Final Report

Synthesis and Characterization of 6FDA-Durene Polymer Based Mixed Matrix Membrane

by

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Dissertation submitted in partial fulfilment of the requirements for the Bachelor of Engineering (Hons) (Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

____
(DR YEONG YIN FONG)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
December 2012

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.

(HON LIAN HUNG)

ABSTRACT

In the present work, a series of mixed matrix membranes were synthesized. The polymer matrix was based on a polymer synthesized from 2,2'-bis (3,4-dicarboxyphenyl) hexafluoropropanedianhydride and durene diamine (6FDA-Durene). The inorganic fillers used were zeolite imidazolate framework (ZIF-8) and silicoaluminophosphate zeolite 34 (SAPO-34) respectively, with the weight percent ranging from 0 to 4.5 wt%. The morphologies of the resulting membranes were compared. From the comparison, the maximum loading of the inorganic particles that can be incorporated into the polymer matrix before phase separation between the inorganic particles and polymer matrix occurs is determined.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Natural gas is an important energy resource. The primary constituent of natural gas is methane (CH_4). Other low-boiling hydrocarbons such as ethane can also be present in the gas stream, along with some amounts of impurities such as sulphur compounds, carbon dioxide, and nitrogen; the exact composition of the raw natural gas differs from well to well (Guo & Ghalambor, 2005). In the context of gas processing, sulphur compounds and carbon dioxide represent a threat to equipment and pipelines as they are capable of forming corrosive acids on exposure to water (Kidnay & Parrish, 2006). In particular, carbon dioxide can also form undesirable dry ice in cryogenic processing of liquefied natural gas. Furthermore, the heating value of the natural gas is lowered depending on the carbon dioxide concentration as it is incombustible. The problem is especially significant in the Southeast Asia region, where CO_2 abundance can range from less than 10% to greater than 90% (Imbus, Katz, & Urwongse, 1998). Various technologies have been developed to remove carbon dioxide from natural gas, e.g. absorption by alkanoamines, condensation processes, and adsorption. An established technology is CO_2/CH_4 gas separation by membranes (Dortmundt & Doshi, 1999), which can offer significant advantage over more conventional processes in terms of energy and cost savings.

In industrial applications, apart from the need for desirable mechanical properties, two important performance parameters are the permeability and the selectivity. The selectivity or ideal separation factor refers to the ratio of permeability between two components being separated, whereas permeability is defined as the transport flux per unit transmembrane driving force per unit membrane thickness (Koros, Ma, & Shimidzu, 1996). A high selectivity gives rise to better separation, whereas a high permeability reduces pressure drop losses associated with the membrane separation because by definition less driving force is needed per unit transport flux. Unfortunately, it has been found that in polymeric membranes, attempts to increase the permeability generally lead to a loss in selectivity, i.e. an upper limit exists

(Robeson, 2008). Developing a membrane material retaining both characteristics remains a challenge.

Mixed matrix membranes (MMM) are an approach that attempts to overcome this shortcoming by incorporating dispersed solids with favourable gas separation properties into the membrane matrix, e.g. zeolites. Using suitable inorganic fillers, an increase in overall selectivity can be achieved (Noble, 2011) with minimal reduction in permeability. MMMs are potentially applicable to CO_2/CH_4 gas separations.

1.2 PROBLEM STATEMENT

Referring to Robeson's upper bound line, the performance of polymeric membranes have an upper bound (Robeson, 2008). Mixed matrix membranes have the potential to exceed the upper bound limit and therefore can be applied to CO_2/CH_4 separation by developing a right kind of mixed matrix membrane. However, the separation performance of a mixed matrix membrane can fall below expectation. It has been proposed that this is caused by improper interfacial contact between the solid phase and the bulk polymer phase. The loading of the inorganic filler and its size could affect the phase behaviour. Therefore, it is desirable to determine the maximum loading of inorganic filler that maintains the morphology of the membrane and does not cause phase separation between the membrane and the inorganic particles.

1.3 OBJECTIVE AND SCOPE

The objective of the present research is to study the effect of the inorganic particle loading on the 6FDA-Durene polymer membrane morphology and to determine the optimum loading of the inorganic particles that can be incorporated into the 6FDA-Durene polymer matrix before phase separation occurs.

The scope of the present work includes:

1. To synthesize a 6FDA-Durene polymer.
2. To synthesize mixed matrix membranes by adding SAPO-34 and ZIF-8 as inorganic fillers into6FDA-Durene polymer.

Based on existing literature, 6FDA-durene is selected as the material for the polymer membrane because it has high CO_2 permeability but low CO_2/CH_4 selectivity, and it is desired to improve the selectivity by adding inorganic fillers. SAPO-34 and ZIF-8 are selected as the inorganic fillers due to their high CO_2/CH_4 selectivity. More details are available in Chapter 2. The synthesis of the inorganic particles is carried out by group members.

1.4 RELEVANCE AND FEASIBILITY

The importance of the project is emphasized in the problem statement. In particular, the knowledge gained from this project will aid future polymer and membrane synthesis with application to CO_2/CH_4 gas separation. Given the short time frame, the scope is suitably selected such that it can be completed on time. For details, the planning is given in the Gantt chart (Chapter 3: Methodology).

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE TECHNOLOGY IN CO_2/CH_4 SEPARATION

Proven methods of CO_2/CH_4 separation include physical or chemical absorption, cryogenic processes, pressure-swing or temperature-swing adsorption by solids, and separation by membranes (Kohl & Nielsen, 1997). Among the various technologies, membrane separation processes have the advantage of being compact in size, requires few pieces of rotating equipment, and easy to scale up. However, due to their modular nature, there is no economy of scale associated with the use of membrane technology. Membrane separation systems typically require multiple stages or some degree of recycling (Olajire, 2010).

Membranes are generally classified into two broad classes, inorganic and organic/polymeric membranes. Inorganic membranes are classified based on the material used, e.g. metals and ceramics. Organic membranes are generally divided into rubbery and glassy types. Shekhawat, Luebke, & Pennline (2003) reported that most industrial permselective membrane processes for gas separation utilize glassy polymeric membranes because of their high gas selectivity and good mechanical properties. Polymeric membranes separate components by the solution-diffusion mechanism, thus differences in the solubility and mobility of the gas pair in the membrane needs to be significant for effective separation to take place (Rufford et al., n.d.).

2.2 POLYMERIC MEMBRANE SELECTION AND SYNTHESIS

2.2.1 Membrane Selection

Cellulose acetate (CA) is the most commonly used polymeric membrane in acid gas separations in the industry. Other materials include polyimide (PI) and perfluoropolymers. A good review is available by Scholes, Stevens, & Kentish (2012). Although CA membranes are widely used, there are some limitations, e.g. susceptible to plasticization. Polyimide membranes in general appear to be a better alternative due to its higher permeability and selectivity. In particular, 6FDA-based membranes are of particular interest and offer advantages against PI membranes based on other dianhydrides(Xiao, Low, Hosseini, Chung, & Paul, 2009).

For a 6FDA-based membrane, the choice of the diamine component is vast and affects the gas separation performance. Table 1 shows a comparison of various 6FDA-based membranes and their published performance data *sorted by selectivity* (Budiyono et al., n.d.; Xu & Xu, 1998; Lin & Chung, 2001; Kim, Park, So, Ahn, & Moon, 2003; Xiao et al., 2009; Chen, Rodrigue, & Kaliaguine, 2012; Liaw et al., 2012; Scholes et al., 2012).

