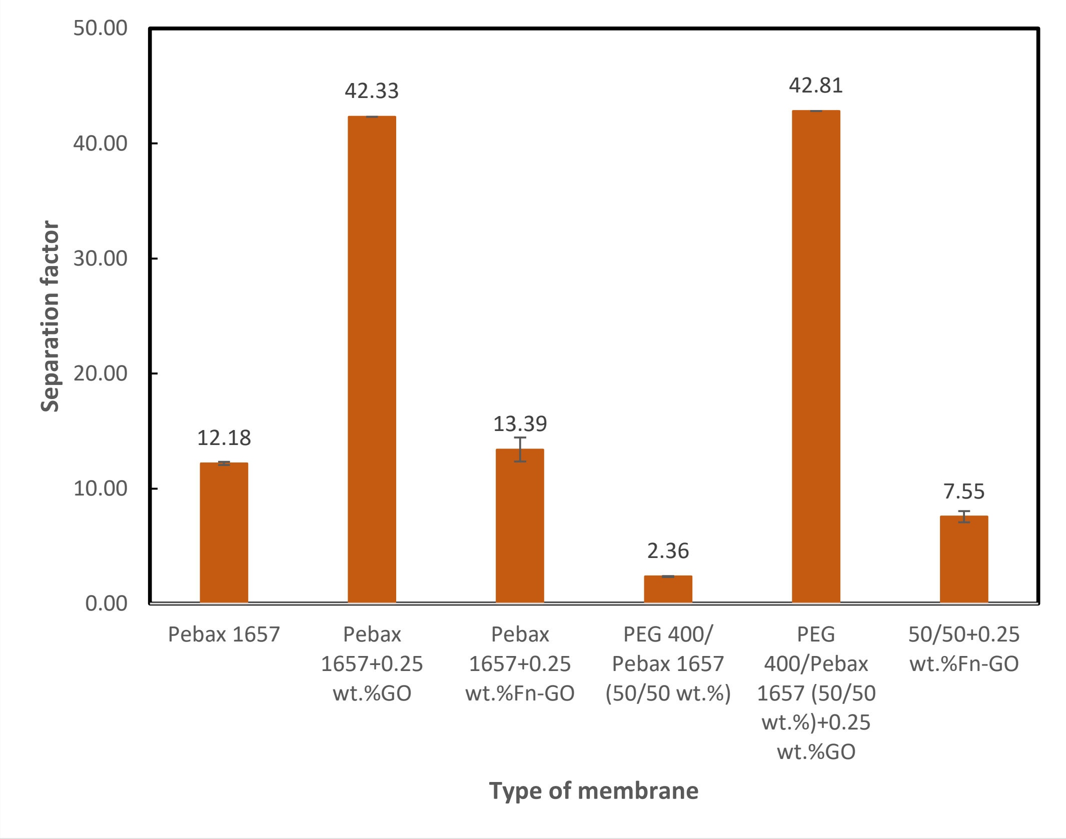


Figure 4.25 The comparison of different membrane conditions on separation factor (Feed flowrate: 80 ml/min, Trans-membrane pressure: 5 bar, Temperature: 35 °C)

The permeance of CO_2 increased when PEG 400 was added to Pebax 1657 matrix as can be seen from Figure 4.23. PEG 400/Pebax 1657 in the weight ratio of 50/50 showed a higher CO_2 permeance for both with and without GO addtion condition. At 0.25 wt.% GO in PEG 400/Pebax 1657 blended matrix showed the best performance for of both CO_2 permeance and separation factor was achieved as shown in Figure 25. The addition of Fn-GO might increase transport pathway for gases to travel through the membrane. That is why GO addition showed an enhanced separation factor.

On the other hand, EDA functionalized GO exhibited a slight increase in separation factor for pure Pebax 1657 while decreased the separation factor in 50/50 wt.% polymer blended. Many researches have been studied on amine functionalized graphene oxide in polymer matrix and all results have been reported the positive results for membrane improvement via an amine functionalization on the filler used.

All previous studies from researchers have concluded that the amine functionalized GO acted as selective carrier for CO_2 over CH_4. Furthermore, amine functionalized GO from other studies showed a better separation factor and permeability compared to their unmodified GO [6].

