SOLID-LIQUID-POLYMER MIXED MATRIX MEMBRANES FOR GAS SEPARATION: SILICONE RUBBER MEMBRANES FILLED WITH NAX AND KY ZEOLITES ADSORBED PEG

Sitthikiat Boonchoo

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การศึกษาการแยกก๊าซโดยใช้เยื่อเลือกผ่านเนื้อผสมของแข็ง-ของเหลว-พอลิเมอร์: เยื่อเลือกผ่านซิลิโคนที่ประกอบด้วยซีโอไลต์โซเดียมเอกซ์และเควายซึ่งดูดซับโพลีเอทิลีนไกลคอล

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ก๊าซคาร์บอนไดออกไซด์เป็นหนึ่งในองค์ประกอบหลักที่พบในแก๊สธรรมชาติและแก๊สชีวภาพ เมื่อมีปริมาณของก๊าซคาร์บอนไดออกไซด์สูงจะทำให้เกิดปัญหาคือ การลดลงของค่าความร้อนเชื้อเพลิง (Heating value) และการสึกกร่อนของผิววัสดุ มากไปกว่านั้นการปลดปล่อยก๊าซคาร์บอนไดออกไซด์ออกสู่บรรยากาศยังเป็นต้นตอสำคัญในการเกิดภาวะเรือนกระจก ด้วยเหตุนี้การแยกก๊าซโดยใช้เยื่อเลือกผ่าน (Membrane technology) จึงได้รับความสนใจเนื่องจากศักยภาพในการแยกก๊าซ เยื่อเลือกเนื้อผสม (Mixed matrix membranes, MMMs) จึงถูกศึกษาและพัฒนาเพื่อนำข้อดีของวัสดุอินทรีย์และวัสดุอนินทรีย์มารวมกันในเยื่อเลือกผ่านตัวเดียวกัน ในการศึกษานี้ เยื่อเลือกผ่านเนื้อผสมของแข็ง-ของเหลว-พอลิเมอร์ที่มีโพลิเอทิลีนไกลคอลเป็นสารเติมของเหลว ซีโอไลต์โซเดียมเอกซ์ (NaX)และซีโอไลต์เควาย (KY) เป็นสารเติมของแข็ง และซิลิโคนเป็นพอลิเมอร์ถูกเตรียมโดยการวิธีเคลือบสารละลายบนผิวของแผ่นรองรับ (Solution-casting method) และทำการทดสอบการซึมผ่าน (Permeability) และการเลือกผ่าน (Selectivity) โดยใช้อุปกรณ์ทดสอบเยื่อเลือกผ่านที่อุณหภูมิห้องและความดัน 50 ปอนด์ต่อตารางนิ้ว ของแข็งผสมระหว่างซีโอไลต์โซเดียมเอกซ์และเควายสามารถเพิ่มประสิทธิภาพในการแยกก๊าซคาร์บอนไดออกไซด์ออกจากก๊าซมีเทน โดยเยื่อเลือกผ่านเนื้อผสมที่มีสัดส่วนของซีโอไลต์โซเดียมเอกซ์และเควายเท่ากับ 0:1 ทดสอบแล้วได้ค่าการซึมผ่านของก๊าซคาร์บอนไดออกไซด์และการเลือกผ่านระหว่างก๊าซคาร์บอนไดออกไซด์และก๊าซมีเทนสูงที่สุดเมื่อเปรียบเทียบระหว่างเยื่อเลือกผ่านเนื้อผสมของแข็ง-พอลิเมอร์ เนื่องจากจากซีโอไลต์เควายมีความเป็นเบสมากกว่าซีโอไลต์โซเดียมเอกซ์จึงทำให้ประสิทธิภาพในการแยกก๊าซคาร์บอนไดออกไซด์สูงกว่า เมื่อเปรียบเทียบประสิทธิภาพการแยกก๊าซระหว่างเยื่อเลือกผ่านเนื้อผสมของแข็ง-พอลิเมอร์และของแข็ง-ของเหลว-พอลิเมอร์ โพลิเอทิลีนไกลคอลที่ดูดซับบนซีโอไลต์ส่งผลต่อการแยกก๊าซได้อย่างมีประสิทธิภาพในเพิ่มค่าการซึมผ่านของก๊าซคาร์บอนไดออกไซด์และการเลือกผ่านระหว่างก๊าซคาร์บอนไดออกไซด์และก๊าซมีเทน

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Sitthikiat Boonchoo : Solid-Liquid-Polymer Mixed Matrix Membranes for Gas Separation: Silicone Rubber Membranes Filled with NaX and KY Zeolites Adsorbed PEG. Advisor: Prof. THIRASAK RIRKSOMBOON, Ph.D.

Carbon dioxide (CO_2) is one of the major constituents of natural gas and biogas. The presence of high CO_2 content causes some serious problems including reduction of heating value and corrosion of equipment's surface. Additionally, CO_2 emission is the main issue of the greenhouse effect. In consequence of these problems, membrane technologies have drawn much attention as potential techniques for gas separation. mixed matrix membranes (MMMs) have been studied and developed to provide the synergistic effect of inorganic and organic materials on membranes. In this study, PEG/NaX:KY/SR mixed matrix membranes (PZS MMMs) were prepared by the solution casting method using NaX and KY zeolites as the solid fillers, PEG as the liquid additive, and silicone rubber as the continuous phase. The fabricated PZS MMMs were evaluated through permeance and selectivity for the single gas measurements using a membrane testing unit at room temperature and a pressure of 50 psig. The combination of NaX and KY zeolites showed the improvement in gas separation CO_2/CH_4 gas separation. The PZS MMM with NaX/KY zeolite mass ratio of 0:1 yielded the highest CO_2 permeance and CO_2/CH_4 selectivity among the solid-polymer MMMs prepared. KY zeolite was more effective than NaX zeolite in term of higher CO_2 permeability and CO_2/CH_4 selectivity due to the basicity. PEG adsorbed into the zeolites effectively influenced the gas separation performance, CO_2 permeance and CO_2/CH_4 selectivity in comparison between solid-polymer and solid-liquid-polymer mixed matrix membranes.

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CHAPTER 1
INTRODUCTION

Carbon dioxide (CO_2) is one of the major greenhouse gases (GHGs) which causes environmental impact leading to global warming. CO_2 is an acidic gas found industrially in natural gas, flue gas and biogas. The presence of CO_2 causes corrosion to the surface of equipment; moreover, it must be removed from gas streams to upgrade natural gas and biogas to meet the specifications of fuel gases and prevent CO_2 emission to the atmosphere. Various CO_2 capture technologies have been developed to effectively remove CO_2 from gas streams. Membrane technology has been an interesting and promising technique because of its advantages: low cost, simplicity of operation, and low energy consumption compared to other conventional separation technology.

Polymeric membranes were widely applied in membrane materials for the reason of low cost and processability. However, the intrinsic property of polymer does not provide the impressive gas separation performance because of limitation, trade-off between the permeability and selectivity under Robeson's upper bound. To enable feasibility of industrial applications of polymeric membranes, it is necessary to improve the gas permeability and selectivity by combining the high-performance materials with polymeric membranes. Consequently, the inorganic fillers which have high gas separation performance are dispersed in polymeric membranes. This kind of membrane is called mixed matrix membranes (MMMs). MMM has the prospects to attain both high permeability and selectivity relative to neat polymeric membranes, resulting from the incorporation of inorganic fillers with their inherent superior separation properties. Zeolites known as porous inorganic materials have been widely studied as fillers dispersed in mixed matrix membranes, because of their excellent gas separation performance. Owing to the very different physicochemical properties of organic and inorganic materials, the compatibility of inorganic fillers and polymer becomes the most considerable issue determining the accomplishment of gas separation. To settle the incompatibility of filler and polymer, Low molecular weight materials (LMWMs) are applied to mixed matrix membranes by filling the space between filler particles and polymer chains; therefore, the polymer-filler interface region is improved. Additionally, LMWMs being CO_2-philic materials can also significantly improve the gas permeability and selectivity of membranes. The combination of two inorganic fillers in the same polymer membrane is so interesting and attractive. When the combined fillers incorporated polymer membranes are successful, the mixed matrix membrane will take advantage of both fillers, resulting in the substantial enhancement of gas separation performance.

The purpose of this study is to investigate the gas separation performance of MMM composed of silicone rubber (SR) as polymer continuous phase, NaX and KY zeolites as inorganic fillers, and polyethylene glycol (PEG) as a liquid additive. This MMM is cast on Cellulose acetate supporting membrane. MMMs are fabricated by solution-casting methods and solvent evaporation methods. For measurement of gas separation performance, the single gas permeability is measured at the inlet pressure of 50 psi and the temperature of 25°C.

CHAPTER 2
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical Background

2.1.1 Polymeric Membranes

Membrane separation is an energy efficient and economical technology in the field of gas separation. Polymeric membranes currently dominate gas separation processes because of the mechanical property and the easy processability.

In the area of membrane technology for gas separation, the gas transport mechanism of polymeric membrane is based on solution-diffusion mechanism. This mechanism mainly consists of three steps: (1) adsorption of molecules on the membrane surface, (2) diffusion of molecules through the membrane, and (3) desorption of molecules on the other side of membranes. The gas separation performance is evaluated by two parameters: permeability (P) and selectivity (α) (Alqaheem *et al.*, 2017).

Permeability (P), the permeation of molecules through the membrane, is the product of diffusivity (D) and solubility (S), expressed as Equation 2.1.

$$P = D \times S \tag{2.1}$$

Diffusivity (D) is the mobility of individual gas molecules passing through the available space in the membrane, and solubility (S) is the ability of molecules dissolved in the membrane.

Experimentally, the permeability can be calculated based on the flux according to Equation 2.2.

$$P = J \frac{\Delta L}{\Delta P} \tag{2.2}$$

where J is the flux (volumetric flow rate per unit area), ΔL is the membrane thickness, and ΔP is the pressure difference across the membrane.

The other parameter used to evaluate the separation performance is selectivity (α), the ability to separate two species. It is the ratio of their permeabilities expressed as Equation 2.3.

$$\alpha_{AB} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \cdot \frac{S_A}{S_B} \tag{2.3}$$

The polymers can be classified to two types: glassy and rubbery polymers. Glassy polymers which operate below their glass transition temperature (T_g) are rigid and brittle. These kinds of polymers have low chain mobility. In contrast, rubbery polymers which operate above T_g are flexible and soft. Moreover, rubbery polymers tend to have higher permeation but lower selectivity. On the other hand, glassy polymer provides higher selectivity but lower permeability. Due to a trade-off between permeability and selectivity (Robeson, 2008), as schematically illustrated in Figure 2.1, it is difficult to obtain high performance of both permeability and selectivity at the same time by using polymeric material as the membrane.

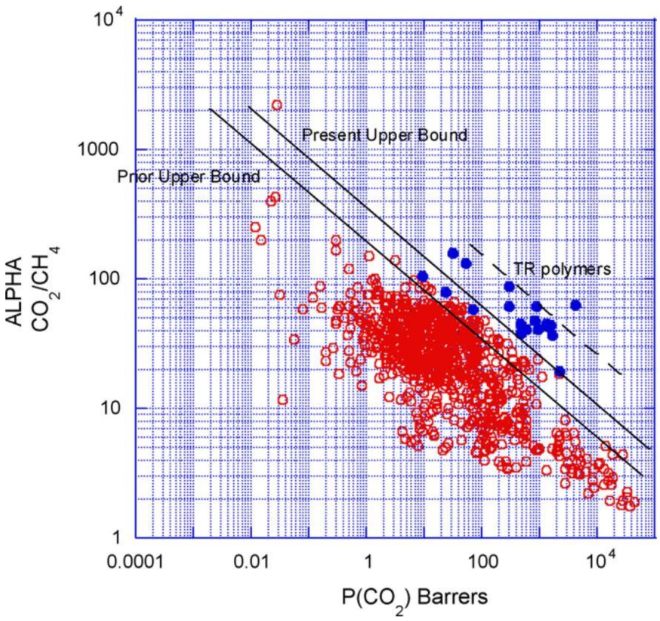

Figure 2.1 The Robeson's upper bound of CO_2 and CH_4 (Robeson, 2008).

2.1.2 Zeolites

Zeolites are crystalline aluminosilicate minerals with microporous structure. The porous structures of the zeolite can accommodate cations in it by adsorption and ion exchange. The general formula of the zeolite structure is as follows

$$M_{x/n}\left[(AlO_2)_x(SiO_2)_y\right]\cdot zH_2O$$

where M and *n* are the structure cation (alkali- or alkaline-earths, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}) and its valence, respectively, *x* and *y* denote the total number of the tetrahedra in each unit cell, and *z* is the number of water molecules in each unit cell. Some of the more important zeolite types, most of which have been used in commercial applications as shown in Table 2.1. Based on their origin, zeolites are divided into natural zeolites such as chabazite, faujasite, and mordenite, and synthetic ones such as types A, X, Y, and ZSM-5 zeolites. The advantage of natural zeolites is their innate low cost. Although synthetic zeolites have relatively high costs, the drawbacks of impurities and chemical composition alteration are avoided.

