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# Performance Prediction of ZIF-8/Polymer Blend Mixed Matrix Membrane by Permeation Models for $CO_2/CH_4$ Separation

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**Abstract :** Mixed matrix membranes (MMM) with moderate filler loading have been shown to improve the transport properties of polymers and its blends for many gas separations. Currently, the main focus of the research is to invent the new membranes materials and its combinations for gas separation. PES/PSF (80/20%) blend with dispersed inorganic porous zeolitic imidazolate framework (ZIF-8) MMM were fabricated at 10, 20 and 30% ZIF-8 loading by the solvent evaporation method using solvent N-methyl-2 pyrrolidone (NMP). Membranes were characterized in terms of thermal stability by using thermal gravimetric analyzer (TGA) and it was found that, due to addition of ZIF-8 nano particle, the developed membranes exhibit the improved thermal stability and adequate contact between filler particles and the polymer chains with the thickness in the ranges of 90 μm to 100 μm. For the pure gas permeation, the effect of ZIF-8 loading at 3 atmosphere on permeability (Barrer) and selectivity were investigated. By the addition of 10 w/w % ZIF-8 into polymer blend, increased the permeability about two times for gases $CO_2$ and $CH_4$, while the ideal selectivity shows a slight loss (~15 to 16 %) for pure PES/ PSF blend membrane. For the higher ZIF-8 loadings (≥ 30 w/w %) permeability's were increasing but selectivity gets started to reduce rapidly due agglomeration of nanoparticles , but it was found that, still the selectivity improvement with the addition of filler into glassy polymer blend up to 25% and 30% loading.

The theoretical prediction predicts the good agreement of experimental and calculated relative permeability at lower loading of ZIF-8, but at higher loading the absolute average relative error percent (AARE %) was found higher. The models predicted under ideal morphology, result confirmed that, decrease in the AARE % in the order of, Maxwell model > Lewis-Neilson model > Singh model. Hence, Singh model was found to be in a better agreement with the experimental data for the prediction of relative permeability of $CO_2$ in PES/PSF blend polymer MMM at different volume fraction of ZIF-8. It was observed that, addition of 15 to 25 w/w % ZIF-8 was suitable as an optimum filler loading for membrane formulation.

**Keywords :** Mixed Matrix Membrane, Zeolitic Imidazole Framework (ZIF-8), Gas separation, Permeability, Permeation models, polymer blend.

## 1. Introduction

The current necessity is to invent the new membrane materials and its combinations to develop environmental friendly and energy efficient gas separation processes such as natural gas, biogas separation and many more applications such as hydrogen, oxygen–nitrogen separation, vapor–vapor separation, and dehydration of air[1]. Due to low capital cost, modest energy requirement and ease to fabricate, research on polymeric membrane has expanded much attention in the last two decades. Polymeric membranes provide many advantages and its performance is studied by Robeson's trade-off curve shows relation between selectivity and permeability[1].

Inorganic fillers such as carbon molecular sieve, various types of zeolite, carbon nano tubes, and activated carbon etc. posses separation properties surpass Robeson's trade-off limit, were initially embedded into polymer to improve separation performance but, inorganic fillers shows poor interaction with polymer matrix and often lead to defective membranes. Developing defect-free mixed matrix membranes remains major challenge[2,3]. Mostly membranes defected through particle agglomeration, un-selective voids formation, filler pore blockages and sieve-in-cage morphology affect its effectiveness. The Metal organic frameworks (MOFs) as potential filler due to organic linkers present in the structure have good interaction with polymers. Besides, MOFs consist of large surface area, high adsorption capacity, ease of modifications and high affinity towards certain gas[4,5].

Among MOFs and its sub-groups, zeolitic imidazole framework-8 (ZIF-8) is widely investigated MOFs[6,7,8] and it has porous crystalline structure with M-Im-M angle (M= metal) near to 145°, coincident with the Si–O–Si angle found in many zeolites[7,8,9]. ZIF-8 has found sodalite (SOD) topology and a pore size of 0.34 nm[6,8,10]. It has large pores of 11.6 $A^0$ which is approximatly two times larger than SOD zeolite and pores are accessible through small channels (3.4 $A^0$). It exhibits thermal stability up $400^0$C and it has a BET surface area around 1300 to 1600 $m^2$/gm or even more[6,8,10,11]. It shows good chemical stability against polar and non-polar solvents[9], reorientation of its structure at high pressure and mechanical strength. Textural properties of the ZIF-8 is shown in Table-1[8,11,12].

