Synthesis and Characterization of Polyvinyldene Fluoride/ Low Density

Polyethylene/ Montmorillonite Mixed Matrix Membrane for CO$_2$ Removal

by

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13396

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical)

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CERTIFICATION OF APPROVAL

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Approved by,

_____

(Dr. Oh Pei Ching)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 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.

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(SRINIVASAN SIVARAMAN)

ABSTRACT

Membrane gas separation technology has taken in a new form in its application through the growing branches of mixed matrix membrane (MMM). The existing usage of polymeric membranes is fairly insufficient to meet the demand of the industry due to its lack in stability and separation capabilities, even though they are competitively advantageous over the conventional separation methods. The MMM developed by introducing inorganic fillers into the polymeric matrices, is significantly improvised in its separation properties with trivial loss in membrane stability. The properties attained by the MMM combines the advantageous characteristics of high permeability and flexibility of the polymer; and high selectivity, thermal and chemical stability of the inorganic particles. With a wide range of polymeric and inorganic material being implemented into the MMM concept, this project is aimed to synthesize asymmetric nanoclay-polyvinyldene fluoride (PVDF)-low density polyethylene (LDPE) MMM by incorporating various amount of montmorillonite (MMT) nanoclay mineral into the polymer matrix. The development of this PVDF/LDPE/MMT MMM is intended specifically for separation of CO_2 from natural gas (CH_4). The MMMs were fabricated via dry-wet phase inversion technique with N,N-dimethylacetamide (DMAc) used as solvent and distilled water as the coagulant. The fabricated MMMs were characterized using field emission scanning electron microscopy (FESEM) and thermal gravimetric analysis (TGA) to study the thermal properties and surface morphology of the membrane. Permeability and selectivity of the resultant membrane towards CO_2/CH_4 separation is investigated through gas permeation tests. The morphology of the membranes highly depends on the clay mineral loading as validated by FESEM. PVDF/LDPE/3wt% MMT MMM exhibits the highest CO_2 permeance and CO_2/CH_4 selectivity relative to the pristine PVDF/LDPE membrane.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1   Background of Study

Intensified growth in the global energy demand for natural gas has resulted in the development of unconventional gas reserves that were formerly regarded as not economically viable. Effective and efficient transportation of the natural gas are of the highest importance, as significant natural gas reserves are mostly situated further from the major gas markets (Rufford et.al, 2012). Liquefied Natural Gas (LNG) production from these gas reserves, intended for long distance transportation, present huge challenges to its gas processing.

Gas sweetening in natural gas processing is a process intended to refine natural gas by removal of acidic gas such as carbon dioxide (CO_2). In the petrochemical industry, specifically in natural gas plants, CO_2 removal from the produced natural gas is the stepping stone for its further processing. CO_2 level as high as 80% is commonly found in the produced natural gas streams. Transportation of this gas requires concentrations of below 2%. Presence of CO_2 degrades the calorific value and compressibility of the natural gas (Zhang, Sunarso, Liu, & Wang, 2013). Its corrosive properties in the presence of water may lead to equipment and pipeline damages if not substantially removed from the gas stream (Rezakazemi, Ebadi, Montazer, Ismail, & Matsuura).

Absorption, adsorption, cryogenic distillation and membrane separation are the widely used technologies in this natural gas purification. Over the years, significant improvements on these technologies are made with the aim of optimizing production costs, gas quality requirements and environmental purposes (Shimekit, & Mukhtar, 2012). Conventional industrial methods of CO_2 separation utilizing solvents such as in scrubbers, packed towers, bubble columns and spray towers, thermal and pressure swing adsorption and cryogenic distillation frequently results in flooding, weeping, excessive loading, foaming, and entrainment (Zhang, Sunarso, Liu, & Wang, 2013).

Besides of its full maturity of the separation process, these conventional methods normally involve complicated equipments, high energy consumption and capital costs.

The promising features of membrane separation technology such as energy efficiency, process simplicity, ease of scale-up and reliable high selectivity, have placed in a competitive advantage over the other separation methods. The membranes could be classified into polymeric membranes, inorganic membranes and mixed matrix membranes. However, it is important to note that although membrane technology is highly reliable for gas separations, huge challenges are always present in maintaining the performance of the membrane for long-term operation. This is encountered for both the polymeric and inorganic membranes. Most of these membranes lacks on the resilience in practical conditions, which poses a big challenge for their industrial scale applications (Zhang, Sunarso, Liu, & Wang, 2013).

Mixed matrix membranes (MMMs), consisting of inorganic fillers incorporated into a polymer matrix, present a viable opportunity for improving the separation performances of polymeric membranes whilst retaining the desirable characteristics of inorganic fillers. In fact, a wide range of inorganic fillers such as clays, zeolites and carbon molecular sieves have been utilized for a variety of applications (Shimekit, & Mukhtar, 2012). Yet, the selection of suitable polymer-inorganic components remains a challenge in order to prepare defect-free MMMs with good adhesion between the two phases.

Polymeric materials like polyvinylidene fluoride (PVDF), polyetherimide (PEI) and polysulfone (PSF) have been widely used in gas separation applications. PVDF in general exhibits better separation properties compared to other polymeric materials. Interestingly, low density polyethylene (LDPE), attaining superior hydrophobic characteristics, have been highly advantageous for industrial scale gas separation applications. Attempt of combining PVDF and LDPE into a membrane matrix were carried out in this research, thereby incorporating the advantageous properties of both polymers.

Montmorillonite (MMT), a type of clay from the smectite family, has been employed predominantly in polymer-clay nanocomposite synthesis. It shows promise as inorganic filler to enhance the barrier properties of polymeric materials (Hashemifard,

Ismail, & Matsuura, 2011). There is also evidence that clay increases the polymer structure's free-volume; which in turn enhances the gas separation properties of membrane.

In this study, MMMs were prepared from hybrid materials made of PVDF, LDPE and MMT using dry/wet phase inversion method. The effects of the presence of the clay inorganic fillers on the structure of the MMMs were investigated through its morphology and physical features.

1.2   Problem Statement

Membrane separation technologies potentially offer significant advantages over the rest of the gas separation options. They are highly attractive for their ability in low energy requirements, compact plant footprints and no phase change involved (Rufford et.al, 2012). Applications of polymers into gas separation membranes undoubtedly grew huge interest as potential solution for energy efficient gas separation technologies. However, a few disadvantages of this polymeric membrane have setback their potential development in the scale of industry. Concerns on their permeability, selectivity, thermal and chemical stability have placed a limit over their industrial scale applications. PVDF and LDPE membranes are much similar to these concerns, even though they have some advantages over other polymeric membranes. Inorganic membranes have encountered the drawbacks of polymeric membranes, however, their high cost of development and fragility have made them less susceptible for industrial applications (Rufford et.al, 2012). Solution that gained attention to these problems is the incorporation of inorganic and polymeric materials into mixed matrix membranes (MMMs). In practical applications, however, fabrication of MMM is not easy, as the compatibility of both phases is an important factor in determining its separation performance.

1.3   Objectives

1. To elucidate the casting solution formulation for synthesis of PVDF/LDPE and PVDF/LDPE/MMT membranes using dry-wet phase inversion technique.
2. To determine the optimum blend of PVDF/LDPE polymeric membrane.
3. To study the effect of MMT clay loading on PVDF/LDPE/MMT Mixed Matrix Membrane (MMM) formation.

4. To characterize the resultant membranes using field emission scanning electron microscopy (FESEM) and thermal gravimetric analysis (TGA).

5. To investigate the performance of the developed membranes for CO_2/CH_4 gas separation.

1.4 Scope of Study

This research focuses on the development of PVDF/LDPE/MMT MMM for CO_2 separation from natural gas. In this study, montmorillonite is used as nanofillers to synthesize flat sheets of the MMM via dry-wet phase inversion technique. The optimum blend of PVDF/LDPE polymer and the effect of MMT loading on PVDF/LDPE/MMT MMM fabrication are investigated. The morphology and thermal stability of the resultant membranes are determined using various characterization tools such as field emission scanning electron microscopy (FESEM) and thermal gravimetric analysis (TGA). Gas permeation study is performed to determine the permeability and selectivity of the membranes towards CO_2/CH_4 separation.

1.5 Relevancy of Project

Emerging technology of mixed matrix membranes for CO_2 separations have placed urgency in their rigorous development. Research on selecting the best pair of polymeric and inorganic materials for the MMM is always an ongoing process for membrane developers. Better separation performances are expected for every newly developed MMM, comparing to its precursors. Calling on this challenge, this research project is highly relevant to be carried out to encounter performances of different polymers and inorganic materials combination, in the case of this project is the PVDF, LDPE polymers and MMT inorganic nanoclay.

The project may indicate positive results or at least provide some background works for further developments of MMM. Guidelines for the methodologies designed for this research were obtained from relevant sources with close monitoring by the author's supervisor. Moreover, the dry-wet phase inversion technique used in this research for MMM development is widely accepted for synthesizing gas separation membranes. In overall, this project has high potential in contributing towards the industry demand of membrane developments for effective and efficient separation of CO_2 from natural gas.

1.6   Feasibility of Project

The proposed project is subjected for completion within a time frame of 28 weeks. With the availability of materials, equipments and facilities in the university, the time allocated is fairly adequate to produce results. Figure 1.1 illustrates the Gantt chart of activities planned for the entire project duration.

The estimated time required to prepare individual membranes are shown in Table 1.1.

