Synthesis and Characterization of SAPO-34/6FDA-Durene Mixed Matrix Membrane for CO_2 Capture

by

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14384

Dissertation submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

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Approved by,

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(Dr. Yeong Yin Fong)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

CHUA LIN KIAT

ABSTRACT

Membrane separation has become a promising technology in CO_2 removal from natural gas sweetening recently. In the present research, a series of SAPO-34/6FDA-durene mixed matrix membranes (MMMs) were developed to remove the CO_2 from CH_4. The MMMs were fabricated by incorporating different compositions of SAPO-34 fillers into 6FDA-durene polymer matrix. SAPO-34 fillers modified with (3-Aminopropyl)-triethoxysilane (APTES) were synthesized and incorporated into 6FDA-durene polymer matrix in order to study their effects on the membrane defects, as well as their effects on the performances of the resulting MMMs towards the gas separation. The resulting SAPO-34 and silane-modified SAPO-34 were characterized by using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM), whereas all the fabricated MMMs were characterized by using Energy Dispersive X-ray (EDX) and SEM. The performances of the membranes in CO_2/CH_4 separation were tested by using CO_2 membrane cell filter test rig (CO_2MCEF). The morphology of the silane-modified MMMs showed the improvement on the compatibility between the polymeric and inorganic phases. EDX results showed that the inorganic SAPO-34 particles were evenly distributed in the polymer matrix and no phase separation was found. However, all MMMs showed lower separation performance compared to pure 6FDA-durene membrane mainly due to large inorganic particles size, moisture contact, poor interfacial adhesion and polymer matrix rigidification.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Carbon dioxide (CO_2) is a greenhouse gas mainly found in the combustion product of fossil fuels, natural gas stream, biogas and landfill gas. The purpose of removing CO_2 from those gas streams, especially natural gas stream is to obtain a purified fuel with enhanced energy content and to prevent corrosion problems in the gas transportation system. These reasons have driven the development of CO_2 gas separation process technology. One of the separation technologies that have successfully gained the attention is the membrane-based technology. Membrane technology has emerged as a potential process in natural gas sweetening (CO_2/CH_4) apart from adsorption, absorption and cryogenic process due to its high energy efficiency, simple in design and construction of membrane modules and environmental compatibility (Zhang, Sunarso, Liu, & Wang, 2013).

Natural gas sweetening is a purification process to remove the acidic gases such as CO_2, hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) before it is compressed and delivered for sale. The presence of CO_2 in the natural gas will lower its caloric value and thus, lower the selling value of natural gas. Moreover, the presence of acidic CO_2 containments in the gas stream will corrode and damage the equipments and pipelines with the presence of water in the transportation and storage system, and hence reduces the process plant efficiency (Zhang et al., 2013)

Membrane-based technology uses membrane materials such as polymeric membrane, inorganic membrane and mixed matrix membrane (MMM) to separate CO_2 from natural gas. Generally, the permeation and selectivity are the two common basic performance characteristics of a membrane. Permeability can be defined as the ability of permeate to pass through a membrane, while selectivity of the membrane is the ratio of permeability of the more permeable component to that of the less permeable (Goh, Ismail, Sanip, Ng,

& Aziz, 2011). Higher permeability decreases the amount of membrane area used, thus reduces the capital cost of membrane units, while higher selectivity will increase the purity of gas product. Despite the membrane separation process is energy efficient, operating and capital cost savings, ease of process design and operation, the development of the high performance membrane material still possesses a big challenge in membrane technology. It is difficult to maintain the high performance and consistency of a membrane over a long period.

The performance of the existing membranes such as polymeric membrane is limited by Robeson's upper bound limit while inorganic membrane has a low mechanical properties and high manufacturing cost (Goh et al., 2011; Zhang et al., 2013). Therefore, MMM becomes a new class of membrane materials that is potential to enhance the current membrane technology by overcoming the limitations of the polymeric membrane and inorganic membrane. The incorporation of inorganic fillers in a polymer matrix is expected to increase the permeability, selectivity, or both compared to the current existing membrane materials.

Recent literature reviews reported that SAPO-34 promotes high CO_2 selectivity, and incorporation of SAPO-34 in polymer matrix could produce a MMM with better CO_2/CH_4 gas separation (Junaidi, Khoo, Leo, & Ahmad, 2014). Therefore, in the present research, new type of MMM namely SAPO-34/6FDA-durene is developed. Besides, a chemical-modified SAPO-34 which can improve the interface and reduce the voids during the MMM fabrication is synthesized and used as inorganic fillers in MMM. Characterization and separation performances of the resulting membranes would be studied.

1.2 Problem Statement

Even though polymeric membrane possesses advantages of mechanical properties, reproducibility and relative economical processing capability, but this membrane material has demonstrated a trade-off between the permeability and selectivity, which is known as Robeson's upper bound limit (Robeson, 2008). Robeson's upper bound limit is an inverse relationship exists between the permeability and selectivity, where more permeable polymer is generally less selective and vice versa. In order to enhance the gas separation performances, mixed matrix membrane (MMM) has been developed to transcend the upper bound limit.

In MMM fabrication, inorganic fillers are normally dispersed at a nanometer level in a polymer matrix. The resulting material possesses the favorable properties of inorganic filler and polymeric membrane, thus its performance in gas separation could surpass the trade-off issue. Another challenge in the development of MMM is to obtain a good compatibility or interfacial contact between the continuous polymer matrix and inorganic fillers. Incompatibility of polymer and filler phases during the formation of MMM may deteriorate the gas separation performance of the resulting membrane and leads to the void formation (Cong, Zhang, Radosz, & Shen, 2007). The formation of these non-selective voids at the interface allows the bypassing of gases and hence, decreases the selectivity and permeability of the resulting MMM.

The incorporation of SAPO-34 fillers in polymer matrix always leads to the poor compatibility between the two phases (Li, Guan, Chung, & Kulprathipanja, 2006). However, it was found that the application of silane coupling agents on the surface of SAPO-34 zeolite can improve the interfacial strength between these two phases. The selection of appropriate silane groups and their effect towards the separation performance of MMM remain as new tasks to be discovered.

Besides, the loading of inorganic fillers and their particle size will affect the morphology and performances of MMM. The synthesis of inorganic fillers in smaller size and optimum loading of inorganic fillers in MMM can minimize the void volumes, and thus increase the performances of the MMM.

Therefore, better understanding on the improvement and optimization of MMM process to overcome the abovementioned problems remains as a challenging topic for future investigation and development.

1.3 Objectives & Scopes

The primary purpose of this research is to synthesis a high permeability and selectivity membrane for separation of carbon dioxide (CO_2) from natural gas.

There are several objectives and scopes to be achieved in this research project. These objectives are:

1. To synthesis 6FDA-durene polymer, SAPO-34 and silane-modified SAPO-34 particles.
2. To fabricate mixed matrix membranes (MMMs) by incorporating different loadings of SAPO-34 and silane-modified SAPO-34 as inorganic fillers into 6FDA-durene polymer.
3. To characterize the resulting particles and membranes by using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX).
4. To study the performance of the resulting MMMs in CO_2/CH_4 separation.

1.4 Relevancy & Feasibility

Mixed matrix membrane (MMM) is an emerging membrane material in membrane-based separation technology that can be used to separate carbon dioxide (CO_2) from natural gas. It is synthesized by incorporating porous inorganic fillers in a polymer matrix. MMM is a potential material that can overcome the limitations of the polymeric and inorganic membrane. This research is feasible within the scopes identified and the time allocated. The first half of this research is focused on the literature study of the related researches as well as project planning. While the second half of the research would be focused on the experimentation and results collecting. The results collected would then be analyzed and investigated critically.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Dioxide/Natural Gas Separation Technology

Carbon dioxide (CO_2) is the main component of the greenhouse gases. The accumulation of CO_2 in the environment will lead to severe global warming issues. Global CO_2 Budget 2013 reported that global CO_2 emissions achieved 36 billion metric tons in year 2012. Human activities such as open burning and transportation will contribute to the large amounts of CO_2 emissions. CO_2 can also be found in the natural gas stream, biogas from anaerobic digestion, landfill gas, combustion product of fossil fuel and product of coal gasification. Natural gas reserves are usually contaminated with 70% of CO_2 and N_2, but pipelines specifications for natural gas normally require a CO_2 concentration below 2-3% (Venna & Carreon, 2011). Besides, CO_2 will reduce the heating value of natural gas, and it is acidic and corrosive with the presence of water in the transportation and storage system. Therefore, the separation of CO_2 from CH_4 is very important in many industrial processes especially in natural gas sweetening.

The conventional separation methods employed for CO_2 separation process include chemical absorption by reactive solvents, pressure swing adsorption (PSA), temperature swing adsorption (TSA) and cryogenic separation (Basu, Khan, Cano-Odena, Liu, & Vankelecom, 2010). The conventional separation method is operated at a high temperature and pressure, and it yields high purity and efficiency. However, these conventional separation methods usually involve substantially complicated equipment, higher energy consumption and capital cost.

Therefore, as an alternative, membrane separation technology appears to be a potential and efficient method for gas separation. It becomes an attractive separation approach due to its fast and energy efficient process without any phase changes. Membrane separation technology uses membrane as a thin barrier between miscible fluids to separate a mixture, such as CO_2 and natural gas mixture. During the separation process, a driving force such as concentration or pressure differential is used to transport a selective component across the membrane. Membrane is a promising material for CO_2/CH_4 separation due to its advantages which include high efficiency and stability, low operating and capital cost, less energy required, simple process design, ease of operation as well as environmental friendly (Goh et al., 2011).

However, although membrane separation technology is promising in gas separation, it is difficult to maintain the membrane performance and consistency in long term operation. Most membranes do not have the resilience in practical industry conditions (Zhang et al., 2013). A high performance membrane used in natural gas sweetening should possess good chemical, thermal and mechanical stability, high CO_2 permeability, and high selectivity towards CO_2 and natural gas separation (Freemantle, 2005).

Membrane materials are classified into polymeric membrane, inorganic membrane and mixed matrix membrane (MMM). They would be discussed in details in the following sections.

2.2 Polymeric Membrane

Polymeric membrane, particularly glassy polymer is currently the dominant material for gas separation process such as natural gas sweetening, landfill gas recovery, hydrogen recovery and purification, flue gas separation and air separation (Bastani, Esmeili, & Asadollahi, 2013).This is because polymeric membrane possesses the advantages of mechanical properties, reproducibility, flexibility to be processed into different modules and relative economic processing capability.

Polymeric membranes are classified into porous and non-porous membrane. Porous membrane has rigid, highly voided structure with randomly distributed and interconnected pores (Goh et al., 2011). The separation in polymeric membrane is dependent on the molecular size and pore size distribution. Non-porous membranes or dense membranes consist of a dense film where the permeate molecules are absorbed and diffused through the membrane matrix under the driving force of a concentration, pressure, or electrical potential gradient (Goh et al., 2011). The mechanism of the gas transport is determined by the diffusivity and solubility of the permeant molecules in the membrane material. The transport of gas molecules in polymeric membrane is usually based on solution-diffusion mechanism. Polymer materials such as polyimide (PI), cellulose acetate (CA), polysulfone (PSF), polyethersulfone (PES) and polycarbonates (PC) have been used to fabricate the polymeric membranes for gas separation (Zhang et al., 2013). Polymer materials such as PI and CA have been commercially used in CO_2/CH_4 separation (Han & Lee, 2011). Other glassy polymers such as PSF, polyethermide (PEI), polymer of intrinsic microporosity (PIM) and Matrimid are still undergoing tremendous researches to improve the membrane performance (Zhang et al,. 2013). Table 1 shows the CO_2/CH_4 separation performances of polymeric membranes.

Even though polymeric membranes dominate the current CO_2 separation membrane technologies due to their low cost, outstanding mechanical stability and other advantages, but they still suffer from either low permeability or low selectivity. The performance of polymeric membrane is governed by the Robeson's upper bound limit (Robeson, 2008). Robeson's upper bound limit is an inverse relationship exists between the permeability and selectivity. High permeability polymeric membrane always has a low selectivity and vice versa. Figure 1 shows the trade-off of CO_2 permeability versus CO_2/CH_4 selectivity for gas separation. It can be seen that only minority of the membranes fall above or close to the curve. Besides, commercial polymeric membrane also suffers from an issue of plasticization, where the CO_2 concentration in the feed stream is high (Zhang et al., 2013). CO_2-induced plasticization is a phenomenon where the CO_2 permeability increases as a function of pressure while the selectivity decreases (Ismail & Lorna, 2002).