**Table 1. Textural Properties of the ZIF-8**

| MOF Type | Pore topology | Pore diameter (nm) | BET Surface area $m^2$/gm | Approximate Particle size (nm) |
|---|---|---|---|---|
| ZIF-8 | Cage/ Window | 1.16 /0.34 | 1214-1650 | 170 |

Another important concern about MMM is the amount of filler loading, particle size of filler material in determining the gas transport properties of the mixed matrix membrane. High filler loading would provide higher penetrant-filler interaction with increase in performance, but that leads to particles agglomeration, directly reflect on membrane production cost and deteriorating its performance. In contrast, incorporating smaller amount of fillers gives appropriate improvement on membrane separation properties. Lowest filler loading with significant improvement of membrane performance would be the ideal MMM[5,13].

$CO_2$ has a smaller kinetic diameter 0.33 nm compared to $CH_4$ gas, and much upper critical temperature compared to $N_2$ and $CH_4$ as shown in above table-2. The lesser kinetic diameter and prominent critical temperature (higher condensability) of $CO_2$ support in higher diffusion rate and solubility coefficients and hence higher permeability compared to $N_2$ and $CH_4$.

**Table 2. General Properties of Gases $CO_2$, $N_2$ and $CH_4$**

| Gas | Molecular Mass (g/mol) | Critical Temperature ($^0$K) | Kinetic Diameter (nm) |
|---|---|---|---|
| $CO_2$ | 44 | 304 | 0.33 |
| $N_2$ | 28 | 126 | 0.36 |
| $CH_4$ | 16 | 190 | 0.38 |

Polyethersulfone (PES) and polysulfone (PSF) is commercially attractive polymers due to its high chemical resistance, thermal degradation and stability to oxygen. The glass transition temperature (Tg) of these polymer PES and PSF are $220^0$C and $185^0$C[14]. The gas transport properties of polymers lie near the upper bound line on the central region of Robeson's plot for desirable attractive gas pairs like $CO_2/CH_4$, $H_2/CH_4$. *N*-Methyl-2-pyrrolidone (NMP) solvent is most suitable to dissolve polymers due to its strong dissolving power for many components. It has the chemical formula of $C_3H_3ON$, and boiling point of $153^0$C[15].

Polymer blending concept is considered as a time and cost effective method to develop new material combination with desirable properties by tuning the blend ratio, which may not found in the individual polymers. Polymer blend membranes are fabricated by combination of glassy- glassy or galssy rubbery polymers. Basu et. Al. [16] prepared PSF/PI blend membrane and found improved separation performance of CO2/$CH_4$ under harsh conditions of temperature and pressure. Han et al[17] also blend PES/PI for $O_2$ /$N_2$ separation and found increase in permeability.

It can be also possible to prepare the membrane with addition of filler such as CMS in polymer to improve the performance and strength of membrane. Kulprathipanja et al[18] prepared PES- zeolite-A MMM membrane and studied the effects of polymer chain regidification, zeolite pore size, pore blockage etc . Hafiz Abdul Mannan et. al.[19] prepared and study the characterization of PSF/ PES blend membrane with improved thermal stability and found good blending with enhance performance of $CO_2$ separation.

Several theoretical models[20] have been used to predict the performance of MMMs. Theoretical analysis predicts that, the permeation of gases through mixed matrix membranes is a difficult problem. Due to close relationship between thermal and electrical conduction and with permeation in composite materials; these conductivity models are established to find permeability of MMMs[21]. Initially the most useful correlation was established by Maxwell (1954) to investigate the permeability. Electrical potential and flux through membrane establish similarities in trend, allowing the Maxwell model to predict the mixed matrix membrane performance[20,21,22]. In other models with incorporation of different geometries of particles was proposed by Singh and illustrate a correlation term in place of physical porosity and thermal conductivity as a function and thermal conductivity model with replacing thermal conductivity by permeability[23]. While the Lewis and Neilsen (1970) and Neilsen (1973) was originally proposed model for the elastic modulus of composites and then can be adopted for the permeability calculation[20-23].