Table 1: Brief comparison of some 6FDA-based membranes

Diamine	CO_2/CH_4 Selectivity	Permeability of CO_2 (Barrer)	Permeability of CH_4 (Barrer)
DAP on PES	79	38.6 (gpu)	0.5(gpu)
TAPOB	75	7.4	0.1
mDDS	74	2.3	0.03
6FmDA	64	5.1	0.1
HAB	60		
DAFO on PES	60		
DAFO	60	7.7	0.1
CDA	57	17.1	0.3
DAF	54	11.3	0.2
mPDA	50	10	0.2
44ODA	49	16.7	0.3
34ODA	49	6.1	0.1
3BDAF on PES	48		
pDDS	47	16	0.3
DABA on PES	47	26.3 (gpu)	0.6 (gpu)
MDA	45	19.3	0.4
IPDA on PES	43		
IPDA	43	30	0.7
6FpDA	40	63.9	1.5
APPS on PES	39		
PPTI-1	35	23.1	0.7
DATPA	34	23	0.7
ECDA	33	33.8	1.0
BAPAF on PES	23	24.6 (gpu)	1.1 (gpu)
Durene	20	677	33.7
TPEQ		12.6	
TPER		5.13	
ODA		20	

It was noticed that durene diamine exhibits a high permeability for carbon dioxide, although the selectivity for CO_2/CH_4 is relatively low (Lin & Chung, 2001). Thus 6FDA-dureneis selected for synthesis and modification in this study. By incorporating inorganic fillers having high CO_2/CH_4 selectivity, it is expected that the mixed matrix membrane will demonstrate improved properties, especially selectivity, over the original dense film membrane. The structure of the 6FDA is shown in Figure 1. The structure of the durene diamine is shown in Figure 2.

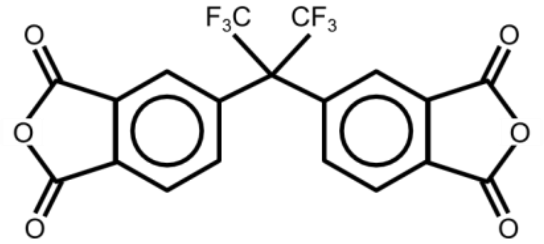


Figure 1: Structure of 6FDA

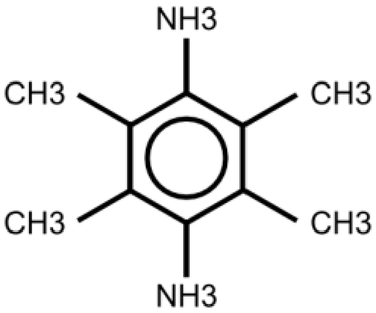


Figure 2: Structure of durene diamine

2.2.2 Materials Preparation

This section describes how other researchers have purified the materials used in synthesizing 6FDA-Durene mixed matrix membranes. 6FDA can be purified by sublimation (Y. Liu, Wang, & Chung, 2001). Polymer grade 6FDA can be purified by drying “at 180 °C for at least 12 hours under vacuum (~5 torr) prior to use” (Farr, 1999, p. 103). 6FDA can also be purified by “[drying] at ~180 °C under vacuum for at least 12 hours prior to use” (Dunson, 2000, p. 127). Durene diamine can be purified by recrystallization from methanol (Y. Liu et al., 2001). Y. Liu et al. purified NMP by “distill(ing) at 42 °C under 1 mbar after drying with molecular sieves”. In most syntheses, acetic anhydride, triethylamine, methanol, and THF are used as received.

2.2.3 Polyamic Acid Preparation

In 6FDA-durene polymer both species are used in equimolar amounts. The two reaction steps are polyaddition and polycondensation. The first step is to mix the two monomers in a polar aprotic solvent, typically NMP (1-methyl-2-pyrrolidinone). (Other suitable solvents include dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and dimethylacetamide (DMAc).) A more basic solvent leads to a higher reaction rate (Ratta, 1999;Dunson, 2000). The reaction rate is also affected by the choice of the diamine and dianhydride (Bregg, 2007). Usually the diamine is added first, followed by the dianhydride such that the chances of the dianhydride reacting with the diamine are higher than the chances of it being hydrolyzed by any trace amounts of water present in the solvent (Farr, 1999). The intermediate from this first step is termed a polyamic acid (Figure 3).

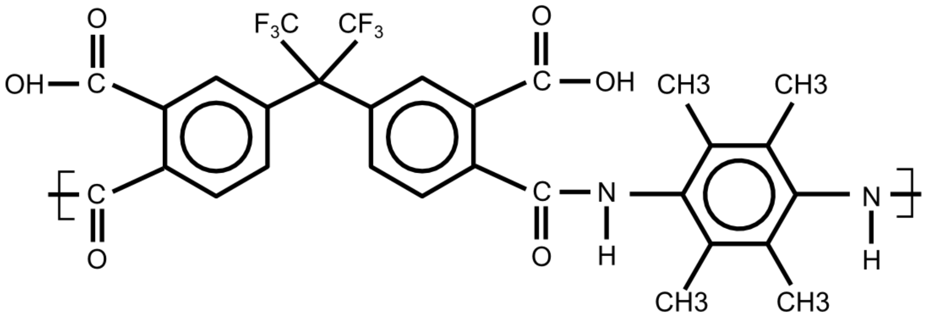


Figure 3: Polyamic acid synthesized from 6FDA and durene diamine

2.2.3 Imidization

Once the polyamic acid is formed, ring closure is then promoted via thermal or chemical imidization (Figure 4). Thermal imidization is conducted by heating the polyamic acid to induce the removal of water (polycondensation). Chemical imidization is more complicated and involves the use of a dehydrating agent such as acetic anhydride to remove the water species in an amount of slightly excess than the equimolar amount of water produced by the reaction, and a tertiary amine catalyst e.g. pyridine and beta-picoline (Edman & White, 2003). In the case of 6FDA-Durene two mols of water is evolved per mol of polymer formed. In one synthesis example, the amount of water used was 10% excess of the equimolar amount (Vora, 2003, p. 612). Edman & White also reported that the catalysts are “used in varying amounts up to several moles per mole of anhydride dehydrating material". In another example for synthesis of 6FDA-durene,the amount of triethylamine is used is 4 parts acetic anhydride to 1 part triethylamine (Y. Liu et al., 2001).

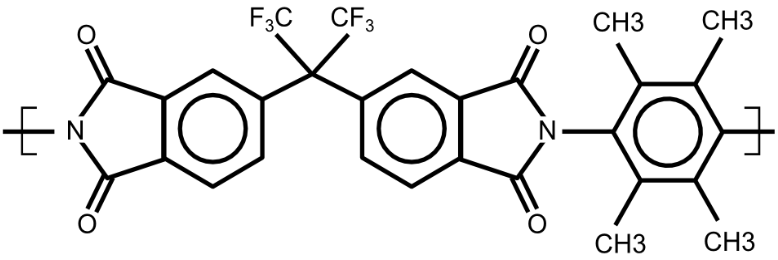


Figure 4: 6FDA-durene polymer structure

2.2.4 Dense Flat Sheet Membrane Formation

The polymer is first dissolved in a solvent with a high solubility for the polymer, e.g. tetrahydrofuran (THF) or dichloromethane (DCM). The solution is then casted on a flat surface, e.g. Petri dish, and the solvent evaporated thermally. A vacuum atmosphere can be used during heating to ensure thorough removal of solvent, e.g. (Kusworo, Ismail, Mustafa, & Matsuura, 2008).