In order to overcome the inherent limitations of polymeric membrane, researches are underway for alternative membrane materials for effective separation of CO_2 from natural gas.

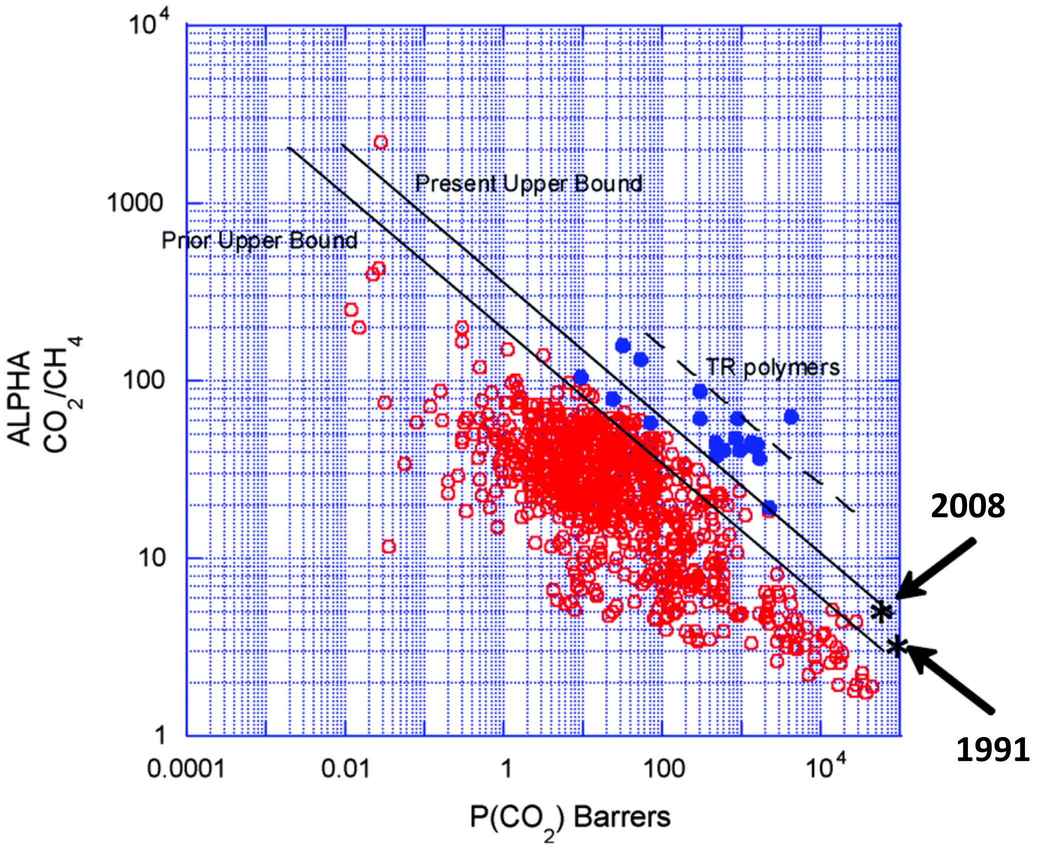


Figure 1: Trade-off curve between selectivity and permeability of CO_2/CH_4 gas separation (Robeson, 2008; Zhang et al., 2013)

Table 1: CO_2/CH_4 separation performances of polymeric membranes

Membrane Material	Pressure (bar)	Temperature (^oC)	CO_2 Permeability		CO_2/CH_4 Selectivity	Reference
			Value	Unit		
6FDA-BAPAF	30	21	24.6	GPU	22.8	Kim, Park, So, Ahn, & Moon (2003)
6FDA-DAP	30	21	38.6	GPU	77.8	Kim et al. (2003)
6FDA-DABA	30	21	26.3	GPU	47	Kim et al. (2003)
6FDA-1, 5-NDA	10	35	22.6	Barrer	49	Chan, Chung, Liu, & Wang (2003)
6FDA-pPDA	10	35	15.3	Barrer	-	Lin, Vora, & Chung (2000)
6FDA-Durene	10	35	458	Barrer	16.1	Liu, Chng, Chung, & Wang (2003)
6FDA-Durene/mPDA (50:50)	10	35	84.6	Barrer	29.9	Liu et al. (2003)
6FDA-Durene/NDA (75:25)	10	35	274	Barrer	21.1	Chan et al. (2003)
6FDA-Durene/pPDA (80:20)	10	35	230	Barrer	-	Lin et al. (2000)
6FDA-DAM	2	25	390	Barrer	24	Bae et al. (2010)
Matrimid®5218	34.5	35	10	Barrer	35.5	Vu, Koros, & Miller (2003)
Matrimid®5218	2.66	35	9.52	Barrer	39.8	Ordoñez, Balkus Jr, Ferraris, & Musselman (2010)

2.3 Inorganic Membrane

Inorganic membrane is increasingly being investigated due to its attractive characteristics and advantages over the polymeric membrane for many gas separation processes. Inorganic membrane can be categorized as porous and non-porous. Porous inorganic membranes such as zeolite and carbon molecular sieve (CMS) are favorable for CO_2/CH_4 gas separation due to their superior selectivity to polymeric membrane. According to Carreon, Li, Falconer, & Noble (2008), SAPO-34 zeolite membrane on porous α-alumina supports exhibited the CO_2/CH_4 selectivity range from 86 to 171 with CO_2 permeability of 20,000-40,000 Barrer.

Non-porous inorganic membranes are attractive for high temperature (above 400^oC) application only when the amount of ionic defects in these membranes are enough to allow the appreciable ionic movement and, thus, high conductivity. Non-porous inorganic membrane is represented by a dual phase membrane containing mixed conducting oxide ceramic (MCOC) and molten carbonate phases (Anderson & Lin, 2010; Li, Rui, Xia, Anderson, & Lin, 2009; Rui, Anderson, Lin & Li, 2009).

The ability of inorganic membrane to withstand high temperature for long time and the resistance to harsh operating environment have brought it to be a promising material for application in membrane reactors in industrial processes. Moreover, inorganic membranes also have a higher throughput and longer lifespan compared to polymeric membrane.

Different inorganic membrane will exhibit different gas separation performance. It is selective to certain gas pair’s separation. Table 2 shows the CO_2/CH_4 gas separation performances of inorganic membranes. The unique characteristic of inorganic membrane makes it demonstrates high gas flux and selectivity. Nevertheless, inorganic membrane is limited to the severe operating conditions due to the high manufacturing cost and low reproducibility. Besides, inorganic membrane is also facing the drawback of poor mechanical properties. It is brittle and usually with low surface-to-volume ratio (Goh et al., 2011). Furthermore, the presence of other gas components such as water and hydrogen sulfide (H_2S) may cause negative effects to the CO_2 separation performance of the membrane (Li, Alvarado, Noble, & Falconer, 2005). Therefore, inorganic membrane is still not a commercialized material to use in industrial applications.

Table 2: CO_2/CH_4 separation performances of inorganic membranes

Membrane Material	Pressure (bar)	Temperature (°C)	CO_2 Permeability		CO_2/CH_4 Selectivity	Reference
			Value	Unit		
SAPO-34 zeolite (on porous stainless steel tube)	2.2	22	1045.9	GPU	120	Li, Falconer, & Noble (2006)
KY zeolite (on porous alumina tube)	1	30	2091.8	GPU	40	Hasegawa, Tanaka, Jeong, Kusakabe, & Morooka (2002)
DDR zeolite (on porous alumina disk)	5	28	7.0×10^{-8}	$mol/(m^2sPa)$	220	Tomita, Nakayama, & Sakai (2004)
Zeolite-T	5	30	0.70×10^{-8}	$mol/(m^2sPa)$	70.8	Mirfendereski, Mazaheri, Sadrzadeh, & Mohammadi (2008)
Zeolite-T	1	35	4.60×10^{-8}	$mol/(m^2sPa)$	400	Cui, Kita, & Okamoto (2004)
ZIF-8 (on porous α-alumina)	1.4	22	1.69×10^{-5}	$mol/(m^2sPa)$	7	Venna & Carreon (2009)
CMS 550-2	3.4	35	1250	Barrer	63	Vu et al. (2003)
CMS 800-2	3.4	35	43.5	Barrer	200	Vu et al. (2003)
Silicate^{-1}	1.01	30	589.84	GPU	4.3	Zhu, Hrabanek, Gora, Kap teija, & Moulijn (2006)

2.4 Mixed Matrix Membrane

Due to the limitations of the polymeric membrane and inorganic membrane, a new membrane material which is known as mixed-matrix membrane (MMM) have been introduced to overcome the restrictions of the polymeric membrane and inorganic membrane. This emerging membrane material is expected to enhance the existing membrane-based separation technology by overcoming the polymer-inorganic phase separation problems. Besides, the MMM produced should also improve the compatibility between the polymer matrix and inorganic fillers as well as defect-free.

MMM is fabricated by incorporating the inorganic fillers as dispersed phase in a continuous polymer matrix:

Inorganic fillers + Polymer matrix → Mixed matrix membrane

Different combinations of inorganic phase in polymer matrix will synthesis the MMM with different membrane performances. The choice of the polymer matrix and the inorganic filler particles with different loadings are the two important parameters that will affect the morphology and performance of the MMM. In order to choose the most suitable continuous polymer phase and dispersed inorganic phase in the MMM fabrication, the gas transport mechanism and the gas component transporting through the membrane should take into consideration (Chung, Jiang, Li, & Kulprathipanja, 2007). Table 3 shows the CO_2/CH_4 gas separation performances of MMM.

The incorporation of inorganic fillers in polymer matrix should synthesis an ideal membrane material which possesses high permeability, high selectivity and high chemical, thermal and mechanical stability (Freemantle, 2005). The effective permeability of the MMM is calculated by using the Maxwell model, as shown in equation 1 (Noble, 2011). This equation is valid for spherical particles in dilute suspensions where the interaction between the particles is negligible.

$$P_{eff} = P_c\left[\frac{P_d + 2P_c - 2\emptyset_d(P_c - P_d)}{P_d + 2P_c + 2\emptyset_d(P_c - P_d)}\right] \text{ ---------- } (1)$$

P_{eff} is the effective permeability of the MMM, P_c is the permeability of the continuous polymer phase, P_d is the permeability of the dispersed inorganic phase and $\emptyset_d$ is the volume fraction of the dispersed phase.

Table 3: CO_2/CH_4 separation performances of mixed matrix membranes

Mixed Matrix Membrane (MMM) Composition		Pressure (bar)	Temperature (°C)	CO_2 Permeability		CO_2/CH_4 Selectivity	Reference
Polymer	Inorganic Filler			Value	Unit		
6FDA-DAM	ZIF-90 (15 wt%)	2	25	720	Barrer	37	Bae et al. (2010)
6FDA-DAM	MOFs (0%)	2	25	390	Barrer	24	Bae et al. (2010)
6FDA-ODA	UiO-66	10	35	50.4	Barrer	46.1	Nik, Chen, & Kaliaguine (2012)
6FDA-ODA	Al-MIL-53-NH2 (32 wt%)	10	35	14.5	Barrer	80	Chen, Vinh-Thang, Rodrigue, & Kaliaguine (2012)
6FDA-Durene	ZIF-8 (33.3 wt%)	3.5	35	1552.9	Barrer	-	Wijenyaka et al. (2013)
PC	Zeolite 4A	-	-	4.6	Barrer	51.8	Cite in Goh et al. (2011)
PES	Zeolite 4A	-	-	6.7	Barrer	28.7	Cite in Goh et al. (2011)
PES	A zeolite with silver ion exchange (50 wt%)	10	35	1.2	Barrer	44	Cite in Goh et al. (2011)

PDMC	SSZ-13 zeolite	-	-	88.6	Barrer	41.9	Cite in Goh et al. (2011)
PI	MWCNTs (1 wt%)	-	-	14.3	Barrer	10	Cite in Goh et al. (2011)
PIM-1	ZIF-8 (43 vol%)	1	23	6300	Barrer	14.7	Bushell et al. (2013)
PSF	SAPO-34E	4.48	25	706	GPU	31	Junaidi, Khoo, Leo, & Ahmad (2014)
Matrimid®9725	ZIF-8 (30 wt%)	10	35	22	GPU	20	Basu, Cano-Odena, & Vankelecom (2011)
Matrimid®5218	ZIF-8 (30 wt%)	4	22	28.72	Barrer	24.9	Song et al. (2012)
Matrimid®5218	ZIF-8 (40 wt%)	2.66	35	24.55	Barrer	27.84	Ordoñez et al. (2010)
Ultem®1000	CMS 800-2 (35 vol%)	3.4	35	4.48	Barrer	53.7	Vu et al. (2003)

2.4.1 Materials Selection for Development of Mixed Matrix Membrane

In this research, SAPO-34 crystals and 6FDA-durene are selected as the inorganic fillers and polymer matrix, respectively to synthesis the mixed matrix membrane (MMM). SAPO-34 particles are incorporated into 6FDA-durene polymer to fabricate the MMM that can enhance the CO_2/CH_4 gas separation process. Characterization and the performances of the resulting MMM are studied. The literatures and reasons for investigating these combinations are discussed in the following sections.