Table 1.1.   Estimated duration for individual membrane fabrication

Membrane preparation stages	Duration (hours)
Polymer preparation/drying	24
Polymer/Nanoclay solution preparation	12
Solution degassing	4
Membrane casting	1
Membrane treatments	24
Drying	24
Total Duration	**89**

The time allocated for the membrane preparation is 15 weeks, as in the Gantt chart proposed. Number of days required to complete an individual membrane synthesis is approximately 5 days including the standby period. A total of 11 membrane sheets including pristine PVDF/LDPE membrane and PVDF/LDPE/MMT mixed matrix membrane were to be fabricated. Simultaneous membrane preparations may include two at a time.

Therefore,

= 11 membranes × 0.5 week/membrane × 5 days/week

= **27.5 days**

This gives a period of 6 whole weeks excluding the weekends. The allocated time in the planner for the membrane preparations deemed to be sufficient, taking into consideration of the non-productive time as well.
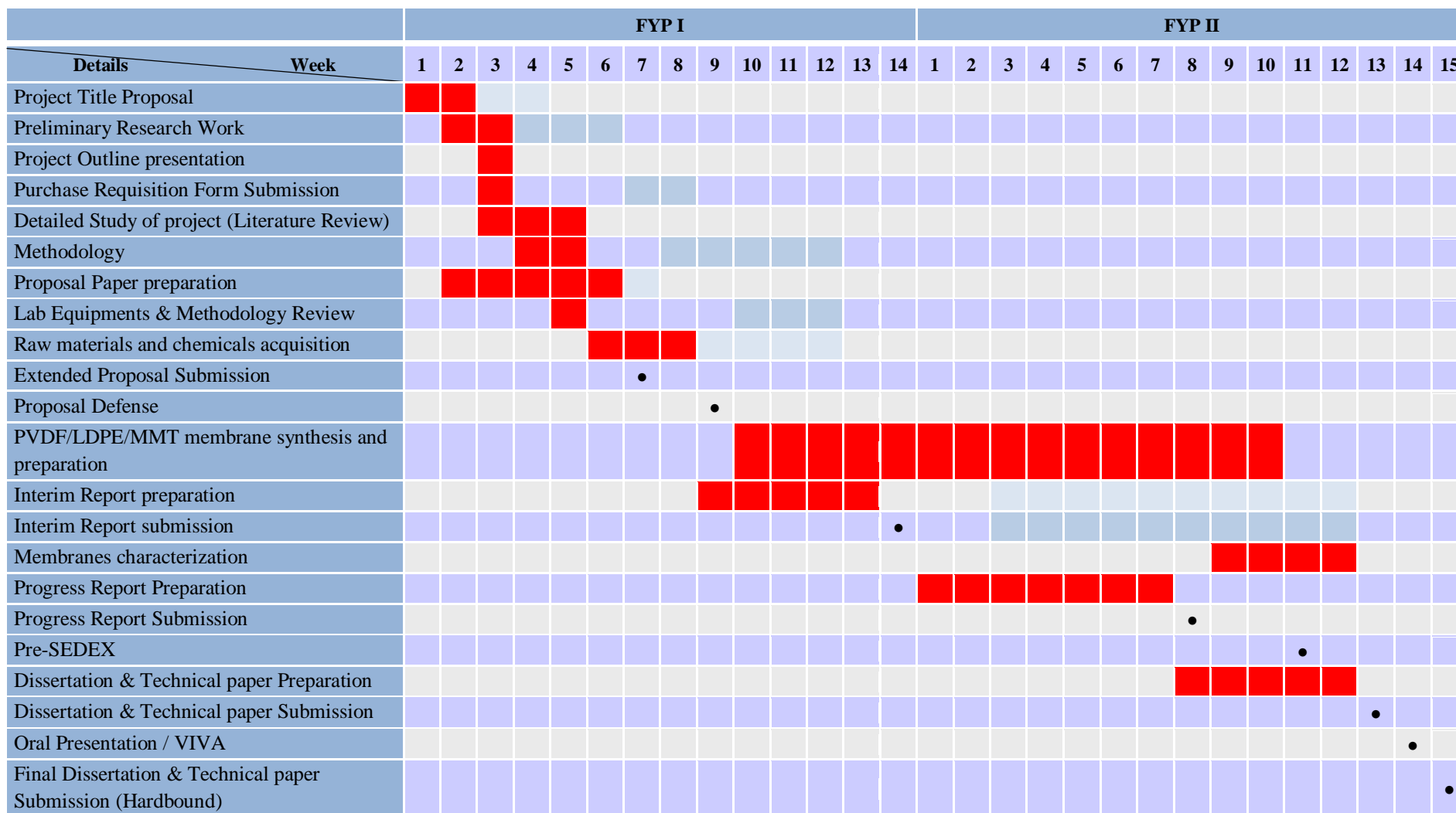
Details \ Week	FYP I														FYP II														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Project Title Proposal	■	■																											
Preliminary Research Work		■	■																										
Project Outline presentation			■																										
Purchase Requisition Form Submission			■																										
Detailed Study of project (Literature Review)			■	■	■																								
Methodology				■	■																								
Proposal Paper preparation	■	■	■	■	■	■																							
Lab Equipments & Methodology Review					■																								
Raw materials and chemicals acquisition						■	■	■																					
Extended Proposal Submission							●																						
Proposal Defense									●																				
PVDF/LDPE/MMT membrane synthesis and preparation										■	■	■	■	■	■	■	■	■	■	■	■	■	■	■					
Interim Report preparation									■	■	■	■	■																
Interim Report submission														●															
Membranes characterization																									■	■	■	■	
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Oral Presentation / VIVA																												●	
Final Dissertation & Technical paper Submission (Hardbound)																													●

Figure 1.1.   Gantt chart and Key Milestones

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CHAPTER 2
LITERATURE REVIEW

2.1 Gas Separation Membrane Technology

Methods commonly used for separation of CO_2 gases from natural gas include cryogenic distillation, adsorption, scrubbers and bubble columns. Development of new separation technology that are more cost effective and energy efficient emerged high as these conventional separation methods have drawbacks especially on their energy consumption and cost efficiency.

On this emerging technology, membrane gas separation serves as the viable option especially for the natural gas processing industry. Growth in membrane separation applications is relatively high and is increasing exponentially (Baker, 2001). Achieving greater separation efficiency, being cost effective, yield faster separation in compact modules and less space utilization are some of the great advantages of gas separation membrane which makes it highly reliable for applications in the industry.

Table 2.1. Gas separation membrane applications. Source: Reza & Amir (2010)

Common Gas Separation	Application
CO_2/CH_4	Natural gas treatment, Acid gas treatment
H_2/CH_4	Hydrogen refining
H_2/N_2	Ammonia synthesis
H_2/CO	Syngas processing
H_2O/CH_4	Natural gas dehydration
H_2S/CH_4	Sour gas treatment
He/N_2	Helium recovery
H_2O/Air	Dehumidification of air
O_2/N_2	Oxygen purification

Commercialization of gas separation membranes for natural gas processing was first established in the year of 1980's. The principle behind the membrane separation for CO_2 removal is the solution-diffusion mechanism. Gas separation membranes functions based on the diffusivity of different compounds rather than the molecular size basis (David & Kishore, 1999).

The permeation flux or permeability of a membrane for a particular gas could be defined as;

$$\frac{P_i}{l} = \frac{1}{A\Delta p}\frac{dV_i}{dt}$$

where V_i is the volume of gas permeated through membrane (cm^3, STP), A is the effective membrane area (cm^2), t is the permeation time (s) and Δp is the trans-membrane pressure drop (cmHg).

Permeability is not affected by the membrane properties alone but also the process conditions (Δp). Membrane selectivity towards CO_2 is obtained by calculating CO_2 permeability ratio to other components (i.e. methane, CH_4). It determines how effective the membrane permeates CO_2 in comparison to other components. As an example, for membrane selectivity of 30 towards CO_2/CH_4 separation, CO_2 diffuses the membrane 30 times faster than CH_4.

Selectivity measurements are as follows;

$$\alpha_{i/j} = \frac{(P_i/l)}{(P_j/l)}$$

where $\alpha_{i/j}$ is the selectivity of gas i to gas j, P_i/l and P_j/l are the permeability of the respective gas penetrants.

Both permeability and selectivity are important considerations when determining the performance of a membrane. Membranes of high permeability require less area for the separation process, thereby lowering the system cost. Higher selectivity membranes allow greater removal of CO_2 compared to the component of interest, which yields higher value of the product (David, & Kishore, 1999).

However, high permeability in CO_2 does not always results in high selectivity, though achieving these combined properties are an ongoing aim for membrane researchers. In

normal practices of obtaining a good membrane, highly selective membrane is prepared to the thinnest possible, to enhance its permeability. However, reduction in its thickness results in an extremely brittle membrane and therefore unusable (David, & Kishore, 1999).

2.1.1   Polymeric membranes

Polymeric membranes are the focus of commercialization for gas separation membranes because of their ease of manufacture (Scholes, Stevens, & Kentish, 2012). However, of the many hundreds polymeric membranes developed at research scale, only a few of them have reached commercialization.

Membranes can be further branched into porous and non-porous membranes. Porous membranes are firm and possess numerous voids with randomly distributed interconnected pores. Gas permeation in porous structures are based on the permeate characteristics and the membrane properties itself such as pore size and its distribution (Reza, & Amir, 2010). Porous membranes functions similar to the conventional filter, where molecules having a wide range of sizes could be effectively separated by the membrane. Porous membranes generally exhibit high permeability but inherent low selectivity values.

