

**Effects of Halloysite Nanoclay Filler on
Mixed Matrix Membrane (MMM)
for CO₂ Removal**

by

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14802

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

JANUARY 2015

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CERTIFICATION OF APPROVAL

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Approved by,

(DR. OH PEI CHING)

UNIVERSITI TEKNOLOGI PETRONAS
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JANUARY 2015

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.

(KUAN CHUAN HONG)

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ABSTRACT

Membrane separation technology plays an important role in natural gas CO₂/CH₄ separation. Mixed matrix membrane (MMM) is one of the many types of membrane used and its advantage over other types of membrane is that it has the mechanical strength and cheap production cost of organic membrane, in the same time have the superior selectivity – permeability trade off of inorganic membranes. There are various combinations when it comes to synthesis of MMM. Generally, an inorganic filler is embedded into a polymeric matrix to form MMM. One of the combinations never ventured by researchers is the polysulfone (PSf) – halloysite MMM. This project aims to elucidate the casting formulation of pristine PSf membrane (a type of organic membrane) and to study the effects of halloysite nanoclay filler in PSf membrane. The membranes synthesized will be characterized using FESEM, TGA, and DSC. The first part of the project involves synthesis of membranes using pure polysulfone and a mixture of polysulfone – halloysite nanoclay fillers. In the second part of the project, the membranes synthesized are characterized using analytical tools. The effects of halloysite nanoclay fillers in polysulfone membrane are investigated and the best composition will be determined. The best MMM chosen is 20wt% PSf – 3wt% halloysite mixed matrix membrane. It has a decomposition temperature of 519.18°C. The total remaining residue after heating the membrane up to 730°C is 27.63wt%. The glass transition temperature, T_g of the membrane is 184.34°C.

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ABBREVIATIONS AND NOMENCLATURES

PSf	: Polysulfone
MMM	: Mixed matrix membrane
FESEM	: Field emission scanning electron microscopy
TGA	: Thermogravimetric analysis
DSC	: Differential scanning calorimetry

CHAPTER 1: INTRODUCTION

1.1 Background

Carbon dioxide (CO₂) is the largest contributor to global warming. In the past five years, 34 billion tons of CO₂ emission is recorded globally [1]. Common sources of CO₂ are natural gas streams, flue gas from fossil fuel combustion, and biogas from anaerobic digestion [2]. The separation of CO₂ from methane gas (CH₄) is important in many industrial processes, for example increasing the calorific value of natural gas, natural gas sweetening and landfill gas purification [3]. Therefore, effective and economically feasible techniques to remove CO₂ from CH₄ streams are highly sought and attract great interests.

There are several methods or techniques used to separate gases, either to isolate a single product or to produce multiple products. Compared to other gas separation techniques such as swing adsorption techniques (i.e. pressure swing adsorption, vacuum swing adsorption, and temperature swing adsorption), cryogenic distillation and amine absorption [2, 4], membrane gas separation technologies are comparatively less developed and hence less widely used. Generally, membrane gas separation uses the characteristic of a partially permeable membrane which allows the unwanted gas (i.e. carbon dioxide, CO₂) to pass through the membrane and be removed, while the desirable gas (i.e. methane gas, CH₄) remains in the original airstream.

Synthetic membranes used in membrane gas separation technologies are divided into two types – organic membranes (i.e. polymeric membranes) such as polyethylene, polyamides, cellulose acetate, polysulfone, etc. as well as inorganic membranes (i.e. ceramic membranes) such as silicon carbide, montmorillonite, halloysite, etc [2, 5-7]. Organic materials-based membranes are characterized by their lower costs, better processability, and their intrinsic properties of gas transportation [2, 7, 8]. Comparatively, inorganic materials-based membranes provides stronger capabilities to differentiate gas species in spite of high temperature, pressure conditions and harsh environments [2, 6, 9].

Mixed matrix membranes (MMM), also known as hybrid membranes, are a combination of both inorganic and organic membranes. It contain a separating layer

made of continuous phase (usually a polymer) embedding a second, dispersed phase, the chemical nature of which is different [2, 6, 10, 11]. The combination of two different materials with different gas diffusivity and solubility into a new membrane allows an optimal combination of high permselectivity (selectivity, permeability) of the inorganic component with the characteristic of ease of production of the polymeric component.

1.2 Problem statement

The current CO₂/CH₄ separation membrane technologies are led by organic membranes due to their cheaper production costs, and the nature of them being easily shaped into both flat sheets and hollow fibers. It is also relatively easy to scale them up to whichever industrial size [2]. However, organic membranes suffer from either low selectivity or permeability. They form an inverse relationship and can be observed in Robeson's upper bound curve [2, 12, 13].

Inorganic membranes, on the other hand, has the capability to maintain a superior selectivity and permeability at high temperature and pressure [2, 7] However, the use of inorganic membranes are limited due to their expensive nature as well as reproducibility problems in the preparation steps when it comes to industrial scale [2, 6, 9].

Polysulfone-halloysite mixed matrix membrane has not been reported in past studies, and hence the casting solution formulation for the MMM has to be investigated in order to determine the best solvents to be used, and also the weight percentages of all the components used in the fabrication of the MMM.

1.3 Objectives of study

The objectives of this study are as follows:

1. To elucidate the casting solution formulation for synthesis of pristine polysulfone (PSf) membrane.
2. To study the effects of halloysite nanoclay filler on mixed matrix membrane fabrication.
3. To characterize the resultant membranes using various analytical tools (FESEM, TGA, DSC, etc.).

1.4 Scope of study

The variation of compositions of inorganic membrane component (halloysite nanoclay filler), organic membrane component (polysulfone – PSf), and solvent (N-Methyl-2-pyrrolidone – NMP) will result in different level of performance of the mixed matrix membrane. The characteristics of a decent MMM that will be observed are permselectivity, ease of production, and its durability.

There are several variables that can be altered throughout the study. Firstly, the optimal weight percentage of polysulfone in the pristine polymeric membrane mixture can be determined by trial and error method. Secondly, the effects of the composition of halloysite nanoclay fillers in polysulfone can be observed. The weight percentage of the other components (solvents and non-solvent) will also change the performance of the membrane.

Tests will be done on the membranes casted, with different weight percentage of polysulfone and halloysite in order to determine their qualities. The tests that can be done are field-emission scanning electron microscope (FESEM) test, thermal gravimetric analysis (TGA) test, and differential scanning calorimetry (DSC) test.

1.5 Project feasibility

The expected experimental process flow are summarized in Table 1:

Table 1: Estimated duration per trial

	Step	Estimated Duration
1	Drying of raw halloysite filler and polysulfone powder	24 hours
2	Sonication of halloysite in solvent mixture	30 minutes
3	Dispersion (stirring) of halloysite in solvent mixture	6 hours
4	Dissolving polymer in solvent mixture	24 hours
5	Sonication of MMM mixture	2 hours
6	Leaving the mixture to 'stand up' overnight	12 hours
7	Membrane casting	30 minutes
8	Water coagulation bath	24 hours
9	Post treatment (methanol and <i>n</i> -hexane bath) (optional)	3 hours
10	Drying time	24 hours
TOTAL		96 hours

- Total experiments: 20 (can be done in parallel)

- Planned schedule: Refer to Gantt chart below.

This project is allocated eight months to be completed. It is believed that there is ample time to complete the project objectives. According to Table 1, the parameters of membrane to be studied have been chosen carefully in order to suit the timeline given for this project. Besides, a reasonable and detailed planning has been devised for each part of the project, this is so that the project can be completed within the planned timeframe and will produce a good outcome by the end.

CHAPTER 2: LITERATURE REVIEW / THEORY

2.1 The Robeson's curve

The CO₂/CH₄ gas pair is the second most investigated gas pair for membrane separation [13]. For the case of organic membranes used for CO₂/CH₄ gas separation, they are commonly cheap and easily synthesized, but often suffer from either low selectivity or permeability. They form an inverse relationship and can be observed in Robeson's upper bound curve [2, 12, 13].

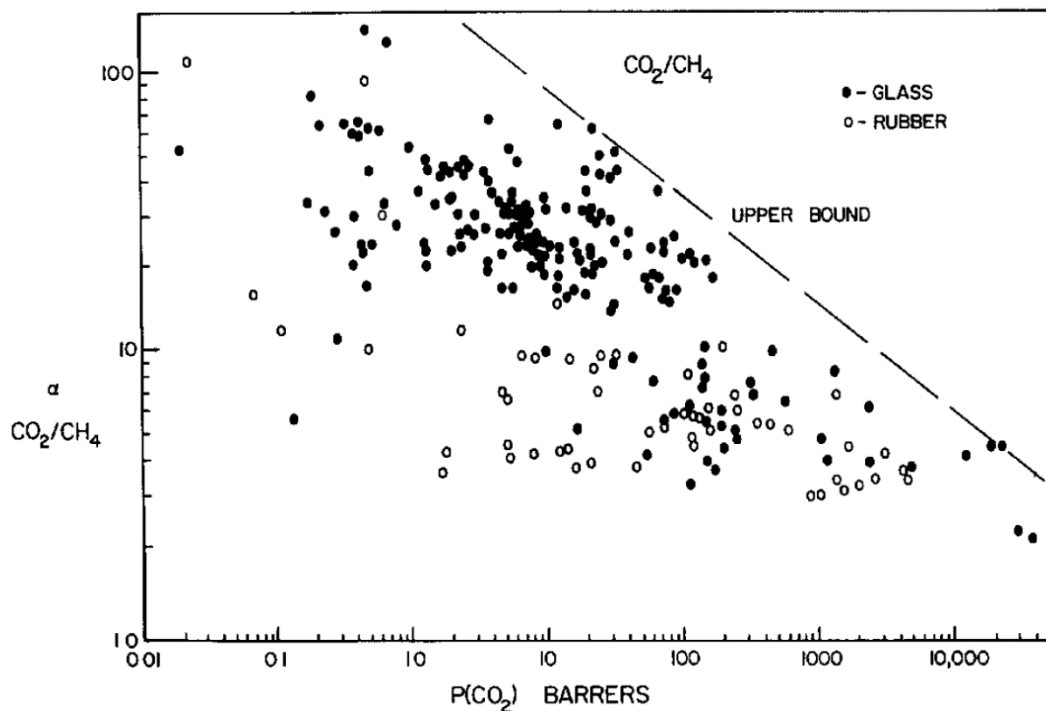


Figure 1: Upper bound correlation for CO₂/CH₄ separation (1991)[12]

The first upper bound correlation (Robeson's curve) study on CO₂/CH₄ gas pairs was done in 1991, as shown in Figure 1. A review of the initial upper bound for the new upper bound correlation for CO₂/CH₄ gas separation was done by Robeson in 2008, as shown in Figure 2. The results only show a modest shift in the upper bound, which means that the use of polymeric membrane in CO₂/CH₄ gas separation is still very limited due to the low tradeoff between selectivity and permeability.