Table 2.1 Commercial zeolites and their cations, pore size, and Si/Al ratios (Bakhtyari *et al.*, 2020)

Zeolite	Cation	Pore size (Å)	Si/Al ratio
3A	K^+	3.0	1.0
4A	Na^+	3.8	1.0
5A	Ca^{2+}/Mg^{2+}	4.3	1.0
10X	Ca^{2+}	7.8	1.2
13X	Na^+	8.0	1.2
Y	K^+	8.0	2.4
Mordenite	Na^+	7.0	5.0
ZSM-5	Na^+	6.0	31.0
Silicalite	-	6.0	∞

Zeolites are promising inorganic porous materials which have excellent separation performance and stability. Zeolites have several structures which have different chemical composition and physicochemical properties; thereby, they are widely used in various applications such as catalysis, gas separation, and ion exchange. Transport mechanism through zeolites is based on adsorption, diffusion, and desorption, respectively. For gas separation, the pore size of zeolites acts as an important role to determine the success in separation. When a permeable molecule allows to pass through but does not allow another molecule to pass through or pass through with slower rate. This separation mechanism is called molecular sieving. For this reason, pore structure of zeolite and characteristics of penetrant are the important parameters determining the success in gas separation. The properties of each gas are shown in Table 2.2, such as different kinetic diameters and critical temperatures. The zeolite selection is essential for any applications.

Table 2.2 Physical properties of CO_2, CH_4, N_2, O_2, and H_2 (Bastani *et al.*, 2013)

Physical properties	Gas molecules				
	CO_2	CH_4	N_2	O_2	H_2
Molecular weight	44.01	16.04	28.01	31.99	2.02
Kinetic diameter (Å)	3.3	3.8	3.64	3.46	2.89
Density (at 0°C, 1 atm, g/L)	1.977	0.72	1.25[a]	1.429	0.0899
Critical temperature (°C)	31	82.1	-147.1	-118.6	-240.2
Critical pressure (atm)	72.9	45.8	33.5	49.77	12.8
Critical density (g/mL)	0.468	0.162	0.311	0.436	0.031
Viscosity (at 21°C, 1 atm, cp)	0.0148	0.0106[b] 0.0116[c]	0.017 0.0174	0.019[d]	0.0087[e]

[a] At 20°C. [b] At 4.4°C. [c] At 37.8°C. [d] At 0°C. [e] At 15°C.

In commercial adsorption processes for CO_2 capture, Types A, X, and Y zeolites are the most utilized ones (Bakhtyari *et al.*, 2020). The structural unit of type X and Y zeolites is the Faujasite (FAU) demonstrated in Figure 2.2 and the general information is shown in **Table 2.3**. They have a large cavity in FAU called the "supercage" (which should really be called a supercavity). Owing to the large cavity, X and Y zeolites have been used for the CO_2 adsorption process.

Table 2.3 The general information of FAU structure type (Broach, 2010)

Type material	Faujasite (FAU)
Chemical formula	$|(Ca,Mg,Na)_{29}(H2O)_{240}|[Al_{58}Si_{134}O_{384}]$ **-FAU**
Space group	Cubic, Fd-3m, a = 24.74 Å
Pore structure	Three-dimensional 12-ring
Mineral forms	Faujasite
Synthetic forms	Beryllophosphate X, Li-LSX, LZ-210, SAPO-37, siliceous Na-Y, zeolite X (Linde X), zeolite Y (Linde Y), zincophospate X

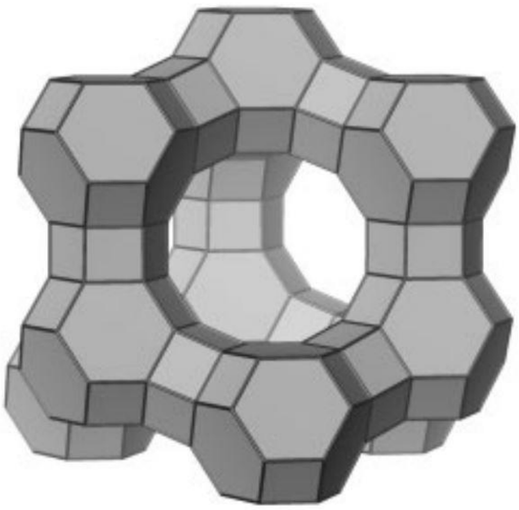

Figure 2.2 Framework structure for FAU zeolite formed by linking sodalite cages through double six-rings (Broach, 2010).

The faujasite framework possesses the largest central cavity pore. In the fully hydrated state, the central cavity pore of the faujasite framework can accommodate about 235 water molecules, while in the fully dehydrated state, it results in almost 50% void fraction. The free diameter of the aperture of the faujasite framework, which is formed by 12-membered oxygen rings, is approximately 7.4Å. Type X and Y zeolites possess a similar framework to that of faujasite but with different Si/Al ratio shown in Table 2.4. Due to the different Si/Al ratio between them, this affects the total acidity of the zeolite. Zeolite acidity increases in strength as the molar ratio of Si/Al decreases due to the strength of the electro-static field in the zeolite and increase in the number of acid sites (Kulprathipanja and James, 2010). For this reason, zeolite X, Si/Al ratio of 2.5, is more acidic than zeolite Y, Si/Al ratio of 4.8. The cations can alter acidity or enhance the basic strength of zeolites in the following order: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Moreover, the replacement of cations through ion exchanges results in the adjustment of the pore dimensions of the zeolite channels. For CO2, which is an acidic gas, the interaction between the acidic and basic sites of zeolite and CO_2 is the important parameter for separation performance.

Table 2.4 Typical properties of common zeolites (Kulprathipanja and James, 2010)

Zeolite type	Channel system	Pore openings (Å; hydrated form)	Typical SiO_2/Al_2O_3 mole ratio	Theoretical ion exchange capacity (meq/g; Na form, anhydrous)
Anlcime	One-dimensional	2.6	4	4.9
Chabazite	Three-dimensional	3.7 × 4.2 and 2.6	4	4.9
Clinoptilolite	NK	4.0 × 5.5, 4.4 × 7.2 and 4.1 × 4.7	10	2.6
Erionite	Three-dimensional	3.6 × 5.2	6	3.8
Ferrierite	Two-dimensional	4.3 × 5.5 and 3.4 × 4.8	11	2.4

Phillipsite	Three-dimensional	4.2 × 4.4, 2.8 × 4.8 and 3.3	4.4	4.7
Zeolite A	Three-dimensional	4.2 into alfa-cage; 2.2 into beta-cage	2	7.0
Zeolite L	One-dimensional	7.1	6	3.8
Mordenite	Two-dimensional	2.9 × 5.7	10	2.6
Zeolite Omega	One-dimensional	7.5	7	3.4
Silicate-1	Three-dimensional	(5.7-5.8) × (5.1-5.2)	50	0.63
Zeolite X	Three-dimensional	7.4 into supercage; 2.2 into beta-cage	2.5	6.4
Zeolite Y	Three-dimensional	7.4 into supercage; 2.2 into beta-cage	4.8	4.4

2.1.3 Mixed Matrix Membranes (MMMs)

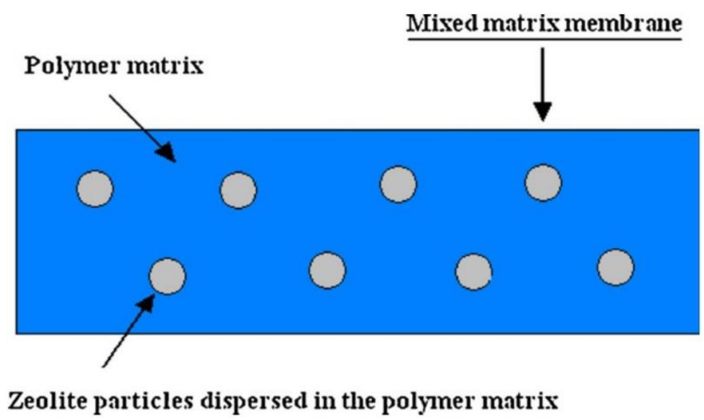

Figure 2.3 Schematic of the mixed matrix membrane (Bastani *et al.*, 2013).

Mixed matrix membranes (MMMs) illustrated by Figure 2.3 are well known to enhance the gas separation performance of polymeric membranes to overcome the Robeson's upper bound. Generally, it consists of a polymer as a continuous phase and an inorganic filler as a dispersed phase. The incorporation of inorganic filler and polymer can lead to the synergistic effect of both materials. Inorganic materials provide enhancement of gas separation performance in terms of permeability and selectivity while retaining the advantages of polymeric materials.

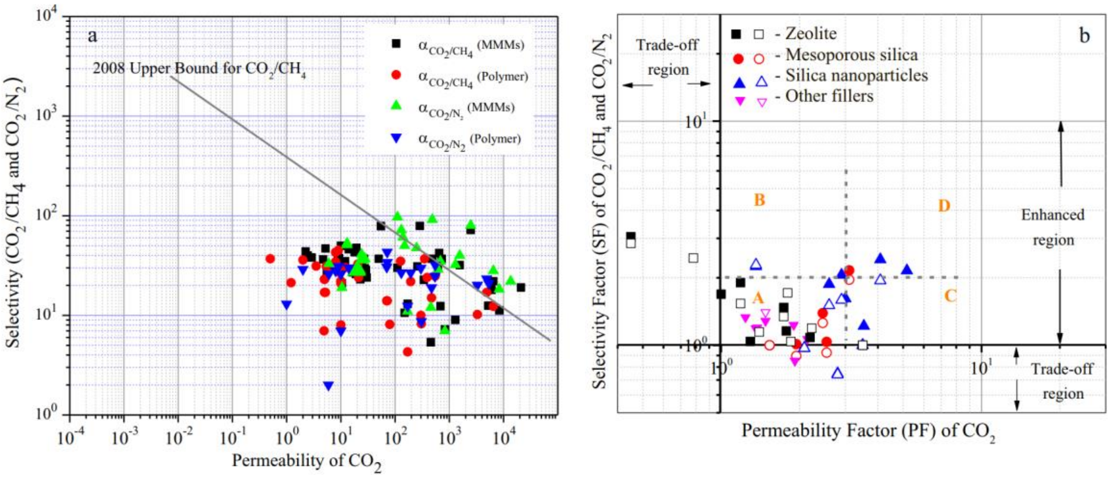

Figure 2.4 Zeolite-based filler in mixed matrix membranes of CO_2 gas separation; (a) Gas separation performance of MMMs compared to 2008 upper bound for CO_2/CH_4. (b) Permeability and selectivity factors of CO_2/CH_4 (filled) and CO_2/N_2 (unfilled) respectively (Vinoba *et al.*, 2017).

As seen in Figure 2.4, inorganic materials, such as zeolite, mesoporous silica, silica nanoparticles, and others, can improve the CO_2 permeability and selectivity from trade-off region to enhanced region. For these results, these inorganic materials as solid fillers can enhance the separation performance of polymeric membranes. However, the factors to succeed in development of MMMs depends on several key factor including the compatibility between polymer and filler, the gas separation characteristic of polymer and filler, filler concentration, and defect in MMMs (Bastani *et al.*, 2013; Cheng *et al.*, 2018; Rezakazemi *et al.*, 2014). The compatibility and adhesion between polymer and filler is the important issue that affects the overall performance of MMMs. For this reason, many approaches have been introduced and studied to modify the outside surface of the zeolite particles to improve the compatibility between the zeolite particles and the polymer matrix (Liu and Kulprathipanja, 2010) including small organic molecules, sizing agents, surface treatment agents, electro-stabilizing additives, and low molecular weight materials (LMWMs).

2.1.4 Low Molecular Weight Materials (LMWMs)

To improve compatibility between inorganic filler and polymer, there are several methods to improve compatibility. The promising and convenient method is the addition of a third component into solid-polymer mixed matrix membranes. The third component can be located in several ways, as schematically illustrated in Figure 2.5, In addition to improving compatibility, the introduction of this component can optimize gas separation performance in terms of increase in CO_2 diffusion selectivity, CO_2 solubility selectivity, and the fractional free volume.