Compared to this study, a different trend was observed when amine functionalized GO was incorporated in polymer matrix for CO_2/CH_4 gas separation. The separation factor decreased. The functionalized graphene oxide is assumed to be the dominant factor to affect the membrane performance. As mentioned earlier in filler properties, functionalized GO showed an amorphous structure while the unmodified GO showed a crystalline structure which implies that excess amine might destroy the crystallization of graphene oxide. The amorphous structure of functionalized graphene oxide caused a disorganized structure. A large d spacing and also a big size of filler due to an accumulation were thus obtained in the functionalized GO. This led to a worse CO_2/CH_4 separation performance.

4.4.3 Comparison of membrane with other researches

Both 0.25 wt.% of GO in Pebax 1657 composite membrane and 0.25 wt.% of GO in PEG 400/Pebax 1657 blended composite membrane showed the good separation performance. In this section, all membrane conditions were plotted with Robeson's upper bound in order to compare the performance with other researches. The results of comparison was shown in Figure 4.26.

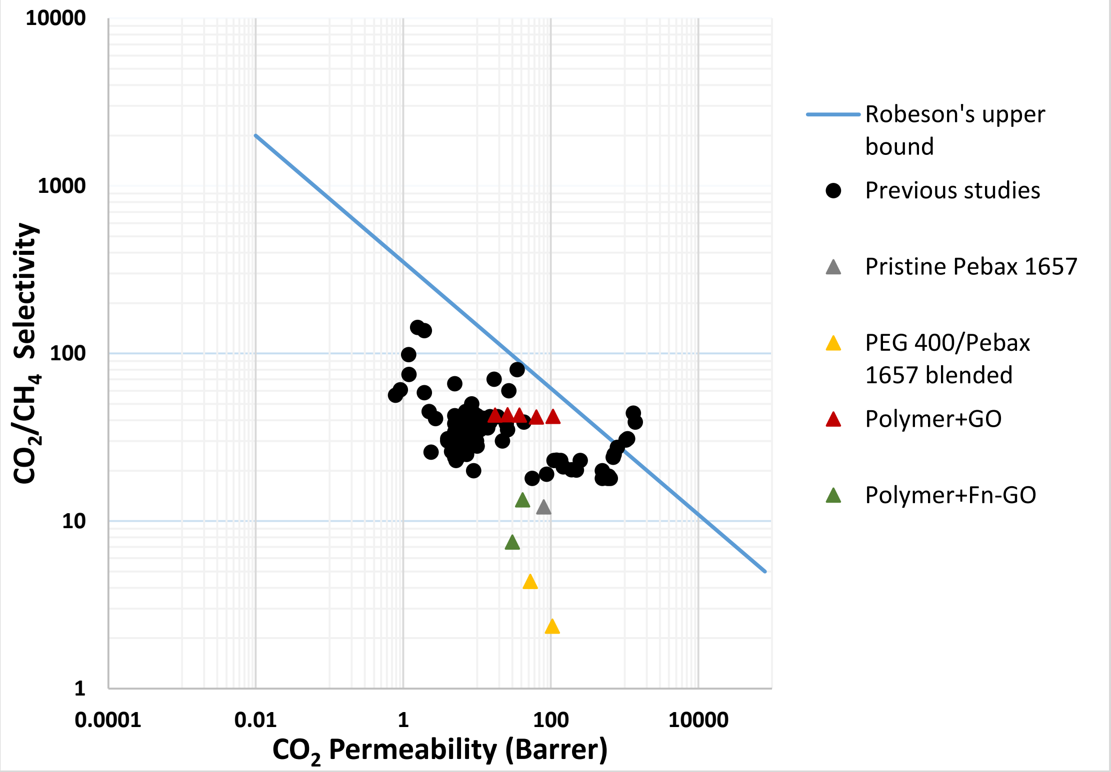


Figure 4.26 The comparison of different membrane conditions with Robeson's upper bound

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Composite membranes of PEG 400/Pebax 1657 blended polymer with graphene oxide (GO) and functionalized graphene oxide (Fn-GO) additions were successfully developed. The optimal operating condition for testing was carried out with two considered parameters, including feed flowrate and trans-membrane pressure. Moreover, the effect of each factor has been investigated and the resultant composite membranes were summarized below.

5.1 The effect of feed flowrate on membrane performance

In this research, the testing condition was carried out at constant temperature (35 °C) and constant trans-membrane pressure (3 bar). The feed flowrate was varied from 30 ml/min to 130 ml/min. The results showed that at 80 ml/min provided the highest CO_2/CH_4 separation factor for Pebax 1657 composite membrane. The increment of feed flowrate could reduce the concentration polarization. Thus, more CO_2 could able to diffuse through membrane. However, increasing feed flowrate higher than 80 ml/min resulted to reduce CO_2/CH_4 selectivity. Therefore, at 80 ml/min of feed flowrate considered as the suitable feed flowrate for pristine Pebax 1657 composite membrane.

