2^3 FRACTIONAL FACTORIAL DESIGN FOR PVDF/PEBAX FILM COMPOSITE SYNTHESIS ON GAS SELECTIVITY STUDY

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Abstract— One of the key indicators for membrane film excellencies is by having a good ideal selectivity, and it is defined as the permeability ratio of two pure gases which be separated. This study was focusing on factors screening and interaction study between involved factors in film development on gas selectivity by employing 23 fractional factorial design (FFD). A total of four factors; Pebax concentration, bath temperature, evaporation times and quenching times which obtain from past research was chose to run simultaneously and ideal selectivity was chose as a single respond. Order of contribution was found to be as follows; Pebax concentration > quenching times > bath temperature > evaporation times, while the most impacting factors towards gas selectivity was Pebax concentration (main effect), evaporation times - Pebax concentration (interaction effect), quenching times (main effect). The outcome of the study indicates a very strong judgement in utilizing FFD to minimize and eliminate factors by considering the interaction among the factors involves in membrane film development for a perfect gas selectivity.

Index Terms— ***Factorial design, membrane optimization, factor screening, gas separation, composite membrane***

1. INTRODUCTION

Many research have been done on how to improve gas selectivity and performance in film composite development. Material concentration contributes to a better membrane synthesis. Some said that porosity and void can be minimized with an increasing polymer concentration [1]. But that is in the case of porous media. Selective material works a bit different way as they will be coated on top of the porous substrate. The selective material was suggested to be very dilute as a concentrated solution could thicken the layer, increase the mass transfer resistant and lead to loss in gas selectivity.

Defect in composite membranes is either incomplete coverage of the porous support or solution penetration by the thin selective solution. These two factors related to each other due to relationship between solution concentration and morphological changes. If the concentration is too low, the tendency of penetration is high thus incomplete coverage of the film structure could occur, but, if it is too high, the film composite will have a thicker structure and the selectivity will drop drastically. Perfect range of Pebax suggested from recent study is around 3% to 5% in its respective binary solution [2,3,4]. In this range, researcher believed that even though there is a possibility of pore penetration, yet it still allows the gas transport excellently.

Solvent and non-solvent interaction in membrane occur in water bath where phase inversion is taking place. The condition of precipitation bath could affect the morphological changes of the film form. Every structural change might be due to the molecular entanglement which restrict the change mobility during film formation. The process of de-mixing of the solvent and non-solvent rapidly occurs in the coagulation environment where the verification takes place and the structure are completely frozen. Oprea and Ciobanu (2007) in their work of the effect of bath temperature towards membranes morphology found out that at low bath temperature there will be a cellular porous structure enclosed with continuous polymer matrix phase and as the bath temperature increase, they start to observe a very symmetric 'sponge structure' across the film [5].

The aggregation of molecules at low bath temperature decrease the formation of uniform porous structure and possibly form a stiff dense film. At elevated temperature, molecules have a better chance and great mobility to arrange themselves faster and form a symmetrical film [5]. The morphological in dry-wet phase inversion techniques are strongly depends on the demixing rate either it is an instantaneous or delay. Macrovoid (finger-like cavities) region mostly associated with the instantaneous demixing of the solvent and non-solvent while the formation of spongy porous structure appointed to the delay demixing. The study of effect of Coagulant bath temperature (CBT) done by Amirilargani et al. (2009) jotted a significant finding when they said increase of CBT in range of 0 – 25 °C have improved the formation of surface porosity from a dense region to a fine pores structure across the film top to bottom [6].

Phase inversion during film development also found to influenced the film physical morphology thus influenced the gas selectivity during separation process. The first period where the polymer precipitate is left to vaporize in an open air for a specific period on the casting support (glass) and then move to the second period which is the quenching step in a non-solvent bath. The longer evaporation time will cause the film interface concentration and area with high polymer concentration form a thicker and dense skin. Tsay and McHugh (1991) observed an increasing anisotropic spongy sublayer with an increasing of evaporation time [7]. This pores formation behaviour is related to the nucleation and growth mechanism of the polymer. The quenching step can take up to 48 hours as the procedure lead to membrane precipitation. The period of quenching depends on the material used to prepare the dope solution and the dynamic movement of the solvent and non-solvent.

The FFD is a screening method where all variables are varied together rather than the traditional 'one-at-a-time' techniques to stimulate the interaction between N design variables [8]. A range of minimum and maximum values of each N variables must be identified. The experiment design with two-level upper bound and lower bound of the N variables is called 2N-1 factorial. It is the first order-model that have a smaller number of runs. In the past, application of FFD in membranes development has shown a great potential for this purposed [9,10]. Design Expert was used to initiate the experimental design and study the interaction effect among the factors.

