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Optimizing CO_2/CH_4 Separation Performance of Modified Thin Film Composite Pebax MH 1657 Membrane Using a Statistical Experimental Design Technique

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ABSTRACT

In this research, statistically based experimental design (central composite design, CCD) was applied to analyze and optimize the effect of PEG-ran-PPG (10-50 wt%) as a blending polymer and CuBTC (0-20 wt%) which is a metal organic framework (MOF) as a nano filler on the CO_2 permeance and CO_2/CH_4 ideal selectivity of Pebax MH 1657/ polysulfone thin film composite membrane. In fact, the beneficial properties of polymer blending and mixed matrix membranes (MMMs) have been combined. Based on the regression coefficients of the obtained models, the CO_2 permeance was notably influenced by PEG-ran-PPG mass content, while the mass content of CuBTC has the most significant effect on the CO_2/CH4 ideal selectivity. Experimental and statistical results showed that under the optimum conditions (PEG-ran-PPG: 32.76 wt% and CuBTC: 20 wt%), nearly 620% increase in the CO_2 permeance and 43% enhancement in the CO_2/CH_4 ideal selectivity was observed compared to the neat Pebax membranes.

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1. Introduction

The increase in the atmospheric concentration of greenhouse gases, such as carbon dioxide, is the main cause of the current global warming trend which is one of the most serious problems in the world [1]. Among different technologies for CO_2 (the major greenhouse gas) removal which is found in flue and natural gas stream, membrane technology can be one of the promising ways to solve serious global problems due to its flexible, energy efficient, economical and environmentally friendly characteristics [2,3] The chemical and mechanical characteristics of polymeric membranes have made them as attractive materials for gas separation due to their flexibility, environmentally friendly, cost and energy effective characteristics, as well as high permeation and selectivity with easy processability [4].

In this research, two techniques were applied to modify the CO_2 separation properties of the selective layer of Pebax MH 1657/Polysulfone polymeric membranes. CuBTC or MOF-199, which has a three-dimensional network with the main channels being 0.9 nm in diameter surrounded by tetrahedral pockets [5], was used as filler to have the beneficial properties of mixed matrix membranes (MMMs). Also, poly (ethylene glycol)-ran-poly (propylene glycol) (PEG-ran-PPG) copolymer, which combines the benefits of PEG (high selectivity) with those of PPG (high permeability, amorphous), can be an out-standing additive to Pebax. Therefore, in the present work, CuBTC (0-20 wt%) and PEG-ran-PPG (0-50 wt%) were added to the top layer of Pebax MH 1657/polysulfone composite membrane. Central composite design (CCD) (a statistical experimental design technique) was employed to investigate the influence of CuBTC and PEG-ran-PPG mass contents on CO_2 permeance and CO_2/CH_4 selectivity of composite membranes. By obtaining a model, the optimum mass contents were determined in order to maximize both the CO_2 permeance and CO_2/CH_4 selectivity at the same time.

2. Gas Pernation Measurements

The single gas permeation test of the prepared composite membranes was done for CO_2 and CH_4 gasses using a constant pressure apparatus at 30°C temperature with feed pressure of 3 bar. The gas permeance values in GPU (10^{-6} cm^3 (STP)/cm^2 s cmHg) and the ideal selectivity were calculated as:

$$Permeance = \frac{P}{l} = \frac{Q}{A(p_2 - p_1)} \quad (1)$$

$$\alpha_{CO_2/CH_4} = \frac{Permeance\ CO_2}{Permeance\ CH_4} \quad (2)$$

where P is permeability, Q is the volumetric permeate gas flow rate (cm^3 (STP)/s), l is selective layer thickness (cm), A the effective membrane area (cm^2) for gas permeation, p_1 and p_2 are the feed and permeate side pressures (cmHg), respectively. Each gas permeation value represents an average of 2 replicates.

3. Experimental Design

Central composite design (CCD), which is the most popular response surface method (RSM), was used to design the experiment. 5 central points, 4 axial points and $2^2 = 4$ full factorial points, was employed for the two variables (Table 1). To set specific values for the upper and lower levels, the central composite inscribed (CCI) type was applied (α=0.7071). The Design Expert software (version 6.0.10, Stat-Ease, Inc., Minneapolis, USA) was used for analysis of the obtained data. To predict the optimal point, results of the experimental design were fitted with a quadratic polynomial equation, explained as follows:

$$Y= a_0+ a_1X_1+ a_2X_2+ a_{11}X_1^2 + a_{22}X_2^2 + a_{12}X_1X_2 \quad (3)$$

The response functions (Y) represents CO_2 permeance and CO_2/CH_4 ideal selectivity. The coefficients of the polynomial were represented by a_0 (constant term), a_1 and a_2 (linear effects), a_{11} and a_{22} (quadratic effects), and a_{12} (interaction effects), which the significance of the each coefficient in the above model was selected or rejected based on the p-value. The terms that statistically found non-significant ($p>0.05$) were removed from the initial model. Some additional permeation tests were conducted to verify the validity of the statistical experimental design.