Apparently, non-porous membranes are higher in selectivity but lower in their permeability values. Non-porous membranes are prepared through thermal extrusion or solution casting methods. Polymeric membranes generally come under the non-porous category in which the gas separation takes place by the solution-diffusion mechanism. Refer Figure 2.1.
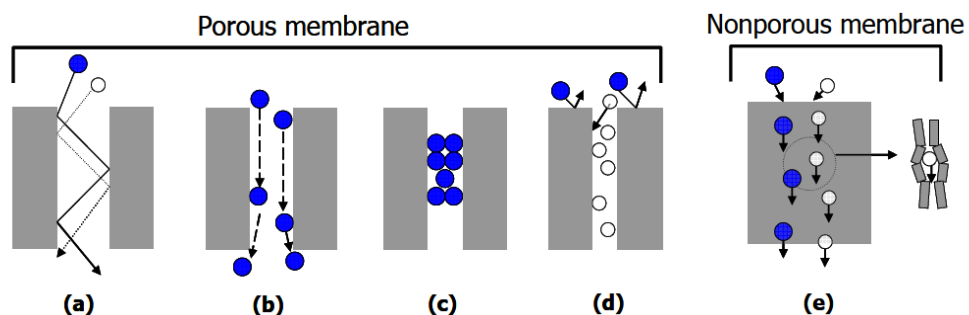

Figure 2.1.   Schematic representation of membrane based gas separations. (a) Knudsen-flow separation, (b) surface-diffusion, (c) capillary condensation, (d) molecular-sieving separation, and (e) solution-diffusion mechanism.

The solution-diffusion mechanism takes in a form of three steps; absorption or adsorption at the surface of membrane, activated diffusion through membrane pores, and finally desorption at the other side of the membrane.

Polymeric membranes can be further categorized into rubbery or glassy polymer, based on their glass transition temperature properties. Glassy polymers are highly selective but less in their permeability performances (Adewole, Ahmad, Ismail, & Leo, 2013). In contrary, rubbery polymers possesses high permeability but lower selectivity. More often, polymeric membranes lacks in their thermal and chemical stability. Table 2.2 displays the permeability and selectivity of CO_2/CH_4 gas separation for a range of polyimide membranes.

Table 2.2. CO_2 permeability and CO_2/ CH_4 selectivity for a range of polyimide membranes. Source: Scholes, Stevens & Kentish (2012)

Polymer	Pressure	Temp. (°C)	CO_2 permeability (Barrer)	CH_4 permeability (Barrer)	CO_2/CH_4
Matrimid 5218	10 bar	35	6.5	0.19	34
Matrimid 5218	2 bar	35	5.39	0.15	36
6FDA-TAPOB	1 bar	25	7.4	0.098	75
ODPA-TAPOB	1 bar	25	0.63	0.0064	98
PMDA-TAPOB	1 bar	25	3.3	0.066	50
6FDA-DATPA	10 bar	35	23	0.68	34
ODPA-IPDA	10 bar	35	0.301	0.0064	47
6FDA-6FpDA	10 bar	35	63.9	1.5	39.9
6FDA-6FmDA	10 bar	35	5.1	0.08	63.8
DAD-6FDA	300 psi	25	381	15.24	25
DAM-6FDA	300 psi	25	691	48.7	14.2
DDBT-BPDA	10 bar	50	8.2	0.24	34.2

2.1.2 Inorganic membrane

Limited performance in extreme conditions and barriers to abrasion and chemical attack of polymeric membranes has resulted towards the application of inorganic

membranes (Reza, & Amir, 2010). Inorganic membranes are highly selective and permeable thus having superior separation properties than polymeric membranes.

However, inorganic membrane comes with drawbacks of expensive and low mechanical strength thus rendering it to be mass produced in industrial scale. Adding to that, presence of components such as hydrogen sulfide and water induces negative effect towards CO_2 separation capabilities of the inorganic membrane (Zhang, Sunarso, Liu, & Wang, 2013). Research on modifying the surface properties of the inorganic membranes is being conducted, in order to counter the wettability effect on the membrane by water.

In addressing the issues concerning the polymeric and inorganic membranes, researches have expanded the idea of embedding nano-structured inorganic materials into the polymer matrix, thus incorporating the advantages of both the polymeric and inorganic membrane. This has led to the development of mixed matrix membranes (MMM) that potentially attains enhanced permeability and selectivity relative to their existing polymeric membranes.

2.2   Mixed Matrix Membranes (MMM)

MMMs are heterogeneous membranes composed of inorganic particles embedded in the polymeric membrane matrix (Zhang, Sunarso, Liu, & Wang, 2013). The addition of inorganic particles has three major effects imposed on their respective membranes in which they functions as molecular sieves to enhance the permeation properties of the membrane, modifies the structure of the membrane matrix to enhance its permeability and may even function as a barrier towards the gas permeation performance of the membrane.

Mixed matrix membranes are potential of having higher selectivity and permeability, enhanced thermal and chemical stability relative to their polymeric membrane (Reza, & Amir, 2010). Adding to that, the fragility of inorganic particles is hindered by the flexibility of the polymer matrix. Permeability of MMM is dependent on both the characteristics of the inorganic filler and polymer in use. However, superior gas separation properties of the MMM is majorly contributed by the inorganic filler's capability in molecular sieving.
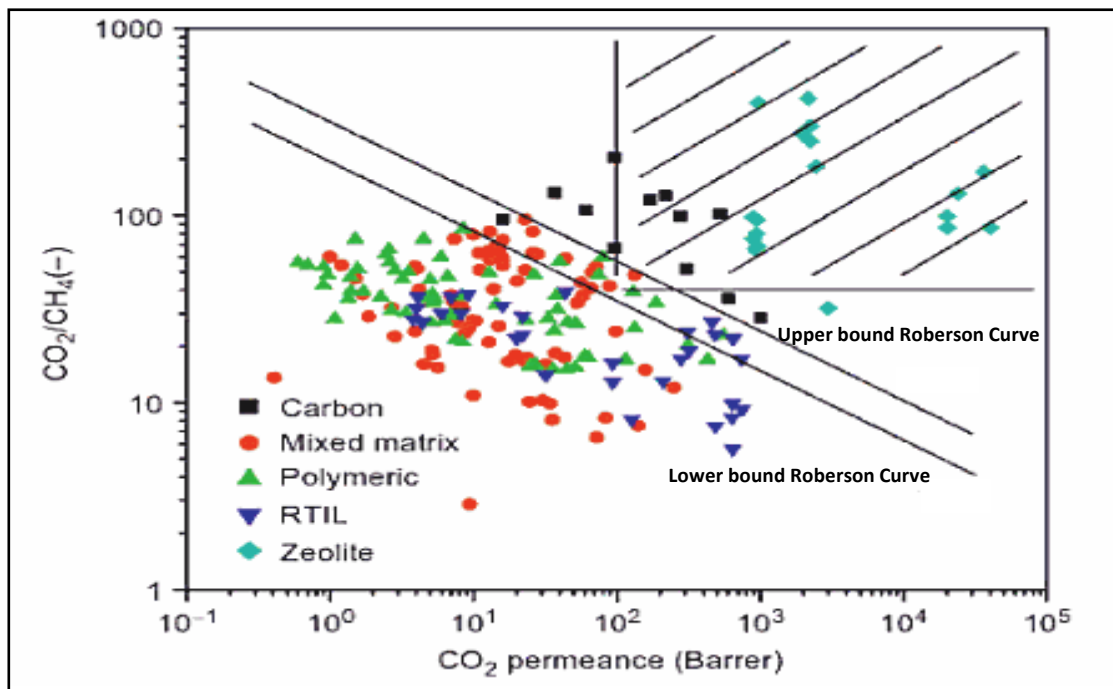
Figure 2.2.   Roberson Curve

Gas separation membranes basically have a trade-off between their permeability and selectivity performance as illustrated in the Robeson curve. Polymeric membranes are situated below the upper bound curve, signifying its low performance in gas separations. Theoretical works have concluded the presence of an asymptotic limit in the Robeson upper bounds trade-off curves, for the polymeric membrane separation capabilities. In return, works focused at developing membranes having the ability of performing well beyond the upper bound curve has focused on the mixed matrix membranes (Reza, & Amir, 2010).

Major challenge of developing MMM is to have effective distribution of inorganic particles in the polymer matrix. Inorganic particles disperse relatively poor in the polymer matrix and tend to agglomerate. This may result in the formation of stress convergence points which reduces the mechanical stability of the membrane and thus making it brittle (Zhang, Sunarso, Liu, & Wang, 2013).

To eliminate the defects of the MMM formed, few guidelines were proposed;

1. *Priming.* During the dope solution preparation, the inorganic particles are added to the solvent prior to the polymer. This ensures efficient polymer layer coating onto inorganic particles.

2. ***Choice of polymer material and inorganic filler***. Selection of polymer material is essential as it decides the transportation properties of the membrane. Inorganic fillers are selected based on their size, shape and their compatibility with the polymer matrix. Smaller inorganic particle provides larger polymer/particle interfacial area, thus improving the capability of the membrane in gas separations. In addition, smaller particles are significant for formation of thin and delicate MMMs.

3. ***Prevention of particle sedimentation and agglomeration.*** To prevent agglomeration of the inorganic particles which is mainly due to its sedimentation, high concentration of polymer solution is used. By this, the solution prepared would be highly viscous, thus slowing the particle sedimentation. The use of ultra-fine crystallites has signifcant reduction in the sedimentation rate.

4. ***Optimization of morphology interface.*** Polymers having flexible chain structure at practical conditions, forms excellent MMM. Polymers with lower glass transition temperature surround inorganic particles more evenly, forming an ideal MMM. Polymers of high glass transition temperature are incorporated with plasticizers to provide higher degree of flexibility to the membrane formed.