2. MATERIALS AND METHODS

A. Materials

Polyvinylidene fluoride (PVDF) pallets and Polyether block amide under trade name Pebax 1657 was supplied by Sigma Aldrich and Arkema France respectively. Two analytical grade solvents, ethanol and N-Methyl-2-pyrrolidone (NMP) was purchased from Fisher Scientific. Two tanks of 99.9% purify CO_2 and CH_4 gas was used for gas permeation experiment. Both polymer pellets were oven dried at 60ºC for 24 hours before the dope preparation.

B. PVDF Substrate Preparation

15 wt% of PVDF pellets was uniformly stirred in 85 wt% NMP at 90ºC for 7 hours. After ensuring the complete homogeneity of the dope solution, it was then left for 24 hours at room temperature for degassing purpose to release any air bubble build up in the solution. The procedure was proceeded with dope casting with film applicator setting set to 0.03 mm knife gap, room temperature and 100 rpm of casting speed. Utilizing the dry/wet phase inversion technique, the casting plate was left to vaporize for 10 s to 240 s before it was completely immersed in a non-solvent medium (water bath) for 6 hours to 24 hours to let the liquid-liquid demixing take place. The wet PVDF film was then hanging to dryness at room temperature for another 24 hours. The complete experimental design with all parameter range was tabulated in Table 1.

C. PVDF/Pebax film composite development

Pebax 1657 coating solution was prepared first by dissolving 3 – 5 wt% of the pellets in 70:30 ethanol:water mixture at 80ºC until a clear homogenous solution was obtained. To ensure the consistency of the layer made, 5 mL of the Pebax 1657 coating solution was prepared in a flat dish. PVDF film was dip coated into the dish for 3 times, where there is a 15 minutes times interval in between the dip procedure. For a complete solvent vaporization, the film composite was further dried at 60°C for 12 h.

D. Gas Permeability Setup

The selectivity data was obtained by measuring the permeation rate of gas species through the develop membrane film. Single gas permeation setup was prepared as in Figure 1. CO_2 and CH_4 were tested individually by flowing each species at 2 bars toward the membrane cell, and the flow rate of the permeate was measured by the bubble flow meter. The effective cell area was 19.63 cm^2 with 5 cm film diameter.

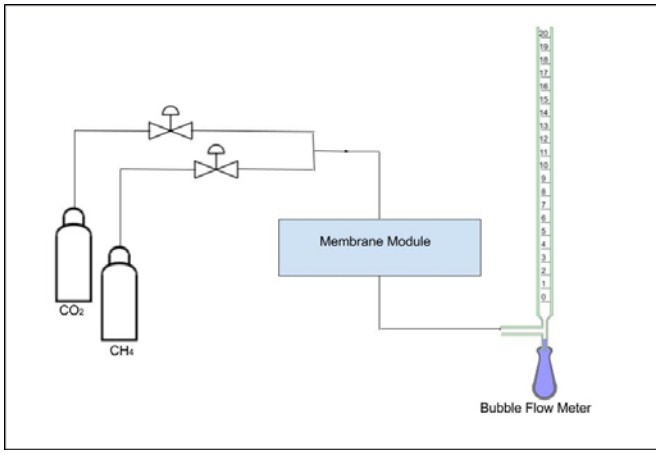

Figure 1: Gas permeability set-up

The permeability calculation was done by Equation 1 and it was expressed Barrer, where;
1 Barrer = 1 x 10-10 cm^3 (STP) cm/(cm^2scmHg). Taking the conversion factor into account, Equation 2 can be directly used to find the gas permeability in Barrer.

$$P = \frac{lV}{AtΔp}\ (cm^3cm(stp))/(cm^2scmHg)] \quad \text{Eq. 1}$$

$$P(Barrer) = \frac{1X10^{10}lV}{AtΔp} \quad \text{Eq. 2}$$

where P represent the film permeability in barrer, l is the film thickness in cm, A is the effective membrane area in cm^2, V is the volume in cm^3 displaced in time t(s) and Δp is the transmembrane pressure expressed in cmHg. The membrane selectivity is given in Equation 3, it is the membrane ability to separate two gases (A and B). It is the permeability ratio of species A and B respectively.

$$\alpha_{AB} = \frac{P_A}{P_B} \quad \text{Eq. 3}$$

E. Factorial Design Methodology

For this purpose of study, the factors screening was aided by Design Expert 7.6.1 to analyze the factors interaction for the gas selectivity output. The end result of first order polynomial was expected from this study to fit the following model;

$$y = b_o + \sum_{i=1}^{n} b_i x_i \quad \text{Eq. 4}$$

Where y represents the predicted response, b_o is the constant coefficient, n is the number of factors involved, b_i is the linear parameter coefficient and x_i denoted the two-way interaction parameter coefficient. The FFD experimental factors and running were performed as shown in Table 1.