2.4.1.1 SAPO-34

SAPO-34 zeolite is a silicoaluminophosphate molecular sieve with the composition $(Si_xAl_yP_z)O_2$, where x = 0.01-0.98, y = 0.01-0.60 and z = 0.01-0.52. Figure 2 shows the framework structure of SAPO-34. Li, Falconer, & Noble (2006) reported that SAPO-34 molecular sieve has a 0.38 nm framework pore diameter; which is similar in size to CH_4 but larger than CO_2. SAPO-34 has high CO_2/CH_4 selectivity due to its remarkable molecular sieving, combination of differences in diffusivity and enhanced competitive CO_2 adsorption properties (Venna & Carreon, 2011; Li et al., 2006). Adsorption isotherms showed that CO_2 adsorbs more strongly than CH_4 on SAPO-34 crystals (Li et al., 2006). Li et al. (2006) reported that SAPO-34 membrane showed separation selectivity as high as 95 and CO_2 permeability of 1433 Barrer. Due to these advantages, SAPO-34 receives great attention as inorganic fillers in mixed matrix membrane (MMM) fabrication.

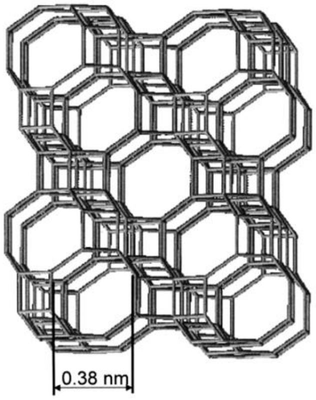


Figure 2: Framework structure of SAPO-34 (Venna & Carreon, 2011)

However, it was found that there is a challenge in incorporating SAPO-34 fillers in the polymer phase, which is the poor compatibility between these two phases. The recent research found that there are some methods that can improve the interfacial strength between these two phases in order to enhance their membrane performance. One of them is the silane (chemical) modification of the surface of SAPO-34 zeolite with silane coupling agent, such as (3-Aminopropyl)-triethoxysilane (APTES). Silane coupling agent is a silicon-based chemical which contains two types of reactive groups, namely organic and inorganic groups in the same molecule (Junaidi, Khoo, Leo, & Ahmad, 2014). By introducing the silane coupling agent, it may modify the surface properties of SAPO-34 zeolite from hydrophilic to hydrophobic, and increase SAPO-34 affinity to the functional groups of the polymer matrix (Li et al, 2006).

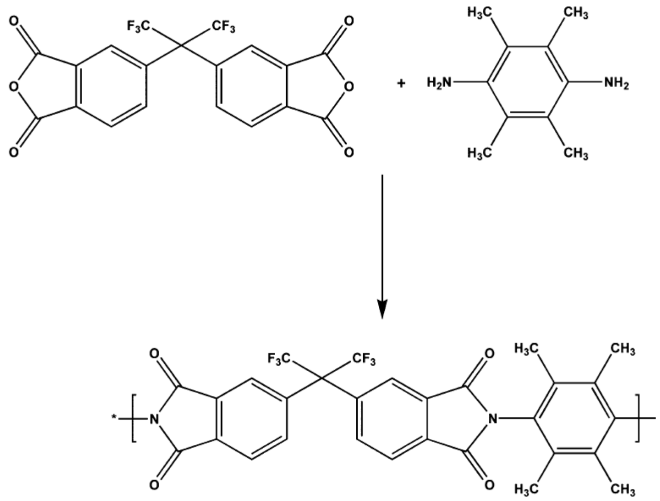
However, even though the application of silane coupling agent in the inorganic phase can improve the interface and reduce the voids in the membrane, but it may increase the gas transport resistance across the membrane, and decrease the permeability and selectivity of the membrane if an improper silane coupling agent is selected. Therefore in the present research, APTES is introduced on SAPO-34 zeolite surface to study their effects on the separation performance of mixed matrix membrane (MMM). APTES can react with hydroxyl groups, amino groups and other functional groups from zeolite and polymer matrix to improve the compatibility between the two phases (Zhang et al., 2013). Hibshman et al. (2003) found that the organosilicate can be covalently bonded to the polyimide matrix.

In the present research, SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs are fabricated to compare their performances towards the CO_2/CH_4 gas separation.

2.4.1.2 6FDA-Durene

6FDA-durene is a type of aromatic Polyimide (PI) materials. Referring to Table 1, 6FDA-durene shows the highest CO_2 permeability, which is 458 Barrer. 6FDA-durene becomes an ideal polymer phase in mixed matrix membrane fabrication due to its excellent thermal and mechanical properties. It shows a good intrinsic gas separation performance as compared to other 6FDA-based polyimides (Liu, Chng, Chung, & Wang, 2003).

6FDA-durene is synthesized by using the chemical imidization method. Figure 3 shows the synthesis scheme and the molecular structure of 6FDA-durene that is used to fabricate the mixed matrix membrane (MMM) for CO_2/CH_4 gas separation.



6FDA-durene

Figure 3: Synthesis scheme of 6FDA-durene (Wijenayake et al., 2013)

The four methyl groups that are present in the diamine moiety increase the gas diffusivity and solubility, and inhibit the dense chain packing, thus increase the membrane permeability (Chan, Chung, Liu, & Wang, 2003; Liu, Wang, Liu, Chng, & Chung, 2001).

Due to these advantages, 6FDA-durene is selected as the polymer phase in the MMM fabrication. The synthesis procedure of 6FDA-durene is prepared in the methodology sections.

2.4.2 Challenges in Mixed Matrix Membrane Fabrication

Even though mixed matrix membrane (MMM) possesses high performances in gas separation technology, but there are some challenges in the development of MMM that will reduce its performances.

One of the major challenges in MMM fabrication is the dispersibility of inorganic fillers in the polymer matrix. In ideal situation, the dispersed inorganic phase should evenly distribute in the continuous polymer phase. Overloading of inorganic fillers will cause the agglomeration of inorganic fillers in the MMM and hence, reduces the gas permeability. Therefore, an optimum loading of inorganic fillers is important to maintain the morphology of the membrane and to avoid the phase separation between the polymer phase and the inorganic phase.

Another problem that is faced by MMM is the incompatibility between the inorganic fillers and the polymer matrix. This condition will create the separate phases in MMM and deteriorate the gas performance of the membrane. The improper/poor interfacial contact between the dispersed phase and the continuous phase will lead to the formation of void volume as illustrated in Figure 4. The formation of non-selective voids at the interface will allow the bypassing of gases, which in turn decreases the membrane selectivity (Goh et al., 2011). One of the effective methods that can be used to eliminate the interfacial voids is by applying the silane coupling agent into the inorganic phase prior to the fabrication of MMM. Silanes can react with hydroxyl groups, amino groups and other functional groups from zeolite and/or the polymer matrix to improve the compatibility between the phase boundaries (Zhang et al., 2013).

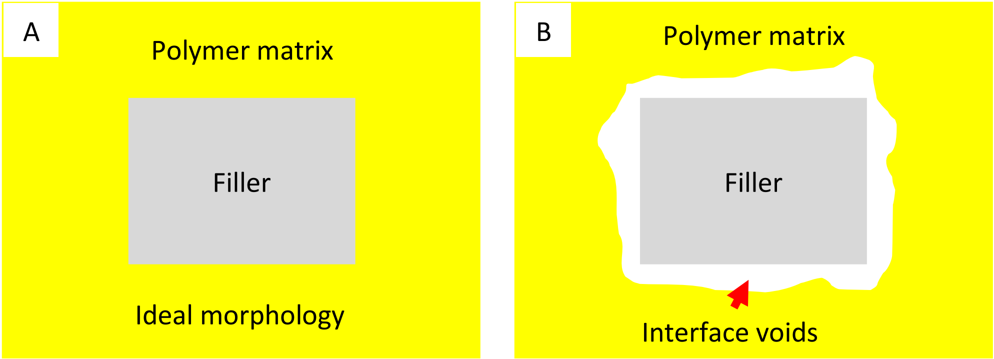


Figure 4: Schematic diagram of (A) ideal morphology of MMM and (B) interface voids between inorganic filler and polymer matrix

The next factor that will affect the performance of the MMM is the particle size of the inorganic fillers (Noble, 2011). The average filler particle size should be in nano-scale regime and uniform in shape. This is because smaller particles possess higher surface area/volume ratios. It will enhance the mass transfer of gas molecules across the membrane and hence, increases the performance of the membrane.

CHAPTER 3

METHODOLOGY

3.1 Flow Chart of Research Methodology

The overall research methodology is shown in Figure 5.

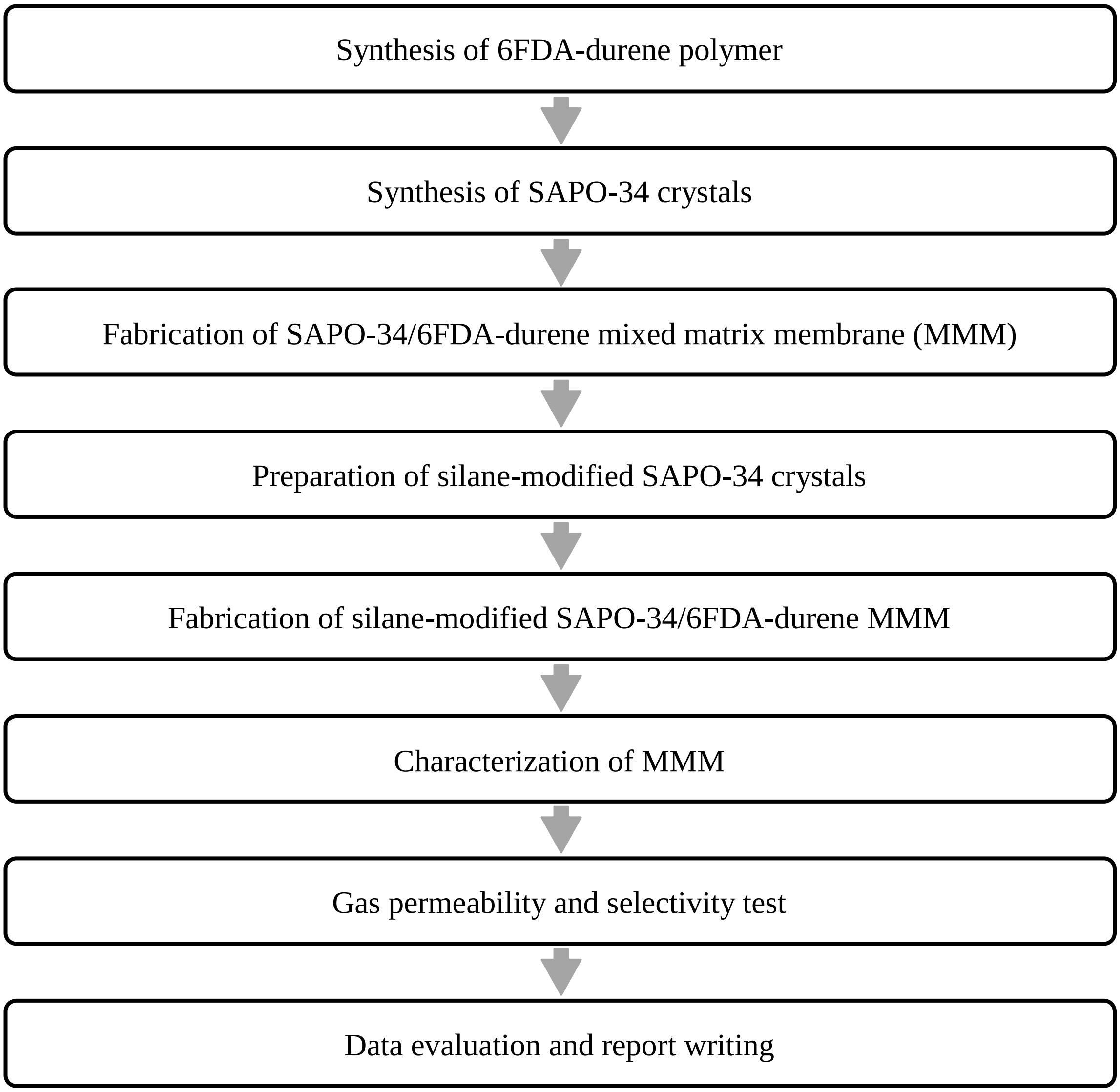


Figure 5: Flow chart of overall research methodology

3.2 Materials

The materials and chemicals used in the present research are as follows:

- 4, 4’-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99% purity, Sigma-Aldrich) monomers are purified by vacuum sublimation prior to use.
- 2, 3, 5, 6-Tetramethyl-p-phenylenediamine (durene-diamine, 99% trace metals basis, Sigma-Aldrich) monomers are purified by re-crystallization in methanol prior to use.
- The solvent, N-methyl-2-pyrolidone (NMP) is purified by using a rotary evaporator.
- Propionic anhydride (PA, ≥98% purity, Merck) and triethylamine (TEA, ≥99% purity, Merck) are used as received.
- Methanol (≥99.9% purity, Merck) and dichloromethane (≥99.8% purity, Sigma-Aldrich) solvent are used as received.
- Phosphoric acid (H_3PO_4, 85% aqueous solution, Merck).
- Aluminium triisopropylate ($C_9H_{21}AlO_3$, ≥98% purity, Merck).
- Tetraethylammonium hydroxide (TEAOH, ~40% aqueous solution, Sigma Aldrich) template solution.
- Tetraethyl-orthosilicate (TEOS, ≥99% purity, Merck).
- Toluene (99.8% purity, Sigma-Aldrich).
- The silane coupling agent, (3-Aminopropyl)-triethoxysilane (APTES, ≥ 98% purity, Sigma-Aldrich) is used without further purification.

3.3 Equipments

The equipments that are used in the present research are as follows:

- **Vacuum sublimation equipment** is used to purify the 6FDA monomers.
- **Rotary evaporator** is used to purify the N-methyl-2-pyrolidone (NMP).
- **Vacuum oven** is used to dry the polymer precipitates, SAPO-34 crystals, cast films of 6FDA-durene and mixed matrix membrane (MMM). It is also used to anneal the dense films of 6FDA-durene and MMM.
- **Teflon-lined synthesis reactor** is used to carry out the hydrothermal synthesis of SAPO-34 crystals.
- **Furnace** is used to calcine the SAPO-34 crystals in air condition.
- **Sonicator** is used to evenly disperse the SAPO-34 crystals in the polymer solution.
- **X-ray Diffraction (XRD)** is used to verify the presence of SAPO-34 in the resulting MMM.
- **Fourier Transform Infrared Spectroscopy (FTIR)** spectrometer is used to determine the functional groups and silane-modified grafting present in SAPO-34 crystals.
- **Scanning Electron Microscope (SEM)** is used to study the morphology of the MMM.
- **Energy Dispersive X-ray (EDX)** is used to study the dispersion of fillers in the MMM.
- **CO_2 membrane cell filter test rig (CO_2MCEF)** is used to test the performance of the MMM in CO_2/CH_4 separation.

3.4 Experimental Procedure

3.4.1 Synthesis of 6FDA-Durene Polymer

The synthesis of 6FDA-durene polymer was carried out by using the chemical imidization method (Wijenayake et al., 2013; Liu et al., 2001). The experimental procedure was as follows:

1. Durene-diamine monomers were dissolved in purified NMP. Nitrogen purge was applied throughout to reduce the side reactions that would occur when the solution was exposed to the air which contains oxygen and water moisture.
2. Equal-mole of 6FDA monomers were added to the solution to obtain a 21 wt% concentration.
3. The mixture was stirred for 24 hours at room temperature under nitrogen purge to obtain polyamic acid (PAA) solution.
4. Propionic anhydride and triethylamine were added slowly to the PAA solution for chemical imidization, with the mole ratio of propionic anhydride/ triethylamine to 6FDA of 4:1. The mixture was stirred for 24 hours at room temperature under nitrogen purge to form 6FDA-durene polyimides.
5. The polyimides were precipitated in methanol and then washed with methanol for several times.
6. The wash solution was filtered and the collected polymer precipitates were dried at 150 ℃ in vacuum oven for 24 hours to remove any wash solution residue.

3.4.2 Synthesis of SAPO-34 Crystals

SAPO-34 crystals were synthesized by hydrothermal synthesis method reported by Askari & Halladj (2012) as follows:

1. A gel with molar composition of Al_2O_3: P_2O_5: 0.6 SiO_2: 2 TEAOH: 70 H_2O was prepared by mixing $C_9H_{21}AlO_3$, TEAOH and deionized water. The mixture was stirred for an hour at room temperature to form homogeneous solution.

2. Silica source (TEOS) was added into the mixture and stirred for 2 hours. After that, with continuous stirring, H_3PO_4 was added drop wise to the solution. The solution was further stirred for an hour.
3. The gel solution was then transferred into the Teflon-lined synthesis reactor for hydrothermal growth. The hydrothermal synthesis was carried out at 200^oC for 24 hours.
4. After synthesis, the solid products were recovered and washed three times by centrifuging with deionized water.
5. The products were dried in oven at 110^oC overnight.
6. The as-synthesized crystals were calcined in furnace at 550^oC in air for 6 hours to remove the organic template molecules.

3.4.3 Preparation of Silane-Modified SAPO-34 Crystals

The synthesis of silane-modified SAPO-34 crystals was carried out by using the procedure as follows (Li et al., 2006):

1. A mixture of 120 ml toluene, 4.8 ml silane coupling agent (APTES) and 0.6 g SAPO-34 crystals was stirred for 24 hours at room temperature under nitrogen purge.
2. SAPO-34 crystals were filtered with toluene and then washed three times by centrifuging with methanol to remove the unreacted silane.
3. The silane-modified SAPO-34 crystals were dried in oven at 110^oC overnight.

3.4.4 Preparation of 6FDA-Durene Dense Film

6FDA-durene dense film was prepared as follows (Liu et al., 2002):

1. A 3% w/v solution of polymer in dichloromethane was prepared and filtered through a 1 μm filter to remove the non-dissolved materials and dust particles.
2. The solution was stirred for 1 hour and then slowly poured into a Petri dish on a leveled clean glass plate.
3. The Petri dish was covered with a piece of glass and a small gap was kept for slow solvent evaporation at room temperature overnight.

4. The cast film was dried in an oven at 60 ℃ for 24 hours without vacuum and another 24 hours with vacuum. Then, the oven temperature was increased from 60 to 250 ℃ at a heating rate of 25 ℃/hour.
5. The dense film was annealed at 250 ℃ for 24 hours and then slowly cooled down in the oven.

3.4.5 Preparation of SAPO-34/6FDA-Durene and Silane-Modified SAPO-34/6FDA-Durene Mixed Matrix Membrane

The mixed matrix membrane (MMM) with inorganic fillers loadings was prepared by using the method as follows (Wijenayake et al. 2013):

1. SAPO-34 dispersion and polymer solution were prepared separately. SAPO-34 crystals of 5, 10, 15 and 20 wt% were added to the dichloromethane in separate vials, and stirred and sonicated for 2 hours (alternating 30 minutes stirring followed by 30 minutes sonication) to produce SAPO-34 dispersion.
2. 6FDA-durene polymer was added to the dichloromethane and stirred for 1 hour to produce polymer solution.
3. 10% of the polymer solution was added to the SAPO-34 dispersion (priming). The mixture was stirred and sonicated for 2 hours.
4. The remaining polymer solution was added and the mixture was further stirred and sonicated for 2 hours, and finally stirred for 2 hours.
5. The mixture was casted on a Petri dish and the Petri dish was covered with a piece of glass. A small gap was kept for slow solvent evaporation at room temperature overnight.
6. The membrane was then removed from the Petri dish. The cast film was dried in an oven at 60^{o}C for 24 hours without vacuum and another 24 hours with vacuum. Then, the oven temperature was increased from 60 to 250 ℃ at a heating rate of 25 ℃/hour.
7. The membrane was annealed at 250 ℃ for 24 hours in the vacuum oven, then cooled down to room temperature naturally prior to the removal from the vacuum oven.

Silane-modified SAPO-34/6FDA-durene MMM was synthesized by using the same procedure as SAPO-34/6FDA-durene MMM fabrication. The amount of silane-modified SAPO-34 crystals loaded was 5, 10, 15 and 20 wt% as well.

3.4.6 Characterization of Mixed Matrix Membrane

Mixed matrix membrane (MMM) was characterized by using the following methods:

1. The presence of SAPO-34 in the resulting MMM was verified by the pattern of the X-ray Diffraction (XRD).
2. The functional groups and silane-modified grafting present in SAPO-34 crystals were determined by using the Fourier Transform Infrared Spectroscopy (FTIR).
3. The morphology of MMM was studied by using the Scanning Electron Microscopy (SEM).
4. The dispersion of fillers in the MMM was studied by using the Energy Dispersive X-ray (EDX).

3.4.7 Gas Permeability and Selectivity Test

The performance of the resulting mixed matrix membrane (MMM) on CO_2/CH_4 separation were tested by using the CO_2 membrane cell filter test rig (CO_2MCEF) as shown in Figure 6. The operating parameters were as follows:

- Temperature: 25^{o}C
- Feed pressure: 5 bar
- Feed composition: 100% CO_2 and 100% CH_4

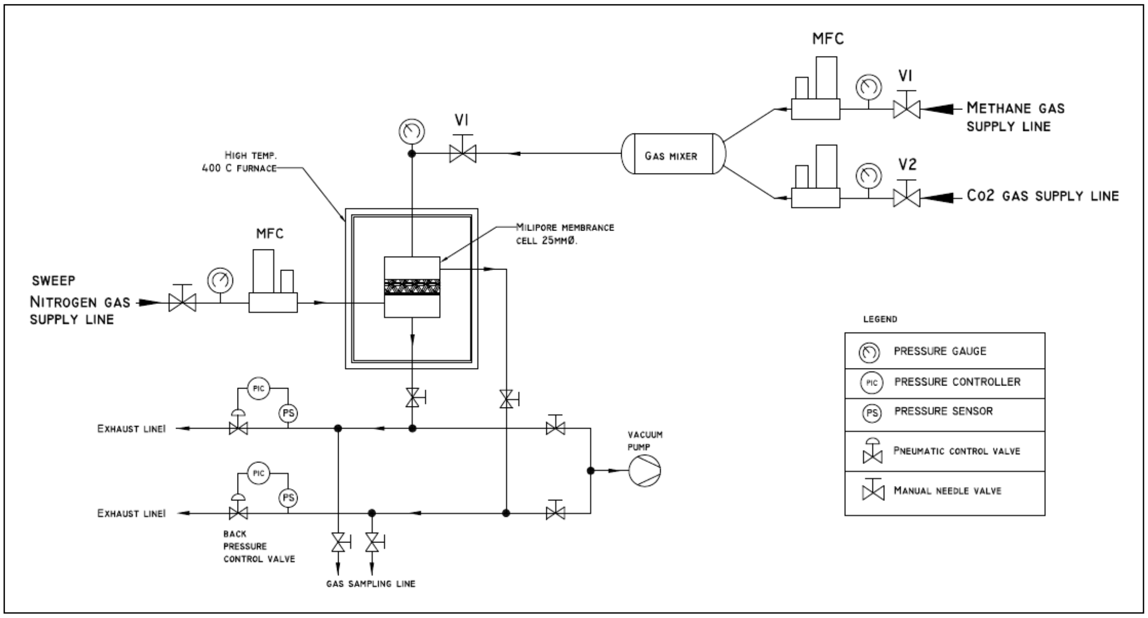


Figure 6: CO_2 membrane cell filter test rig (CO_2MCEF)

The permeability of CO_2 and CH_4 were calculated by using equation 2 and 3, respectively (Ismail & Lai, 2004).

$$P_{CO_2} = \frac{Q_{CO_2} l}{A \Delta p} \text{ ---------- (2)}$$

$$P_{CH_4} = \frac{Q_{CH_4} l}{A \Delta p} \text{ ---------- (3)}$$

P_{CO_2} is the permeability of CO_2 in Barrer (1 Barrer = 1 x 10^{-10} cm^3 (STP) cm/cm^2 s cmHg), P_{CH_4} is the permeability of CH_4 in Barrer, Q_{CO_2} is the volumetric flow rate of CO_2, Q_{CH_4} is the volumetric flow rate of CH_4, l is the membrane skin thickness, A is the membrane effective surface area, while Δp is the pressure difference across membrane.