2.3   Polyvinyldene Fluoride (PVDF) Polymer

Polyvinyldene fluoride (PVDF) is a semi-crystalline polymer consisting of a crystalline phase and an amorphous phase. Refer Figure 2.3 for the molecular structure of PVDF.
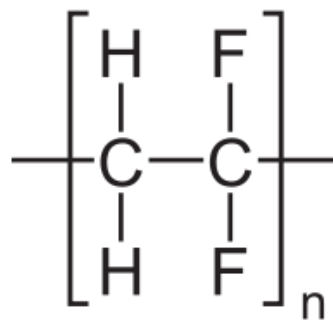

Figure 2.3.   PVDF polymeric structure

PVDF is synthesized through the free radical polymerization of 1, 1-difluoroethylene. Water with peroxy compounds are used as the synthesis medium for PVDF. This polymer has a density of around 1.78 g/cm^3 and a melting point of 177°C. The crystalline phase of the PVDF polymer is responsible for its thermal stability while the amorphous phase provides flexibility towards its membranes (S.A. Hashemifard, 2011). PVDF are relatively stable to chemical attacks including acids, oxidants and halogens.

PVDF are widely used in the electronics industry as they make good insulators. PVDF are highly flexible, having low thermal conductivity and high heat resistance. Despite of all these, PVDF have also been applied in the membrane field for various purposes. The polymer is popularly used to mobilize proteins, due to its non-specific affinity for amino acids. In gas separations, PVDF membranes are developed for removal of CO_2 from Nitrogen.

PVDF is valued for its toughness, stability and distinct engineering advantages. However, in gas separation applications, PVDF highly lacks on the hydrophobic properties which makes it less susceptible for industrial scale applications.

2.4   Low Density Polyethylene (LDPE) Polymer

Low Density Polyethylene (LDPE) is a thermoplastic polymer made from ethylene monomers. LDPE is within the range of density of 0.910-0.940 g/cm^3 of the numerous polyethylene grades. It can withstand a temperature of up to 95°C. LDPE have good resistance to chemicals such as acids, alcohols, bases and esters but they are less crystalline compared to other polymers. LDPE is widely consumed in containers, bottles and commercial plastic bags manufacturing. Figure 2.4 shows the typical molecular structure of LDPE.
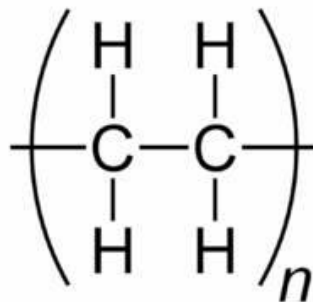

Figure 2.4.   LDPE polymeric structure

LDPE polymers are highly advantageous for industrial scale gas separation applications due to its superior hydrophobic characteristics. Membrane contactors commonly used in industrial gas separations are dominated by wetting problems, which refers to the increase in the membrane's mass transfer resistance. The increased resistance is a resultant of the penetration of the absorption liquid into the pores of the membrane that eventually lead to the decrease in the mass flux of the membrane over time (Ahmad, Mohammed, Ooi, & Zeo, 2013). Hydrophobic polymeric materials are required in place to counter the wetting problems, in which LDPE serves to be a viable option.

Studies involving LDPE membranes for CO_2 separation have been conducted over the years and it is still ongoing. In a study involving deposition of LDPE layer on the PSF membrane surface, conducted by Ahmad, Mohammed, Ooi, & Zeo (2013), the creation of the LDPE layer on the membrane surface results in a lotus-like membrane morphology which is responsible for its high hydrophobicity. The hydrophobic layer generated exhibits a 152° contact angle and a mean roughness of 4.8 times greater than the original layer. Reduction of CO_2 absorption flux in the LDPE coated membrane is only 14% after 1 day of operation and eventually stabilizes after 7 days. In contrast, the plain membrane experiences a reduction of 43% of its initial absorption flux within 1 day and a continuous decline of its flux over time.

In another study involving the fabrication of hydrophobic hollow fiber membrane for CO_2 capture in membrane contactors, LDPE was selected for its low commercial price and for its better chemical stability compared to other polyolefins. In the study, LDPE membrane was prepared using the melt-extrusion coupled with salt-leaching technique instead of the dry-wet phase inversion technique.

Table 2.3.　　　Physical properties of Low Density Polyethylene (LDPE).
Source: Azom.com (2013)

Physical properties of LDPE	
Density (g/cm^3)	0.91
Tensile Strength (MPa)	11
Flexural Modulus (GPa)	0.24
Water Absorption (%)	0.01
Dielectric Strength (MV/m)	27
Melting Temp. Range (°C)	230-275
Mould Shrinkage (%)	5
Mould Temp. Range (°C)	15-35

2.5　　Montmorillonite (MMT) Clay

Montmorillonite (MMT) are soft phyllosilicate minerals that occurs naturally in the form of clay. MMT belongs to the smectite family, whereby having a central octahedral sheet between two tetrahedral sheets.
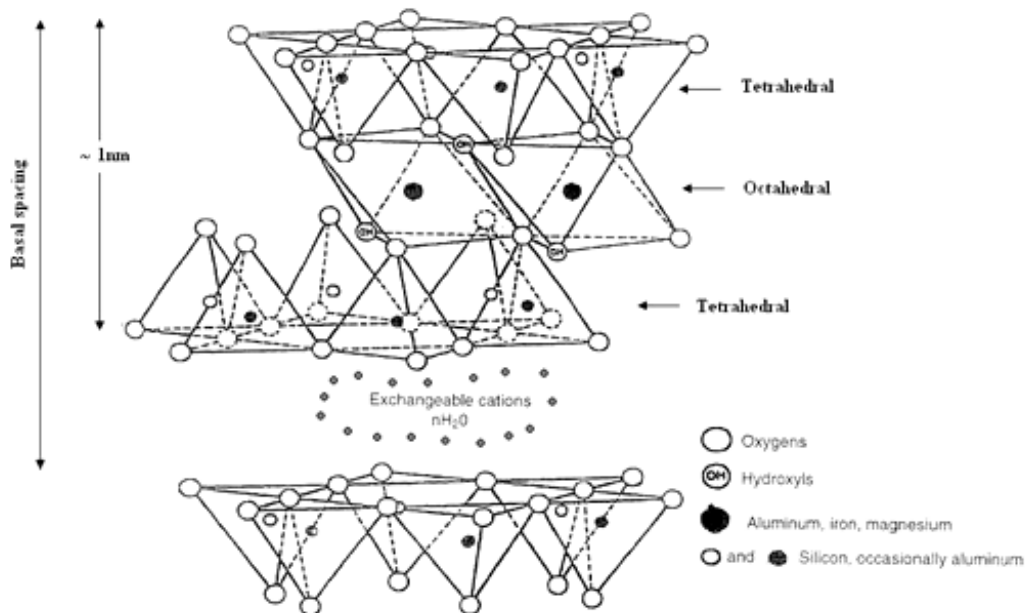

Figure 2.5.　　　Molecular structure of MMT

Over the past years, aluminosilicate mineral clays are dominant in synthesizing composite membranes, primarily used to enhance the mechanical properties of the

membrane. However, less attention have been devoted to aluminosilicate clays when MMT was introduced. A research by Liang et al. (2012) on the PES/MMT mixed matrix membrane has indicated enhanced thermal stability of the membrane compared to its pristine membrane, through the thermal gravimetric analysis. This improvement was contributed by the good thermal properties attained by the MMT inorganic fillers.

Incorporating inorganic fillers into the membrane matrix restrain the movement of molecules through the membrane, thus increasing its selectivity. However, only up to certain extent that optimum concentration of MMT could be added to get positive results. This is because; large amount of fillers will tend to agglomerate and induce formation of large voids in the membrane structure which eventually results in high permeability and low selectivity membranes (Chia-Yu Liang et. al., 2012).

CHAPTER 3
METHODOLOGY

3.1   Apparatus and Materials

Table 3.1.   List of Chemicals required

No.	Chemicals	Amount
1	Polyvinydene Fluoride (PVDF) polymer	250 g
2	Low Density Polyethylene (LDPE) polymer	250 g
3	Dimethylacetamide (DMAc)	2.5 Liter
4	Montmorillonite (MMT) clay	20 g
5	Distilled Water	3 Liter
6	Ethanol	2.5 Liter

Table 3.2.   List of Apparatus and Glassware required

No.	Apparatus / Glassware	Amount
1	Spatula	1
2	Tray (for coagulation bath)	2
3	Measuring cylinder	2
4	Beaker	2
5	Smooth glass plate (for membrane casting)	1
6	Casting knife	1
7	Covered bottle	3

Table 3.3.   List of Equipments required

No.	Equipments	Amount
1	Electronic balance	1
2	Hot plate stirrer	1
3	Ultrasonic degasser	1

3.2   Membrane Preparation Procedure

3.2.1   Preparation of PVDF/LDPE membrane

1. Polyvinyldene fluoride (PVDF) and low density polyethylene (LDPE) powder was prepared by drying it in an oven for 24 hours at a temperature of 80°C to remove any trapped moisture.

2. The LDPE powder was first dissolved slowly in Dimethylacetamide (DMAc) at 85°C under agitation using a hot plate stirrer and stirred moderately until the polymer dissolves completely.

3. The PVDF powder was then added slowly to the stirring solution. Dope solutions of 25wt% with different PVDF/LDPE polymer blends (95:5, 90:10, 85:15, 80:20, 75:25, and 70:30) were prepared. Refer Table I in the Appendix for details of the samples prepared.

