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EXPERIMENTAL DESIGN AND RESPONSE SURFACE MODELING OF PI/PES-ZEOLITE 4A MIXED MATRIX MEMBRANE FOR CO_2 SEPARATION

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Abstract

This paper investigates the effect of preparation of polyimide/polyethersulfone (PI/PES) blending-zeolite mixed matrix membrane through the manipulation of membrane production variables such as polymer concentration, blending composition and zeolite loading. Combination of central composite design and response surface methodology were applied to determine the main effect and interaction effects of these variables on membrane separation performance. The quadratic models between each response and the independent parameters were developed and the response surface models were tested with analysis of variance (ANOVA). In this study, PI/ (PES)–zeolite 4A mixed matrix membranes were casted using dry/wet phase inversion technique. The separation performance of mixed matrix membrane had been tested using pure gases such as CO_2 and CH_4. The results showed that zeolite loading was the most significant variable that influenced the CO_2/CH_4 selectivity among three variables and the experimental results were in good agreement with those predicted by the proposed regression models. The gas separation performance of the membrane was relatively higher as compare to polymeric membrane. Therefore, combination of central composite design and response surface methodology can be used to prepare optimal condition for mixed matrix membrane fabrication. The incorporation of 20 wt% zeolite 4A into 25 wt% of PI/PES matrix had resulted in a high separation performance of membrane material.

Keywords: Mixed matrix membrane, Response surface, Central composite design CO_2 separation.

Nomenclatures

A	Membrane affective surface area, cm^2
l	Membrane skin thickness, cm
P	Permeability
Q_i	Volumetric flow rate of gas i

Greek Symbols

$\alpha_{i/j}$	Ideal separation factor
β_{ij}	Interaction effect
β_j	Linear effect
β_{ii}	Squared effect
β_o	Offset term
Δp	Pressure difference across membrane, cmHg
δX	Step change

1. Introduction

The gas separation process by polymer membranes for natural gas processing, landfill gas recovery, air separation and hydrogen recovery have received much attention during the past several decades [1]. It is well known that the glassy polymer membranes perform well in separations of mixtures of gases such as O_2/N_2, H_2/CO, and N_2/CO_2. However, there are challenges in preparing membranes with improved anti-plasticization and desirable combination of both high selectivity and high permeability for CO_2 removal that are as competitive as other gas separation processes. Good physical and gas separation properties ensure polymers to be considered as membrane materials for gas separation. However, the investigation of polymer material such as polyimide for gas separation has been challenged by the upper bound trade-off limitation between the productivity and the selectivity [2, 3]. Meanwhile, the rigid porous materials such as carbon molecular sieves and zeolites are poor in processability and difficulty in forming defect-free membranes of practical meaning continue in spite of their superior gas separation properties. To overcome the drawbacks of both polymeric and molecular sieve materials, mixed matrix membranes have been extensively and intensively examined for gas separation during the past two decades.

The materials are fabricated by incorporating the molecular sieves into the polymer matrix. Mixed matrix membranes have been recognized as a promising alternative to the conventional membranes. Kulprathipanja et al. at UOP (Universal Oil Products) were the first group to observe that the O_2/N_2 selectivity increases from 3.0 to 4.3 when increasing silicalite content in the cellulose acetate matrix [4]. It has been generally found that when using rubbery polymers as the membrane matrix, the contact between the polymer matrix and the molecular sieve is satisfactory owing to the highly flexible polymer chain. According to Jia et al. [5], the incorporation of silicalite into silicone rubber (PDMS) membranes increased the O_2/N_2 selectivities from 2.14 to 2.92 in comparison to pure PDMS. Duval et al. [6] studied carbon molecular sieve and zeolite such as silicalite-1, 13X and KY as filler. They observed that membrane with the filler such as silicalite, 13X and KY could increase the selectivity by 13.5% to 35%, respectively. They also concluded that molecular sieves did improve the gas separation performance of mixed matrix membrane. Currently, the research focuses more on the glassy polymers [7]. Meanwhile,

the major problem of mixed matrix membranes using glassy polymers is adhesion between the polymer phase and the external surface of the particle. It seems that the weak polymer-filler interaction makes the filler tend to form voids in the interface between the polymer and filler. Therefore, the resultant membranes generally have deteriorated selectivity.

