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Preliminary study on gas separation performance of flat sheet mixed matrix (PVDF/Zeolite)

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Abstract. Membrane separation has attracted a lot of attention over the last years mainly due to its separation ability, operational capability and economical viability. Mixed matrix membrane (MMM) combines the superior transport and selectivity properties of inorganic membrane materials and the excellent fabrication properties of organic polymers. This emerging technology can be utilized to purify biogas which can be used in a variety of applications. In this study, flat sheet mixed matrix membranes were synthesized with different percentages of N-Mehtyl-2-pyrrolidone (NMP) as solvent, Polyvinylidene Fluoride (PVDF) as the polymer matrix and zeolite 4A as the dispersed fine particles, membrane A (80: 20: 0), membrane B (80: 18: 2), membrane C (80: 15: 5), and membrane D (75: 15: 10) respectively. The membranes were fabricated using dry/wet phase inversion method. The membrane's performance in terms of permeability and selectivity was examined using the single gas permeation device. The general trend was that, the permeability of the two gases (CO_2/CH_4) decreased with the increase of the pressure (0.5, 1, 1.5) bar. Membrane D was found to be suitable to separate the pair gas (CO_2/CH_4) as the permeability was 65623.412, Barrer and 15587.508, Barrer respectively, and its selectivity for was 4.21 at 0.5 bar.

1. Introduction

Generally, membranes for gas separation can be categorized as inorganic membranes and organic membranes depending on the constituent materials. Inorganic membranes exhibit excellent selectivity because of their regular pore structures[1]. On the other hand, academic investigators and industrial suppliers have employed organic polymers as asymmetric nonporous membranes that offer many desired properties including low operating cost and ease of construction and excellent processability [2]. And the latest emerging membrane with the potential for many applications involves mixed matrix membranes (MMM). The concept of mixed matrix membrane is the combination of polymeric membranes and inorganic membranes such as zeolite, activated carbon, and carbon nanotube. Inorganic molecular sieving materials have high separation performance properties and have the potential to surpass Robeson 2008 trade-off limit compared to polymeric membranes which are bounded by the trade-off limit [3]. The Polymer chose and the structure of the membrane are key aspects in selecting the appropriate membrane fabrication method. Phase inversion, interfacial polymerization, stretching,

and track-itching, are by far the most used techniques for membrane preparation. Phase inversion is defined as a process where a homogeneous polymer can be transformed from a liquid state to a soled state [4]. On the other hand, interfacial polymerization is One the most important techniques for commercial preparation of thin-film composite (TFC), (NF), and (RO) membranes [5].

Nowadays gas separation membranes find many applications such as hydrogen separation, oxygen–nitrogen separation, natural gas separation (carbon dioxide separation, dehydration, and dew point adjustment), vapor–vapor separation, and dehydration of air [6]. Membrane is one of the main methods of treatment of landfill gas mainly because of its lower energy requirements and capital investment cost as compared with the traditional separation techniques such as cryogenic distillation, pressure swing adsorption, and chemical absorption[7]. For an effective use of biogas as potential vehicle fuel, it has to be enriched in methane and this primarily achieved by carbon dioxide removal which then enhances the energy value of the gas to give longer driving distances with a fixed gas storage volume [8].

In this research, based on its unique features that the mixed matrix membrane (MMM) provides, it has been selected as a feasible method for CO_2/CH_4 separation. MMM combines the superior transport and selectivity properties of inorganic membrane materials (zeolite) and the excellent fabrication properties of organic polymers (PVDF). The aim of the study is to fabricate flat sheet mixed matrix membrane for CO_2/CH_4 biogas separation and test its permeability and selectivity. As well, it aims to characterize the membrane physically by scanning electron microscopy (SEM).

