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2^3 fractional factorial design for polymer based thin film composite (TFC) membrane synthesis for CO_2/ CH_4 separation

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Abstract. Membrane technology is dominating the industry as an attractive approach for biogas purification due to its outstanding performance. Recently, there have been intensive efforts in the development of better separation efficiency of membrane which include altering the materials and modifying the methods in preparing the membrane. A well-formed membrane is when they achieved both high permeability and excellent separation ability. Therefore, this study is focusing on identifying the best processing factors in PVC/Pebax thin film composite (TFC) membrane development towards CO2/CH4 separation by employing 23 fractional factorial design (FFD). A total of three factors; immersion times (5 & 15 min), Pebax concentration (1 & 5 wt%) and number of coating layers (1 & 4) were chosen to run simultaneously with CO2 permeability and ideal selectivity as the responses for this study. The results show that the most influential factors that affect the permeability are immersion time and Pebax concentration, while for selectivity are Pebax concentration and number of coating layer. The best condition was known to maximize the permeability and selectivity. The identified conditions were immersion time for 15 min, Pebax concentration at 5wt% and 4 layers of coating which gave CO2 permeability and gas selectivity of 19612 Barrer and 7.15, respectively. The outcome of this study indicates that FFD was suitable to minimize and eliminate factors by considering the interaction among the factors involves in membrane film synthesis for excellent gas separation performance. Besides, the existence of Pebax layer was verified by visual interpretation using Scanning electron microscopy (SEM) and Fourier Transform Infrared (FTIR).

1. Introduction

Biogas is a form of renewable energy sources that can be found during anaerobic digestion of organic substrates in industry waste, agriculture residues, sewage sludge as well as household [1]. The composition of biogas depends on the type of feedstock being digested. Primarily, it consists of methane (CH_4) which is around (35%–70%) and carbon dioxide (CO_2) (30%–65%) [2]. Due to richness of CH_4, biogas can act as vehicle fuel, electricity and power production as well as for injection into grid as an alternative of natural gas [3]. Nevertheless, the presence of high concentration of the acidic gas CO_2 may cause equipment and pipeline corrosion as well as reduction effect on the heating value of the gas, which restricts its practical application. Therefore, it is essential to separate CO_2 from the gas stream to meet the pipeline specification and the standard requirements for biogas utilization, which requires CO

concentration below 2 mol% for pipeline system and high purity of CH_4 (> 95 mol%) for use as vehicle fuel [4-5]. There is a wide range of gas separation according to different circumstances used for the CO_2 removal from gaseous compounds, such as absorption, adsorption, membranes and cryogenic distillation [6]. Among these technologies, membrane–based technology is promising which offers several advantages over others competing separation such as low operating cost, ease of scale-up and maintenance operation, lack of chemical disposal [7].

Different types of membrane materials are commercially available in the market and polymeric membranes have attracted maximum attention by the researchers due to its good mechanical properties, easier process, simplicity, and thermal stability [8]. Despite having excellent properties, they also have their own inherent limitation. An obvious issue is the trade-off between permeability and selectivity as shown in Robeson's upper bound curves [9]. Over the last few decades, many researchers have been working on developing a new kind of membrane called thin film composite (TFC) membrane. Commonly, TFC membrane comprises of two main layers; a microporous polymeric substrate and a thin selective layer on top of a thick substrate's surface as shown in Figure 1. The combination of stable support layer and high permeable selective layer was believed to enhance the selectivity–permeability trade-off [10]. However, few characteristics of the membrane such as pore diameter, thickness and surface roughness influenced the performance of the TFC membrane. Therefore, selecting the best conditions in preparing the TFC membrane is important in order to fabricate an excellent separation efficiency of TFC membrane.
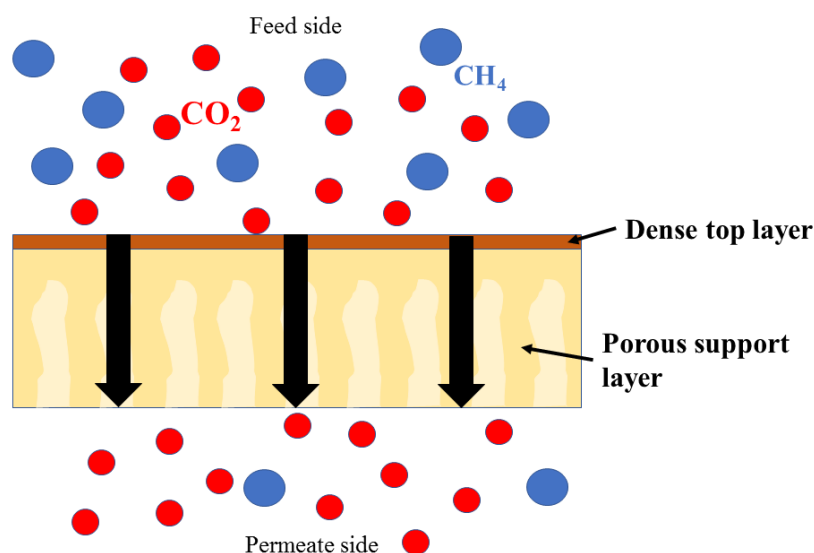

Figure 1. Schematics of thin film composite membrane.

Membranes can be synthesized in a different manner via modifying the key factors which influence the morphology of the membrane. TFC development consists of several key factors starting from material selection, casting technique and coating procedure. Commonly, the porous support layer was prepared via dry/wet phase inversion method. The process includes casting polymer solution on a glass plate and subsequently immersing in a non-solvent bath, where mass transfer takes place involving the interchange of solvent and non-solvent, by diffusion and convection [11]. Explained by Strathmann and Kock [12], in terms of thermodynamic and kinetic, the duration of the immersion, either fast or delayed demixing processes can lead to various types of membrane morphological structure. Hence, providing an optimum length of immersion time is required in order to produce defect free TFC membrane.

In many real structures of membrane, some non-ideal morphology such as polymer chain rigidification, particle pore blockages and interface void formation often occurred that reduce the performance of the membrane. According to Zarshenas et al. [13], higher polymer concentration produced dense membrane which led to the reduction of separation performances. Similar to the preparation of top selective layer in TFC membrane, having a higher concentration of coating solution

will increase the viscosity which led to a thicker layer, hence, increasing the mass transfer resistant throughout the membrane causing lower gas permeability. On top of that, a dilute solution is suggested for the top selective top to be coated on top of the support layer. However, the presence of large voids and free volume in porous support layer might lead to solution penetration by the selective solution that causes pore blockage and reduce the gas permeability drastically [14]. Therefore, choosing a perfect range of polymer loading for selective layer is important to prepare an ideal morphology of TFC membrane. In recent study, at lower concentration of Pebax (< 5 wt% in its binary solution), a membrane defects free can be produced.