2.3 INORGANIC FILLERS

The mixed matrix membrane is formed by the addition of inorganic fillers into the membrane polymer matrix. Conventional fillers such as zeolites and carbon molecular sieves have been studied extensively; alternative fillers such as metal organic frameworks have also been reported in CO_2/CH_4 gas separation using mixed matrix membranes (Goh, Ismail, Sanip, Ng, & Aziz, 2011).

Zeolites are microporous crystalline compounds made up of atom groups comprising elements such as Si and Al arranged in a tetrahedral structure (Ghobarkar, Schäf, & Guth, 1999). These atoms groups are coordinated to oxygen atoms. SAPO-34 is of particular interest in separation, catalytic, and adsorption technology because of its chemical and thermal stability (Li, Falconer, & Noble, 2004). In the context of CO_2/CH_4 separation, SAPO-34 demonstrates good separation performance; the pore mouth of this zeolite is comparable in size to the kinetic diameter of CH_4 but larger than that of CO_2, and selective adsorption is therefore possible (Ashraf Talesh, Fatemi, Hashemi, & Emrani, 2010). SAPO-34 membranes has in fact been applied to CO_2/CH_4 gas separation with reasonable success; the separation selectivity were observed to be as high as 290 (Chew, Ahmad, & Bhatia, 2011; Li et al., 2010).

2.4 MIXED MATRIX MEMBRANES

Despite mixed matrix membranes not being a new concept, very few attempts to increase the gas separation performance via mixed matrix membranes (MMMs) have been reported (Aroon, Ismail, Matsuura, & Montazer-Rahmati, 2010). The failure of MMMs to achieve their expected performance can be attributed to compatibility between the polymer material and inorganic filler, size of the inorganic filler particles, particle agglomeration, interface morphologies, pore blockage, and polymer chain rigidification around inorganic particles (Chung, Jiang, Li, & Kulprathipanja, 2007). To date, the exploration of mixed matrix membranes remains challenging because there is no reliable and standard approach to identify suitable materials for the mixed matrix membrane (Chung et al., 2007).

Most polyimide MMMs were based on Matrimid and/or copolymers. 6FDA-based MMMs applied to CO_2/CH_4 gas separation are quite rare. In line with the scope of this study, the performance of some existing 6FDA-based MMMs are reviewed in Table 2 (Pechar, Tsapatsis, Marand, & Davis, 2002; Tena et al., 2010; Nik, Chen, & Kaliaguine, 2012).

Table 2: CO_2/CH_4 gas separation performance for 6FDA-based MMMs

Polymer	Inorganic filler	CO_2/CH_4 selectivity	Permeability of CO_2 (Barrer)	Permeability of CH_4 (Barrer)
6FDA-ODA	UiO-66	46.1	50.4	1.10
	NH2-UiO-66	51.6	13.7	0.27
	MOF-199	51.2	21.8	0.43
	NH2-MOF-199	59.6	26.6	0.45
	UiO-67	15.0	20.8	1.40
6FDA-6FpDA-DABA	ZSM-2	24.2	16.0	0.33
6FDA-6FpDA	γ-alumina	36	70	
	Silanized alumina	51	51	
	PVP coated alumina	36	70	

2.5 SUMMARY

CO_2 removal from natural gas is an established technology. However, there are limitations on the performance of the membrane, especially in terms of permeability and selectivity. The performance is limited by the Robeson upper bound mentioned earlier. Mixed matrix membranes are an approach to overcome this weakness. The idea is that by incorporating inorganic fillers with high CO_2/CH_4 selectivity into the polymer matrix, the overall selectivity will increase while ideally maintaining the permeability. However, phase separation may occur when the inorganic filler loading is too high. Researchers have typically used less than 5 wt% loading. A suitable candidate for this study is 6FDA-durene because they have high permeability but low CO_2/CH_4 selectivity. SAPO-34 and ZIF-8 is hypothesized to be suitable as the inorganic filler because they exhibit high CO_2/CH_4 selectivity of up to 290 (Chew et al., 2011; Li et al., 2010).

CHAPTER 3

METHODOLOGY

3.1 MATERIALS

Durene diamine and 2,2'-Bis (3,4-Dicarboxyphenyl) hexafluoropropanedianhydride (6FDA) monomers were used as received. N-methyl-pyrrolidinone (NMP) solvent was purified using a rotary evaporator. Methanol solvent was used as received. Acetic anhydride (AA) and triethylamine (TEA) were used as received. Deionised water with a conductivity of less than 16 MΩ·cm was used.

3.2 PREPARATION OF 6FDA-DURENE POLYMER

The synthesis of 6FDA-Durene polymer using the chemical imidization method is outlined below (Y. Liu et al., 2001).

1. Durene diamine monomers were dissolved in purified NMP. Stirring was continued for one hour to ensure that all the monomers have dissolved. Nitrogen purge was applied throughout to minimize side reactions that will occur when the solution is exposed to oxygen and water moisture from air.
2. 6FDA monomer was added and allowed to react with the durene diamine monomers. Stirring is continued under nitrogen purge.
3. After 24 hours, a viscous polyamic acid (PAA) solution formed in the reaction flask.
4. Acetic anhydride and triethylamine were added to the solution to allow chemical imidization to occur. The reaction mixture was stirred under nitrogen for another 24 hours.
5. The reaction mixture was then precipitated using a suitable precipitating agent. Excess monomers were washed off from the polymer precipitate by immersing the precipitate into the wash solution. The final polymer precipitate was collected by filtering off the wash solution.
6. The collected polymer was dried at 110 °C in an oven to remove any residual wash solution.

The synthesis steps are conveniently summarized in Figure 5 below.

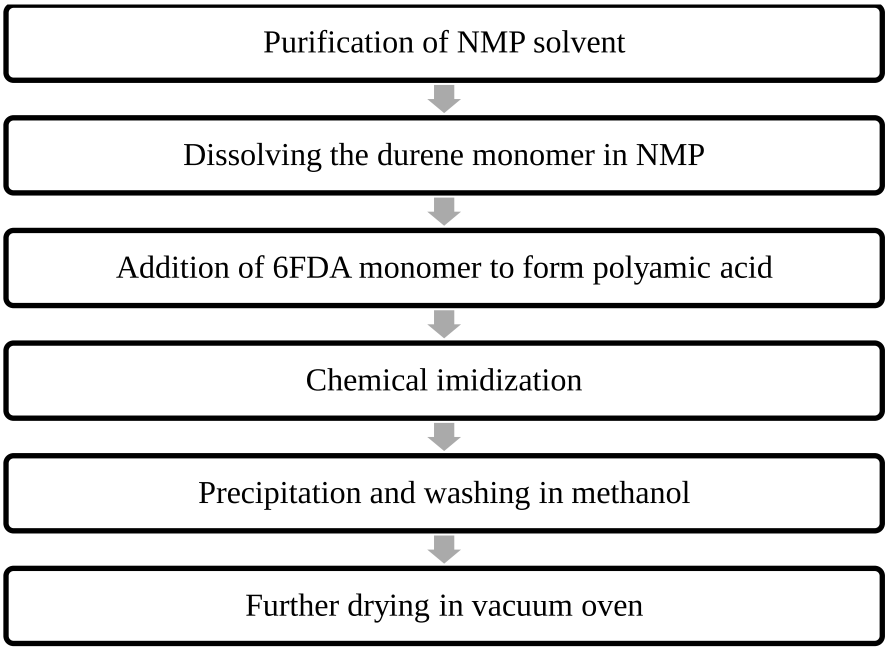


Figure 5: Steps to synthesize the polymer

3.2 PREPARATION OF MIXED MATRIX MEMBRANES

The preparation of mixed matrix membranes using the chemically-imidized polymer is described below. Various organic solvents were tested and the type used for each synthesis run is listed in Chapter 4 (Results and Discussion).

