Optimization of ZIF-8 Filler loading in Mixed Matrix Membrane for Gas Separation by Permeation Models

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Abstract— **Performance of Mixed matrix membranes (MMM) depends upon the filler loading to improve the transport properties of polymer matrix blends for gases. The objective of this study is to optimize the effect of synthesized filler loading (ZIF-8) on the relative permeability of prepared mixed matrix membranes and validate the various theoretical models at 8 bar operating pressure.**

Membranes were prepared by using pure Polyethersulfone/Polysulfone (PES/PSF) blend and PES/PSF/Zeolitic Imidazolate Framework-8 (PES/PSF/ZIF-8) based asymmetric mixed matrix membrane at loading of ZIF-8 filler from 0 to 30% using solvent-evaporation method. The characterization spectra's FTIR and TGA of prepared membranes indicates that the blends were miscible and compatible. The effect of ZIF-8 loading on gas permeability and selectivity for prepared mixed matrix membrane for pure gas mixture (1:1 ratio of CO_2 and CH_4) were further analysed by using gas chromatography.

Comparative investigation of experimental results with theoretical for selected theoretical models for relative permeability (P_r) of CO_2 at 8 bar pressure for different values of volume fraction (ϕ_d), found in good agreement at optimum loading of 15 to 25% of ZIF-8. The overall observations and findings confirmed that, the PES/PSF blends were miscible and provide good compatibility with ZIF-8 particles at this loadings, have great potential for applications in gas and vapour separation.

Keywords— **Mixed matrix membranes (MMM), Zeolitic Imidazolate Framework-8, Permeability, Permeation models, Polymer blend.**

I. INTRODUCTION

Mixed matrix membrane consists of combination of two or more chemically different materials, the continuous phase is a matrix and the other constituent is the reinforcement, in the form of molecular sieves particles added into the matrix to improve or alter the matrix properties [1]. It has micro porous and nanoporous material adsorption and sieving properties, the process ability and flexibility of polymer, improvement in resistance to heat, corrosion and chemical degradation.

Metal-organic frameworks (MOFs) [2] and its subclass Zeolitic Imidazolate framework (ZIF-8) [3] are an promising class of nanoporous materials comprising metal centres connected by various organic linkers to create one, two and three dimensional porous structures with tuneable pore volumes, surface areas, and chemical properties. As a coordination network, MOF's are mechanically less stiff and brittle compared to zeolite. It has found many applications in membrane gas separation, in selective gas adsorption, hydrogen storage, catalysis and sensing [4].

To fabricate a MMM, material selection for matrix and sieving material are the key feature in order to have a membrane with good chemical strength and excellent separation performance. The objective of this study is to optimize the effect of synthesized filler loading (ZIF-8) on the relative permeability of prepared mixed matrix membranes and validate the various theoretical models at 8 bar operating pressure.

II. LITERATURE REVIEW

The critical literature review prevail that, the gas separation by polymeric membrane started in early of 1970, but by mixed matrix membranes [5], it has been studied extensively since 1990. Since then, MMM has undergone enormous development to achieve to its current state. In the last 20 years, this MMM technology was upgraded to very advanced stage by utilization of different inorganic molecular sieve materials used as nano fillers.

Blending between the inorganic fillers [6,7] like carbon nano tubes, zeolite, metal oxides, silica and silica nano particles, MOF, with glassy and rubbery polymers to prepare a mixed matrix or hybrid membrane [8,9,10] has been worked out successfully.

This convenient material combination for industrial gas separations, has become an important research issue in recent years was focused in this work. A number of glassy and rubbery polymers have been used to fabricate the gas separation membranes [11]. However despite of several advantages, the separation performance of polymeric membranes is limited by upper bound trade off between selectivity and permeability discovered by Robeson in 1991 [12]. Since then researchers tried to enhance the performance of membranes i.e. permeability and selectivity by different techniques including mixed matrix approach, chemical cross-linking, composite and hybrid membranes and polymer blending [13].

It was observed that, even though numerous advantages of inorganic material, membrane performance is still below the expectations, due to membrane defects, cracks, and voids, retention of surface area [7,14], uniform dispersion and processing problems [15]. Major technical barrier is the preparation of well dispersed and wetted additives at high loading. There is prime importance to study the material selection of organic and inorganic phases, and its preparation techniques [16]. The study shows that, using filler like ZIF-8 into polymer matrix would overcome several difficulties in developing MMM by providing superior dispersion in polymer matrix, high contact of polymer-filler even at lower filler loading by using separation properties of both polymer and filler [1,17].