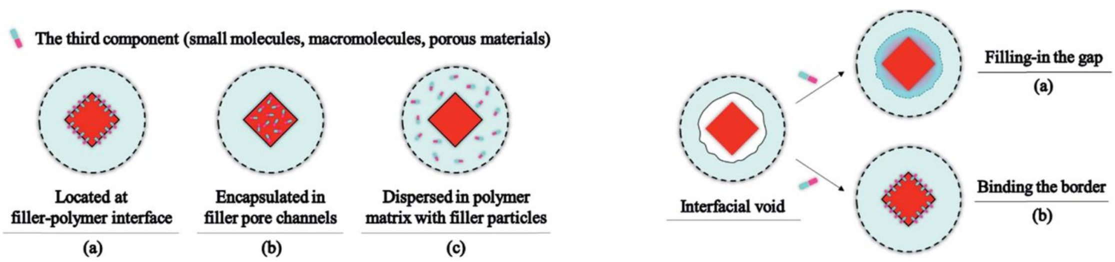

Figure 2.5 Schematic illustration of possible existing forms of the third component in solid-liquid-polymer MMMs and interfacial void healing by the third component (Guo *et al.*, 2019).

Macromolecules have long molecular chains, abundant functional groups, and good compatibility with polymer matrix, which result in filling the gaps between filler and polymer matrix, introducing a large amount of CO_2-philic functional groups into MMMs, or bridging the filler and polymer matrix through covalent or noncovalent interactions. Macromolecules commonly used, as schematically demonstrated in Figure 2.6, are O-containing or N-containing materials, such as polyethylene glycol (PEG) and its derivatives, polydopamine (PDA), polyethyleneimine (PEI) and some other polymers. The presence of polar functional groups that provide affinity for CO_2 results in the enhancement of CO_2 separation (Guo *et al.*, 2019).

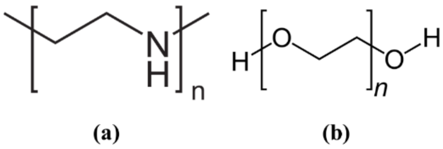

Figure 2.6 Chemical structures of PEI (a) and PEG (b).

2.2 Literature Reviews

Junaidi et al. (2013) examined the gas separation performance of SAPO-44 zeolite incorporated PSf polymeric matrix. The well-dispersed homogeneous MMMs could be achieved when SAPO-44 was loaded less than 5 wt.% in MMMs. In consequence of higher zeolite loading, the particle agglomeration and interfacial void were formed, and then the separation performance was severely declined. They reported that the filler modification was required to embed more filler loading without defect on MMM. Zarshenas et al. (2016) investigated the gas separation performance of NaX/Pebax®1657 mixed matrix membranes. They found that the addition of nano-zeolite NaX led to the agglomeration at 4 wt.% of zeolite contents. The gas permeation results showed that the incorporation of nano-zeolite NaX impacted on the gas separation performance of Pebax®1657. The ideal selectivity of CO_2/N_2 improved but the permeabilities of all gases passing through the MMMs decreased. Zhao et al. (2019) prepared mixed matrix membrane consisting of Matrimid and Li/Na-ZSM-25. The MMM incorporating low zeolite loading (5 wt.%) was well dispersed homogeneous, further increase in zeolite loading came up with filler agglomeration and precipitation of zeolite particles. Due to ZSM-25 addition, the results revealed that the CO_2 permeance increased but the CO_2/CH_4 selectivity decreased. The reason for this was the presence of filler-polymer interfacial defect enhancing both CO_2 and CH_4 permeation. Ahmad et al. (2021) studied the gas separation performances of SSZ-16 zeolite dispersed in a 6FA-based PI matrix. The fabricated MMMs could remarkably enhance CO_2 permeability about 2 times, while the selectivity was still the same as a pristine polymeric membrane. The best performance was found at 5 wt.% SSZ-16 zeolite dispersed in PI. When the zeolite loading was too high, the sedimentation of filler occurred in MMM. Resulting from defects on MMM, it negatively impacts the overall performance of the membrane. Surya Murali et al. (2014) introduced 4A zeolite to Pebax®1657 to investigate the gas separation performance of MMMS. The prepared MMMs were well dispersed without defects on MMMs at low zeolite content. 4A/Pebax®1657 MMMs increased the permeability of all gases as well as the ideal selectivity of CO_2/CH_4 compared to the neat polymeric membrane.

Many research groups have studied the incorporation of zeolite as inorganic filler into polymeric membranes and reported in the same way. Although zeolite showed significant enhancement in the gas separation performance of MMMs, the compatibility between zeolite and polymer is the issue leading to the negative impact in terms of separation performance and mechanical strength on membranes. The physicochemical properties between polymer and zeolite are completely different; consequently, the incorporation of zeolite in the polymeric matrix always encounters defects on MMMs. This results in the formation of interfacial void and agglomeration of zeolite in the polymeric matrix. To improve polymer-zeolite compatibility, plenty of approached, such as silanation, thermal annealing, priming, and Grignard treatment, have been studied and developed recently (Bastani *et al.*, 2013; Rezakazemi *et al.*, 2014). One of the convenient modifications is an addition of additive or low molecular weight materials (LMWMs) to MMM (Bastani *et al.*, 2013; Cheng *et al.*, 2018). These additives fill the available space in the membrane. The voids are fulfilled, thus. Moreover, the surface of zeolites is coated by additives, and then the polymer-zeolite interaction is also improved. In addition to improvement of interfacial morphology, the materials which have affinity to penetrant will be selected to improve both compatibility and separation performance. For CO_2 separation membrane, CO_2-philic material, especially polyethylene glycol (PEG), has been selected and studied due to the existence of an oxygen polar group in the structure (Kargari and Rezaeinia, 2020). PEG enhances CO_2 separation in the reason of a favorable ether-CO_2 interaction. Reijerkerk et al. (2010) studied the effect of PEG-PDMS as an additive on the gas separation performance. They simultaneously combined the permeable polymers, PDMS and PEG, in the same membrane. The addition of PDMS-PEG to PEBAX®1657 increased CO_2 permeability about 5 times. Conversely, the CO_2/N_2 and CO_2/CH_4 selectivity decreased. Loloei, Moghadassi, et al. (2015) introduced a low molecular weight polyethylene glycol (PEG 200) to Matrimid®5218 to investigate the effect of PEG in the form of a blended-polymeric membrane. The addition of PEG 200 led to increase both permeability and selectivity. From the most improved membrane (Matrimid®5218/PEG 200 (95:5)), the CO_2 permeability and CO_2/CH_4 selectivity were improved about 25% and 14%, respectively. Loloei, Omidkhah, et al. (2015) examined the effect of a liquid additive, PEG 200, on Matrimid®5218/ZSM-5 MMMs' performance. They found that PEG 200 improved the interface between zeolite and polymer. The incorporation of PEG 200 and ZSM-5 in polymeric membrane significantly enhanced the gas separation performance of a neat Matrimid®5218. 5 wt.% PEG and ZSM-5 in Matrimid®5218 yielded an increase in CO_2 permeability about 50% and CO_2/CH_4 selectivity about 72%. Castro-Muñoz et al. (2019) fabricated ternary mixed matrix membranes (Matrimid®5218/ZIF-8/PEG 200) to investigate the effect of PEG as CO_2-philic additives. They obtained a homogeneous dispersion of ZIF-8 particles in a polymeric matrix. The addition of PEG 200 enhanced the CO_2/N_2 selectivity of Matrimid®5218-PEG blend membranes, while the incorporation of PEG 200 in MMMs could not improve the CO_2/CH_4 selectivity. Although CO_2 permeability significantly improved, the permeabilities of other gases were also improved by a reason of enhancing motion of the polymer chain. Nadeali et al. (2020) introduced PEG (MW 550) to improve the filler-polymer compatibility and the gas separation performance. The results showed that the existence of PEG in PEBAX/PEG550 (30 wt.%)/CA (0.5%) could remarkably improve the CO_2 permeability from 122.71 to 632.60 Barrer compared to the neat membrane. Furthermore, the selectivity of CO2/CH4 was also enhanced from 20.76 to 59.83. Wang et al. (2014) investigated the effect of PEG on mixed matrix membranes to obtain well – dispersed MWCNTs in MMM and improve the CO_2 permeability and selectivity. The results showed that PEG could reduce the filler agglomeration by improving the surface hydrophilicity of MWCNT. The incorporation of PEG could lead to enhancing the CO_2 permeability and selectivity of CO_2/light gas. Azizi *et al.* (2017) introduced PEG to modify the surface of TiO_2 nanoparticles and investigate the effect of PEG and TiO_2 nanoparticles on CO_2 and CH_4 permeability and CO_2/CH_4 selectivity. They reported that the presence of PEG modified TiO_2 particles could prevent the filler agglomeration and achieve well-dispersed MMMs. The gas separation performance was also improved due to the influence of PEG and TiO_2.

Some researcher groups have not only studied the capability of molecular sieving but also the ability to adsorb a liquid additive inside pores of porous filler to obtain the advantages of liquid additive and prevent the additive leakage. The hybrid membranes called solid-liquid-polymer mixed matrix membranes have been studied recently (Rezakazemi *et al.*, 2014). They combine adsorbed liquid additive, filler, and polymer in the same membrane. Mahmoudi et al. (2015) introduced PEG (MW 200) as a liquid additive into PEBA/NaX mixed matrix membranes to investigate the improvement in CO_2/CH_4 separation. They found that the homogeneous dispersion of NaX particles was achieved. Due to the addition of PEG, the surface roughness was reduced as well. Compared to neat PEBA membrane and NaX/PEBA membrane, the PEG addition significantly improved the CO_2 permeability and CO_2/CH_4 selectivity. Besides, the gas separation performance of this work was located above Robeson's upper bound. Chultheera et al. (2017) introduced PEG 400 as a liquid additive into activated Carbon (AC)/Silicone rubber (SR) MMMs to examine the enhancement in CO_2 separation performance and the capability to adsorb liquid PEG in pores of AC. The results showed that 10 wt.% PEG/AC/SR/CA MMM achieved the best selectivity (14.12) compared to AC/SR/CA MMM (5.98). Besides, they found that the existence of AC in MMM could also enhance the performance and prevent the leakage of liquid additives. When the separation performance between PEG/SR/CA MMM and PEG/AC/SR/CA MMM were compared, the CO_2 permeability and CO_2/CH_4 selectivity were improved from 83.63 to 114.82 GPU and 6.31 to 12.42, respectively. Poogkasorn (2018) inspected the gas separation performance of the liquid-solid-polymer mixed matrix membranes consisting of NaX as an inorganic filler, PEG 400 as a liquid additive, and a silicone rubber as polymer matrix. The results showed that PEG adsorbed NaX significantly improved the CO_2/CH_4 selectivity compared to the neat silicone rubber on the CA support membrane. Khonkhlong (2019) studied the addition of KY zeolite as a filler embedded by PEG and dispersed in a silicone rubber. They found that the simultaneous incorporation of KY zeolite and PEG 400 in SR yielded the highest CO_2/CH_4 selectivity compared to both neat SR and KY/SR MMMs. They reported that there was additive leaking from filler, resulting in lowering the gas separation performance.

Some research groups have tried to find new approaches to develop mixed matrix membranes. They attempted to combine two kinds of fillers within the same polymer matrix. They expected that this approach might yield the synergistic effect on gas separation performance of MMMs. Zornoza et al. (2011) incorporated two types of fillers, including metal-organic framework (MOF) and zeolite in the same membrane. They reported that the different surface properties of two fillers facilitated the dispersion and disaggregation of fillers in MMMs. The combination of MOFs (HKUST-1 and ZIF-8) and silicalite-1 zeolite significantly enhanced the CO_2 permeability; nevertheless, the CO_2/light gas selectivity was unimproved. Galve et al. (2013) investigated the combination of MCM-41 mesoporous silica and JDF-L1 microporous titanosilicate incorporated into copolyamide to improve the H_2 separation performance. The existence of JDF-L1 in MCM-41/PI MMM resulted in good dispersion of MCM-41 within the membrane. Besides, the H_2 permeability and H_2/CH_4 selectivity improved as well. They revealed that the gas performance of JDF-L1/MCM-41/PI MMM was in the attractive zone in the Robeson diagram. Valero et al. (2014) combined MCM-41 mesoporous silica and NH2-MIL-53(Al) metal-organic framework in the same MMM. They found that the presence of MCM-41 particles aided the formation of MOF agglomeration. In addition to good dispersion of filler, synergistic effects of two fillers resulted in superior gas separation performance.

