

# COMPARISON BETWEEN TREATED AND UNTREATED ZEOLITE TOWARDS THE PERFORMANCE OF POLYETHERSULFONE MIXED MATRIX MEMBRANES (MMMs) FOR O<sub>2</sub>/N<sub>2</sub> GAS SEPARATION

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**Abstract.** Mixed Matrix Membranes (MMMs) is one of the alternative ways to increase the performance of plain polymeric membrane. In this study, the performance of MMMs using treated zeolite and the ones using untreated zeolite were compared to see the effect of the coupling agent towards the separation of O<sub>2</sub> and N<sub>2</sub>. The polymer solution contains Polyethersulfone (PES) as the polymer, N-Methyl Pyrrolidone (NMP) as the solvent and distilled water (H<sub>2</sub>O) as the non-solvent. For the MMMs using treated zeolite, the zeolite was first treated using Aminopropyl-Trimethoxysilane (APTMS), a silane coupling agent before inserted into the polymer solution. For both types of MMMs, the zeolite concentration between 5 to 20 wt % were applied. The dry/wet phase inversion methods were used to produce the asymmetric flat sheet membrane. The prepared membranes were coated with silicone and N-Hexane in order to decrease the surface defect of the membrane. The best performance had found for membranes using treated zeolite where the selectivity was 3.3 for 15 % zeolite concentration at 3 bar operating pressure compare to the untreated zeolite. As a conclusion, it believe that surface modification of zeolite plays an important role to the incompatibility of zeolite and polymer to the formation of large free voids and it affected the overall selectivity and permeability.

## Introduction

Membrane can be defined as a thin barrier between two bulk phases and it is either a homogeneous phase or a heterogeneous collection of phases [1]. The membrane is a permselective barrier that permits the transport of some component and retains others. The use of membranes has been widely developed from microfiltration and reverse osmosis for water filtration until the application of artificial organs in medical field [2]. Another renowned membrane application is in gas separation since it is the most preferable method to separate gases compared to cryogenic separation and absorption in cost-wise perspective [3, 4].

However the plain polymeric membrane performance is limited by the selectivity/permeability limitation. As the permeability of plain polymeric membrane increase the selectivity of the preferable gas will decrease and the same results will be obtain vice versa. This phenomenon can be observed by the Robeson 1981 selectivity/permeability upper bound limit graph where this graph compiled the results of various research that were using plain polymeric membrane to separate gases [5]. Therefore, researchers have find ways to increase the selectivity and permeability of the plain polymer membranes and one of it is by adding another material into the polymer solution. One of these filler materials is called Zeolite [6]. Zeolite is actually an inorganic material mostly found in minerals compound and it can be represented by the the following chemical formula:



where y is 2 or greater, M is the charge balancing cation, such as sodium, potassium, magnesium and calcium, n is the cation valence and w represents the moles of water contained in the zeolitic voids [7]. The insertion of zeolite into the plain polymer matrix is specifically to increase the selectivity of the preferable gas since zeolite at optimum concentration will form a channel that can only allow the gases with certain sizes and retain larger gases [8]. To use the zeolite, several

approaches have been done by other worker. One of it is just by adding the zeolites into the dope formulation without any alteration [9] and the other one is by first treating the zeolite with certain chemical, then will the zeolite inserted into the dope formulation [10].

The first approach, that was not to modify the zeolite original properties showed the original performance of the zeolite and the real condition between the zeolite and the polymer when they are together. While the other method that was treating the zeolite with certain chemical has modified the zeolite properties in order to suit the polymer condition. Both of these methods have been used in this study and the results with its comparison for both methods are discussed later in the discussion section.

## Experimental

### 2.1 Materials selection

Polyethersulfone (PES) was chose to be the polymer in this research. PES was dried for 4 hours at the temp of 150°C before usage. 1-methyl-2-pyrrolidone with formula molecular of C<sub>5</sub>H<sub>9</sub>NO also known as NMP was used as the solvent and distilled water was be the non solvent additives. The coagulation medium used in this study also water along with methanol. This research used zeolite 4A was bought from Sigma Aldrich Cheme GmbH, Steinheim, Germany. For the treated zeolite method, 3-Aminopropyl- trimethoxysilane was selected as a coupling agent for zeolite 4A and PES. It is a product form Acros Organics BVBA. The APTMOS was mixed with mixture of ethanol and distilled water. The ethanol used in this research was bought from R&M Chemicals (Essex, UK) as 99.7% V/V denatured.

