

# Development and Performance Prediction of Polyethersulfone-Carbon Molecular Sieve Mixed Matrix Membrane for CO<sub>2</sub>/CH<sub>4</sub> Separation

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Natural gas contains some impurities like acid gases (CO<sub>2</sub> & H<sub>2</sub>S), which can affect the environment. Currently, the main focus of the research is to invent the new membranes materials for gas separation. Native polyethersulfone (PES) and PES/carbon molecular sieve (CMS) mixed matrix membranes were fabricated by solvent evaporation method using N-Methyl-2-pyrrolidone (NMP) as solvent. The final membranes were characterized in term of morphology and thermal stability by using field emission scanning electron microscopy (FESEM) and thermal gravimetric analyser (TGA). FESEM analysis of developed membranes was revealed that the final membranes have acceptable contacts between filler particles and the polymer chains with the thickness in the ranges from 51.37 μm to 67.68 μm. CMS inorganic particles were dispersed well within organic (polymer) matrix. Due to the addition of CMS the developed membrane exhibit the improved thermal stability. In the pure gas permeation, the effect of CMS loading and variable pressures (2, 4, 8 and 10 bar) on permeance and selectivity was analysed. Gas permeance and selectivity test portrayed that addition of different loading of CMS showed a better gas separation performance as compared to pure PES membranes. The results showed that the CO<sub>2</sub> permeance and CO<sub>2</sub>/CH<sub>4</sub> selectivity was increased with increasing CMS loading. The CO<sub>2</sub> permeance and CO<sub>2</sub>/CH<sub>4</sub> selectivity were increased from 50.86 GPU to 122.20 GPU and 3.08 to 10.33 at 2 bar pressure. The performance of membranes was predicted by using current numerical model of mixed matrix membranes. The current results showed that this work will be the substantial contribution in the gas separation technology.

## 1. Introduction

Extensive research has been performed to study new technologies which offer practical alternatives to traditional energy-intensive technologies (Etoumi et al., 2014). Membrane technology applied to the separation of gases competes with conventional unit operations like distillation, absorption, and adsorption on the basis of economics, safety, environmental and technical aspects (Bernardo and Clarizia, 2013). Due to high stability, ease of operation, reliability and high energy efficiency (Baker, 2002) membrane technology is preferred choice for CO<sub>2</sub> capture and natural gas purification (Mannan et al., 2013). Mixed matrix membranes (MMMs) contain inorganic dispersed phase in the organic polymer matrix. These membranes show superior performance than polymeric and inorganic membranes. MMMs possess some advantages like good processability, low capital cost and mechanical properties (Chung et al., 2007). Many studies have been carried out to incorporate the different type of inorganic filler like carbon molecular sieve (CMS) (Nasir et al., 2015), zeolite (Goh et al., 2011), SAPO-34 (Mohshim et al., 2014) in a polymer matrix to develop MMMs. Some researchers obtained higher performance than pure polymeric

membranes (Zhang et al., 2008). Some other researchers found lower performance than native polymeric membranes. This low performance was due to some difficulties like voids formation, poor compatibility, blockage of filler particles and rigidification of polymer chain (Mahajan et al., 2002). The performance of MMMs can be affected by the different parameters like pressure, temperature, composition and type of filler etc. Feed pressure is an important parameter for glassy MMMs. The solubility and permeance of gases increase with the increase of feed pressure (Khan et al., 2011).

Theoretically, the transport of gases through mixed matrix membranes is a complex problem. Several theoretical models have been used to predict the performance of MMMs. Due to close relationship between thermal/electrical conduction and permeation in composite materials; the conductivity models are readily adapted to permeability of species in MMMs (Hashemifard et al., 2010). A comparative summary of various models has been reviewed by Petropoulos (Petropoulos, 1985). A useful model was developed by Maxwell (1954) to predict the permittivity of a dielectric. Due to similarities in electrical potential and the flux through membrane equations, allowing the Maxwell model to predict the performance of mixed matrix membranes.

This study proposes the effect of pressure and CMS loading on the performance of PES-CMS mixed matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation and theoretical prediction of performance by using one of the existing models.

## 2. Materials and methods

### 2.1 Materials

A commercial Ultrason® E6020P Polyethersulfone (PES), purchased from BASF® (Germany) was used as base polymer. It has a molecular weight of about 50,000 g/mol. The solvent, N-methyl-pyrrolidinone (NMP) was purchased from Merck® Germany. The filler particles, carbon molecular sieve (CMS) was purchased from Japan Enviro Chemical®. The PES and CMS were also dried overnight in the oven to remove absorbed moisture.