2. Experimental Set up
2.1. Material
Pallet of analytic grade Polyvinylidene fluoride (PDVF) with 177°C melting temperature, the inorganic filler material, Zeolite 4A with particle size 8-12mesh, and biotech grade N-Mehtyl-2-pyrrolidone, NMP with 99.5% purity, were bought from Sigma Aldrich. The two gases CO_2 and CH_4 which were utilized for gas permeation test were provided by Chemical Engineering Laboratory, Universiti Malaysia Pahang, which were utilized for gas permeation.

2.2. Preparation of Dope Solution
The dope solution was prepared be mixing the PVDF solution with the zeolite particles. The PVDF was dissolved in the NMP solvent and stirred with magnetic stirrer at 180°C for 6 hours. Then the zeolite was added to the PVDF solution according to the ratio given in the Table 1. Then continuously the dope was stirred for almost 3 hours at 180°C to ensure its homogeneity. Finally, the stirring was stopped and the gas bubbles in the dope were released by leaving the solution at room temperature for at least 72h [9]. Figure 1. illustrates the dope solution preparation steps.

Table 1. The component ratio of dope solution.

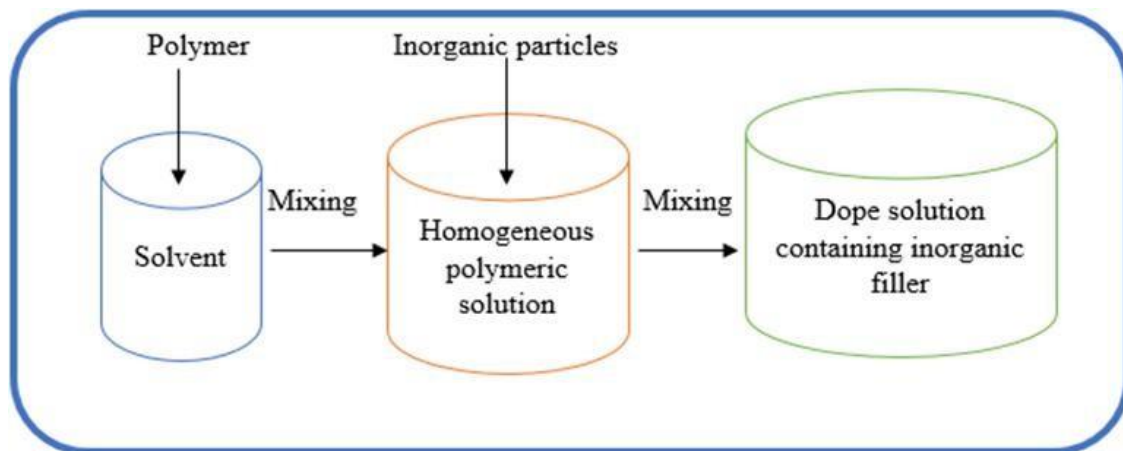| Membrane type	PVDF (wt.%)	Zeolite (wt.%)	NMP (wt.%)
A	20	0	80
B	8	2	80
C	15	5	80
D	15	10	75

Figure 1. Method to produce dope solution for mixed matrix membrane [6].

2.3. Membrane Casting

The casting solutions were left at the room temperature for 24 h to de-gas to avoid bubbles. Then they were casted uniformly on a glass plate at room temperature with a knife gap of 0.2 mm. After it was subjected to air for 30s, the casted film was immersed into coagulation bath. The formed membrane was taken out of the coagulation bath to a container containing fresh running water to remove the excessive (NMP) solvent. Last, the wetting membrane was dried in air at room temperature until a dry flat sheet membrane was achieved.

2.4. Permeability Test

The single gas permeation device was used to test the membrane performance. CO_2 and CH_4 were tested separately by using different pressure set (0.5, 1, 1.5) bar, and the permeability's of the two gases were measured by the bubble flow meter as illustrated in Figure 2. The gas permeability was calculated using equation 1. and it was expressed in Barrer [1 barrer = $1*10^{-10}$ cm3 (STP) cm/ (cm2scm Hg)]. The gas permeability in Barrer can be found by utilizing Equation 2, but the conversion factor has to be considered.

$$P = \frac{LV}{At\Delta p} \tag{1}$$

$$P(\text{Barrer}) = \frac{1*10^{10}*LV}{At\Delta P} \tag{2}$$

Where P is permeability, L is membrane thickness, V is gas volume in cm3 displaced in t(s), A is effective membrane area, ΔP is pressure difference across the membrane. Equation 3. is membrane selectivity which is the membrane ability to separate the pair gas and it is the ratio of CO_2 and CH_4 permeabilities.