### 2.2 Zeolite Surface Modification

This process was done prior to dope solution formulation for the MMMs using treated zeolite. This method was used to alter the zeolite surface compatibility with PES [10]. The zeolite 4A was dried in an oven at 80°C for 24 hours prior to the modification. 200 ml ethanol solution was prepared (95% ethanol, 5% distilled water) and it was stirred with APTMOS and zeolite 4A for 4 hours under room temperature. Based on a study by Shu Shu [11] for 5g of zeolite 4A, 5ml of APTMOS was used. The mixture was then filtered through a filter paper and the residue was washed thoroughly with ethanol to remove the unreacted silane. Finally, the modified zeolite was dehydrated at 110 °C for 2 hours in a vacuum oven to remove the adsorbed water vapor or other organic vapors before it was ready to be used in preparation of dope solution.

### 2.3 Dope Solution Formulation

Dope solution formulation was done by adding all four materials which are PES, NMP, Zeolite 4A and distilled water into the casting solution preparation system. The same methods were used throughout the formulation for both MMMs with treated zeolite and the ones with untreated zeolite. Before the insertion of PES, PES was dried for 4 hours at the temp of 150°C. zeolite need to be dried for 2 hours at the temperature of 110°C prior to the addition into the casting solution due to its hydrophilic properties. The weight percentage of each chemical used for dope solution formulation is listed in Table 1

Table 1: Dope formulation for MMMs

	Concentration (wt %)			
PES	30	30	30	30
NMP	60	55	50	45
Zeolite 4A	5	10	15	20
Distilled H <sub>2</sub> O	5	5	5	5

At first zeolite was added into the solvent and stirred for 1 hour. After that, PES was inserted into the NMP-Zeolite solution and stirred for about 2 and a half hour. Next the distilled water was inserted and stirred for another hour and a half. After stirring of the dope formulation, the solution was degassed under vacuum for 3 hours in the ultrasonic bath to remove any micro bubbles inside the solution.

## 2.4 Membrane Casting

A layer solution was poured on a glass plate. Using a stainless steel casting knife, the solution poured was slowly spread to have a smooth and uniform layer. Next, the plate and the membrane were inserted into the water bath for 1 day. After that it was washed with methanol for 1 day before it is dried at room temperature for 48 hours.

## 2.5 Membrane Coating

In order to repair the skin layer from any defects, the membranes were coated because during membrane fabrication, the membrane skin layer suffer from some defects. These defects caused by gas bubbles, dust particles and support fabric imperfections, can be very difficult to eliminate. To overcome these problems, coating method was applied. The membrane was cut into circular area of 12.57 cm<sup>2</sup>. Then the skin layer of the membrane was dip into 3 wt% of silicone in n-hexane for 5 minutes and placed in oven at temperature of 40°C for 15 minutes. After that the membrane is left at room temperature for 24 hours.

## 2.6 Permeation test

Pure O<sub>2</sub> and N<sub>2</sub> gases were applied in the permeation test to identify the membrane performance. The volume of the gas permeates were determined by using bubble flow meter. The bubble flow meter consist of a burette containing soap solution and the expansion of bubble over time was the permeates flow rate.

Equation 2.1 and Equation 2.2 was used for calculation.

$$P = \frac{Q}{A \times \Delta P} \quad \text{-(Eq-2.1)}$$

$$\alpha = \frac{P_A}{P_B} \quad \text{-(Eq-2.2)}$$

P = Pressure normalized flux ( $\frac{cm^3}{cmHg \ s \ cm^2}$ )

Q = Permeates flow rate ( $cm^3 / s$ )

A = Effective area of membrane ( $cm^2$ )

$\Delta P$  = The pressure applied to the membrane ( $cmHg$ )

## Results and Discussions

3.1 Comparison on the Permeability and Selectivity of the Polyethersulfone MMMs with untreated and treated zeolite.

### 3.1.1 Performance of MMMs with untreated zeolite

Permeability is the rate at which any compound permeates through a membrane while the selectivity of a membrane can be defined as the ability of a membrane to accomplish a given separation [6]. In this research was intend to produce MMMs with high gas permeability and at the same time the MMMs will also possess the high selectivity of O<sub>2</sub> towards N<sub>2</sub>.