### 2.2 Preparation of flat sheet membranes

MMMs were prepared by simple method "solvent evaporation method". The PES concentration in NMP is 20 wt. %. The CMS loadings in the casting solution were 10 and 30 wt. %. The CMS was added in NMP and stirred for 15 min and then sonicated for 30 min. CMS particles were primed by adding 10 wt. % of the total amount of PES and stirred the solution till the complete mixing of PES. Then remaining amount of PES added into the solution and stirred overnight. Then membranes were cast on glass plate by using the automatic casting machine. The cast membranes were placed in oven at 160 °C for 24 h.

### 2.3 Characterization of membranes

The morphology of all developed membranes was characterized by variable pressure field emission scanning electron microscopy (VPFESEM, Zeiss Supra 55 VP). The thermal stability of developed membranes was investigated by Thermogravimetric analysis (TGA) by using the Analyzer STA 6000 system (Perkin Elmer). The samples were heated up to 800 °C at a rate of 10 °C/min.

### 2.4 Gas performance test of membranes

Single gas (CO<sub>2</sub> and CH<sub>4</sub>) permeation through membranes was carried out by constant volume variable pressure method. The impurities of both gases were higher than 99 %. The permeation test was conducted at 25 °C with feed pressure 2, 4, 8, and 10 bar. The following Eq(1) and Eq(2) were used to calculate the permeance and selectivity of gases through membranes.

$$\frac{P_{CO_2}}{l} = \frac{J_{CO_2}}{\Delta p} \quad (1)$$

where  $\frac{P}{l} = \text{Permeance}$  ,

$$J_{CO_2} = \text{Flux } \alpha_{CO_2/CH_4} = \frac{\frac{P_{CO_2}}{l}}{\frac{P_{CH_4}}{l}} \quad (2)$$

### 3. Results and discussion

#### 3.1 Morphology of membranes

The qualitative analysis of flat sheet pure PES, PES-10 % CMS and PES-30 % CMS mixed matrix membranes were determined by FESEM characterization. The micrographs of the membranes are shown in Figure.1 (a), (b) and (c), which exemplify the cross section of developed membranes at high magnification. The high magnification micrographs were obtained to identify the true structure of membranes. All developed membranes are dense and non-porous. The FESEM images reveal that the distribution of CMS particles is uniform at acceptable limits. But there are some interface voids formed in particle – polymer interface. This is due to the solvent evaporation during membrane formation (Moore and Koros, 2005). The micrographs also show some agglomeration of CMS particles, especially at higher loading of CMS.

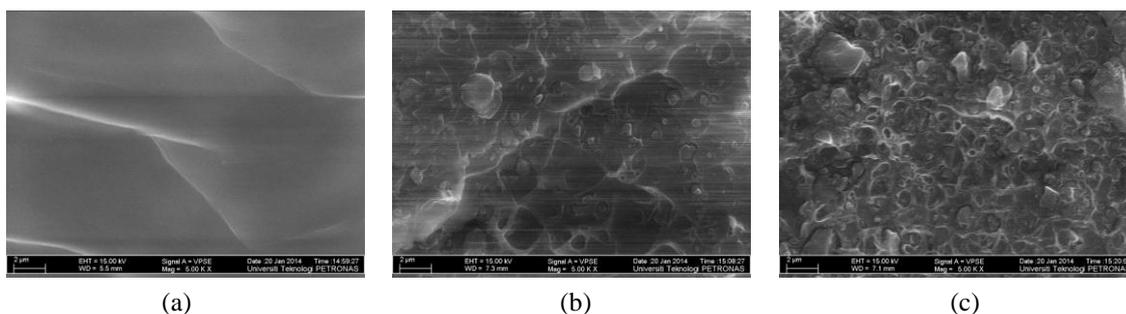


Figure 1: FESEM micrographs of (a) pure PES membrane, (b) PES-10 wt. % CMS and (c) PES-30 wt. % CMS

#### 3.2 Thermogravimetric analysis (TGA) of membranes

The thermal stability is an important factor in order to carry out the various separation processes at higher temperatures. For that purpose thermogravimetric analysis was performed in order to explain the impact of CMS particles when incorporated into the PES membrane. Figure 2 shows the results obtained for all pure PES and mixed matrix membrane with 10 wt. % and 30 wt. % CMS at a heating rate of 10 °C/min.