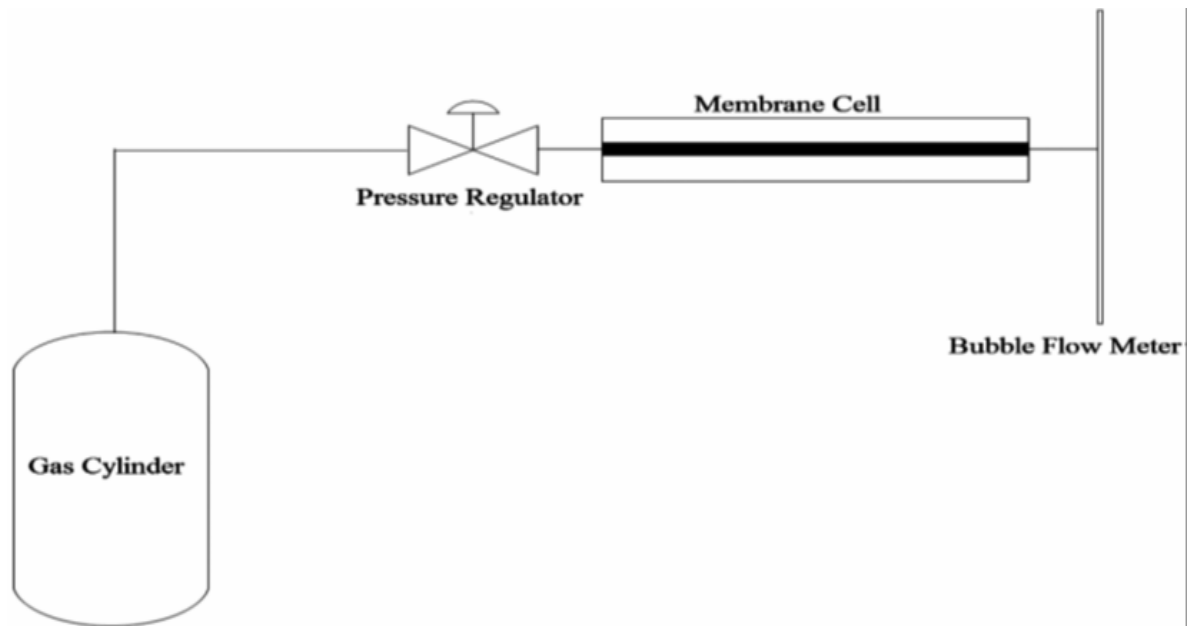$$\alpha_{CO2/CH4} = \frac{P_{CO2}}{P_{CH4}} \tag{3}$$

Figure 2. Single gas permeation device [10].

2.5. Membrane Characterization
A Scanning Electron Microscopy, SEM is used for the characterization of the membrane. SEM device is to examine the membrane morphology. The sample was fractured in liquid nitrogen and then inserted into the SEM device for cross sectional view of membrane. The size of pores on SEM micrograph that is scanned by a computer is calculated using the Sigmascan software.

3. Result and discussion
3.1 Performance of the membrane
The single gas permeation device was utilized to carry out the test. Table 2 shows the data that was obtained from the test to calculate the permeability and the selectivity of the two gases. The general trend is that, all four membranes showed an increase in permeability when there was a decrease in pressure. It is obvious that, membrane D at pressure 1.5 bar exhibits the highest selectivity of CO_2 among all other membranes, and that believed to be due to the loading rate of the fine zeolite particles which decreased the free volume of the membrane, thus influencing the gas transport behaviour. Then followed by membrane C, B and A at the same pressure 1.5 bar.