The literature review demonstrate that, the performance of MMMs can be affected by the various different parameters like temperature, pressure, composition of membrane and type, size of filler etc. Feed pressure is an important parameter for mixed matrix membranes. The solubility and permeability of gases increase with the increase of feed pressure[24]. After investigation of various materials, process and casting parameters, we confirm that, in order to develop high performance MMM at low to moderate filler loading, nano filler with good polymer-filler interaction is necessary with combination of polymer blend with nano filler loading to enhance the physico-chemical properties of materials. But interestingly not much study is available in the literature for blend of glassy polymers with fillers loading and specifically ZIF-8 loading. Therefore in the present work blending of PES/PSF (80/20% blend ratio) with ZIF-8 nano particle was carried out to prepare flat sheet polymer blend membrane. This study put forward the effect of ZIF-8 loading on the performance of PES/PSF blend- ZIF-8 mixed matrix membranes for $CO_2/CH_4$ separation and theoretical prediction of performance by using three different existing models[23]. The predicted relative permeability of the different MMM was validated with comparing different experimental data and existing model to find out the optimum loading range of filler loading.

## 2. Materials and methods

### 2.1 Materials

Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$], methanol were obtained from Fisher Scientific and 2-methylimidazole [$C_4H_6N_2$] was obtained from Sigma-Aldrich (India). Polyethersulfone (PES) [Radel A-100 grade] and Polysulfone provided by Solvay. n-Hexane and *N*-Methyl-2-pyrrolidone (NMP) were purchased from Merk. All chemicals were used as received without any further purification.

## 2.1 Membrane preparation

The morphology and the transport properties of mixed matrix membranes are strongly related to the types of polymer, nano filler materials, solvents, and the additives used in fabrication. Solvent-evaporation method was used for preparation of the membranes. Polymer and ZIF-8 were dried at $80^0$C and $180^0$C overnight before using in the membrane synthesis. Two different types of membranes were prepared in this study, pure PES/PSF blend membrane and PES/PSF (80/20%) with different percentage of ZIF-8 membranes.

Asymmetric flat sheet neat membrane was prepared by casting solution consisted of Polyethersulfone (PES), Polysulfone (PSF) and NMP. Overnight dried PES and PSF was added into the solvent NMP step by step in order to prevent a sudden increase in the viscosity of solution and ease of stirring. Then, the solution was stirred for overnight by a magnetic stirrer. Casting process was performed by hand-casting at ambient atmosphere. Asymmetric flat sheet MMM was prepared by overnight dried ZIF-8 was dispersed in the solvent NMP in three or four steps according to the amount of ZIF-8. Between each two steps, the solution was ultrasonicated for 20 to 30 min in order to ease the dispersion and minimize the agglomeration of ZIF-8 particles in the solution. After completing the ZIF-8 addition, PES and PSF was primed by adding 15 wt % of the total amount so as to increase the compatibility between ZIF-8 and PES/PSF and the solution was stirred for overnight by a magnetic stirrer. Then, remaining amount of PES/ PSF was added to the solution in three or four steps with 20 to 30 minute ultrasonication in between the steps and again the solution was stirred for overnight. While the PES/ PSF concentration was kept constant, the ZIF-8 contents in the membranes were varied between 10- 30 w/w % and then, membrane undergoes "curing" at 40 to 50°C overnight. [25,26].

## 2.2. Gas permeation

Single pure gas (99.99% purity) $CO_2$ and $CH_4$ permeation through membranes was carried out by constant volume variable pressure method as shown in fig 1. The permeation test was conducted at $35^0$C with feed pressure 3 bar while permeate side was opened to atmosphere with a designed membrane permeation cell. Circular membrane discs with an effective permeation area of 7.069 $cm^2$ were used. Permeability 'P' of 1 barrer corresponding to $10^{-10}$ related to cubic centimeters per second (volume at STP) was calculated by using following equation:

$$\text{Pemeability}\left(P_{CO_2}\right) = \frac{\text{Gas flow rate}\left(V_{CO_2}\right) \times \text{Membrane thickness (l)}}{\text{Area (A)} \times \text{Pressure drop } (\Delta P)} \text{--------(1)}$$