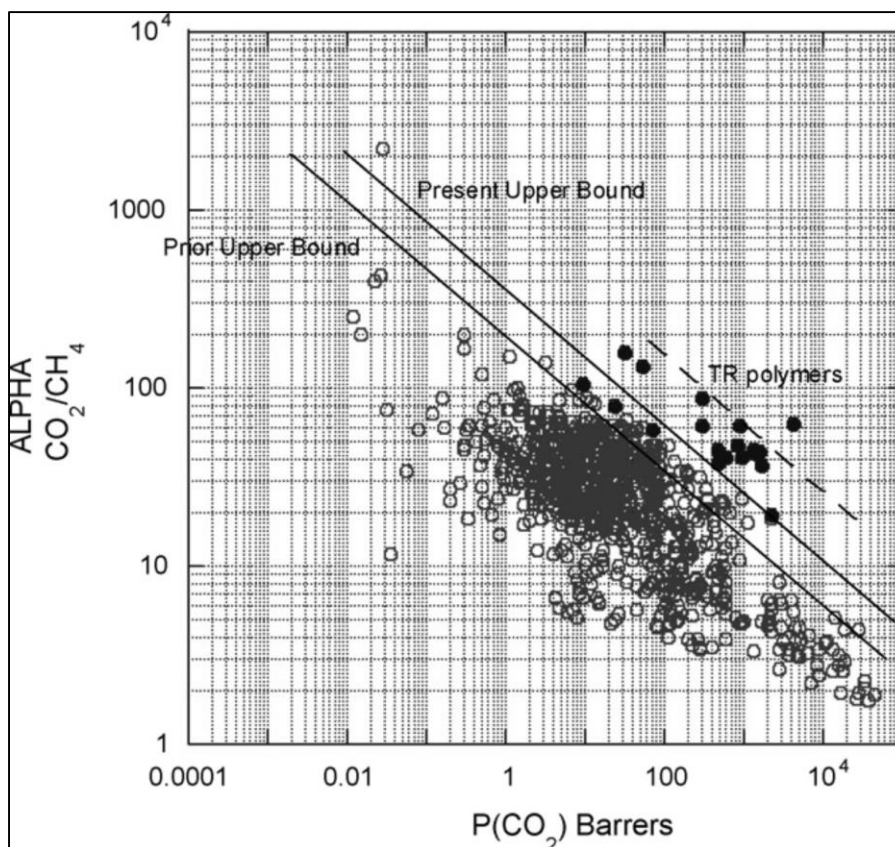


Figure 2: Upper bound correlation for CO₂/CH₄ separation (2008) (TR: Thermally rearranged.)[13]

2.2 Polymer characteristics and comparison

Polyimide (PI) and cellulose acetate (CA) based membranes have been mainly used for CO₂/CH₄ separation commercially [2] due to their relatively low cost and their status as a high performance polymer. Their excellent glass transition temperature (T_g) and high tradeoff for selectivity/permeability made them better choices for various gas separation applications [14]. However, PI is prone to plasticization in high pressure CO₂ environment as they plasticize at 8 bar pressure [14-16]. Plasticization pressure refers to the point of concentration of carbon dioxide passed through the membrane where the polymer matrix starts to swell and expands, resulting in lower selectivity.

On the other hand, polysulfone (PSf) exhibits similar traits to PI and CA. PSf is one of the most investigated glassy polymer membrane material used for CO₂/CH₄ separation. Its properties are being extensively explored for gas separation because of its superior chemical stability and mechanical strength compared to other polymers [17]. However, PSf have a plasticization pressure at 30 bar pressure [2, 14, 18]. Figure 3 shows the comparison of plasticization pressure for different polymers.

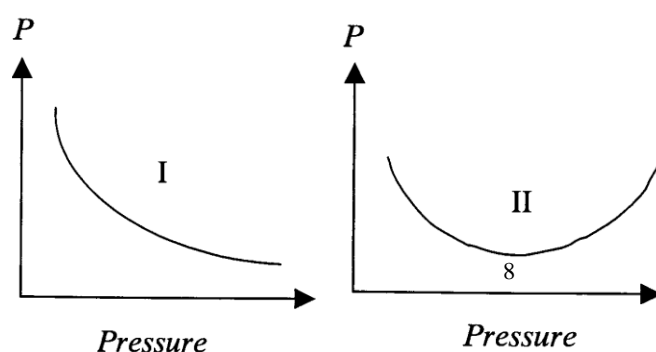


Figure 3: Plasticization pressure for different polymers. From left: I – PSf, PC; II – PI[15]

Other than plasticization pressure and the membranes' mechanical strength, two more factors that must be considered are the membranes' CO₂ permeability and CO₂/CH₄ selectivity. They indicate the performance of the membrane in the industry. The permeability indicating the extent of the membrane allowing CO₂ to pass through the pores, and selectivity indicating the effectiveness of the membrane to differentiate between CO₂ and CH₄, separating them from the gas stream and the permeate.

Table 2 below summarizes the important factors for five different polymer membrane materials – CA, PI, polyamide (PA), polycarbonate (PC), and PSf.

Table 2: Summary of CO₂/CH₄ separation performance for different membranes.

Membrane	CO ₂ Permeability (Barrer)	CO ₂ /CH ₄ Selectivity	Plasticization Pressure (bar)	Ref.
CA	2.5 (GPU)	20.0	55	[19]
PI	10.0	35.7	8	[20]
PA	11.0	36.3	-	[21]
PC	2.0	27.2	30	[10]
PSf	80.7 (GPU)	40.2	30	[22]

2.3 Halloysite nanoclay filler

Halloysite, also known as endellite in certain Eurasia countries, is under the kaolinite-serpentine group. The chemical formula for dehydrated halloysite is Al₂Si₂O₅(OH)₄.

The main constituents of halloysite are silica and aluminium, in the form of SiO_2 and Al_2O_3 respectively [23].

Halloysite fillers have a large diameter of lumen making them potentially suitable for the accommodation of a range of molecule guests from large molecules such as proteins to light gas molecules including CO_2 and CH_4 [24].

2.4 Dry/wet phase inversion method

There are three common processes to manufacture a polymer membrane: dry, wet, and dry/wet. Dry process is named so because the manufacturing process does not involve the immersion in coagulation bath, and the gas permeation rate is usually low due to a thicker selective layer [16, 18, 25]. In wet process, the polymer solution composition is immersed into a coagulation bath, and phase separation phenomena occur due to the diffusional exchange of solvent and non-solvent [18], but they are generally unstable and requires further treatment [25].

In order to produce a defect free membrane with an ultra-thin top layer that doesn't require too much post treatment, Pinnau and Koros developed a new technique in 1991 – dry/wet phase inversion method [18, 25]. In a typical dry/wet process, two solvents are used, one being the more volatile solvent and another less volatile solvent, which have different affinity with the non-solvent used. The mixture is then sonicated and left free standing for evaporation before being immersed into a coagulation bath (usually water) [18].

In the coagulation bath, the exchange of solvents and non-solvent will occur. The solvent will then evaporate. During the solvent evaporation, a thin skin layer of solidified polymer is formed on the top of casting film. During the exchange process, the non-solvent will diffuse into the solution through the thin solid layer while solvent diffuses out.

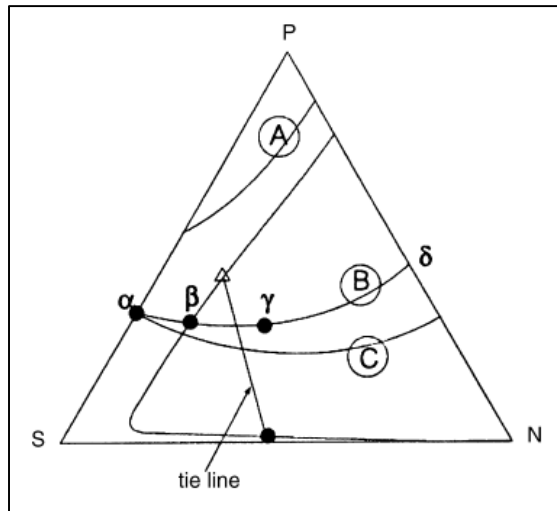


Figure 4: Schematic representation of mass transfer path of dry/wet phase inversion method [26]

The composition change in the film is illustrated in Figure 4 by the 3 paths (A, B, and C). The axis of the triangles are represented by initial polymer fraction (P), solvent outflux (S), and nonsolvent influx (N). Path A starts with high initial polymer fraction and does not cross the phase separation line, resulting in homogenous and dense polymeric membrane. Path B starts with a lower initial polymer fraction compared to Path A, and has a relatively low ratio of the rate of solvent outflux to nonsolvent influx, resulting in an asymmetric structure. Path C starts with the same polymer fraction as Path B, but having an even smaller ratio of solvent outflux to nonsolvent influx. The polymer fraction at the densification point is not high enough to form a continuous polymer-rich phase, resulting in a mechanically weak membrane that is too porous [26, 27].