Table 1: FFD experimental design

Runs	Factor 1 A: Evaporation time (s)	Factor 2 B: Quenching time (h)	Factor 3 C: Bath temperature (°C)	Factor 4 D: Pebax concentration (%)	Response Selectivity
1	10.00	6.00	30.00	3.00	53.57
2	240.00	6.00	30.00	3.00	31.03
3	10.00	24.00	30.00	3.00	55.88
4	240.00	24.00	30.00	3.00	33.33
5	10.00	6.00	55.00	3.00	59.21
6	240.00	6.00	55.00	3.00	27.58
7	10.00	24.00	55.00	3.00	64.75
8	240.00	24.00	55.00	3.00	35.32
9	10.00	6.00	30.00	5.00	63.80
10	240.00	6.00	30.00	5.00	56.66
11	10.00	24.00	30.00	5.00	62.63
12	240.00	24.00	30.00	5.00	59.60
13	10.00	6.00	55.00	5.00	59.92
14	240.00	6.00	55.00	5.00	56.66
15	10.00	24.00	55.00	5.00	63.42
16	240.00	24.00	55.00	5.00	58.90

3. RESULTS AND DISCUSSION

A. *Statistical Analysis of Gas Selectivity*

Gas selectivity obtained from this study was tabulated in Table 1 with the lowest and highest data jotted at 27.58 and 64.75 respectively. The highest selectivity came from the film samples cast at the following condition; 10 s evaporation time, 24 h quenching time, 55°C bath temperature and 3 wt% Pebax concentration.

The input response was analyzed for the significance of the regression model in the Design Expert Software and the analysis of variance (ANOVA) was given in Table 2. For a chemical process design, R2 for an accepted model must be in range of 0.9 to 1. From the ANOVA analysis in Table 2, this design experiment has generated 0.99 for R2, 0.9263 for “Pred R-Squared” and 0.9698 for “Adj R-Squared”. The "Pred R-Squared" is in sensible assertion with the "Adj R-Squared", this two must be within 0.2 from each other to ensure the reliability of the model. If both R are widely differed the model might be unstable for future used [11]. The indication of model satisfactory gave by the "Adeq Precision" and it does measure the signal to noise ratio. It is the judgement factor whether the model is perfect or not to navigate the design space and able to predict the response. A ratio greater than 4 is desirable [12]. From the analysis, the “Adeq Precision” of 20.850 indicates an adequate signal.

The Model F-value of 61.15 implies the model is significant. It is a test for comparing model variance with the residual or error variance. It is calculated by dividing model mean square by residual mean square. There is only a 0.01 % chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.05 indicate model terms are significant. In other word, if the Prob > F value is less than 0.05, then the term in the model have a significant effect towards the response. In this case A, B, D, and AD are significant model terms for this design.

Coefficient of the variation, C.V. % expressed the standard deviation as a percentage of the mean. It is used to measure the spread of data to describe amount of variability related to the mean and a good fit should have C.V. less than 10 %. PRESS is a Predicted Residual Error Sum of Squares where it measures the ability of the model of this design experiment to perform and predict the response of a new experiment. A small figure is desirable for this part. The final mathematical models developed for this experimental design as given by design expert are as shown in Equation 5.

$$\text{Selectivity} = +52.65 - 7.76A + 1.59\,B + 0.58C + 7.56D - 0.85AC + 5.51AD + 0.79BC - 1.05CD \quad \text{Eq. 5}$$

where A is the evaporation time, B is the quenching time, C is the bath temperature and D is the Pebax concentration while AC, AD, BC and CD is the interaction between the factors.

Table 2: ANOVA table of the regression model

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F	
Model	2447.74	305.97	61.15	< 0.0001	significant
A-Evaporation time	962.78	962.78	192.43	< 0.0001	
B-Quenching time	40.27	40.27	8.05	0.0252	
C-Bath Temperature	5.38	5.38	1.07	0.3343	
D-Pebax Concentration	913.98	913.98	182.68	< 0.0001	
AC	11.55	11.55	2.31	0.1724	
AD	486.07	486.07	97.15	< 0.0001	
BC	9.99	9.99	2.00	0.2005	
CD	17.73	17.73	3.54	0.1018	
Residual	35.02	5.00			
Cor Total	2482.76				
Std. Dev.	2.24		R-Squared	0.9859	
Mean	52.65		Adj R-Squared	0.9698	
C.V. %	4.25		Pred R-Squared	0.9263	
PRESS	182.98		Adeq Precision	20.850	

B. *Effect of Process Parameters and Interaction on Selectivity*

The selectivity is straightforwardly identified with all the process variables investigated, either as a main or as a part of an interaction effect, as expressed prior. The explanation behind anticipating the selectivity is to build up a model, to help in the choice of a proper range for the film synthesis optimization. The pareto chart for the selectivity, as outlined in Figure 2, highlights the order of the main and interaction parameter effects, which at last influence the selectivity model.