For statistical calculations, the relation between the coded values and actual values are described by Eq. (4), where X_i is the coded value of the variable, X_i is the actual value of the variable, X_0 is the actual value of X_i at the center point, and ΔX is the step change value of the variables.

$$x_i = \frac{X_i - X_0}{\Delta X} \tag{4}$$

Table 1. Factors and their levels for experimental design (CCI)

Factor	Low axial level (-1)	Low factorial level (-α: -0.7071)	Center point (0)	High factorial (+α: +0.7071)	High axial level (+1)
X1: PEG-ran-PPG (wt.%)	10	15.86	30	44.14	50
X2: CuBTC (wt.%)	0	2.93	10	17.07	20

4. Results and Discussion

As described in the experimental design section, the CCD method was used to investigate the effect of both PEG-ran-PPG and CuBTC mass contents on the membrane separation process at the same time. The permeation properties of a series of membranes based on CCD design have been done at 30°C and 3 bar and the results are presented in Table 2. All the experiments were performed two times and the average results were reported. Also the experiments did not perform based on the run number.

Table 2. Experimental design matrix of CCD and actual responses (30°C, 3 bar)

Point type	Run no.	Independent variables		Response variables	
		X_1	X_2	Y_1	Y_2
		(PEG-ran-PPG (wt.%))	(CuBTC (wt.%))	(CO_2 permeance) (GPU)	CO_2/CH_4 ideal selectivity
Factorial	1	10 (-1)	0 (-1)	13.8	16.3
Factorial	3	10 (-1)	20 (+1)	23.0	22.8
Factorial	3	10 (-1)	20 (+1)	23.0	22.8
Factorial	4	50 (+1)	20 (+1)	80.0	17.8
Center	5	30 (0)	10 (0)	43.8	21.1
Center	6	30 (0)	10 (0)	43.8	21.1
Center	7	30 (0)	10 (0)	43.7	21.1
Center	8	30 (0)	10 (0)	43.7	21.1
Center	9	30 (0)	10 (0)	43.8	21.1
Axial	10	15.86 (-α)	10 (0)	24.0	20.0
Axial	11	44.14 (+α)	10 (0)	65.5	17.8
Axial	12	30 (0)	2.93 (-α)	42.2	18.0
Axial	13	30 (0)	17.07 (+α)	54.7	23.2

The statistical significance of the model equations and the model terms was evaluated by the F-test (analysis of variance (ANOVA)). The model and lack of fit p-value, the coefficient of determination (R_2), adjusted R_2 (adj-R_2) and the coefficient of variance (CV) along with the calculated regression coefficient of the model equations (based on the coded factors) are presented in Table 3. Also the individual significance (F-value and p-value) of each coefficient for each response variable is shown in Table 4.

Table 3. Regression coefficients (based on the coded values) and evaluation of mathematical models for the response variables

Regression coefficient	Response variables	
	CO_2 Permeance (Y_1)	CO_2/CH_4 Ideal selectivity (Y_2)
a_0	45.09	20.86
a_1	27.51	-1.43
a_2	7.03	2.46
a_{12}	-1.99	-3.10
a_{22}	2.36	0.30
a_{12}	1.97	1.10
Regression (p-value)	0.0001[a]	<0.0001[a]
Lack of fit (p-value)	0.42[b]	0.63[b]
R^2	0.987	0.958
Adj-R^2	0.978	0.929
CV (%)	6.01	3.24

[a] Significant ($p<0.0001$).
[b] Not significant ($p>0.05$).

As shown in Table 3, the p-value for the CO_2 permeance and CO_2/CH_4 ideal selectivity were 0.0001 and <0.0001 respectively, (p-value < 0.05), which indicates that the models were statistically significant with a confidence interval of 99.99%. Also, the lack of fit is not significant which shows that the models are suitable to predict the responses. The quality of fit of the prediction equation expresses by the coefficient of determination (R_2) [6]. The R_2 for the models were 0.987 for Y_1 and 0.958 for Y_2 which indicates that the models were suitable for adequate representation of the real relationship among the variables. Since addition of a variable to the model will always increase R_2, regardless of whether the additional variable is statistically significant or not, it is recommended to use adj-R_2 (it should be over 90%). The adj-R_2 will not always increase as variables are added to the model. Moreover, the values of coefficient of variance (CV) were 6.01% and 3.24% for the CO_2 permeance and CO_2/CH_4 ideal selectivity, respectively. The CV is a measure of reproducibility of the model. As a general rule, if the CV is not greater than 10%, a model can be considered reasonably reproducible [7].

