Plasticization and Aging Effect on Polysulfone (PsF) Based Mixed Matrix Membrane in Carbon Dioxide Permeation

by

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16812

Dissertation submitted in partial fulfilment of

the requirements for the

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr. Yeong Yin Fong)

UNIVERSITI TEKNOLOGI PETRONAS
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May 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.

SHUSHILAN PILLAI A/L RAMACHANDRAN

ABSTRACT

Polysulfone (PsF) membranes which undergo plasticization during gas separation involving CO_2 is a rising issue that has to be dealt with. Plasticization which is an irreversible process causes the disentanglement of polymer chains at high pressure observed by the depression of the glass transition temperature, Tg. Another problem faced by the polymeric membranes such as PsF aging which is the deterioration of the membranes performance with time. Mixed matrix membranes which contains the mixture of polymeric membranes and inorganic particles makes use of the advantages of both the components, making it the new approach in the membrane separation technology. In the present work, PsF/ZIF-8 mixed matrix membrane was fabricated and their structural properties was characterized using analytical tools such as scanning electron microscope and energy dispersive X-ray. The resultant membranes underwent plasticization and aging test in CO_2 permeation. The resultant data showed that the membranes fabricated using different loadings of ZIF-8 improved the aging duration of the membrane. Pure PsF membrane showed a 49.97% permeation reduction due to aging after 30 days. The MMM with 5 wt% ZIF-8 showed a 47.54% permeation reduction while the 20 wt% ZIF-8 MMM showed a 5.99% permeation reduction. The membranes shows and increase in resistance towards aging effect with the increase in the amount of loading of ZIF-8.The resultant mixed matrix membrane also showed improvements in permeation towards CO_2. However, no significant improvements towards plasticization was discovered from the mixed matrix membrane fabricated in the present work.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The synthetic membrane technology is used in a large industrial scale for various industries. The membrane technology is a relatively new technology which is still being researched on as it has not been perfected. There are various types of membranes reported in the literature such as liquid membranes, ceramic membranes and polymeric membranes (Julian and Wenten, 2012).

With pressing environmental concerns, scientist and researchers from all over the world are figuring out ways to trap and prevent greenhouse gasses from being emitted into the atmosphere. One of the major research would be carbon dioxide CO_2 removal. Polymeric membrane is the most common type of membrane used in the separation of gasses today. Polymeric materials such as polysulfone (PsF), polyethersulfone (PES), and polyimide (PI) exhibit high selectivity coefficients and acceptable permeability values for separation of gas mixture. From the list of polymeric membranes, Polysulfone is extensively explored for gas separation due to its low price, easy synthesis, long life, good thermal stability, chemical stability, and mechanical strength (Ismail A.F and Lorna W, 2002). Polysulfone membrane though cheap and useful, it possess weakness. In CO_2 separation, polysulfone membrane shows CO_2 induced plasticization and aging (Hadi,N.A and Ismail,A. F, 2014). Therefore, many approaches have been reported in overcoming these problem. Currently, researches has found an ingenious way to solve this arising problem. The solution is altering the current polymeric membrane into a mixed matrix membrane.

Mixed matrix membranes is a relative new type of membrane materials which combining the benefits of both polymeric and inorganic material with improved performance such as enhancing the gas permeability and selectivity. Mixed matrix membranes are obtained by embedding numerous types of fillers such as carbon molecular sieves, mesoporous molecular sieves, activated carbon, silica or conductive polymers, but mostly zeolites into a polymer matrix (Zimmerman C.M et al., 1997). Inorganic molecular sieves like zeolites and carbon molecular sieves are excellent materials with diffusivity selectivity significantly higher than polymeric materials (Zimmerman C.M et al., 1997).

1.2 Problem Statement

In order to enhance the properties of the membrane, the permeability and selectivity values of membranes should be as high as possible for industrial gas separation applications to work efficiently and effectively. Polymeric membrane though currently being used for CO_2 removal, it shows limitations such as plasticisation and aging effect towards certain gasses. This problem could be reduced with the introduction of mixed matrix membranes. Although mixed matrix membranes shows improvements in performance for CO_2 removal, the problem in CO_2 plasticization and aging effect are yet to be overcome. Plasticization and aging effect still remain a challenging issue.

Therefore, in the present work mixed matrix membrane ZIF-8/PsF were fabricated and tested. Different loading amounts of ZIF-8 were incorporated into to PsF. These MMM were then subjected to CO_2 permeation testing in order to study the behaviour of the membrane in plasticization and aging.

1.3 Objectives and Scope of Study

The aim of this study is to:

1. To fabricate a series of ZIF-8/PsF mixed matrix membranes by incorporating different loading of ZIF-8 into PsF polymer matrix
2. To characterize the resultant mixed matrix membranes using Scanning Electron Microscope (SEM) , and Energy-Dispersive X-ray spectroscope (EDX)
3. To test the CO_2 plasticization and aging on the resultant membranes.

1.4 Relevancy & Feasibility

Mixed matrix membranes are the latest breakthrough in the membrane technology to overcome limitations faced by polymeric membranes. Mixed matrix membranes is able to sustain the easy of fabrication as well as cost while improving the high intrinsic permeability and selectivity of the membrane. The timeframe given to complete this project is sufficient with the first portion of the project being an in depth study of the literature which the second half focuses on casting the membranes and testing it. The data obtained from the test would be analysed thoroughly.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Dioxide/Natural Gas Separation Technology

Since the pre-industrial age, it was observed that there was an increase of 100 ppm of CO_2 in the atmosphere which has led to the increase in the world's temperature by 1°C. (Florides G.A and Christodoulides P ,2009). Thus, with the ever growing population, it is clear that this problem has to be dealt with. With the drastic increase in greenhouse gases in the atmosphere, a larger scope of gases which includes carbon dioxide is being researched on to figure out methods to capture it successfully. However, this is not the only reason to why CO_2 separation is highly being researched on. The first commercial interest in the separation of CO_2 from flue gas was its application for enhanced oil recovery (EOR) (Herzog et al., 1997). Application of CO_2 for EOR started in the 1970s and has proved to be an effective economic approach over the years (Long et al.,2006).Chemical absorption such as absorption with monoethanolamine (MEA) solvent, membrane separation, cryogenic fractionation, and adsorption using molecular sieves are some of the methods used today for the capture of these gasses (Goulumb et al., 2010) .

CO_2 found in oil wells along with CH_4 and other useful hydrocarbons is an undesired impurity which is able to reduce the caloric power of natural gas. This issue brings loss to gas processing plants and thus is a significant problem which has provoked the development of CO2 separation technologies.

2.2 Polymeric Membrane

Membrane technology is highly sort after and is a major researched technology as it has the capability of reducing the capital cost and energy consumption as compared to other capture methods used (Kapantaidakis G.C. et al., 1996). Membrane technology which incorporates both the advantages of chemical absorption and membrane separation (Gabelman and Hwang S.T, 1999) is now highly being explored. The major challenges faced today in the membrane industry are penetrant-induced plasticization, physical aging, conditioning and poor balance between permeability and selectivity (Ismail A.F and Lorna W, 2002). Membrane technologies are also highly being researched on due its robustness. Most oil fields are located in remote areas and also require robust and long lasting equipment to carry out operations continuously. Membrane separation system which utilises not moving parts makes it highly researched.

The ever expanding industry of membranes is due to the increase in concerns of the world's climate situations as well as the usage of certain gasses which is economically viable. Polymeric membranes are one of the most used membranes in various industries today due to their higher separation performance, requires less processing area, and does not require solvent regeneration (Kim.S , 2013). Polymeric membranes are synthetic membranes derived from polymers. There are various types of polymeric membranes which are selected based on its characteristics and function. Polymeric membranes can be split into two categories that are commercially available for gas separations which are glassy and rubbery membrane (Kapantaidakis G.C. et al., 1996).

Glassy membranes are rigid and glass like which operates below the glass transition temperature while the rubbery membranes are flexible, soft and operate above the glass transition temperature. Glass polymeric membranes are more popular in the industry due to its high selectivity. However, glass polymeric membrane has low permeability. The rubbery polymeric membranes has the high permeability but low selectivity (Mustaq A et al., 2013) .Table 1 shows the different types of membranes used in industries.

TABLE 1. Common polymers used in industrial gas separation membrane (Zhong, 2012).

RUBBERY POLYMERS	GLASSY POLYMERS
Poly(dimethylsiloxane)	Cellulose acetate
Ethylene oxide/propylene oxide-amide copolymers	Polyperfluorodioxoles
	Polycarbonates
	Polyimide
	Poly(phenylene oxide)
	Polysulfone

Polymeric membranes works the same way all other membranes would. It operates based on the same principle which is observed in osmosis process which is the spontaneous net movement of solvent molecules through a partially permeable membrane into a region of higher solute concentration, in the direction that tends to equalize the solute concentrations on the two sides (Paul D. , 2004). Hence the driving force of the separation is pressure gradient between the membrane layers. Polymeric membranes are used commercially to separate air which is mainly targeted in separating different mixtures of air, for example to separate carbon dioxide from natural gas. The most common polymers in membrane synthesis are cellulose acetate, Nitrocellulose, and cellulose esters (CA,CN, and CE), polysulfone (PS), polyether sulfone (PES), polyacrilonitrile (PAN), polyamide, polyimide, polyethylene and polypropylene (PE and PP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyvinylchloride (PVC) (Nunes S.P and Peinemann K.V , 2001). The most common membrane used in industries nowadays are the polysulfone membrane which will be discussed later in the section. Table 2 shows various applications of membrane-based gas separation in industries.

TABLE 2. Various applications of membrane-based gas separation in industries (P.S. Goh, 2011).

GAS SEPARATION	APPLICATIONS
O_2/N_2	Oxygen enrichment, inert gas generation
H2/hydrocarbon	Refinery hydrogen recovery
H_2/N_2	Ammonia purge gas
H_2/CO	Syngas ratio adjustment
CO_2/hydrocarbon	Acid gas treatment, greenhouse gas capture
H_2O/hydrocarbon	Natural gas dehydration
H_2S/hydrocarbon	Sour gas treating
He/hydrocarbon	Helium separation
He/N_2	Helium recovery
Hydrocarbon/air	Hydrocarbon recovery
H_2O/air	Air dehumidification

Polymeric membrane may seem like the best alternative for the industry as a separating and capturing technology, however it has yet to be perfected. Some of the problems faced are plasticization and aging effect. Figure 1 below shows the plasticization phenomena of polymeric membranes. One method used to overcome this problem is by the fabrication of mixed matrix membrane which consists of inorganic fillers and polymer matrix which could improves certain limitations depending on the type of inorganic filler added. Mixed matrix membranes will be discussed in the later section.

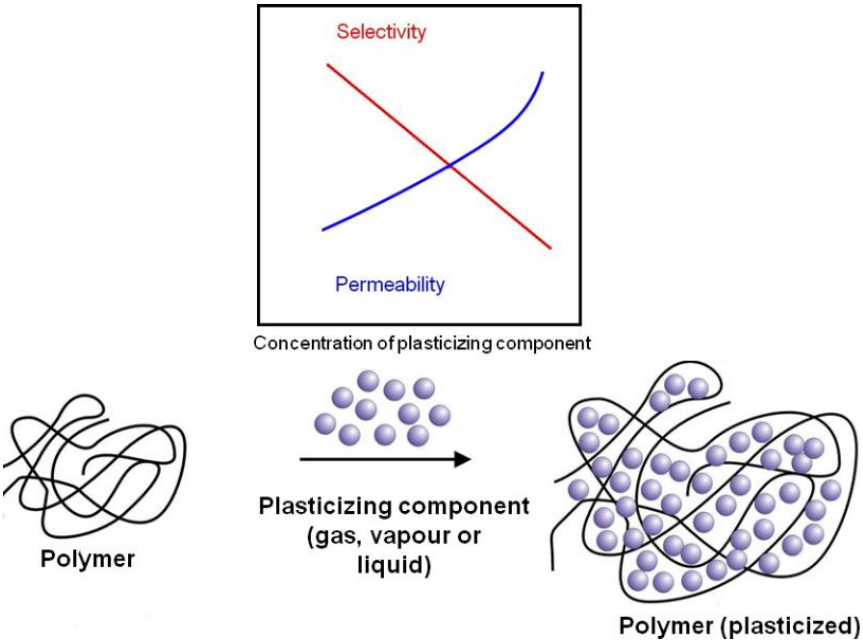


FIGURE 1. Plasticization phenomena of polymeric membranes (Ritter, 2010).