Figure 3 shows a perturbation plot highlighting the effect of all parameters on the selectivity. The perturbation plot allows the effect of all factors at a particular point in the design space to be compared. This type of display does not show the effect of interactions. Instead, the lines represent the behaviors of each factor while holding the others in a constant ratio (center point by default). In the case of more than one factors this type of display could be used to find those factors that most affect the response.

The order of the level of significance of the positive effects of the film composite synthesis parameters on the selectivity follows the order: (D) > (AD) > (B) > (BC) > (C) while the order of the level of significance of the negative effects on the selectivity is as follows: (A) > (CD) > (AC). Henceforth, if

large amounts of selectivity are to be gotten, the main three most impacting impacts for control are as per the following:

1. Pebax Concentration (Main Effect)
2. Evaporation Time × Pebax Concentration (Two-way Interaction Effect)
3. Quenching Time (Main Effect)

The primary factor most affecting the selectivity appears to be the main effect of the Pebax Concentration. The coating solution was manipulated 3 % (level -1) and 5% (level +1), which later dip coated with PVDF film for 3 times. CO_2 permeability increase with increase in Pebax 1657 concentration mainly cause by the reducing of pore blockage. Because of large voids and free volume in PVDF substrate, the lower Pebax 1657 concentration make the solution very dilute and penetrate deep into membranes matrix. Beside the pore blockage of the porous support, having a different concentration could make the polymer itself become compact and decrease in gas transport ability. From a general view, the skin layer solution concentration highly dependent on the porous support structure in a way that the larger the void form in support film, the higher Pebax 1657 skin solution concentration needed to achieve a perfect film composite but still few factors regarding Pebax solution preparation needed to be taking care such as solution gelation and mixture stability.

The second factor most affecting the selectivity is the two-way interaction effect between the Pebax concentration and the Evaporation Steps. The relationship between the two factors is as illustrated in Figure 4. The understanding of perfect film composite is a simple analogy, of which the perfect composite made by the combination of excellent well shaped porous support layer and a beautifully coated dense skin layer with a wide adsorption side. From the interaction plot, the highest response came from the shorter evaporation time (10 s) with high Pebax 1657 concentration (5%) while the lowest response from the combination of highest evaporation time (240s) and lowest Pebax 1657 concentration (3%). The trend of the effectiveness of the factors towards the response mostly influenced by the evaporation time, as selectivity decrease with increase of evaporation time. A conclusion can be made saying that 10 s is enough for the solution to vaporize and create a perfect top thin dense skin layer for the PVDF film before it can be transfer to the quenching bath.

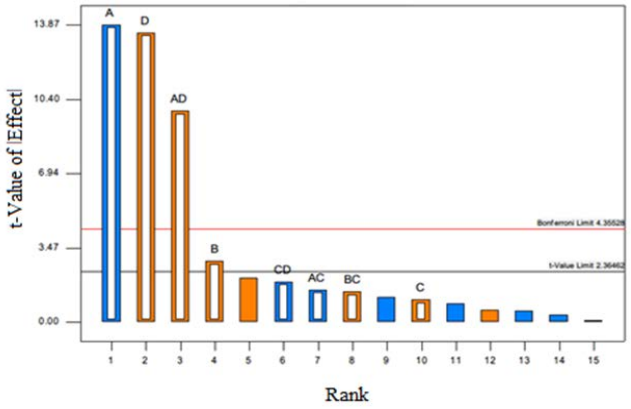

Figure 2: Pareto chart of main and interaction effect of film composite synthesis parameter (orange: positive effect and blue: negative effect)