1. The inorganic particles (1.5 – 4.5 wt%) were added to the organic solvent. (For the control, no inorganic particles are added.)
2. The synthesized polymer was redissolved using the organic solvent containing the inorganic particles. The polymer solution was then placed in a sonic bath to help disperse the particles.
3. The polymer solution was cast on a Petri dish using a syringe (with a syringe filter, which does not remove the nanosize inorganic particles).
4. The membrane film was finally produced by drying off the solvent in a vacuum oven at 60 °C at 60 mbar for 48 hours. The phase separation of the particles with the membrane, if any, can then be observed.

For the thermal imidization method, the NMP containing the inorganic particles is used to dilute the viscous PAA solution to 13 wt% polymer in NMP solvent. The thermal imidization is then carried out. The diluted PAA solution was cast on a Petri dish after being filtered using a syringe filter. It is then dried using a vacuum oven at 60 °C at 60 mbar for 48 hours. This drying step is necessary to remove the solvent in the polymer matrix prior to imidization. A thin film was produced on the Petri dish, which was imidized by heating it under vacuum at 200 °C at 60 mbar for another 48 hours.

3.3 PROJECT ACTIVITIES & KEY MILESTONES

There are two key project activities, i.e. are the synthesis of the 6FDA-Durene polymer and its modification to become mixed matrix membranes. The modification is done via the incorporation of inorganic particles SAPO-34 and ZIF-8. The phase separation of the membranes is then observed to determine the optimum loading of the inorganic particles before phase separation between the polymer matrix and inorganic particles occur. Table 3 shows the key milestones of the project.

Table 3: Key milestones of the project

Milestone	Completed
Confirmation of title and supervision	16/6/2012
Preparation of synthesis procedures, literature review, etc.	29/7/2012
Booking of lab equipment and purchase of chemicals	15/8/2012
Synthesis of polymer	24/11/2012
Synthesis of mixed matrix membrane	30/11/2012
Characterization of mixed matrix membrane	7/12/2012

3.4 TOOLS REQUIRED

In addition to standard lab apparatus (glassware, stirrer set, etc.), important equipment for the completion of the study includes the rotary evaporator, oven, vacuum oven, and a sonicator. Analytical equipment required includes thermal gravimetry analysis (TGA) equipment for the determination of the decomposition temperature of the synthesized polymer.

3.5 GANTT CHART

Table 4 and Table 5 show the planning and Gantt chart for the project.

Table 4: Gantt chart for FYP I

Month:	May		June				July				Aug					Sept	
Item Week:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Confirm supervision and title	x	x	x	x													
Paperwork, procedures, interim report draft					x	x	x	x	x	x							
Booking of lab equipment and purchase of chemicals							x	x	x	x	x	x	x				
Preparation for proposal defence							x										
Proposal defence								x	x								
Synthesis of polymer													x	x	x		
Submission of interim report														x	x		
Study week, exam week, sem break															x	x	x

Table 5: Gantt chart for FYP II

Month:	Sept		Oct				Nov					Dec				Jan	
Item Week:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Synthesis of polymer	x	x	x	x	x	x	x	x	x	x							
Progress report (submit 5/11)					x	x											
Synthesis of mixed matrix membrane							x	x	x	x	x						
Characterization of mixed matrix membrane									x	x	x	x	x				
Documentation, data analysis, report writing, poster preparation										x	x	x	x				
Pre-EDX											x						
Draft report submission												x					
Dissertation + technical paper submission													x				
Oral presentation													x	x	x		
Study week, exam week, sem break															x	x	x

CHAPTER 4

RESULTS AND DISCUSSION

4.1 PREPARATION OF 6FDA-DURENE POLYMER

The polymer synthesis runs are listed in Table 6 below (NMP: N-methyl-pyrrolidinone).

Table 6: Results of polymer synthesis runs using different wt% monomers in NMP

Polymer batch	Weight percent of monomers in NMP solvent (wt%)	Precipitated in methanol	Precipitated in water	Remarks
1	22.5	No	Not tested	Yield was insufficient to test precipitation in water
2	25.0	No	Yes	Short precipitate strands and small flakes were formed
3	27.5	No	Yes	Both short and long precipitate strands were formed
4	30.0	No	Yes	Long precipitate strands were formed
5	32.5	No	Yes	Long and thick precipitate strands were formed

The polyamic acid was first synthesized using 22.5 wt% of monomers in NMP solvent and subsequently imidized to polyimide by the addition of acetic anhydride (AA) and triethylamine (TEA). It was observed that the viscosity of the solution is very low. This is attributed to using the monomers as received. Impurities in the mixture solution lead to side reactions that lower the average molecular weight (hence viscosity) of the polyamic acid (PAA). The resulting polymer also dissolved in the original precipitating agent (methanol) due to the low degree of polymerization and no polymer was recovered. In order to increase the molecular weight of the polymer form, further synthesis runs were applied: 25 wt%, 27.5 wt%, 30 wt% and

32.5 wt% monomers in NMP, respectively. Each synthesis run consumes about seven days.

The rationale for increasing the concentration of the monomers is based on the fact that the main chain-forming reaction proceeds faster than the side reactions (higher rate constant, hence the “main” reaction). Therefore, for an increase in the concentration of the monomers, the rate of reaction of the main reaction will increase more quickly than the side reactions. It is assumed that the reactions are of similar reaction orders. When the weight percent of the monomer in the reaction mixture was increased, it was observed that the PAA solution formed becomes more viscous.

During the precipitation step, when methanol was used as the precipitating agent, all polymer solutions failed to produce any precipitate. This can be attributed to the degree of polymerization still being insufficient to withstand the dissolving effect of methanol. Deionised water was used as an alternate precipitating agent and the polymer successfully precipitated. The precipitate strand was longer for solutions with higher weight percent monomer (only flakes and short strands were formed for low wt% solutions). This is evidence that the polymer produced using a higher weight percent of monomers in the NMP solvent has a higher molecular weight. The different degrees of precipitation are illustrated in Figure 6, Figure 7, and Figure 8 respectively.