The selectivity of CO_2/CH_4 was determined by the ratio of the permeability of CO_2 and CH_4 as shown in equation 4 (Ismail & Lai, 2004).

$$\propto_{CO_2/CH_4} = \left(\frac{P_{CO_2}}{P_{CH_4}}\right) \text{ ---------- (4)}$$

3.5 Project Activities and Key Milestones

The main activities of this research were to synthesis the membrane and to conduct the membrane performance test towards gas separation. Inorganic fillers SAPO-34 crystals, silane-modified SAPO-34 crystals as well as the polymer of 6FDA-durene were synthesized prior to the fabrication of mixed matrix membrane (MMM). MMM was fabricated by incorporating the inorganic fillers into the polymer matrix. The resulting SAPO-34 and silane-modified SAPO-34 were characterized by using the X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM), whereas the fabricated MMM was characterized by using the Energy Dispersive X-ray (EDX) and SEM. The performance of the MMM in CO_2/CH_4 gas separation was evaluated by using the CO_2 membrane cell filter test rig (CO_2MCEF) in order to determine the optimum loading of the inorganic particles into the polymer phase. Table 4 shows the key milestones of the present research.

Table 4: Key milestones of the research

Progress	Date of Completion
Confirmation of research topic	29th May 2014
Problem identification, literature review and preparation of experimental procedure for membrane synthesis	19th June 2014
Synthesis of 6FDA-durene polymer	24th July 2014
Synthesis of SAPO-34 crystals	26th September 2014
Preparation of 6FDA-durene dense film	3rd October 2014
Fabrication of SAPO-34/6FDA-durene MMM	3rd October 2014
Preparation of silane-modified SAPO-34 crystals	10th October 2014
Fabrication of silane-modified SAPO-34/6FDA-durene MMM	17th October 2014
Characterization of MMM	13th November 2014
Gas permeability and selectivity test	21st November 2014

3.6 Gantt Chart

Table 5 shows the Gantt chart of the present research work.

Table 5: Gantt chart

No.	Project Activities	Final Year Project 1														Final Year Project 2													
		Week																											
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Confirmation of project topic	■	■																										
2	Preliminary research work		■	■	■	■																							
3	Submission of extended proposal						■																						
4	Proposal defense								■	■																			
5	Project work continuous									■	■	■	■																
6	Synthesis of 6FDA-durene polymer									■	■																		
7	Submission of interim draft report													■															
8	Submission of interim report														■														
9	Synthesis of SAPO-34 crystals															■													
10	Preparation of 6FDA-durene dense film																■												
11	Fabrication of SAPO-34/6FDA-durene mixed matrix membrane (MMM)																■												
12	Preparation of silane-modified SAPO-34 crystals																	■											
13	Fabrication of silane-modified SAPO-34/6FDA-durene MMM																		■										
14	Characterization of MMM																			■	■	■	■						
15	Gas permeability and selectivity test																				■	■	■	■					
16	Submission of progress report																						■						
17	Pre-SEDEX																								■				
18	Submission of draft final report																									■			
19	Submission of dissertation (soft bound)																										■		
20	Submission of technical paper																										■		
21	Viva																											■	
22	Submission of project dissertation (hard bound)																												■

CHAPTER 4

RESULTS AND DISCUSSION

4.1 6FDA-Durene Polymer

6FDA-durene polymer was synthesized by using the chemical imidization method. 6FDA-dianhydride and durene-diamine monomers were purified prior to the synthesis of 6FDA-durene polymer. Figure 7 and 8 show the purified 6FDA dianhydride and durene-diamine monomers, respectively.

Figure 7: Purified 6FDA-dianhydride monomers

Figure 8: Purified durene-diamine monomers

Purified 6FDA-dianhydride and durene-diamine monomers were dissolved in purified NMP solvent in order to prepare 21 wt% of monomers in solution. Polymerization was carried out under nitrogen purge at room temperature to form polyamic acid (PAA). The process was followed by chemical imidization by adding propionic anhydride (PA) and triethylamine (TEA) to convert PAA to polyimide. Figure 9 shows the 6FDA-durene polyimide formed. It was observed that the polyimide formed was viscous with light yellowish appearance.

Figure 9: 6FDA-durene polyimide after synthesis

The 6FDA-durene polyimide produced was then precipitated with methanol. Methanol was used as precipitating agent as it will dissolve the unreacted monomers after the chemical imidization, and retain the 6FDA-durene polyimide structure. The polyimide was washed with methanol for several times for solvent exchange before drying in the vacuum oven at 150^{o}C for 24 hours. Figure 10 shows the 6FDA-durene polyimide after drying.

Figure 10: 6FDA-durene polyimide after drying

6FDA-durene polyimide was successfully synthesized. It was used as the polymer matrix in the fabrication of mixed matrix membrane (MMM).

4.2 SAPO-34 Crystals

SAPO-34 crystals were synthesized by hydrothermal synthesis method as reported by Askari & Halladj (2012). During the preparation of SAPO-34, the gel solution with molar composition of Al_2O_3: P_2O_5: 0.6 SiO_2: 2 TEAOH: 70 H_2O was prepared before it was transferred into the Teflon-lined synthesis reactor for hydrothermal growth. The solid products which contained SAPO-34 particles were recovered and centrifuged with deionized water upon completion of synthesis. Figure 11 shows the SAPO-34 crystals before drying in the oven at 110^{o}C overnight.

Figure 11: SAPO-34 crystals before drying

The dried crystals were calcined with air in the furnace to eliminate TEAOH template from SAPO-34 framework. The final products of SAPO-34 crystals after calcination are shown in Figure 12.

Figure 12: Final products of SAPO-34 crystals after calcination

The SEM image of SAPO-34 crystals is illustrated in Figure 13. It was observed that the particles have a smooth external surfaces and displaying cubic shape morphology, which is typical of SAPO-34 crystals. The crystals have an average size of ~2 µm.

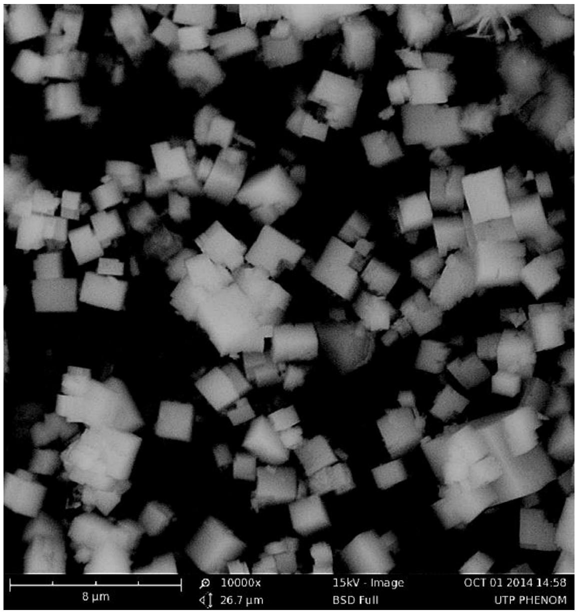


Figure 13: SEM image of SAPO-34 crystals. The scale bar (8 µm) is represented by 4 grids

The XRD pattern of SAPO-34 crystals is shown in Figure 14. The XRD pattern exhibited the identical characteristic peaks at 2-theta values of 9.5^o, 15.2^o and 20.8^o approximately, which correspond to the standard XRD pattern of SAPO-34 crystals as reported by Robson & Lillerud (2001), confirming the formation of SAPO-34 phase.

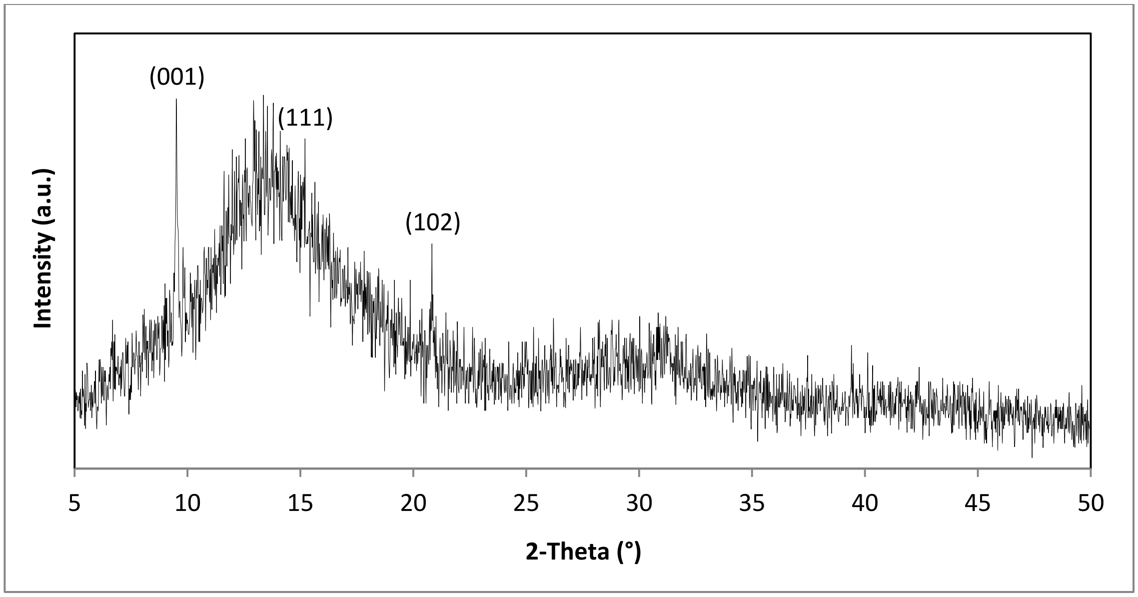


Figure 14: XRD pattern of synthesized SAPO-34 crystals

The synthesized SAPO-34 crystals were then used as the inorganic phase to fabricate the mixed matrix membrane (MMM).

4.3 Silane-Modified SAPO-34 Crystals

Silane-modified SAPO-34 crystals were prepared by mixing the silane coupling agent (APTES) and toluene with the as-synthesized SAPO-34 crystals. The mixture was stirred under nitrogen purge as shown in Figure 15.

Figure 15: Stirring of silane-modified SAPO-34 crystals mixture under nitrogen purge

The silane-modified crystals were filtered and washed with toluene and methanol, respectively to remove the unreacted silane before drying in the oven.