However in this section will only be discussing the performance of coated membranes since an uncoated membrane produced unreliable results. The uncoated membranes mostly suffer from severe surface defects that lead to the existence of pin holes and these pin holes will provide an alternative path for the gases to pass through the membrane. The mechanism of the gas transport will be governed by the Knudsen and Poiseuille Flow, gas flow mechanism through holes and gaps [11]. An ideal membrane gas separation must have a selective layer that should be defect free so that gas transport takes place exclusively by solution-diffusion, not by poorly selective flow through pores [12]. Therefore the best solution is by coating the MMMs and the performance of the coated MMMs is selected to be discussed. The performances of MMMs with untreated zeolite are summarized by Fig 1(a) to Fig 1(e).

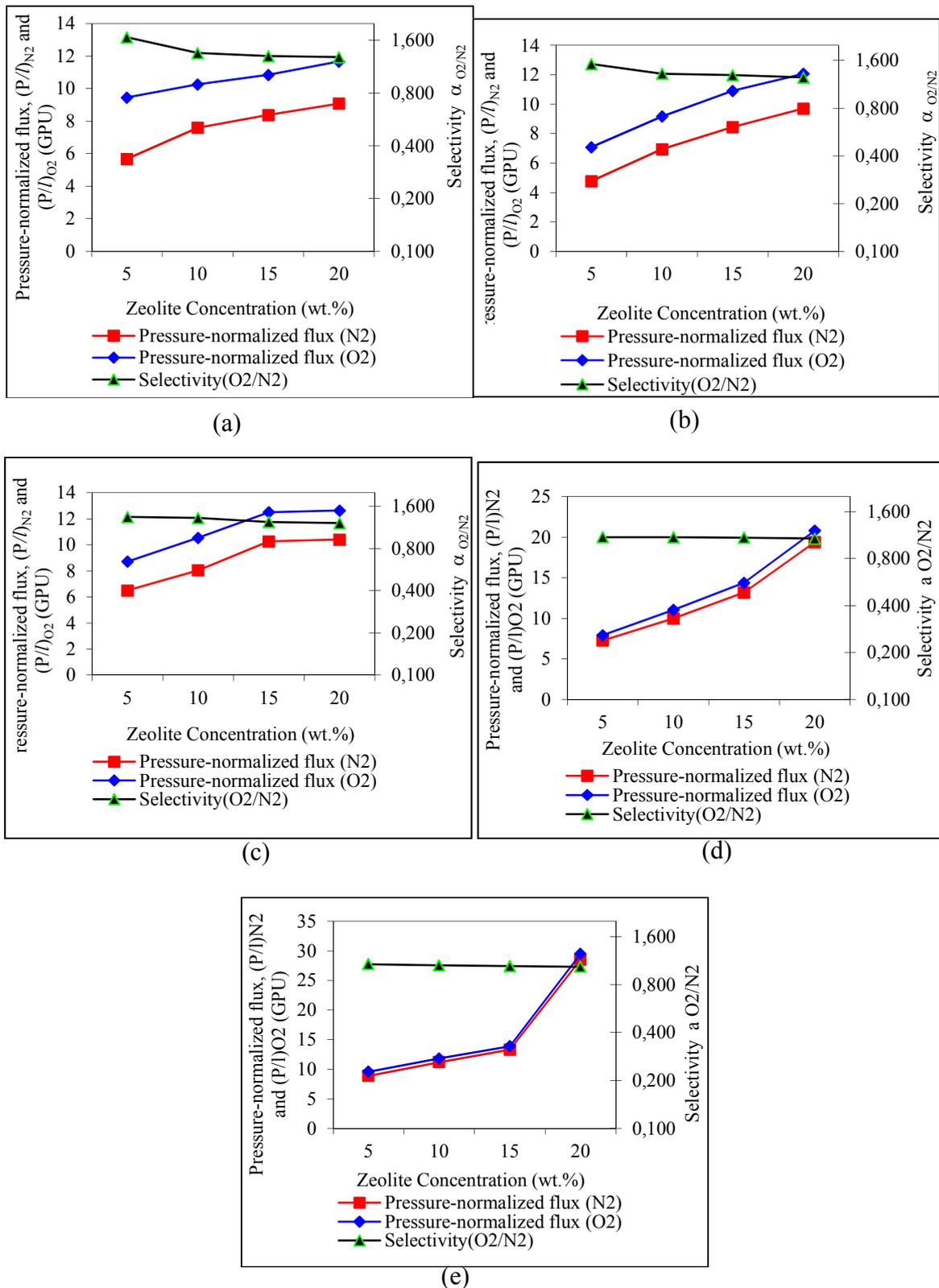


Fig 1: Performance of Polyethersulfone MMMs with various untreated zeolite concentration at difference pressure. (a) 1 bar, (b) 2 bar, (c) 3 bar, (d) 4 bar, (e) 5 bar

Fig1(a) to 1(e) shows that each of the MMMs with untreated zeolite possess high permeability for every concentration. The highest pressure normalized flux for O2 is 29.5 GPU and it was observed on the MMMs with 20 wt% zeolite loading rate at 5 bar while for N2, the highest pressure normalized flux is 28.5 also exhibits by MMMs with 20 wt% at 5 bar. However at this highest permeability of the gas species, the selectivity was very low, 1.03. For each concentration of

zeolite, it can be observed that the selectivity is nearly the same (near to 1.0) and suggesting that the insertion of untreated zeolite does not give any effect towards the membrane performance. This is due to the formation of gaps and voids in the MMMs matrix. The incompatibility of the zeolite and polymer forcing them to push each other away and due to this condition, gaps and voids forms around the interface between these two materials. Just like the earlier explanation on the gas transport through pore flow mechanism, the gaps and voids provides an escape route for the gases to bypass the selective skin layers. With the existence of this alternative way, both of the gases have equal chance to pass through the membrane and producing high permeability with low selectivity.