Table 4. The significance of coefficients for each response variable

Regression coefficient	**Response variables**			
	CO_2 Permeance (Y_1)		**CO_2/CH_4 Ideal selectivity (Y_2)**	
	F-value	**p-value**	**F-value**	**p-value**
Linear effects				
X_1 (PEG-ran-PPG (wt.%))	511.67	<0.0001*	24.92	0.0016*
X_2 (CuBTC (wt.%))	33.45	0.0007*	73.35	<0.0001*
Quadratic effects				
X_{12}	0.48	0.5093	21.17	0.0025*
X_{22}	0.68	0.4368	0.19	0.6742
Interaction effects				
X_{12}	2.11	0.1897	11.78	0.0110*

*Significant at p<0.05.

4.1. CO_2 Permeance

The results of ANOVA analysis (Table 4) indicated that the linear effects of PEG-ran-PPG mass content ($p<0.0001$) and CuBTC mass content ($p=0.0007$) were significant on the CO_2 permeance (Y_1), whereas quadratic and interaction effects were not significant. By considering the values of coefficients, the CO_2 permeance (Y_1) was notably influenced by the PEG-ran-PPG mass content. As shown in Figure1, the CO_2 permeance is increased by addition of both PEG-ran-PPG and CuBTC concentrations. When the amount of PEG-ran-PPG and CuBTC increase up to 50 wt.% and 20 wt.% respectively, the CO_2 permeance attains 80 GPU (almost 10 times of the CO2 permeance of neat Peabx). PEG is well known for its high CO_2 permeability and CO_2/light gas selectivity [8]. The quadrupole interaction between the polar ether units in PEG segments and CO_2 molecules, resulting in the high CO_2 solubility and thereby permeability in the system. Also the high flexibility of the EO units enhances the diffusivity of CO_2 molecules [8,9-11]. The higher content of EO in the system due to addition of PEG to the neat Pebax copolymer, increases the favorably interaction of EO units with CO_2. Also the presence of PPG, which is fully amorphous and its permeability is a factor 4 to 5 higher than that of PEG [12], increases the permeability. The extra methyl side group ($-CH_3$) in PPG compared to PEG hinders close chain packing and increases the FFV and permeability of the membrane, at the cost of lower selectivity as a result of the reduced polarity of the system [13]. On the other hand, CuBTC separate CO_2 and CH_4 gases based on the different electrostatic interactions between the gases and the MOF framework. The improved CO_2 permeability due to addition of CuBTC particles can be attributed to the facilitated diffusion of CO_2 through the MOF pores. CuBTC has a three-dimensional network with intersectional pores, the main channels being 0.9 nm in diameter surrounded by tetrahedral pockets of 0.5 nm diameter. The tetrahedral pockets and main channels are connected by triangular windows of 0.35 nm [5]. The strong quadrupole moment of CO_2has higher affinity toward unsaturated Cu sites compared to CH4, leading to more CO_2 sorption.

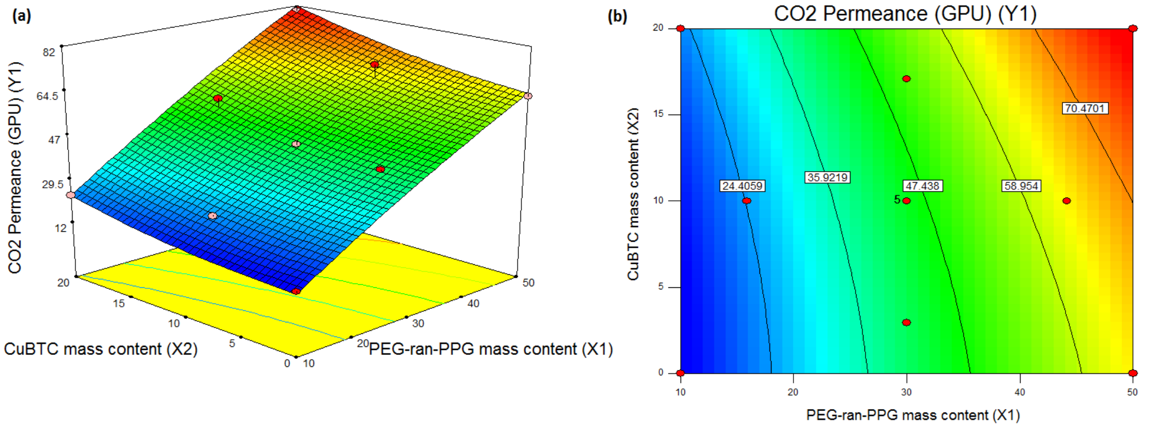

Figure1. 3D surface (a) and contour (b) plots of CO_2 permeance at different PEG-ran-PPG and CuBTC mass contents