All common composite membrane preparation method includes separate casting, direct coating [15], gas phase deposition [16] and interfacial polymerization [17]. At present, dip–coating is one of the most widely used techniques to prepare composite membranes due to its simplicity [18]. Different number of coating layers produced different thickness. The thickness of the selective layer is also found to influence the gas separation performance [19]. In Abdul Wahab et al. [20] recent work, they identified that too thin selective layer could not make any different to the gas selectivity. However, too thick selective layer may cause an increase in mass transfer resistance throughout the membrane, causing membrane's performance drop significantly. Generally, selecting the best thickness of selective layer is vital to form a defect–free TFC membrane with perfect separation efficiency.

Consequently, the aim of this study is to identify the independent factors (input variables) that have the highest contribution on the responses (output variables). The independent factors that have been selected in this study are immersion time of polyvinyl chloride (PVC) cast solution in non-solvent bath (water), concentration of polyether block amide (Pebax) and number of coating layer while CO_2 permeability and ideal selectivity were chosen as the responses. Currently, factorial designs are one of the promising methods used to obtain empirical models relating process response to process factors, and have proved their effectiveness. Therefore, two level factorial analysis (TLFA) factorial design was employed in this study to find the best factor that contributes the most in fabricating a perfect PVC/Pebax TFC membrane.

2. Methods

2.1 Materials
Polyvinyl Chloride (PVC) in powder form and dimethylformamide (DMF) solvent in liquid form were purchased from Sigma Aldrich. Polyether block amide under trade name Pebax 1657 and ethanol solvent were supplied by Arkema France and Fisher Scientific, respectively. Two tanks of CO_2 and CH_4 gases used for gas permeation experiments with purity of 99.9% were acquired from Air Products.

2.2 PVC substrate preparation
13 wt% of PVC powder was magnetically stirred in 87 wt% DMF at 90 °C for 7 h till complete dissolution, it was then left for 24 h at room temperature for degassing purpose to release any air bubbles formed in the solution. Then, the dope solution was casted on a clean glass plate with film applicator setting set to 0.03 mm knife gap, room temperature and 100 rpm of casting speed. Employing the dry/wet phase inversion technique, the casting plate was immediately immersed in a non-solvent medium (water bath) at 25 °C for 5 to 15 min to let the liquid–liquid demixing take place. Water is selected as the bath medium due to its high miscibility with DMF which can cause a fast solvent–non-solvent exchange. Then, the PVC substrate film was dried at room temperature for another 24 h to achieve complete drying.

2.3 PVC/Pebax Film Composite Membrane formation
Pebax 1657 coating solution was prepared by dissolving 1–5 wt% of the pellets in 70:30 ethanol:water mixture at 80 °C until a clear, dilute and homogenous solution was formed. Then, for the preparation of TFC membrane in laboratory scale, dip–coating method was used. 5 mL of the Pebax 1657 coating solution was poured on a flat dish. Then, the PVC substrate film was dip coated into the dish for 1 to 4 times, with 30 min time interval in between the dip procedure. Then, the prepared TFC membrane was dried in an oven at 60 °C for 24 h for complete solvent vaporization.

2.4 Single Gas Permeation Test Setup

Permeability test were run individually for each CO_2 and CH_4 through single gas permeation test by allowing them to flow at 2 bar and room temperature (25 ± 5 °C) toward the membrane cell and bubble flow meter was used to measure the flow rate of permeate. The single gas permeation setup was prepared as illustrated in Figure 2. Test module membranes with effective cell area and diameter, 19.63 cm^2 and 5 cm, approximately were used. The selectivity data was obtained by measuring the permeability of each gas species through the newly synthesized membrane. To measure the permeability of single gas, Equation (1) was expressed in GPU [1 Barrer= $1\times10^{-10}cm^3(STP)cm/(cm^2scmHg)$] [21]. After considering the conversion factor, equation (2) was obtained which can be directly used to calculate the gas permeability in Barrer.

$$P\ (\text{GPU}) = \frac{lV}{At\Delta p} \frac{(\text{cm}^3\text{cm(stp)})}{(\text{cm}^2\text{scmHg})} \tag{1}$$

$$P\ (\text{Barrer}) = \frac{1\times10^{10}lV}{At\Delta p} \tag{2}$$

where P is the permeability, l is the thickness of the membrane in cm, V is the volume in cm^3, t is the time taken (s), A is the effective membrane area in cm^2, and Δp is the transmembrane pressure expressed in cmHg. The ideal selectivity (α) of a membrane between two gases, A and B, can be expressed through permeability ratio of fast gas (A) to slow gas (B) as shown in equation (3) [22].
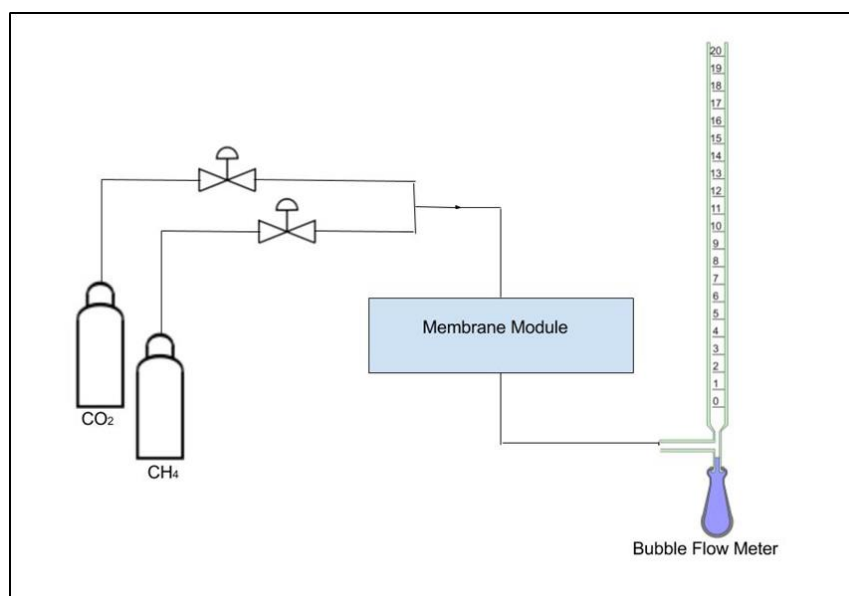
$$\alpha_{AB} = \frac{P_A}{P_B} \tag{3}$$

Figure 2. Gas permeability experimental setup

2.5 Factorial Design Methodology

The experimental matrix design and analysis of data were performed using Design Expert software (Version 7.1.6). The effects of several independent factors to process responses were explored by using a 2^3 fractional factorial design. Three factors that were chosen include immersion time, concentration of Pebax and number of coating layer and the responses were based on the CO_2 permeability and gas selectivity. A total of 8 runs were performed in this study. The summary of factors and responses utilized in the design are shown in table 1. Multiple linear regression analysis (MLRA) and analysis of variance (ANOVA) were used to develop mathematical models containing the notable terms.