2.2.1 Polysulfone Membrane

The polysulfone membrane (PSF) is a thermoplastic polymer which contains the subunit aryl-SO2-aryl, the defining feature of which is the sulfone group. PSF is rigid, transparent and strong provided the temperature is between -100^oC and 150^oC.Its glass transition temperature which is the temperature region where the polymer transitions from a hard, glassy material to a soft, rubbery material is at 185 ^oC (Ismail A.F and Lorna W, 2002). Although polysulfone membrane has been commercially used, it shows limitations and properties drawbacks.

Polysulfone membrane undergoes penetrant induced plasticization from gases such as CO_2. This is a major drawback from allowing the PSF membrane to achieve its highest potential. By definition, plasticization is a pressure dependent phenomenon caused by the dissolution of certain penetrants within the polymer matrix which disrupts the chain packing and enhance inter-segmental mobility of polymer chains. (Youchang et al.,2009) . Plasticization is an irreversible process as it permanently alters the structure of the membrane. The pressure at which the permeability starts to increase with increasing pressure is referred to as the plasticization pressure, which is shown in Figure 2. CO_2-induced plasticization is a phenomenon where the CO_2 permeability increases as a function of pressure while the selectivity decreases.

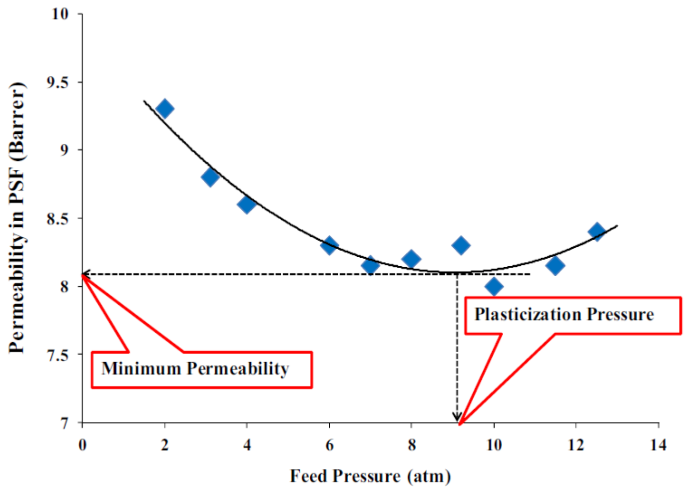


FIGURE 2. Plasticization Pressure of PsF membrane (Colin A. Scholes, 2010).

Researches are also unsure of the aging effect of PSF membranes which is usually dependent of the penetrant. Membranes can only function optimally for a given time for after which degrades due to the aging effect (Scholes C.A et al., 2010). The structure of glassy polymeric membranes which are in non-equilibrium state always tries to achieve equilibrium state spontaneously but slow. This process is known as physical aging which is able to dramatic change the gas transport properties of the membranes (Fua Y.J et al, 2008) .It is currently assumed that the active layer controls membrane selectivity and fluxes, but the porous support can also slightly affect them (Johnson and Benaventeb, 1992). For this reason, modifications of the active or the porous sub layers of composite membranes, which can be due to diverse circumstances (particle deposition, aging, cleaning agents, radiation, etc.), can cause important changes in their transport parameters, as has been reported by different authors (Musale and Kulkarni ,1997); (Paul and McCaig, 1999).

2.3 Mixed Matrix Membrane

The application of polymeric membranes are increasing mainly due to its ability to reduce capital cost and its environmental friendliness .Today , polymeric membranes is used for hydrogen separation, nitrogen recovery, oxygen and nitrogen enrichment, and natural gas purification. (Sinyoung Hwang, 2015). However, polymeric membranes are far from being perfect as their performance deteriorates with time and other factors. Due to the challenges faced by polymeric membranes, mixed matrix membranes were developed. Mixed matrix membranes are actually a mixture between polymeric membranes and inorganic membranes as shown in Figure 3 (Ismail A.F and Lorna W, 2002).

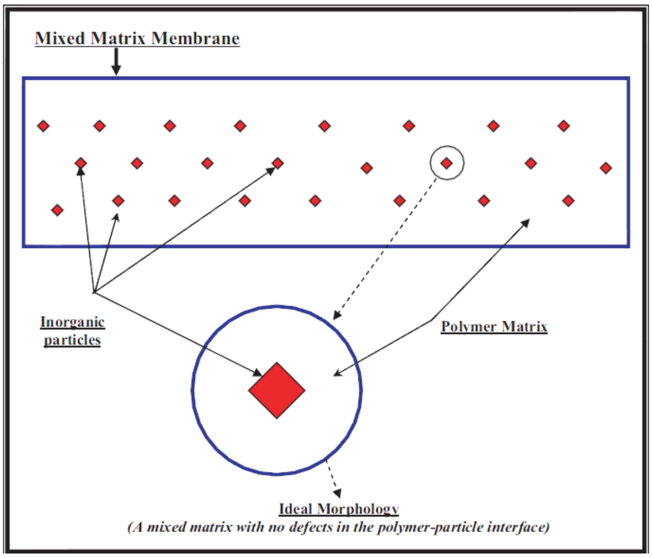


FIGURE 3. Schematic diagram of an ideal MMM (A.F. Ismail, 2002).

Mixed matrix membranes however differs in performance. The difference depends not only on the type of polymers and inorganic fillers used but also differs when different quantities of the same mixture is used. Hence several factors must be considered before casting MMM. Knowing the gas transport mechanism and the gas component transporting through the membrane is important in determining the type of membrane needed (Chung T.S et al., 2007). A desirable MMM would have high permeability, high selectivity and high chemical, thermal and mechanical stability (Freemantle, 2005).

Two major problems exist in making a PsF based MMM which inorganic material the compatibility of the PsF and material inorganic. These problems causes the selectivity of the membranes to decrease. To overcome the first problem, the composition of the inorganic material in PsF matrix should not be too much (Julian and Wenten, 2012). Some action, such as inorganic molecular sizing (Rafizah Wand Ismail A.F , 2008), zeolite surface modification with silane (Khan A.L et al.,2010) , and particle functionalization can overcome the second problem. Table 3 shows the gas transport properties for various mixed matrix membranes.

TABLE 3. PsF based MMM gas transport properties based on inorganic material type.

Inorganic Material	**Wt-%**	**Permeability (barrer)**		**CO2/CH4 selectivity**	**Reference**
		CO_2	**CH_4**		
Zeolite ZSM-5	0	1.3624	0.2833	4.809	(F. Dorosti, 2011)
	10	1.513	0.3419	**4.4253**	
	20	1.5977	0.5505	**2.9023**	
Zeolite 13X	0	6.5	1.5	**4.3**	(Gur, 1994)
	10	6.1	0.26	**23.5**	
	20	6.1	0.32	**19**	
Carbon Nanotube	0	3.9	0.17	**23.55**	(S. Kim Y. L., 2013)
	10	5.19	0.28	**18.41**	
	15	4.52	0.28	**16.09**	
Silica MCM-41	0	4.5	0.17	**23**	(J.S. Chiou, 1985)
	10	6.6	0.29	**23**	
	20	7.8	0.34	**23**	
Silica MCM-48	0	4.46	0.17	**25.88**	(S. Kim E. M., 2006)
	10	8.45	0.33	**25.47**	
	20	18.21	0.77	**23.58**	

2.3.1 ZIF-8

Zeolitic Imidazole Framework-8, ZIF-8 is porous crystalline structure which is a sub branch of Metal organic frameworks (MOF). ZIF-8 particles have metal nodes (usually zinc or cobalt) and imidazolate (or imi- dazolate derivative) ligands as organic linkers. (R. Banerjee, 2008) . ZIF-8 has a structure with M-Im-M angle (M=metal, Im= imidazolate) near to 145°, coincident with the Si–O–Si angle found in many zeolites (Hadi N.A, 2014). ZIF-8 is a highly researched ZIF structure due to its potential for catalysis and gas separation. Due to ZIF-8 ultra-microscopy along with having high thermal and chemical stability, it is used as a filler in MMM (Park K.S, 2006). Figure 4 shows the structure of the ZIF-8 framework. (Cravillon J., 2006). ZIF-8 particles is also reported to have reorientation of its structure at high pressure and high mechanical strength (Tan J.C , 2010).

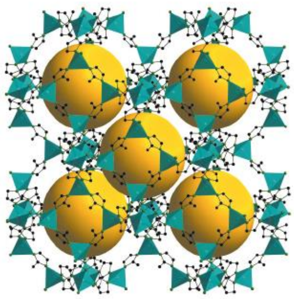


FIGURE 4. Structure of ZIF-8 Framework (J. Cravillon, 2011)

ZIF-8 is being used as an inorganic filler in MMM fabrication by due to its promising properties. However, results may differ corresponding to different type of parameters. One parameter studied is the filler loading. An increased filler loading increase its separation performance, but eventually leads to particles to agglomerate and deteriorating its performance(Car A.,2006) ;(Zhang Y.,2008). Minimum filler loading with significant improvement of membrane performance would be the ideal MMM (Hadi N.A,2014).This project is aimed to determine whether this type of MMM with different composition is able to reduce the plasticization and aging effect which is normally faced by PSF membranes in CO_2 separation.

ZIF-8 is specifically chosen in the present research as it is found that it has the ability to increase the permeance of CO_2 better as compared to other types of ZIF crystals. Table 4 below summarizes the performance of different types of ZIFs membranes.

TABLE 4. CO_2 permeance for different types of ZIF membranes (Lai et al.,2014)

Type of ZIF membrane	**Feed Pressure (kPa)**	**Temperature (K)**	**CO_2 permeance ($x10^{-7}molm^{-2}sPa^{-1}$)**	**CO_2/CH_4 selectivity**
ZIF-8	139.5	298	240	7
ZIF-7	100.0	493	0.035	1.13
ZIF-69	101.3	298	1.0	4.6
ZIF-90	101.3	473	0.348	2.22
ZIF-9-67	NA	298	15.8	0.3

CHAPTER 3

METHODOLOGY

3.1 Flow Chart of Research Methodology

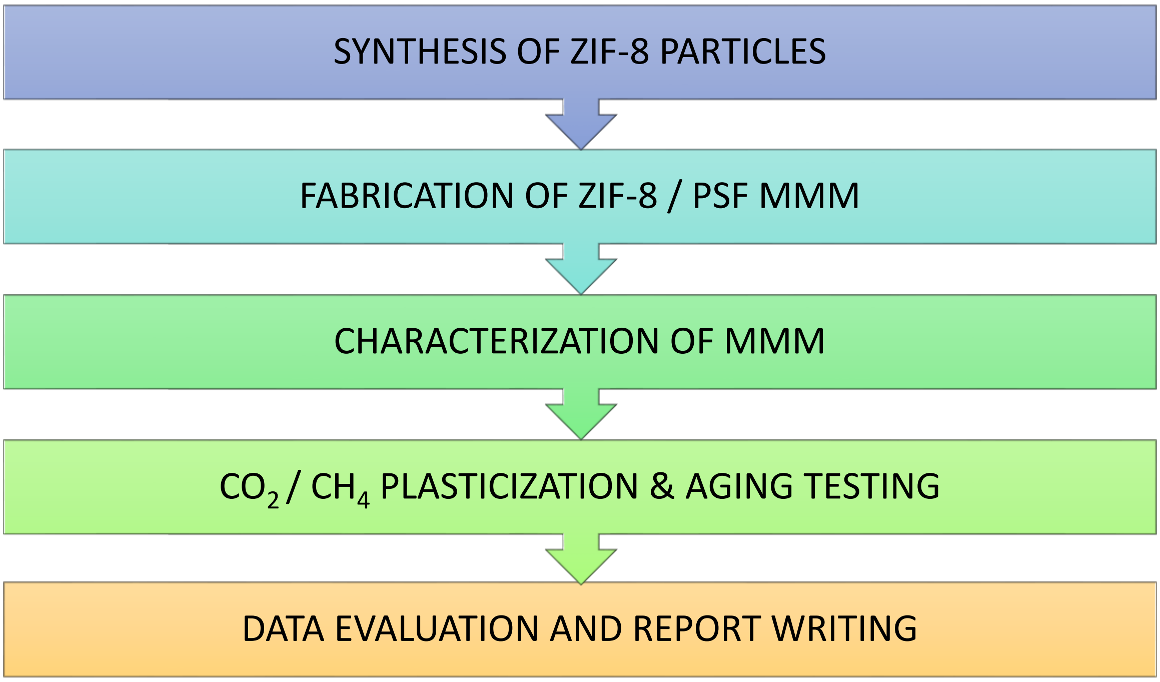


FIGURE 5. Flow Chart of Research

Figure 5 shows the flow chart of the research methodology in the present work. The first step in this project is to synthesis ZIF-8 inorganic particles. These particles would later be added to the polysulfonate polymeric membrane for the fabrication of mixed matrix membrane. The resultant mixed matrix membranes were characterized using SEM and EDX. After that, the membrane were tested for it CO_2 induced plasticisation and aging behaviour. Finally, the data were analysed.