2.5 Mixed matrix membrane

Mixed matrix membrane (MMM) utilizes two or more different materials, usually an organic polymer and an inorganic filler that come with distinct difference in certain properties such as chemical nature, selectivity, and permeability. The inorganic fillers are added to work as ‘sieves’ to the polymeric matrix, which can improve selectivity significantly, given that proper fillers are chosen to match its polymer counterpart [3, 6, 14, 28]. Figure 5 shows the schematic diagram of how a typical MMM functions.

In a successful MMM, the polymer portion of the membrane are supposed to be attached closely to the outer surface of the inorganic fillers [3, 6, 14, 28], like shown

in Figure 6. The organic and inorganic components of a MMM is determined by the industrial need, as well as the cohesiveness between the two components [28, 29]. For the case of a defect-free MMM, the polymer will determine the minimum membrane performance while the inorganic filler will increase the selectivity of the membrane during gas separation.

In the case of poor decision during the polymer and inorganic filler selection stage, four different types of ‘defect’ may be formed – sieve-in-a-cage, matrix rigidification, leaky interface, and plugged sieve [28]. Figure 7 demonstrates the defects and their respective gas transport through the MMM.

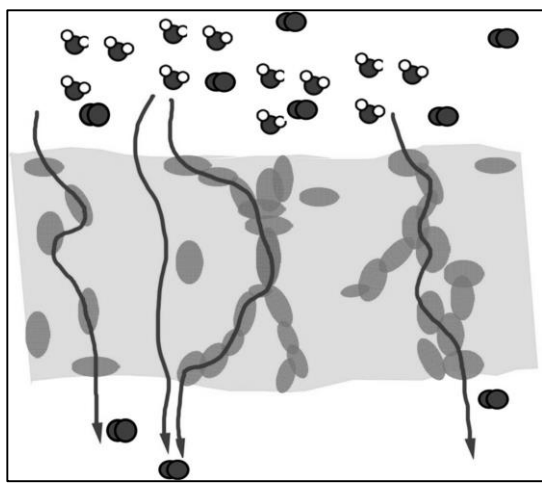


Figure 5: Schematic diagram of MMM [28]

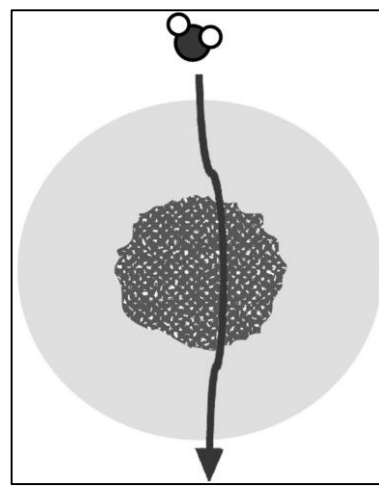


Figure 6: Ideal gas transport properties [28]

Voids are formed between the polymer matrix and inorganic fillers in the case of ‘sieve-in-a-cage’. With the presence of these voids, the gas molecules will travel through the empty space instead of the filler, resulting in higher permeability, but the selectivity will be the same, or even lower than pure polymer matrix, which is undesirable because the membrane will not be able to filter out the unwanted product [3, 6, 30, 31]. ‘Leaky interface’ is a special type of ‘sieve-in-a-cage’ but with even more permeability.

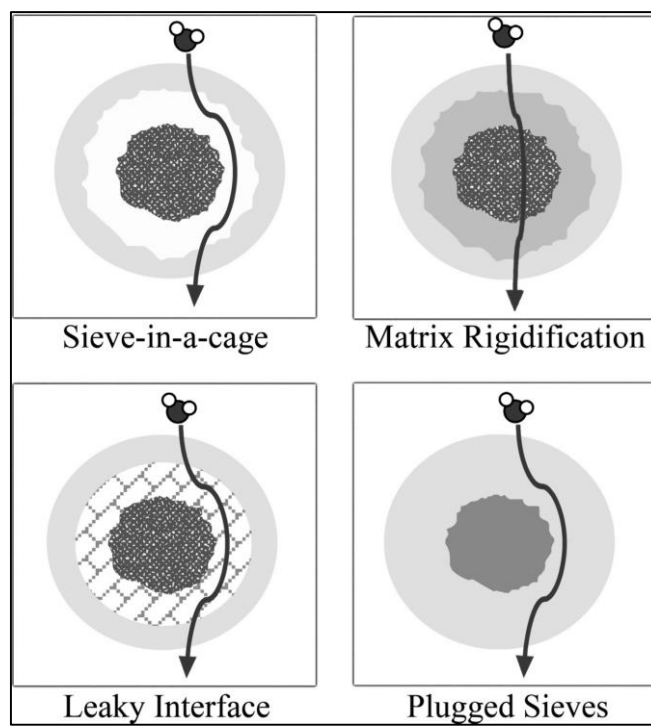


Figure 7: Non-idealities / flaws in MMM[28]

In the case of ‘matrix rigidification’, a rigidified or hardened layer of polymer is formed in between the polymer matrix and inorganic filler. As the name suggests, it immobilize the polymer chains near that area [28], lowering gas sorption and hence lowering the permeation of gas as well. Inorganic filler pores sealed by either the solvent or the rigidified polymer will cause ‘plugged sieve’, in which the sieve pore blockage decreases membrane permeability with no change in selectivity [28].

2.6 Synthesis of pristine polymer membrane and mixed matrix membrane

As mentioned above, the pristine polymer membrane in this study is casted using the dry/wet phase inversion method. In order to cast a defect-free membrane, 10 wt% of the polymer will be added into the solvent mixture and stirred for four hours on a heated magnetic stirrer, forming a ratio of 90/10 wt% solvent/polymer solution [6, 28, 32], before adding the remaining wt% of polymer into the solution. The solution is then stirred overnight to ensure complete dissipation of polymer into the solvent.

The membrane is then casted as a flat sheet using a casting knife, as shown in Figure 8. After casting, the membrane will then be immersed into a coagulation bath

for 24 hours, in order for the solvent exchange to occur and form a solidified polymer outer layer. Next, the membrane will be sent for optional post treatments – further immersion in other drying agents such as methanol and *n*-hexane or membrane coating. Regardless of post treatment done, the membrane will then need to be vacuum oven dried and air dried for 24 hours [6, 24, 28, 32, 33].

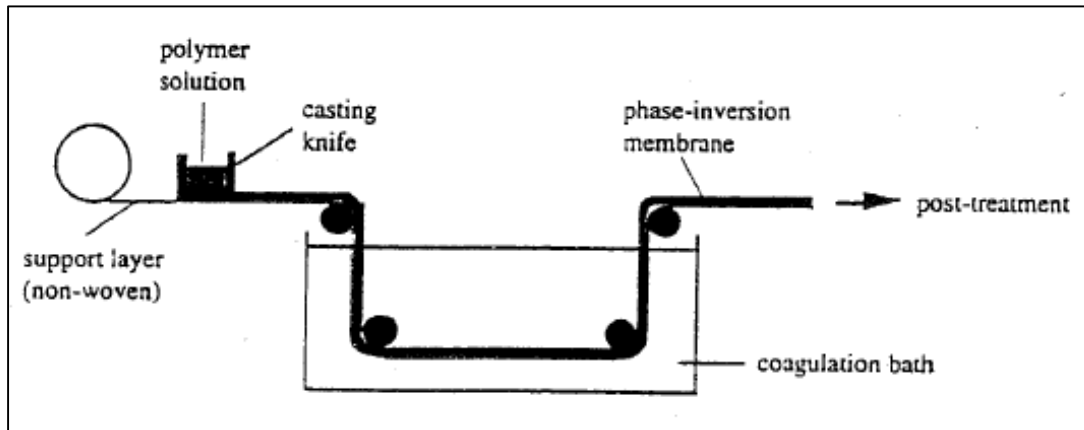


Figure 8: Flat membrane synthesized by phase inversion method[16]

Generally, the procedure for a mixed matrix membrane synthesis is the same as a polymer membrane, with the additional step of dissolving the inorganic fillers into the solvent mixture beforehand. The inorganic filler + solvent mixture will also need to be sonicated and stirred thoroughly for about six hours until all of the nanotube fillers dissolve completely in the mixture [6]. Figure 9 shows a visual flow on how inorganic filler is implemented in a general polymer membrane to form mixed matrix membrane. Two methods of casting are also shown in the figure [28].