Various methods have been proposed to improve the polymer-filler contact. Kusworo et al. [8] reported that the shear rate affected the separation performance of zeolite mixed matrix membrane. Duval et al. [6] proposed fabrication of mixed matrix membrane at above glass transition temperature, while Ismail et al. [9] investigated the effect of silane agent to reduce interface`defects between zeolite and polyethersulfone to enhance the separation performance of zeolite-PES mixed matrix membrane. In another papers, Ismail et al. [10] was also studied the effect of thermal annealing to increase the O_2/N_2 selectivity using PI/PES-zeolite mixed matrix membrane. In the current reaseach, thermal annealing was subjected into PI/PES-zeolite mixed matrix membrane to increase CO_2/CH_4 selectivity. In this research was also investigated the best processes parameters in the production of PI/PES blending-zeolite mixed matrix membrane using full factorial design and central composite design. The other researchers have suggested selection criteria for materials and preparation protocols in order to meet the transport characteristics necessary to form high separation performance of mixed matrix membrane [11]. By incorporating carbon molecular sieve (CMS) into commercial glassy polymers, Ultem and Matrimide 5218, Vu et al. [12] reported that mixed matrix membranes with these CMS particles showed enhancement by up to 40-45% in CO_2/CH_4 selectivity over the intrinsic selectivity of the pure Ultem and Matrimide polymer. The separation performance of the mixed matrix membrane was improved due to application of polymer coating on molecular sieve for removing the interface defects. Pechar et al. [13] applied zeolite L as molecular sieve into polyimide matrix. The carboxylic acid group was used to facilitate the adhesion of zeolite surface to the polymer matrix to reduce the delamination of the polymer from the zeolite.

Experimental designs are commonly performed in the study of empirical relationship, in terms of a mathematical model, between one or more measured responses and a number of variables or factors [14]. Experimental design and mathematical modelling techniques are mathematical tools normally used to optimize a process. Traditional methods of optimization involved changing one independent variable while fixing the others at a certain level. Experiment design techniques were developed to allow the gathering of maximum process information with reduced number of experiments. Experimental design techniques usually depend on empirical model structure in order to interpret experimental data and provide optimum process conditions. In general, response surface methodology (RSM) allows an empirical model to be built from data collected from a minimal set of systematically designed experiments. The RSM integrates mathematical and statistical techniques and was essentially developed from numerical method [15]. The RSM is initiated with an experimental design commonly called design of experiment (DOE) to screen model parameters before going to the optimization process [16]. Statistical technique has been successfully applied in the field of quality experimental work [17, 18].

Ismail and Lai [17] studied the main effect and interaction effects on the membrane fabrication using response surface methodology. In their work, they use full factorial experimental design in order to obtain the main effects on the

membrane performance. Ismail and Lai also concluded that the polymer concentration, solvent ratio and shear rate were among the dominant factors on the membrane fabrication for obtaining high performance membrane. The effects of composition of the aqueous phased used on the interfacial polymerization of thin film composite were studied by Idris et al. [18]. They used response surface methodology and central composite design to develop mathematical model and to optimize the aqueous solution in the thin film fabrication. These studies demonstrate that combination of central composite design and response surface methodology was succesfully used for modeling some operating parameters in the fabrication of thin film composite. Therefore, in this paper was to develop an alternative preparation of mixed matrix membrane using polyimide and polyethersulfone blends for CO_2/CH_4 separation with different loading of zeolite as inorganic filler. The effects of preparation conditions such as polymer blending composition and polymer concentration on the dope solution were also investigated.

This paper was also studied the optimal process parameters in fabrication of symmetric flat sheet mixed matrix membrane (MMM) using statistical methods. Full factorial design was applied in planning the experiment to determine the effect of the process variables in the fabrication of mixed matrix membrane and to evaluate the gas separation performance. The response surface methodology and central composite design were used in optimization experiments and iterative regression analysis to determine the maximum gas selectivity.

2. Materials and Methods

Polyimide (Matrimide 5218) resin was supplied by Alfa Aesar Johnson Mattew Mexico and polyethersulfone by Solvay Advanced Material (USA). The polymers were dried in a vacuum oven at 120^{o}C overnight before dope preparation; N-methyl-pyrrolidinone (NMP) from Merck was used as the solvent due to its low toxicity. The inorganic filler molecular sieve involved was zeolite 4A from Aldrich and the particle size was 1 µm. In order to remove the adsorbed water vapour or other organic vapors, all zeolite particles were dehydrated at 300^{o}C for 3 hours before use. The chemical structure of the polyimide and polyethersulfone are shown in Fig. 1.