3.2 Materials

The materials which are used for this research project are as follows:-

I. Synthesis of ZIF-8

- 2-Methyimidazole , H-MeIM
- Methanol
- Zinc Nitrate Hexahydrate, Zn(NO3)2•6H2O,

II. Fabrication of ZIF-8 / PsF Mixed Matrix Membrane

- Polysulfone, PsF
- N,N-Methylpyrrolidone , NMP

3.3 Equipments

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

- Casting Knife
- Stirrer
- Centrifuge
- CO_2 membrane cell filter test rig (CO2MCEF)
- Vacuum oven
- Scanning Electron Microscope (SEM)
- Energy-dispersive X-ray spectroscope (EDX)

3.4 Experimental Procedure

3.4.1 Synthesis of ZIF-8

- A solution of 2-methyimidazole (6.489g, 79.04 mmol) was prepared and dissolved in 200 mL of methanol under stirring in a magnetic bar
- A second solution of zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$, (2.933 g, 9.87 mmol) was prepared and dissolved in 200mL of methanol
- The prepared solution of zinc nitrate hexahydrate was then rapidly poured into the solution of 2-methyimidazole and stirred with a magnetic bar for an hour.
- The cloudy solution was centrifuged using 7800 rpm for 5 minutes to separate the nanocrystals and the solution
- The nanocrystals was washed with fresh methanol for 3 times and dried overnight at 85 °C in oven.

3.4.2 Synthesis of PsF Membrane

- The polymer solution consisted of 25 wt. % of polysulfone, and 75 wt. % of NMP.
- 3.125g polysulfone pallets was mixed in the NMP solution at ambient temperature for 10h.
- Prior to casting, the solution was degassed for 4 h and left at standing still for 24 h to eliminate micro-bubbles trapped in the solution.

- The flat sheet layer membrane was prepared by pouring the casting solution onto a clean flat glass plate and casted by using casting knife with 0.25 mm gap at ambient temperature and left it to evaporate for 30seconds.

- Then, the glass plate with a flat layered solution was immersed in the DI water bath to perform flat sheet layer and left for 24 hours

- After that, the fabricated membrane was solvent-exchanged with methanol for 2h and followed by drying in open air.

3.4.3 Synthesis of Mixed Matrix Membrane (PsF / ZIF-8)

- A mixture containing 10 wt% PsF and NMP was prepared in a separate bottle (labelled B) and was let to stir for 2 days until it becomes homogenous.

- A separate mixture containing 90 wt% PsF and NMP was prepared in a separate bottle (labelled A) and was let to stir for 2 days until it becomes homogenous.

- A priming mixture consisting of 5 wt% ZIF-8 was added to NMP (labelled C).The solution was let to stir for 2 hours and then sonicated for 30 minutes. This step was repeated twice.

- Solution C was added to the bottle containing solution B and was let to stir for 4 hours. The solution was then sonicated for 30 min.

- After sonicating, the solution was added into bottle A and was stirred vigorously for 1 day.

- The MMM was then casted. The flat sheet layer membrane was prepared by pouring the casting solution onto a clean flat glass plate and casted by using casting knife with 0.25 mm gap at ambient temperature and left it to evaporate for 30seconds.

- Then, the glass plate with a flat layered solution was immersed in the DI water bath to perform flat sheet layer and left for 24 hours
- After that, the fabricated membrane was solvent-exchanged with methanol for 2h
- The finished membrane was then air dryed for 3 days.
- The procedure was repeated by varying the loading of ZIF-8 to 10 wt% and 20 wt%.

TABLE 5. Formulation of MMM components

	PsF	**NMP**	
Pure PsF (g)	3.125	9.375	12.500

Particle Loading (wt%)	5	10	20
Particle Loading (g)	0.156	0.313	0.625

		90%	**10%**	**Priming**
	NMP (g)	6.375	2.000	1.000
5%	**PSF (g)**	2.672	0.297	0
	ZIF-8 (g)	0	0	0.156
	NMP (g)	6.000	2.000	1.375
10%	**PSF (g)**	2.531	0.281	0
	ZIF-8 (g)	0	0	0.313
	NMP (g)	5.375	2.000	2.000
20%	**PSF (g)**	2.250	0.250	0
	ZIF-8 (g)	0	0	0.625

3.4.4 Characterization Of Mixed Matrix Membrane

I. Scanning Electron Microscopy (SEM) – (Hitachi TM 3030) were used to analyse the morphology of MMM

II. Energy-Dispersive X-Ray Spectroscopy (EDX) – (Bruker Quantax 70) were used to study the dispersion of ZIF-8 particles in the resultant MMM.

3.4.5 Gas Permeability and Selectivity Test

CO_2 membrane cell filter test rig (CO_2MCEF) is the equipment used to test the plasticization and aging effect of the mixed matrix membrane. The selected testing conditions are as follows:-

- Gas: CO_2
- Temperature: 25^{o}C
- Feed pressure: - 1-9 bar
- Aging duration: 1 month (Checked every 5 days up to 30 days)

To calculate the permeance of an asymmetrical membrane for pure gases, the following equation is used:-

$$\left(\frac{P}{l}\right) = \frac{Q}{A\,\Delta p}$$

Where

P is the the permeability of membrane
Q is the volumetric flow rate of gas
Δp is the pressure difference across membrane
A is the membrane effective surface area
l is the membrane thickness

3.5 Project Activities and Key Milestones

The main path of the project is to fabricate MMM and to test its CO_2 plasticization and aging effect. The polymer matrix used in the present work is Polysulfone (PsF) and the inorganic filler used is ZIF-8. The membrane were casted using different compositions of the inorganic fillers and the testing were conducted to check whether these MMMs would be able to overcome the plasticization and aging behavior which are normally faced by PSF membrane. Table 6 shows the key milestones of the research.

TABLE 6. Key Milestone

PROGRESS	DATE OF COMPLETION
Confirmation Of Research Topic	28th January 2015
Problem Identification , Literature Review And Proposal Preparation	27th February 2015
Proposal Defense	19th March 2015
Synthesis Of ZIF-8	25th March 2015
Synthesis Of Pure Psf Membrane And MMM	30th May 2015
Performance Test Of Membranes	17th July 2015
Characterization Of Membranes	24th July 2015

3.6 GANTT CHART

Table 7 and table 8 shows the Gantt chart in the present research

TABLE 7. Gantt chart for FYP I

No	Project Activity	FINAL YEAR PROJECT 1														FYP 1
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	
1	Introductory Lecture With The Coordinator															
2	Title Selection															
3	Confirmation Of Project Topic															
4	First Meeting With Supervisors															
5	Preliminary Research Work															
6	Submission Of Extended Proposal															
7	Proposal Defence															
8	Project Work Starts															
9	Submission Of Interim Draft Report To Supervisors															
10	Submission Of Final Interim Report (After Correction)															
11	Submission Of Marks By Supervisors															

TABLE 8. Gantt chart for FYP II

No	Project Activity	FINAL YEAR PROJECT 1														FYP 2
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	
1	Synthesis of pure PsF membrane															
2	Mixed Matrix Membrane fabrication															
3	Permeability testing															
4	Submission of progress report															
5	Mixed Matrix Membrane characterization															
6	Pre-SEDEX															
7	Submission of dissertation															
8	Submission of technical paper															
9	Viva															
10	Submission of hardbound dissertation															

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Plasticization

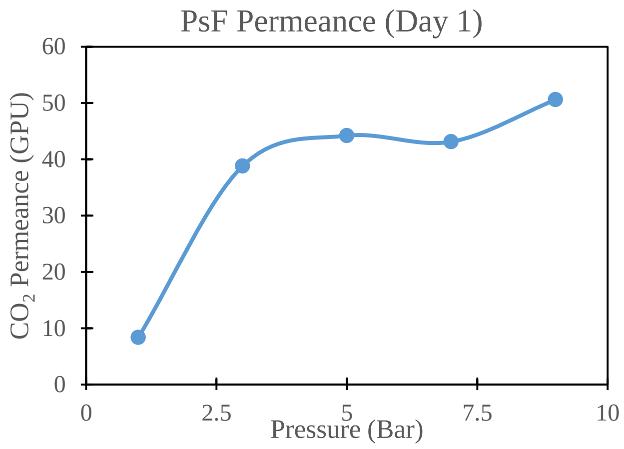
4.1.1 Pure PsF Membrane

Figure 6 shows the permeation of CO_2 through a pure PsF membrane. The permeance of CO_2 increases with pressure up till pressure 5 bar on Day-1. The membrane then exhibits a decrease in CO_2 permeance at 7 bar which after this point increases. This phenomena is known as plasticization

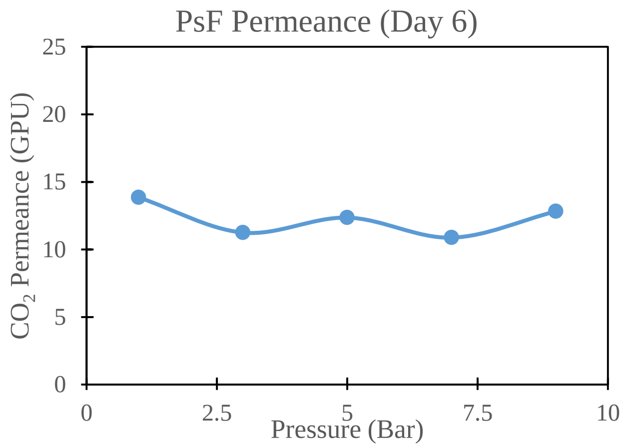
Figure 6 (a) also shows some unusual trend of CO_2 permeance at pressure 1 bar and 3 bar where the CO_2 permeance is relatively low. The permeance of CO_2 should slightly decrease with increase in pressure up to the plasticization point. (Colin A. Scholes, 2010) This phenomena is caused by the insufficient vacuum time of the pressure before taking the reading. Figure 6 (b) shows the similar trend with the plasticization pressure at 7 bar.

After day 13, based on Figure 6 (c) there is an increase in permeance with an increase in pressure. The sudden increase in permeance shows that the membrane has undergone plasticization. The plasticization occurred as a result to aging effect. Apart from that, moisture contamination of the membrane also caused this to occur as the membrane is aged at room conditions.