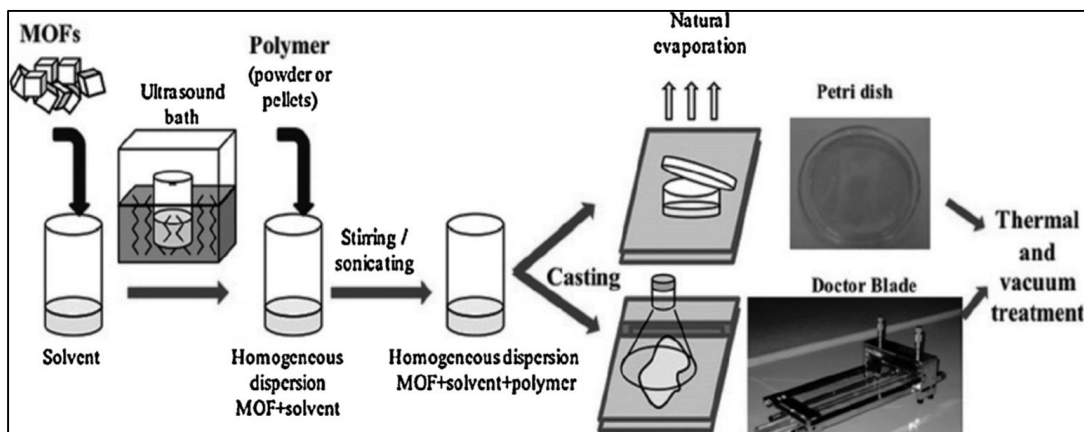


Figure 9: General Procedure of MMM synthesis[28]

CHAPTER 3: METHODOLOGY / PROJECT WORK

3.1 Overall research methodology

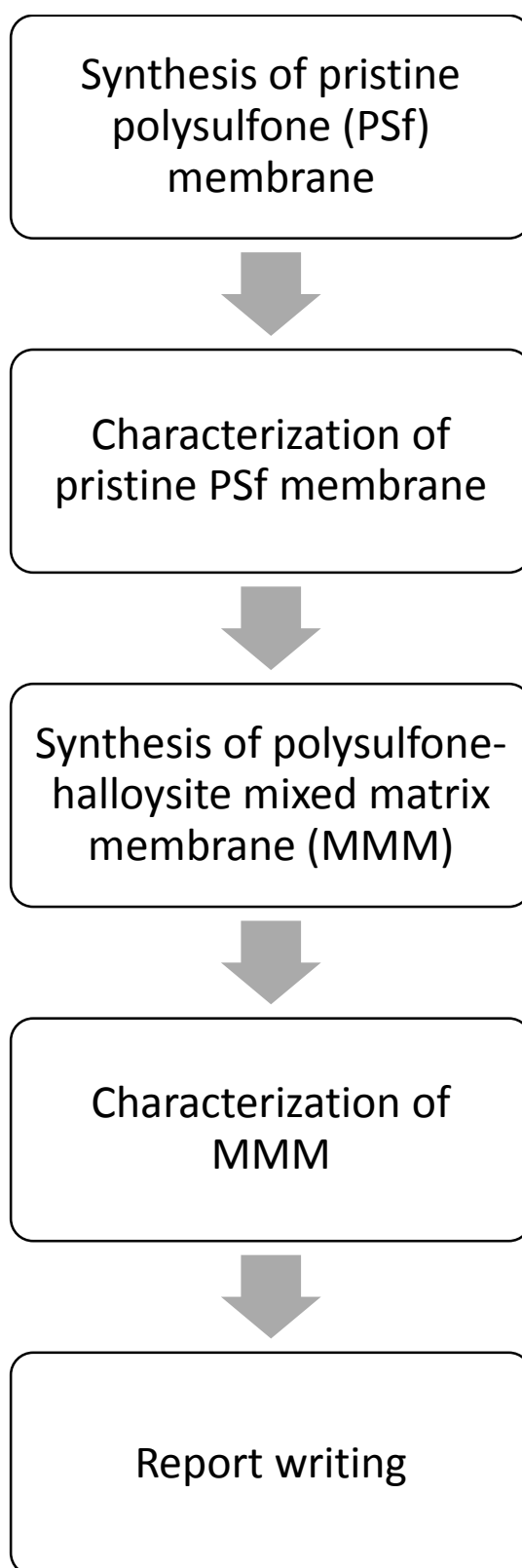


Figure 10: Overall research methodology

3.2 Gantt Chart

Task / Week	FYP 1														FYP 2																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Exam 1	Exam 2	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Introduction to FYP / First Briefing	█	█																													
Obtain Project Title / Meeting with Supervisor			█																												
Literature Review / Finding polymer to be used / Preparing the procedure for membrane casting			█	█	█																										
Procurement of Lab Space, Equipment, and Chemicals				█	█	█																									
Submission of Extended Proposal						█	█																								
Synthesis of Pristine Polymer (PSf) Membrane							█	█	█	█	█	█	█	█																	
Determination of optimal PSf wt% in the Pristine Polymer Membrane														●																	
Proposal Defence								█	█																						
Submission of Interim Draft Report											█																				
Submission of Interim Report													█																		
Determination of the Effects of Halloysite wt % on the Membrane														█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	
Determination of optimal Halloysite wt % in the PSf-Halloysite Mixture																								●							
Submission of Progress Report																															
Characterization of casted membranes																															
Pre-SEDEX																															
Submission of Draft Final Report																															
Submission of Dissertation (soft bound)																															
Submission of Technical Paper																															
Viva																															
Submission of Project Dissertation (hard bound)																															

3.3 Chemicals / glassware / equipment List

Table 3: Chemicals / Glassware / Equipment List

Type	No	Name	Amount	Supplier/Brand
Chemicals	1	Halloysite	20 g	Sigma Aldrich
	2	Polysulfone (PSf)	54 g	Solvay
	4	N-methyl-2-pyrrolidone	96.1 mL	Merck
Glassware	1	Beaker	50 mL x3	Duran
	2	Beaker	25 mL x3	Duran
	3	Measuring cylinder	10 mL x1	Duran
	4	Measuring cylinder	25 mL x1	Duran
	5	Filter funnel	N/A	Duran
	6	Stirring bar	N/A	Duran
	7	Glass plate	5	Duran
	8	Flat bottom centrifuge tubes	5	Duran
Equipment	1	Electronic balance	1	Mettler Toledo
	2	Hotplate magnetic stirrer	3	Favorit
	3	Stopwatch / Timer	3	N/A
	4	Ultrasonic degasser	1	Fisherbrand
	5	Casting knife	1	Plasmost
	6	Coagulation bath	N/A	N/A
	7	Oven	N/A	Carbolite
	8	FESEM (Supra55 VP)	N/A	Zeiss
	9	TGA (STA 6000)	N/A	Perkin Elmer
	10	DSC (DSC Q2000)	N/A	Research Instruments

3.4 Synthesis of pristine polysulfone membrane

In the first phase of this study, the casting solution formulation for synthesis of pristine polysulfone (PSf) membrane will be elucidated. The polymer powder will be Commercial Udel[®] polysulfone, PSF (Solvay Advanced Polymer) and the solvent used to dissolve the polysulfone powder will be N-methyl-2-pyrrolidone (NMP) – 99.5% purchased from Merck.

3.4.1 Experimental procedure

- (i) 5g of PSf powder is left in the oven for 24 hours at 80°C to remove moisture.
- (ii) 8.6mL of NMP is measured and mixed into a 25mL beaker.
- (iii) 2.132g of the dried PSf powder is weighed using an electronic balance and added into the 25mL beaker.
- (iv) The mixture is stirred without heating for 24 hours
- (v) The homogeneous solution is sonicated and degassed for 4 hours.
- (vi) After sonication and degassing, the solution is left standing overnight.
- (vii) The solution is sonicated and degassed for 30 minutes, followed by standing for 30 minutes.
- (viii) The solution is poured onto a glass plate, and casted using a casting knife.
- (ix) The glass plate is immersed into a water coagulation bath for 24 hours.
- (x) The membrane is left to air dry at room temperature for 24 hours.

3.5 Synthesis of polysulfone-halloysite mixed matrix membrane

In the second phase of this study, halloysite nanoclay filler will be added into the mixture to study on the effects of halloysite nanoclay filler on mixed matrix membrane fabrication.

3.5.1 Experimental procedure

- (i) 5g of PSf powder and 1g of halloysite nanoclay filler are left in the oven for 24 hours at 80°C to remove moisture.
- (ii) 8.5mL of NMP is measured and mixed into a 25mL beaker.
- (iii) 0.107 of the dried halloysite nanoclay filler is weighed using an electronic balance and added into the 25mL beaker.
- (iv) The mixture is transferred into a flat bottom centrifuge tube and sonicated for 1 hour at 40°C.
- (v) The mixture is then stirred for 5 hours at 40°C at the 25mL beaker.
- (vi) 2.145g of the dried PSf powder is weighed and added into the 25mL beaker.
- (vii) The mixture is stirred for without heating for 24 hours.
- (viii) The homogeneous solution is sonicated and degassed for 4 hours.
- (ix) After sonication, the solution is left standing overnight.
- (x) The solution is sonicated and degassed for 30 minutes, followed by standing for 30 minutes.
- (xi) The solution is poured onto a glass plate, and casted using a casting knife.
- (xii) The glass plate is immersed into a water coagulation bath for 24 hours.

(xiii) The membrane is left to air dry at room temperature for 24 hours.

Figure 11 summarizes the steps needed to complete the synthesis of pristine polysulfone membrane (first phase) and polysulfone-halloysite MMM (second phase)

