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Optimization of the Preparation of Hydrophobic Isotactic Polypropylene Flat Sheet Membrane by Response Surface Methodology Design

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Membrane contactor (MC) is a cost effective solution that able to reduce the release carbon dioxide into the atmosphere.The membrane applies in a MC system are highly hydrophobic, high surface porosity, low mass transfer resistance and high resistance to chemicals in the feed streams.In this study, Response Surface Methodology (RSM) design consists of 2-Level Factorial and Centre Composite Design, which were performed for screening and optimization respectively, on the production of isotactic Polypropylene (iPP) microporous flat sheet. The results obtained from the analysis of variance of contact angle, showed that the impacts of drying temperature and drying time are much more important than polymer concentration and immersion time in methanol. The most optimum membranes prepared in this experiment were membranes with the contact angle value of 106.22° by the interacting factors of dry temperature and dry time, which are 54.96°C and 18.64 minutes respectively.The regression equation obtained from the 2-Level Factorial and

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Central Composite Design can be expected to apply in the preparation of iPP membranes using diphenyl ether (DPE) diluents and can reasonably predict and optimize the performance of the iPP membranes.

Keywords: Thermally induced phase separation; isotactic polypropylene; hydrophobic membrane; 2-level factorial; central composite design.

ABBREVIATIONS

A : *Polymer concentration (wt%)*
B : *Immersion time (hr)*
C : *Drying temperature (°C)*
D : *Drying time(min)*
k : *Degrees of freedom associated with SSR*
R^2 : *Coefficient of determination*
Xi : *Coded value of the ith independent variable*
X_i^* : *Uncoded ith independent variable at the center point*
ΔXi : *Step change value*
Y : *Response*

GREEK SYMBOLS

β_0 : *Constant coefficient*
β_1/ β_2 : *Linear coefficient*
β_{11}/ β_{22} : *Quadratic coefficients*
β_{12} : *Quadratic interaction coefficients*

1. INTRODUCTION

Membrane contractor (MC) or gas-liquid membrane contactor plays an important role this day as a solution of the mass transfer resistance problem in membrane separation process between two or more phases. In conjunction with this subject, numerous of studies about the membrane contractor have been done and develop for a lot of gas absorption process application in industries.

MC has offered a highly specific area, higher volumetric mass transfer rate, easier to linear scale up and does not require a large space as the way to minimize the carbon dioxide (CO_2) gas emission and reduce cost compared to the traditional equipments [1,2]. The MC is a system that consists of the combination of the gaseous, liquid absorbent and hydrophobic membrane. It provides a barrier between two phases from dispersion with one another when these two phases being separated through a membrane [3,4,5). Due to many reasons and advantages, gas adsorption or MC was putting itself at a high level of attention by industries and researchers [1,6]. A good membrane used for MC has high hydrophobicity, high surface porosity, low mass transfer resistance and high resistance to chemicals in the feed streams [7].

The hydrophobicity of membranes prepared was measured by the contact angle of water droplets on the membrane surfaces. A few researchers agree that improving the hydrophobicity of membrane can increase the membrane long term performance [8] by providing a high specific surface area, increasing the selectivity by absorption liquid and increasing the driving force of flux even at a low concentration [9].

Polymeric membranes have main characteristics of the polymer material such as polarity and the main effect of the permeation process is steric [10]. As for the polymer with higher molecular weight, which will contribute to small inter-connect structure, that is why researchers commonly use polypropylene (PP), polyethylene (PE), polytetrafluorethylene (PTFE) and poly (vinylidene fluoride) (PVDF) [9]. The polymeric material not only lowers molecular weight which attributes to the slower phase separation rate, but possesses high hydrophobicity and low surface energies [10,11]. Table 1 shows the comparison of PP-based and other commercial polymers in term of surface energies. The aqueous solution having lower values will generally spread on materials of higher surface tension values, thus it is one of the important fundamental to make sure that the material for hydrophobic membranes to have a longer performance period. There is indirectly proportional relationship between surface tension and the contact angle value of the polymer material. The highest contact angles were shown for PTFE whereby PP has a second highest contact angle while both of them have the lowest surface tension polymer material. Out of these polymers, iPP was chosen for this study due to the low cost, high hydrophobility, low surface energies, great mechanical properties, thermal stability and chemical resistance polymer [12,13,14].