The porous solid nano sized crystals of zeolitic imidazolate framework (ZIFs) [3] is new material consist of of imidazolate linkers and metal ions with structure similar to zeolite. It exhibit permanent porosity, high hydrothermal and chemical stability [18]. Because of their molecular sieving effect, facile synthesis and compatible with the polymers, it reveals its importance during preparation of mixed matrix membrane [4]. ZIFs-8 material is found as valued filler by reason of organic linkers exist in its structure [5] and superior interface with polymer. Moreover, ZIFs consist of huge surface area, high adsorption capacity; easy to modify and high affinity towards certain gas, gives the edge for ZIFs to be applied as filler. This material demonstrate fine chemical stability against solvents, reorientation of its structure at high pressure and high mechanical strength [5,17, 19] separation properties [6,20] and membrane performance.

Literature review was carried out on fabrication of defect free MMM by homogeneous blending [21] of inorganic particles in a polymer matrix blend, similar to the ordinary polymeric membrane by the phase inversion method [19,22, 23]. Particle size less than 100 nm and spherical shaped nanoparticles will be preferred for the best suspension in the blends and is less likely to settle during casting of the membrane. Also pre-coating of the crystal by polymers is another approach found, to promote better interaction between the polymer and MOF/ZIF particles [7,23,24]. To enhance the membrane strength and durability in the severe environment, particle loading is the other most important aspect must be taken in to consideration.

Blending of polymers [22, 25] is considered as an effective method to develop materials with attractive properties, which are not found in individual polymers [21,26]. A wide range of properties can be obtained by tuning the blend ratio. Polymer blend membranes [22] are prepared by blending glassy or rubbery polymers together. M. Rezakazemi et al. [13] have reviewed the concept and material modifications, strategies for MMM development and overview of current status and future directions. Also Han et al. [25] reported the blending of PES/PI and found increased permeability for O_2/N_2 separation. PSF/PI blend membrane studied by Basu et al. [27] in his study found improved separation performance of CO_2/CH_2 under harsh conditions of temperature and pressure. PSF/PI blend membranes studied by Rafiq et al. [28] and found better thermal stability and separation for CO_2/CH_4 mixture. Ahmad Fauzi Ismail et al. [29] has studied PI/PES polymer blending and the effect of PI/PES concentration and zeolite loading on dope solution to investigate gas separation performance and found sieve-in a-cage morphology and higher performance than neat polymeric membrane. These studies indicate that, blending of PSF and PES with different ratio has definitely improved the overall separation effect. But interestingly no study was found in literature, to the best of knowledge and critical review, for PES/PSF polymer blends and PES/ PSF polymer blends with ZIF-8 as nano filler.

Hence, in the present work, blending of PES/PSF and PES/ PSF polymer blends with ZIF-8 as nano filler was carried out, to prepare flat sheet membranes and effect of ZIF-8 loading with respect to change in pressure were studied for pure and mixed gas separation (CO_2/CH_4). The polymer- polymer interaction and thermal stability of prepared blend membranes are characterized [25, 30] by FTIR and TGA and compared with pure polymeric blend. Permeability of CO_2 and CH_4 gases in the pressure range of 3-12 bars was evaluated to find out the selectivity.

III. THEORETICAL EVALUATION AND MATHEMATICAL MODELLING

The analysis of relative permeability of CO_2 by pure blend of PES/ PSF and blend of PES/PSF with dispersed phase (ZIF-8) MMM studied by Maxwell, Modified Singh and Lewis–Nielson models [31, 32, 33] and evaluated experimental results with theoretical to validate the models and to investigate the best suitable model and it was also helpful to find the addition of optimum filler loading for membrane formulation up to pressure 12 bar. These studies evaluate that the effect of ZIF-8 loading on the performance of PES/PSF-ZIF-8 blend mixed matrix membranes for CO_2/CH_4 separation at a range of operating parameters. The solubility and permeability of gases increases with increasing pressure [34, 35].