Figure 6: Low MW precipitate formed using 22.5wt% monomers in NMP solvent

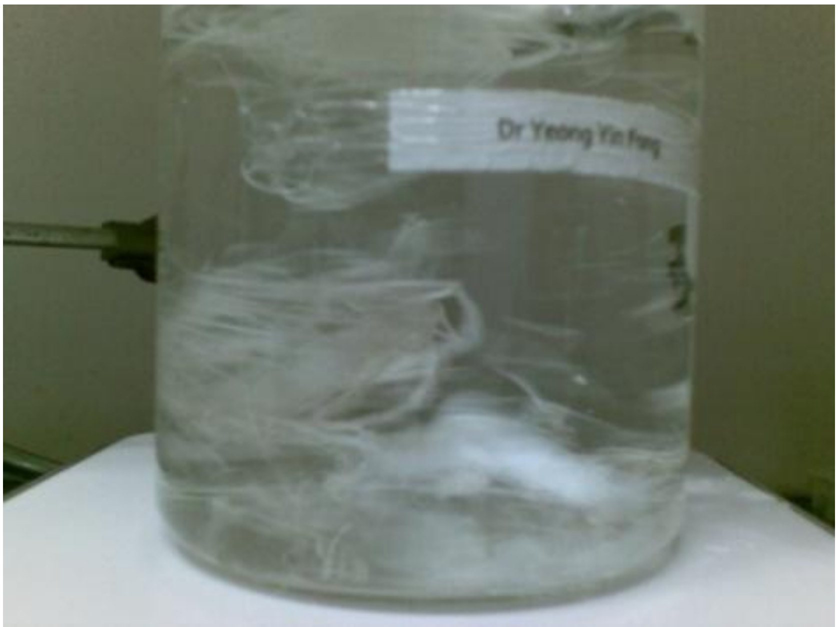


Figure 7: High MW precipitate formed using 30.0 wt% monomers in NMP solvent

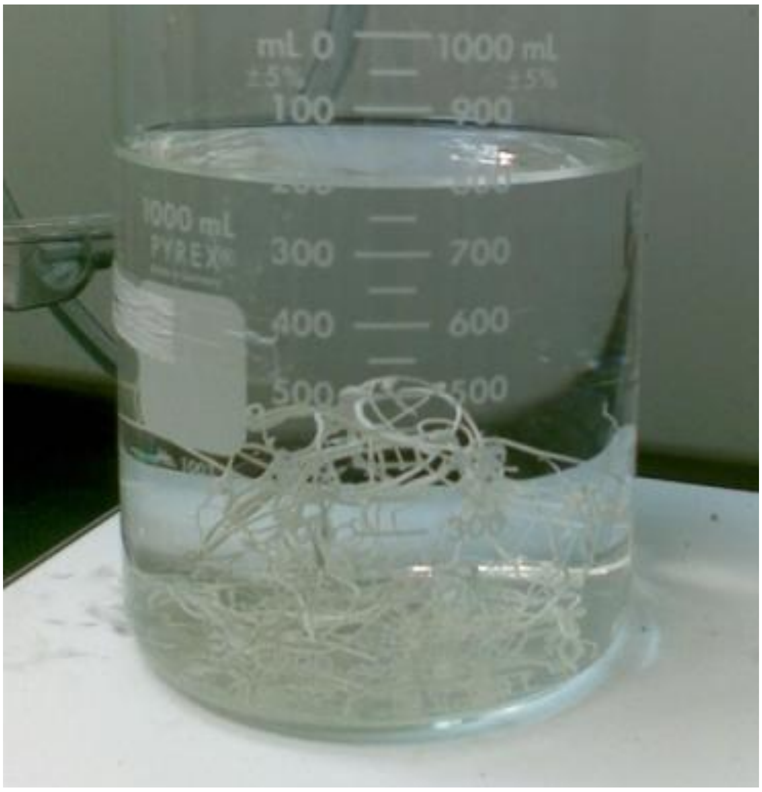


Figure 8: High MW precipitate formed using 32.5 wt% monomers in NMP solvent

All precipitates were collected and dried in an oven at 110 °C for 1.5 days. The TGA curve for the precipitate (using polymer batch 2) is presented in Figure 9.

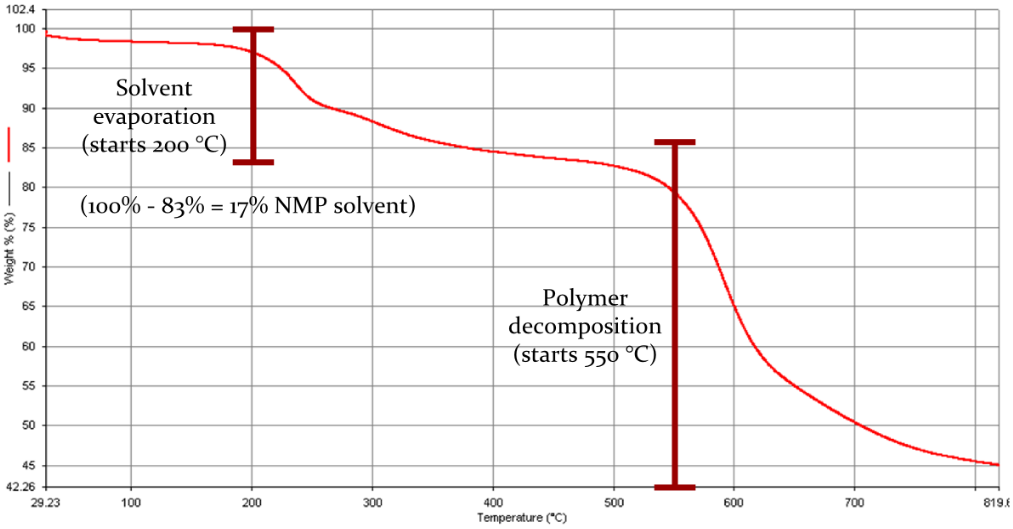


Figure 9: TGA curve for synthesized polymer

Two weight loss regions were observed in the TGA curve. The first weight loss region starts at 200 °C and is attributed to incomplete solvent removal during the washing step. The recommendation to this is to increase the frequency of changing the washing agent, which was done in all subsequent syntheses (every 4 hours during daytime). The second weight loss region occurs at 550 °C and is attributed to the polymer decomposition. The decomposition temperature agrees well with the decomposition temperature of 6FDA-Durene polymer in the literature (Y. Liu et al., 2001), proving that the desired polymer is synthesized.

Other limitations that resulted in the failure of the initial stage of polymer synthesis were as follows:

1. The purity of the monomers and synthesis solvent. The presence of impurities in the polymer solution could significantly affect polymer chain formation. This was mainly due to the lack of suitable equipment to purify the monomers (e.g. sublimation port).
2. Nitrogen purging of the nitrogen flask. Improper set up conditions may lead to the presence of air in the reaction flask, leading to undesirable side reactions ultimately resulting in a low overall molecular weight.

To sum up the results from this section: **6FDA-Durene polymer was successfully synthesized. When a higher weight percent of monomers in NMP solvent is used in the synthesis of 6FDA-Durene polymer, the polymer formed has a higher molecular weight.** This is seen from the 1) reaction mixture being more viscous, and 2) the precipitate strands being longer and thicker.

4.2 MEMBRANE FORMATION

4.2.1 Introduction

In order to form a membrane, the dried polymer precipitates from the previous section were redissolved in a solvent and cast on a glass plate. The different types of solvent used are summarized in Table 7 (NMP: n-methyl-pyrrolidinone; THF: tetrahydrofuran; DCM: dichloromethane). Membranes H and I were formed using the thermal imidization route.