5.2 The effect of trans-membrane pressure on membrane performance

The effect of trans-membrane pressure on membrane performance was investigated. Trans-membrane pressure from 3 to 7 bar was applied in the operation. Regardless of feed flowrate and temperature, pressure increment decreased CO_2 permeance due to the membrane compaction resulting in free volume reduction and restriction of penetrating gas molecules. It could be concluded that 3 bar of trans-membrane pressure was the suitable testing condition for pristine Pebax 1657 composite membrane.

5.3 The effect of GO addition on membrane performance

The increasing of GO content in selective layer of composite membranes could able to enhance CO_2/CH_4 separation factor. However, the CO_2/CH_4 separation factor was constant even though the GO addition enhanced. The increasing of GO loading led to reduction of CO_2 permeance due to the rigidity of membrane.

5.4 The effect of PEG 400 addition on membrane performance

The effect of PEG 400 blended with Pebax 1657 was investigated. At 50 wt.% loading of PEG 400 in Pebax 1657 matrix provided slightly increasing of CO_2 permeance. While separation factor dramatically dropped when PEG 400 was incorporated in Pebax 1657matrix because PEG 400 caused the loose chain of Pebax 1657.

5.5 The effect of combined additives on membrane performance

In conclusion, each additive provides a different function affected to membrane performance. Composite membrane of PEG 400/Pebax 1657 blended with graphene oxide (GO) and functionalized graphene oxide (Fn-GO) on PEI support membrane were successfully developed. Compared with pristine Pebax composite membrane, PEG 400/ Pebax 1657 blended with 0.25 wt.% graphene oxide (GO) showed the excellent performance with separation factor of 42.81 and CO_2 permeance at 13.07 GPU. The main function of GO was to increase in separation factor while PEG 400 was added to increase CO_2 permeance. Nevertheless, ethylenediamine functionalized graphene oxide (Fn-GO) exhibited the worse membrane performance which contradicted to other researches. This probably caused by the excess of ethylenediamine added in GO fillers resulting in disordered state and poorly ordered along the different stacking directions as proved by XRD analysis.

5.5 Recommendations

In this thesis, composite membrane of PEG 400/Pebax 1657 blended polymer with graphene oxide (GO) and functionalized graphene oxide (Fn-GO) additions were successfully developed. However, the amine functionalized graphene oxide should be synthesized with other methods in order to achieve the appropriate properties for CO_2/CH_4 gas separation. The experiment should be carried out in humidified condition in order to increase the membrane performance. Moreover, further characterization especially DSC should be done to explain more on membrane performance of polymer blend.

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APPENDIX

APPENDIX A: Gas chromatography calibration curve

Gas chromatography was equipped with membrane testing system to analyze the composition of gas for feed, permeate and retentate streams. A calibration curve was generated by running various dilutions of the CO_2 mole fraction and plotted against CO_2 GC area fraction. The obtained CO_2 calibration curve for CO_2 in different concentrations is shown in Figure A.1.