CHAPTER 3
METHODOLOGY

3.1 Objectives

1) To study the effect of NaX/KY zeolite mass ratios on CO_2/CH_4 gas separation performance of the MMMs
2) To investigate the synergistic effects of NaX, KY, PEG, and silicone rubber on CO_2/CH_4 gas separation performance of MMMs

3.2 Scope of Research

To achieve the objectives of this study, the following scope of work is proposed:

1) The amount of silicone rubber was 20 wt.% with respect to hexane.
2) The amount of zeolite dispersed in each membrane was 4.76 wt.% with respect to silicone rubber and hexane.
3) The amounts of PEG adsorbed NaX and KY zeolites were 2.94 and 3.85 wt.% with respect to zeolite, silicone rubber, and hexane.
4) The size of solid fillers was smaller than 80 mesh or 180 µm.
5) The thickness of the fabricated membrane was 16 mils (1 mil = 10^{-3} in).
6) The membranes were prepared at room temperature and atmospheric pressure.
7) The gas permeances of all membranes were determined at room temperature, inlet pressure of 50 psi.
8) The sequence of tested gases was N_2, CH_4, N_2, CO_2, and N_2, respectively.

3.3 Materials and Equipment

Equipment:

1) The in-house membrane testing apparatus
2) Oven (ED056, Binder World)
3) Casting knife
4) Glass plate
5) Magnetic stirrer

Chemicals:

1) Silicone rubber (KE-1300T/CAT-1300, Shin-Etsu, Japan, CAS No. 63394-02-5)
2) Zeolites (NaX and KY, Honeywell UOP, USA)
3) Polyethylene glycol (Carbowax PEG 400, Dow Chemical, Malaysia, CAS No. 25322-68-3)
4) Cellulose acetate (Semipermeable film, Honeywell UOP, USA)
5) Carbon dioxide (HP, 99.99%, Air Liquide, Thailand, CAS No. 124-38-9)
6) Nitrogen (HP, 99.99%, Air Liquide, Thailand, CAS No. 7727-37-9)
7) Methane (HP, 99.99%, Air Liquide, Thailand, CAS No. 74-82-8)
8) n-Hexane (AR, 99%, Aldrich, Thailand, CAS No. 110-56-3)
9) Ethanol (AR, 99.9%, Aldrich, Thailand, CAS No. 64-17-5)

3.4 Experimental Procedures

3.4.1 PEG Impregnated into Zeolite Preparation

Zeolites were mashed and sieved to be smaller than 180 μm or 80 mesh. The sieved zeolite was dried at 120°C for 5 h to get rid of the moisture. To prepare a 60 vol.% PEG solution, PEG *MW*-400 was dissolved in ethanol. The PEG solution was stirred about 30 min or until the solution was homogeneous. After that, the resulted PEG solution was impregnated dropwise onto the zeolite until it was wetted. The PEG impregnated zeolites were dried at 80°C for 12 h to evaporate the solvent.

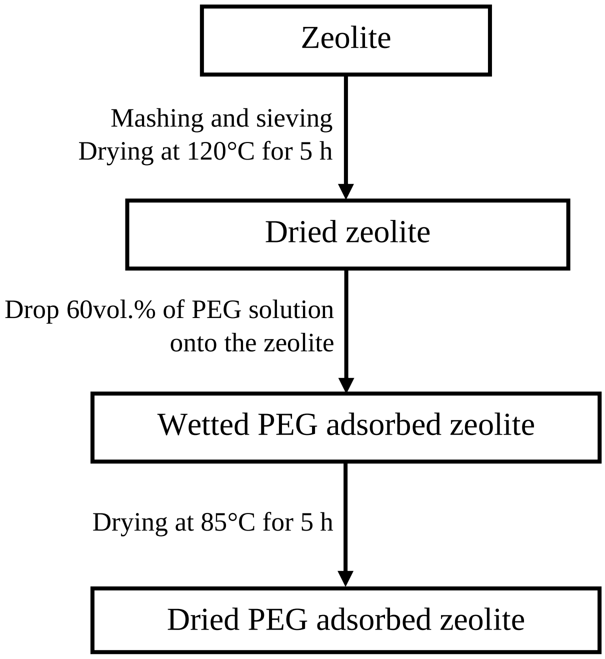

Figure 3.1 Flow diagram of the PEG adsorbed zeolite preparation.

3.4.2 Membrane Preparation

All the membranes were prepared via the casting and solvent evaporation methods. Firstly, the desired amount of each filler was dispersed in hexane and then sonicated for 15 min to break aggregation among the fillers. The elastomer part of silicone rubber was added to the dispersion and was stirred for 2 h to enable complete dissolution of polymer. The solution was sonicated for 15 min prior to adding the curing agent. The resultant solution was stirred further for 2 h and then cast on a supporting membrane. The cast membrane was dried at room temperature for 1 h and then at 85°C for 5 h to evaporate the residual solvent from the membrane. Thickness of the different membrane samples prepared in this study was 16 mils.

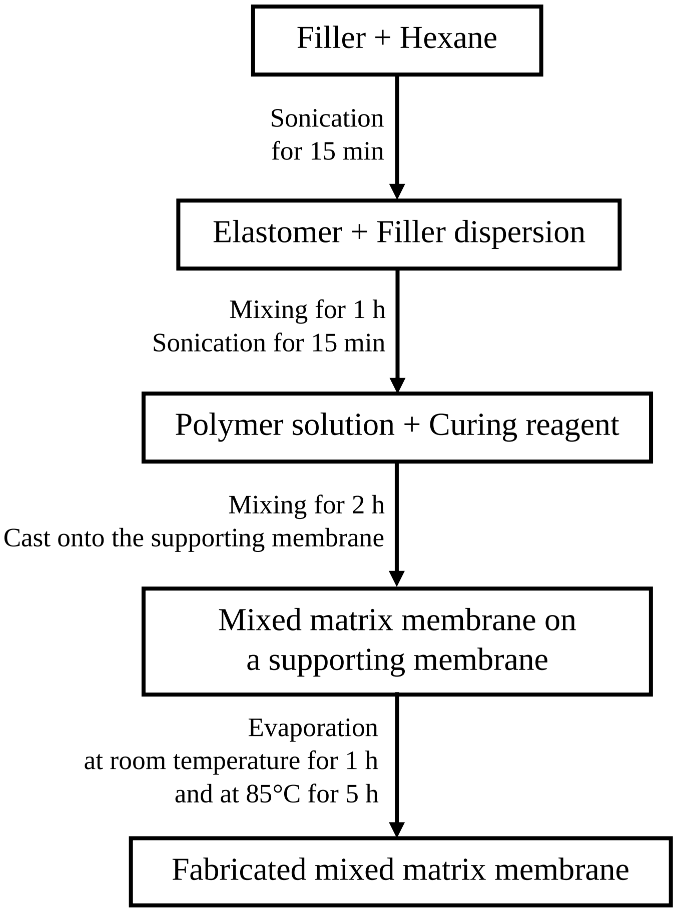

Figure 3.2 Flow diagram of the MMM preparation.

Table 3.1 The chemical composition of fabricated membranes

Membrane	Polymer (wt.%)	Zeolite		PEG (wt.%)		Supporting membrane
		Loading (wt.%)	Mass ratio (NaX:KY)	NaX	KY	
SR/CA	Silicone rubber (20wt.%)	-	-	-	-	Cellulose acetate
NaX:KY/SR/CA		4.76	1:0	-	-	
			3:1			
			1:1			
			1:3			
			0:1			
PEG/NaX:KY/SR/CA		4.76	1:0	2.94	3.85	
			3:1			
			1:1			
			1:3			
			0:1			

3.4.3 <u>Gas Permeance Measurements</u>

The experimental setup used for the determination of gas permeability is schematically shown in Figure 3.3. The fabricated membrane was shaped into a 7.5 cm-diameter circle and then placed in a membrane testing unit with an O-ring sealing around the edge. The testing unit was pressurized at 50 psig on the feed side, whereas the permeate side was at an atmospheric pressure (1 atm) and at room temperature. After the testing system was steady, the gas flux was measured using a bubble flow meter. The sequence of gases passing through the membrane was N_2, CH_4, N_2, CO_2, and N_2. The gas permeance was calculated according to Eq. (2.1).

$$\frac{P_A}{L} = \frac{J_A}{\Delta P_A}$$

where P_A/L is the gas permeance in GPU, J_A is the penetrant diffusive flux through the membrane (cm^3/cm^2-s) and ΔP_A is the change in partial pressure across the membrane (cmHg). The ideal CO_2/CH_4 selectivity was determined according to Eq. (2.3).

$$\alpha_{ij} = \frac{P_i}{P_j}$$

where α_{ij} is the selectivity between i and j gases, P_i and P_j are the gas permeabilities of i and j gases, respectively.

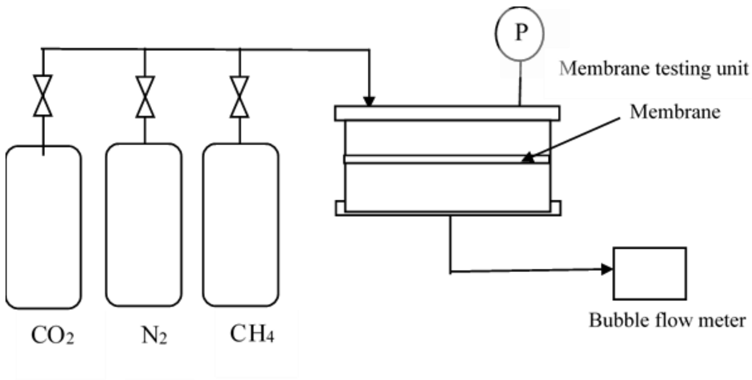

Figure 3.3 Schematic diagram of the single gas permeance measurement.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Gas Permeance and Selectivity

4.1.1 Silicone Rubber Membranes

To determine the separation performance, there are two important parameters influencing penetrants passing through polymeric membranes, namely solubility (S) and diffusivity (D). The solubility depends on the condensability of the penetrants and interaction between the penetrant and polymer. The other one, diffusivity, is determined by polymer chain mobility and physical characteristics of penetrants (Alqaheem *et al.*, 2017). The product of these two factors is called permeability (P). Permeability is used to evaluate how much the penetrant can pass through a membrane. To evaluate which species is more permeable, selectivity (α) is the ratio of permeability between two penetrants. For both parameters, the selection of polymer is an important issue for success in polymeric membrane separation.

Permeance was determined from steady-state permeation rates of CO_2, CH_4, and N_2 through the membranes. The volumetric flow rates were collected using a bubble flow meter at room temperature, inlet pressure of 50 psi. The single gas permeances were determined by using Eq. (2.1) accordingly.

Table 4.1 Gas permeances and selectivities for silicone rubber on cellulose acetate supporting membrane and cellulose acetate supporting membrane

Membranes	Gas permeance (GPU)			Selectivity	
	CO_2	CH_4	N_2	CO_2/CH_4	CO_2/N_2
CA[1]	213.51	10.52	8.52	23.88	25.07
SR/CA[2]	155.43	4.71	3.69	32.91	42.17

[1] CA = Cellulose acetate supporting membrane

[2] SR/CA = 20 wt.% silicone rubber on cellulose acetate supporting membrane

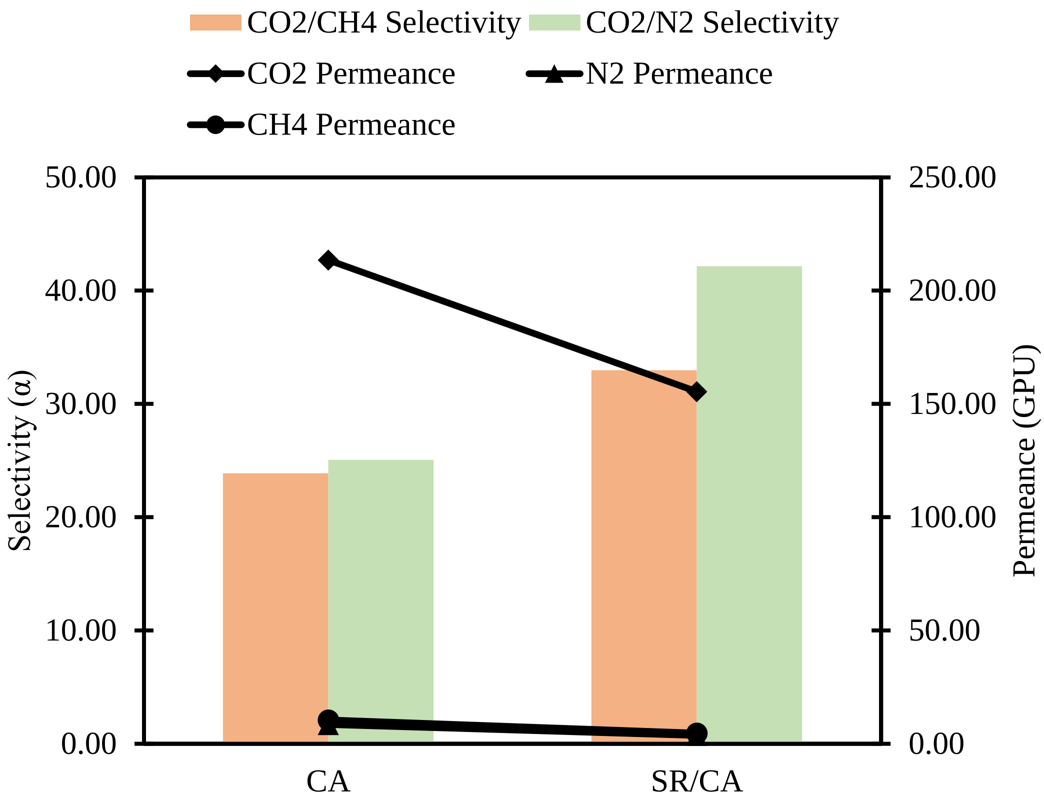

Figure 4.1 Comparison of gas permeance and selectivity between silicone rubber on cellulose acetate (SR/CA) and cellulose acetate (CA) membranes.