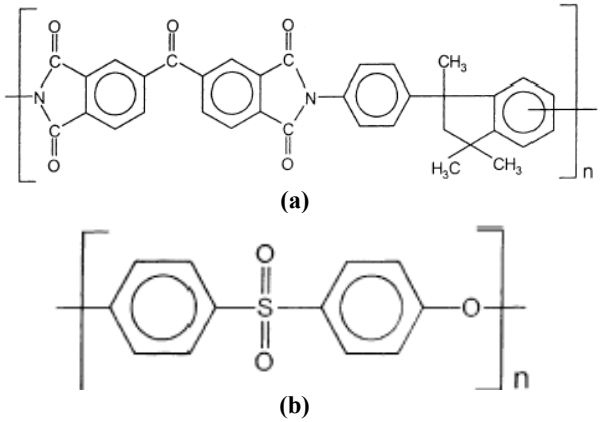

Fig. 1. Chemical structure of (a) Polyimide and (b) Polyethersulfone.

In this study, the polymer solution was consisted of 20-30 wt% polymer (blend PI/PES, 20-30/80-70), and 75% NMP + 15-30 wt% zeolite loading in total solid. Mixed matrix dopes are prepared as two parts: a sieve suspension and a polymer solution which are then mixed together. The sieve suspension is typically of low viscosity, whereas the polymer solution is concentrated and highly viscous. This is necessary to produce casting dope in approximately 20 wt%-25 wt% total solids. The homogeneous polyimide and polyethersulfone were prepared according to the following procedure; the inorganic molecular sieve particles were dispersed into the solvent and stirred for 24 hours then followed by the addition of a desired amount of polyimide. The solution was agitated with a stirrer at least 24 hours to ensure complete dissolution of the polymer. Next, a desired amount of polyethersulfone was added to this homogenous solution. This solution was further agitated by stirring at high speed for at least 2 days to form homogenous solution and at 60^{o}C. Once the casting dope was ready, the film was casted using pneumatically controlled casting machine. After a homogeneous solution was obtained, the solution underwent degassing procedures to remove gas bubbles by vacuuming the solution for 20 minutes. The solution was poured onto a clear, flat and smooth glass plate placed on a trolley. Stainless steel support casting knife was used to spread the solution to a uniform thickness by using a pneumatic casting machine. Mixed matrix membranes after the air drying were dried in an oven at 280^{o}C for 20 min. After the treatment the membranes were cooled down slowly to room temperature. The treated membrane after being subjected to heat treatment methods were tested using permeation test system. The permeation test involved the use of gas permeation cell in which the membrane was placed on a sintered metal plate and pressurized at the feed side. Gas permeation rates were measured by a constant pressure system using a soap bubble flow meter. Figure 2 illustrates the gas permeation cell set up.

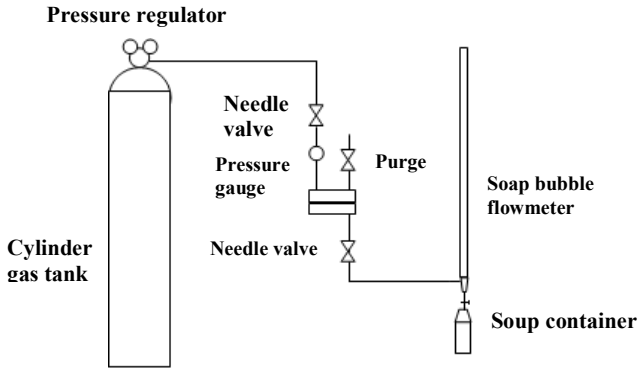

Fig. 2. Flat sheet membrane gas permeation measurement set up.

The permeability can be calculated using the following equation:

$$P = \frac{Q_i l}{\Delta p A} \tag{1}$$

where Q_i is the volumetric flow rate of gas "*i*" at standard temperature and pressure (cm^3), Δp is the transmembrane pressure difference (cmHg), l is the

membrane thickness (cm) and A is the effective membrane area (cm^2). Permeability is expressed in barrers (10^{10} cm^3 (STP) cm/ s cmHg cm^2). The ideal separation factor for gas *i* to gas *j* is defined by:

$$\alpha_{i/j} = \frac{(P)_i}{(P)_j} \tag{2}$$

The fabrication parameters were optimized using a technique called the response surface methodology [16]. A central composite design and full factorial design were employed in this regard. Three independent experimental variables, namely, total solid content (X_1), polymer blend composition (X_2) and zeolite loading in the total solid (X_3) were selected as controlled factors. The lower, upper, and centre point of the design were coded as -1, 1, 0 and α, where + 1 denotes high level, -1 low level, α = 2 k (k = number of variables or factors) is the star point, and 0 corresponds to the centre point. The star points were added to the design to provide curvature estimation for the model. Based on the type of experimental design used, 16 experiments were needed.