4. The solution was left to stir for approximately 12 hours.

5. After stirring, the resulting homogenous solution was degassed for 4 hours and left overnight at room temperature to remove the gas bubbles in the solution.

6. The solution then was poured onto a smooth glass plate, placed on an even surface. Stainless steel casting knife was used to spread the solution to a uniform thickness.

7. The cast solution is allowed to evaporate at ambient condition for 10 minutes before being immersed into the coagulation bath.

8. After being immersed in the coagulation bath for 1 day, the membrane were then detached and immersed in ethanol for at least an hour.

9. The membrane was then air-dried for 24 hours at room temperature.

3.2.2 Preparation of PVDF/LDPE/MMT mixed matrix membrane

1. Polyvinyldene fluoride (PVDF), low density polyethylene (LDPE) and montmorillonite (MMT) was prepared by drying it in an oven for 24 hours at a temperature of 80°C to remove any trapped moisture.

2. The MMT was first dissolved slowly in Dimethylacetamide (DMAc) at 85°C under agitation using a hot plate stirrer and stirred moderately until it dissolves completely.

3. The LDPE powder followed by the PVDF powder was then added slowly to the stirring solution. Dope solutions of 25wt%; 85:15 (PVDF/LDPE) polymer blend with different concentration of MMT (1, 3, and 5wt%) were prepared. Refer Table II in the Appendix for details of the samples prepared.

4. The solution was left to stir for approximately 12 hours.

5. After stirring, the resulting homogenous solution was degassed for 4 hours and left overnight at room temperature to remove the gas bubbles in the solution.

6. The solution then was poured onto a smooth glass plate, placed on an even surface. Stainless steel casting knife was used to spread the solution to a uniform thickness.

7. The cast solution is allowed to evaporate at ambient condition for 10 minutes before being immersed into the coagulation bath.

8. After being immersed in the coagulation bath for 1 day, the membrane were then detached and immersed in ethanol for at least an hour.

9. The membrane was then air-dried for 24 hours at room temperature.

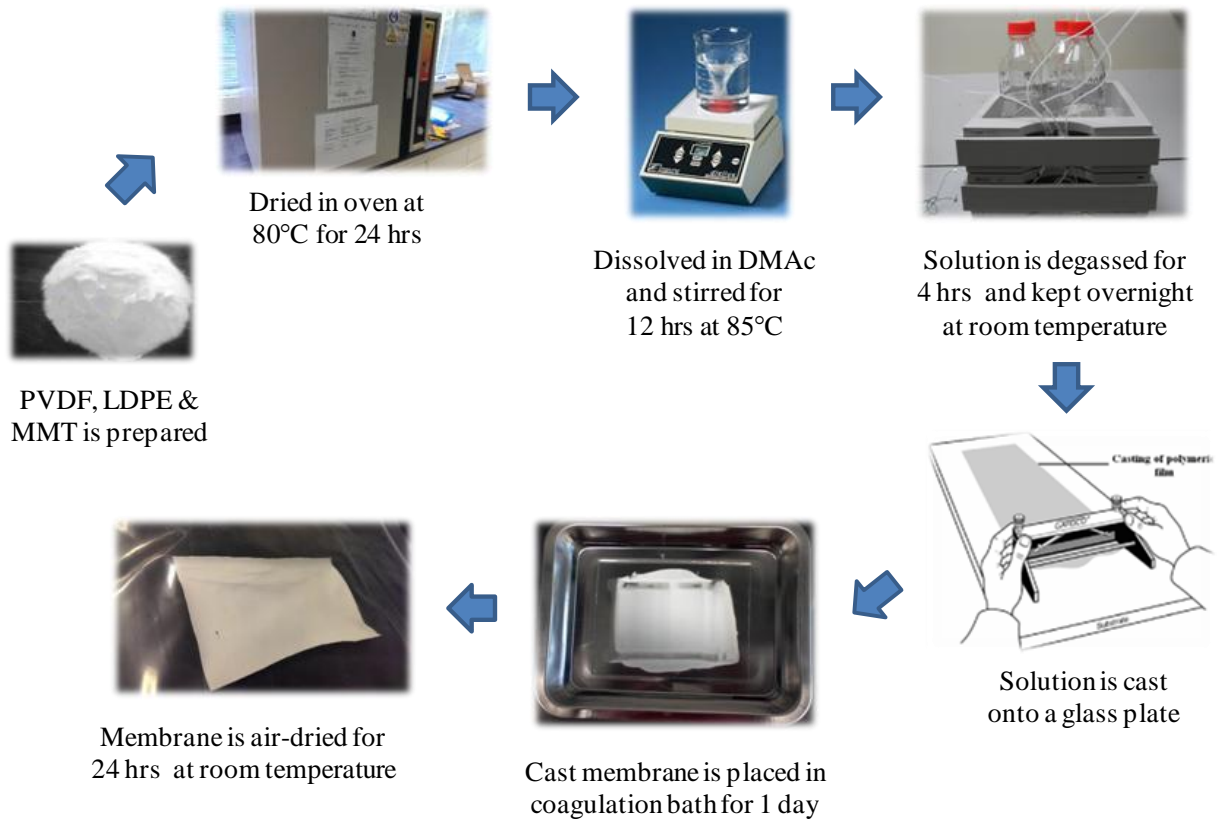### 3.2.3 Membrane preparation flow chart

Figure 3.1. Membrane preparation flow chart

3.3 Membrane Characterization and Gas Permeation Test

The prepared membranes were subjected to various characterizations such as field emission scanning electron microscopy (FESEM), thermal gravimetric analysis (TGA) and gas permeation tests. Characterization and gas permeation tests were intended to investigate the quality and performance of the synthesized membrane in terms of its morphological structure, thermal stability and gas separation properties. Table 3.4 briefly explains on the characterization techniques and gas permeation tests undertaken.

Table 3.4.   Membrane Characterization and Gas Permeation Test

Field Emission Scanning Electron Microscopy (FESEM)

- **Purpose:** To investigate the extent of adhesion between PVDF and LDPE polymers; and MMT inorganic fillers in the membrane matrix formed.
- **Procedure:** Sample is sputter coated with Gold/Palladium and mounted on aluminium holder with copper tape. The sample is viewed under an operating acceleration voltage of 15.0kV under magnifications up to 2000×.

Thermal Gravimetric Analysis (TGA)

- **Purpose:** To determine the weight changes of the membrane corresponding to a range of temperature, under a controlled atmosphere.
- **Procedure:** The test is carried out in a range of 40–700°C using 20°C/min of heating rate under nitrogen atmosphere. The decomposition temperature is determined at the point where 5% weight loss occurred.

Gas Permeation Test

- **Purpose:** To investigate the permeability of CH_4 and CO_2 gases and determine the selectivity of the membrane towards CO_2 separation.
- **Procedure:** The permeation test utilizes a gas permeation cell where the membrane was placed in between the cells and pressurized at the feed side. Permeation tests were conducted at 25°C and a pressure of 2 bar. the membrane was tested with pure gas of 99.97% purity in the sequence of CH_4 and CO_2. The permeation rate of the individual gases was determined using a constant-pressure method and a soap bubble flow meter.

CHAPTER 4
RESULTS AND DISCUSSION

4.1   Results

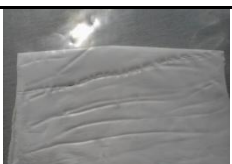Preliminary study of determining the optimal blend of PVDF/LDPE polymer mixture was conducted prior to the preparation of mixed matrix membranes. The study was based on the physical properties of the membrane formed. Parameters observed for evaluating the membranes include brittleness, surface tension, elasticity and smoothness of the membrane surface. Five samples of membranes having different composition of the PVDF/LDPE polymers were successfully prepared. The overall concentration of polymer in the dope solution was fixed to 25wt% as it was determined to be optimal for PVDF membranes. The results obtained for the membrane samples are described as in Table 4.1.

It was observed that membrane sample S3 possess the characteristics of a good membrane. Surface tension of the membrane was observed to be increasing as more of the amount of LDPE is being added into the casting solution. In contrary, the elasticity of the membranes reduces with decreasing amount of PVDF present in the membrane. PVDF provides essential structural support to the membrane thus enhancing the mechanical stability attained. Less wrinkles were observed in sample S3, thereby resulting in a smooth surfaced membrane.

From this preliminary study conducted, sample S3 having a composition of 85:15 PVDF/LDPE polymer blend exhibited the optimal membrane characteristics, thus, subsequently selected for further development into mixed matrix membranes. In this regard, varying amount of MMT inorganic fillers was added to the optimal polymer blend casting dope, resulting in the synthesis of mixed matrix membranes having different loading of the inorganic fillers. Effect of this MMT loading into the PVDF/LDPE polymer matrix was validated through various characterization techniques, which are further discussed in the following chapters.

Table 4.1.   Observations of the prepared membranes

Sample	PVDF/LDPE blend ratio	Synthesized Membrane	Surface Tension	Elasticity	Brittleness
S1	95:05		Moderate	High	Not Brittle
S2	90:10		Moderate	High	Not Brittle
S3	85:15		High	High	Not Brittle
S4	80:20		High	Moderate	Not Brittle
S5	75:25		High	Moderate	Not Brittle

4.2   FESEM Characterization

Preliminary studies have shown that, composition of 85:15 PVDF/LDPE polymer blend forms better membranes than other compositions utilized in the study. The results were validated through the FESEM characterizations obtained. The characterization was aimed to investigate the extent of adhesion between the PVDF and LDPE polymers in the membrane matrix formed.