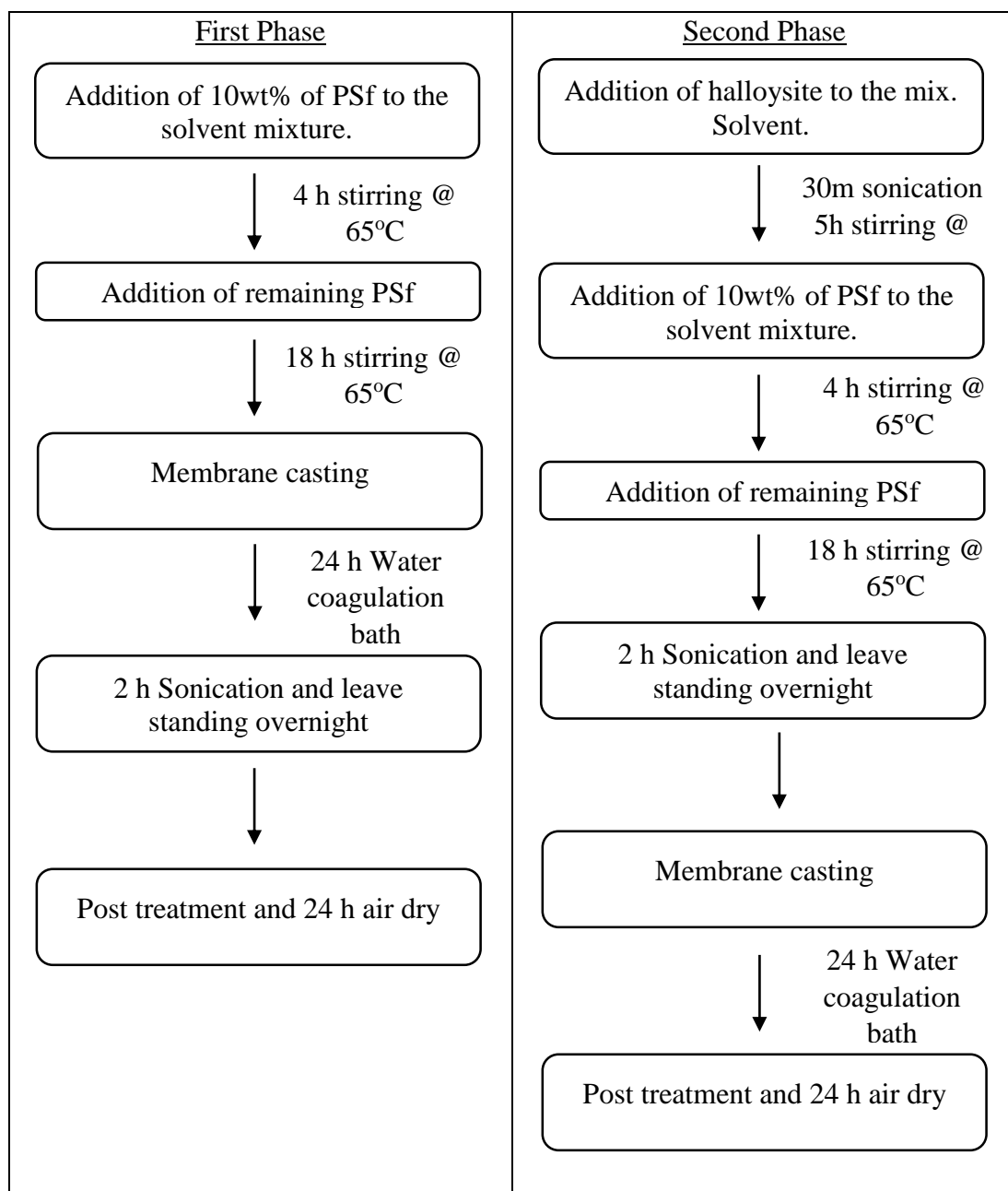


Figure 11: Process flowsheet / Sequence of Work

3.6 Characterization tests

3.6.1 Field emission scanning electron microscopy (FESEM) test

As mentioned before in Section 2.3, mixed matrix membrane are considered defect if there are voids that are too big between the polymer matrix and the inorganic filler molecule. Field emission scanning electron microscope (FESEM) is utilized to investigate the extent of the adhesion between the inorganic filler particle and polymer matrix [6].

Field emission scanning electron microscopic (FESEM) tests will done on selected pristine polymer membrane and mixed matrix membrane samples. Sample membrane size of 2cm x 3cm will be used for the test. Cross sectional view and plan view of the membrane will be done using FESEM at various magnifications.

3.6.2 Thermogravimetric analysis (TGA)

Thermal gravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere [34]. In the case of gas separation membranes, TGA is used to investigate the thermal stability of hybrid films [14].

Thermal gravimetric analysis (TGA) will be performed on both the pristine polymer membrane and mixed matrix membrane. Selected samples will be heated from 30 up to 800°C at the heating rate of 10°C min⁻¹, under nitrogen atmosphere, with a nitrogen flow rate of 20 mL min⁻¹ [6, 33].

3.6.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique designed to determine how heat capacity (C_p) of a particular material is changed by temperature. A sample of material with its mass weighed is heated and the changes in its heat capacity are tracked [24].

In this study, DSC is only conducted on the mixed matrix membrane, to determine its glass transition temperature (T_g). Glass transition temperature refers to the temperature where glassy polymers starts to reforms into rubbery polymers.

Differential scanning calorimetry (DSC) will be performed on the membrane samples to determine the glass transition temperature (T_g) of the mixed matrix membrane. The membrane samples will be cut into smaller pieces, weighed and placed onto a pre-weighed crucible. The membrane samples will be heated at temperature ranges of 30 – 400°C at a heating rate of 10°C min⁻¹ in the first cycle to remove the heat signature [6], and then cooled from 400°C to 30°C with the same cooling rate. The same procedure is repeated for a second cycle, and the T_g will be determined as the midpoint of the transition region during the second cycle [6, 33].

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Membrane synthesis

Table 4 shows the pristine membranes synthesized, with their respective composition of polysulfone (PSf). This preliminary study was conducted to determine the optimum composition of PSf for elucidating the dope solution. It was found that membranes at different composition exhibited different physical traits.

Figure 12 shows an example of defect-free membrane. In this case, the 20 wt% pristine PSf membrane displayed the optimum characteristics among the testing range of 15-25 wt%. This optimal PSf composition was within the acceptable range reported by Julian and Wenten [18]. Hence, 20 wt% of PSf was used in the subsequent synthesis of mixed matrix membrane (MMM) with varying loading of halloysite nanoclay filler ranging from 3 wt% to 5 wt%.

Polysulfone-halloysite MMM exhibits similar physical appearance as pristine polysulfone membrane, as the same solvent – NMP was used in both pristine and MMM synthesis. In order to determine further which filler composition has the best physical characteristics and adhesion with the polymer matrix, various characterization tests were performed.

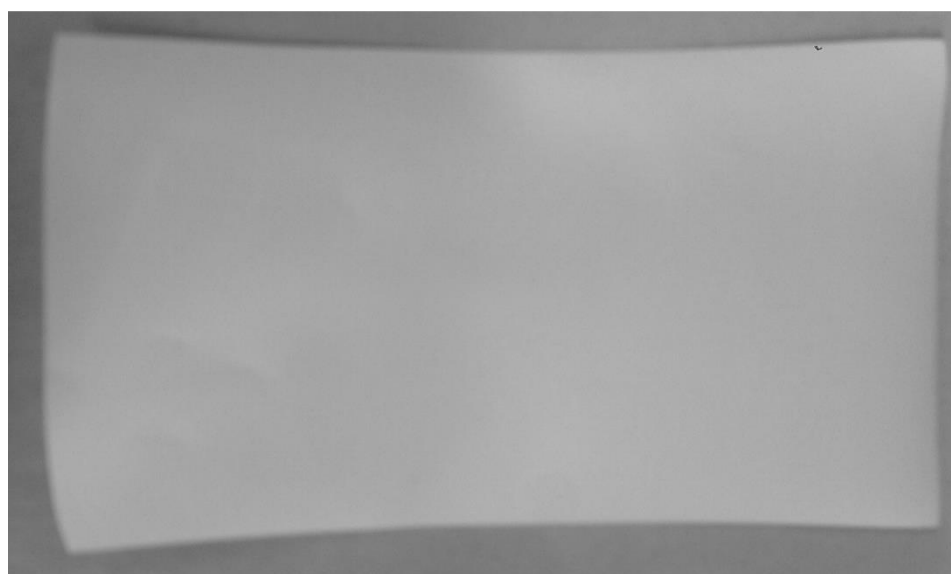


Figure 12: Defect-free polysulfone membrane (20 wt%)

Table 4: Membranes synthesized

Sample No.	Composition (wt%)	Remarks (Visual Observation)
1	15% PSf	Wrinkles formed
2	20% PSf	Defect-free
3	25% PSf	'Powdery' feel due to migration of polymer to the surface

4.2 FESEM

4.2.1 Membrane Morphology (Top Views)

Figure 13(a) shows the top view of a pristine 20 wt% PSf membrane. Pores can be observed to be distributed evenly among the polymer matrix.

Figure 13(b) shows the top view of a MMM with 3 wt% loading. Compared to the MMM with 1 wt% loading, the pores of the polymer matrix were very visible and the halloysite fillers were well distributed throughout the polymer matrix. However, agglomeration was observed. Small voids can also be observed between the halloysite filler and the polysulfone matrix, showing weak adhesion of the filler with the polymer matrix.

Figure 13(c) shows the top view of a MMM with 5 wt% loading. Similar with 3 wt% halloysite loading, the halloysite fillers were well distributed throughout the polymer matrix. Nevertheless, agglomeration increased as compared to 3 wt% loading. Interfacial contact between the filler and polymer matrix deteriorated, resulting in more void formation.

In general, PSf – halloysite MMM exhibits excellent filler dispersion and adequate adhesion between the polymeric matrix and inorganic fillers. However, agglomeration of particles is very noticeable and this is expected to reduce the selectivity of the membrane.