According to this design, the total number of treatment combinations is 2k + 2k + no, where 'k' is the number of independent variables and no is the number of experiments repeated at the centre point. The experimental plan and levels of independent variables are shown in Table 1. For statistical calculation, the variables Xi have been coded as xi according to Eq. (3):

$$xi = (Xi - Xo)/\delta X \tag{3}$$

where xi is the dimensionless coded value of the i^{th} variable, *Xi* is the natural value of the i^{th} variable, *Xo* is the value of the *Xi* at the center point, and δX is the step change, respectively.

Table 1. Factorial central composite experimental design for fabrication of flat sheet mixed matrix membrane.

Run	Coded Variables		
	Total solid, wt%	Polyimide content, wt%	Zeolite Loading, wt%
1	22.5	20	15
2	22.5	20	25
3	22.5	30	15
4	22.5	30	25
5	27.5	20	15
6	27.5	20	25
7	27.5	30	15
8	27.5	30	25
9	25	25	20
10	20.6	25	20
11	29.41	25	20
12	25	16.18	20
13	25	33.82	20
14	25	25	11.18
15	25	25	28.82
16	25	25	20

Response surface methodology was applied to the permeability and selectivity data using the commercial Statistica Stat Software version 6. The statistical experiment design provides second order polynomial equation for the

prediction of the effects of experimental variables and their interactions on the response variables. Each response Y can be represented by a quadratic model of the response surface, here with three independent variables as shown in Eq.(4)

$$Y_i = \beta_o + \sum_{j=1}^{3} \beta_j x_j + \sum_{i<j} \beta_{ij} x_i x_j + \sum_{j=1}^{3} \beta_{jj} x_j^2 \quad (4)$$

where Y_i is the predicted response (permeability of CO_2 and CH_4 or selectivity of CO_2/CH_4), β_o the offset term, β_j the linear effect, β_{ij} the interaction effect, β_{jj} the squared effect. In this study, the CO_2 and CH_4 permeability and the selectivity of CO_2/CH_4 were obtained as the responses of the experiment. Response contour and surface plots, analysis of variance and standard deviation were generated with Statistica Stat Software version 6. The statistical analysis of the model was performed in the form of analysis of variance (ANOVA). This analysis included the Fisher's F-test (overall model significance), its associated probability p(F), correlation coefficient R, and determination coefficient R^2 which measure the goodness of the fitted regression model. It also includes the student's *t-value* for the estimated coefficients and the associated probabilities p(t). For each variable, the quadratic models were represented as contour plots (2D) and surface plots (3D).

3. Results and Discussion

3.1. Optimization of PI/PES-zeolite mixed matrix membrane fabrication using response surface methodology

In this study, full factorial design (FFD) and central composite design (CCD) were systematically performed to investigate the main factor of fabrication parameters and the relationship with the mixed matrix membrane performance. A response surface methodology and central composite design were used in optimization experiments and iterative regression analysis to determine the maximum gas permeability and selectivity. Hence, the dominating factors that were likely to be the most important and influential could be diagnosed in order to optimise flat sheet mixed matrix membrane formation process. A complete full factorial design with central composite design for experimental data of this study was conducted by using Statsoft Statistica version 6. The effects and interactions of total solid/polymer concentration (X_1), composition of polymer blending (X_2) and zeolite content (X_3) on carbon dioxide permeability and CO_2/CH_4 selectivity for PI/PES-zeolite mixed matrix membranes were investigated. The experimental value and predicted responses for 16 trials runs carried out are presented in Table 2. The coefficients of the model developed for the three responses were estimated with multiple regression analysis on the experimental data. The following second order polynomial equations, Eqs. 5 and 6, provided the predicted responses for carbon dioxide permeability and CO_2/CH_4 selectivity, respectively.