4.2. CO_2/CH_4 Ideal selectivity

As revealed in Table 4, the CO_2/CH_4 ideal selectivity (Y_2) was significantly influenced by the linear effects of both independent variables (p=0.0016 for X_1 and p<0.0001 for X_2). The results also indicated that the quadratic effect of PEG-ran-PPG mass content significantly (p=0.0025) influenced the CO_2/CH_4 ideal selectivity. Moreover, the interaction effect between PEG-ran-PPG and CuBTC mass contents, was significant (p=0.0110). The 3D response surfaces and counter plots were employed to determine the interaction of the independent variables on the CO_2/CH_4 ideal selectivity (Y_2) (Figure 2). As it can be seen in Figure 2, the higher CO_2/CH_4 ideal selectivity was achieved at high CuBTC mass content and medium PEG-ran-PPG concentration. Also, based on the model regression coefficient, the CuBTC mass content has the most significant effect on the response and the interaction effect between PEG-ran-PPG and CuBTC has a positive effect on the selectivity. The CO_2/CH_4 ideal selectivity of Pebax/CuBTC MMMs increased about 19% at 20 wt.% MOF. While, at 50 wt.% of PEG-ran-PPG without addition of MOF, a slight decrease at the CO_2/CH_4 ideal selectivity (nearly 4%) was observed. The presence of both PEG-ran-PPG and CuBTC at the same time in the membrane structure resulted in an enhancement in the CO_2/CH_4 ideal selectivity, and at 20 wt.% of MOF and 30 wt.% of PEG-ran-PPG the membrane ideal selectivity reached to 23.7 which is nearly 45% higher than that of the neat polymeric one. The separation properties of MMMs are mainly affected by the transport properties of both continuous and dispersed phases and also the morphology of the interface. The high CO_2 selectivity of Pebax over other gases is obtained by high CO_2/light gas solubility selectivity, as the quadrupolar CO_2 display desirable interaction with the ether oxygen linkages, favoring the solubility of the polar CO_2 over the non-polar gases like H_2, N_2 and CH_4. Also, the selective adsorption of CuBTC toward CO_2 increases the permeability of CO_2 compared to CH_4, which affects the CO_2/CH_4 selectivity. The particles agglomeration and the presence of non-selective voids in the polymer/filler interface has a negative effect on the MMM selectivity. The addition of PEG-ran-PPG to the Pebax/MOF system increases the FFV and flexibility of the polymer chains and consequently enhances the filler/polymer interface (as confirmed by DSC analysis), which has a positive influence on the overall CO_2/CH_4selectivity of the membrane. On the other hand, the selectivity of PPG based block copolymers is lower than that of PEG based block copolymers because of the lower size sieving ability as well as the lower CO_2 solubility (due to the reduction in the polarity of the system) [14]. But, due to existence of PEG near the PPG in the PEG-ran-PPG copolymer, and favorable interaction of polar CO_2 molecules with them, the severe reduction in the selectivity of Pebax/PEG-ran-PPG membranes did not observe.

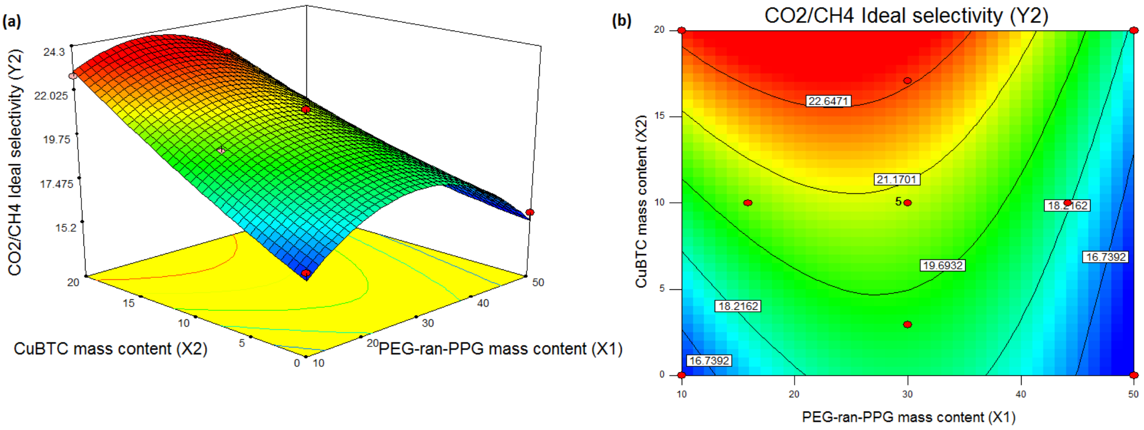

Figure 2. 3D surface (a) and contour (b) plots of CO_2/CH_4 ideal selectivity at different PEG-ran-PPG and CuBTC