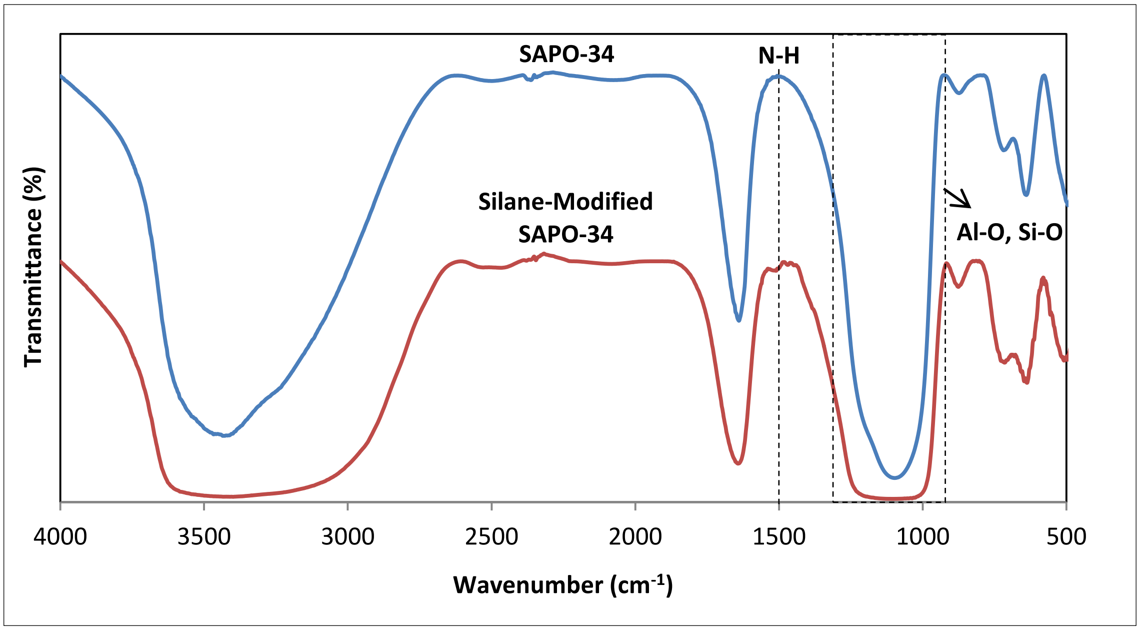


Figure 16: FTIR spectra of SAPO-34 and silane-modified SAPO-34 crystals

Figure 16 shows the FTIR spectra of SAPO-34 and silane-modified SAPO-34 crystals. The significant band between the wavenumber of 900-1350 cm^{-1} in the FTIR spectra for both samples indicates the asymmetric vibration modes of Si-O and Al-O group in SAPO-34. A band of N-H at around 1450-1550 cm^{-1} was observed in the spectra of silane-modified SAPO-34. This result shows that the silane group was successfully grafted onto the SAPO-34 structure.

4.4 Mixed Matrix Membranes

Mixed matrix membranes (MMMs) were fabricated by incorporating different loadings of SAPO-34 inorganic fillers in 6FDA-durene polyimide. In the present research, 5, 10, 15 and 20 wt% of SAPO-34 and silane-modified SAPO-34 crystals were successfully added into the 6FDA-durene polymer matrix to synthesis total of eight MMMs (Four SAPO-34/6FDA-durene MMMs and four silane-modified SAPO-34/6FDA-durene MMMs). Pure 6FDA-durene membrane was fabricated as a reference membrane. Prior to membrane fabrication, 6FDA-durene polymer, calcined SAPO-34 and silane-modified SAPO-34 crystals were dried at 110^{o}C overnight to remove excess moisture. During the fabrication of MMM, SAPO-34 dispersion and polymer solution were prepared separately before mixing. The mixture was then stirred and sonicated for 2 hours alternately by using the priming method. Figure 17 shows the sonication process of SAPO-34/6FDA-durene mixture in the sonicator.

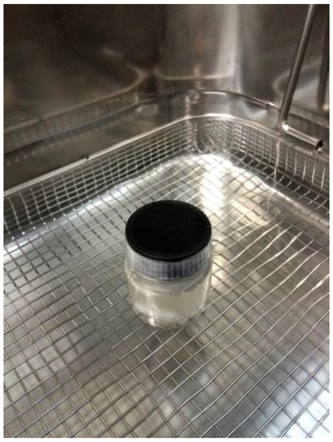


Figure 17: Sonication of SAPO-34/6FDA-durene mixture in sonicator

After the mixture was further stirred for 2 hours, it was casted on Petri dish and covered with a glass plate overnight for slow solvent evaporation as illustrated in Figure 18.

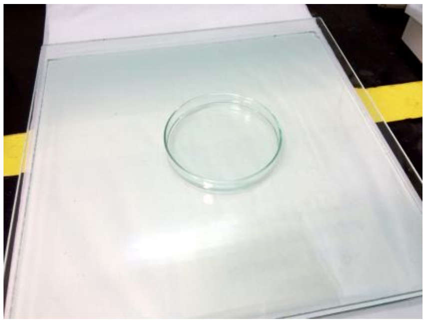


Figure 18: Slow solvent evaporation of casted membrane

After the resulting MMM was peeled off from the Petri dish, it was then dried and annealed in the vacuum oven.

Figure 19 shows the fabricated SAPO-34/6FDA-durene MMMs, while Figure 20 shows the fabricated silane-modified SAPO-34/6FDA-durene MMMs with different loadings of SAPO-34 fillers.

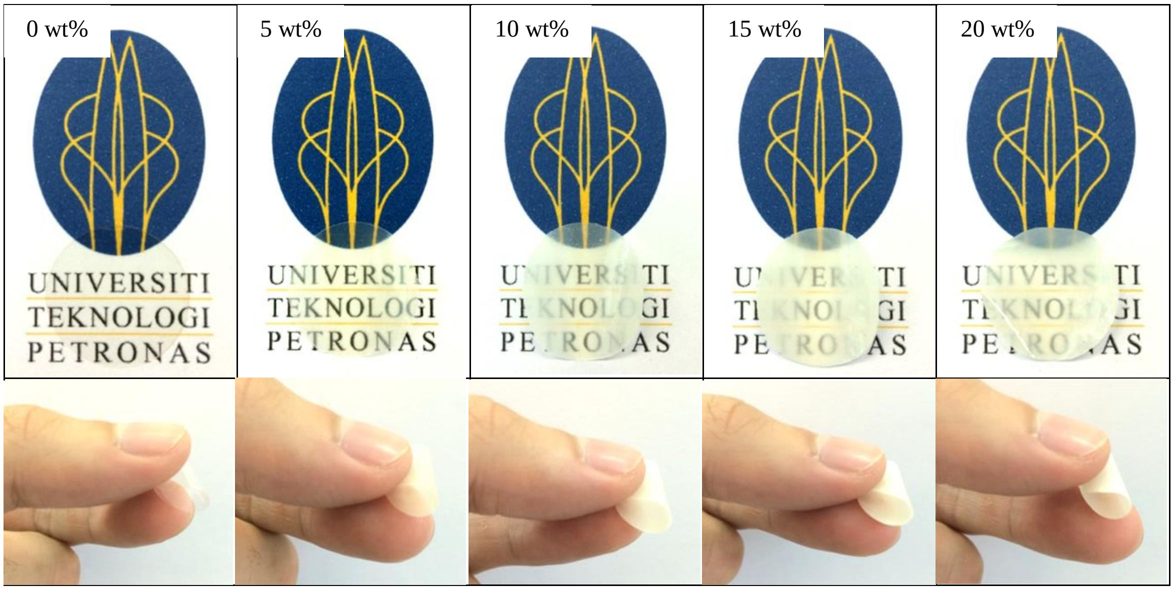


Figure 19: SAPO-34/6FDA-durene mixed matrix membranes with 0, 5, 10, 15 and 20 wt% SAPO-34 loadings

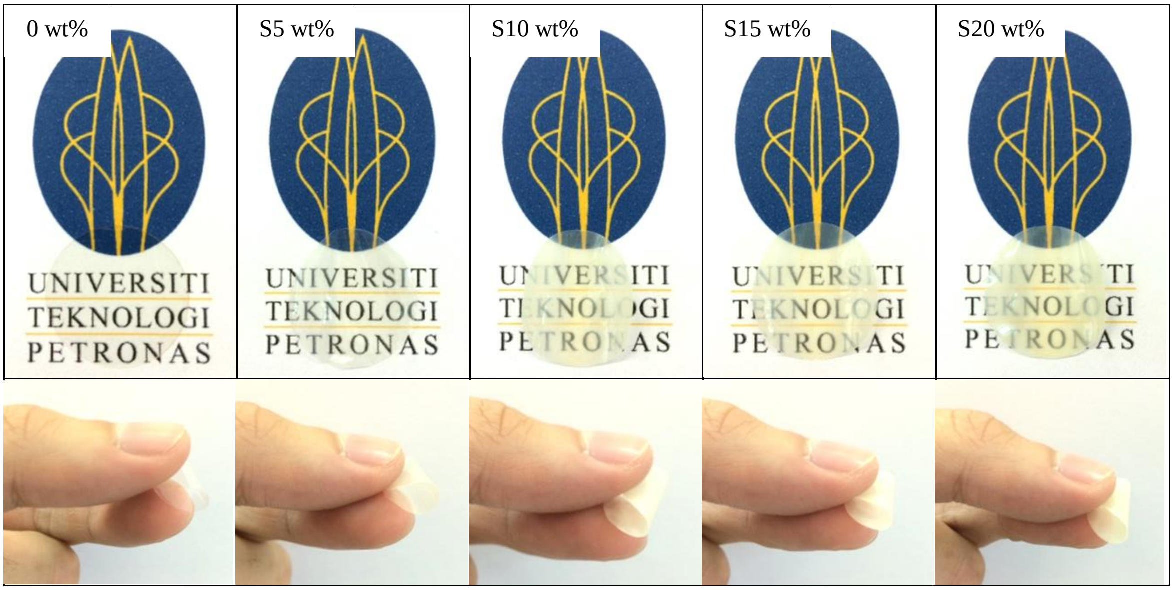


Figure 20: Silane-modified SAPO-34/6FDA-durene mixed matrix membranes with 0, 5, 10, 15 and 20 wt% silane-modified SAPO-34 loadings

From Figure 19 and 20, it was observed that the fabricated MMMs were transparent and possessed good mechanical property. There was no crack on the resulting MMMs and with ductile and bendable property. The transparency characteristic of silane-modified SAPO-34/6FDA-durene MMMs was found better than SAPO-34/6FDA-durene MMMs. It might be due to the modification effect of APTES on the surface properties of SAPO-34. In general, all fabricated MMMs have good physical appearance and mechanical property.

4.5 Characterization of Mixed Matrix Membrane

4.5.1 Scanning Electron Microscopy

The morphology of the resulting mixed matrix membrane (MMM) was studied by using the Scanning Electron Microscopy (SEM). Figure 21 and 22 depict the SEM images of cross-section view of 6FDA-durene dense film and MMMs with and without silane-modification of 5, 10, 15 and 20 wt% SAPO-34 fillers. The thickness of all membranes was between 35-45 μm.