The highest selectivity was exhibits by MMMs with 5 wt% untreated zeolite with 1.67 at 1 bar. In fact, for all the pressure applied the highest selectivity was shown by MMMs with 5 wt% zeolite. This is because, at 5 wt% zeolite loading rate, less zeolite particle contained by the membrane matrix. The incompatibility still exist between the zeolite and the polymer and the voids in the interface still can form, however since less zeolite is incorporated therefore less gaps and voids formed in the MMMs with 5 wt% zeolite. Thus, the Knudsen flow and Poiseuille flow decreases due to lack of pores and these produced the highest selectivity.

### 3.1.2 Performance of MMMs with treated zeolite

The performance of MMMs with untreated zeolite are summarized by Figure 2(a) to Figure 2(e). The different results were obtained in Figure below compared to the untreated zeolite MMMs. Each of the MMMs for every concentration does not show the same selectivity results for all pressure applied. The trend from the graph suggesting that with the increase of the zeolite concentration, the selectivity between O<sub>2</sub> and N<sub>2</sub> gas also increase. The results came out differently compared to the untreated zeolite MMMs because of the formation of siloxane bond that provide a string that can attached between zeolite, an inorganic material, and PES, an organic material. These bonds allow the membrane to have a better structure that can assist with the gas separation, thus increases the selectivity. With the existence of these strings, voids and gaps are not formed at the interface of the zeolite and polymer. Therefore, without these gaps and voids, no alternative pathways provided to the gas species and the only way they can pass through in by the selective skin layers.

With the increasing of the zeolite concentration, the zeolite particle supposed to form interconnected channels. The interconnected channel will provide a easier path for intended gas to permeates and at the same time retain the other gas. With these two component, selective skin layer and interconnected channel of zeolite, the gas will only pass through the membrane by solution-diffusion mechanism and molecular sieve mechanism. Even so, it cannot be said that the membranes is defect free and no pores are form on the skin surface, but with the insertion of treated zeolite into MMMs matrix, the pore flow mechanism will not be the governing mechanism to transport gas. For the treated zeolite MMMs, the best performance was observed on MMMs with 15 wt% zeolite loading rate with selectivity of 3.3 at 3 bar.