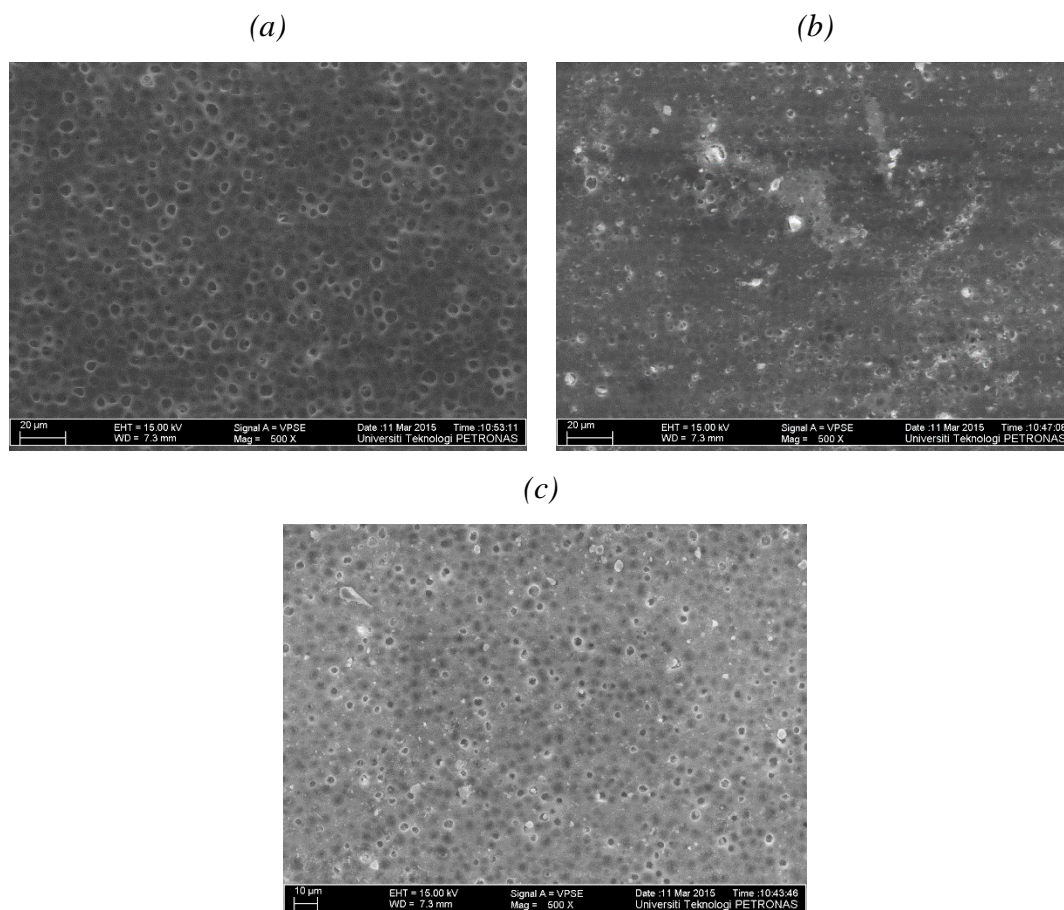


Figure 13: Top views of fabricated membranes (500x magnification). (a): Pristine 20 wt% PSf membrane; (b): 3 wt% halloysite loading MMM; (c): 5 wt% halloysite loading MMM

4.2.2 Cross Sectional Morphology

Figure 14 shows the cross sectional views of all the membranes analyzed. The casting thickness of the membranes was 200 μ m, nevertheless, as expected, the thickness reduced after drying. Table 5 tabulates the final thickness of the membranes.

Table 5: Thickness of fabricated membranes

Membrane Status	Thickness (μ m)
Pristine 20 wt% PSf	98.67
3 wt% Halloysite	99.84
5 wt% Halloysite	102.7

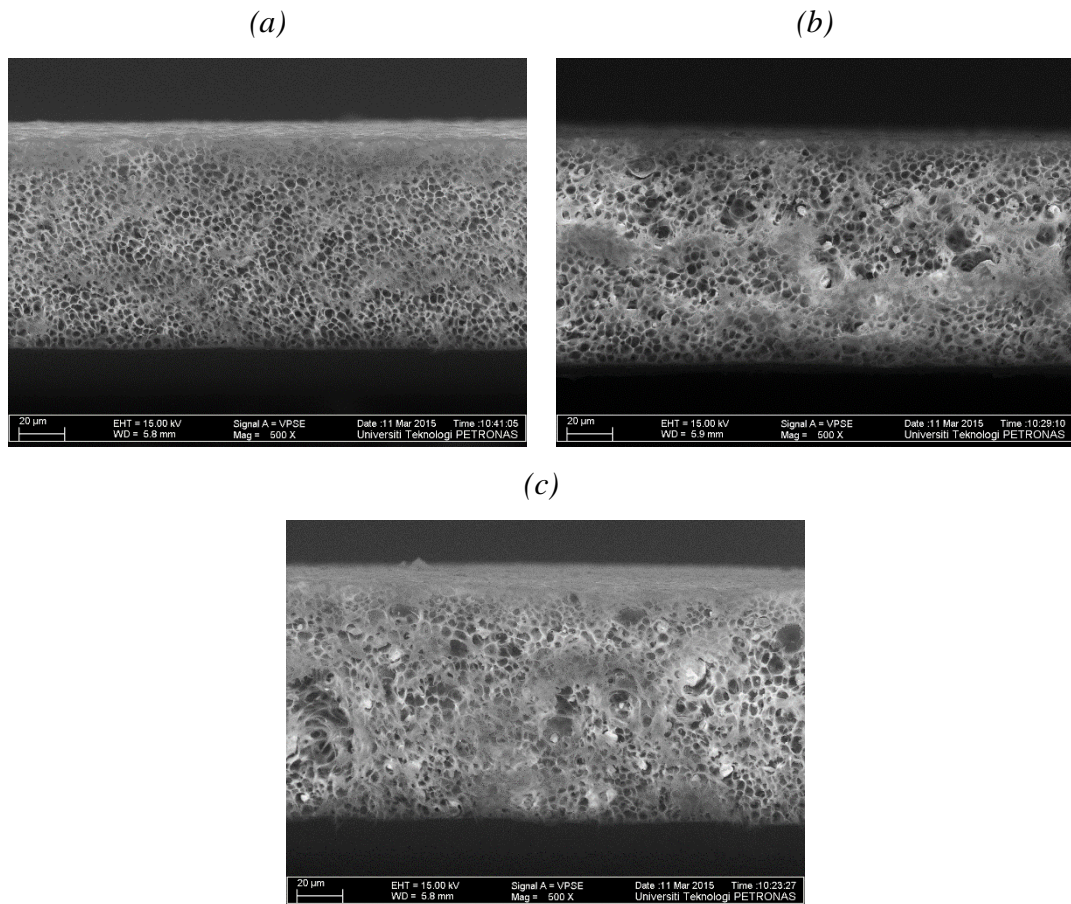


Figure 14: Cross sectional views of fabricated membranes (500x magnification). (a) Pristine 20 wt% PSf membrane; (b): 3 wt% halloysite loading MMM; (c): 5 wt% halloysite loading MMM

Figure 14(a) shows the cross sectional view of a pristine 20 wt% PSf membrane. Pores can be observed to be distributed evenly among the polymer matrix.

Figure 14(b) shows the cross sectional view of a MMM with 3 wt% halloysite loading. In line with the top view of the same membrane, the halloysite fillers are well distributed throughout the polymer matrix, and slight agglomeration can be observed. Poor adhesion between the polymer matrix and inorganic fillers can also be observed at certain parts of the membrane.

Figure 14(c) shows the cross sectional view of a MMM with 5 wt% halloysite loading. Similar to the MMM with 3 wt% loading, the halloysite fillers are well distributed throughout the polymer matrix, but agglomeration of halloysite was more significant. There appeared to be larger agglomerates due to increased halloysite loading. The adhesion between the polymer matrix and the inorganic fillers also deteriorated as compared to MMM with 3 wt% loading.

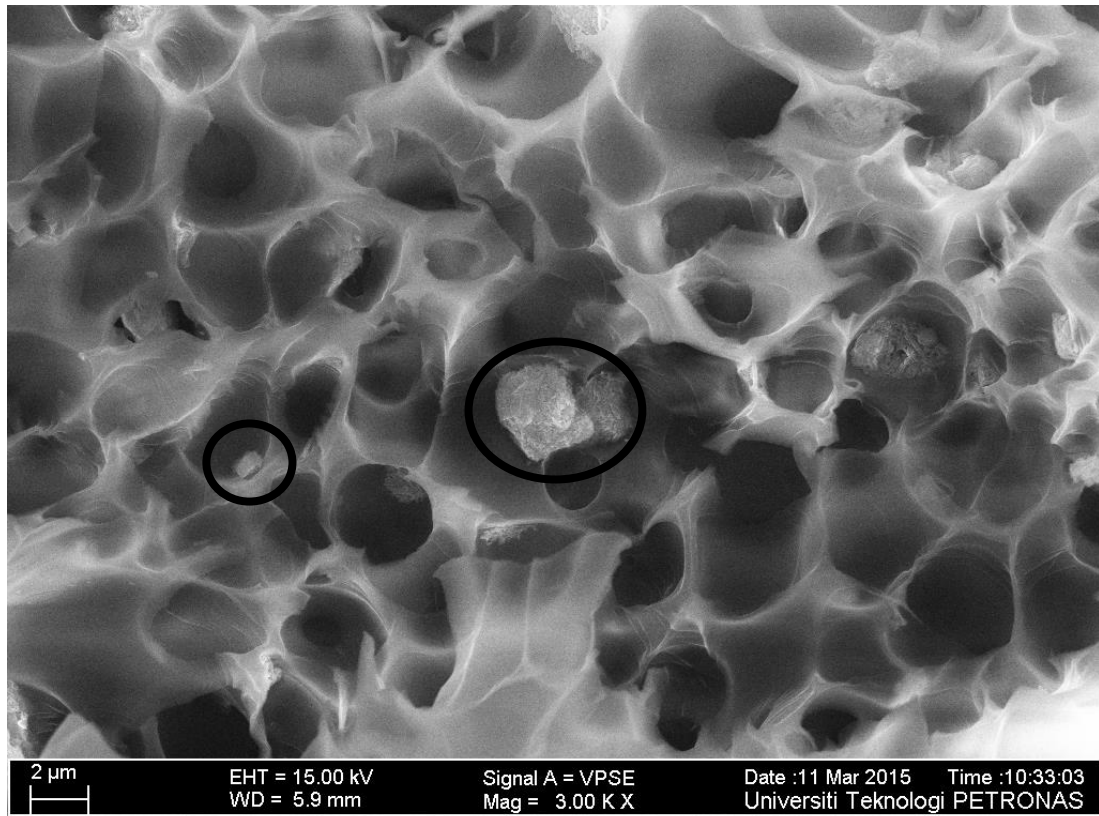


Figure 15: Cross sectional view of 3 wt% halloysite loading membrane (3000x magnification)

Figure 15 shows a zoomed in cross sectional view of MMM with 3 wt% halloysite loading at 3,000x magnification. Slight agglomeration can be observed (highlighted in the big circle), compared to a single particle (highlighted in the small circle). The zoomed in cross sectional view also shows a good dispersion rate of the inorganic fillers.