The effective membrane area be 'A' ($cm^2$), and't' is the time of permeation (s) and the 'Δp' is the transmembrane pressure drop (cmHg) [10]. The unit of volumetric gas flow rate is ($cm^3$, STP), and permeability usually is Barrer, where,

$$\text{Barrer} = 1 \times 10^{-10} \frac{cm^3\,(STP)\,cm}{cm^2\ s\ cmHg} \qquad \text{--------(2)}$$

Selectivity was obtained using Equation (2):

$$\alpha_{\frac{i}{j}} = \frac{\left(\frac{y_i}{y_j}\right)\text{permeate}}{\left(\frac{x_i}{x_j}\right)\text{feed}} \qquad \text{------------(2)}$$

Where, $x_i$ and $y_i$ are mole fractions of component 'i' in the gas mixture in the feed and permeate sides respectively.

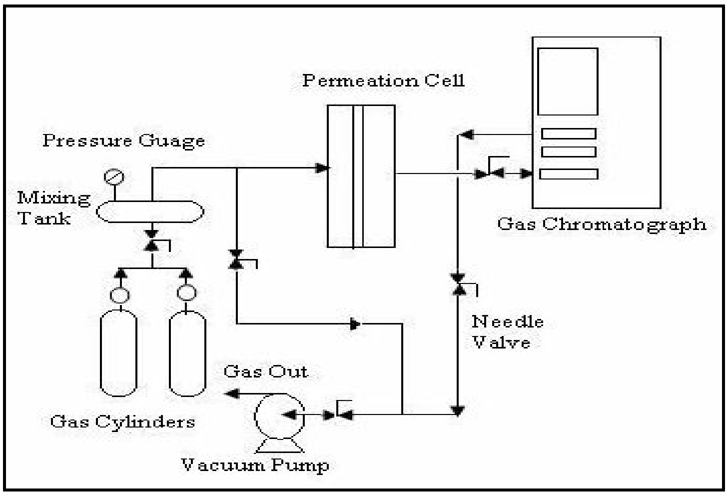



**Fig.1. Gas permeation experimental set-up**

## 3. Permeation models for performance prediction

The gas separation performance of developed mixed matrix membrane can be predicted by the several theoretical models[20] as functions for the gas permabilities of the continuous PES/ PSF and dispersed phase (ZIF-8). Maxwell, Singh and Lewis–Nielson models has been discussed for the prediction of relative permeability of $CO_2$ by mixed matrix membrane[21-23,27].

### 3.1. Maxwell model

The Maxwell model (1954) was initially developed for electrical conductivity of the particulate composites and it can be useful and adopted for the calculation of permeability as,

$$P_r = \frac{P}{P_m} = \left[\frac{2(1-\phi)+(1+2\phi)\lambda_{dm}}{(2+\phi)+(1-\phi)\lambda_{dm}}\right] \qquad \text{---------- (1)}$$

Where, $P_r$ - relative permeability of species; P - effective permeability of species in mixed matrix membrane; $P_m$ - permeability of species in matrix (continuous phase); Φ- volume fraction of filler particles; $\lambda_{dm} = P_d/P_m$ - the permeability ratio; $P_d$ - permeability of species in dispersed phase[20-22,28].

### 3.2. Singh Model

The new model for the effective thermal conductivity of polymer composites has been proposed by Singh[23]. In this model, a structure like cylindrical lattice with regular distribution of spheres was considered. In this model, with incorporation of different geometries of particles and consider non linear flow of heat flux lines which generated by the differences in thermal conductivities of the constituent phases. This equation state a two phase model to predict permeability of mixed matrix membrane. The Singh thermal conductivity model with replacing thermal conductivity by permeability, is reported as below,

$$P_r = 1 + 3.74\left[\frac{\lambda_{dm}-1}{\lambda_{dm}+2}\right] * \phi^{2/3} \qquad \text{----------- (1)}$$

$$\lambda_{dm} = \frac{P_d}{P_m} \qquad \text{-------------- (2)}$$

### 3.3. Lewis and Nielson model

The Lewis and Nielson (1970) and the Nielson (1973) model[21,22,28] was formerly projected for the elastic modulus of composite and can be implemented for the permeability prediction as:

$$[P_r = ] \; [P/P_m] = [(1+2[\lambda_{dm}-1)/(\lambda_{dm}+2)]\phi)/(1-[\lambda_{dm}-1)/(\lambda_{dm}+2)]\phi\psi)]$$

Where,

$$\psi = 1 + \left[\frac{1 - \phi_m}{\phi_m^{2}}\right]\phi \qquad ---------- (4)$$

$\phi_m$ - is the maximum volume packing fraction of filler particles; $\phi_m$ = 0.64 for random close packing of uniform spheres[20,21].