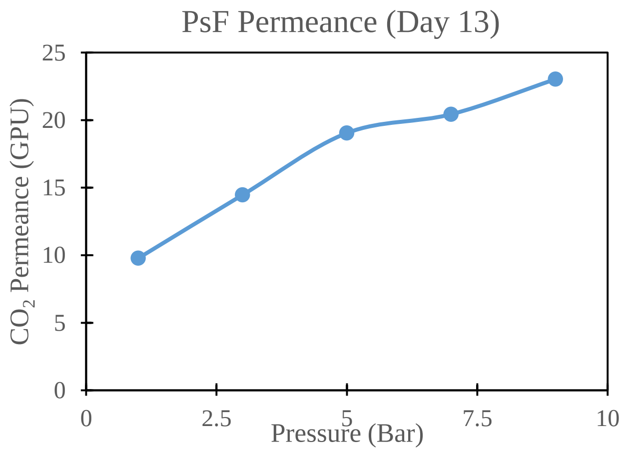
(a)


PsF Permeance (Day 1)
CO_2 Permeance (GPU)
60
50
40
30
20
10
0
0
2.5
5
7.5
10
Pressure (Bar)

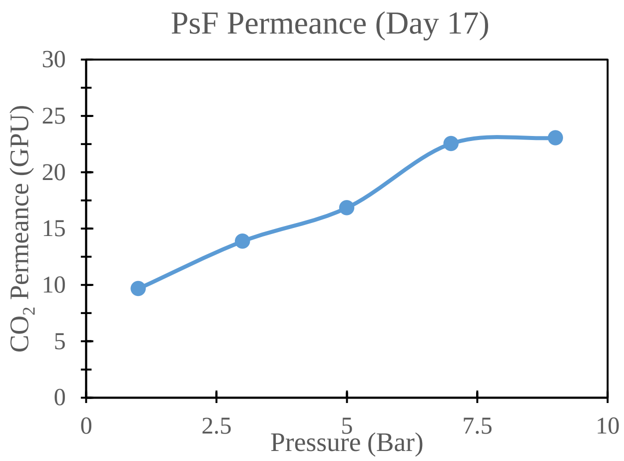
(b)


PsF Permeance (Day 6)
CO_2 Permeance (GPU)
25
20
15
10
5
0
0
2.5
5
7.5
10
Pressure (Bar)

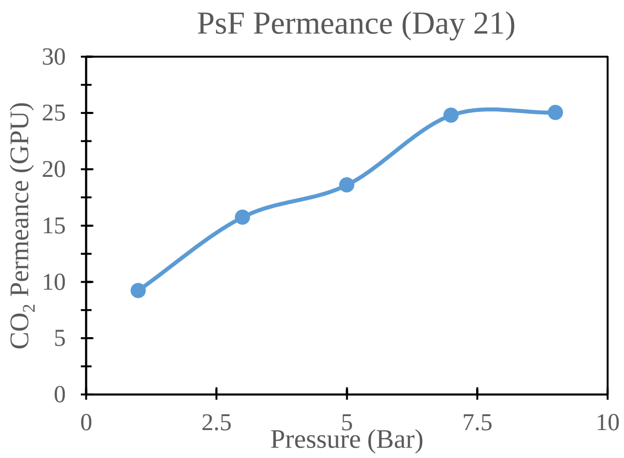
(c)


PsF Permeance (Day 13)
CO_2 Permeance (GPU)
25
20
15
10
5
0
0
2.5
5
7.5
10
Pressure (Bar)

(d)



(e)



(f)

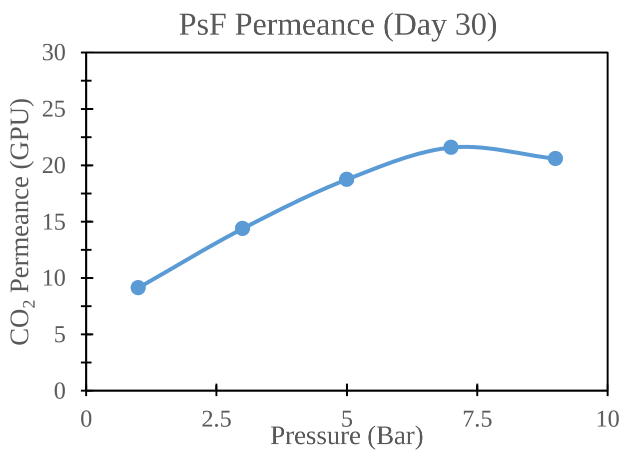
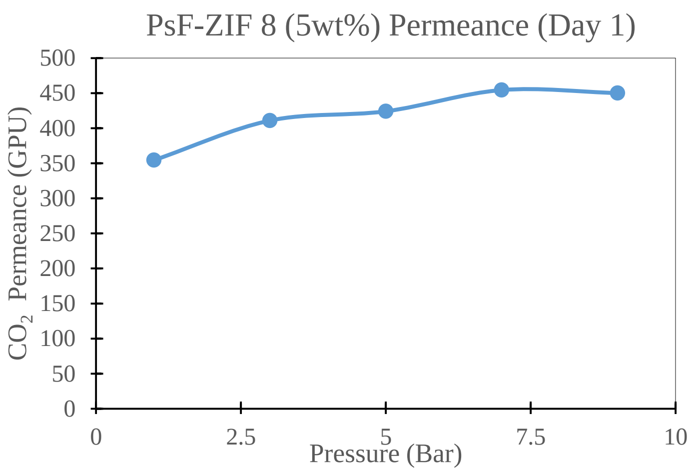


FIGURE 6: CO_2 Permeance of Pure PsF membrane on (a) Day-1, (b) Day-6 , (c) Day-13 , (d) Day-17 , (e) Day-21 and (f) Day-30

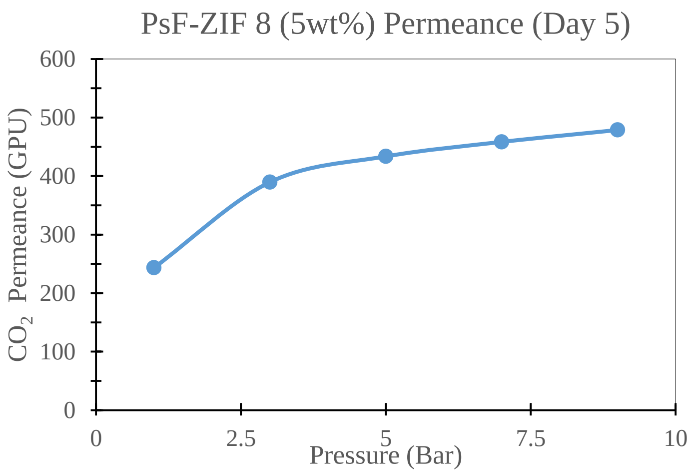
4.1.2 PsF / ZIF-8 (5wt %) Mixed Matrix Membrane

Figure 7 (a) below shows the permeance of CO_2 in a mixed matrix membrane composed of PsF and 5 wt% loading of ZIF-8. From the figure it can be seen that the permeance of CO_2 increases with the incorporation of ZIF-8. Based on the study conducted, it can also be concluded that the incorporation of ZIF-8 particles into PsF shows no improvement towards the plasticization. However, the research shows that the MMM undergoes plasticization since the trial on day-1.This could be due to the water moisture contamination of the MMM.

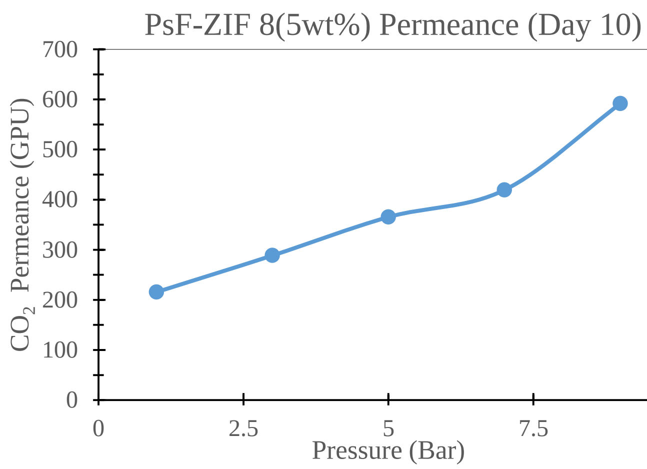
(a)



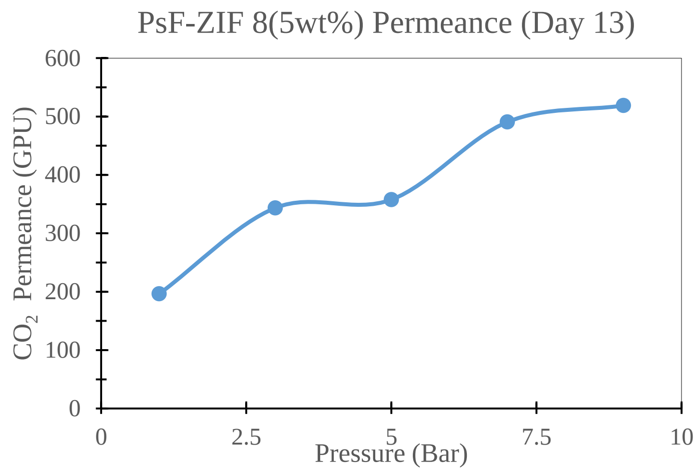
(b)



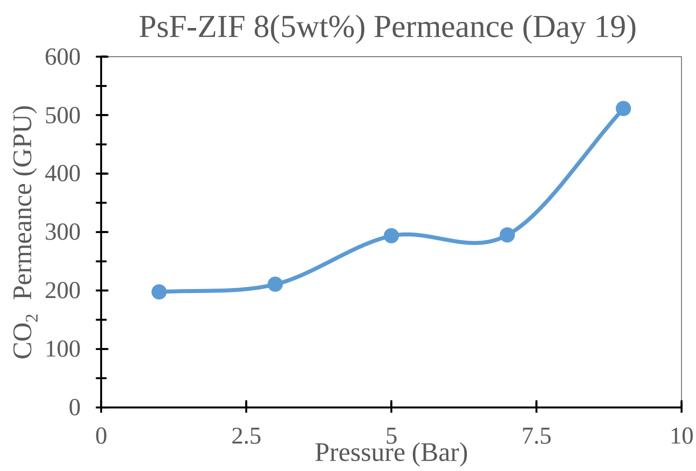
(c)


PsF-ZIF 8(5wt%) Permeance (Day 10)
CO_2 Permeance (GPU)
Pressure (Bar)
0
100
200
300
400
500
600
700
0
2.5
5
7.5
10

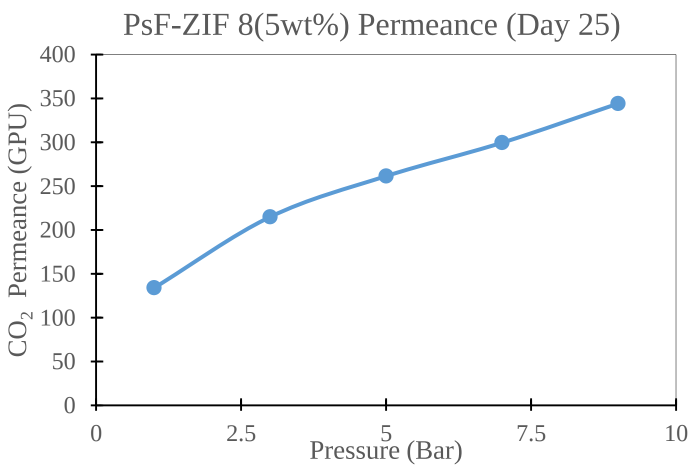
(d)


PsF-ZIF 8(5wt%) Permeance (Day 13)
CO_2 Permeance (GPU)
Pressure (Bar)
0
100
200
300
400
500
600
0
2.5
5
7.5
10

(e)


PsF-ZIF 8(5wt%) Permeance (Day 19)
CO_2 Permeance (GPU)
Pressure (Bar)
0
100
200
300
400
500
600
0
2.5
5
7.5
10

(f)



(g)

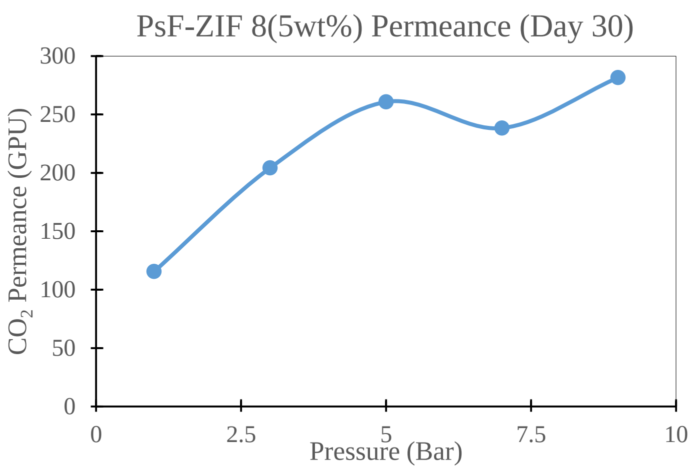
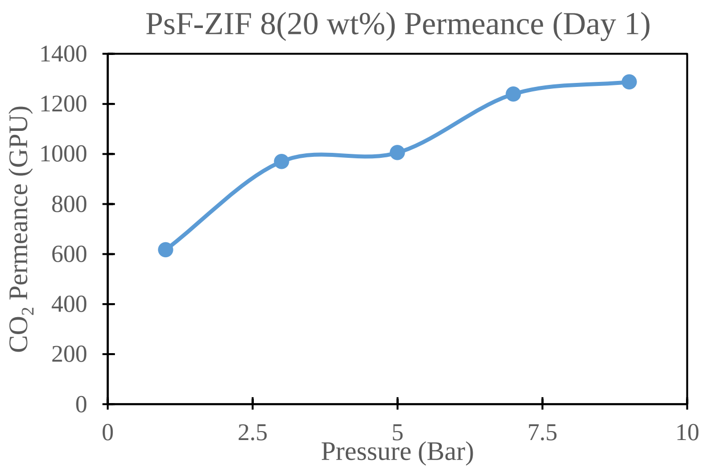