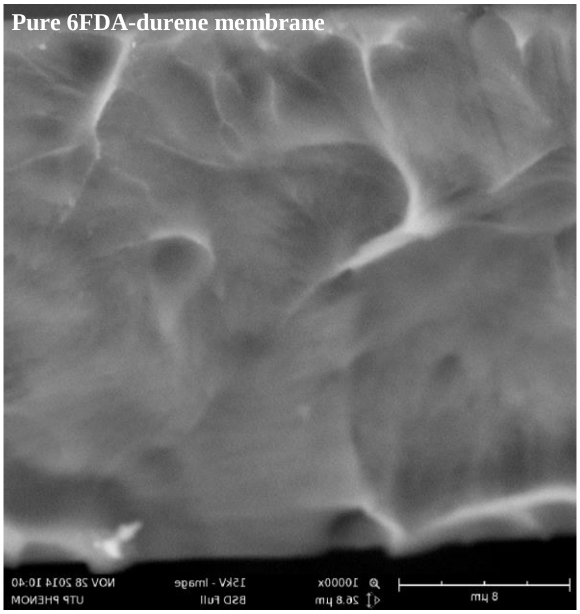


Figure 21: Cross-section SEM image of pure 6FDA-durene membrane

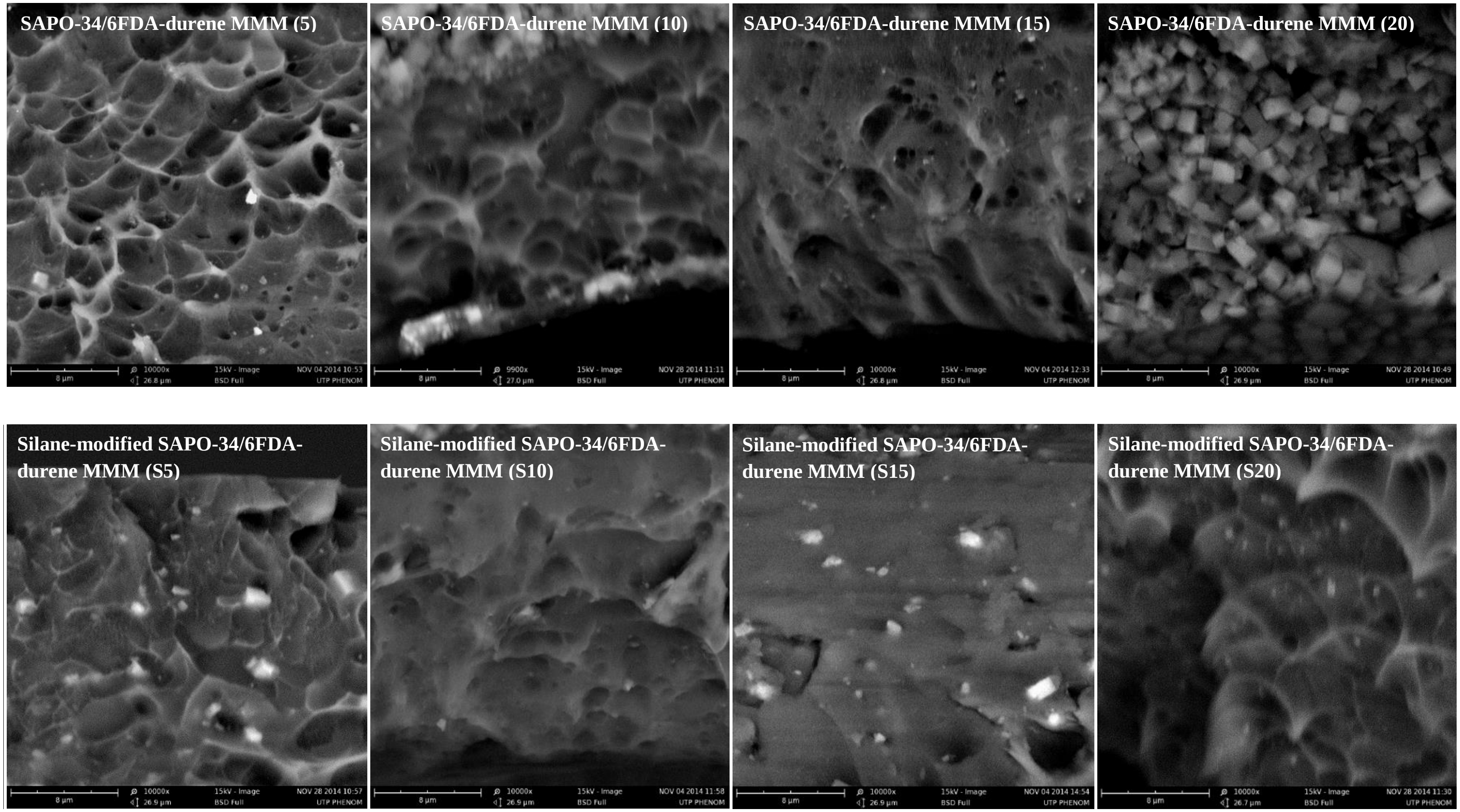
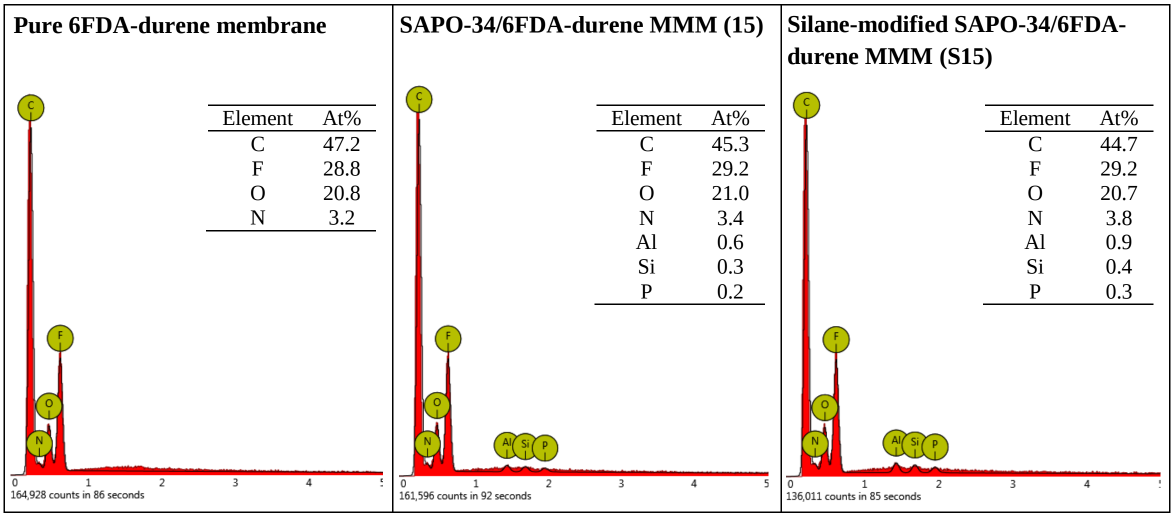


Figure 22: Comparison of cross-section SEM images of SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs. (5, 10, 15 and 20) and (S5, S10, S15 and S20) represent the loadings of SAPO-34 and silane-modified SAPO-34 in wt%, respectively

The purpose of introducing the silane coupling agent on the surface of SAPO-34 is to improve the compatibility between the polymeric and inorganic phases. From the SEM images as shown in Figure 22, it was observed that the interfacial void or defect was improved between the polymeric and inorganic phases for silane-modified SAPO-34/6FDA-durene MMMs as compared to the SAPO-34/6FDA-durene MMMs. The filler particles were detached to the polymer matrix without forming significant phase separation between the two boundaries.

4.5.2 Energy Dispersive X-ray

Energy Dispersive X-ray (EDX) was carried out to study the dispersion of SAPO-34 fillers in the mixed matrix membrane (MMM). Figure 23 shows the EDX data of the pure 6FDA-durene membrane, SAPO-34/6FDA-durene MMM loaded with 15 wt% SAPO-34 and silane-modified SAPO-34/6FDA-durene MMM loaded with 15 wt% silane-modified SAPO-34.



Pure 6FDA-durene membrane

Element	At%
C	47.2
F	28.8
O	20.8
N	3.2

SAPO-34/6FDA-durene MMM (15)

Element	At%
C	45.3
F	29.2
O	21.0
N	3.4
Al	0.6
Si	0.3
P	0.2

Silane-modified SAPO-34/6FDA-durene MMM (S15)

Element	At%
C	44.7
F	29.2
O	20.7
N	3.8
Al	0.9
Si	0.4
P	0.3

Figure 23: EDX data of pure 6FDA-durene membrane, SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMM. (15) and (S15) represent the loadings of SAPO-34 and silane-modified SAPO-34 in wt%, respectively

The main elements that presence in pure 6FDA-durene are carbon (C), fluorine (F), oxygen (O) and nitrogen (N), while SAPO-34 contains the elements of aluminium (Al), silicon (Si) and phosphorus (P). The amount of each element was presented in atomic percentage (at%). From Figure 23, it was verified that pure 6FDA-durene membrane contains only C, F, O and N with the amount of 47.2, 28.8, 20.8 and 3.2 atomic %, respectively. For SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs, it was verified that the elements of SAPO-34 (Al, Si and P) were presence in the resulting MMMs.

Figure 24 displays the EDX mapping for SAPO-34/6FDA-durene MMM loaded with 15 wt% SAPO-34, while Figure 25 displays the mapping for silane-modified SAPO-

34/6FDA-durene MMM loaded with 15 wt% silane-modified SAPO-34. The images in both figures showed that SAPO-34 particles were uniformly dispersed in 6FDA-durene polymer matrix. No agglomeration and phase separation was found in both MMMs.