In terms of permeability, membrane D was the highest permeable to CO_2 65623.412 Barrer followed by membrane C, B and A 57980.535, 41725.869 and 30415.773 Barrer respectively. For CH_4 permeability, it very clear that membrane B was the highest permeable 36092.877 Barrer followed by membrane C, A and D, 32082.557, 26538.880, and 15587.508 Barrer respectively. On the other hand, the least permeable membrane for both gases CO_2 and CH_4 were membrane A with permeability 11577.692 Barrer and membrane D 7573.786 Barrer respectively, and this gas transport behavior could be attributed the slow gas diffusion through the membranes. plot of the membrane's permeability results that obtained from the test verses different set of pressure showed in Figure 3.

Table 2. The Performance of the Membranes.

NMP: ZEOLITE	PVDF:	Pressure, Bar	PCO$_2$ (Barrer)	PCH$_4$ (Barrer)	Selectivity CO$_2$/CH$_4$
80: 20: 0 A		0.5	30415.773	26538.880	1.15
		1	15154.568	12381.776	1.22
		1.5	11577.692	8797.776	1.32
80: 18: 2 B		0.5	41725.869	36092.877	1.16
		1	18782.232	17394.157	1.08
		1.5	18556.987	9663.420	1.92
80: 15: 5 C		0.5	57980.535	32082.557	1.80
		1	23590.115	13594.303	1.70
		1.5	19996.607	9238.820	2.16
75: 15: 10 D		0.5	65623.412	15587.508	4.21
		1	26735.464	7573.786	3.53
		1.5	16113.251	6146.083	2.62
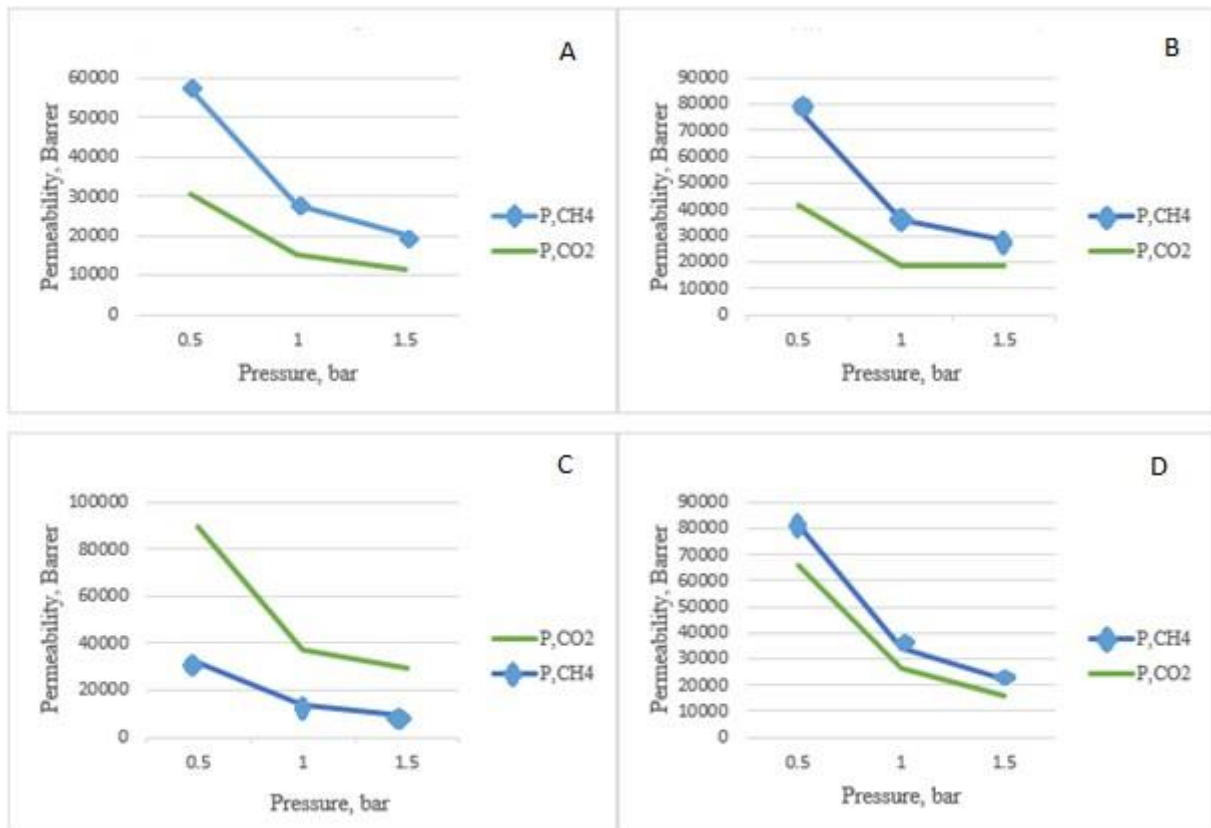
Figure 3. Permeability, Barrer of Membranes: A (80: 20: 0), B(80: 18: 2), C (80: 15: 5) and D (75: 15: 10) VS Pressure, bar.