FIGURE 7. CO_2 Permeance of PsF/ZIF-8 (5wt%) MMM on (a) Day-1, (b) Day-5 , (c) Day-10 , (d) Day-13 , (e) Day-19 , (f) Day-25 and (g) Day-30

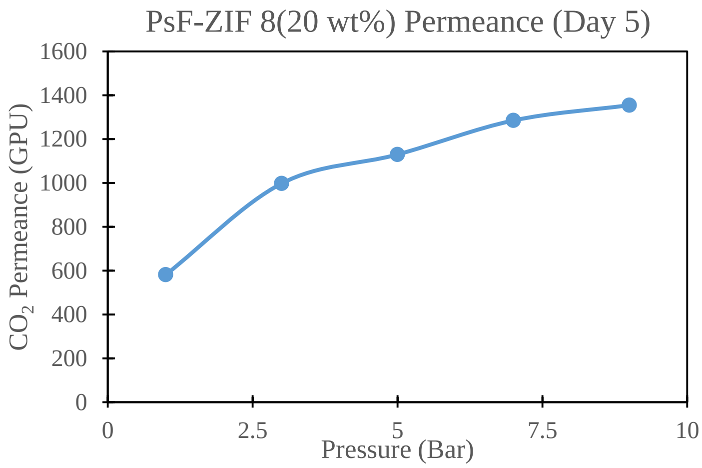
4.1.3 PsF / ZIF-8 (20wt %) Mixed Matrix Membrane

Figure 8 (a) shows the permeance of CO_2 in a mixed matrix membrane composed of PsF and 20 wt% loading of ZIF-8 .The permeance of CO_2 increases drastically when 20 wt% of ZIF-8 is incorporated into the membrane. From the research, it can be concluded that the increase in inorganic filler causes the increase in permeation of CO_2 through the membrane. However, it is observed that even with the incorporation of ZIF-8 particles into PsF, there are no improvement towards the plasticization. It is observed from figure 8 shows that the MMM undergoes plasticization since the trial on day 1.

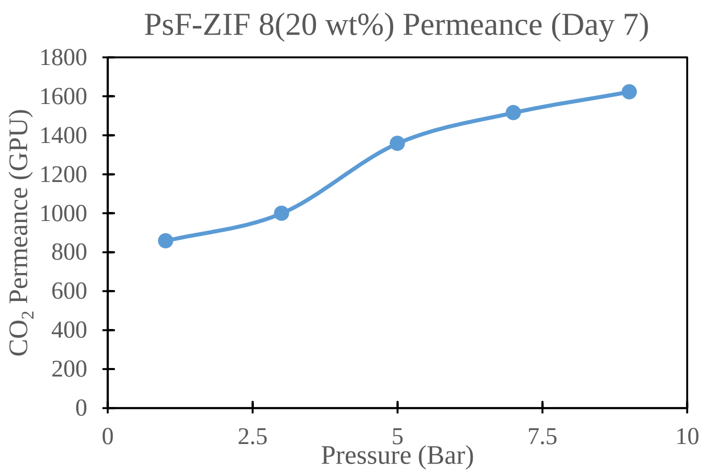
(a)



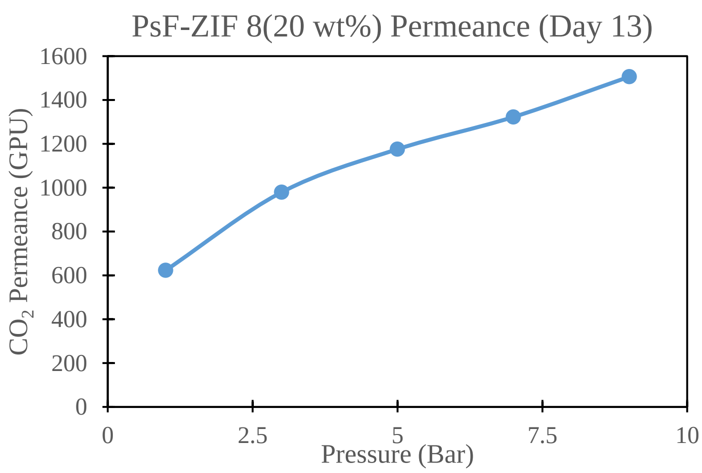
(b)



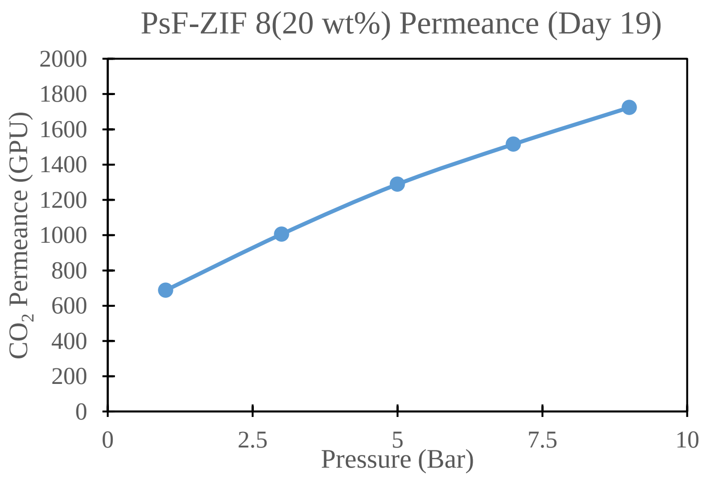
(c)


PsF-ZIF 8(20 wt%) Permeance (Day 7)
CO2 Permeance (GPU)
1800
1600
1400
1200
1000
800
600
400
200
0
0
2.5
5
7.5
10
Pressure (Bar)

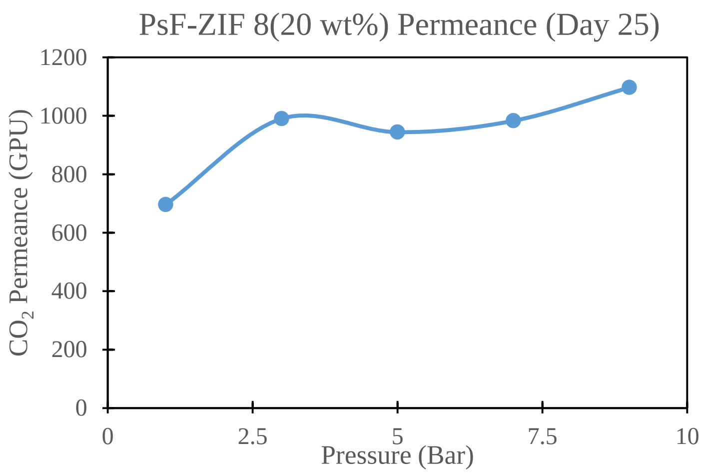
(d)


PsF-ZIF 8(20 wt%) Permeance (Day 13)
CO2 Permeance (GPU)
1600
1400
1200
1000
800
600
400
200
0
0
2.5
5
7.5
10
Pressure (Bar)

(e)


PsF-ZIF 8(20 wt%) Permeance (Day 19)
CO2 Permeance (GPU)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
2.5
5
7.5
10
Pressure (Bar)

(f)



(g)

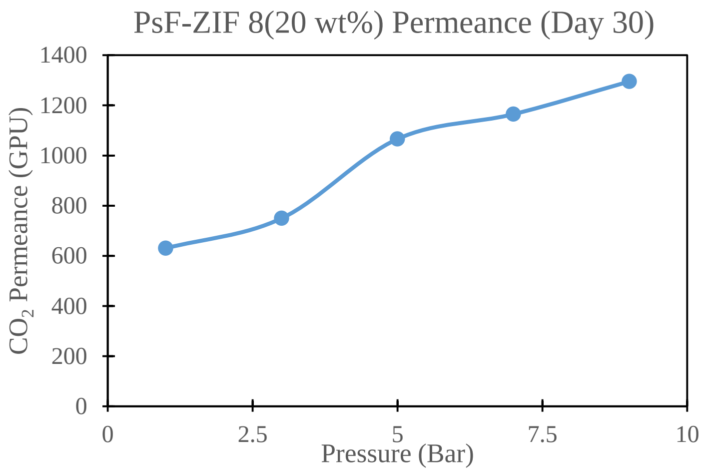


FIGURE 8. CO_2 Permeance of PsF/ZIF-8 (20 wt%) MMM on (a) Day-1, (b) Day-5, (c) Day-7, (d) Day-13, (e) Day-19, (f) Day-25 and (g) Day-30

4.1.4 Comparison of Permeance and Plasticization trend

Figure 9 shows the CO_2 permeance of pure PsF and MMM . Based on the figure it can be seen that there is no improvement in plasticization when ZIF-8 particles are incorporated to PsF membranes. Plasticization occurs at 7 Bar for pure PsF. The 5wt% and 20 wt. % shows that the membrane has already undergone plasticization. The plasticization occurs due to the contamination of the membrane due to the storing conditions of the membranes. The membrane could be contaminated by water moisture as well as other gasses. However, it can be seen that there is an increase in permeation of CO_2 as more ZIF-8 is added. Hence it can be concluded that by incorporating ZIF-8 into PsF, permeation of CO_2 increases.

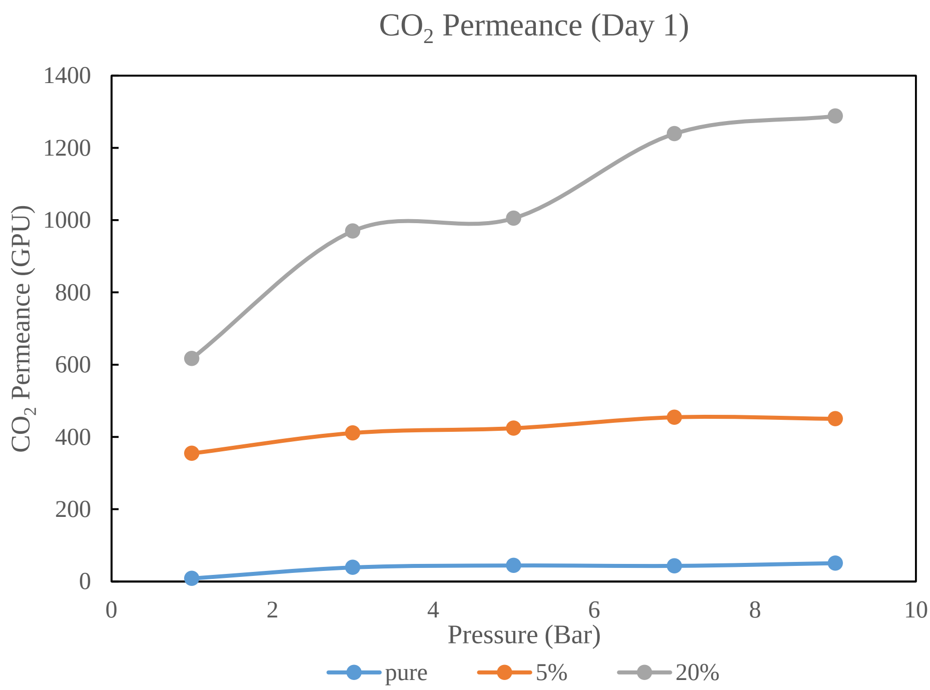
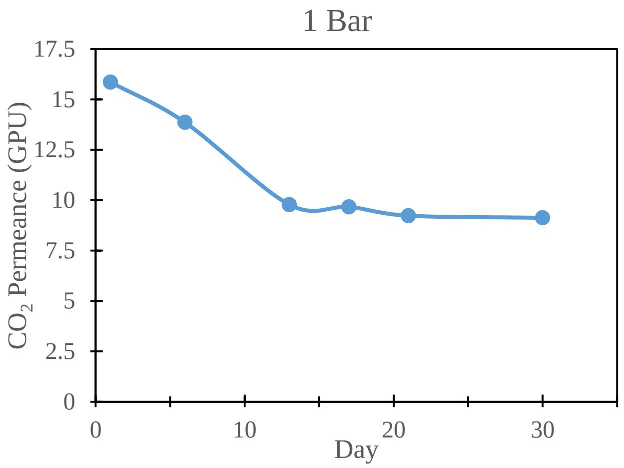