A. Maxwell Model:

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

$$Pr = {}^{P}/_{P_m} \; ; \quad \lambda = {}^{P_d}/_{P_m} = \text{Permeability ratio} \qquad (2)$$

Pm- Permeability of polymer matrix i.e. continuous phase (PES/PSF is known from experiment); *P*- Effective permeability of species in MMM; *Pr* - Relative permeability ratio; Φ - Volume fraction of dispersed phase; P_d - Permeability of dispersed particle or filler particle. Φ_d - Volume fraction of dispersed ZIF-8 filler particle. It is assumed that, P_d will be same for all pressure range (3 -12 bars) [36].

A. Modified Singh Model

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

$$\lambda_{dm} = \frac{P_d}{P_m} \; ; \; \lambda_{dm} = \frac{P_d}{P_m} = \frac{\beta}{\gamma} \; ; \; \beta = (2+\delta^3)\lambda_{dm} - 2(1-\delta^3)\lambda_{im} \qquad (4)$$

$$\gamma = (1+2\delta^3) - (1-\delta^3)\lambda_{di} \qquad (5)$$

$$\lambda_{di} = \frac{P_d}{P_i}; \qquad (6)$$

$$\lambda_{im} = \frac{P_i}{P_m} \qquad (7)$$

B. Lewis – Neilson model

$$P_r = \frac{P}{P_m} = \left[\frac{1+2\,[\lambda_{dm}-1)/(\lambda_{dm}+2)]\phi}{1-[\lambda_{dm}-1)/(\lambda_{dm}+2)]\phi\psi}\right] \tag{8}$$

Where,

$$\psi = 1 + \left[\frac{1-\phi_m}{{\phi_m}^2}\right]\phi \tag{9}$$

The terms ϕ_m - is the maximum volume packing fraction of filler particles ; The value of ϕ_m = 0.64 for random close packing of uniform spheres

C. Absolute Average Relative error percentage

$$\%\,AARE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{(Pcal-Pexp)}{Pexp}\right| \tag{10}$$

Where, *N*- is the number of membranes.

The experimental results were compared with the theoretically calculated relative gas permeability *(P_r)* for all developed MMM are shown graphically. Permeability through micro porous material does not depend upon pressure [36]. Theoretical permeability value for pure ZIF-8 [dispersed phase (P_d) of filler] membrane at 10 bar pressure for CO_2 was considered as standard values for pure ZIF-8 [36, 37].

IV. Materials and Methods

A. Filler Selection

The gas transport properties of MMM are strongly associated to the types of polymer [11], solvent used, filler porous materials and the additives used during fabrication. Zeolitic imidazolate framework (ZIFs) is an emerging class of porous solid nano sized crystals comprised of imidazolate linkers and metal ions with structure similar to zeolite. It exhibit permanent porosity and high hydrothermal and chemical stability. ZIF-8 has a BET surface area 1300 -1600 m^2/gm [2,4,5, 8], has a high selective adsorption capacity to CO_2, which is a desirable property for development of selective membrane materials. Due to their molecular sieving effect, facile synthesis and compatible with the polymers, it reveals its importance during preparation of mixed matrix membrane [3].

B. Materials

The polymers, Polyethersulfone (PESU) and Polysulfone (PSF) were used in the fine powder form with an average molecular weight of 63,000 g/mol were supplied by Solvay Specialties India Pvt. Ltd. and it was washed and dried before being used. Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] and methanol, *N*-Methyl-2-pyrrolidone (NMP) solvent were procure from Fisher Scientific ltd. and 2-methylimidazole [$C_4H_6N_2$] was get from Sigma-Aldrich (India). All materials and solvents were utilized as it is without any further purification.

C. Membrane Preparation

Solvent-evaporation method was used for preparation of the mixed matrix membrane [20]. Two types of membrane, MO (neat), M_2 (20% ZIF-8), were fabricated by polymer blend ratio of 80/20 % PES/PSF. Asymmetric flat sheet pure PES/PSF blend membrane was prepared by step by step adding overnight dried polymers at 85^0C to 170^0C in solvent NMP by under controlled viscosity of solution and then stirred overnight by magnetic stirrer. Between each steps, the solution was ultra-sonicated for 18 to 20 min. in order to ease the dispersion and curtail the agglomeration of particles in the blend solution, then casted on glass plate at ambient condition followed by "curing" at 45 to 50°C overnight.