Table 1. Summary of design, factors and responses.

Study type	Initial design		Design model		Runs
Factorial	2 Level Factorial		3FI		8
Factors	Symbols	Unit	Type	Low actual	High actual
Immersion time	A	min	Numeric	5	15
Pebax concentration	B	wt%	Numeric	1	5
Number of coating layer	C	layer	Numeric	1	4
Responses	Symbols	Unit	Analysis		
CO_2 permeability	P	Barrer	Factorial		
CO_2/CH_4 selectivity	S		Factorial		

2.6 Membrane Characterization

The cross-section morphology of the membrane was analyzed using scanning electron microscope (SEM, Hitachi/TM3030 Plus, Japan). To obtain a clear image and smooth cutting surface of the TFC membrane, it was freeze and fractured in liquid nitrogen without any part of the membrane affecting the cutting surface. Next, fourier transform infrared spectroscopy (FTIR, Nicolet AVATAR 370 DTGS with measurement wavelength range of 4000–500 cm^{-1}) was used to study the chemical information and examine the existence of each functional group of molecules in the TFC membrane. It allowed the membrane to absorb different kinds of wavelength produced from a beam and the output data were computerized to get the desired data in the form of wavenumbers, cm^{-1}. The high wavenumber region is best for investigating the thin selective layers that may present on top of the PVC layer, while the lower wavenumber region can be used to study the chemistry of both the Pebax selective layer as well as the PVC support layer.

3. Results and Discussions

3.1 Screening of Factors Affecting on the Gas Selectivity

The screening of factors that contributed on gas permeability and selectivity were carried out using 2^3 fractional factorial designs as shown in Table 2. The single gas permeation measurement is used to obtain the selectivity of CO_2/CH_4. To increase accuracy, three samples of membranes for each run were prepared and tested. Then, the average of gas permeation rate and selectivity results were reported and utilized in this work. The CO_2 permeability ranged from 7994.09 to19612.4 Barrer and the selectivity ranged from 2.55 to 7.15.

Table 2. 2^3 Fractional Factor Design analysis using Design Expert software with its respective responses.

Run	Factor 1: Immersion time (min)	Factor 2: Pebax concentration (wt%)	Factor 3: Coating layer	Response 1: CO_2 permeability (Barrer)	Response 2: CO_2/CH_4 Selectivity
1	5	1	1	15329.1	2.55
2	15	1	1	13336.5	3.48
3	5	5	1	7994.09	7.03
4	15	5	1	13319.8	7.05
5	5	1	4	10817.3	4.03
6	15	1	4	9614.5	4.83
7	5	5	4	14420.2	7.15
8	15	5	4	19612.4	7.15

3.2 Analysis of Variance of (ANOVA)

The input response was analyzed for the significance of the regression model in the Design Expert Software. The significance of the model was confirmed by the analysis of variance (ANOVA) as shown

in Table 3 and 4. The significance of a regression equation was checked using F-values while the p-values were used to check the significance of each coefficient towards the response. The model terms are significant if the p-value is less than 0.05.

Based on the ANOVA results, the F-values obtained were high, 230.62 for CO_2 permeability and 2176.06 for CO_2/CH_4 selectivity while the p-values identified were very low, 0.0043 for CO_2 permeability and 0.0005 for CO_2/CH_4 selectivity, indicating that good models are implied. The model terms that have significant effects towards permeability and selectivity were A (immersion time), B (Pebax concentration), C (coating layer), AB (immersion time and Pebax concentration), and BC (Pebax concentration and coating layer).

R-squared (R^2) from the ANOVA was used to indicate how close the data to the fitted regression line. For a chemical process design, a good fitting model should have R^2 value in range of 0.9 to 1. The design experiment for both CO_2 permeability and selectivity have generated $R^2 > 0.9983$, predicted $R^2 > 0.9939$ and adjusted $R^2 > 0.9723$. The predicted R^2 is in reasonable agreement with the adjusted R^2 since the difference between this two are within 0.2. In other words, the design model of the experiment is in accurate description of experimental data which indicated the relationship between the variables and the responses is reliable. The indication of model satisfactory gave by the adequate precision where it measures the signal to noise ratio. A ratio greater than 4 is desirable. From the analysis, the adequate precision for permeability and selectivity were 47.37 and 108.98, respectively, indicating an adequate signal. To express the permeability and selectivity as a function of independent variables, the final empirical model in terms of actual factors are shown in Equation (4) and (5).

$$P = + 20808.95 - 331.19A - 3506.15B - 2245.32C + 171.42\,AB + 873.02BC \qquad (4)$$
$$S = + 0.36 + 0.11A + 1.33B + 0.58C - 0.02\,AB - 0.11\,BC \qquad (5)$$

where P and S are referred as the responses, CO_2 permeability and CO_2/CH_4 selectivity, respectively. A is immersion time, B is Pebax concentration and C is number of coating layer.

**Table 3.** ANOVA table for the regression model (CO_2 permeability).

Source	Sum of Squares	Mean Square	F- Value	p-value Prob> F	
Model	9.248E+007	1.850E+007	230.62	0.0043	significant
A- Immersion time	6.702E+006	6.702E+006	83.57	0.0118	
B- Pebax Concentration	4.881E+006	4.881E+006	60.86	0.0160	
C- Coating Layer	2.514E+006	2.514E+006	31.35	0.0304	
AB	2.351E+007	2.351E+007	293.10	0.0034	
BC	5.488E+007	5.488E+007	684.23	0.0015	
Residual	1.604E+005	80201.12			
Cor Total	9.264E+007				
R-Squared	0.9983				
Adj R-Squared	0.9939				
Pred R-Squared	0.9723				
Adeq Precision	47.37				

Table 4. ANOVA table for the regression model (CO_2/CH_4 selectivity).