4.2.2 Use of chemically imidized polymers

Initially, polymers from batch 4 above was redissolved in THF solvent at 12 wt%, then cast on a Petri dish and dried in an oven at 50 °C (Membrane D). The resulting membrane was cracked. It was suspected that the solvent THF evaporates too quickly, causing a mismatch between the solvent and dissolved polymer resulting in a cracked membrane. This led us to try using NMP as the solvent (Membrane E) to dissolve the polymer. The drying temperature was adjusted upwards to 80 °C to accommodate the higher boiling point of NMP. The resulting membrane was still cracked due to improper drying condition. Next (Membrane F), THF solvent was used with the solvent being evaporated at ambient conditions. The resulting membrane is still cracked. This result indicated that THF is not a suitable solvent to cast the 6FDA-Durene membrane. Polymer from other batches were tested sequentially (C, B, A), but the cracking persisted. Polymer batch 5 was synthesized at this time and tested, but the membrane still did not form well. Based on these results, the following inferences were made:

1. Although the molecular weight of the PAA is high as shown by the viscosity of the solution, it is apparently still not enough for the formation of a smooth membrane.
2. The presence of impurities in the polymer solution could affect the membrane formation process. The polymerization and imidization process is very sensitive to the presence of impurities, which leads to unwanted side reactions that compete with the main reaction.
3. The chosen solvent may not be suitable for the membrane formation. The original solvent described in literature (DCM) was unable to dissolve the

polymer precipitate, leading to the use of NMP and THF as alternatives. It is suspected that the rate of solvent evaporation may be causing the cracks as well, therefore different drying conditions were employed (oven and ambient drying, respectively).

Figure 10: DCM cannot redissolve the polymer

4. Inadequate polymer mass was used for the membrane formation. This inference is made based on the decrease in the degree of cracking when more of the polymer is redissolved (at same weight percent in solvent).
5. The cast membrane is fragile and cracks easily because it is too thin. This is seen during thermal imidization (see next section), where the degree of cracking decreases when the same amount of solution was cast onto a Petri dish with a smaller diameter (so the thickness is higher). Furthermore, the fragments of the membrane are larger (i.e. the cracks are further separated from one another).
6. Presence of unreacted monomers in the final polymer precipitate. In the casting step, the polymer solution is redissolved in THF or NMP solvent and cast onto a Petri dish and dried in a normal oven. It was found that both samples cracked suggesting that the rate of evaporation is inappropriate. Also, little strands of “impurities” were visible on the membrane, which are likely unreacted monomers that were not washed out during the washing step using deionised water.

The membrane films that are cast from the 6FDA-Durene polymer synthesized using the chemical imidization method are also not transparent. In one case black strands were observed in the membrane film (Membrane D). It is suspected that the presence of unreacted monomers which could not be removed during the washing step affects the transparency. In order to test the suitability of deionised water as the washing agent, the monomers were each dissolved in deionised water. It was found that durene diamine dissolved completely but 6FDA did not dissolve in the deionised water. This observation is probably because of its high molecular weight of 6FDA and the dianhydride group is insufficient to interact with water for complete solvation. Therefore, the choice of deionised water is not suitable because it only dissolves one of the two monomers. In future synthesis, a different solvent is needed such that it dissolves both the monomers but leaves the polymer chain undisturbed.

Figure 11 shows the 6FDA-Durene membranes synthesized using chemically imidized polymers.

Table 7: Results of membrane formation

Membrane batch	Polymer batch	Solvent to redissolve	Polymer weight percent in solvent (wt%)	Drying method	Cracked?	Transparent?	Remarks
-	1	-	-	-	-	-	(No precipitate yield, see Section 4.1)
-	2	DCM	12	-	-	-	Polymer failed to redissolve in DCM.
A	2	THF	12	Ambient	Cracked	No	Both the membrane films formed are not transparent. This is attributed to insufficient washing of the precipitate. In subsequent polymer syntheses the washing duration is increased from 1.5 days to 2.5 days
B	2	NMP	12	Ambient	Cracked	No	
C	3	THF	12	Ambient	Cracked	Semi-transparent	Yield only enough for one membrane batch synthesis, suspect losses during filtration
D	4	THF	12	Oven 50 °C	Cracked	Transparent	Black strands observed – washing of polymer was not enough to remove monomers?

E	4	NMP	12	Oven 80 °C	Cracked	Transparent	Severe cracking into very small fragments
F	4	THF	12	Ambient	Cracked	Transparent	Moderate cracking is observed
G	5	NMP	12	Oven 60 °C	Cracked	Transparent	The film has turned yellow, indicating oxidation of NMP
H	5 (PAA)	NMP	13	Oven 75 °C	Significantly less cracks	Very clear and transparent	PAA was used because thermal imidization is to be employed for this batch
I	6 (PAA)	NMP	13	Oven 60 °C	Significantly less cracks, cracked into larger pieces	Very clear and transparent	A smaller glass plate was used, resulting in a thicker membrane with better mechanical properties