$$Y_{CO2} = 7.887 + 0.203\ X_1 + 0.195\ X_2 - 1.308\ X_3 - 2.135\ X_1^2 - 1.031\ X_2^2 - 1.31\ X_3^2 - 0.233\ X_1X_2 - 0.493\ X_1X_3 - 0.723\ X_2X_3. \quad (5)$$

$$Y_{CO2/CH4} = 46.088 + 3.282\ X_1 + 4.289\ X_2 - 5.337\ X_3 - 9.264\ X_1^2 - 8.09\ X_2^2 - 9.913\ X_3^2 - 5.732\ X_1X_2 + 0.077\ X_1X_3 - 1.182\ X_2X_3. \quad (6)$$

The quality of the models can be judged from their coefficients of correlation, R and R^2. The R value for the CO_2 permeabilities and the CO_2/CH_4 selectivities are 0.97 and 0.96, respectively, indicating a fairly good agreement between the

experimental and predicted values from the models. From Tables 3 and 4, the values of R^2 for the CO_2 permeabilities and CO_2/CH_4 selectivities are 0.93, and 0.96, respectively implying 93%, and 96% of the total variation in the two responses are attributed to the experimental variables. The adequacy of each model was further checked with the analysis of variance (ANOVA) [15, 16] as shown in Tables 3 and 4. In ANOVA, the sum of squares of the total variation of each response is broken down into two components, i.e., regression and residual. The F-value for the regression is defined as MSreg/MSres, where MSreg is the mean square of regression, obtained by dividing the sum of squares of regression by the degree of freedom. MSres is the mean square of residual. The test of significance of the fitted regression model is based on the following hypothesis:

(i) Null hypothesis (H_0): all of the β_j (excluding β_0) is zero

(ii) Alternative hypothesis (H_A): at least one of the β_j (excluding β_0) is not zero

The null hypothesis (H_0) is true if the F-value < F table ($F_{p-1, N-p, \alpha}$), which means that alternative hypothesis (H_A) is rejected. Here p-1 denotes level significance, while N-p, α expresses degrees of freedom with respect to regression and residual error, respectively. On the contrary, if the F-value > F Table ($F_{p-1, N-p, \alpha}$) the null hypothesis is rejected and the alternative hypothesis is true.

Table 2. Factorial central composite design three variables with the observed responses and predicted values.

Run	Y_o CO_2/CH_4	Y_p CO_2/CH_4	% Errors
1	30.16	27.92	7,43
2	24.32	23.68	2,63
3	37.84	39.12	3,38
4	33.56	32.52	3,10
5	38.18	36.86	3,46
6	36.42	32.78	9,99
7	38.32	36.60	4,49
8	30.27	30.15	0,40
9	46.12	46.09	0,07
10	28.45	28.78	1,16
11	31.87	34.57	8,47
12	26.43	29.72	12,45
13	37.54	37.29	0,67
14	34.26	35.37	3,24
15	24.04	25.96	7,99
16	45.72	46.09	0,81

$YpCO_2/CH_4$ = Predicted CO_2/CH_4 selectivity
Yo CO_2/CH_4 = Observed CO_2/CH_4 selectivity

In general, the calculated F value should be several times greater than the tabulated value for a good model. If the value of F is greater than the tabulated F $F_{(p-1, N-p, \alpha)}$, then the null hypothesis is rejected at the α level of significance and implies that the variation accounted by the model is significantly greater than the unexplained variation. The results in Tables 3 and 4 indicate that F values for CO_2 permeability, and CO_2/CH_4 selectivity which are 9.79 and 8.33, respectively. These values are greater than the tabulated $F_{(p-1, N-p, \alpha),}$, value of 3.37. Therefore, the null hypothesis is rejected, and the Fisher F test demonstrates a 95% confidence level (α= 0.05). Consequently, the three models developed are correct and adequate. The

F-value shows a statistically significant regression at 5% level of significance (95% confidence level). In this case, the null hypothesis (H_0) is rejected at 5% level of significance based on the marked F-value [13, 14] implies that at least one of the independent variables contributes significantly to the model.

Table 3. ANOVA for the CO_2 permeability.

Source	Sum of squares	Degree of freedom	Mean square	F_{Value}	$F_{0.05\ Value}$ (Table)	R^2
SS regression	20.27	9.00	2.25	9.8	3.37	0.94
S.S. error	1.38	6.00	0.23			
S.S. total	21.65					

Table 4. ANOVA for the CO_2/CH_4 selectivity.