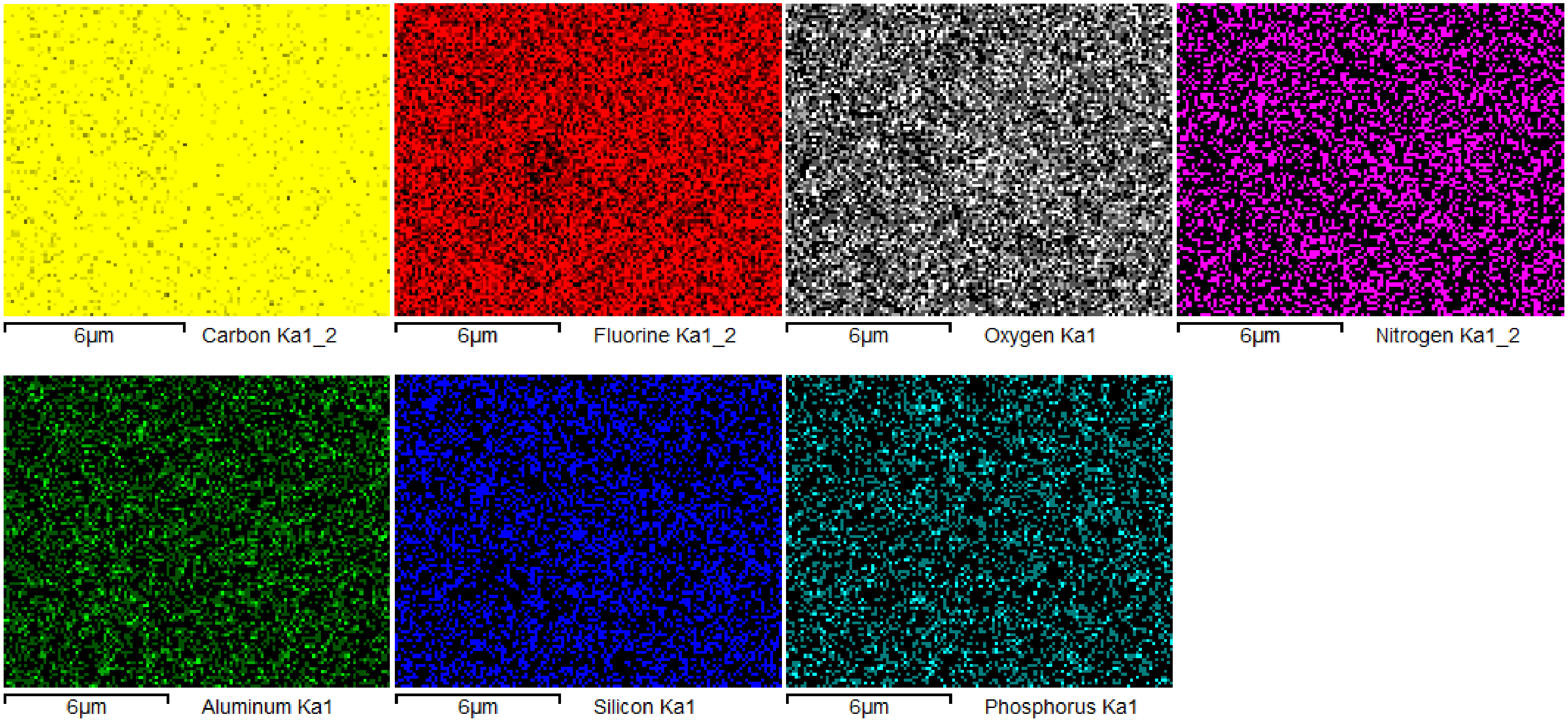


Figure 24: EDX mapping of SAPO-34/6FDA-durene MMM loaded with 15 wt% SAPO-34

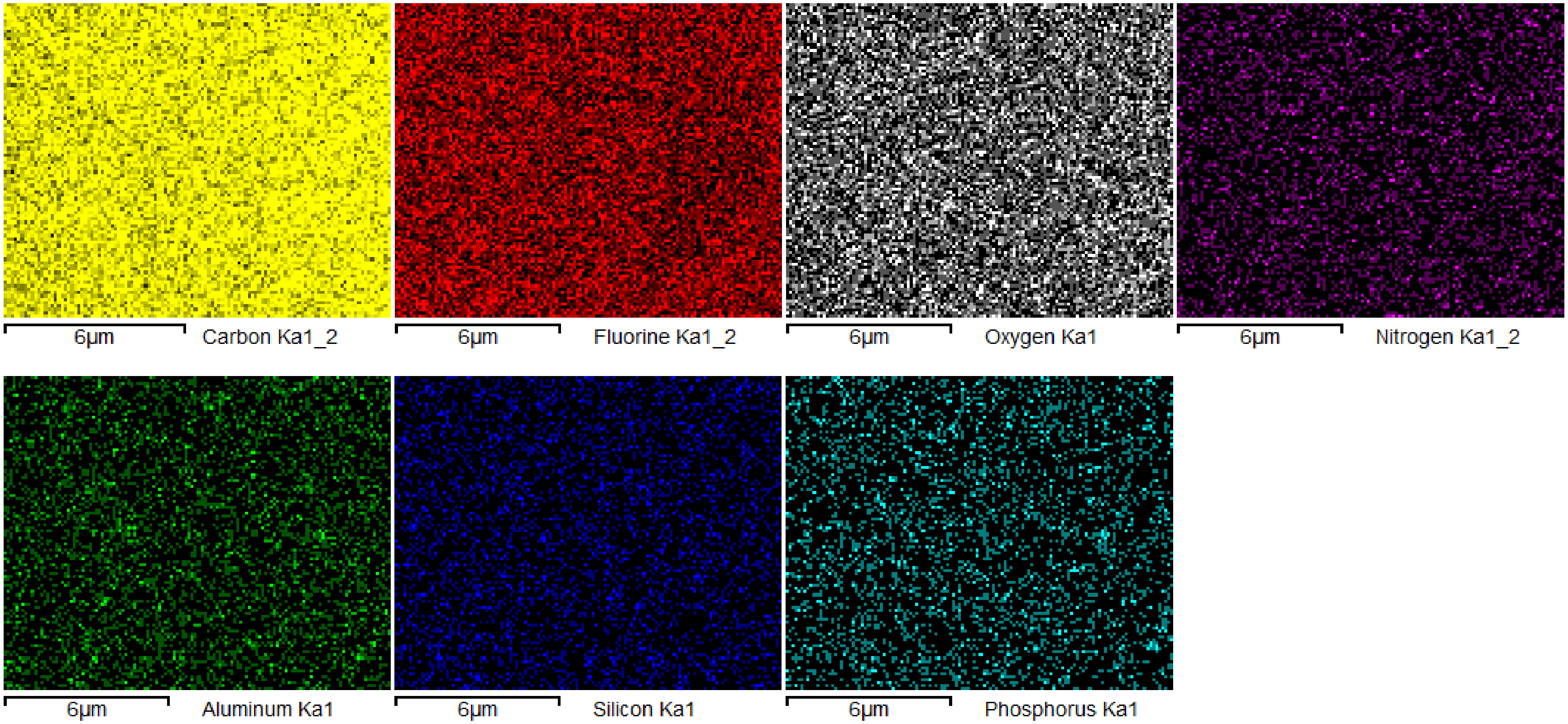


Figure 25: EDX mapping of silane-modified SAPO-34/6FDA-durene MMM loaded with 15 wt% silane-modified SAPO-34

4.6 Gas Separation Performance

In the present research, the permeability of the carbon dioxide (CO_2) and methane (CH_4), and CO_2/CH_4 selectivity of the resulting mixed matrix membranes (MMMs) were determined. The membranes were tested in the CO_2 membrane cell filter test rig (CO_2MCEF) at pressure of 5 bar and room temperature of 25^oC. The results of the separation performance were summarized in Table 6.

Table 6: Permeability and CO_2/CH_4 separation selectivity at 25^oC and 5 bar

Mixed Matrix Membrane (MMM)	Permeability		CO_2/CH_4 Ideal Selectivity
	Carbon Dioxide, CO_2 (Barrer)	Methane, CH_4 (Barrer)	
6FDA-durene	408.23	18.71	21.82
5 wt% SAPO-34 in 6FDA-durene	239.50	23.28	10.29
10 wt% SAPO-34 in 6FDA-durene	206.97	21.49	9.63
15 wt% SAPO-34 in 6FDA-durene	251.32	26.10	9.63
20 wt% SAPO-34 in 6FDA-durene	217.72	24.95	8.73
5 wt% silane-modified SAPO-34 in 6FDA-durene	183.61	16.39	11.20
10 wt% silane-modified SAPO-34 in 6FDA-durene	166.32	15.35	10.84
15 wt% silane-modified SAPO-34 in 6FDA-durene	243.93	24.39	10.00
20 wt% silane-modified SAPO-34 in 6FDA-durene	235.87	24.95	9.45

For the pure 6FDA-durene membrane, the results of the gas permeability and the selectivity of CO_2/CH_4 separation are comparable to the results reported by Liu, Chng, Chung, & Wang (2003). However, it was found that the permeability of CO_2 and CO_2/CH_4 selectivity of the resulting MMMs decrease significantly as compared to the pure 6FDA-durene membrane. Several justifications are made to discuss the possible causes of the abovementioned results:

1. Large inorganic particles size and moisture contact penetrated the gas diffusion. Typical SAPO-34 particles have a bigger size (~ 2μm) as compared to other inorganic particles. Due to the large size of SAPO-34, sedimentation of particles might occur during the fabrication of MMM. However, the effect of large

particles size seems to be less towards the gas separation performance of MMM. Different particles size might be the factor for the variation of permeability and selectivity results. Besides, the resulting MMM might get contact with the air moisture in the surrounding before conducting the gas permeability and CO_2/CH_4 selectivity study. Gas molecules were unable to penetrate through the pores of SAPO-34 due to the pores blockage, and thus degraded the performance of the MMM.

2. Poor interfacial adhesion created interfacial void. Even though the morphology of the resulting MMMs showed the improvement on the compatibility between the polymeric and inorganic phases, there might still have some minor interface voids existed in the MMM. Gas molecules could easily penetrate into the membrane via the interfacial void generated because void provides the path with the least resistance. Thus, it will deteriorate the selectivity of the resulting membranes.
3. Formation of rigidified polymer layer at SAPO-34/6FDA-durene interphase (matrix rigidification). Rigidified polymer might form in the resulting MMM and caused the immobilization of polymer chains at SAPO-34/6FDA-durene interphase, which will reduce the gas sorption and permeation (Manson & Chiu, 1973). The formation of matrix rigidification is illustrated in Figure 26 (A). Rigidified polymer might seal the SAPO-34 pores and caused the pores blockage, which is known as “plugged sieves” (Rezakazemi, Amooghin, Rahmati, Ismail, & Matsuura, 2014), as demonstrated in Figure 26 (B). Thus, the gas permeability and selectivity would be affected.

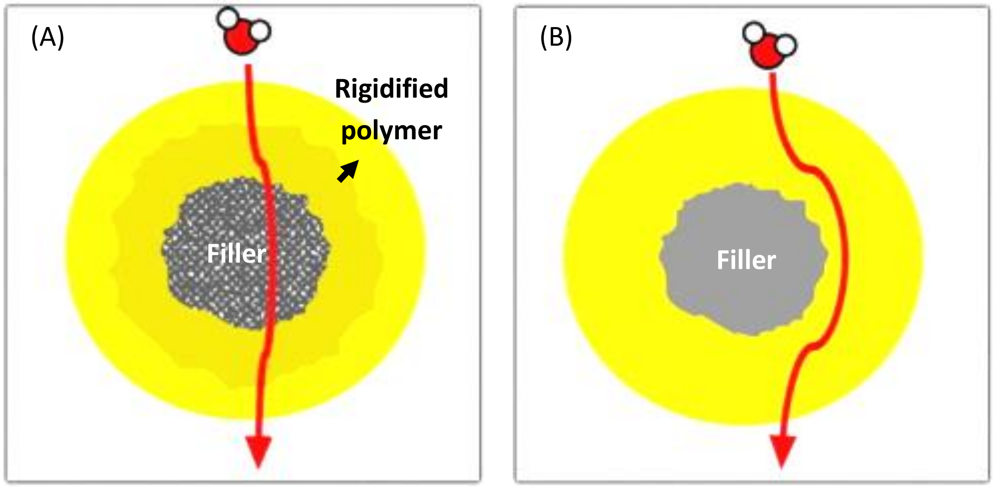


Figure 26: Schematic diagram of (A) matrix rigidification and (B) plugged sieves (Rezakazemi, Amooghin, Rahmati, Ismail, & Matsuura, 2014)

Besides, there was no significant improvement on the CO_2/CH_4 selectivity of the resulting MMMs after introducing the silane coupling agent (APTES) in the inorganic phase. Theoretically, the application of silane group should improve the interfacial strength between the polymeric and inorganic phases, and thus enhance the membrane selectivity. Therefore in this context, the selection of appropriate silane group and its effect towards the separation performance of MMM is an important consideration in fabricating a chemical-modified membrane.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In the present research, 6FDA-durene polymer, SAPO-34 and silane-modified SAPO-34 crystals were successfully synthesized prior to the fabrication of mixed matrix membrane (MMM). 6FDA-durene polymer was synthesized by chemical imidization method while SAPO-34 crystals were synthesized by hydrothermal synthesis method. SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs were successfully fabricated by incorporating different loadings (5, 10, 15 and 20 wt%) of inorganic fillers in polymer matrix. The MMMs fabricated were transparent and showed good mechanical property in which they were ductile and bendable. No crack was found on all fabricated MMMs.

The formation of SAPO-34 phase was verified by the SEM morphology and XRD pattern. APTES was successfully used as the silane coupling agent to prepare the silane-modified SAPO-34 crystals. The FTIR spectra showed that silane group was successfully grafted into the SAPO-34 structure. The cross-section SEM morphology of the fabricated MMMs generally showed the improvement on the compatibility between the polymeric and inorganic phases. The formation of interfacial voids and defects were reduced in the silane-modified SAPO-34/6FDA-durene MMMs as compared to the SAPO-34/6FDA-durene MMMs. No significant phase separation was formed between the two boundaries. The objective to improve the compatibility between the two phases through silane-modification on the surface of the inorganic fillers was successfully achieved. EDX results showed that inorganic SAPO-34 was well distributed in the polymer matrix. No agglomeration was found in the EDX mapping for both SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs. EDX results also verified the presence of SAPO-34 in the resulting MMMs. The amount of each element in the membranes was presented in atomic %.

In this research, the gas separation performance of the resulting MMMs was successfully conducted by using the CO_2 membrane cell filter test rig (CO_2MCEF). However, the permeability of CO_2 and CO_2/CH_4 selectivity of the resulting MMMs decreased significantly for all the resulting MMMs, compared to the pure 6FDA-durene membrane. Several possible causes such as large particles size of SAPO-34, moisture contact with MMM, poor interfacial contact between the polymeric and inorganic phases, and polymer matrix rigidification were justified.

In general, all fabricated SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs exhibited excellent characterization results. Modifications and process optimization are needed in later works to improve the performances of MMM in gas permeability and CO_2/CH_4 separation selectivity.

5.2 Recommendation

There are several recommendations and modifications that can be done in future to improve the synthesizing processes, characterization results and gas separation performances of SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene mixed matrix membranes (MMMs):

1. Priming process of polymer and SAPO-34 solutions mixture. The time allocated for stirring and sonication of the polymer and SAPO-34 solutions mixture can be adjusted or extended in order to achieve better priming process (obtain good dispersion between the two solutions).
2. Gas permeability and CO_2/CH_4 selectivity test. The MMM is suggested to be heated in the vacuum oven at 110^oC overnight to remove the excess moisture that might contain in the MMM. The molding of MMM before putting into the test rig must be handled more carefully in order to avoid any defect and moisture contact to the MMM. Besides, it is encouraged to vacuum the molded membrane overnight after putting it into the test rig to remove the gas molecules or impurities that might attach to the MMM, in order to enhance its gas separation performance.

3. Selection of appropriate silane group. The selection of suitable silane group is the main concern for the preparation of silane-modified inorganic fillers. Other types of silane coupling agents such as methoxy silanes: 3-Aminopropyltrimethoxysilane (APTMS), N-(2aminoethyl)-3-aminopropyl-trimethoxysilane (AAPTMS) and other amine agents can be used instead of APTES to study their effects in inorganic phase towards the gas separation performance of MMM. This is because different silane group will graft differently with inorganic phase and exhibits different performance results. According to Junaidi, Khoo, Leo, & Ahmad (2014), methoxy silane is more readily in hydrolysis reaction compared to ethoxy group.
4. Optimum loading of inorganic fillers. The loadings of 5 to 20 wt% of SAPO-34 and silane-modified SAPO-34 in 6FDA-durene polymer matrix might be too high for the fabrication of SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs. Therefore, a lower loading of 1 to 3 wt% of SAPO-34 and silane-modified SAPO-34 can be considered for future fabrication of these types of membranes.
5. Characterization of MMM. The resulting membrane can be further characterized by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA is used to study the thermal stability while DSC is used to study the amount of heat required to increase the temperature of a sample.

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