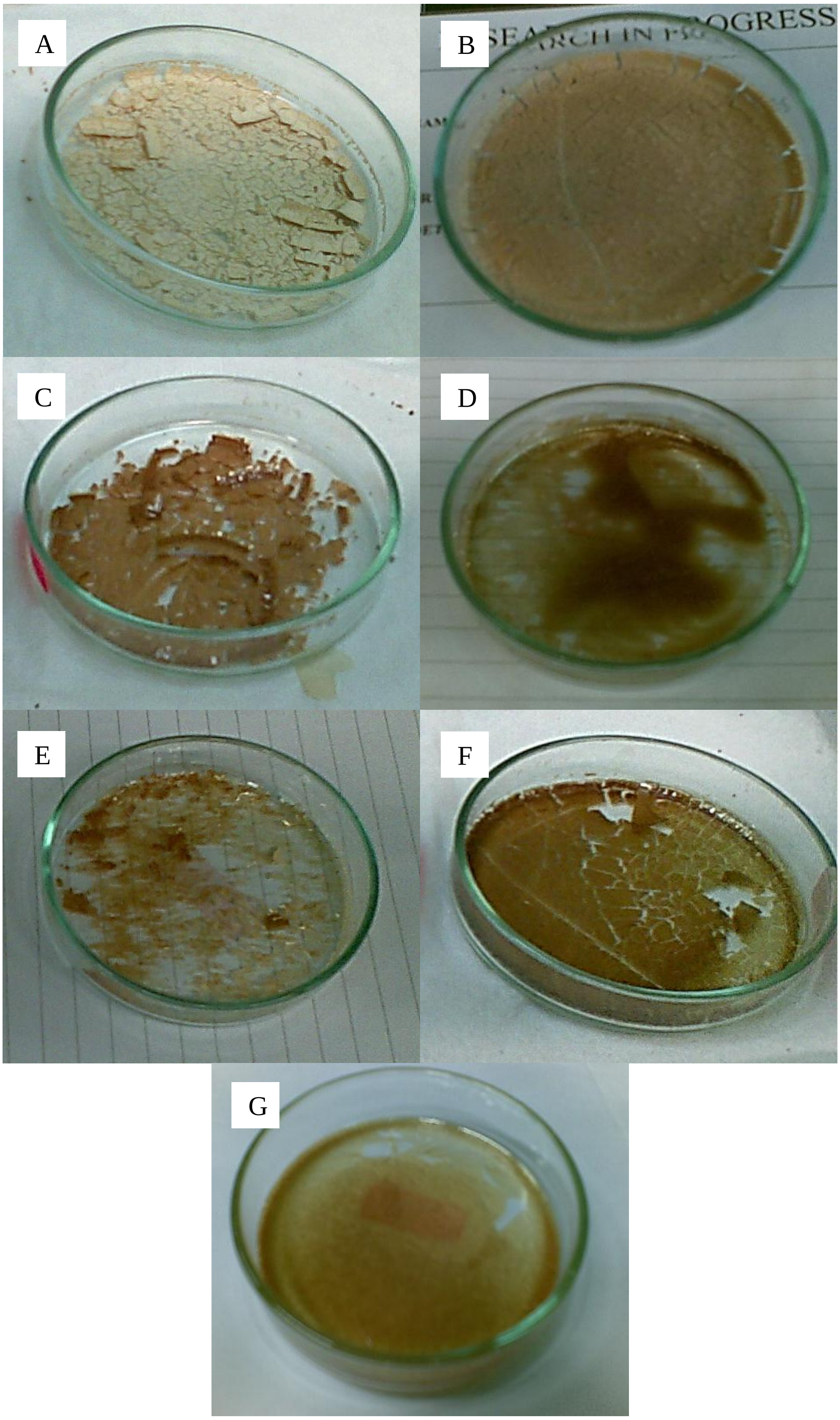


Figure 11: Close up images of 6FDA-Durene membranes

4.2.3 Use of thermal imidization method

In an attempt to address the problem of cracking, the thermal imidization method for membrane formation was applied. After the formation of the polyamic acid, the PAA solution was diluted to 10 wt%, filtered with a syringe filter, and cast on a glass plate. It is then dried in a vacuum oven at 50 mbar and 75 °C for 2 days. The resulting film is clear and transparent with minor cracks, as shown in the left part of Figure 12. This film will later be thermally imidized using a temperature ramp from 50 °C to 200 °C at a rate of 25 °C per hour. The right part of Figure 12 shows a membrane with even less cracks (larger membrane fragments obtained). The improvement is believed to be caused by the use of a higher polymer weight, resulting in a thicker membrane. These two films will be used as the control for comparison of the transparency and clarity of the mixed matrix membrane.

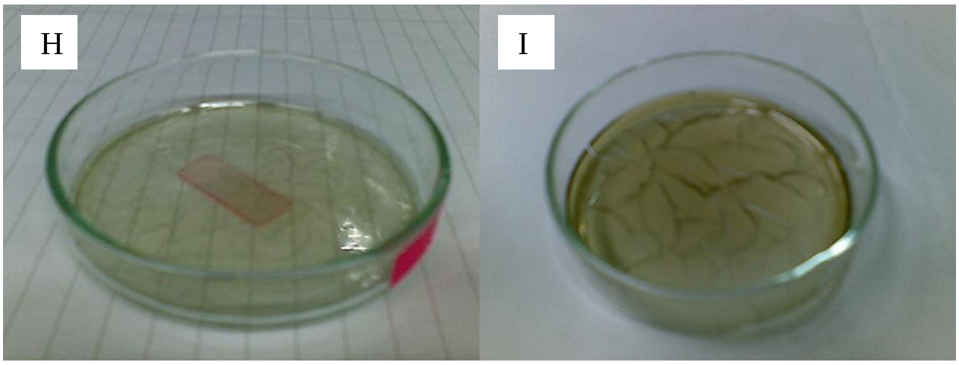


Figure 12: 6FDA-Durene membranes (left: Membrane H; right: Membrane I)

4.2.4 Summary

To sum up the major and important results from this section: **The casting of *polyamic acid* and subsequent thermal imidization gives a better membrane formation in terms of less cracking compared to using the chemical imidization method, where the *polyimide polymer* is redissolved and cast.** A thicker membrane has better mechanical properties and exhibits less cracks. Also, to get a clear and transparent membrane, the washing step during the polymer synthesis is very important because the presence of unreacted monomers and impurities results in non-transparent membrane morphology.

4.3 PREPARATION OF MIXED MATRIX MEMBRANES

The thermal imidization method gives control membranes that are clear with significantly less cracks. Therefore, the mixed matrix membranes will be synthesized using this method.

Initially, 7wt% inorganic filler loading was used to synthesize the mixed matrix membrane. However, during the sonication step, it was observed that the particles were already unable to dissolve and disperse evenly in the solution. This means that if the membrane is cast phase separation between the polymer matrix and inorganic particles will definitely occur. Based on this information, the experiment range for the inorganic filler loading is set to 0 wt% to 4.5 wt% at increments of 1.5 wt%. Table 8 lists the mixed matrix membranes (MMM) cast in the present work.

Figure 13: 7 wt% inorganic filler loading appears cloudy even after sonication

Table 8: Results of mixed matrix membranes synthesis

Membranes	Inorganic filler, wt%	Clear?	Transparency	Remarks
MMM0 (Control)	-	Yes	Yes	No cracks
MMM1	SAPO34-1.5wt%	Yes	Yes	No cracks
MMM2	SAPO34-3.0wt%	Yes	Yes	No cracks
MMM3	SAPO34-4.5wt%	Yes	Yes	Minor crack at one side
MMM4	ZIF8-1.5wt%	Yes	Yes	No cracks
MMM5	ZIF8-3.0wt%	Yes	Yes	No cracks
MMM6	ZIF8-4.5wt%	Yes	Yes	No cracks

The TGA curve for the control membrane is shown in Figure 14 below. It exhibits similar characteristic peaks as the previous TGA curve. In the temperature range 0 to 300 °C, there is nearly 40% mass loss. The mass loss prior to 200 °C is caused by the formation of water condensate on the membrane prior to the analysis, which we found out after the fact. Regardless, the important point is that the polymer decomposition occurs at 550 °C, in agreement with the literature value. The resolution of the TGA curve is very low and peak broadening is clearly affecting the results. In future analysis, a lower temperature ramp should be used.