Source	Sum of Squares	Mean Square	F- Value	p-value Prob> F	
Model	25.50	5.10	2176.06	0.0005	significant
A- Immersion time	0.38	0.38	161.44	0.0061	
B- Pebax Concentration	22.75	22.75	9707.71	0.0001	
C- Coating Layer	1.16	1.16	494.43	0.0020	
AB	0.36	0.36	154.83	0.0064	
BC	0.85	0.85	361.89	0.0028	
Residual	4.688E-003	2.344E-003			
Cor Total	25.51				
R-Squared	0.9998				
Adj R-Squared	0.9994				
Pred R-Squared	0.9971				
Adeq Precision	108.98				

3.3 Pareto Chart

Pareto chart highlights the order of the main and interaction parameter that affects the permeability and selectivity models. The pareto chart in Figure 3(a) illustrates the main and interaction effects of the factors for CO_2 permeability. The immersion time (A) shows the highest contribution towards permeability followed by Pebax concentration (B) and number of coating layer (C). There were two positive interaction effects between BC and AB. Positive effect referred to increase of permeability as the value of factor increased and vice versa. Figure 3(b) demonstrates the main and interaction effects of the factors for CO_2/CH_4 selectivity. The order of the TFC membrane synthesis parameters that give positive effects towards selectivity is B > C > A, while the order of the parameters that bring negative effects on the selectivity is BC > AB.
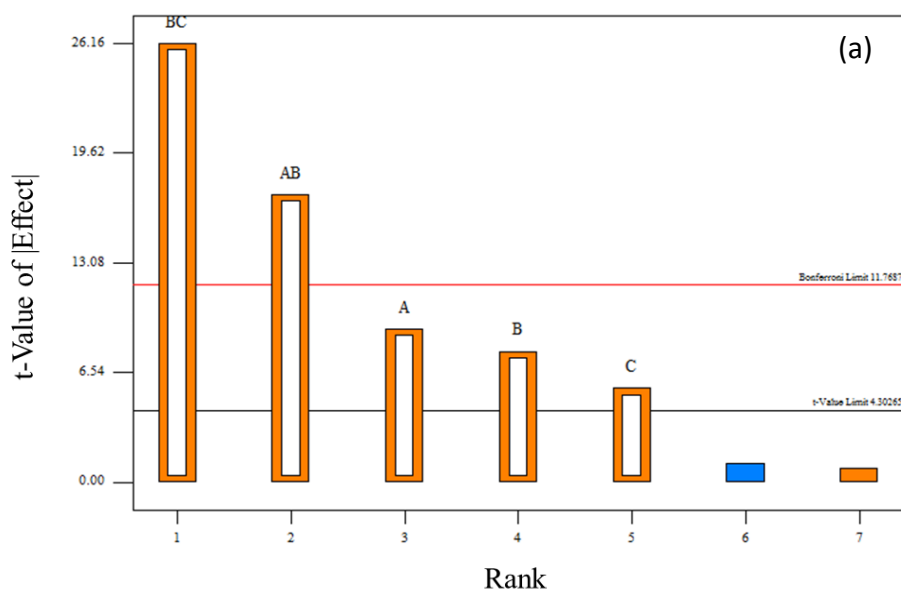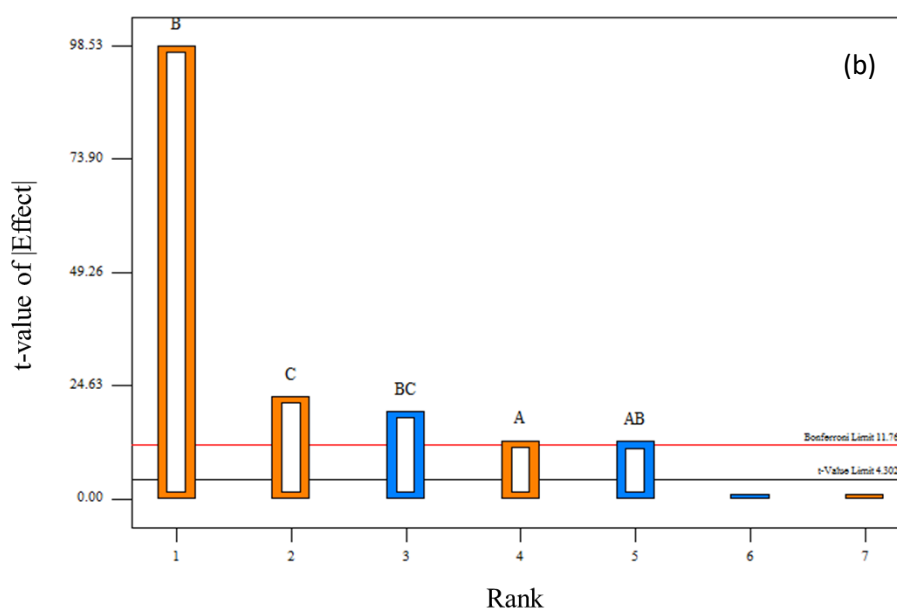
Figure 3. Pareto chart of main and interaction effect between TFC membrane synthesis parameters for (a) CO_2 permeability and (b) CO_2/CH_4 selectivity (orange: positive effect and blue: negative effect).

3.4 Effect of Process Parameters on CO_2 Permeability

The primary factor that provides a significant change to the membrane permeability was the length of the immersion time, which is the duration for the polymer precipitation process to occur. The large finger-like pores structure presence in the substrate is formed by the rapid rate of precipitation of the polymer from the cast solution during its immersion in the bath of non-solvent. The morphological changes are directly related to the immersion time where the longer it takes to immerse, the well-dispersed structure can be obtained. Therefore, a longer immersion time is required to allow the rest of the solvent slowly come out from the polymer. In this study, the immersion time was varied from 5 to 15 min for each sample. Based on Figure 4(a), the permeability increased with increased in immersion time which was due to complete dissolved solvent, forming a defect free porous membrane that creates an easy path for CO_2 gas to pass through the membrane. These results are in good agreements with the results in SEM as shown in Figure 9.