Figure 16 shows a zoomed in cross sectional view of MMM with 5 wt% halloysite loading at 3,000x magnification. Slight agglomeration can be observed (highlighted in the big circle), compared to a single particle (highlighted in the small circle). There appeared to be larger agglomerates due to increased halloysite loading (highlighted in the biggest circle). The zoomed in cross sectional view also shows a good dispersion rate of the inorganic fillers.

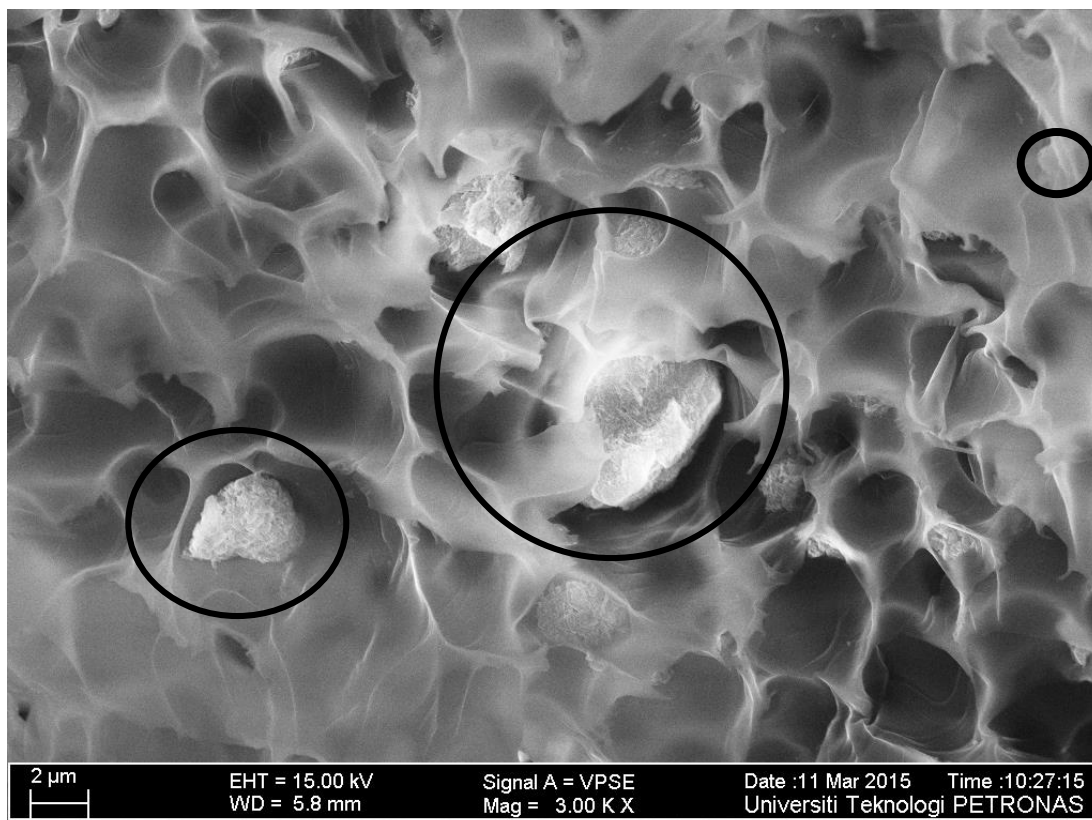


Figure 16: Cross sectional view of 5 wt% halloysite loading membrane (3000x magnification)

4.3 TGA

4.3.1 Individual TGA Curves

Figure 17 shows the thermogravimetric analysis curves for all four fabricated membranes. Figure 17(a) shows the TGA analysis curve for pristine 20 wt% PSf membrane. The peak of the derivative weight curve indicates that the decomposition temperature of the membrane is at 543.09°C. The second peak of the graph is exhibited due to possible contamination of the membrane during the analysis, as pristine membranes are only supposed to display one peak (due to its pure nature). Besides, the mass of the membrane is completely diminished at the end of the experiment, which may be due to its weak resistant towards high temperature, or equipment failure.

Figure 17(b) shows the TGA analysis curve for 3 wt% halloysite loading MMM. The peak of the derivative weight curve indicates that the decomposition temperature of the membrane is at 519.18°C. This shows a decrease in decomposition temperature compared to the pristine membrane. Similar to the previous MMM, a drop in decomposition temperature compared to the pristine PSf membrane can be observed, and might be due to the lack of adhesion between the inorganic fillers and the polymer

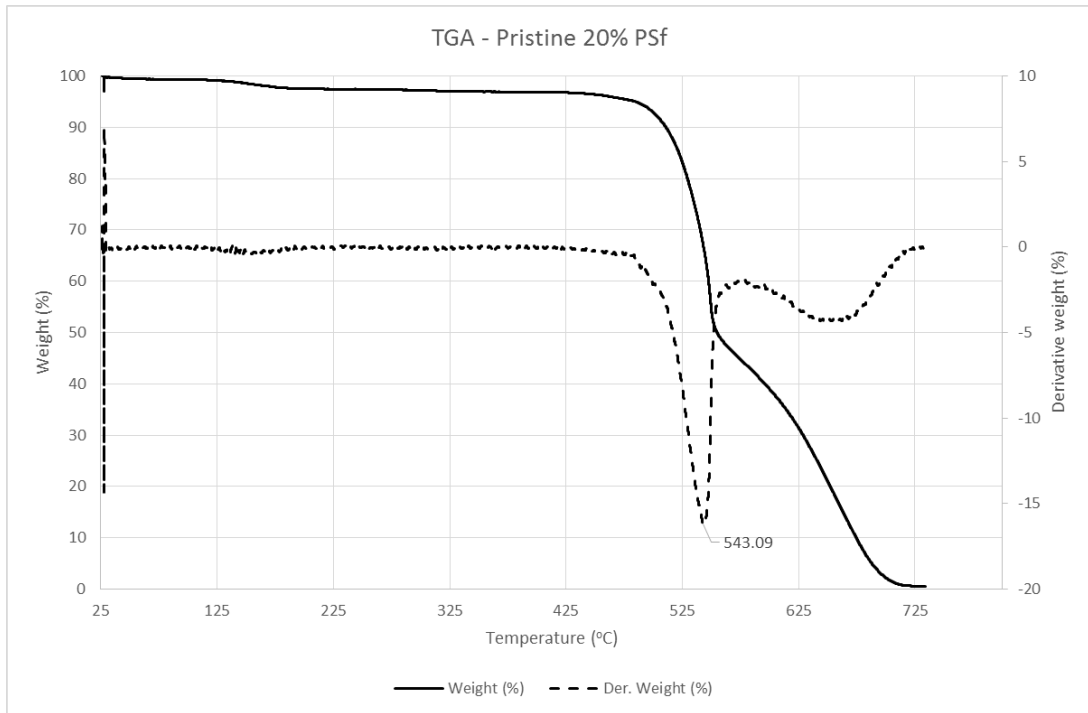
matrix. Higher loading of halloysite filler here gives lower decomposition temperature, which is due to worse adhesion of the filler and the polymer matrix.

Figure 17(c) shows the TGA analysis curve for 5 wt% halloysite loading MMM. The peak of the derivative weight curve indicates that the decomposition temperature of the membrane is at 528.48°C. This shows a decrease in decomposition temperature compared to the pristine membrane, but shows an improvement compared to the 3 wt% halloysite loading MMM. Similar to the 3 wt% halloysite loading MMM, a drop in decomposition temperature compared to the pristine PSf membrane can be observed, and might be due to the lack of adhesion between the inorganic fillers and the polymer matrix.

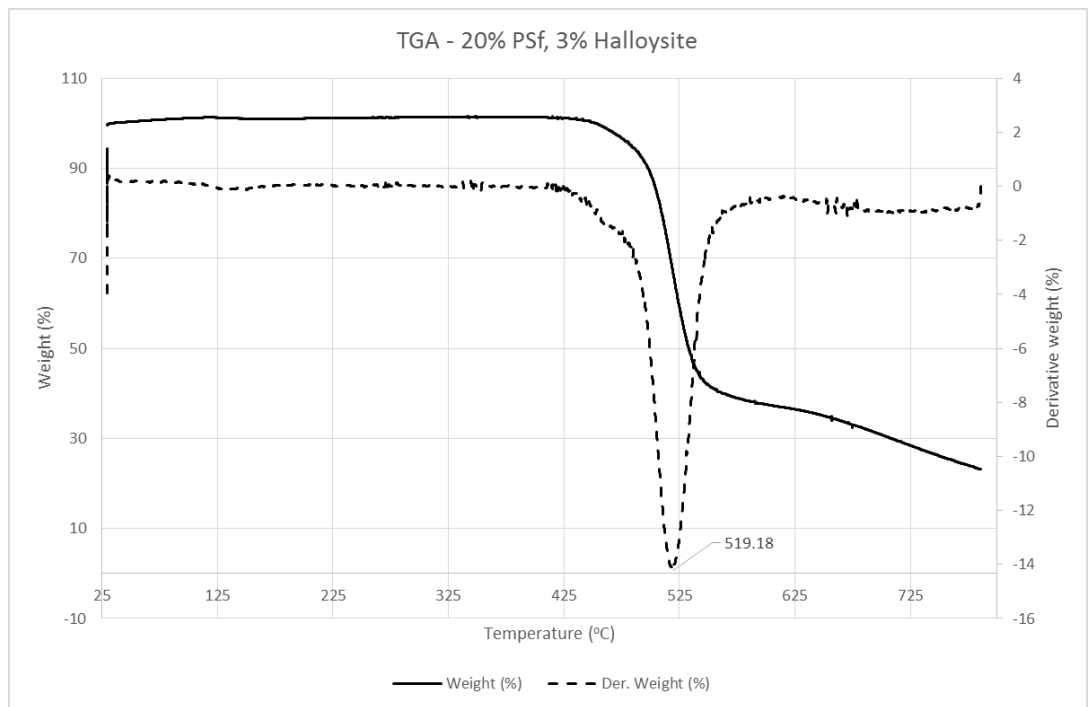
The decomposition temperatures of the fabricated membranes can be determined by looking at the peak of the derivative weight % line of each graph. The decomposition temperature determines the strength of a membrane to a certain extent and is important in differential scanning calorimetry as it gives the range of possible glass transition temperature of the membranes. The decomposition temperatures are tabulated in table 6. There are a lot of noise present in the graphs, which may be due to small defects in the membrane pieces used in the analysis, or incomplete cleaning of the equipment prior to analysis (contaminated with previous samples). In general, incorporation of halloysite fillers into PSf membrane will reduce the decomposition temperature, and hence lowering the heat resistance of the membrane. However, increase in halloysite loading will increase the decomposition temperature of the MMM.