## 4. Results and discussion

### 4.1. Phase purity of ZIF-8

The phase purity of ZIF-8 crystalline powder was characterized by XRD (X -Ray Diffractometer) [9,25]. XRD is a non destructive analysis to measure wavelength of sample and to identify structure. The XRD will release X-rays to the sample and the X-Rays diffracted at different angles and intensity by CuKa irradiation with a wavelength (λ) 1.54 $A^0$ at room temperature. The schematic graphical representation of synthesized ZIF-8 crystalline powder by room temperature synthesis method and synthesis procedure of ZIF-8 crystals[15] by using de-ionized water and by using methanol has been studied in our earlier work[13].

### 4.2. Thermo gravimetric analysis (TGA)

The developed membranes were characterized by thermo gravimetric analysis (TGA) to analyze the thermal stability of by using the thermal analyzer model DTG simultaneous DTA-TG apparatus (Shimadzu). The changes in thermal properties of the mixed matrix membrane will be detected by using TGA. The small amount of sample weight 5 to 10 mg were heated up to 900 $^0$C at a rate of $10^0$C/min at nitrogen atmosphere to determine weight loss with respect to temperature as shown in fig 2. The thermal behavior of a polymer can be characterized rapidly over a wide range of temperature; it was observed that there was no loss till $190^0$C it means that membrane are free of moisture. There are two weight loss curves between $190^0$C to $210^0$C and $450^0$C to $680^0$C. The first curve shows that membrane have some residual solvent but in the safe range. Due to addition of inorganic filler the residue of membrane has increased. It shows that the ZIF-8 particles have good interaction with the polymer blend. In the range of $450^0$C to $680^0$C there was almost 88 to 97 % weight loss has been observed due to degradation of polymers. By addition of ZIF-8 the stability of the membrane has increased. It was also observed that the residue weight of MMM was higher than pure blend. The increase of residue was suggesting an interaction of ZIF-8 with polymer.

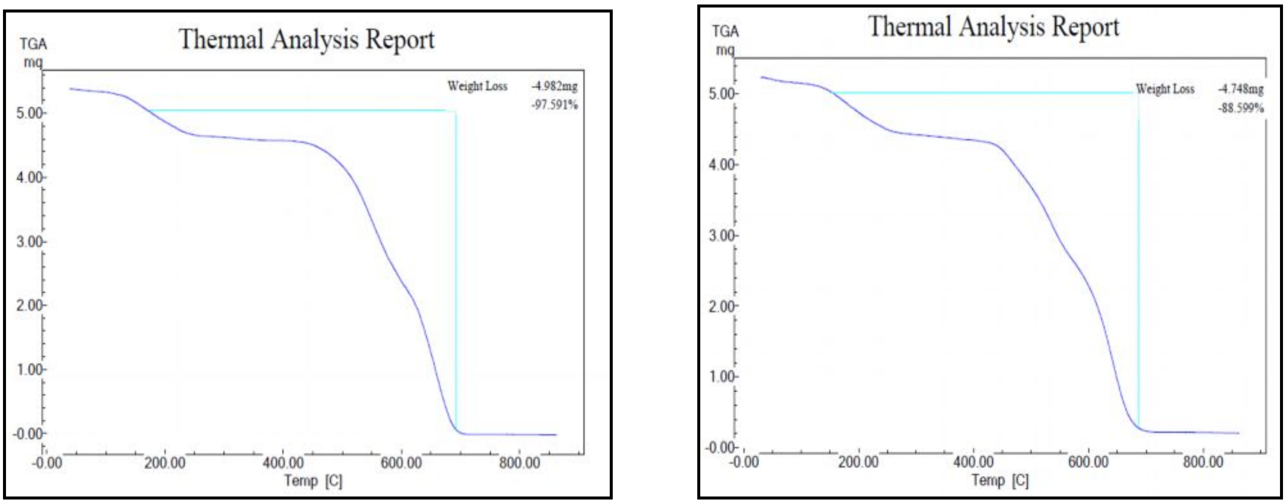
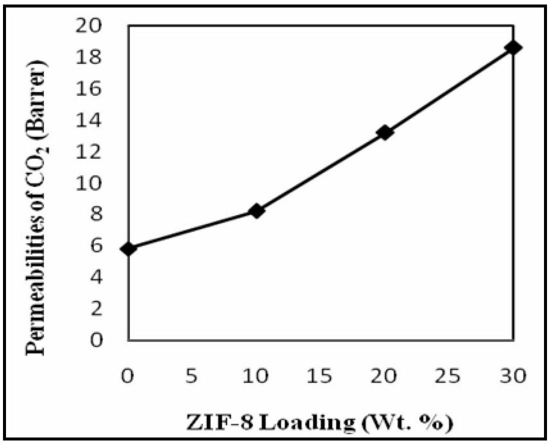