Gas permeance and CO_2/CH_4 selectivity are shown in Table 4.1 and Figure 4.1. After silicone rubber was cast on cellulose acetate, the CO_2, N_2, and CH_4 permeances declined about 73%, 43%, and 45%, respectively. Conversely, the CO_2/CH_4 selectivity is inclined about 38% and 68%, respectively. It is clearly seen that silicone rubber as a polymeric membrane can improve the gas separation performance in terms of selectivity, although gas permeance decreases. Penetrants pass through rubbery polymer, silicone rubber, via a transient gap of sufficient size to accommodate the penetrants (Chultheera *et al.*, 2017). As a result, gas permeance of SR/CA decreases. Since CO_2 permeance is higher than the others because of its smaller kinetic diameter and facile condensability, the permeance of CO_2 was higher than the permeance of N_2 and CH_4 leading to increase in CO_2/CH_2 selectivity

4.1.2 Mixed Matrix Membranes of Combination of NaX and KY Zeolites Incorporated in Silicone Rubber (NaX:KY/SR/CA)

In this section, solid-polymer mixed matrix membranes were fabricated and investigated the effect of mass ratio of NaX and KY zeolites on their CO_2/CH_4 gas separation performance. 4.76 wt.% of zeolites were incorporated in 20 wt.% silicone rubbers as a continuous phase which in turn was cast on a cellulose acetate supporting membrane. Gas permeance and selectivity were determined and reported in Table 4.2.

Table 4.2 Gas permeances and selectivities for NaX and KY zeolites incorporated silicone rubber on cellulose acetate supporting membrane

Membranes	Gas permeance (GPU)			Selectivity	
	CO_2	CH_4	N_2	CO_2/CH_4	CO_2/N_2
NaX:KY, 1:0/SR/CA	46.98	4.81	4.11	9.76	11.44
NaX:KY, 3:1/SR/CA	65.44	5.52	5.15	11.87	12.72
NaX:KY, 1:1/SR/CA	75.06	5.79	4.12	12.98	18.23
NaX:KY, 2:1/SR/CA	96.43	4.99	3.62	19.34	26.62
NaX:KY, 0:1/SR/CA	150.11	6.00	4.17	25.01	35.98

Notes

[1] NaX:KY, Y:Z/SR/CA = 4.76 wt.% NaX and KY zeolites with NaX to KY zeolite mass ratio of Y:Z incorporated silicone rubber cast on cellulose acetate supporting membrane.

Zeolite content was calculated with respect to the total weight of silicone rubber and zeolites.

GPU = $1\cdot10^{-6}$ $cm^3(STP)/cm^2\cdot s\cdot cmHg$

As shown in Table 4.2 and Figure 4.2, with increasing the content of KY zeolite, the results reveal an increase in CO_2 permeance. The highest CO_2 permeance is obtained from the membrane with NaX/KY ratio of 0:1 that was ca. 150 GPU. In contrast, the CO_2 permeance of the membrane with NaX/KY ratio of 1:0 was ca. 47 GPU. In addition, the CO_2/CH_4 selectivity of the membrane with NaX/KY ratio of 0:1 is higher than that of membrane with NaX/KY ratio of 1:0. Clearly, KY zeolite is better in gas separation than NaX zeolite in the form of a solid filler dispersed silicone rubber matrix. Moreover, KY zeolite dominated the gas separation performance of MMMs combined with NaX zeolite in the same membranes. NaX and KY zeolites have no significant difference in pore size; therefore, the factor determining gas separation performance does not depend on the kinetic diameter of gases. Conversely, acid-base interaction becomes an aspect for CO_2/CH_4 gas separation. It was implied that the basicity of KY zeolite is stronger than NaX zeolite. In other words, NaX zeolite is more acidic or less basic than KY zeolite (Bakhtyari *et al.*, 2020). The theoretical ion exchange capacity of zeolites X and Y is listed in Table 2.4. The ion exchange capacity of Y zeolite is lower than that of X zeolite. Although zeolite with a lower Si/Al ratio, that is KY zeolite in this study, has obviously a lower cation density and acid-basic sites, the performance of KY zeolite as solid filler is still better than that of NaX zeolite. This behavior could be resulted from the lower occupancy in the cages resulting in more spaces for gas diffusion and less steric hindrance (Busca, 2017). Additionally, the high density of Na^+ ions on type X zeolite covers and masks part of the basic oxygen ions in orthosilicate (Busca, 2017). In addition to Si/Al ratio and ion exchange capacity, the cation is another parameter considered. Potassium ion (K^+) which is a stronger basic cation than sodium ion (Na^+) results in good interaction with an acidic gas (Bakhtyari *et al.*, 2020; Kulprathipanja and James, 2010). Owing to the increment of CO_2 permeance, CO_2/CH_4 selectivity is enhanced with increasing the amount of KY in combination of zeolite.

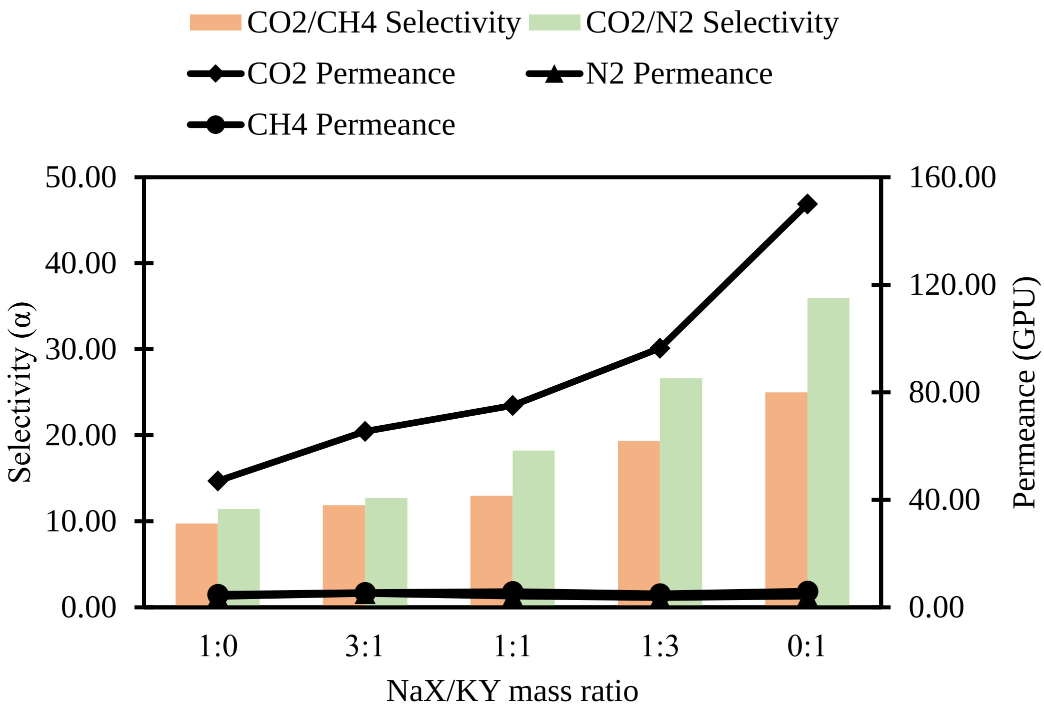

Figure 4.2 Comparison of gas permeance and selectivity among solid-polymer mixed matrix membranes with varying the mass ratio of NaX to KY zeolites.

4.1.3 <u>Mixed Matrix Membranes of Combination of PEG Adsorbed NaX and KY Zeolites Incorporated in Silicone Rubber (PEG/NaX:KY/SR/CA)</u>

In this section, solid-liquid-polymer mixed matrix membranes were investigated for the effect of mass ratio of PEG adsorbed NaX and KY zeolites on CO_2/CH_4 gas separation performance. Polyethylene glycol (PEG) (MW = 400), as a liquid polymer, was used to improve CO_2 permeance and CO_2/CH_4 selectivity due to its affinity for CO_2. It was reported that liquid PEG can leak from the membrane (Chultheera *et al.*, 2017) and then affect the CO_2/CH_4 gas separation performance. In previous works, individual NaX and KY zeolites were introduced to accommodate and stabilize liquid PEG to prevent the leakage (Poogkasorn 2018, Khonkhlong 2019). In this study, NaX and KY zeolites were combined and impregnated with 2.96 and 3.85 wt.%, respectively. The 4.76 wt.% of PEG/zeolite particles were incorporated in 20 wt.% silicone rubbers as a continuous phase and then cast on cellulose acetate supporting membrane. Gas permeance and selectivity were observed and reported in the following section.

Table 4.3 Gas permeances and selectivities for PEG adsorbed NaX and KY zeolites incorporated silicone rubber on cellulose acetate supporting membranes

Membranes	Gas permeance (GPU)			Selectivity	
	CO_2	CH_4	N_2	CO_2/CH_4	CO_2/N_2
PEG/NaX:KY, 1:0/SR/CA	66.00	2.95	2.06	22.35	32.10
PEG/NaX:KY, 3:1/SR/CA	113.43	4.63	3.25	24.52	34.91
PEG/NaX:KY, 1:1/SR/CA	105.48	3.99	3.21	26.43	32.84
PEG/NaX:KY, 1:3/SR/CA	86.60	3.29	2.61	26.32	33.23
PEG/NaX:KY, 0:1/SR/CA	97.80	4.13	2.94	23.69	33.27

Notes

PEG/NaX:KY, Y:Z/SR/CA = 2.96 wt.% PEG adsorbed NaX and 3.85 wt.% PEG adsorbed KY with NaX to KY mass ratio of Y to Z (4.76 wt.% zeolite) incorporated silicone rubber cast on cellulose acetate supporting membrane.

PEG content was calculated with respect to the total weight of silicone rubber, zeolite, and PEG.

Zeolite content was calculated with respect to the total weight of silicone rubber and zeolite.

GPU = $1 \cdot 10^{-6}$ $cm^3(STP)/cm^2 \cdot s \cdot cmHg$

Table 4.3 and Figure 4.3 show the effect of PEG adsorbed zeolite filler mass ratio on membrane performance. When CO_2/CH_4 gas separation performances of MMMs with PEG-NaX/PEG-KY ratio of 1:0 and 0:1 are compared, the results reveal that the CO_2 permeance of membrane containing PEG-KY, 97.80 GPU, is higher than that of membrane containing PEG-NaX, 66.00 GPU. about 48%. This is due to the characteristic of zeolite as described in the previous section. KY zeolite has a lower density of cation on zeolite structure resulting in more space and less steric hindrance. For this reason, KY zeolite could impregnate liquid PEG (3.85 wt.%) more than NaX zeolite (2.98 wt.%). This is confirmed by the literature (Khonkhlong, 2019;

Poogkasorn, 2018). CO_2 permeance tends to decrease after the highest CO_2 permeance is observed. PEG-to-PEG interaction and higher amounts of PEG adsorbed zeolite result in the precipitation and agglomeration of solid fillers during membrane preparation. Agglomeration and precipitation of solid fillers were obviously found in the case of PEG-KY particles. For this reason, the membrane performance could be deviated from the expectation. Even though CO_2 permeance decreased, it rose again for membranes containing PEG-KY. KY zeolite as a solid filler performs better than NaX zeolite as a solid filler despite the lower number of solid particles. In terms of CO_2/CH_4 selectivity, CO_2/CH_4 selectivities of membranes dispersing PEG-NaX and PEG-KY are 22.35 and 23.69, respectively. Consequently, there is no significant difference in selectivity between them. The highest CO_2 permeance is yielded from MMM with PEG-NaX/PEG-KY ratio of 3:1. Meanwhile, the highest CO_2/CH_4 selectivity is 26.4 obtained from the membrane with PEG-NaX/PEG-KY ratio of 1:1. Although the loss of solid filler occurred, CO_2/CH_4 separation performance was improved compared to some previous works. To compare CO_2/CH_4 separation performance among solid-liquid-polymer MMMs having the same supporting membranes, the membrane with PEG-NaX/PEG-KY ratio of 1:1 has CO_2 permeance of 105.48 GPU which is higher than that of PEG-NaX (96.49 GPU) and PEG-AC (91.70 GPU). In addition to CO_2 permeance, CO_2/CH_4 selectivity (26.43) is higher than that of PEG-NaX (16.30) and of PEG-AC (14.12) about 162% and 187%, respectively. Moreover, filler loading for this work was also less than the mentioned works (Khonkhlong, 2019; Poogkasorn, 2018). It is suggested that the combination of NaX and KY zeolites shows synergetic effect on CO_2/CH_4 separation performance.