Table 6: Decomposition temperature of the fabricated membranes.

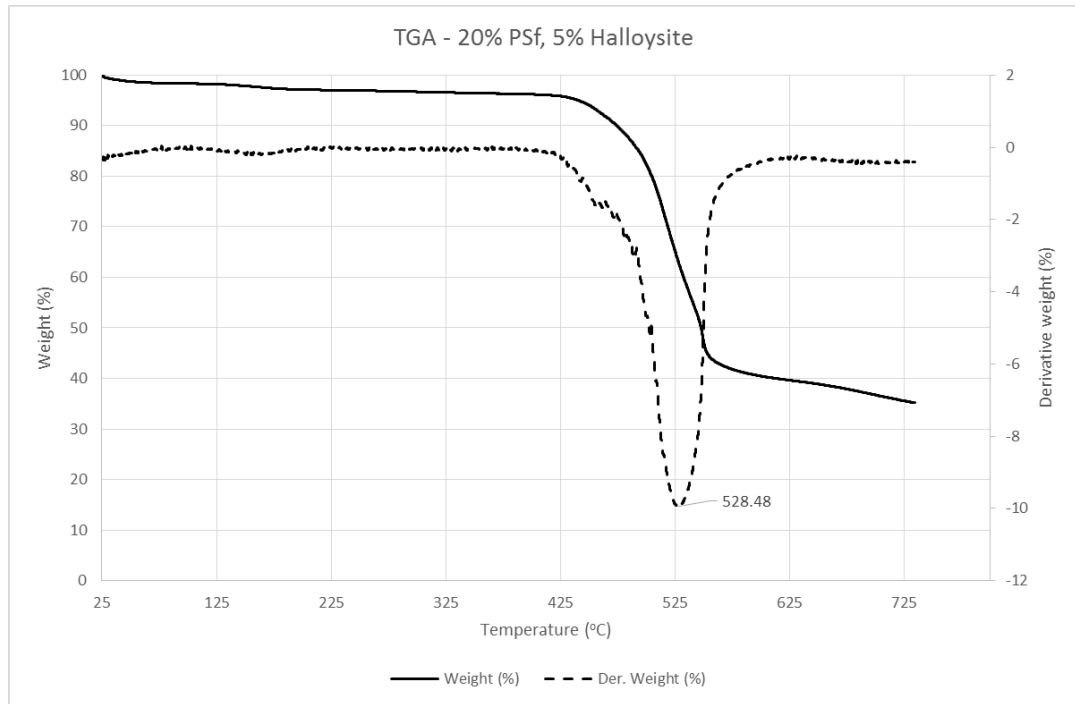
Membrane Status	Decomposition temperature (°C)
Pristine 20 wt% PSf	543.09
3 wt% halloysite loading	519.18
5 wt% halloysite loading	528.48



(a)



(b)



(c)

Figure 17: Individual TGA curves (a) Pristine 20 wt% PSf membrane (b) 3 wt% halloysite loading MMM (c) 3 wt% halloysite loading MMM

4.3.2 Combined TGA Curve

Figure 18 shows the weight loss all the four membranes analyzed. The remaining weight % of the membrane is displayed in the graph after exposed to high temperature of more than 730°C. The 20 wt% pristine PSf membrane curve shows that there are no residue left after being exposed to 730°C, compared to the other MMM that has remaining residue. This contradicts with the TGA analysis earlier which shows that pristine PSf membrane is more inert to temperature as it has a higher decomposition temperature. This can be due to contamination during one of the analysis, or equipment failure. However, this is in agreement with literature reviews that state that mixed matrix membrane has higher temperature resistance compared to pristine organic membrane due to incorporation of inorganic fillers [6].

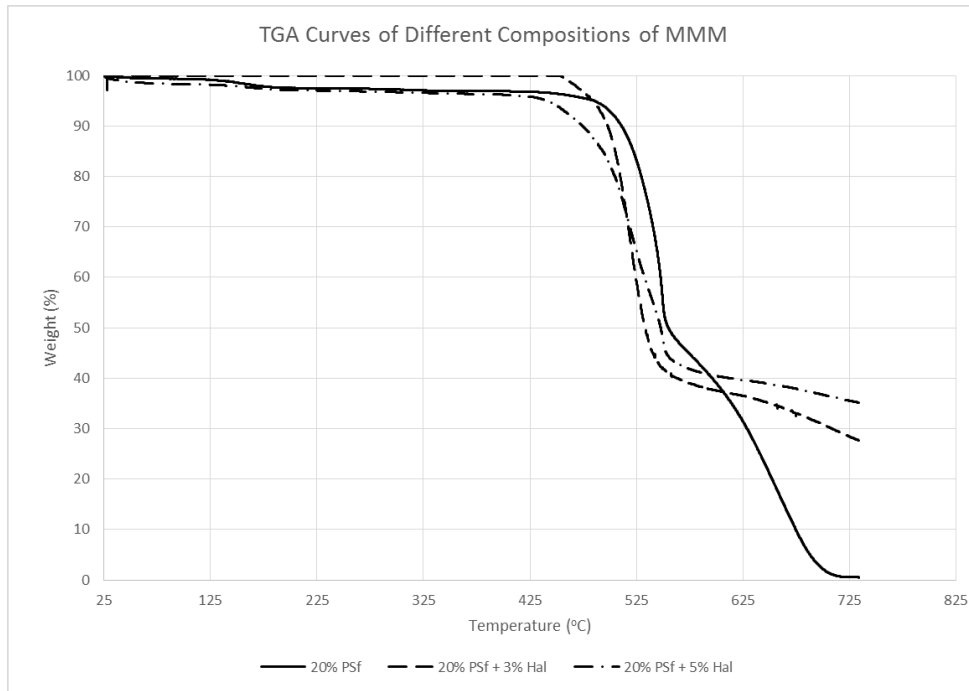


Figure 18: TGA curves of different compositions of membranes

4.4 DSC

Differential scanning calorimetry is done on the four samples, and the glass transition temperatures, T_g are tabulated in table 7. The influence of the addition of different loads of halloysite in polysulfone polymer is illustrated. The temperatures are all above the pristine PSf polymer T_g . It can be concluded that the structure of the membrane is getting more crystalline as the load of halloysite fillers is increased.

Table 7: Glass transition temperature of the fabricated pristine PSf membrane and PSf-halloysite MMM

Membrane Status	T_g (°C)
Pristine 20 wt% PSf	178.34
3 wt% halloysite loading	184.34
5 wt% halloysite loading	189.60

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

The effects of halloysite nanoclay fillers in polysulfone membrane are analyzed in the project. Pristine polymer membrane with 20wt% of polysulfone is chosen as the basis to synthesize the mixed matrix membrane (MMM) as it exhibits the best physical characteristics. MMMs consisting of 3wt% and 5wt% of halloysite fillers are then synthesized and all four membranes are analyzed using FESEM, TGA, and DSC.

PSf – halloysite MMM exhibits excellent dispersion of inorganic fillers in the polymer matrix. However, the adhesion between the polymer matrix and the inorganic fillers is not up to expectation, and will cause a drop in selectivity of the membrane, compared to pristine PSf membrane. Agglomeration of particles can also be observed at higher weight percentages of halloysite fillers.

TGA results of the membranes show that the heat resistance of the MMM is generally lower than pristine PSf membrane, which contradicts the literature whereby MMM generally has higher heat resistance compared to pristine organic membrane [6]. The loading of the halloysite fillers in MMM will also affect the heat resistance performance of the MMM. The higher the loading of fillers, the better the heat resistance.

DSC results show that the incorporation of halloysite fillers into pristine PSf membrane will make the membrane more crystalline. The higher the loading of filler, the more crystalline the membrane will become, showing an improvement of MMM compared to pristine PSf membrane.

In general, the 3 wt% halloysite loading MMM exhibits the best traits from all the analytical test done. It has high decomposition temperature, high glass transition temperature, excellent dispersion of halloysite fillers in the polysulfone matrix, and only a small amount of agglomeration and void between the filler and matrix can be observed.

Throughout the project, the author managed to chose the best polymer to be used along with halloysite nanoclay filler. Pristine polysulfone membrane and polysulfone – halloysite mixed matrix membrane are also synthesized and had the effects of halloysite in the membrane studied. The optimal composition of the MMM is also determined. All the objectives of this project are achieved.

As a recommendation for future works, the CO₂/CH₄ gas permeation tests can be done on the fabricated membranes. The values obtained from the tests can be studied, and then the performance of MMM and pristine PSf membrane can be compared. This can be done if the project timeline is further extended. The gas permeation test will give more conclusive results to backup the fact that MMM shows improvement in performance compared to pristine organic membrane.

Another recommendation is to reduce the agglomeration and adhesion of the MMM. In order to reduce the occurrence of this two unwanted scenarios, the stirring and mixing procedure of the dope can be further improved. This can be done by having more sonication and degassing sessions in between the addition of PSf and halloysite powder into the solvent mixture so that the solid components are dispersed more evenly. Besides, the stirring time can also be lengthened or shortened in order to get the best stirring time.

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