The influence of the pressure on the membrane's selectivity was also obvious as the pressure increased there was a decrease in selectivity for membrane C and D, however, the result was a bit different for membrane A and B as the pressure increased there was a decrease in selectivity. Thus, membrane D which consist of 80%, 15%, 10% NMP, PVDF, and Zeolite respectively was regarded as the suitable membrane to separate CO$_2$/CH$_4$ biogas as the selectivity was 4.21 at 0.5 bar. Figure 4 illustrates the selectivity of the membranes versus pressure.
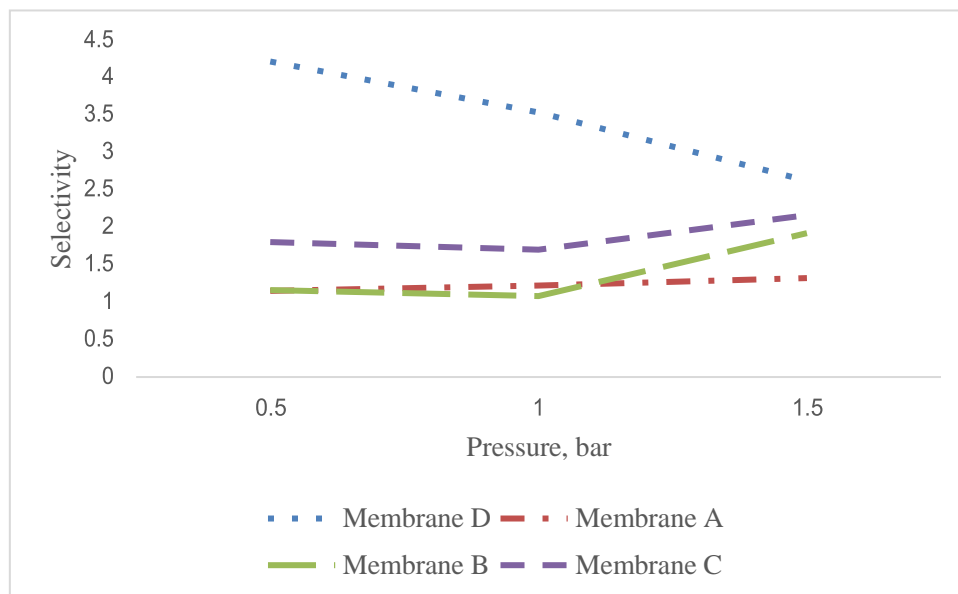
Figure 4. Selectivity of all membranes vs Pressure.