FIGURE 9. CO_2 permeance of pure PsF and MMM

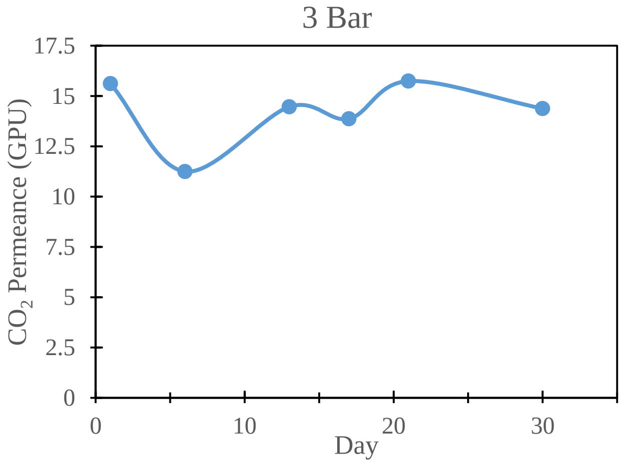
4.2 AGING EFFECT

Figure 10, 11 and 12 shows the aging effect on a pure PsF membrane, PsF/ZIF-8 (5 wt %) and PsF/ZIF-8 (20 wt %) respectively . A similar trend is observed that there is a steady decrease in CO_2 permeance with time. This phenomena is more commonly known as aging effect. This occurs when there is a change in the free volume of the membrane due to the non-equilibrium state of the membrane. Thus the membrane becomes thinner with time. Another reason this happens is also due to the contamination of the membrane due to external factors such as moisture and other gasses.

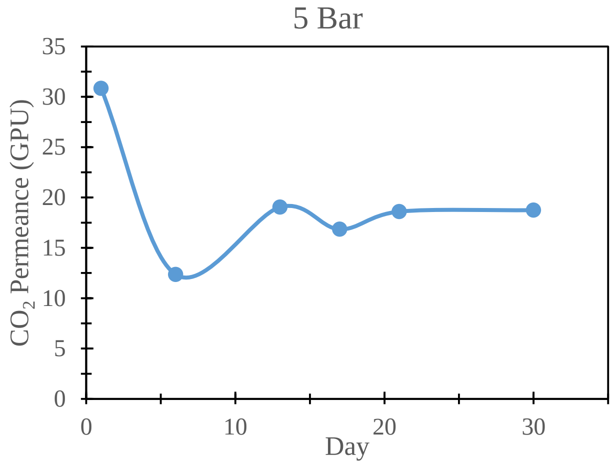
(a)



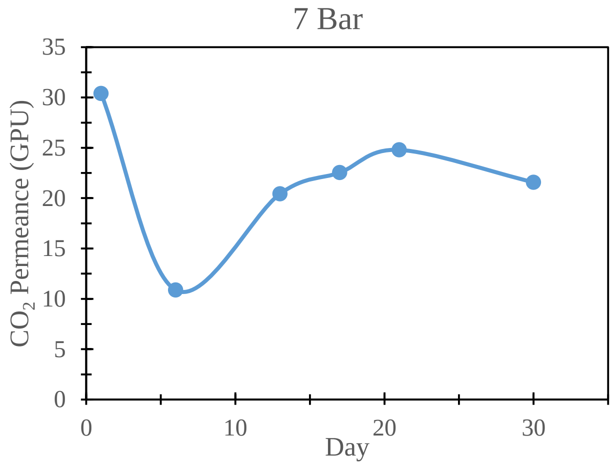
(b)



(c)



(d)



(e)

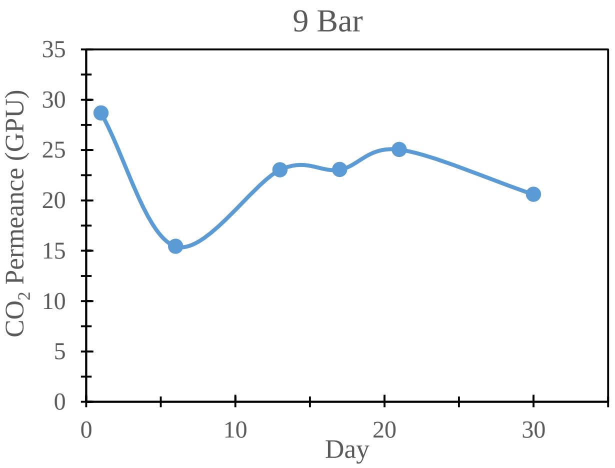
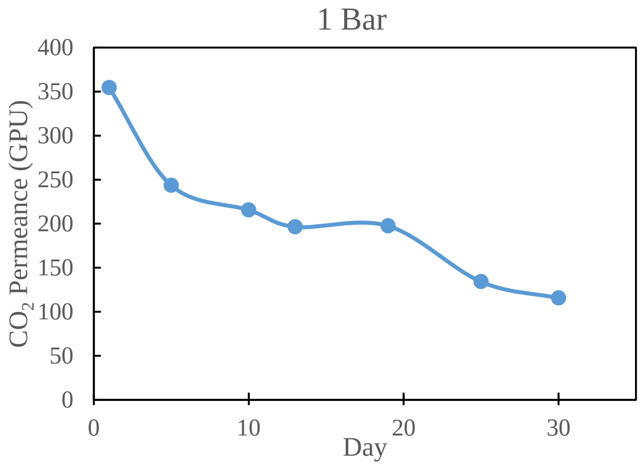


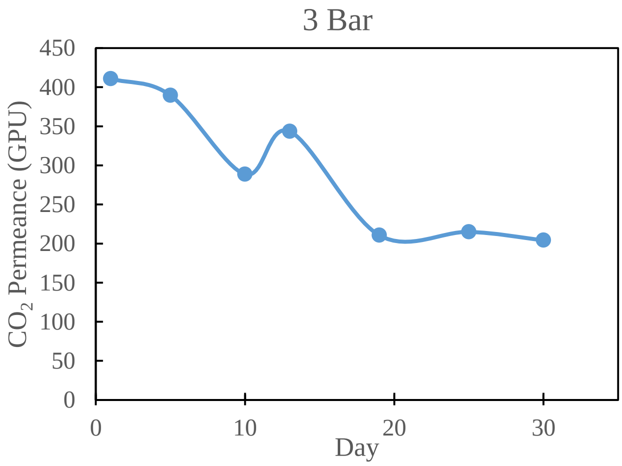
FIGURE 10: Aging of pure PsF membrane at (a)1 Bar , (b) 3 Bar , (c) 5 Bar , (d) 7 Bar and (e) 9 Bar

(a)



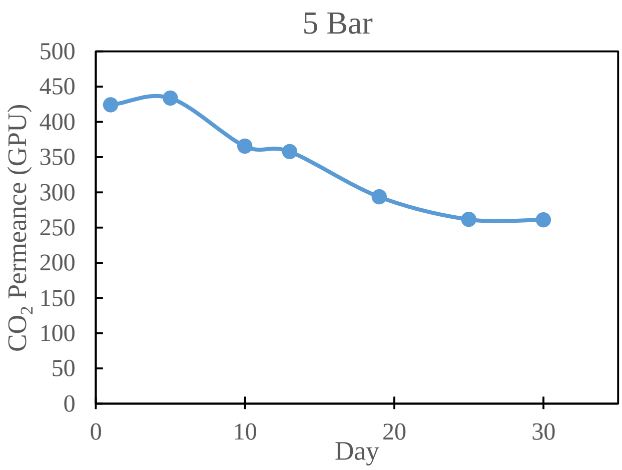
1 Bar
400
350
300
250
200
150
100
50
0
CO$_2$ Permeance (GPU)
0
10
20
30
Day

(b)



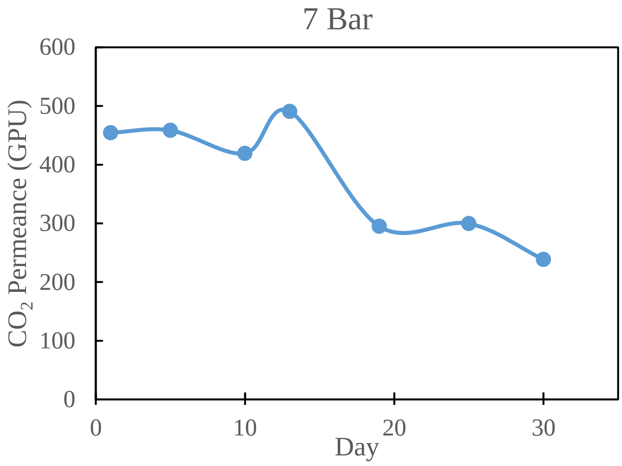
3 Bar
450
400
350
300
250
200
150
100
50
0
CO$_2$ Permeance (GPU)
0
10
20
30
Day

(c)



5 Bar
500
450
400
350
300
250
200
150
100
50
0
CO$_2$ Permeance (GPU)
0
10
20
30
Day

(d)



(e)

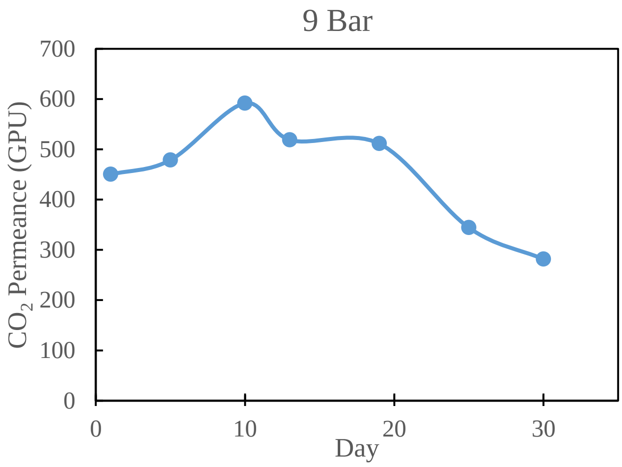
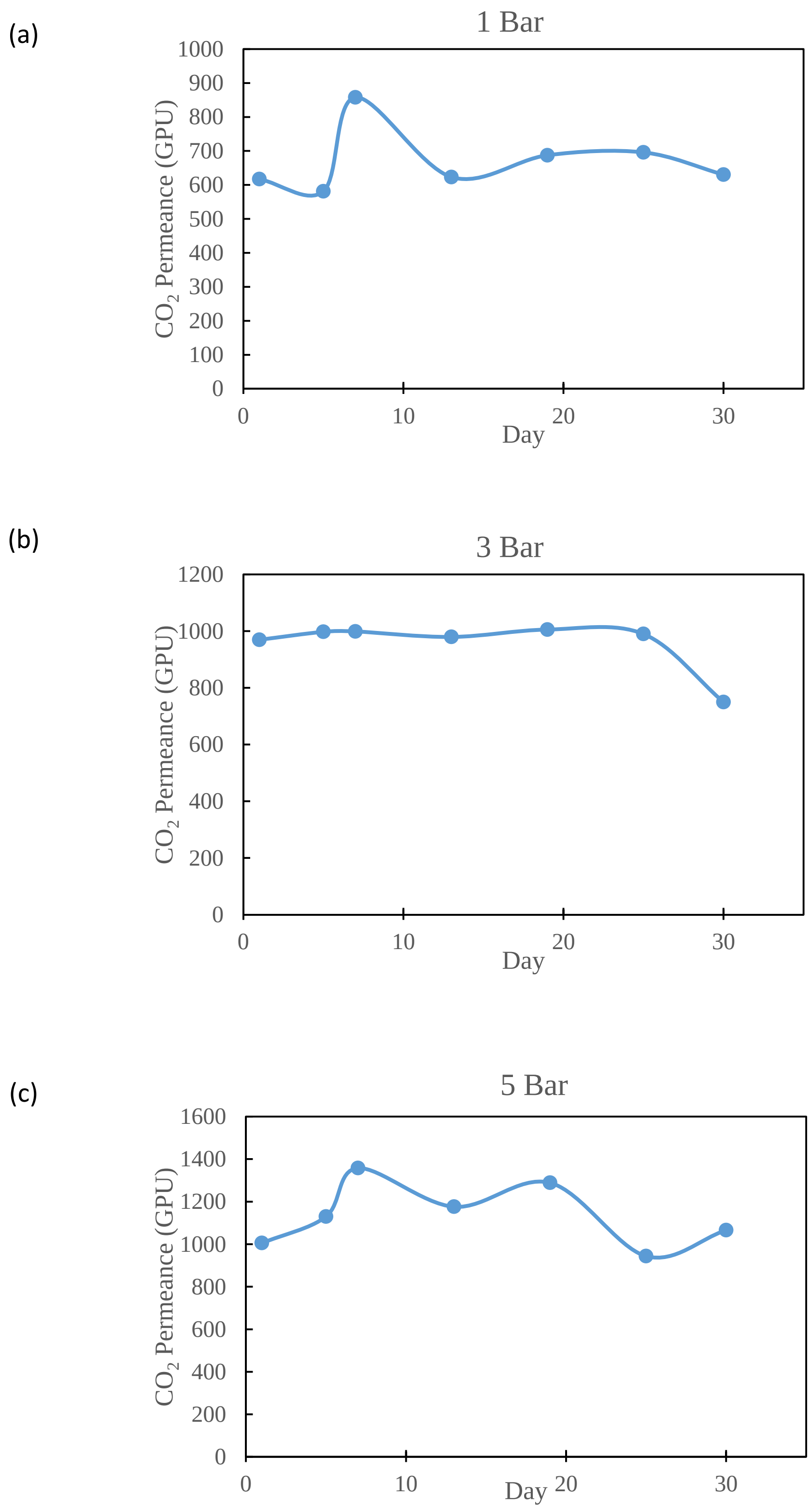
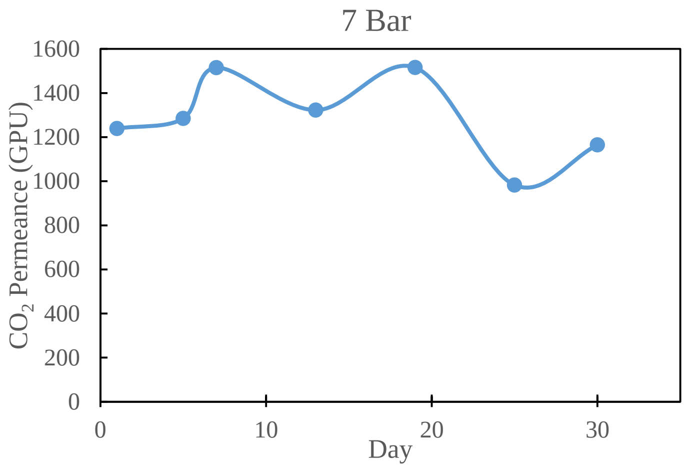