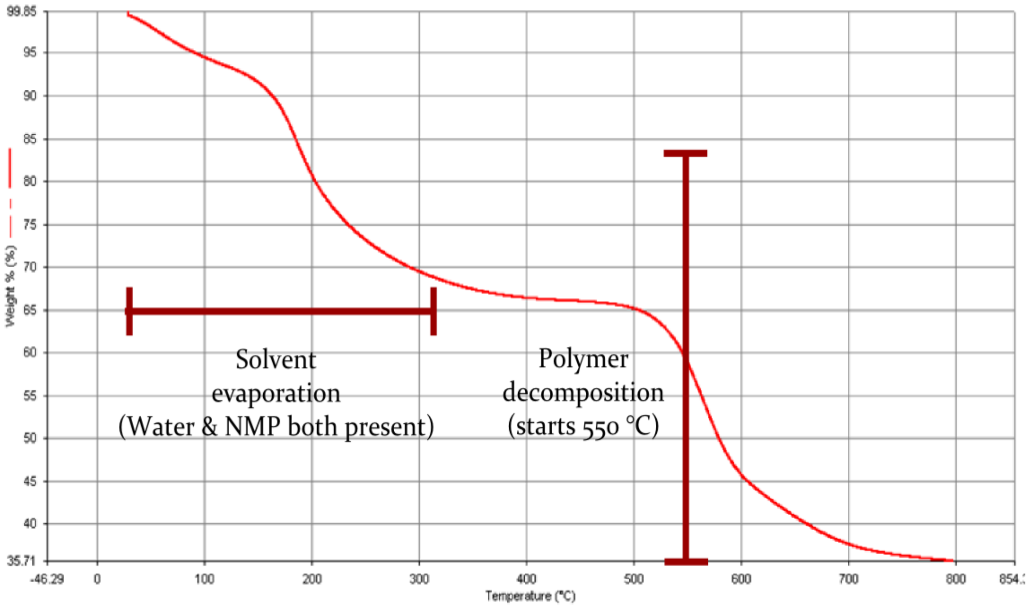
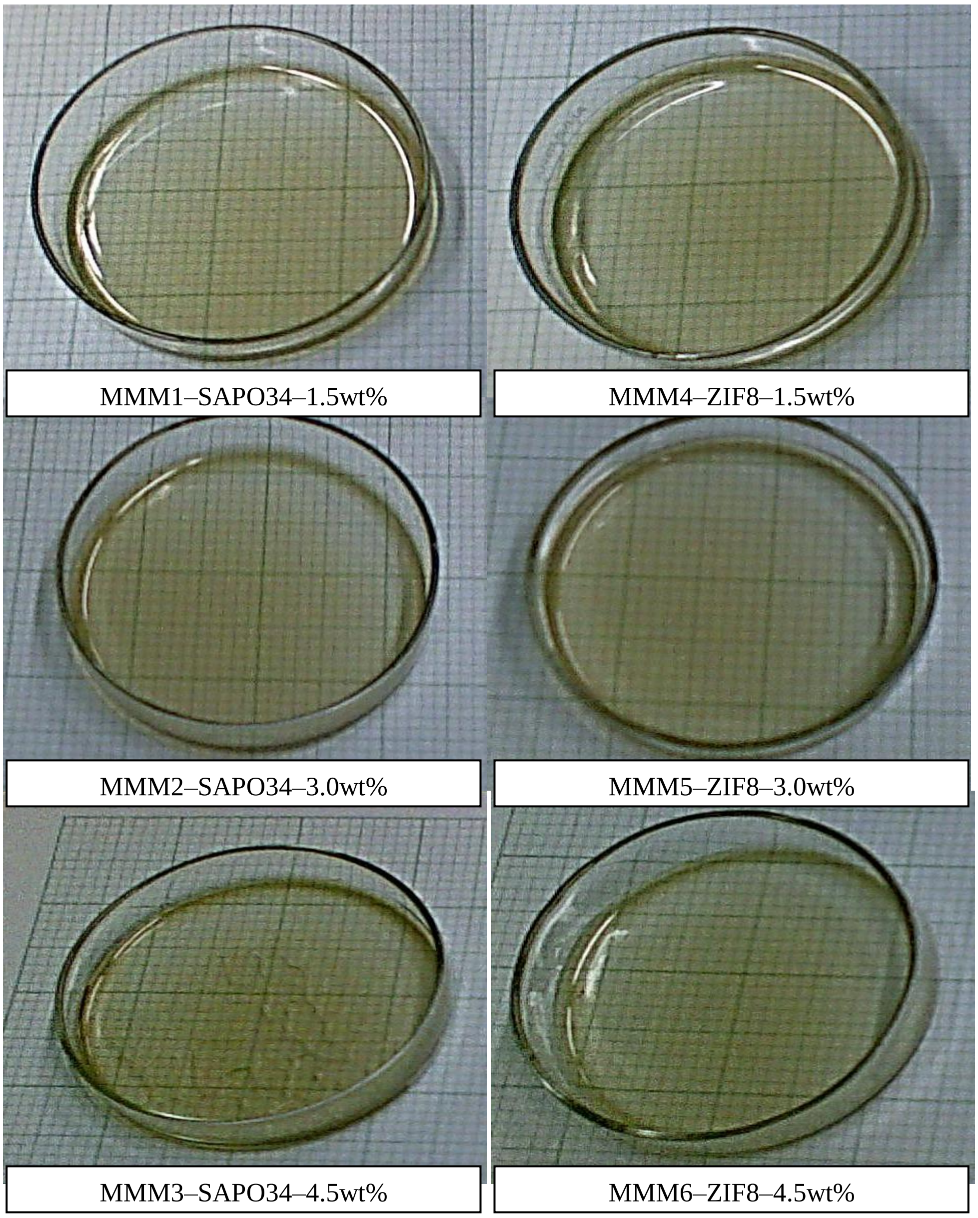


Figure 14: TGA curve for the control membrane

Figure 15shows the synthesized mixed matrix membranes on the Petri dish. The graph paper is used as a scale reference and has a 2x2 mm grid.



MMM1–SAPO34–1.5wt%

MMM4–ZIF8–1.5wt%

MMM2–SAPO34–3.0wt%

MMM5–ZIF8–3.0wt%

MMM3–SAPO34–4.5wt%

MMM6–ZIF8–4.5wt%

Figure 15: Mixed matrix membranes with different inorganic particle loadings

(Left: SAPO-34 inorganic filler; Right: ZIF-8 inorganic filler; top to bottom: 1.5 wt% - 4.0 wt%)

The clarity and transparency of the membrane is compared in Figure 16 below. It was noted that all membranes have similar transparency and clarity.

Figure 16:Comparison of the transparency of the mixed matrix membranes

(from left to right: MMM0–MMM6)

From Figure 16, phase separation has not occurred and the particles are invisible to the naked eye. This means that the 6FDA-Durene mixed matrix membrane is able to accommodate up to 4.5 wt% inorganic particles loading. Since the particles are no longer well dispersed in the polymer solution at a 7 wt% loading (Figure 13), **we can conclude that the maximum loading is in the range of 4.5 to 7 wt%**.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION & RELEVANCE TO THE OBJECTIVES

The synthesis of 6FDA-Durene-based membranes is affected by many factors. The presence of impurities greatly lower the polymerization reaction rate and reduce the molecular weight of the polymer. Using a higher initial weight percent of monomer in the NMP solvent leads to a polymer precipitate of higher molecular weight. A sufficient washing duration is needed to completely wash away the unreacted monomers so that a clear and transparent membrane can be formed. Both using a smaller Petri dish to cast the membrane (increased thickness) and/or increasing the amount of polymer being cast can reduce cracks. Thermal imidization is the preferred synthesis route compared to chemical imidization because the membranes produced are more transparent and have less cracks. This knowledge will make it easier for the future synthesis of 6FDA-Durene membranes for application in CO_2/CH_4 gas separation.

Mixed matrix membranes are synthesized using ZIF-8 and SAPO-34 as the inorganic fillers respectively. The loading of the inorganic particles in the membrane matrix is found to affect the morphology and phase separation of the membrane. In this study it was found that up to 4.5 wt% of inorganic particle loading can be incorporated in the mixed matrix membrane without any problem in terms of phase separation. This knowledge will serve as a guideline for the future synthesis of 6FDA-Durene mixed matrix membranes.

5.2 FUTURE WORK & RECOMMENDATIONS

Parameters that can be adjusted to achieve better membranes in the future include:

1. Monomer purity: The monomers still need to be further purified before use even though they are already electronic grade.
2. Washing solvent: A different washing solvent other than methanol and deionised water should be used. The solvent should be able to dissolve both monomers without dissolving the polymer
3. Drying method: When drying in the oven, the temperature should not be excessively high (60 – 70 °C acceptable). If the temperature is too high, the rapid rate of solvent evaporation may lead to a cracked membrane. When the thermal imidization method is used, the membrane did not form at all when dried in ambient conditions.

Once the mixed matrix membrane is formed successfully, it should be characterized in terms of morphology (using SEM) and tested for the CO_2/CH_4 gas separation performance.

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