Figure 4(b) shows the effect of Pebax concentration to permeability. Similar trend was observed, where increased in Pebax concentration improved the permeability. The high increment of CO_2 permeability was ascribed to the good quadrupolar interactions existed between the CO_2 molecules and the polar groups in Pebax. Even though this TFC is a combination of porous and dense film, the separation achieved successfully due to the existence of Pebax 1657 which is polar material and good CO_2 adsorbent.
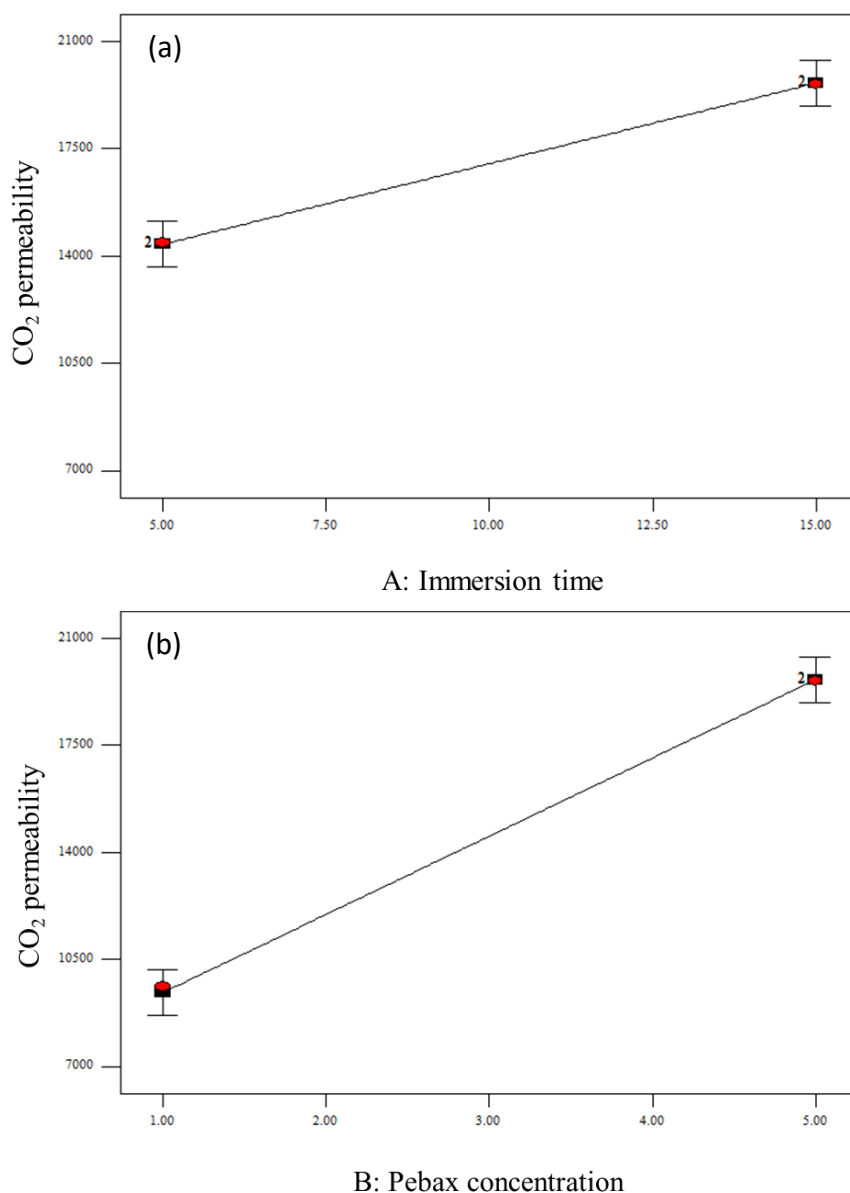
Figure 4. Most effective independent factors in CO_2 permeability; (a) immersion time (A) and Pebax concentration (B).

3.5 Interaction Effects between factors on CO_2 Permeability

Figure 5 shows the interaction effect between Pebax concentration and number of coating layer on CO_2 permeability. It was observed that greater permeability was obtained for 4 coating layers as compared to 1 layer at high Pebax concentration (5 wt%). This observation is due to the presence of more polar groups of Pebax at higher coating layer of Pebax causing more CO_2 molecules being absorbed, resulting in increment of CO_2 permeability. At lower Pebax concentration (1 wt%), permeability of a layer of Pebax was higher than 4 coating layers. This is due to the low Pebax concentration and Pebax coating layer producing thinner selective layer which allows more CO_2 gas passing through the membrane. However, variation of values of Pebax concentration at 1 coating layer of Pebax does not give impact to permeability since the thickness of selective layer is too thin, which does not give any resistant to the gas molecules to diffuse through the membrane layers.
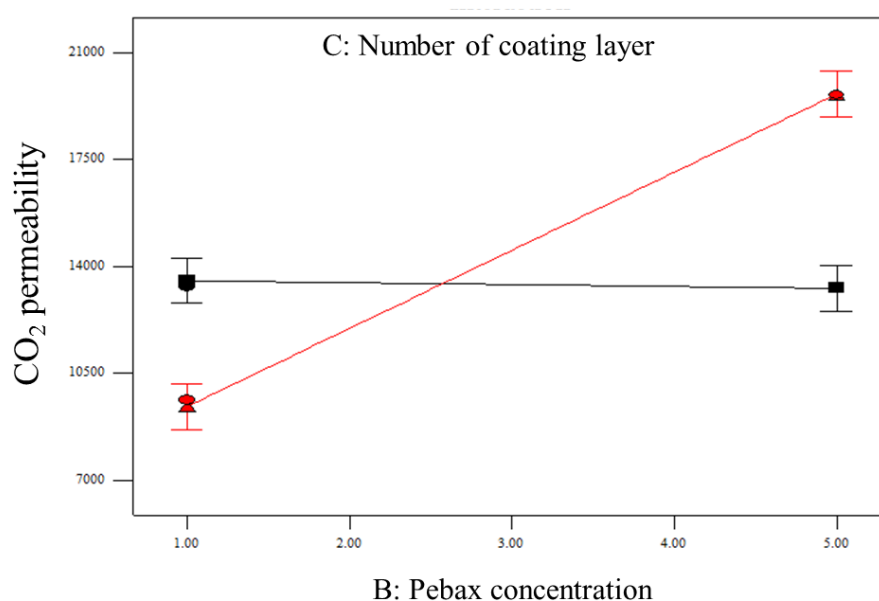
Figure 5. Most effective interaction effect between BC in CO_2 permeability.

3.6 Effect of Process Parameters on CO_2/CH_4 Selectivity

The primary factor most affecting the selectivity is the Pebax concentration. This is attributed to changes of viscosity at different Pebax concentration, where higher polymer concentration increased the viscosity of the solution. The Pebax coating solution was varied from 1 to 5 wt% of Pebax which was later dip-coated on top of PVC substrate in order to further study the role of Pebax 1657 on TFC membrane. According to Zarshenas et al. [13] a lower polymer concentration is preferred in preparing a polymeric membrane because concentrated polymer solution results in a denser membrane which is followed by lower gas permeability. However, different case is applied for the preparation of selective layer where lower concentration of Pebax produced more dilute solution that caused the solution to penetrate deep into large porous structure of the PVC substrate [23]. Hence, causing pore blockage that increased the mass transfer resistant of the gas, reducing the gas transport ability. As can be seen in Figure 6(a), at low Pebax concentration (1 wt%), the selectivity obtained is at the lowest which is 3.72. By increasing the Pebax concentration up to 5 wt%, the selectivity increased up to 7.10. Generally, the selective layer concentration highly depends on the porous substrate pore structure in a way that larger the pore structure in support film requires higher Pebax 1657 concentration solution to achieve a perfect TFC membrane.