3.2. Physical characterization by SEM

After the fabrication of the membranes, they were cut into small pieces and dipped into liquid nitrogen to get a clear cross section. For the coating purpose, the membranes then placed on a metal holder and platinum. The surface morphology of the membranes is illustrated in Figure 5 and Figure 6 In general, the long finger-like structure and the main structures of the four membranes is almost the same. However, the dense membrane which has no zeolite added to it shown in Figure 5A and Figure 6A has a slightly different surface morphology in comparison with the rest of the membranes. Beside finger-like structure, Figure 6A clearly shows a consistent pores diameter. For membranes B, C and D which consist of 2%, 5% and 10% zeolite respectively, illustrate different degrees of disruption of the surface morphology made by the addition of the fine zeolite particles.

As could be seen from Figure 6 with 1000x magnification, the long finger-like structure of the dense membrane with pore diameter of 2.9 µm- 3.4µm, is attributed to the fast coagulation of the solvent NMP and the non-solvent water [11]. This range of pore diameter is not viable for CO2/CH4 separation as the pore diameter of these gases is 3.3x10-4, 3.8x10-4 respectively. There is unbalanced dispersion of the inorganic particles in Figure 6B. Therefore, this membrane displayed many cavities with pores diameter of 1.9µm-2.6µm which were formed during sample preparation by the cleavage of particles. [7] attributed the presence of the voids between the zeolite particles and the polymer chain to the existence of the fine particles in different quantities