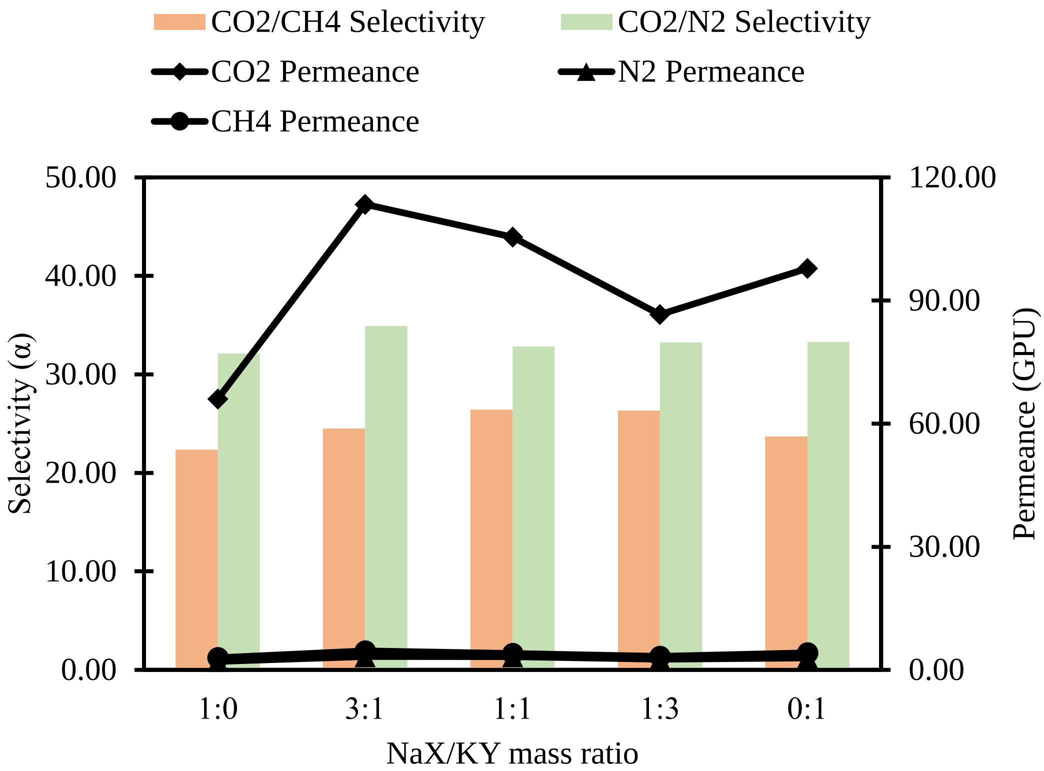

Figure 4.3 Comparison of gas permeance and selectivity among solid-liquid-polymer mixed matrix membranes with varying the mass ratio of NaX to KY zeolites.

4.1.4 Comparison of Gas Separation Performance between Solid-Polymer and Solid-Liquid-Polymer Mixed Matrix Membranes

In this section, CO_2/CH_4 gas separation performance of solid-polymer and solid-liquid-polymer mixed matrix membranes was compared.

From Figure 4.4, it reveals that CO_2 permeance of solid-liquid-polymer MMMs are almost higher than that of solid-polymer MMMs except for the membranes with NaX/KY ratio of 1:3 and 0:1. For membranes with NaX/KY ratio of 1:3 and 0:1, this is mainly caused by loss of PEG/zeolite particles mentioned in the previous section. The most improved CO_2 permeance is achieved for the membrane with NaX/KY ratio of 3:1. This is because of the presence of PEG, a CO_2-philic material, in mixed matrix membranes. PEG containing ethyl ether (EO) unit forms dipole-quadrupole interaction with CO_2 molecules. As a result, PEG prefers to dissolve CO_2 more than other gases (Guo *et al.*, 2019; Loloei, Moghadassi, *et al.*, 2015). In addition to CO_2 permeance, N_2 and CH_4 permeances as shown in Figure 4.5 were suppressed after PEG was impregnated into the pore channel of zeolite. Since PEG is not selective to N_2 and CH_4, it would behave as a pore-blocking material to both gases. For this reason, the decline in N_2 and CH_4 permeance was caused by longer tortuosity of diffusion path or the relatively slow diffusion rate of N_2 (3.64Å) and CH_4 (3.8Å) in pore channels (Zhang *et al.*, 2021). Although the kinetic diameter of CH_4 (3.8Å) is larger than that of N_2 (3.64Å), the results exhibit that CH_4 permeance is higher than N_2 permeance for any membranes. The penetrant gas passes through the polymeric membrane via the solution-diffusion mechanism, therefore, solubility of each gas in polymer is the key parameter determining its permeability. Another key parameter is the critical temperature of gases as shown in Table 2.2. Difference in critical temperature results in different solubility of each gas. The penetrant which has higher critical temperature provides higher solubility on the polymer membrane than the other penetrants which have lower critical temperature. CH_4 has the critical temperature of 82.1°C that is higher than that of N_2 (-147.1°C), therefore, the solubility of CH_4 on silicone rubber is higher than that of N_2. In case of selectivity shown in Figure 4.6, CO_2/CH_4 selectivity of solid-liquid-polymer MMMs is higher than that of solid-polymer MMMs excluding the membrane with NaX/KY ratio of 0:1. The presence of liquid additive, PEG, resulted in the increment of CO_2/CH_4 selectivity by the means of enhancement of CO_2 permeance and decrease in N_2 and CH_4 permeance.

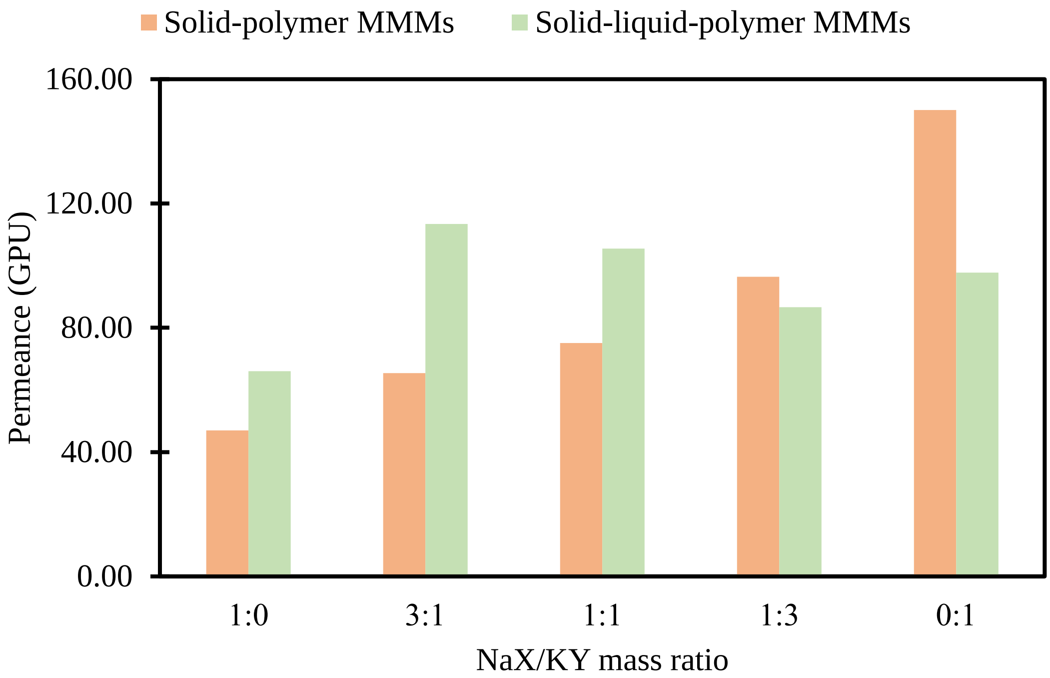

Figure 4.4 Comparison of CO_2 permeance between solid-polymer and solid-liquid-polymer mixed matrix membranes.

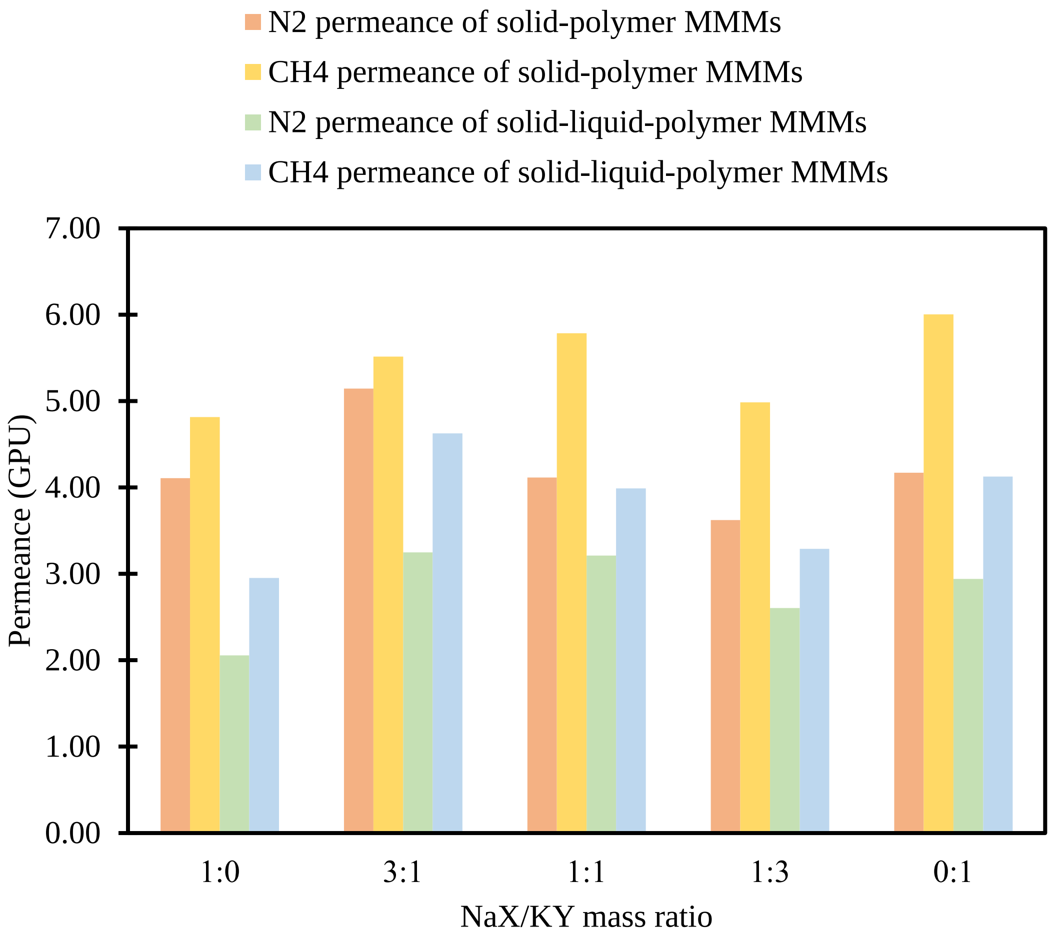

Figure 4.5 Comparison of N_2 and CH_4 permeances between solid-polymer and solid-liquid-polymer mixed matrix membranes.