The second factor that contributes the most in the separation properties (or selectivity) is the number of coating of Pebax. Different number of coating layers produced different thickness of selective layer. Mentioned by An et al. [24], the thickness of the selective layer affects the mass transfer resistance that influenced the entire membrane performance. In homogenous membrane, the researchers agreed that thicker membrane produced greater permeation resistance and lower the flux. The relationship between the selective layer thickness and flux is inversely proportional to each other [25]. As seen in Figure 6(b), it shows that the selectivity increased with an increase in number of coating layers indicating that thicker selective layer enhanced the separation ability of the membrane. This is due to too thin selective layer does not provide any significant resistance to the gas transport for separation to occur leading to high permeation of gases, accompanied by an undesired loss in selectivity. Therefore, the optimum layer was found at 4 coating layers with thickness 13.49 µm, approximately and has given the best selectivity of 5.79. Similar observations are reported in literature during the preparation of Pebax 1657 selective layer on top of PVDF substrate in CO_2/CH_4 separation [20].
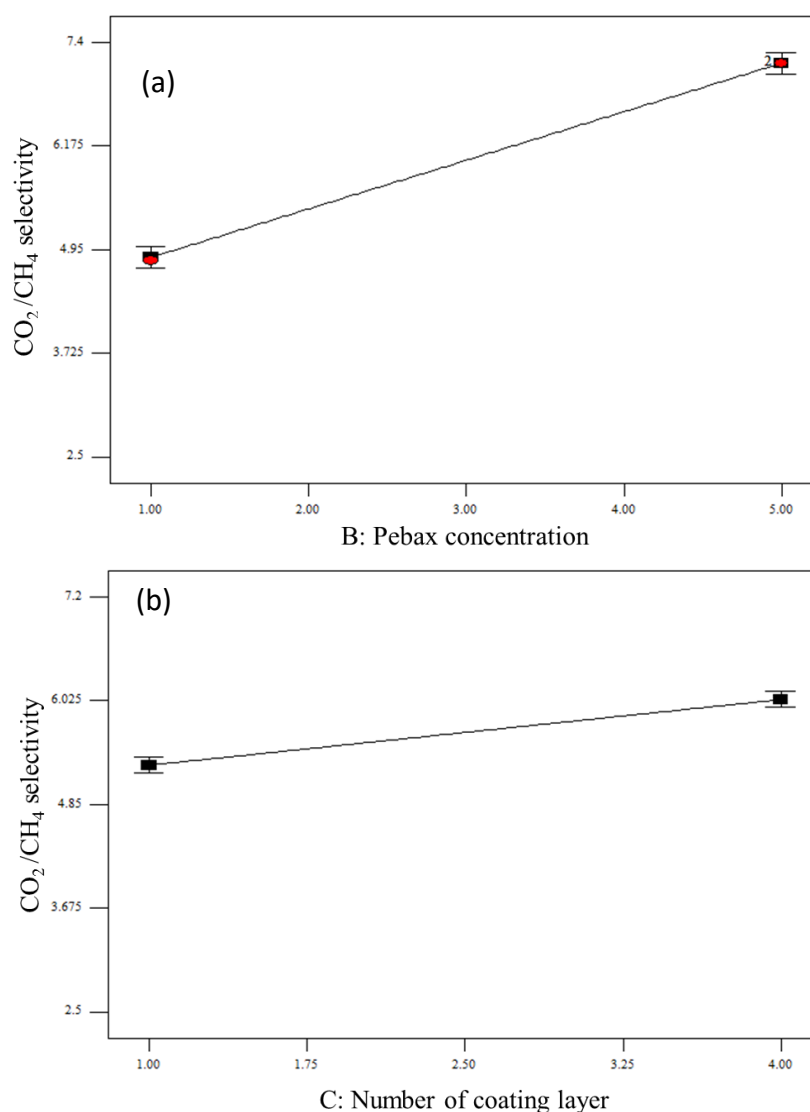
Figure 6. Most effective independent factors in CO_2/CH_4 selectivity; (a) Pebax concentration (B) and number of coating layer (C).

3.7 Interaction Effects between factors on CO_2/CH_4 Selectivity

The interaction effect between Pebax concentration and number of coating layer on CO_2/CH_4 selectivity is illustrated in Figure 7. From the interaction plot, the selectivity was observed to increase with Pebax concentration for both number of coating layers. This phenomenon occurred due to increase in Pebax concentration formed denser selective layer of TFC membrane which restricts the diffusion of gas molecules through the membrane especially CH_4 gas because of its big molecular size [26]. Fortunately, the quadrupolar nature of CO_2 molecules combined with the rubbery nature of Pebax makes it more permeable than CH_4, resulting in increased CO_2/CH_4 selectivity. The highest selectivity was obtained at 5 wt% Pebax concentration with 4 layers of Pebax coating, while the lowest selectivity was from the combination of the lowest Pebax concentration (1 wt%) and number of coating layer (1 layer). At low Pebax concentration, higher number of coating layers shows better separation ability. This observation is due to every layer of Pebax coated on the PVC substrate created a barrier which acts as a resistant and selective mechanism for gas transport, resulting in reduction of CH_4 gas permeability. However, these effects did not significantly affect the permeability of CO_2 due to its smaller kinetic diameter as compared to CH_4 (3.3 Å for CO_2 < 3.8 Å for CH_4), causing an increased in CO_2/CH_4 selectivity [27].
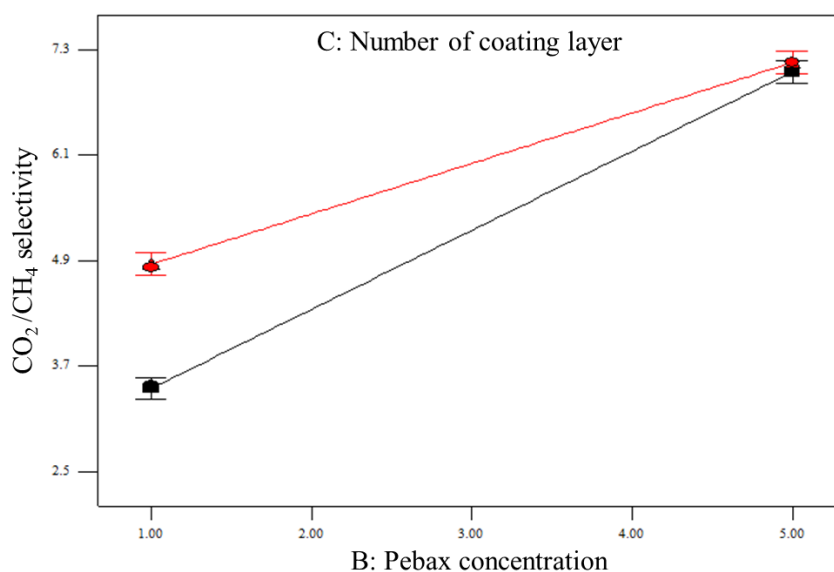
Figure 7. Most effective interaction effect between BC in CO_2/CH_4 selectivity.