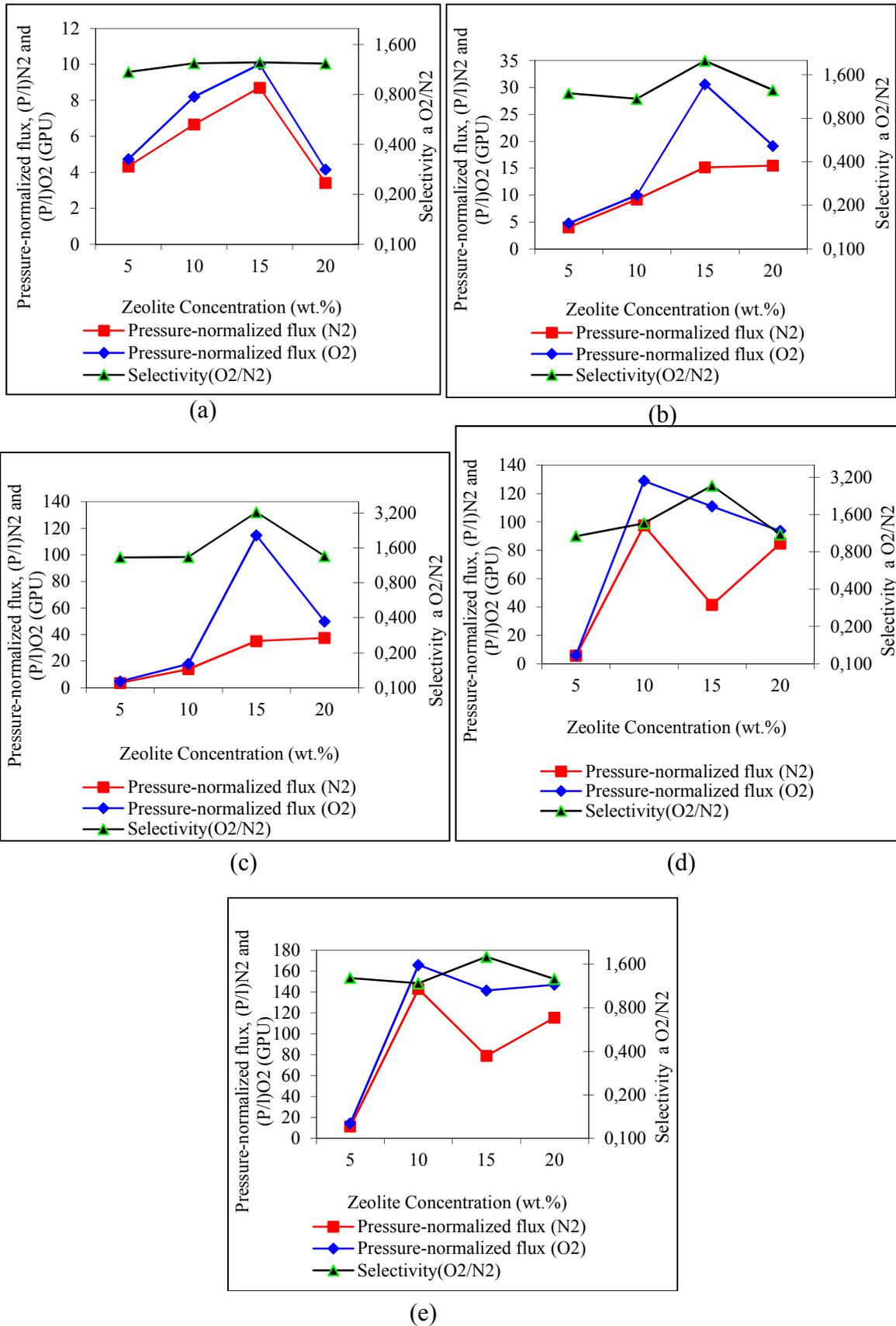


Fig 2: Performance of Polyethersulfone MMMs with various treated zeolite concentration at difference pressure. (a) 1 bar, (b) 2 bar, (c) 3 bar, (d) 4 bar, (e) 5 bar

## Conclusions

From the research of MMMs for gas separation it has already shows that the insertion of inorganic in the plain polymeric membrane can enhance the performance of the membrane. With careful consideration of the zeolite insertion loading for mixed matrix membranes (MMMs) can provide a more optimum performance of permeability and selectivity. In this study, MMMs of polyethersulfone (PES) and zeolite 4A was produced. From all of the experiment, result and study these conclusions can be made:

An ideal MMMs performance should reflects that it is only govern by the solution-diffusion mechanism and molecular sieve mechanism and not pore flow mechanism.