Figure 4.1 illustrates the surface morphology of the polymeric membranes having 90:10, 85:15, and 80:20 compositions of PVDF/LDPE respectively. The resultant membranes are porous. Presence of LDPE particles is highly significant in the 80:20 polymeric membrane as a result of higher loading of the particles. Homogeneous distribution of the LDPE particles is observed across the membrane matrix. The uniform scattering of the LDPE particles across the membrane surface signifies low agglomeration and high compatibility of the polymers.
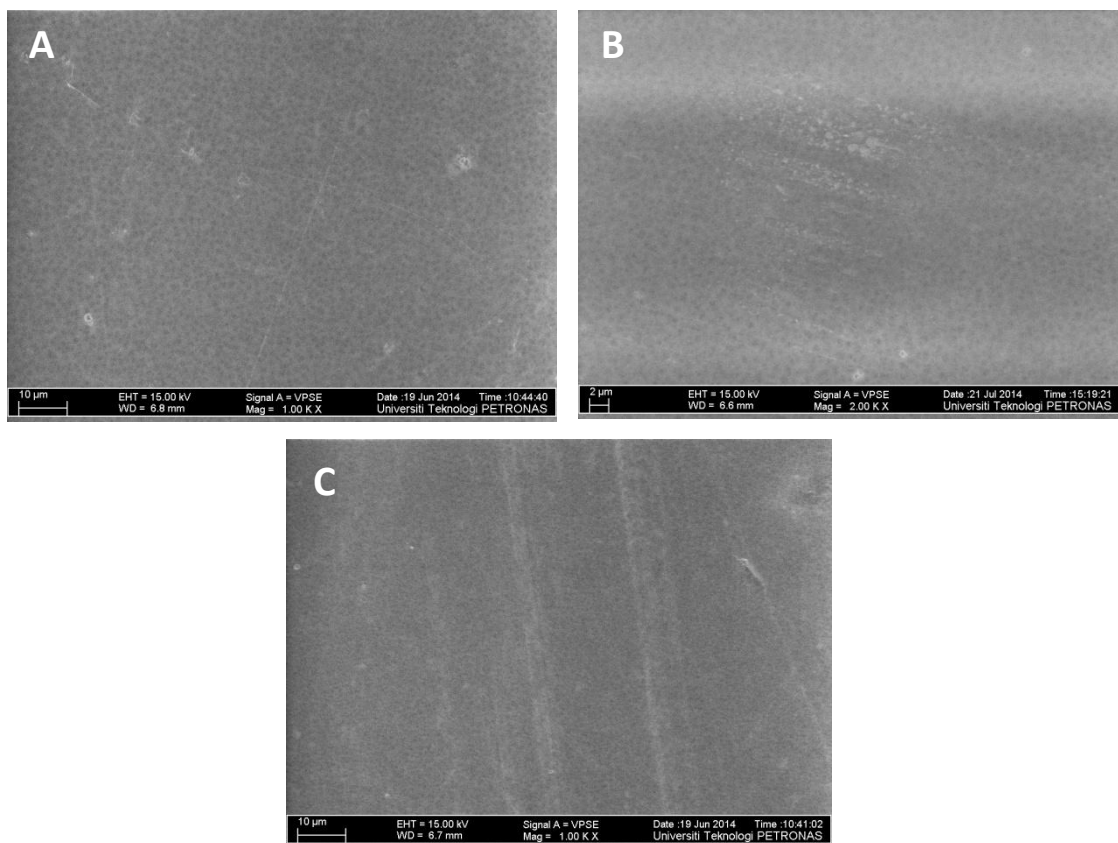

Figure 4.1.   FESEM micrographs of pristine **A)** 90:10 PVDF/LDPE **B)** 85:15 PVDF/LDPE **C)** 80:20 PVDF/LDPE polymeric membrane surface morphology at magnification of 1,000×

Cross-sectional structures of the pristine polymeric membranes having 90:10, 85:15, and 80:20 compositions of PVDF/LDPE are illustrated as in Figure 4.2. Formation of voids featuring finger like patterns were observed in the structure. Good adhesion between PVDF and LDPE is attained in the 90:10 and 85:15, PVDF/LDPE membrane composition, as a result of no any large voids or agglomerations observed across the membrane structure. It therefore signifies good compatibility of PVDF and LDPE particles.

However, significant agglomerations were observed across the membrane having 80:20 composition of PVDF/LDPE, resulting in formation of very large voids. This causes the membrane to experience reduction in its gas separation performance by having lower selectivity towards the molecules of interest. This signifies the presence of limit over the composition of PVDF and LDPE in which to be successfully cast into membranes. Ideally, 85:15 PVDF/LDPE pristine membrane present the characteristics of a good membrane with more of the LDPE loading. This composition therefore is selected for further development into mixed matrix membranes.
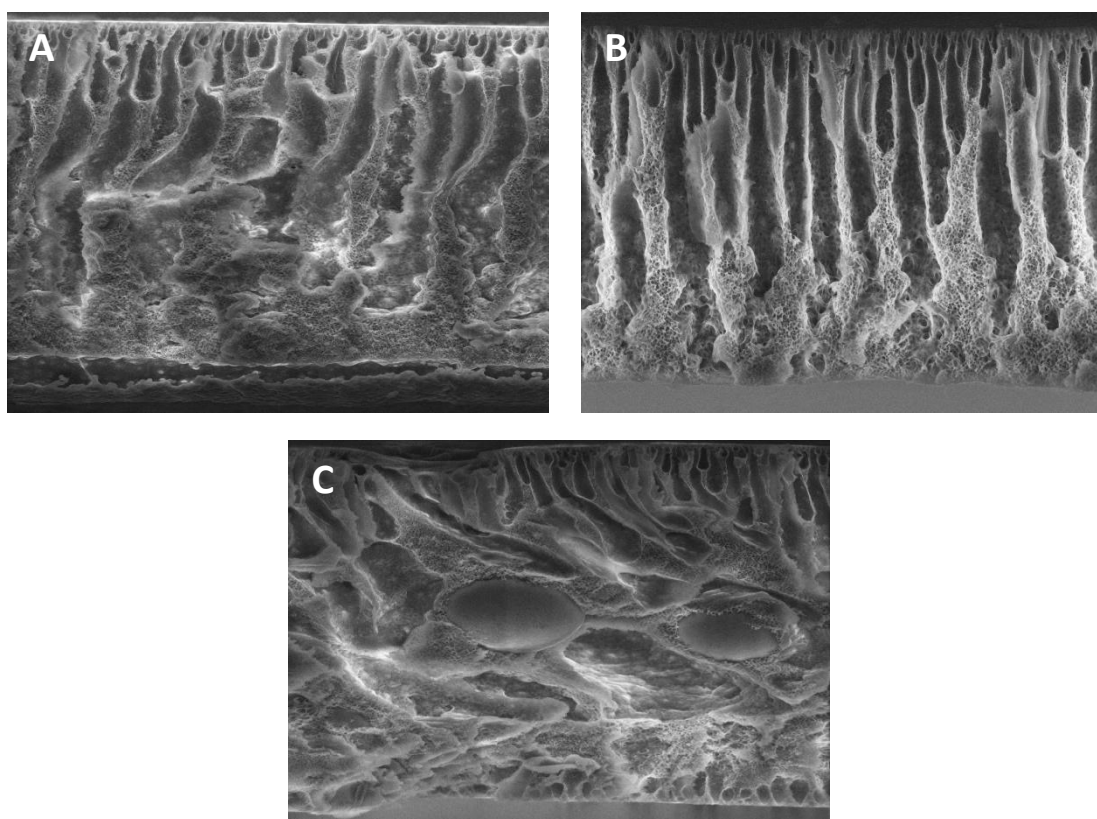

Figure 4.2.　　　FESEM micrographs of pristine **A)** 90:10 PVDF/LDPE **B)** 85:15 PVDF/LDPE **C)** 80:20 PVDF/LDPE polymeric membrane cross sectional structure at magnification of 700×

From the preliminary study conducted, 85:15 PVDF/LDPE polymer blend with 3wt% MMT loading exhibited the optimal membrane characteristics, thus, subsequently selected for further characterization. In this regard, FESEM was performed to investigate the extent of adhesion between MMT inorganic fillers and the PVDF/LDPE polymer matrix. The morphology of the membrane formed is highly significant for its performance in gas separation as it affects the permeability and selectivity of the membrane.

Figure 4.3 illustrates the surface morphology of pristine PVDF/LDPE membrane and PVDF/LDPE/MMT MMM. The measured thickness of the membrane was between 88 to 100 μm. The thickness and structure of the MMM is closely related to the polymer concentration and viscosity of the casting dope as well as the evaporation rate during casting (Ismail, 2003). It can also be noted that both the pristine PVDF/LDPE and PVDF/LDPE/MMT membranes are porous.