Polymer concentration, solvent evaporation time, drying temperature and drying rate are among the parameters that were considered in this experiment.

Table 1. The surfaces tension and contact angle of the polymer based material

Polymer name	Surface tension (Dynes/cm)	Contact angle (Approximate)
Polytetrafluoroethylene (Teflon) (PTFE)	18	109
Polyvinylidene Fluoride (PVDF)	25	89
Polypropylene (PP)	29	102
Polyethylene (PE)	31	96
Polystyrene	33	66
Polysulfone	41	70

The best range of initial concentration studied by researchers were 13, 15, 20 and 30 wt%. The range of concentrations was successfully produced the cellular pore structures membrane [11-15]. Evaporation is a crucial stage to produce the microporous membrane and to prevent pores from wetted. There are two stages of evaporation in this membrane preparation. The first stage after the casting or molding the membrane, typically, the membrane will quench immediately into water bath for the phase separation to occur. Then the second stage of evaporation is by immersing in solvent namely methanol or ethanol, for total diluent extraction from the membrane. The evaporation's purpose is to force the diluent from membrane will leave the holes known as porous on the membrane. After membranes immerse in the solvent, some of the solvent are trapped inside the pores. Thus, to make sure there is liquid free inside the pores, the membrane should be dry in the oven or leave it at room temperature for a certain time.

The purpose of the Screening by 2-Level Factorial Design (FFD) was to determine which factors influencing the outcomes the most and how the factors interact with each other, while CCD was applied for process optimization. There were a few studies exploring the RSM in the membrane field. Xiangli et al. has used RSM in their research to optimize the preparation condition on the polydimethylsiloxane (PDMS)/ceramic composite membrane [16]. Another optimization study using RSM on the membrane was by Ismail and Lai [17]. To the best our knowledge, no one has reported research on using RSM to optimize the preparation conditions of hydrophobic isotactic Polypropylene (iPP) membranes by Thermally Induced Phase Separation (TIPS) method.

In this article, the preparation of the iPP membranes was established by the TIPS method. The polymer concentration, immersion time in methanol, drying time and drying temperature were considered as dominant preparation parameters. Main effects, quadratic effects and interactions of the variables on membrane contact angle were performed by FFD while the most optimum membranes were analyzed by CCD.

2. EXPERIMENTAL DETAILS

2.1 Membrane Materials and Chemicals

The iPP in pellet form with average molecular weight (Mn) of 250 000 was purchased from Aldrich, as well as solvents (diphenyl ether and methanol). All the chemicals purchased from Aldrich were used without further purification.

2.2 Membrane Preparation using TIPS Technique

Briefly, the iPP were mixed with diphenyl ether in beakers at desired iPP concentration . The beaker was placed in a hot plate while stirred until a homogeneous solution formed shown in Fig. 1. A stainless steel mould was pre-heated on the hot plate. A little portion of homogeneous solution was pour into the mould. The entire assembly was then quenched in water bath to induce phase separation in the sample. Then, membranes were immersed in methanol to exact the remaining diluents in membranes. Microporous membranes were obtained by evaporating the diluents in the oven [18].

2.3 Experimental Design

According to Myers and Montgomery, RSM is a collection of statistical and mathematical methods which were used for developing, improving and optimizing processes [19]. It is an efficient procedure for planning experiments so that the data obtained can be analyzed to yield a valid and objective conclusion. The main goals of RSM are to find an approximating function for predicting future response and to determine factor values that optimize the response function.

For this study, there were two steps involved for obtaining the optimization which are 2-Level Factorial Design (FFD) and Central Composite Design (CCD).

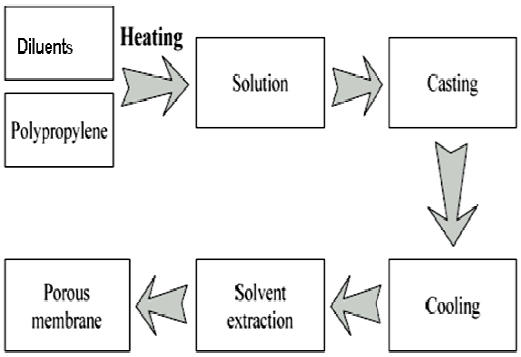

Fig. 1. Preparation of the porous PP membrane using the TIPS method

The factors are also known as input variables or independent variables whereby, the outcome sometimes called response. Any numbers of inputs are considered for this system. But after being analyzed, the factors that do not contribute much to the outcomes will be eliminated. The optimum condition was determined by CCD for input parameters with three to five levels. The optimal data need to be verified by repeating the experiment. Typically second order models were used for this design.