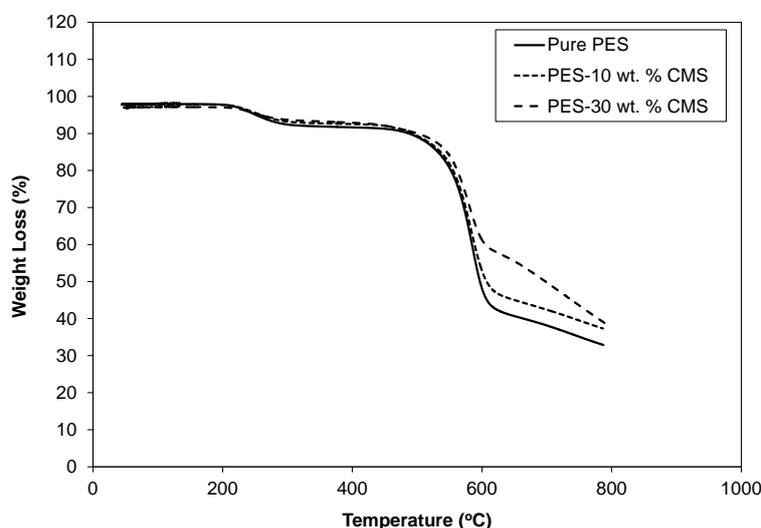


Figure 2: TGA analysis of developed membranes

It is observed that there is no weight loss till 200 °C. It shows that the membranes are free of moisture. There are two weight loss curves between 210 °C to 280 °C and 450 °C to 640 °C. The first curve shows that membranes have some residual solvent. But the percentage of solvent was in a safe range. Due to the addition of inorganic filler the residue of membrane has increased. It shows that the CMS particles have good interaction with the polymer. In the range of 450 °C to 640 °C, there is almost 46 % weight loss

has been observed due to the degradation of PES. By the addition of CMS the stability of membrane has increased. It is also observed that the residue weight of MMM is higher than pure PES. The increase of residue is suggesting an interaction of CMS with polymer (Vilakati et al., 2014).

### 3.3 Gas permeation analysis of developed membranes

The gas permeation properties and selectivity of pure PES membranes and mixed matrix membranes are given in Table 1. Table 1 show that the CO<sub>2</sub> permeance increased with increase in CMS loading and decreased with increase in pressure. It exhibits the glassy nature of membranes. These findings are in good agreement with some previous studies - e.g. using CO<sub>2</sub> (Bos et al., 1999) and specific to separation membranes (Ismail and Lorna, 2002). This non-linear relationship between permeance and pressure indicates the dual sorption mechanism (Paul and Koros, 1976). The permeability coefficient decreases monotonically with the pressure difference across the membrane. The selectivity was increased with increase in pressure. This shows the good interaction of filler particles with polymer matrix. The permeance and selectivity were also increased with the increase of CMS loading. There were almost 140.26 % and 105.27 % increase in CO<sub>2</sub> permeance and selectivity at 2 and 10 bar pressure.

The performance of membranes was evaluated on the Robeson Upper bound curve as shown in Figure 3. As it can be seen that the performance of developed membranes is near to 2008 Robeson upper bound curve for low and high loading of CMS particles. The membrane performance was improved by the addition of CMS at all pressure. The values of permeability and selectivity have not been suppressed. So these results showed that the further improvement is required for these membranes to achieve the upper bound status.

Table 1: Effect of CMS particles and pressure on gas permeance and selectivity

Pressure (bar)	Pure PES	PES-10 wt. % CMS	PES-30 wt. % CMS	Pure PES	PES-10 wt. % CMS	PES-30 wt. % CMS
	CO <sub>2</sub> Permeance (GPU)			CO <sub>2</sub> /CH <sub>4</sub> selectivity		
2	50.86	57.23	122.20	3.08	5.18	10.33
4	42.40	42.51	76.51	4.79	5.47	10.77
8	25.50	31.20	51.76	5.25	6.96	11.04
10	25.14	31.01	44.69	5.40	7.19	11.11