**Fig.2. TGA analysis of developed membrane a) PES/PSF MMM b) PES/PSF with 10% ZIF-8 MMM**

### 4.3. Gas separation measurement

#### 4.3.1. Effect of ZIF-8 loading

The single gas permeability's of pure PES/ PSF blend membrane and PES/PSF (80/20) with ZIF-8 for $CO_2$ and $CH_4$ presented in figure- 3 (a) and (b) and shows that, the single gas permeability of the PES/PSF blend and with ZIF-8 MMMs were increasing with increasing ZIF-8 loadings as compared to the pure PES/PSF blend membrane. Especially, with the addition of 30 w/w % and higher ZIF-8 nano-crystals, the raise in the permeability of $CO_2$ was very strong as compared to the $CH_4$. In literature, there were found similar increasing permeability trends with increasing loadings of nano-size filler materials.



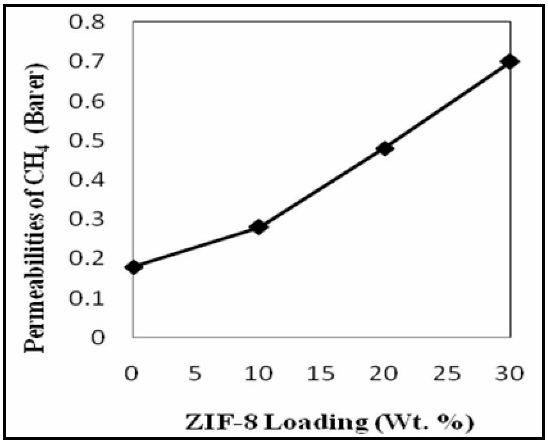




**Fig.3. Effect of ZIF-8 loading on single gas permeability's at $35^0$ C for PES/PSF and PES/PSF/ZIF-8 MMM: a) Pure $CO_2$ gas b) Pure $CH_4$ gas**

However, it was shown in the literature that, if increase the percentage of nano crystals addition, the gas permeability's starts reducing at high pressure for mixed gas. This trend was claimed as the result of reduction in the amount of polymer for gas transport, increase in the diffusion path length for the gas penetrants, and reducing free volume in the membrane due to increasing density. The rise in permeability was observed with increasing ZIF-8 loading may be due to the enhanced free volume and ZIF-8 –polymer interfaces that the gas molecules can cross through the membrane.

#### 4.3.2. Effect of ZIF-8 loading on Selectivity

The selectivity's of the PES/ PSF blend with ZIF-8 MMM for $CO_2/CH_4$ gas pair were also represented figure- 4. The incorporation of ZIF-8 nanofiller at low loadings (< 30 w/w %) improved the performance of the membranes. By the addition of 10 w/w % ZIF-8 into polymer blend, increased the permeability performance about two times for gases $CO_2$ and $CH_4$, while the ideal selectivity for $CO_2/CH_4$ gas pair showed a slight loss (~15 to 16 %). For the higher ZIF-8 loadings (≥ 30 w/w %), while the permeability's are increasing but the ideal selectivity's started to reduce rapidly but still the ideal selectivity's are improved with the addition of filler into glassy polymers blend up to 25% and 30% loadings[28].