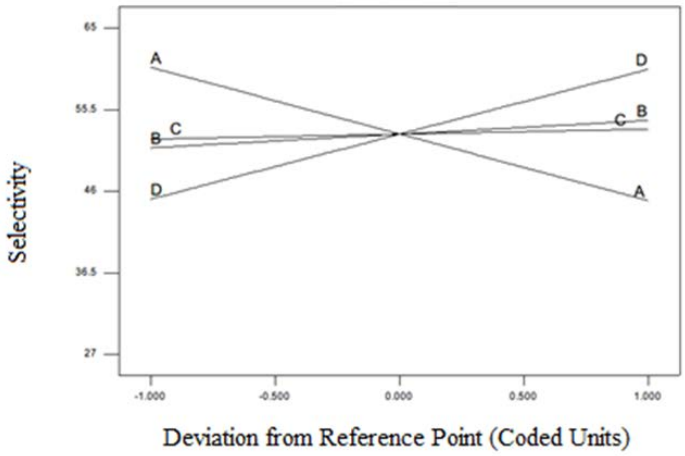

Figure 3: Perturbation plot showing the effect of all parameters on selectivity

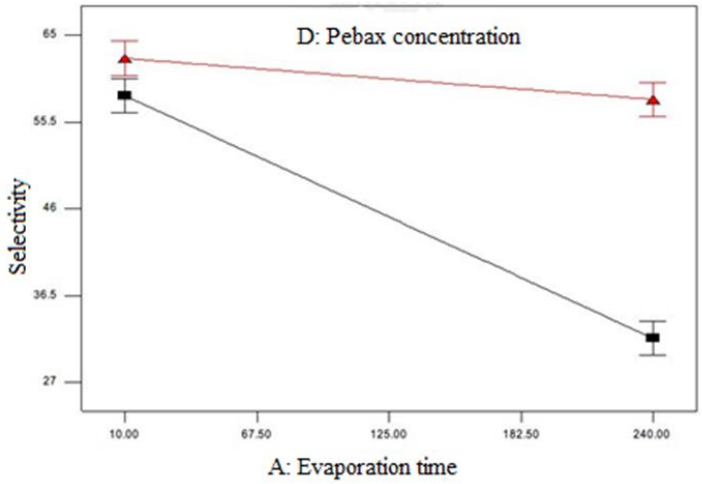

Figure 4: Interaction plot of the most significant interaction effect towards selectivity

C. PVDF/Pebax Film Composite for CO_2/CH_4 Separation

This study illustrated the potential of PVDF/Pebax film composite for biogas separation or in methane purification industry. Table 3 summarized the permeability-selectivity result from this work compared to the latest research regarding the use of Pebax 1657 for CO_2/CH_4 separation. This work is at the top of the list with CO_2 permeability of 393 barrer and selectivity up to 64.75. Pebax is a good CO_2 adsorbent due to the polar characteristic of this coating material that can interact with the permeating species during the separation process. Besides that, the higher condensability rate of CO_2 compared to CH_4 is due to its high critical temperature that help in channeling the gas species pass through the membrane film. It is normal for rubbery and glassy polymeric membranes to scale the gas solubility (or condensability) with gas critical temperature. Besides the two facts, the gas-polymer interaction (condensability and solubility) and penetrant dependent, the interaction of dipole-quadrupole between CO_2 and EO in Pebax 1657 also a driven factor [13]. It is an intermolecular interaction between

the penetrant and the medium where the gas solubility increase with the strong ion attraction.

Table 3: CO_2 permeability and CO_2/CH_4 selectivity data for various work on Pebax 1657

Film Materials	CO_2 Permeability-CO_2/CH_4 Selectivity	References
PVDF/Pebax	393 Barrer - 64.75	This work
TiO2/Pebax 1657/PVC	167 Barrer - 51	(Ahmadpour et al., 2016)
Pebax-1657/4A zeolite	155.7 Barrer - 41.3	(Murali et al., 2014)
ZIF-8/Pebax 1657/PES	758 Barrer - 16.1	(Jomekian et al., 2016)
PVC/Pebax	259.26 Barrer - 34.74	(Ahmadpour et al., 2014)
PEBAX/PEG/POSS	200 Barrer - 15	(Rahman et al., 2013)
Pebax/PEG/MWCNT	70 Barrer - 30	(Wang et al., 2014)
Pebax/amino	361 Barrer - 16	(Zhao et al., 2014a)
PEG/Pebax	80 Barrer - 15.9	(Car et al., 2008)
Pebax/SAPO-34	338 Barrer - 20	(Zhao et al., 2014b)

CONCLUSION

Membranes gas selectivity in response to film development factors was successfully studied by using 23 fractional factorial design. The statistical analysis managed to screen down and eliminate few factors which not so effective in film development for a good gas selectivity. Among the factors, Pebax concentration, quenching time and bath temperature showed positive effect towards the response. The interaction of Pebax concentration and evaporation times was discovered to be the only interaction that contribute to the good gas selectivity in PVDF/Pebax film composite.

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