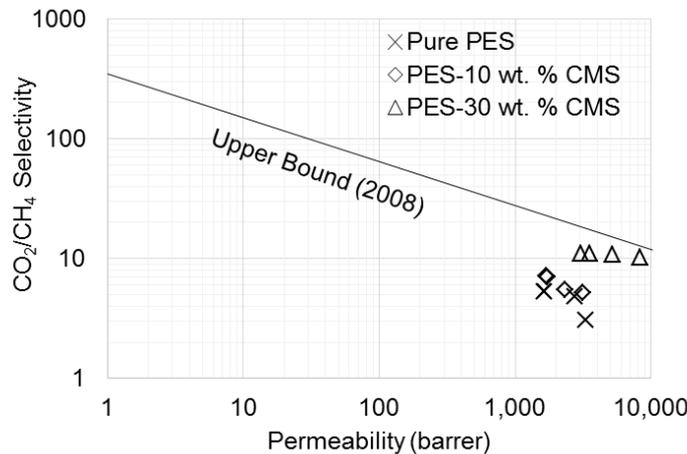


Figure 3: Performance evaluation of developed membranes on Robeson upper bound curve 2008

### 4. Performance prediction of developed membranes

As already mentioned in section 1, the gas performance of developed MMMs can be predicted by Maxwell model. The solution to predict the effective permeability of MMMs with a dilute suspension of CMS can be calculated by the following equation (Maxwell, 1954).

$$P_r = \frac{2(1 - \varphi_d) + (1 + 2\varphi_d)\lambda_{dm}}{(2 + \varphi_d) + (1 - \varphi_d)\lambda_{dm}} \quad (3)$$

where “ $P_r$ ” is the relative permeability ratio of “ $P/P_m$ ”,  $P$  is the effective permeability of species in MMM, “ $P_m$ ” is the permeability polymer matrix, “ $\varphi_d$ ” is the volume fraction of the dispersed phase, and “ $\lambda$ ” is the permeability ratio “ $P_d/P_m$ ”, “ $P_d$ ” is the permeability of dispersed filler particles. Percentage average absolute relative error (AARE %) values were calculated by using the following equation (Yilmaz and Keskin, 2014) and (Shimekit et al., 2011).

$$AARE_i(\%) = \frac{100}{N} \sum_{i=1}^N \left| \frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}} \right| \quad (4)$$

The performance prediction of MMMs was based on the experimental data as shown in Table 1. The pure CO<sub>2</sub> permeance data were obtained for CMS membrane from previous literature (Ahmad et al., 2010). The model parameters are mentioned in Table 2. It assumed that the  $P_d$  will be same for all pressure range (2-10 bar).

Table 3 shows a comparison of the calculated relative permeability “ $P_{r(calc)}$ ” and the experimental relative permeability “ $P_{r(exp)}$ ” by the Maxwell model. It is found that at lower loading of CMS the experimental relative permeability is well predicted by the Maxwell model, but at higher loading of CMS that experimentally obtained relative permeability value was greater than predicted ones. It may be attributed to the agglomeration of CMS particles and interface voids formation around the CMS particles at higher loading, as it was observed in the FESEM analysis (Figure 1).

*Table 2: Model parameters values obtained in present model at 2 bar*

$\varphi_d$	$P_d$ (GPU)	$P_m$ (GPU)	$\lambda_{dm}$
0	1,042	50.86	20.49
0.05	1,042	50.86	20.49
0.13	1,042	50.86	20.49

*Table 3: Comparison of calculate and experimental relative permeability in MMMs by using Maxwell Model*

$\varphi_d$	$P_{r(exp)}$	$P_{r(calc)}$	AARE %
0	1	1	0.00
0.05	1.13	1.14	1.15
0.13	2.40	1.39	42.26

## 5. Conclusions

PES was chosen as a base polymer for the fabrication of MMMs via CMS loading. The CMS loading was 10 and 30 wt. %, to analyse the performance of membranes for pure CO<sub>2</sub> and CH<sub>4</sub> gases. FESEM images exhibited, that CMS particles, at low loading were dispersed uniformly at acceptable limits, but at higher loading some agglomeration of CMS was observed. TGA analysis confirmed the thermal stability of developed MMMs. The gas performance analysis showed that the CO<sub>2</sub> permeance and CO<sub>2</sub>/CH<sub>4</sub> selectivity were higher in PES/CMS MMMs than native PES membrane. Developed MMMs showed the 2.40 fold increase in CO<sub>2</sub> permeance as compared to PES membranes. Similarly the CO<sub>2</sub>/CH<sub>4</sub> ideal selectivity was enhanced 3.35 fold than a pure PES membrane. The theoretical prediction showed the good agreement of experimental and calculated relative permeability at lower loading of CMS, but at higher loading the AARE % value is higher. Therefore the modification in Maxwell model is needed to address interface voids for accurate performance prediction of MMMs. The PES/CMS MMMs showed potential for natural gas sweetening due to increase in selectivity.