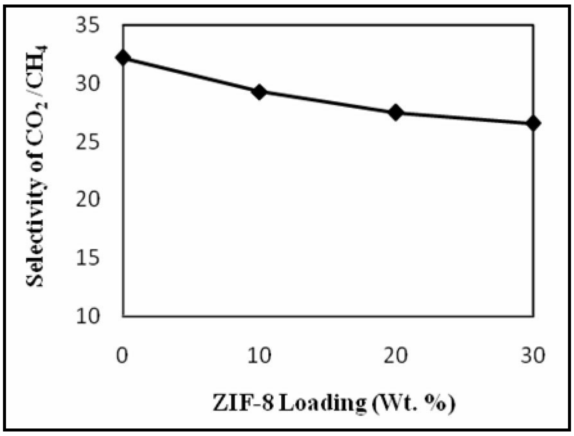



**Fig.4. Effect of ZIF-8 loading on selectivity's for $CO_2/CH_4$ for PES/PSF and PES/ PSF /ZIF-8 MMM at $35^0$ C**

### 4.4. Performance prediction by permeation models

The result of calculated relative gas permeability were compared with the experimental data with the three different existing models i.e. Maxwell, Singh and Lewis-Neilson models in different mixed matrix membrane as shown in fig 5 to 7 in terms of relative permeability (Pr) for $CO_2$ at pressure 3 bar for different values of volume fraction of ZIF-8 ($\phi_d$). it was found that at approximately 15% of loading the Maxwell and Lewis-Neilson models were found that the estimated permeability is very close to the real system and gas transport behavior through MMM's predicts accurately and then start deviating as shown in the fig 6 and 8 with overall % AARE =13.04 for Maxwell model and % AARE = 6.27 % for Lewis-Neilson models. At the same conditions and at same loading, Singh model shows little different results as approximately 20 to 22 % of loading of inorganic porous ZIF-8 the estimated permeability is very close to the real system and gas transport behavior through MMM's predicts accuratly and then start deviating as shown in the fig 7 with overall % AARE = 4.377. It is found that at lower loading of ZIF-8, the experimental relative permeability is well predicted by all evaluated models, but at higher loading of ZIF-8 that experimentally obtained relative permeability value was greater than the predicted values in all models as shown. It may be attributed to the agglomeration of ZIF-8 particles and interfaces voids formations around the ZIF-8 nano particles at higher loading. Moreover, for the models evaluated under the ideal morphology, the result showed a decrease in the absolute average relative error percentage in the following order: Maxwell model> Lewis-Neilson model> Singh model. Hence the Singh model found to be in a better agreement with the experimental data for the prediction of relative permeability of $CO_2$ in PES/PSF blend polymer mixed matrix membrane at different volume fraction of ZIF-8 at experimental conditions.

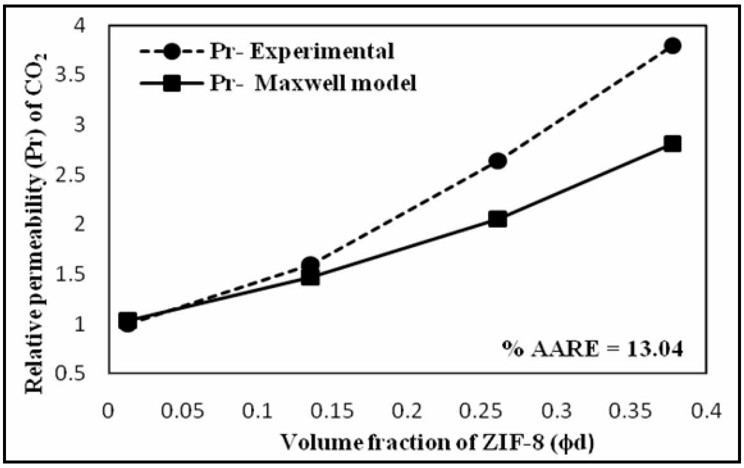



**Fig.5. Comparison of model prediction with experimental data for $CO_2$ at pressure 3 bar for different values of $\phi_d$.**