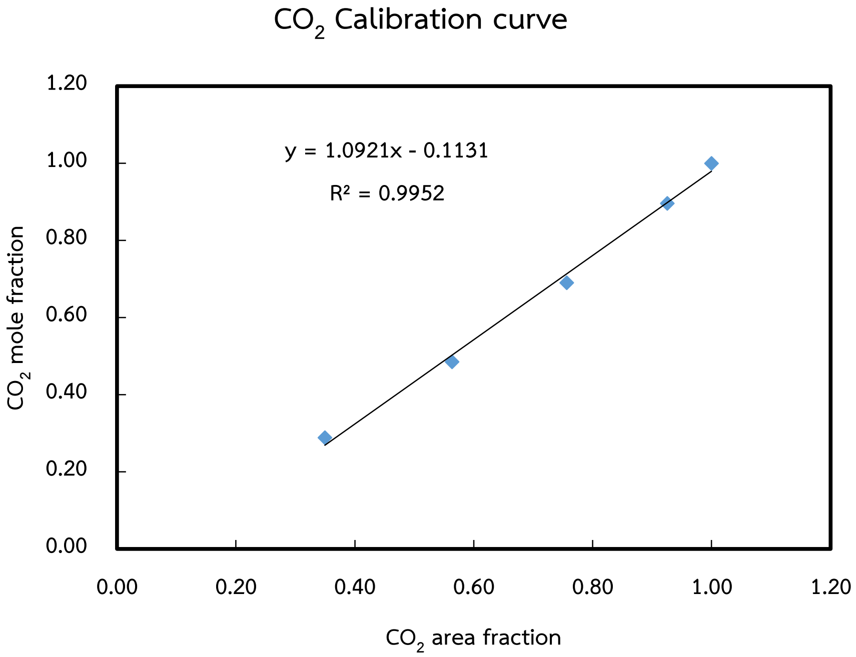

Figure A.1 CO_2 GC calibration curve from this experiment

APPENDIX B: Separation factor and gas permeation calculations

Example of calculation:

Table B.1 Experimental GC area

GC area						
	Feed		**Permeate**		**Retentate**	
	CH_4	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**
	1364690	1879817	12954	272517	1388794	1834116
Area fraction	0.42	0.58	0.04	0.96	0.43	0.57

From obtained GC area fraction, mole fraction can be calculated from equation y=1.0921x-0.1131 where x is GC area fraction and y is mole fraction. Therefore, the mole fraction of gas component in each stream line was summarized in the Table B.2 below.

Table B.2 Mole fraction of gas component in each stream line

Feed		**Permeate**		**Retentate**	
CH_4	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**
0.48	0.52	0.06	0.94	0.49	0.51

Feed gas

Y_{CO2} = (1.0921 x 0.58) – 0.1131 = 0.52

Y_{CH4} = 1-0.52 = 0.48

Permeate gas

Y_{CO2} = (1.0921 x 0.96) – 0.1131 = 0.94

Y_{CH4} = 1-0.94 = 0.06

Retentate gas

Y_{CO2} = (1.0921 x 0.57) – 0.1131 = 0.51

Y_{CH4} = 1-0.51 = 0.49

Calculation of CO_2/CH_4 separation factor

CO_2/CH_4 separation factor can be calculated from equation

$$\text{Separation factor (SF)} = \frac{x_{i,p}/x_{j,p}}{x_{i,f}/x_{j,f}}$$

where $x_{i,p}$ and $x_{j,p}$ is mole fraction of component i and j in permeate side and $x_{i,f}$ and $x_{j,f}$ is mole fraction of component i and j in feed side.

$$\text{Separation factor (SF)} = \frac{0.94/0.06}{0.52/0.48}$$

$$\text{Separation factor (SF)} = 14.46$$

Calculation of CO_2 permeance

➢ Volumetric flowrate

Table B. 3 Volumetric flowrate from experiment

Flowrate (ml/min or cm^3/min)		
Feed	**Permeate**	**Retentate**
80.24	3.37	76.00

Volumetric flowrate (Q) of permeate gas can be calculated from

flowrate x mole fraction

<u>Permeate</u>

$$Q_{CH4} = \frac{3.37\ \mathrm{cm}^3}{\mathrm{min}} \times \frac{1\ \mathrm{min}}{60\ \mathrm{s}} \times 0.06 = 0.0034\ \frac{\mathrm{cm}^3}{\mathrm{s}}$$

$$Q_{CO2} = \frac{3.37\ \mathrm{cm}^3}{\mathrm{min}} \times \frac{1\ \mathrm{min}}{60\ \mathrm{s}} \times 0.94 = 0.0528\ \frac{\mathrm{cm}^3}{\mathrm{s}}$$

Permeate (Volumetric flowrate at STP)

Given operating temperature was at 35°C,

$$Q_{STP} = Q \times \left(\frac{T_{STP}}{T}\right)$$

$$Q_{CH4,STP} = \left(0.0034\ \frac{cm^3}{s}\right) \times \left(\frac{273\ K}{308\ K}\right)$$

$$Q_{CH4,STP} = 0.0030\,\frac{cm^3(STP)}{s}$$

$$Q_{CO2,STP} = \left(\ 0.0528\,\frac{cm^3}{s}\right) \times \left(\frac{273\ K}{308\ K}\right)$$