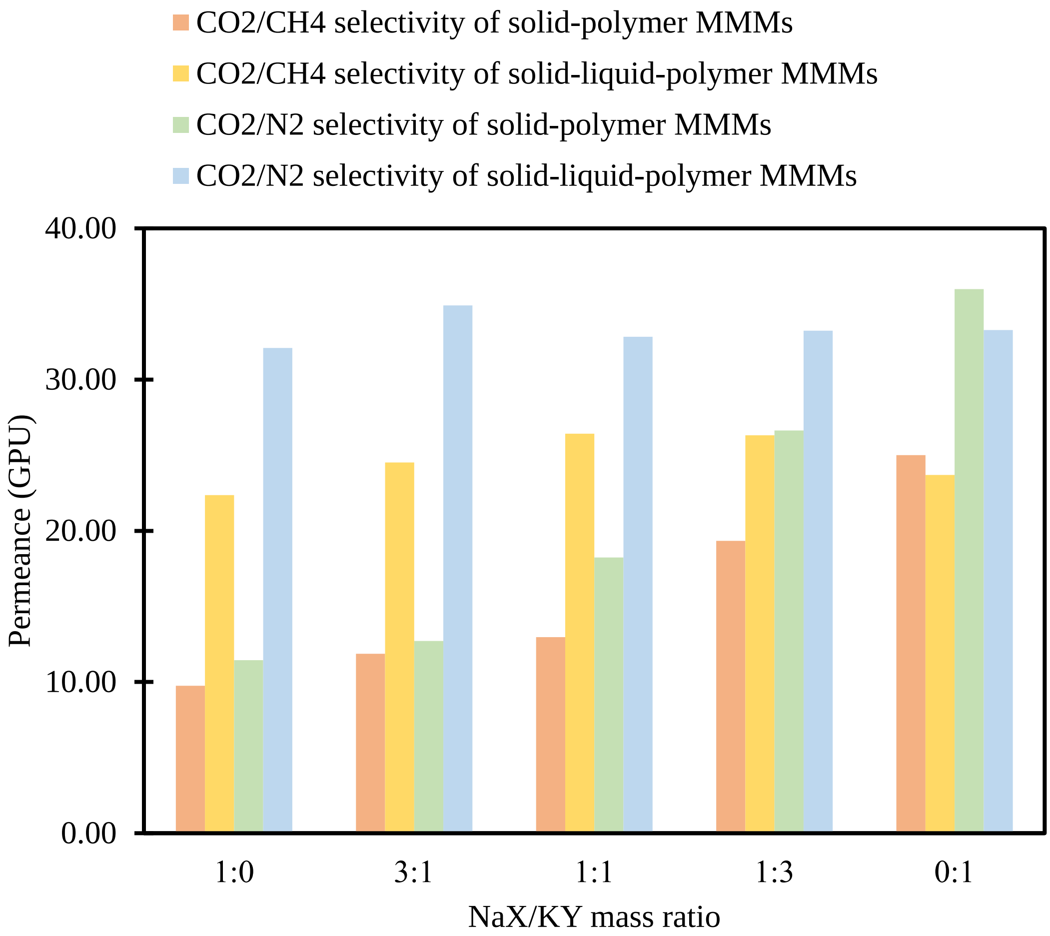

Figure 4.6 Comparison of CO_2/CH_4 and CO_2/N_2 selectivities between solid-polymer and solid-liquid-polymer mixed matrix membranes.

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Polymeric membrane, solid-polymer mixed matrix membranes, and liquid-solid-polymer mixed matrix membranes were fabricated by the solution-casting and solvent evaporation methods. Silicone rubber, NaX and KY zeolites, polyethylene glycol (PEG), and cellulose acetate were used as polymer, solid filler, liquid additive, and supporting membrane, respectively. The gas separation performance was evaluated by determining the permeabilities of CO_2, CH_4, and N_2 and selectivities between the gas pairs. Single gas permeance measurements were carried out at room temperature, inlet pressure of 50 psi, and outlet pressure of 1atm.

In the study of mass ratio of NaX to KY zeolite dispersed polymer matrix for solid-polymer mixed matrix membrane, CO_2 permeance and CO_2/CH_4 selectivity increase with increasing the amount of KY zeolite in the combination of zeolite. It was found that KY zeolite is a better zeolite than NaX zeolite in the form of an inorganic filler dispersed polymeric membrane.

In case of liquid/solid/polymer mixed matrix membranes, PEG impregnated zeolite as a solid filler was dispersed in the polymer matrix. The trend of CO_2 permeance and CO_2/CH_4 selectivity was different from solid-polymer mixed matrix membranes. The reason for this was due to the loss of PEG/zeolite particles during the membrane preparation that negatively impacts on the membrane performance.

By comparing the CO_2/CH_4 gas separation performances of solid-polymer and solid-liquid-polymer mixed matrix membranes, PEG as a liquid additive significantly improves gas separation performance in terms of CO_2 permeance and CO_2/CH_4 selectivity. Furthermore, it can suppress N_2 and CH_4 permeances leading to the enhancement of CO_2/CH_4 selectivity. Among the MMMs studied in this work, the PEG/NaX:KY/SR/CA MMM with NaX/KY ratio of 1:1 is the best performing membrane which provides the highest CO_2/CH_4 selectivity.

5.2 Recommendations

From this work, it was found that PEG impregnated zeolite incorporated in silicone rubber significantly improved CO_2/CH_4 gas separation performance in terms of permeability and selectivity. However, the membrane performance suffers from the loss of PEG/zeolite particles owing to strong PEG-to-PEG interaction. To improve performance of solid-liquid-polymer mixed matrix membrane, the dissolution and dispersion of PEG/zeolite during membrane preparation is an interesting topic for preventing filler precipitation. It is suggested that N-containing materials, such as PEI or PDA, should be considered as liquid filler.

APPENDICES

Appendix A Graphical Abstract

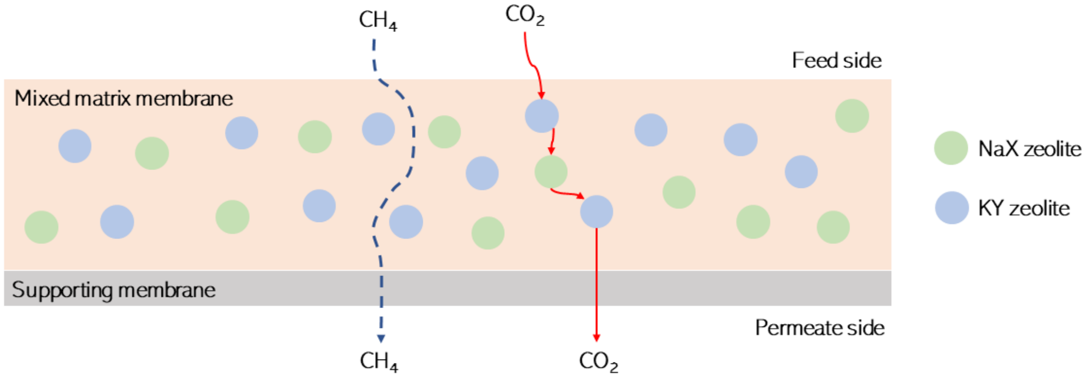

Figure A1 Graphical abstract.

Appendix B Experimental Data Attained from a Supporting Membrane

The experimental fluxed of carbon dioxide (CO_2), methane (CH_4), and nitrogen (N_2) of studied mixed matrix membranes are shown in the following tables.

Table B1 Cellulose acetate supporting membrane (CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
	31.69[a]	170.40	3.86		322.58		
	31.01[a]	174.14	3.94		329.65		
CO_2	30.83[a]	175.15	3.96	3.95	331.58	6.07	330.76
	30.94[a]	174.53	3.95		330.40		
	30.10[a]	179.40	4.06		339.62		
	8.16[b]	7.35	0.17		13.92		
	8.14[b]	7.37	0.17		13.95		
CH_4	8.18[b]	7.33	0.17	0.17	13.89	0.13	13.85
	8.19[b]	7.33	0.17		13.87		
	8.34[b]	7.19	0.16		13.62		
	12.37[b]	4.85	0.11		9.18		
	12.22[b]	4.91	0.11		9.29		
N_2	12.19[b]	4.92	0.11	0.11	9.32	0.08	9.31
	12.16[b]	4.93	0.11		9.34		
	12.09[b]	4.96	0.11		9.39		

[a] Time to reach 90 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min\cdot cm^2$)

[r] Average flux ($cm^3/min\cdot cm^2$)

[f] Permeance ($1\cdot10^{-6} cm^3(STP)/cm^2\cdot s\cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1\cdot10^{-6} cm^3(STP)/cm^2\cdot s\cdot cmHg$)

Permeance of CO_2 = 330.76 GPU

Permeance of CH_4 = 13.85 GPU

Permeance of N_2 = 9.31 GPU

Selectivity of CO_2/CH_4 = 23.88

Selectivity of CO_2/N_2 = 35.54

Appendix C Experimental Data Attained from a SR/CA Membrane.

Table C1 20wt.% silicone rubber on cellulose acetate supporting membrane (20wt.% SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
CO_2	65.99[a] 65.40[a] 65.16[a] 65.82[a] 66.50[a]	81.83 82.57 82.87 82.04 81.20	1.85 1.87 1.88 1.86 1.84	1.86	154.91 156.31 156.88 155.31 153.72	1.23	155.43
CH_4	23.76[b] 24.05[b] 24.15[b] 24.20[b] 24.33[b]	2.53 2.49 2.48 2.48 2.47	0.06 0.06 0.06 0.06 0.06	0.06	4.78 4.72 4.70 4.69 4.67	0.04	4.71
N_2	29.98[b] 31.07[b] 30.87[b] 30.84[b] 31.35[b]	2.00 1.93 1.94 1.95 1.91	0.05 0.04 0.04 0.04 0.04	0.04	3.79 3.66 3.68 3.68 3.62	0.06	3.69

[a] Time to reach 90 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux (cm3/min·cm^2)

[r] Average flux (cm3/min·cm^2)

[f] Permeance ($1\cdot10^{-6} cm^3(STP)/cm^2\cdot s\cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1\cdot10^{-6} cm^3(STP)/cm^2\cdot s\cdot cmHg$)

Permeance of CO_2 = 155.43 GPU

Permeance of CH_4 = 4.71 GPU

Permeance of N_2 = 3.69 GPU

Selectivity of CO_2/CH_4 = 32.97

Selectivity of CO_2/N_2 = 42.17

Appendix D Experimental Data Attained from NaX and KY Zeolites Incorporated in SR/CA Membranes.

Table D1 4.76wt.% zeolite with NaX/KY mass ratio of 1:0 incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (4.76wt.%-NaX:KY, 1:0/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
	31.69[a]	24.59	0.56		46.55		
	31.01[a]	24.09	0.55		45.60		
CO_2	30.83[a]	24.09	0.55	0.56	45.60	1.93	46.98
	30.94[a]	24.77	0.56		46.89		
	30.10[a]	26.56	0.60		50.28		
	8.16[b]	2.63	0.06		4.99		
	8.14[b]	2.61	0.06		4.94		
CH_4	8.18[b]	2.54	0.06	0.06	4.80	0.15	4.81
	8.19[b]	2.47	0.06		4.67		
	8.34[b]	2.47	0.06		4.67		
	12.37[b]	2.21	0.05		4.19		
	12.22[b]	2.19	0.05		4.14		
N_2	12.19[b]	2.14	0.05	0.05	4.05	0.06	4.11
	12.16[b]	2.16	0.05		4.09		
	12.09[b]	2.15	0.05		4.06		

[a] Time to reach 9 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min \cdot cm^2$)

[r] Average flux ($cm^3/min \cdot cm^2$)

[f] Permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

Permeance of CO_2 = 46.98 GPU

Permeance of CH_4 = 4.81 GPU

Permeance of N_2 = 4.11 GPU

Selectivity of CO_2/CH_4 = 9.76

Selectivity of CO_2/N_2 = 11.44

Table D2 4.76wt.% zeolite with NaX/KY mass ratio of 3:1 incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (4.76wt.%-NaX:KY, 3:1/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
CO_2	15.07[a] 15.48[a] 15.92[a] 15.83[a] 15.84[a]	35.83 34.88 33.92 34.11 34.09	0.81 0.79 0.77 0.77 0.77	0.78	67.83 66.04 64.21 64.58 64.54	1.51	65.44
CH_4	20.57[b] 20.57[b] 20.32[b] 20.73[b] 20.79[b]	2.92 2.92 2.95 2.89 2.89	0.07 0.07 0.07 0.07 0.07	0.07	5.52 5.52 5.59 5.48 5.46	0.05	5.52
N_2	22.17[b] 21.92[b] 22.09[b] 22.10[b] 22.10[b]	2.71 2.74 2.72 2.71 2.71	0.06 0.06 0.06 0.06 0.06	0.06	5.12 5.18 5.14 5.14 5.14	0.02	5.15

[a] Time to reach 9 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min \cdot cm^2$)

[r] Average flux ($cm^3/min \cdot cm^2$)

[f] Permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

Permeance of CO_2 = 65.44 GPU

Permeance of CH_4 = 5.52 GPU

Permeance of N_2 = 5.15 GPU

Selectivity of CO_2/CH_4 = 11.87

Selectivity of CO_2/N_2 = 12.72

Table D3 4.76wt.% zeolite with NaX/KY mass ratio of 1:1 incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (4.76wt.%-NaX:KY, 1:1/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
CO_2	13.77[a]	39.22	0.89	0.90	74.24	0.82	75.06
	13.63[a]	39.62	0.90		75.00		
	13.50[a]	40.00	0.90		75.72		
	13.76[a]	39.24	0.89		74.29		
	13.44[a]	40.18	0.91		76.06		
CH_4	19.65[b]	3.05	0.07	0.07	5.78	0.02	5.76
	19.72[b]	3.04	0.07		5.76		
	19.60[b]	3.06	0.07		5.80		
	19.59[b]	3.06	0.07		5.80		
	19.61[b]	3.06	0.07		5.79		
N_2	27.67[b]	2.17	0.05	0.05	4.10	0.03	4.12
	27.25[b]	2.20	0.05		4.17		
	27.63[b]	2.17	0.05		4.11		
	27.75[b]	2.16	0.05		4.09		
	27.65[b]	2.17	0.05		4.11		