D. Gas Permeation

Gas permeation experimentation was carried out by designed and developed experimental set-up at predefined operating conditions for binary gas mixture (CO_2 and CH_4 with 1:1 ratio) for permeation of CO_2 and CH_4 for PES/PSF blend (80/20%) and PES/PSF/ZIF-8 blend mixed matrix membrane for 20 % filler loading at 3 to 12 bar operating pressure at 35^0C and analysed by gas chromatography to calculate the gas permeabilities and selectivity's.

V. Result and Discussion

A. Characterization of Membranes

The graphical interpretation of developed mixed matrix membranes characterization were carried out by Fourier Transform Infrared Spectroscopy (FTIR) and Thermo gravimetric analysis (TGA) and gas analysis were carried out by Gas chromatography.

B. Thermal gravimetric analyser (TGA) of membranes

Thermal gravimetric analyser (TGA) was used for the characterization of membrane for thermal stability. The TGA spectra's of blends of PES/PSF with addition of 20% ZIF-8 mixed matrix membrane are shown in figure-1. The observations and findings from the thermal analysis spectra are summarized in the table-1. Due to addition of ZIF-8 filler in the blends, the residues amount of samples was increased than the pure polymer blends. That shows the good interaction of ZIF-8 filler with the blends and enhances the thermal stability of all the membranes.

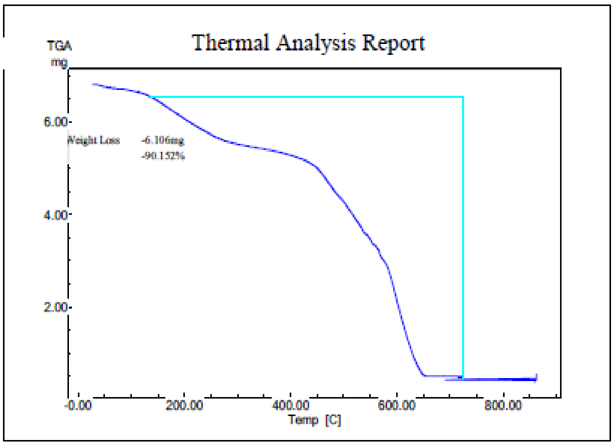

Figure 1: TGA of PES/PSF-20% ZIF-8 Membrane (M2)

TABLE I

DETAILS OF WEIGHT LOSS OF MEMBRANES DURING TGA ANALYSIS

Type of membranes	**Actual weight Loss (mg)**	**Weight loss (%)**	**Average percentage of residue remaining**	**Observed temperature ranges (^{0}C) from TGA spectra's for weight loss of membranes (observations and findings)**			
				0 to 190^{0}C	**190^{0}C to 210^{0}C**	**450^{0}C To 680^{0}C**	**680^{0}C to 850^{0}C**
PES/PSF/ ZIF-8 (20%)	6.106	90.152	Blends of polymers and 10 to 30 % addition of ZIF-8 = 7.782%	No weight loss: membranes were free of moisture and dry	First weight loss occurs: Slight residual solvent present	Second weight loss (86 to 97 %) occurs: degradation of polymers	Small quantity of residue (ZIF-8 filler) remaining

C. *Fourier Transform Infrared Spectroscopy (FTIR) of membrane*

The Fourier Transform Infrared Spectroscopy (FTIR) analysis of developed mixed matrix membranes was as investigated for the interaction between two polymers and its blends with ZIF-8 filler. The FTIR spectra's of, blend of pure PES/PSF, after addition of 20 % ZIF-8 filler were obtained by using FTIR model- Shimadzu-8400S to detect the existence of the functional groups of any other the materials. The observed ranges with respect to percentage transmittance of FTIR spectra's of the blends of PES/PSF with addition of 20 % ZIF-8 mixed matrix membrane are shown in the figure-2. The standard or prescribed and spectral observed FTIR ranges of M_2 (20% - ZIF-8) and mixed matrix membranes are shown in the table-2.

The FTIR spectra's of the prepared membranes shows the structural bonding prepared mixed matrix membranes were obtained within the prescribed ranges mentioned in table-2 and shown on the FTIR spectra's of the samples as shown in figure- 2. The results indicate that PES/PSF blend was a miscible and compatible blend. After addition of ZIF-8 compound, stretching peaks of C-C, C-H, C-O, C-N has been observed and found that, prepared blends are compatible with each other.