$$Q_{CO2,STP} = 0.0468\,\frac{cm^3(STP)}{s}$$

- **Flux (J)**

Membrane affective are = 20.6 cm^2

$$J_{CH4} = \frac{Q_{CH4,STP}}{A}$$

$$J_{CH4} = \frac{0.0030\ cm^3/s}{20.6\ cm^2}$$

$$J_{CH4} = 0.000146\ \frac{cm^3(STP)}{cm^2.s}$$

$$J_{CO2} = \frac{0.0468\ cm^3/s}{20.6\ cm^2}$$

$$J_{CO2} = 0.002272\ \frac{cm^3(STP)}{cm^2.s}$$

- **Permeance (GPU)**

Given trans-membrane pressure was 5 bar (5-0 bar), Absolute feed pressure

$$\mathrm{P_{CH4,Feed}} = \left(0.52 \times 5\ \mathrm{bar} \times \frac{75.0062\ \mathrm{cmHg}}{1\ \mathrm{bar}}\right) + 76\ \mathrm{cmHg}$$

$$\mathrm{P_{CH4,Feed}} = 271.02\ \mathrm{cmHg}$$

$$\mathrm{P_{CO2,Feed}} = \left(0.48 \times 5\ \mathrm{bar} \times \frac{75.0062\ \mathrm{cmHg}}{1\ \mathrm{bar}}\right) + 76\ \mathrm{cmHg}$$

$$\mathrm{P_{CO2,Feed}} = 256.01\ \mathrm{cmHg}$$

Absolute permeate pressure

$$\mathrm{P_{CH4,Permeate}} = 0 + 76\ \mathrm{cmHg}$$

$$\mathrm{P_{CO2,Permeate}} = 0 + 76\ \mathrm{cmHg}$$

$$\frac{\mathrm{P_{CH4}}}{\mathrm{l}} = \frac{\mathrm{J_{CH4}}}{\Delta \mathrm{P_{CH4}}}$$

$$\frac{\mathrm{P_{CH4}}}{\mathrm{l}} = \frac{0.000146}{195.02}\ \frac{\mathrm{cm^3(STP)}}{\mathrm{cm^2.s.cmHg}}$$

$$P_{CH4} = 0.749\ \times 10^{-6}\ \frac{\mathrm{cm^3(STP)}}{\mathrm{cm^2.s.cmHg}}$$

$$\frac{\mathrm{P_{CO2}}}{\mathrm{l}} = \frac{0.002272}{180.01}\ \frac{\mathrm{cm^3(STP)}}{\mathrm{cm^2.s.cmHg}}$$

$$P_{CO2} = 12.62\ \times 10^{-6}\ \frac{\mathrm{cm^3(STP)}}{\mathrm{cm^2.s.cmHg}}$$

1 gas permeation unit (GPU) = 10^{-6} $\mathrm{cm^3}$ (S.T.P)/ (s.$\mathrm{cm^2}$.cm Hg)

Therefore, permeance of CO_2 is 12.62 GPU and separation factor is 14.46

APPENDIX C: Calculation of the spacing between graphene oxide sheets

It can be calculated by the Bragg's law:

$$n\lambda=2d\sin(\theta)$$

where λ is the wavelength of the X-ray beam (0.154 nm), d is the distance between the adjacent GO sheets or layers, θ is the diffraction angle.

As can be seen in Figure 4.18, the diffraction peak position is at $2\theta = 9.94°$, the spacing between which is the spacing between the graphene oxide sheets.

$d=\lambda/2\sin(\theta)=0.154\text{ nm}/2\sin(4.97°)$

$d = 0.888\text{ nm}$

Thus, the distance between the adjacent GO sheets is 0.888 nm

APPENDIX D: The thickness of composite membrane

The dense layer of PEI is about 3.45 ± 1.07 µm and Pebax layer in each condition was measured and presented in Table 4.1;

Table D.1 The thickness of selective layer of membrane prepared with different filler loading.

Membrane condition	**Thickness of selective layer (µm)**
Pebax 1657	6.99 ± 0.29
Pebax 1657 + 0.25 wt.% GO	6.89 ± 1.71
Pebax 1657 + 0.50 wt.% GO	5.46 ± 0.12
Pebax 1657 + 0.75 wt.% GO	3.70 ± 0.51
Pebax 1657 + 1.0 wt.% GO	7.50 ± 0.38

Table D.2 The thickness of selective layer in each membrane condition of polymer blend

Membrane conditions	Thickness of selective layer (µm)
Neat Pebax 1657	6.99 ± 0.29
PEG 400/Pebax 1657 (25/75 by weight)	4.23 ± 0..29
PEG 400/Pebax 1657 (50/50 by weight)	8.47 ± 1.17

VITA

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