The usage of silane coupling agent is an excellent approach to increase the compatibility of the polymer and zeolite. However identification of the right amount of silane coupling agent for different concentration of zeolite should be put into consideration.

The increased in the zeolite insertion, zeolite particles tends to form interconnected channels between particles and this increased the selectivity and permeability of the MMMs.

Best performance of the treated zeolite membrane was observed on MMMs consist of 15 wt% zeolite and operated at 3 bar. The selectivity and pressure normalized flux observed was 3.3 and 114.7 GPU for O<sub>2</sub> and 35.1 for N<sub>2</sub> respectively. The best performance of untreated zeolite membrane was observed on MMMs consist of 5 wt% zeolite operated at 1 bar. The selectivity is 1.67 while the pressure normalized flux were 9.5 GPU for O<sub>2</sub> and 5.7 GPU for N<sub>2</sub>.

## Recommendation

From this study, there are several lacking that needs to be improved and new approach should be applied in order to get a better gas separation performance of the MMMs. Therefore, below are several recommendations for future works:

The usage of silane coupling agent is an excellent approach to increase the compatibility of the polymer and zeolite. Therefore it is better to identify the right amount of silane coupling agent for different concentration of zeolite.

Use other approach such as Grignard reagent to increase the zeolite-polymer interaction and compare its performance with MMMs using silane treated zeolite.

Manual casting of MMMs effect the MMMs preparation since the velocity variable is not constant for each membrane produced. Better results can be obtained by using an automatic casting machine in the future.

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**References**

- [1] Pandey, P. And Chauhan, R.S. (2001). Membranes For Gas Separation. Prog. Polym. Sci. 26:853-893.
- [2] Baker, R.W. (2000). Membrane Technology Applications. Membrane Technology Research, Inc. McGraw Hill.
- [3] Khan, A.L., Odena, A.C., Gutierrez, B., Minguillon, C., Vankelekom, I.F.J. (2010). Hydrogen separation and purification using polysulfone acrylate zeolite mixed matrix membranes. J. Membr. Sci. 350: 340-346
- [4] Sen, D., Kalipcilar, H., Yilmaz, L. (2007).Development of polycarbonate based zeolite 4A filled mixed matrix gas separation membranes. J. Membr. Sci. 303: 194-203
- [5] Robeson, L.M. (1991). Correlation of separation factor versus permeability for polymeric membranes. J.Membr. Sci. 62: 165-185
- [6] Bernado, P., Drioli, E. and Golemme, G. (2009). Membrane Gas Separation: Review/State of the Art. Ind. Eng. Chem. Res. 48: 4638-4663
- [7] Wan Aizan, W.A.R. (2006). Formation and characterization of mixed matrix composite materials for efficient energy gas separation. Faculty of Chemical and Natural Resources Engineering, University of Technology Malaysia.
- [8] Nunes, S.P. and Peinemann, K.V. (2001). Membrane technology in the chemical industry. Wiley VCH.
- [9] Suer, M.G., Bac, N. And Yilmaz, L. (1994). Gas permeation characteristics of polymer zeolite mixed matrix membranes. J. Membr Sci. 91: 77-86.
- [10] Ismail, A.F. Kusworo, T.D. and Mustafa, A. (2008). Enhanced gas permeation performance of polyethersulfone mixed matrix hollow fiber membranes using novel Dynasylan Ameo silane agent. J. Membr. Sci., 63: 5531-5539.
- [11] Wang, R. and Chung, T.S. (2001). Determination of pore sizes and surface porosity and the effect of shear stress within a spinneret on asymmetric hollow fiber membranes. J. Membr. Sci., 188: 28-37
- [12] Paul, D.R. and Yampol'skii, Y.P. (1994). Polymeric Gas Separation Membranes. Chapter 5: Membrane Formation for Gas Separation Processes. CRC Press, Inc.
- [13] Shu Shu.(2007). Engineering the performance of mixed matrix membranes for gas separations. Georgia Institute of Technology.Ph D. Dissertation.