Source	Sum of squares	Degree of freedom	Mean square	F_{Value}	$F_{0.05\ Value}$ (Table)	R^2
SS regression	618.46	9.00	68.72	8.33	3.37	0.93
S.S. error	49.52	6.00	8.25			
S.S. total	667.97					

3.2. Significance of regression coefficients

The results are shown in Table 5 exhibit multiple regression results and the significance of the regression coefficient of the CO_2/CH_4 selectivity model. The significance of the regression coefficient was determined using the student's t tests [13, 14]. In this table, the coefficients with one factor represent the effect of that particular factor, while the coefficients with two factors and those with second-order terms represent the interaction between the two factors and quadratic effect, respectively. A positive sign in front of the terms indicates synergistic effect, while a negative sign indicates antagonistic effect. The *t*-test and p-value is used as a tool to check the significance of each of the coefficients [13]. The p-value is defined as the smallest level of significance that would reject the null hypothesis, H_0. The smaller the magnitude of the *p*-value the more significant is the corresponding coefficient and contributes largely towards the response variable. While, the larger the *t*-test value, the more significant is the corresponding coefficient and consequently, the greater is the distribution of the corresponding model term towards the response variable. From Table 5, it can be seen that the linear term of polymer blending and total solid gave the most significant effect to determine the optimum CO_2/CH_4 selectivity with p-value = 0.030 and 0.074, respectively. Moreover, the zeolite content had significant negative effect with p-value of 0.012. The effect of quadratic of total solid, polymer blending and zeolite content are also significant with *p*-values of 0.00196, 0.00389 and 0.0014, respectively. One interesting factor is the effect of interaction between X_1 and X_2 is considerably important (p-value = 0.0302). The combination of polymer concentration and composition of polymer blending can be used to control the viscosity of the dope solution for fabrication of mixed matrix membrane. Due to the viscous solution, the adhesion between polymer and zeolite can be improved. The improvement of the adherence between polymer and zeolite would produce mixed matrix membrane with high performance in terms of selectivity.

From statistical model, the optimum point for maximum CO_2/CH_4 selectivity is 46.56, respectively. The maximum selectivities can be achieved at the condition of total solid, polymer blending and zeolite content of 25.24, 27.49 and 18.26, respectively. Additional experiments at the optimized reaction

condition were performed to validate the modelling results. As shown in Table 6, the experimental value is 44.67 for CO_2/CH_4, respectively. The percent errors between the experimental and predicted result is 4.05% for CO_2/CH_4 selectivity, respectively. The differences between the experimental and predicted are within the acceptable limit. From these results, it can be verified that the statistical model is a useful tool for giving an accurate prediction of the process. The approach of coupling the response surface methodology (RSM) with central composite design (CCD) is useful for predicting the experimental conditions which would give the optimum CO_2/CH_4 selectivity for fabricated mixed matrix membranes.

Table 5. Multiple regression result and significance of regression coefficient for the CO_2/CH_4 selectivity.

Parameter	Term	Coefficient	*t*-value	*p*-value
βo		46.08857	22.71449	0.000000
β_1	X_1	3.28251	2.15457	0.074634
β_2	X_2	4.28993	2.81582	0.030521
β_3	X_3	-5.33762	-3.50350	0.012772
β_{12}	$X_1 X_2$	-5.73250	-2.82202	0.030274
β_{13}	$X_1 X_3$	0.07750	0.03815	0.970804
β_{23}	$X_2 X_3$	-1.18250	-0.58213	0.581680
β_{11}	X_1^2	-9.26451	-5.20961	0.001996
β_{22}	X_2^2	-8.09129	-4.54989	0.003892
β_{33}	X_3^2	-9.91379	-5.57471	0.001413
R^2	0.86			
R	0.93			

Table 6. Comparison of response between predicted and observed optimize values.

	Total solid, wt%	Polyimide content, wt%	Zeolite content, wt%	Predicted Value	Observed Value	Predicted Error (%)
CO_2/CH_4 selectivity	25.24	27.49	18.26	46.56	44.67	4.05

3.3. Optimization by analysing the response surface contour plots

In order to facilitate a straightforward examination of the effect of the experimental variables on the responses, three dimensional response surface and their corresponding contour plot were constructed using the model. The contours were plotted in the x-y plane. Each contour curve represents an infinite number of responses of two test variables. The maximum predicted permeability and selectivity are indicated by the surface confined in the smallest ellipse in the contour diagram [13, 14].