TABLE II

PRESCRIBED AND OBSERVED FTIR RANGES OF M_2

Compound	**Functional Group**	**Bonding**	**Prescribed Range (cm^{-1})**	**Observed Range (cm^{-1})**
M_2: PES/ PSF-20% ZIF-8	C-C	C-C (CH_3 Bending) (Stretching)	1300-800 (~1375) 1470-1430 Bending	1365.65
	C-N	C-N (Stretching)	1340-1250	1307.78
	C=C C-H	Benzene ring stretching	1650-1400	1496.81
	C=C	Benzene ring stretching, Significant & broad	1650-1400	1589.40
	S=O	S=O Symmetric Asymmetric	1375-1185 1325-1140	1261.81
	C-H	C-H group stretching	3200-2700	3093.92
	O-H	Hydrogen bonding	3700-3200	3452.70

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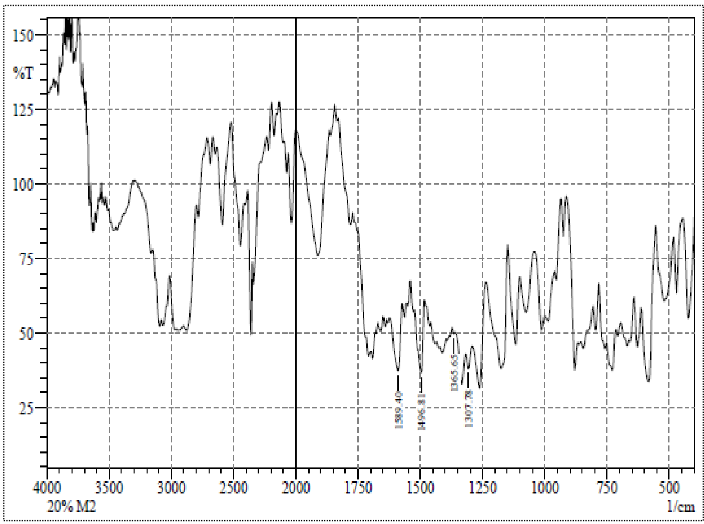

Figure 2: FTIR of pure PES/PSF/-20% ZIF-8 membrane (M_2)

D. *Effect of ZIF-8 loading and feed pressure on mixed binary gas permeation*

The experimental investigation was carried out for mixed gases and studied the effect of loading on mixed gas permeabilities and selectivity's. The figure-3 and figure-4 shows the mixed gas permeabilities of CO_2 and CH_4 of pure PES/PSF blend mixed matrix membrane as a function of pressure for 20 %ZIF- 8 loading and the figure-5 represents the selectivity's for CO_2/CH_4 gas of PES/PSF MMM as a function of feed pressure for different ZIF-8 loading at above said operating conditions.

It was observed that, by increasing the fillers percentage, the gas permeabilities begins reducing at higher pressure for mixed gases. This means that, by reduction in the amount of polymer for gas transport, increases the diffusion path length of the gas penetrant and reduces free volume in the matrix due to rising in the density as a result increasing the permeability due to ZIF-8 loading.

While, the selectivity of CO_2/CH_4 rises with addition of ZIF-8 as pressure rises, but at moderate loading of filler i.e. 20-25 %, selectivity rises very fast. The percentage addition of ZIF-8 was selected as optimum filler loading is 15 to 25 w/w % for membrane formulation considering the excellent permeation performances up to 12 bar pressure. At higher loading of filler, the slight agglomeration was observed.