FIGURE 11. Aging of 5 wt % loading ZIF-8 MMM at pressure (a) 1 Bar, (b) 3 Bar , (c) 5 Bar, (d) 7 Bar and (e) 9 Bar


(a)
1 Bar
CO2 Permeance (GPU)
1000
900
800
700
600
500
400
300
200
100
0
0
10
20
30
Day
(b)
3 Bar
CO2 Permeance (GPU)
1200
1000
800
600
400
200
0
0
10
20
30
Day
(c)
5 Bar
CO2 Permeance (GPU)
1600
1400
1200
1000
800
600
400
200
0
0
10
20
30
Day

(d)



(e)

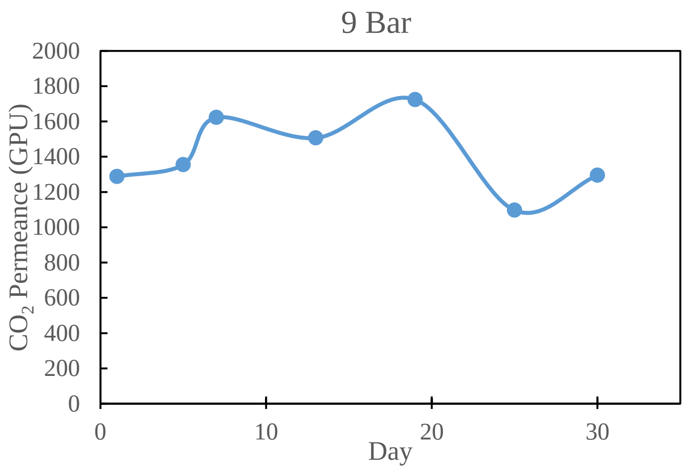


FIGURE 12. Aging of 20 wt% loading ZIF-8 MMM at pressure (a) 1 Bar, (b) 3 Bar, (c) 5 Bar , (d) 7 Bar and (e) 9 Bar

4.2.1 Comparison of Aging Effect

Figure 13 shows the comparison of CO_2 permeance at a pressure 5 Bar for three different types of membrane. Referring to Figure 13, it can be observed that, by incorporating ZIF-8 particles into PsF , the permeance increases drastically .It is also found that the MMM with 20 wt% loading of ZIF-8 shows the highest permeance throughout the testing period.

Another observation that can be made is that all 3 membranes experiences a decrease in permeance with time. This phenomena is known as aging effect. This change can be observed for all 3 membranes.This is mainly due to the insufficient vacuum time during testing

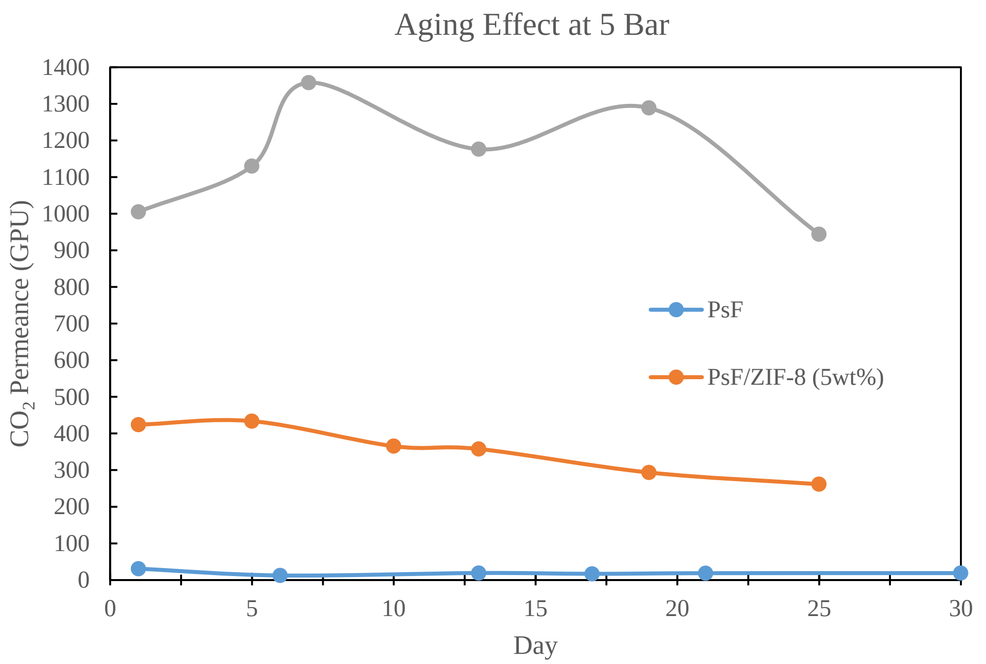


FIGURE 13. Aging Effect at a pressure 5 bar for 3 different types of membrane

TABLE 9 . Data obtained from aging test

Membrane	CO_2 Permeance (GPU)		% Reduction
	Day 1	Day 30	
PsF	43.13	21.58	49.97
PsF/ ZIF-8 (5wt %)	454.40	238.40	47.54
PsF/ ZIF-8 (20wt %)	1239.11	1164.83	5.99

Figure 14 shows the behaviour of 3 types of membrane with time. From the data it can be seen CO_2 permeance of all membranes tested at 7 bar decreases with time. For pure PsF membrane the performance decreases by 49.96% within 30 days. For 5 wt% loading the performance decreases by 47.54% within 30 days while for 20 wt% loading, the performance decrease by only 5.99% within 30 days. Hence it can be concluded that, as the loading increases, the membrane is more resistant towards aging.

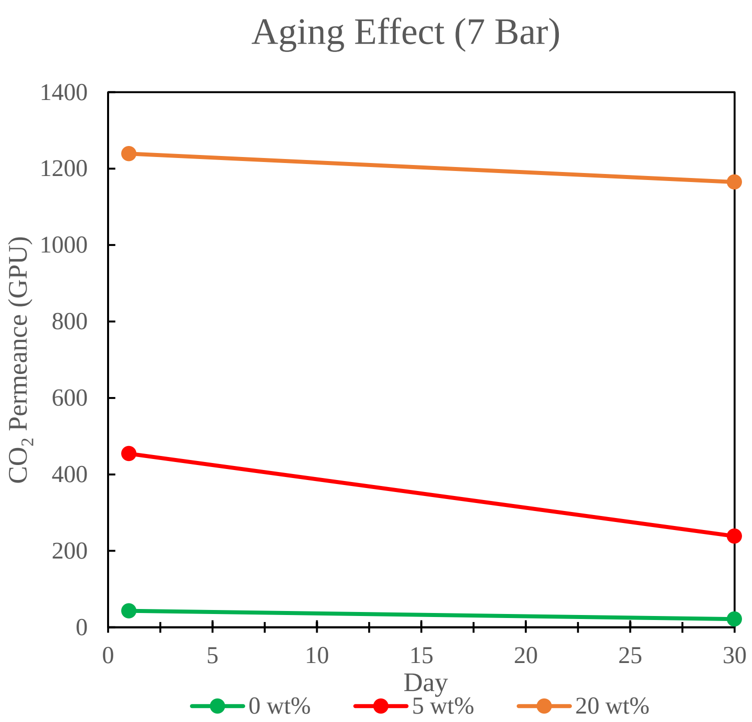


FIGURE 14. Aging Effect at 7 bar for 3 different membranes

4.3 Membrane Characterization

4.3.1 Scanning Electron Microscope Imaging

The morphology of the resulting membrane was studied by using the Scanning Electron Microscopy (SEM).Figure 15 shows the cross section image for (a) pure PsF membrane , (b) PsF/ZIF-8 (5wt%) and (c) PsF/ZIF-8 (20wt%). The thickness of all the membrane is 0.25 mm. From the SEM images it can be seen that the ZIF particles were detached to the polymer matrix without forming significant phase separation between the two boundaries. The SEM imaging also shows even distribution of ZIF-8 particles within the membrane though some agglomeration of particles exists. The agglomeration may be caused due to the insufficient or inefficient mixing of the membrane.