3.3.1. Effect of total solid and polymer blending

The total solid and polymer blending composition were studied for the range of 20-30 wt% and 20-36 wt%, respectively. The response surface for CO_2/CH_4 selectivity in Figs. 3 and 4 is a part of a parabolic cylinder, which shows

a maximum ridge in the experimental domain. By analysing the contour plot in Fig. 4, the optimal CO_2/CH_4 above 46.09 could be obtained between 24-25 wt% of total solid and polymer blending composition = 20 to 25 wt%.

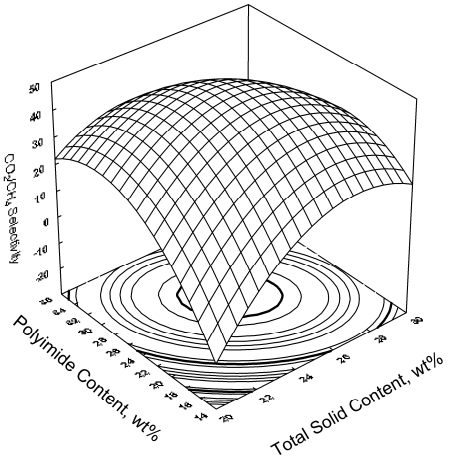

Fig. 3. The surface and contour plot of the effect of total solid content and polymer blending composition on CO_2/CH_4 selectivity at constant level of zeolite loading = 20 wt%.

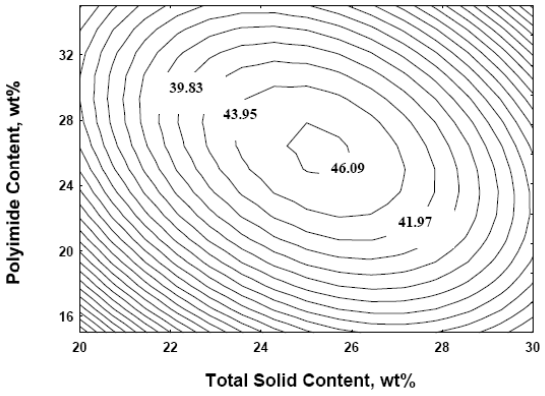

Fig. 4. The contour plot of the effect of total solid content and polymer blending composition on CO_2/CH_4 selectivity at constant level of zeolite loading = 20 wt%.

3.3.2. Effect of total solid and zeolite content

The effects of total solid and zeolite content with constant level polymer blending composition on CO_2/CH_4 selectivity can be seen in Figs. 5 and 6, respectively. Effects of total solid and zeolite content on CO_2/CH_4 selectivity is significant. The CO_2/CH_4 selectivity is increasing within increase of the zeolite addition. Currently, the main problem on the application of mixed matrix membrane for gas separation is its lower selectivity compared to the neat polymeric membrane. The low selectivity in the mixed matrix membrane is caused by the formation of unselective voids in the

membrane; hence, the gas transport is controlled by Knudsen diffusion. The unselective voids are formed due to the weak interaction of inorganic filler such as zeolite with polyimide/polyethersulfone as polymer matrix. Moreover, the determination of suitable zeolite loading is an important factor for successful fabrication of mixed matrix membrane. Therefore, combination of response surface methodology and central composite design can be used to determine the optimum ranges of parameters in the fabrication of mixed matrix membrane to achieve the maximum gas separation performance. The optimum responses values can be clearly observed from the contour plot (Fig. 6) by analysing and tabulating in Table 7.

Table 7. Results obtained from the effect of total solid and zeolite loading at constant polymer blending composition = 25 wt%.

	Total solid, wt%	Zeolite content, wt%	Predicted Value
CO_2/CH_4 selectivity	25	25	46.09

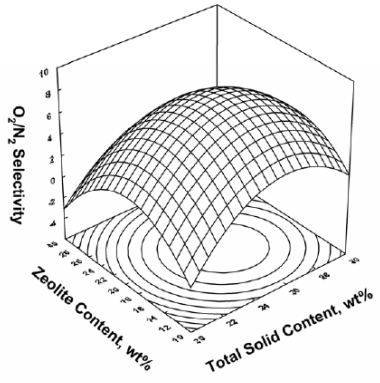

Fig. 5. The surface and contour plot of the effect of total solid content and zeolite content on O_2/N_2 selectivity at constant level of polymer blending composition = 25 wt%.