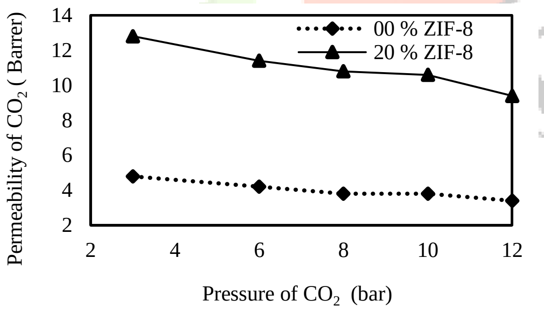

Figure 3: Mixed gas permeabilities of CO_2 of PES/PSF MMM as a function of pressure for different ZIF-8 loading at 35^0C

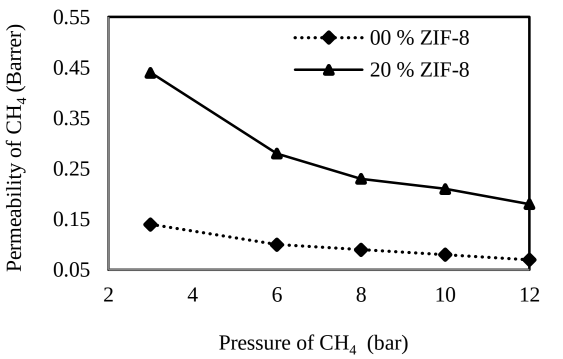

Figure 4: Mixed gas permeabilities of CH_4 of PES/PSF MMM as a function of pressure for different ZIF-8 loading at 35^0C

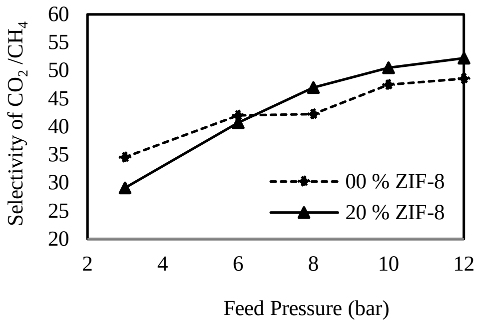

Figure 5: The selectivities for CO_2/CH_4 gas of PES/PSF MMM as a function of feed pressure for different ZIF-8 loading at 35^0C

D. *Model Validation*

By using three models expressions i.e. Maxwell, Modified Singh and Lewis-Neilson Models, all mathematical model variables (parameters) i.e. Φ_d , P_d, Pm , λ_{dm} , ψ etc. and relative permeability of CO_2 i.e. experimental (P_r expt.) and theoretical (P_r cal.) with percentage AARE were calculated all mixed matrix membranes at 8 bar pressure and summarized in the table-3. The graphical interpretation validates the experimental results with theoretically calculated results. Based on the model variables, percentage of AARE were found, that gives actual deviation from the real system. The overall comparison of the selected theoretical models for relative permeability *(Pr)* of CO_2 with experimental data at selected pressures i.e. 8 bars for different values of ϕ_d as shown in the figures- 5.

TABLE III

ESTIMATED MODEL PARAMETER FOR RELATIVE PERMEABILITY *(P_R)* OF MMM OF CO_2 AT 8 BARS

Model	**Membrane Code**	ϕ_d	P_m	$\lambda_{dm} = P_d/P_m$	$P_r = P/P_m$ (Expt.)	ψ	P_r (Cal.)	AARE (%)
Maxwell Model	M0	0.0134	3.8	7105.263	1	NA	1.0407	16.20
	M1	0.1357	6.2	4354.838	1.631		1.4706	
	M2	0.2612	10.8	2500.000	2.842		2.0589	
	M3	0.3773	15.6	1730.769	4.1052		2.8120	
Modified Singh Model	M0	0.0134	3.8	7105.263	1	NA	1.211	0.92
	M1	0.1357	6.2	4354.838	1.631		1.988	
	M2	0.2612	10.8	2500.000	2.842		2.527	
	M3	0.3773	15.6	1730.769	4.1052		2.9498	
Lewis Nelson model	M0	0.0134	3.8	7105.263	1	1.011	1.0408	9.498
	M1	0.1357	6.2	4354.838	1.631	1.119	1.5242	
	M2	0.2612	10.8	2500.000	2.842	1.229	2.2400	
	M3	0.3773	15.6	1730.769	4.1052	1.331	3.5162	