One of the motivations of current membrane research is to develop membranes that surpass the Robeson upper bound, which satisfies both high separation ability (selectivity) as well as high separation speed (permeability). Regarding the CO_2/CH_4 separation, it is shown in Figure 8 that the introduction of Pebax layer on the PVC substrate resulted in a significant enhancement of membrane performance as compared to the uncoated PVC membrane. Besides, two TFC membranes were able to fall beyond the upper bound, and the highest is the TFC membrane prepared at the optimum conditions; 15 min immersion time, 5 wt% Pebax concentration and 4 Pebax coating layers.
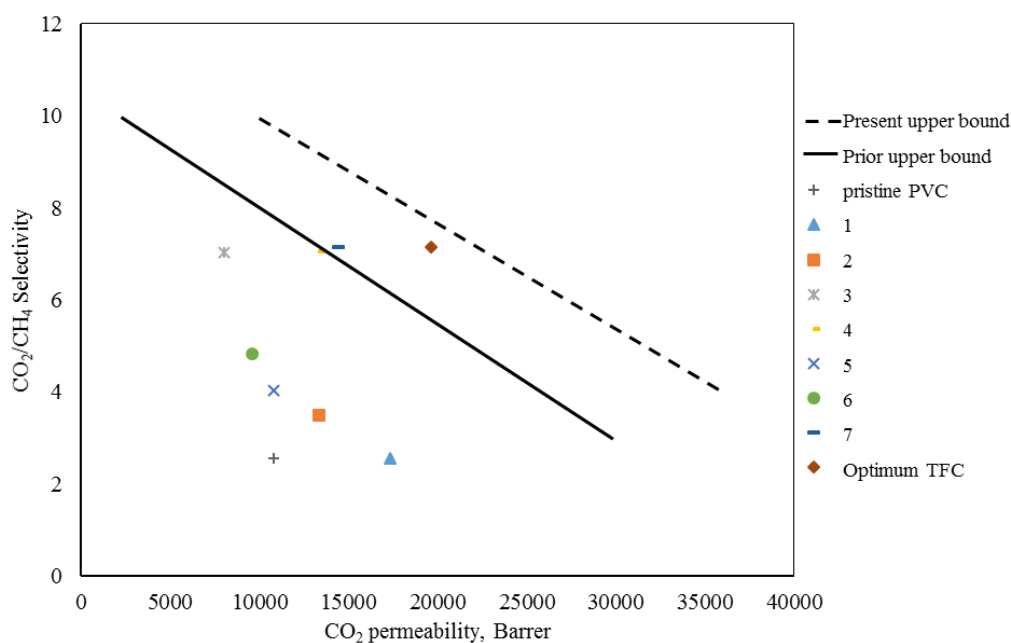

Figure 8. Robeson Upper Bound plot of the pristine PVC and TFC membranes produced in this work.

3.5 Membrane Characterization

3.5.1 Membranes Morphology.
In order to investigate the morphology of the uncoated PVC and PVC/Pebax TFC membranes, SEM images were taken from the cross-section of the membranes. The SEM images revealed that the prepared PVC substrate structures varied with different immersion time. The PVC membrane prepared with 5 min immersion time comprises of spongy like top layer and large void at the bottom (Figure 9(a)). The formation of large void was due to the development of bubble during the short immersion time. Next, the PVC membrane synthesized with 15 min immersion time shows a typical asymmetrical structure, with combination of spongy-like layer and finger-like porous structure (Figure 9(b)). Spongy porous layer is like an open–structure with minimum resistance against the transport of gas molecules while the formation of top finger-like voids in the membrane is believed due to the rapid movement of solvent DMF coming out from the film during phase inversion in water bath. These results indicate that immersion time significantly influenced the physical morphology of the membrane. Hence, 15 min was considered to be the optimal membrane immersion time for the fabrication of a well-defined membrane structure.

As seen from Figure 9(b), a clearly defined morphology with all layers were visible and well adhered to each other. It is obviously observed that the TFC membrane composed of two different layers due to the different physical nature of the polymers; i) a very thin and dense layer on top and ii) a thick and porous membrane, which mainly serves as the support. Besides, there is no adjustment in the PVC inner pore and structure both before (not shown in this paper) and after coating. This is due to the modification was performed by surface–coating, consequently just the surface of the PVC membrane is directly involved with Pebax. The thickness of the selective layer was found to be 13.49 µm.
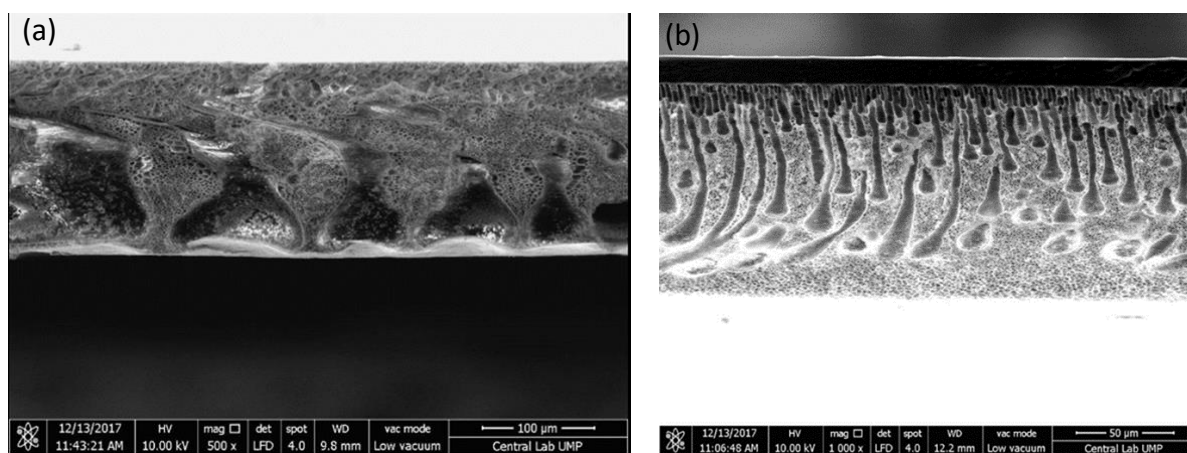

Figure 9. SEM images representing cross-sectional morphologies of (a) pristine PVC membrane and (b) optimum PVC/Pebax TFC membrane.