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**References**

- Ahmad M.A., Rashid N.K.A., Harun W.H.F.W., Hameed B.H., 2010, Effects of polyetherimide pyrolysis temperature on CMS membranes: study on CO<sub>2</sub> permeance and CO<sub>2</sub>/CH<sub>4</sub> permselectivity, *Int. J. Basic Appl. Sci.*, 10, 60-63.
- Baker R.W., 2002, Future directions of membrane gas separation technology, *Ind. Eng. Chem. Res.*, 41, 1393-1411.
- Bernardo P., Clarizia G., 2013, 30 years of membrane technology for gas separation, *Chemical Engineering Transactions*, 32, 1999-2004.
- Bos A., Pünt I.G.M., Wessling M., Strathmann H., 1999, CO<sub>2</sub>-induced plasticization phenomena in glassy polymers, *J. Membr. Sci.*, 155, 67-78.
- Chung T.-S., Jiang L.Y., Li Y., Kulprathipanja S., 2007, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, *Prog. Polym. Sci.*, 32, 483-507.
- Etoumi A., Jobson M., Emtir M., 2014, Hybrid membrane-distillation separation processes, *Chemical Engineering Transactions*, 39, 1075-1080.
- Goh P., Ismail A., Sanip S., Ng B., Aziz M., 2011, Recent advances of inorganic fillers in mixed matrix membrane for gas separation, *Sep. Purif. Technol.*, 81, 243-264.
- Ismail A., Lorna W., 2002, Penetrant-induced plasticization phenomenon in glassy polymers for gas separation membrane, *Sep. Purif. Technol.*, 27, 173-194.
- Khan A.L., Li X., Vankelecom I.F., 2011, Speek/Matrimid blend membranes for CO<sub>2</sub> separation, *J. Membr. Sci.*, 380, 55-62.
- Mahajan R., Burns R., Schaeffer M., Koros W.J., 2002, Challenges in forming successful mixed matrix membranes with rigid polymeric materials, *J. Appl. Polym. Sci.*, 86, 881-890.
- Mannan H.A., Mukhtar H., Murugesan T., Nasir R., Mohshim D.F., Mushtaq A., 2013, Recent applications of polymer blends in gas separation membranes, *Chem. Eng. Technol.*, 36, 1838-1846.
- Maxwell J., 1954, A treatise on electricity and magnetism. Vol. 1, Dover Publications Inc., New York, USA.
- Mohshim D.F., Mukhtar H., Man Z., 2014, The effect of incorporating ionic liquid into polyethersulfone-SAPO-34 based mixed matrix membrane on CO<sub>2</sub> gas separation performance, *Sep. Purif. Technol.*, 135, 252-258.
- Moore T.T., Koros W.J., 2005, Non-ideal effects in organic-inorganic materials for gas separation membranes, *J. Mol. Struct.*, 739, 87-98.
- Nasir R., Mukhtar H., Man Z., Dutta B.K., Shaharun M.S., Abu Bakar M.Z., 2015, Mixed matrix membrane performance enhancement using alkanolamine solution, *J. Membr. Sci.*, 483, 84-93.
- Paul D., Koros W., 1976, Effect of partially immobilizing sorption on permeability and the diffusion time lag, *J. Polym. Sci., Part B: Polym. Phys.*, 14, 675-685.
- Petropoulos J., 1985, A comparative study of approaches applied to the permeability of binary composite polymeric materials, *J. Polym. Sci. Part B: Polym. Phys.*, 23, 1309-1324.
- Shimekit B., Mukhtar H., Murugesan T., 2011, Prediction of the relative permeability of gases in mixed matrix membranes, *J. Membr. Sci.*, 373, 152-159.
- Vilakati G.D., Hoek E.M.V., Mamba B.B., 2014, Probing the mechanical and thermal properties of polysulfone membranes modified with synthetic and natural polymer additives, *Polym. Test.*, 34, 202-210.
- Yilmaz G., Keskin S., 2014, Molecular modeling of MOF and zif-filled mmms for CO<sub>2</sub>/N<sub>2</sub> separations, *J. Membr. Sci.*, 454, 407-417.
- Zhang Y., Balkus Jr K.J., Musselman I.H., Ferraris J.P., 2008, Mixed-matrix membranes composed of matrimid® and mesoporous ZSM-5 nanoparticles, *J. Membr. Sci.*, 325, 28-39.