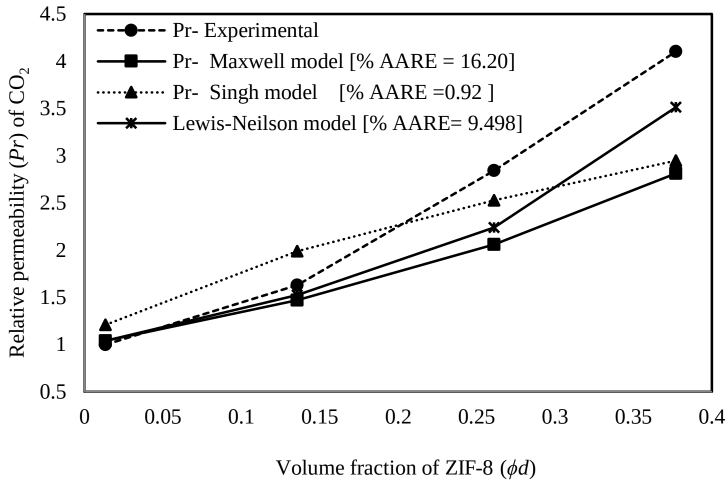

Figure 5: Comparison of experimental data with theoretical models for relative permeability *(Pr)* of CO_2 at pressure 8 bar for different values of ϕ_d

The graphical analysis demonstrate that, up to 15% of ZIF-8 addition, the Lewis-Neilson and Maxwell models were appropriate, as the estimated relative permeability was very close to the real system, but slightly lower than the experimental results up to 8 bars and slightly higher than the experimental results for 10 to 12 bar, afterwards, start deviating for Maxwell and Lewis-Neilson models and found lower than the experimental result as pressure rises.

At the same loading and operating conditions, modified Singh model demonstrate slight different results, about 20 to 22 % loading of ZIF-8, the estimated relative permeability was very close to the real system and found higher than the experimental results 8 bar pressure and then starts deviating and decreasing from the experimental results as pressure rises. The modified Singh model is to be in found good agreement with the experimental results up to 26% loading of ZIF-8 filler. The gas transport behaviour through developed mixed matrix membranes predicts that, all experimental results validated with all theoretical models at lower loading of ZIF-8 at low pressure up to 8 bars.

At higher pressure and loading of ZIF-8 i.e. more than 25 %, experimental results of relative permeability's were found greater than the predicted values for all theoretical models. It assures that, the agglomeration of ZIF-8 particles and interfaces voids formations around the ZIF-8 nano particles at higher loading at high pressure.

It was observed that, modified Singh model establish good agreement with the experimental data up to 8 bar pressure and at around 26% ZIF-8 loading and Lewis- Neilson model for higher pressure up to 12 bar at high loading of ZIF-8 up to 30 %, for the prediction of relative permeability of CO_2. The gas transport behaviour through all developed membranes predicts that, experimental results validated with all theoretical models at lower loading of ZIF-8 (15 to 25%) at low pressure up to 8 bars.

VI. CONCLUSION AND RECOMMENDATIONS

Characterization studies by TGA confirm that, by addition of ZIF-8 in to the polymer blend, the thermal and chemical stability of the mixed matrix membranes was increased. The observation from the TGA spectra, it was concluded that, the residue weight of MMM was higher than pure blend, indicating better interaction of ZIF-8 with polymer blends.

The FTIR spectra of 20 % ZIF-8 filler with PES/PSF blend membranes were obtained to detect the existence of the functional groups with bonding of the materials. The results indicate that, PES/PSF blend was a miscible and compatible blend. After addition of ZIF-8 compound, stretching peaks of C-C, C-H, C-O, C-N has been observed in the standard ranges and found that, prepared blends are compatible with each other.

The experimental result shows that, performance gas separation membranes with uniformly dispersion of fillers at acceptable limit and improvement of permabilities with considerable ideal selectivity due to incorporation of synthesized ZIF-8 crystals into PES/PSF blend polymer matrix.

The 15 to 25 w/w % range of ZIF-8 was selected as best possible filler loading for membrane formulation, considering the excellent binary gas permeation performance at low pressure up to 8 to 10 bars. At higher loading (>30%), agglomeration of ZIF-8 was observed in the membranes that increases the diffusion path length for the gas penetrant and reducing free volume in the membrane matrix due to increasing density.

The comparative study of experimental results with theoretically calculated relative gas permeability of CO_2 for developed MMMs were shown that, the modified Singh model is suitable up to 8 bar pressure and at about 26% ZIF-8 loading.

Thus, the MMM's prepared with moderate nano-filler loading showed that, there is great potential for further improvement and various applications in gas and vapour separation.

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