3.5.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis.
Figure 10 represents the chemical formulas of both PVC and Pebax 1657 which were referred to study and identify the bonding structures in the membrane. The FTIR spectra of pristine PVC and optimum PVC/Pebax TFC membranes over wavenumbers of $4000-500$ cm^{-1} are presented in Figure 11. A peak observed at 1425.64 cm^{-1} belongs to aliphatic CH_3-CH_2 deformation vibration and peaks found at 686.70 cm^{-1} represents the C–Cl stretching, revealing the existence of PVC [28]. New peaks were appeared in TFC membrane spectrum which can be attributed to the addition of Pebax 1657 selective layer on PVC substrate. The presence of Pebax 1657 was observed through several molecule bonding; ether stretching (C–O), amide segment (C=O) and N–H at 1253.86 cm^{-1}, 1640 cm^{-1} and 3404.06 cm^{-1}, respectively. Other peaks in the spectrum of the TFC membrane between 2869 and 2939 cm^{-1} represents

the asymmetric and symmetric stretching of the C−H bond. Table 5 summarized the characteristics absorption of the membranes.
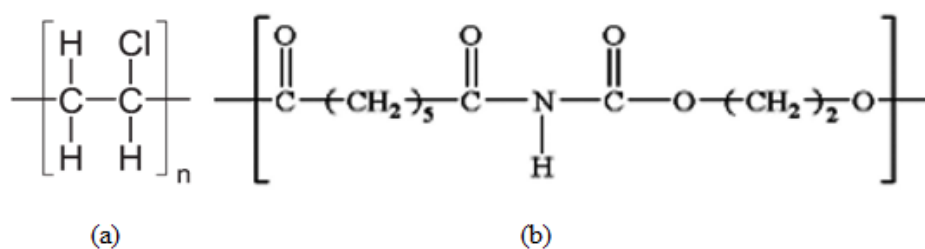

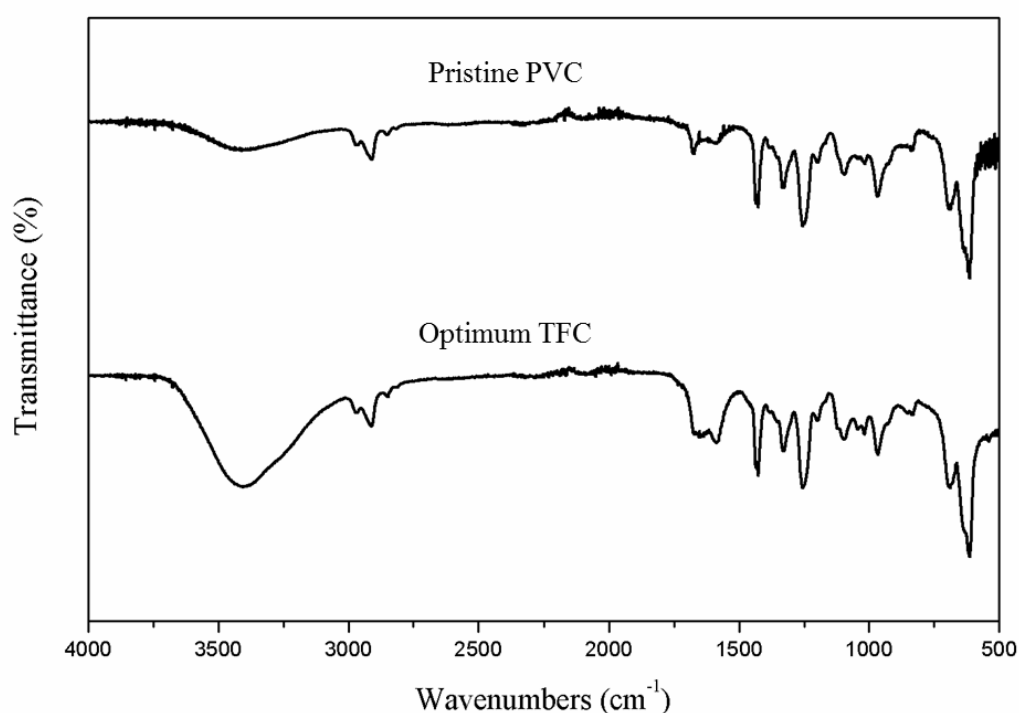**Figure 10.** The chemical structure of (a) PVC and (b) Pebax 1657.

Figure 11. FTIR spectra of pristine PVC and optimum TFC membranes (4000–500 cm^{-1}).

Table 5. Vibrational frequencies of functional groups in PVC and TFC membrane.

Functional Group	Wavenumber (cm^{-1})
PVC	
CH$_3$–CH$_2$ vibration	1425.64
C–H stretch	2867–2817
C–Cl stretching	686.70
C–H bend	1350–1470
Pebax	
N–H stretch (amide)	3404.06
C–O stretch (ether)	1253.86
C=O stretch (amide)	1640
C–H stretch	2860–2925
C–H bend	1350–1470

4. Conclusion

Thin film composite (TFC) membranes comprised of PVC and Pebax 1657, have been successfully developed by dry/wet phase inversion method for PVC substrate and dip–coating technique for the TFC. SEM characterization revealed that different selective layer thicknesses of Pebax 1657 were formed based on different number of coatings made on the PVC film. By having the selective layer, the CO_2 permeability and gas selectivity of the original uncoated PVC film have also been improved. The FTIR analysis confirmed the presence of PVC and Pebax 1657 structures in the TFC. The optimum number of layers was 4 with thickness of 13.49 µm which gave CO_2 permeability and gas selectivity of 19612 Barrer and 7.15, respectively. With the increase in Pebax 1657 concentration, the fabricated TFC surpassed the Robeson upper boundary. To have a good TFC, the selective layer must not be too thin and the coating solution must also not be too diluted as they would cause defects in the TFC.

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