4.3. Optimization and Verification of the Models

The optimization was performed using the Design-Expert software to evaluate an optimum set level of the independent variables leading to the desirable response goals including the highest CO_2 permeance and CO_2/CH_4 ideal selectivity at different importance ratios (CO_2 permeance to CO_2/CH_4 ideal selectivity importance ratios of 1/1 and 1/3). To validate the models generated by CCD, two actual experiments at optimal conditions were carried out. Table 5 presents the results of the experiment conducted at the optimal conditions and showed that the verification experiments and the predicted values from fitted correlations were in close agreement by confidence interval of 95%and confirmed the validity of the models. Under the optimum conditions (PEG-ran-PPG: 32.76 wt.% and CuBTC: 20 wt.%), nearly 620% and 43% increase in the CO_2 permeance and CO_2/CH_4 ideal selectivity was observed, respectively.

Table 5. Optimum conditions and validation experiment results

Independent variables	Optimum condition (wt.%)	Responses	Target	Importance	Correlation predicted	Confirmation experiment
PEG-ran-PPG	35.22	CO_2 permeance (GPU)	maximize	1	59.3	59.8±0.6
CuBTC	20.0	CO_2/CH_4 ideal selectivity	maximize	1	23.0	22.8±0.1
PEG-ran-PPG	32.76	CO_2 permeance (GPU)	maximize	1	55.8	56.2±0.8
CuBTC	20.0	CO_2/CH_4 ideal selectivity	maximize	3	23.2	23.4±0.1

5. CONCLUSION

In this work, PEG-ran-PPG and CuBTC were used to modify the selective layer of Pebax/ Polysulfone composite membrane. The effect of PEG-ran-PPG and CuBTC mass contents were investigated by CCD experimental design. The optimum set of the independent variables was obtained in order to maximize the CO_2 permenace and CO_2/CH_4 ideal selectivity. Under the optimum conditions (PEG-ran-PPG: 32.76 wt.% and CuBTC: 20 wt.%), nearly 620% and 43% increase was observed in the CO_2 permeance and CO_2/CH_4 ideal selectivity, respectively. Since no significant difference ($p<0.05$) was obtained between the actual and the predicted values, the models were verified to predict the responses.

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بهینه‌سازی عملکرد جداسازی غشای بهبود یافته لایه نازک کامپوزیتی Pebax MH1657 با استفاده از روش طراحی آزمایش

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چکیده

در این پژوهش، روش طراحی آزمایش CCD به منظور بهینه‌سازی و تجزیه و تحلیل اثر افزودن پلیمر (10-50 wt%) PEG-ran-PPG بعنوان پلیمر آلیاژکار و ذرات CuBTC (0–20 wt%) که یک نوع MOF بوده بعنوان نانوذرات بر روی تراوایی گاز CO_2 و گزینش‌پذیری CO_2/CH_4 غشای لایه نازک کامپوزیتی Pebax MH 1657/polysulfone مورد استفاده قرار گرفته است. در حقیقت خصوصیات مثبت آلیاژکاری و غشاهای ماتریس آمیخته بصورت همزمان در این پژوهش مورد استفاده قرار گرفته است. بر اساس ضرایب مدل برازش، درصد وزنی PEG-ran-PPG اثر زیادی بر روی تراوایی CO_2 داشته درحالیکه درصد وزنی CuBTC بیشترین تاثیر را بر روی گزینش‌پذیری CO_2/CH_4 داشته است. نتایج آزمایشگاهی و آماری نشان دادند که تحت شرایط بهینه (PEG-ran-PPG: 32.76 wt% and CuBTC: 20 wt%)، تراوایی CO_2 تقریبا ۶۲۰ درصد و گزینش‌پذیری CO_2/CH_4 حدود ۴۳ درصد در مقایسه با غشای Pebax افزایش پیدا کرد.

واژگان کلیدی: جداسازی دی اکسید کربن، Pebax، غشای کامپپوزیتی، روش طراحی آزمایش CCD.