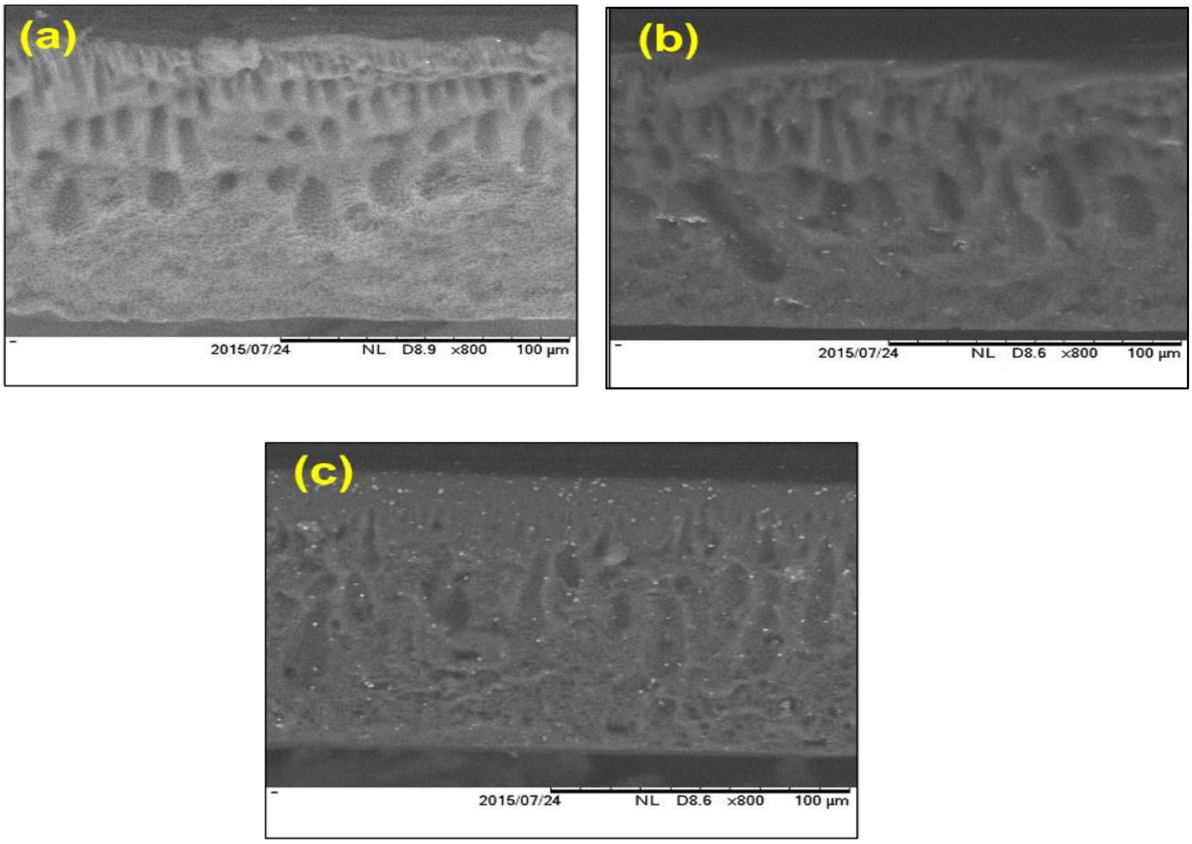


FIGURE 15. Cross section SEM images of (a) Pure PsF (b) PsF/ZIF-8 (5wt%) and (c) PsF/ZIF-8 (20wt%)

4.3.2 Energy Dispersive X-ray

Energy Dispersive X-ray (EDX) was carried out to study the dispersion of ZIF-8 fillers in the mixed matrix membrane (MMM). The main elements that presence in pure PsF are carbon (C) , oxygen (O_2) , aluminium (Al) and sulphur (S) as observed in Figure 16 . The EDX mapping shows a dispersed polymer matrix. Figure 17 and Figure 18 shows the EDX mapping of PsF/ZIF-8 MMM loaded with 5 wt% and 20 wt% ZIF-8 respectively. The main composition of ZIF-8 is zinc (Zn) and silicon (Si). The EDX mapping shows a dispersed membrane although some agglomeration occurs. The agglomeration might be due to the insufficient and ineffective stirring of the membrane.

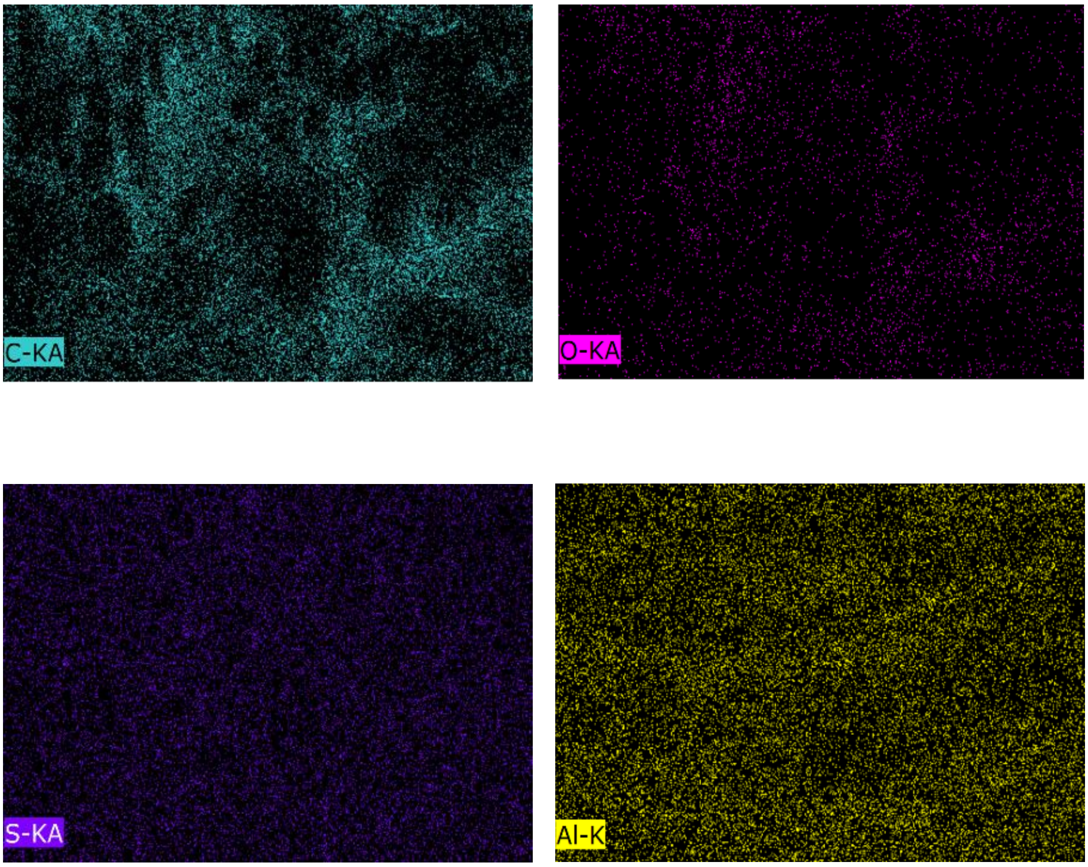


FIGURE 16. EDX Mapping of Pure PsF Membrane

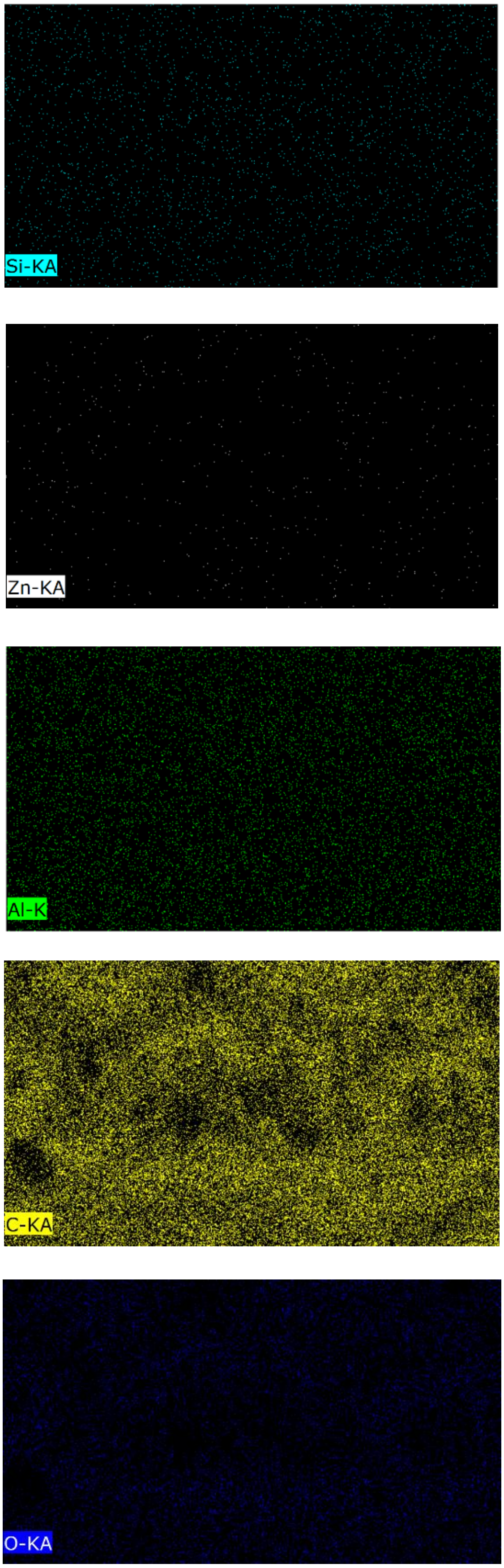


FIGURE 17. EDX Mapping of PsF/ZIF-8 MMM Loaded With 5 wt% ZIF-8

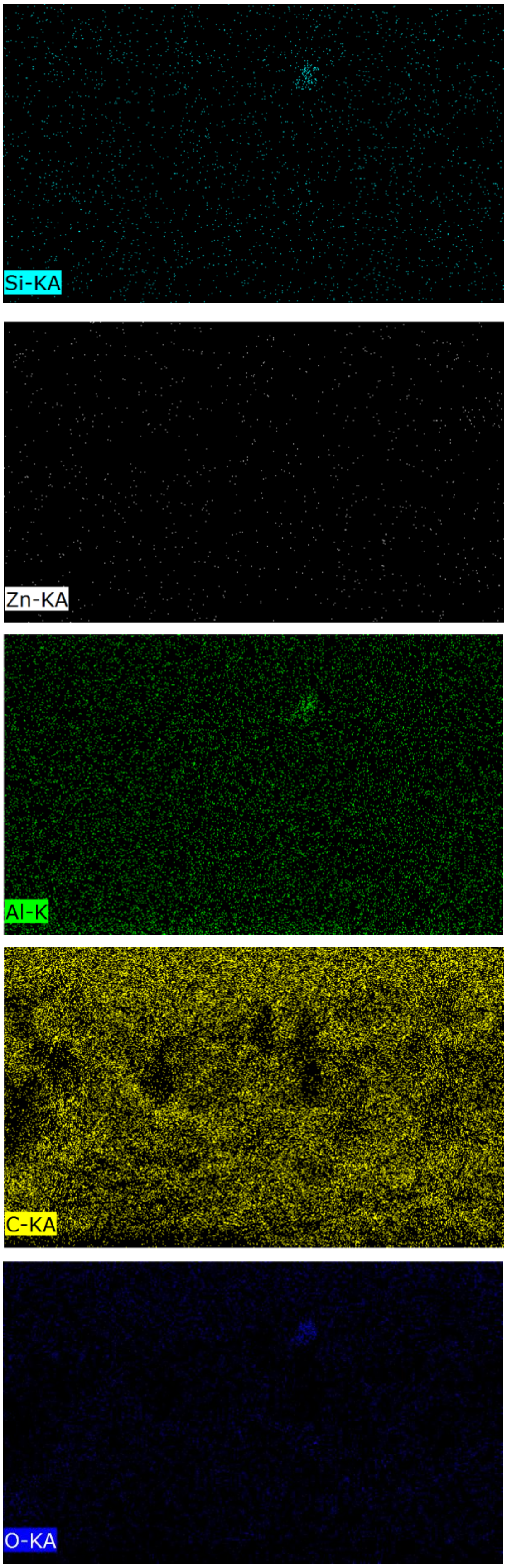


FIGURE 18. EDX mapping of PsF/ZIF-8 MMM loaded with 20wt% ZIF-8

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

It is known that polymeric membranes suffer from plasticization and aging effect when it is used to separate CO_2 .The alternative to overcome this problems is to use mixed matrix membranes which is the combination of polymeric membranes and inorganic fillers. This research were focused on the fabrication of the ZIF-8/PsF for CO_2 plasticization and aging testing.

In this research, the gas separation performance of the resulting MMMs was successfully conducted by using the CO_2 membrane cell filter test rig (CO2MCEF). It is observed that the incorporation of ZIF-8 into PsF based membranes shows significant improvements towards aging effect. The aging effect resistance increases with the increase in loading of ZIF-8 particles. Pure PsF membrane showed a 49.97% permeation reduction due to aging after 30 days. The MMM with 5 wt% ZIF-8 showed a 47.54% permeation reduction while the 20 wt% ZIF-8 MMM showed a 5.99% permeation reduction. Apart from that, it is observed that ZIF-8 increases the permeance of CO_2 of membranes. The permeance increases with the increase in loading of ZIF-8 loading. However, the plasticization of membranes showed no improvement with the incorporation of ZIF-8 particle.

5.2 Recommendation

Future research on this topic can be done by altering the placing the membranes in the test rig throught the testing period. This eliminates contamination of the membrane layer as it is found from this research that contamination by air and water moisture occurs. Apart from that a longer vacuuming period can be done for each test.

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