so more content of the zeolite more increase of the voids size. But unexpectedly membranes C, D with 5%, 10% zeolite content respectively showed smaller pores size of 1.7µm-2.2µm, 0.62µm-1.1µm respectively. And may be attributed to the good homogeneity of the solution which increased the adhesion of the zeolite particles with the polymer structure resulting in perfectly smaller pore sizes.
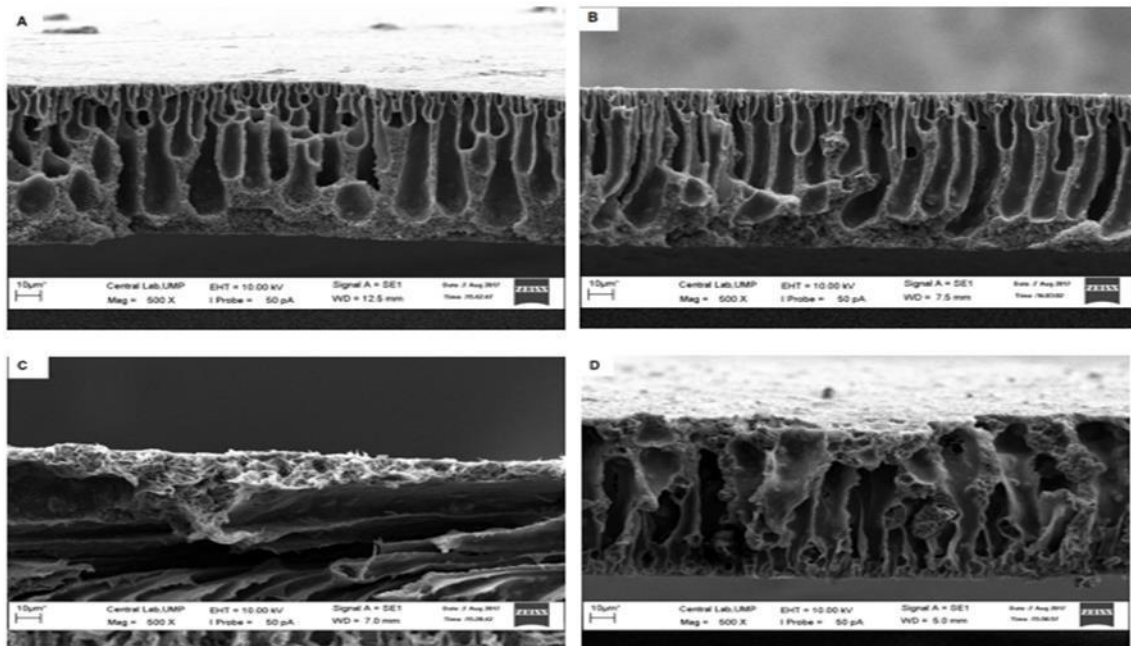
Figure 5. 500X magnification SEM image of NMP, PVDF, Zeolite: A (80: 20: 0), B (80: 18: 2), C (80: 15: 5), D (75: 15: 10).
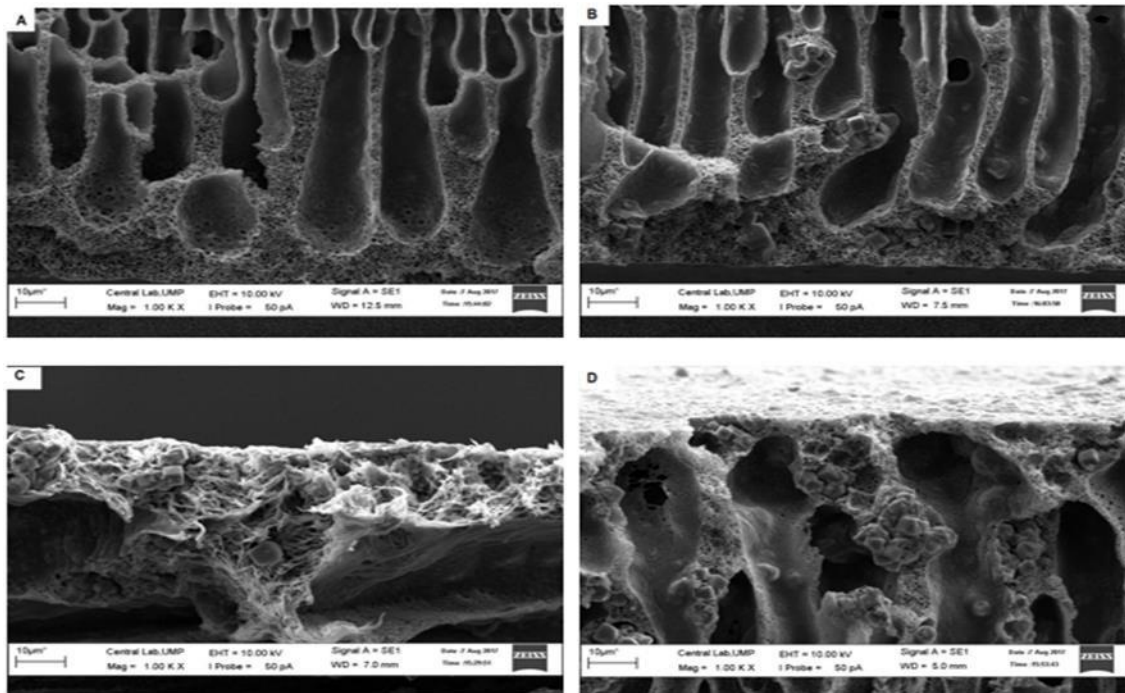

Figure 6. 1000X Magnification SEM image of NMP: PVDF: Zeolite: A (80: 20: 0), B (80: 18: 2), C (80: 15: 5), D (75: 15: 5).

4. Conclusion

In this paper, flat sheet mixed matrix membranes were synthesized with different percentages of N-Mehtyl-2-pyrrolidone (NMP) as solvent, Polyvinylidene Fluoride (PVDF) as the polymer matrix and zeolite 4A as the dispersed fine particles, membrane A (80: 20: 0), membrane B (80: 18: 2), membrane C (80: 15: 5), and membrane D (75: 15: 10) respectively. The membranes were fabricated using dry/wet phase inversion method. The membrane's performance in terms of permeability and selectivity was examined using the single gas permeation device. The general trend was that, the permeability of the two gases (CO2/CH4) decreased with the increase of the pressure (0.5, 1, 1.5) bar. Membrane D was found to be suitable to separate the pair gas (CO2/CH4) as the permeability was 65623.412, Barrer and 15587.508, Barrer respectively, and its selectivity for CO2 was 4.21.

Acknowledgement

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