Homogeneous distribution of inorganic fillers was observed across the PVDF/LDPE/MMT MMM. The inorganic particles scattered uniformly throughout the polymer matrix as a result of low agglomeration of the fillers, aided by the small nano-sized particles and the sonication process.
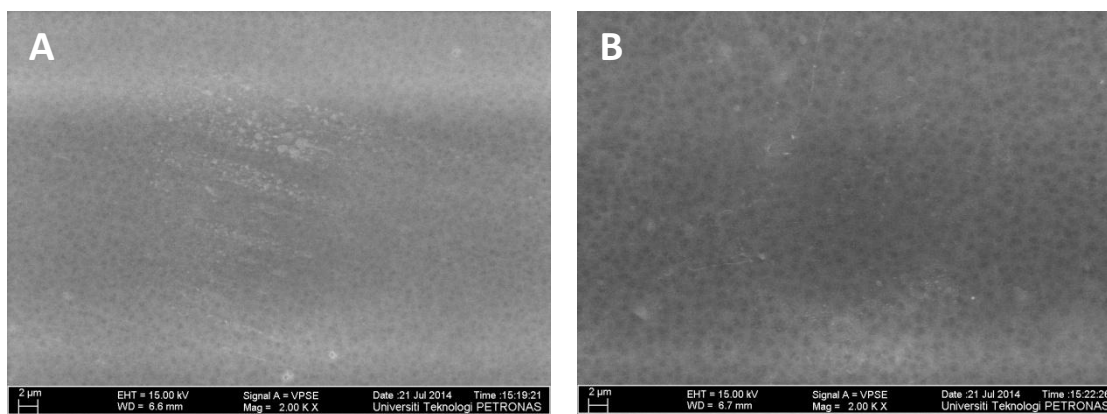

Figure 4.3.   FESEM micrographs of **A)** Pristine PVDF/LDPE **B)** PVDF/LDPE/3% MMT MMM surface morphology at magnification of 1,000×

Figure 4.4 shows the cross-sectional structure of pristine PVDF/LDPE membrane and PVDF/LDPE/MMT MMM. Thin and porous asymmetric structures of finger-like patterns were observed for both membranes. Good adhesion between the inorganic fillers and polymer matrix was attained at 3wt% nanoclay loading. Study by Aroon and colleagues supported this finding, in which nano-sized nonporous fillers such as

MMT was found to provide higher polymer-particle interfacial area and improved interface contact.
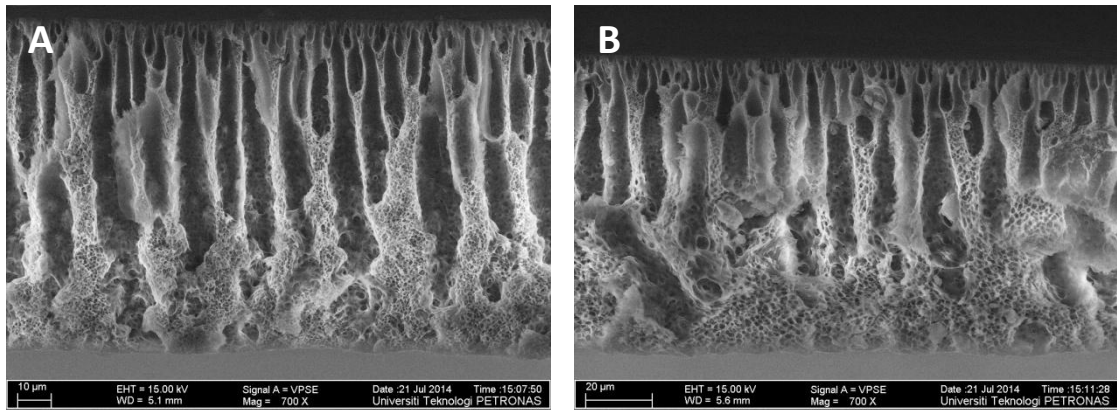

Figure 4.4.   FESEM micrographs of **A)** Pristine PVDF/LDPE **B)** PVDF/LDPE/3% MMT MMM cross-sectional structure at magnification of 700×

4.3   Thermal Gravimetric Analysis (TGA)

Figure 4.5 illustrates the thermal gravimetric analysis of pristine PVDF/LDPE and PVDF/LDPE/MMT MMM samples. Majority weight loss has occurred in the temperature range of 400-550°C for the membrane samples, which was mainly due to the decomposition of LDPE and PVDF. Pristine PVDF/LDPE membrane exhibited a decomposition temperature (T_d) of 480°C, signifying its excellent thermal stability.

Through the addition of MMT inorganic fillers, the mixed matrix membrane formed experiences much lower T_d than that of pristine membrane. The T_d obtained for the MMM at 1, 3 and 5wt% of MMT loading were 420°C, 405°C, and 400°C respectively. It is observed that for increasing filler content in the mixed matrix membrane formed, the T_d eventually decreases. The decreasing trend was more visible for the PVDF/LDPE/5%MMT MMM. Above the temperature of 520°C, the decomposition of MMM eventually reduces and approach stabilization except the PVDF/LDPE/3%MMT MMM. Pristine PVDF/LDPE membrane continues experiencing loss in weight beyond this temperature.
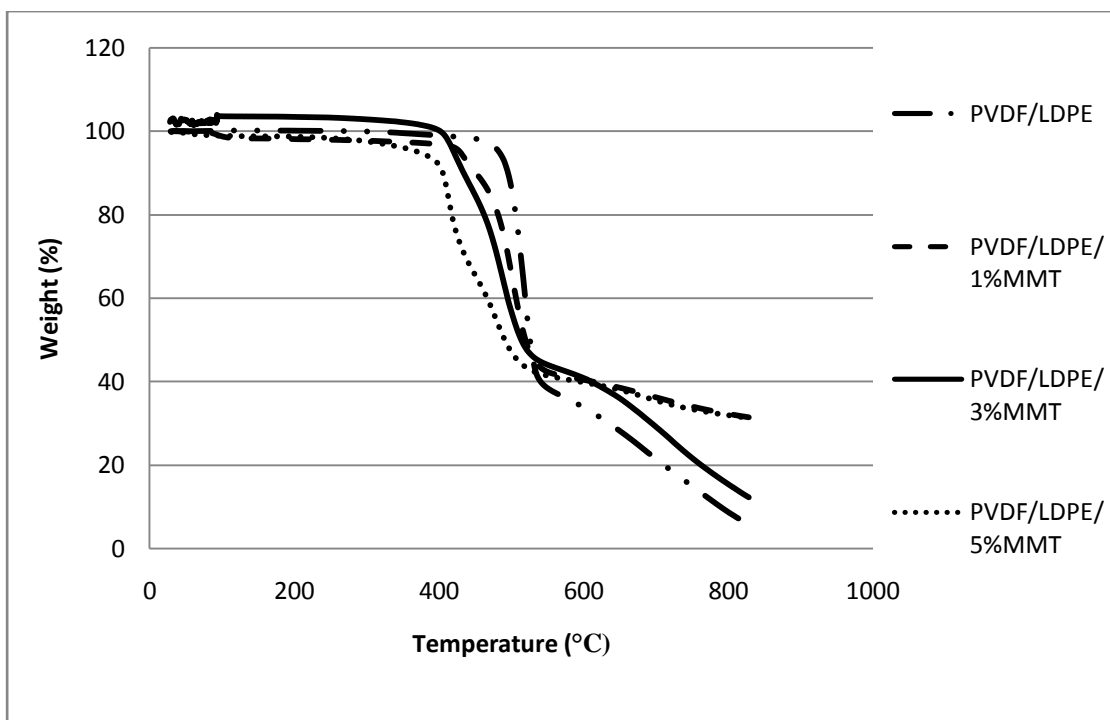
Figure 4.5.   TGA curves of pristine PVDF/LDPE and PVDF/LDPE/MMT MMM samples

Generally, the mixed matrix membranes are expected to possess enhanced thermal stability through the incorporation of inorganic fillers. On the contrary, the addition of MMT into the PVDF/LDPE polymeric membrane matrix has decreased its thermal stability. The results were probably due to the fact that the inorganic fillers might establish reactions with the degradation product of PVDF and LDPE, which caused in the acceleration of the decomposition process.

Similar results were obtained from a study conducted by Shen and Lua (2012) on PVDF membranes, in which incorporation of SiO_2, Zeolite 4A and MCM-41 have decreased the thermal stability of the PVDF matrix. Pure PVDF membranes were noted to attain higher residual weight percent than the PVDF/SiO_2 and PVDF/MCM-41 composite membranes.

4.4   Gas Permeation Test

Gas permeation test is conducted to investigate the permeability of CH_4 and CO_2 gases through the membrane and determine the selectivity of the membrane towards CO_2 separation. Figure 4.6 and 4.7 depicts the influence of MMT loading on the separation properties of MMMs. Interestingly, higher permeability of CO_2 gas was observed for MMM compared to the pristine membrane while both possessed similar

permeability towards CH_4 gases. The MMM exhibited a permeability of 1.572 and 1.042 of the CO_2 and CH_4 gases respectively, compared to the pristine membrane which only exhibited 1.21 permeability of CO_2 and 1.048 permeability of CH_4. A selectivity increment of 30.7% was attained by the MMM towards CO_2/CH_4 gas separation due to better segregation of the inorganic particles in separating CO_2.