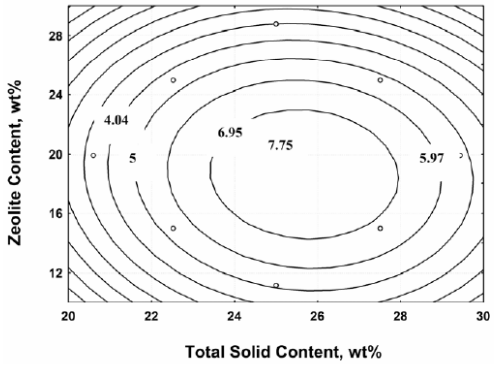

Fig. 6. The contour plot of the effect of total solid content and zeolite content on O_2/N_2 selectivity at constant level of polymer blending composition = 25 wt%.

3.3.3. Effect of polymer blending composition and zeolite content

The effects of polymer blending composition and zeolite loading on CO_2/CH_4 selectivity of mixed matrix membranes can be seen in Figs. 7 and 8, respectively. Again, from contour analysis, the effect of zeolite content on gas separation performance of mixed matrix membrane in terms of CO_2/CH_4 selectivity is significant. Compared to polymer blending composite, increasing zeolite loading in the mixed matrix membrane gave significant effect on the performance of mixed matrix membrane.

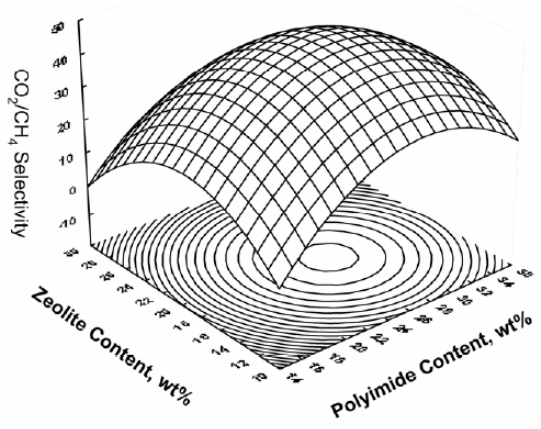

Fig. 7. The surface and contour plot of the effect of polymer blending composition and zeolite content on CO_2/CH_4 selectivity at constant level of total solid content = 25 wt%.

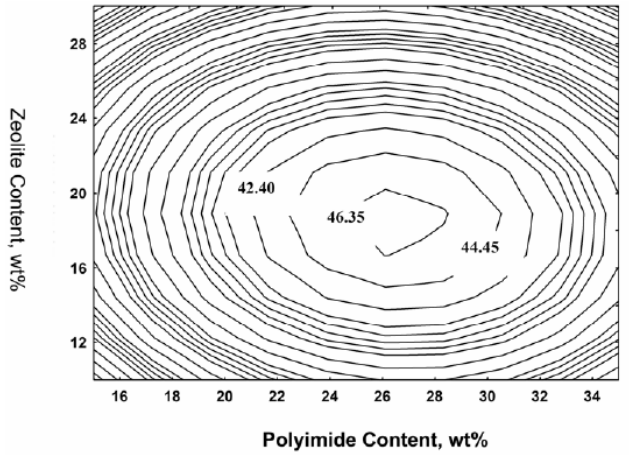

Fig. 8. The contour plot of the effect of polymer blending composition and zeolite content on CO_2/CH_4 selectivity at constant level of total solid content = 25 wt%.

4. Conclusion

This study confirmed that the PI/PES-zeolite 4A with 20 wt% zeolite loading together with the 25 wt% polymer concentration showed the best performance in terms of gas permeability and selectivity for CO_2/CH_4 gas. The response surface methodology (RSM) and central composite experimental design were applied in fabrication of PI/PES-zeolite 4A mixed matrix membranes in order to study the effects of the different parameters involved in membrane fabrication with high permeate flux and selectivity. The main effects and interactions effect for mixed matrix fabrication was successfully developed using response surface methodology. In general, the most significant variables were zeolite content in the total solid followed by composition of polymer blending and polymer concentration. The percent errors between the experimental and predicted using model from response surface methodology result is 4.05% for CO_2/CH_4 selectivity, respectively. The differences between the experimental and predicted are within the acceptable limit. Therefore, the response surface methodology (RSM) with central composite design (CCD) is useful tool for predicting the experimental conditions in the fabrication of mixed matrix membrane.

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