[a] Time to reach 9 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min \cdot cm^2$)

[r] Average flux ($cm^3/min \cdot cm^2$)

[f] Permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

Permeance of CO_2 = 75.06 GPU

Permeance of CH_4 = 5.76 GPU

Permeance of N_2 = 4.12 GPU

Selectivity of CO_2/CH_4 = 12.98

Selectivity of CO_2/N_2 = 18.23

Table D4 4.76wt.% zeolite with NaX/KY mass ratio of 1:3 incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (4.76wt.%-NaX:KY, 1:3/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
	10.51[a]	51.38	1.16		97.26		
	10.73[a]	50.33	1.14		95.27		
CO_2	10.59[a]	50.99	1.15	1.15	96.53	1.06	96.43
	10.71[a]	50.42	1.14		95.45		
	10.47[a]	51.58	1.17		97.64		
	22.30[b]	2.69	0.06		5.09		
	22.60[b]	2.65	0.06		5.02		
CH_4	23.03[b]	2.61	0.06	0.06	4.93	0.07	4.99
	23.01[b]	2.61	0.06		4.94		
	22.94[b]	2.62	0.06		4.95		
	31.13[b]	1.93	0.04		3.65		
	31.92[b]	1.88	0.04		3.56		
N_2	31.35[b]	1.91	0.04	0.04	3.62	0.04	3.62
	31.14[b]	1.93	0.04		3.65		
	31.27[b]	1.92	0.04		3.63		

[a] Time to reach 9 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min\cdot cm^2$)

[r] Average flux ($cm^3/min\cdot cm^2$)

[f] Permeance ($1\cdot10^{-6}cm^3(STP)/cm^2\cdot s\cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1\cdot10^{-6}cm^3(STP)/cm^2\cdot s\cdot cmHg$)

Permeance of CO_2 = 96.43 GPU

Permeance of CH_4 = 4.99 GPU

Permeance of N_2 = 3.62 GPU

Selectivity of CO_2/CH_4 = 19.34

Selectivity of CO_2/N_2 = 26.62

Table D5 4.76wt.% zeolite with NaX/KY mass ratio of 0:1 incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (4.76wt.%-NaX:KY, 0:1/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
CO_2	6.82[a]	79.18	1.79	1.79	149.89	0.60	150.11
	6.78[a]	79.65	1.80		150.77		
	6.79[a]	79.53	1.80		150.55		
	6.85[a]	79.83	1.78		149.23		
	6.81[a]	79.30	1.79		150.11		
CH_4	18.80[b]	3.19	0.07	0.07	6.04	0.05	6.00
	18.85[b]	3.18	0.07		6.03		
	18.77[b]	3.20	0.07		6.05		
	19.01[b]	3.16	0.07		5.97		
	19.18[b]	3.13	0.07		5.92		
N_2	27.25[b]	2.20	0.05	0.05	4.17	0.01	4.17
	27.30[b]	2.20	0.05		4.16		
	27.20[b]	2.21	0.05		4.18		
	27.25[b]	2.20	0.05		4.17		
	27.12[b]	2.21	0.05		4.19		

[a] Time to reach 9 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min\cdot cm^2$)

[r] Average flux ($cm^3/min\cdot cm^2$)

[f] Permeance ($1\cdot 10^{-6} cm^3(STP)/cm^2\cdot s\cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1\cdot 10^{-6} cm^3(STP)/cm^2\cdot s\cdot cmHg$)

Permeance of CO_2 = 150.11 GPU

Permeance of CH_4 = 6.00 GPU

Permeance of N_2 = 4.17 GPU

Selectivity of CO_2/CH_4 = 25.01

Selectivity of CO_2/N_2 = 35.98

Appendix E Experimental Data Attained from PEG Adsorbed NaX and KY Zeolites Incorporated in SR/CA Membranes.

Table E1 2.96wt.% PEG adsorbed on 4.76wt.% NaX zeolite with NaX/KY mass ratio of 1:0 incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (2.96wt.%PEG-NaX, 4.76wt.%-NaX:KY, 1:0/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
	15.38[a]	35.11	0.79		66.47		
	15.49[a]	34.86	0.79		65.99		
CO_2	15.49[a]	34.86	0.79	0.79	65.99	0.30	66.00
	15.58[a]	34.66	0.78		65.61		
	15.50[a]	34.84	0.79		65.95		
	38.80[b]	1.55	0.04		2.93		
	38.37[b]	1.56	0.04		2.96		
CH_4	38.50[b]	1.56	0.04	0.04	2.95	0.02	2.95
	38.44[b]	1.56	0.04		2.95		
	38.20[b]	1.57	0.04		2.97		
	55.01[b]	1.09	0.02		2.06		
	54.94[b]	1.09	0.02		2.07		
N_2	55.80[b]	1.08	0.02	0.02	2.04	0.01	2.06
	55.17[b]	1.09	0.02		2.06		
	55.28[b]	1.09	0.02		2.05		

[a] Time to reach 9 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min \cdot cm^2$)

[r] Average flux ($cm^3/min \cdot cm^2$)

[f] Permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

Permeance of CO_2 = 66.00 GPU

Permeance of CH_4 = 2.95 GPU

Permeance of N_2 = 2.06 GPU

Selectivity of CO_2/CH_4 = 22.35

Selectivity of CO_2/N_2 = 32.10

Table E2 2.96wt.%PEG adsorbed NaX zeolite and 3.85wt.%PEG adsorbed KY zeolite with NaX/KY mass ratio of 3:1 (4.76wt.%zeolite) incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (2.96wt.%PEG-NaX, 4.76wt.%-NaX:KY, 3:1/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
CO_2	9.03[a]	59.80	1.35	1.36	113.21	0.16	113.43
	9.02[a]	59.87	1.36		113.33		
	9.01[a]	59.93	1.36		113.46		
	9.00[a]	60.00	1.36		113.58		
	9.00[a]	60.00	1.36		113.58		
CH_4	24.56[b]	2.44	0.06	0.06	4.62	0.01	4.63
	24.60[b]	2.44	0.06		4.62		
	24.59[b]	2.44	0.06		4.62		
	24.54[b]	2.44	0.06		4.63		
	24.46[b]	2.45	0.06		4.64		
N_2	34.98[b]	1.72	0.04	0.04	3.25	0.01	3.25
	34.91[b]	1.72	0.04		3.25		
	34.90[b]	1.72	0.04		3.25		
	34.91[b]	1.72	0.04		3.25		
	35.06[b]	1.71	0.04		3.24		

[a] Time to reach 1 cm^3 (s)

[b] Time to reach 90 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux (cm^3/min·cm^2)

[r] Average flux (cm^3/min·cm^2)

[f] Permeance ($1\cdot10^{-6}cm^3$(STP)/cm^2·s·cmHg)

[g] Standard deviation of permeance

[h] Average permeance ($1\cdot10^{-6}cm^3$(STP)/cm^2·s·cmHg)

Permeance of CO_2 = 113.43 GPU

Permeance of CH_4 = 4.63 GPU

Permeance of N_2 = 3.25 GPU

Selectivity of CO_2/CH_4 = 24.52

Selectivity of CO_2/N_2 = 31.91

Table E3 2.96wt.%PEG adsorbed NaX zeolite and 3.85wt.%PEG adsorbed KY zeolite with NaX/KY mass ratio of 1:1 (4.76wt.%zeolite) incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (2.96wt.%PEG-NaX, 3.85wt.%PEG-KY/4.76wt.%-NaX:KY, 1:1/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
CO_2	9.64[a] 9.76[a] 9.64[a] 9.72[a] 9.70[a]	56.02 55.33 56.02 55.56 55.67	1.27 1.25 1.27 1.26 1.26	1.26	106.04 104.74 106.04 105.17 105.39	0.57	105.48
CH_4	28.33[b] 28.54[b] 28.42[b] 28.68[b] 28.32[b]	2.12 2.10 2.11 2.09 2.12	0.05 0.05 0.05 0.05 0.05	0.05	4.01 3.98 4.00 3.96 4.01	0.02	3.99
N_2	35.92[b] 35.19[b] 35.58[b] 35.21[b] 34.94[b]	1.67 1.70 1.69 1.70 1.72	0.04 0.04 0.04 0.04 0.04	0.04	3.16 3.23 3.19 3.23 3.25	0.03	3.21

[a] Time to reach 9 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min \cdot cm^2$)

[r] Average flux ($cm^3/min \cdot cm^2$)

[f] Permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

Permeance of CO_2 = 105.48 GPU

Permeance of CH_4 = 3.99 GPU

Permeance of N_2 = 3.21 GPU

Selectivity of CO_2/CH_4 = 26.43

Selectivity of CO_2/N_2 = 32.84

Table E4 2.96wt.%PEG adsorbed NaX zeolite and 3.85wt.%PEG adsorbed KY zeolite with NaX/KY mass ratio of 1:3 (4.76wt.%zeolite) incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (2.96wt.%PEG-NaX, 3.85wt.%PEG-KY/4.76wt.%-NaX:KY, 1:3/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
CO_2	11.72[a] 11.87[a] 11.89[a] 11.81[a] 11.73[a]	46.08 45.49 45.41 45.72 46.04	1.04 1.03 1.03 1.03 1.04	1.04	87.22 86.12 85.98 86.56 87.15	0.57	86.60
CH_4	34.35[b] 34.64[b] 34.55[b] 34.32[b] 34.77[b]	1.75 1.73 1.74 1.75 1.73	0.04 0.04 0.04 0.04 0.04	0.04	3.31 3.28 3.29 3.31 3.27	0.02	3.29
N_2	43.67[b] 43.73[b] 43.35[b] 43.32[b] 43.87[b]	1.37 1.37 1.38 1.39 1.37	0.03 0.03 0.03 0.03 0.03	0.03	2.60 2.60 2.62 2.62 2.59	0.01	2.61

[a] Time to reach 9 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min \cdot cm^2$)

[r] Average flux ($cm^3/min \cdot cm^2$)

[f] Permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

Permeance of CO_2 = 86.60 GPU

Permeance of CH_4 = 3.29 GPU

Permeance of N_2 = 2.61 GPU

Selectivity of CO_2/CH_4 = 26.32

Selectivity of CO_2/N_2 = 33.23

Table E5 2.96wt.%PEG adsorbed NaX zeolite and 3.85wt.%PEG adsorbed KY zeolite with NaX/KY mass ratio of 0:1 (4.76wt.%zeolite) incorporated 20wt.% silicone rubber on cellulose acetate supporting membrane (2.96wt.%PEG-NaX, 3.85wt.%PEG-KY/4.76wt.%-NaX:KY, 0:1/SR/CA)

Gas	Time	Flow[c]	Flux[d]	Avg flux[e]	Permeance[f]	Std. Dev.[g]	Average[h]
CO_2	10.50[a]	51.43	1.16	1.17	97.36	0.31	97.80
	10.45[a]	51.67	1.17		97.82		
	10.44[a]	51.72	1.17		97.92		
	10.41[a]	51.87	1.17		98.20		
	10.46[a]	51.63	1.17		97.73		
CH_4	27.50[b]	2.18	0.05	0.05	4.13	0.01	4.13
	27.50[b]	2.18	0.05		4.13		
	27.42[b]	2.19	0.05		4.14		
	27.59[b]	2.17	0.05		4.12		
	27.56[b]	2.18	0.05		4.12		
N_2	38.67[b]	1.55	0.04	0.04	2.94	0.01	2.94
	38.66[b]	1.55	0.04		2.94		
	38.76[b]	1.55	0.04		2.93		
	38.57[b]	1.56	0.04		2.94		
	38.50[b]	1.56	0.04		2.95		

[a] Time to reach 9 cm^3 (s)

[b] Time to reach 1 cm^3 (s)

[c] Flow rate (cm^3/min)

[d] Flux ($cm^3/min \cdot cm^2$)

[r] Average flux ($cm^3/min \cdot cm^2$)

[f] Permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

[g] Standard deviation of permeance

[h] Average permeance ($1 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)

Permeance of CO_2 = 97.80 GPU

Permeance of CH_4 = 4.13 GPU

Permeance of N_2 = 2.94 GPU

Selectivity of CO_2/CH_4 = 23.69

Selectivity of CO_2/N_2 = 33.27

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