This generally proves higher selectivity in CO_2 separation from CH_4 for the MMM. Increment in performance of the MMM compared to the pristine membrane was justified by good adhesion between the inorganic fillers and the polymer matrix. Incorporation of MMT inorganic fillers into the PVDF/LDPE membrane matrix has shown excellent improvement in both permeability and selectivity of CO_2 separation compared to the pristine PVDF/LDPE membranes. Therefore, MMT has been recognized as promising clay in which to be used as fillers in MMMs.
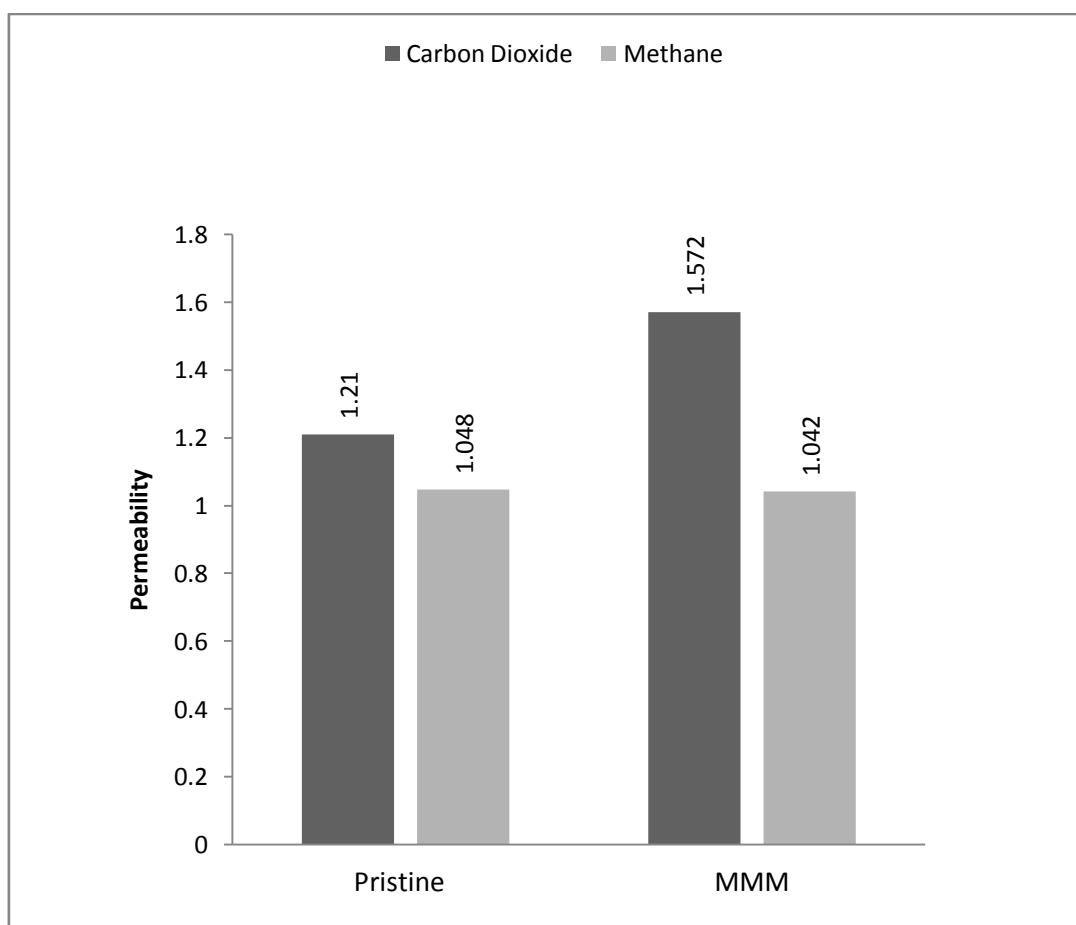

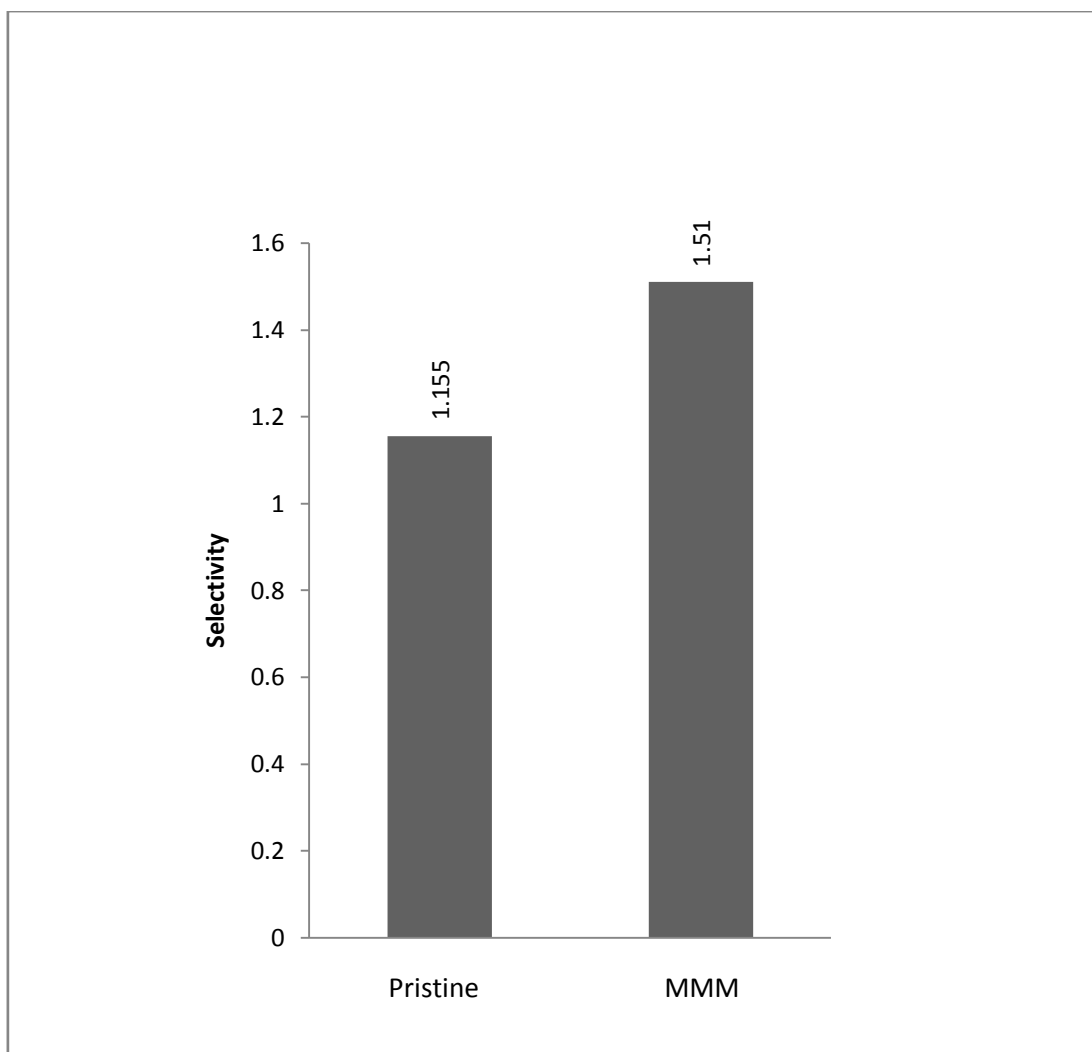Figure 4.6.   Effect of MMT loadings on PVDF/LDPE/MMT MMM CO_2/CH_4 permeance

Figure 4.7.   Effect of MMT loadings on PVDF/LDPE/MMT MMM CO_2/CH_4 selectivity

CHAPTER 5
CONCLUSION & RECOMMENDATIONS

5.1   Conclusion

Flat sheets of pristine PVDF/LDPE membrane and PVDF/LDPE/MMT mixed matrix membrane have been successfully fabricated through the dry/wet phase inversion technique. Optimal concentration of polymer in synthesizing a membrane was determined to be at 25 wt%. Composition of 85:15 PVDF/LDPE polymer blend have exhibited good membrane characteristics through its excellent features of surface tension, elasticity and brittleness. MMMs with this concentration and polymer blend were subsequently fabricated, incorporating 1, 3 and 5wt% of MMT, where 3wt% MMT loading was found to be optimum.

FESEM characterization and gas permeation tests performed showed that the mixed matrix membrane of PVDF/LDPE/3%MMT exhibits enhanced permeability and selectivity compared to the pristine PVDF/LDPE membrane. Good adhesion between inorganic fillers and polymer matrix was obtained for the PVDF/LDPE/3%MMT MMM reflecting its superior gas separation performance. However, thermal gravimetric analysis has shown addition of MMT inorganic fillers into PVDF/LDPE membrane matrix degrades the thermal stability of the resulting MMM formed.

5.2   Recommendations

The following recommendations are suggested for future works implementations on the PVDF/LDPE mixed matrix membrane;

i. Implementing other types of inorganic fillers into the PVDF/LDPE membrane as the substitute for MMT. Examples of the inorganic filler include halloysite nanotubes (HNT), zeolite and silica.

ii. Selecting other solvent or solvent mixtures in the preparing the PVDF/LDPE casting solution which may provide better segregation of the fillers into the polymeric structure.

iii. Experimenting different non-solvent mixtures for the coagulation bath, on the separation performance of the membrane formed.

iv. Implementing different methods of fabricating the membrane such as melt extrusion, wet phase inversion or template leaching techniques; and different membrane structure such as hollow fibers.

v. Investigating the applications of PVDF/LDPE membranes for other gas separations such as H_2/CH_4, H_2S/CH_4 and etc.

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APPENDIX

Table I.   Sample prepared for determining optimal PVDF/LDPE polymer blend

Sample	Polymer wt%	PVDF/LDPE blend ratio	Amount of PVDF (g)	Amount of LDPE (g)	Amount of DMAc solvent (ml)
1	25	95:05	2.9764	0.1567	10
2	25	90:10	2.8200	0.3133	10
3	25	85:15	2.6630	0.4690	10
4	25	80:20	2.5070	0.6270	10
5	25	75:25	2.3498	0.7833	10

Table II.   Sample prepared for determining effect of MMT on PVDF/LDPE MMM

Sample	Polymer wt%	PVDF/LDPE blend ratio	MMT wt%	Amount of PVDF (g)	Amount of LDPE (g)	Amount of MMT (g)
1	24	85:15	1	2.5565	0.4512	0.1253
2	22	85:15	3	2.3435	0.4136	0.3760
3	20	85:15	5	2.1304	0.3760	0.6266