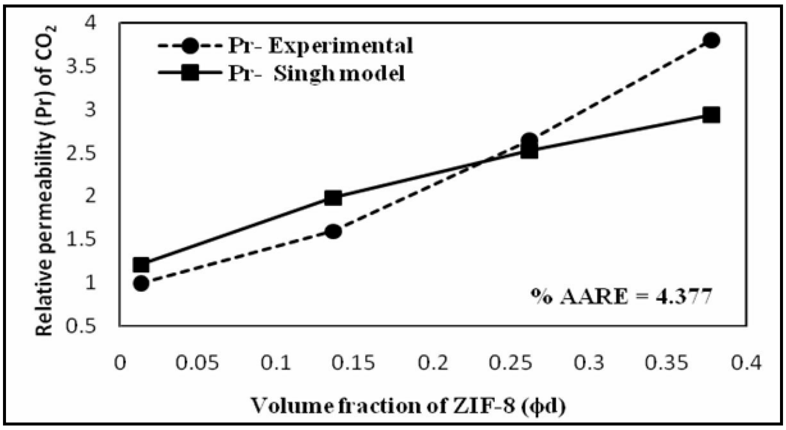



**Fig.6. Comparison of model prediction with experimental data for $CO_2$ at pressure 3 bar for different values of $\phi_d$**

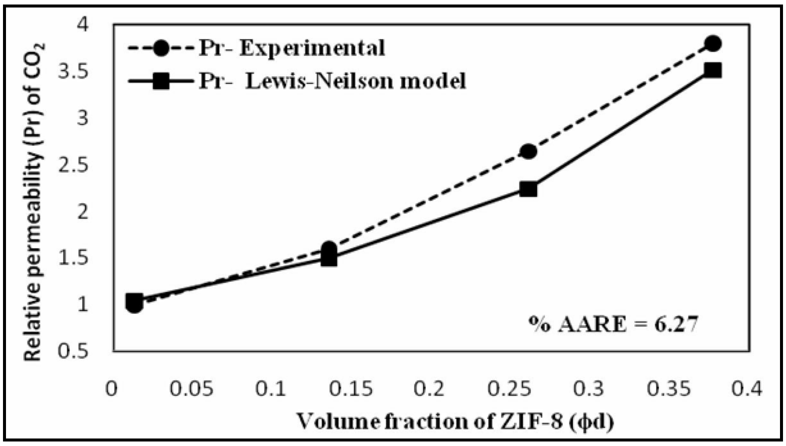



**Fig.7. Comparison of model prediction with experimental data for $CO_2$ at pressure 3 bar for different values of $\phi_d$**

## 5. Conclusion

The incorporation of synthesized ZIF-8 crystals into continuous PES/PSF blend polymer matrix resulted in high performance gas separation membranes with uniformly good dispersion of fillers at acceptable limits and high improvement of permabilities with considerable ideal selectivity. The permeability of gases increased with ZIF-8 loading, while the ideal selectivity showed a slight decrease compared to neat PES/ PSF blend membrane. The addition of 15 to 25 w/w % ZIF-8 was selected as optimum filler loading for membrane formulation considering the permeation performances at 3 bar pressure. At higher loading some agglomeration of ZIF-8 was observed.

The X -Ray Diffractometer (XRD) confirmed the phase purity of ZIF-8 and TGA analysis was confirmed that thermal stability of developed membrane. By addition of ZIF-8 the stability of the membrane has increased. It was observed that there is no loss till $190^0$C it means that membrane are free of moisture. Due to addition of inorganic filler the residue of membrane has increased. It shows that the ZIF-8 particles have good interaction with the polymer blend. In the range of $450^0$C to $680^0$C there is almost 88 to 97 % weight loss has been observed due to degradation of polymers. It is also observed that the residue weight of MMM is higher than pure blend. The increase of residue is suggesting an interaction of ZIF-8 with polymer.

The theoretical prediction showed the good agreement of experimental and calculated relative permeability at lower loading of ZIF-8, but at higher loading the AARE % value is higher. For the models evaluated under the ideal morphology, the estimated results proved a decrease in the absolute average relative error percentage in the following order: Maxwell model> Lewis-Neilson model> Singh model. Hence, Singh model was found to be in a better agreement with the experimental data for the prediction of relative permeability of $CO_2$ in PES/PSF blend polymer mixed matrix membrane at different volume fraction of ZIF-8 at experimental conditions. However continuous work should be done for the further evaluation of the theoretical models with experimental data for the relative permeability of $CO_2$ in polymer blends with ZIF-8 loading at higher pressure. Thus, the MMM prepared with moderate nano-filler loading shows that there will be great potential to be further improvement and various applications in the gas and vapor separation.

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