In developing the regression equation, the test variables were coded according to the following equation:

$$xi = \frac{(Xi - Xi*)}{\Delta Xi}$$

Where x_i is the coded value of the ith independent variable, X_i is the uncoded value of the ith independent variable, X_i^* is the uncoded ith independent variable at the center point and ΔXi is the step change value.

In region of higher curvature, near to the optimum second-order (quadratic) models are commonly used. A quadratic model with two factors, X_1 and X_2, can be written as:

$$Y=\beta_0+\beta_1X_1+\beta_2X_2+ \beta_{11}X_1^{\,2}+\beta_{22}X_2^{\,2}+\beta_{12}X_1 X_2$$

Here, Y is the response for given levels of the main effects X_1 and X_2 and the X_1X_2 term for a possible interaction effect between X_1 and X_2. The constant β_0 is the response of Y when both main effects are 0.

There are a few reasons for why the second order model was typically chosen which are the high flexibility to take a wide variety of functional forms and the high accuracy to the true response surface. It is also easy to estimate the parameter (the β's) using this model. From our practical experience, the second-order models work well in solving real response surface problems.

2.3.1 Two-level factorial design (FFD)

There were four processing variables (factors) that were studied and applied for 2-level factorial design shown in Table 2. The variables investigated were concentration (*A*), immersion time (*B*), drying temperature (*C*) and drying time (D). The response variable measured was contact angle measurement on the membrane prepared for 16 runs. In this design, there was no categorical factor included. The purpose of using this design is to estimate the main effect and interactions. The factorial models have been obtained from experimental design to study all interactions among the considered parameters (polymer concentration (15–25 wt %), immersion time (5-10 h), drying temperature (55-65°C) and drying time (20-60 min) [11,12,13,15,20-24].

2.3.2 Central composite design (CCD)

Dry Temperature and Dry time were the factors which contributed the most and were selected for central point in this design. Whereby, concentration and immersion time which contributed the less are set for a constant. For CCD, only value of dry temperature and dry time were manipulated for optimization. The low and high level of the parameters was determined from the 2-level factorial design shown previously. Table 3 shows the low and high level of each variable.

Design layout, as well as response for the experiment, are shown in Table 4. All the experimental data were mathematically processed and the experimental response models were produced. The optimal operating condition of the membrane molding process was determined by those experimental response models. Basically, CCD analyzes the experimental data with different combination of only 2 factors using a more details range of data for optimizing data. There are 13 runs of experiments, which were used to analyze the data in this design. In this study, the response variable measured was membrane's hydropobicity measured by contact angle value. All membranes prepared show the contact angle

higher than 90° which indicate the hydrophobic membranes characteristic while the highest average contact angle obtained in this experiment is 106°.

2.4 Membrane Surface Analysis

Test System of JY-82 Video Contact Instrument was used to measure the contact angle of distilled water on the PP membrane. A droplet of 5ml distilled water was placed on the membrane surface by a syringe. The contact angles were calculated from a digital video image of the drop on the membrane using an image processing program for the estimation of the contact angle from drop height and width.

2.5 Membrane Morphology Study

The membrane morphology both cross section and surface layer were examined by scanning electron microscopy (SEM) (Carl Zeiss EVO50). The samples were fractured in liquid nitrogen and a small piece was coated with thin platinum layer in vacuum. The other purpose of using this equipment is to analyze the membrane surface to examine the morphology or specifically the membrane structure, pore distribution, defects and presence of impurities.

2.6 Chemicals Composition Study

Chemicals composition study was carried out by using Fourier transform infrared spectroscopy (FTIR) model Nicolet Avatar 370 DTGS. FTIR was performed in order to study the chemical structure of organic molecules and potential structural changes that occurred as a result of the membrane chemical treatment or degradation. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). FTIR spectra of thin films were recorded. Its resulting spectrum represents the molecular absorption and transmission.

Table 2. The design arrangement and experimental results

Run	Factor 1	Factor 2	Factor 3	Factor 4
	A:concentration	B:immersion time	C:dry temperature	D:dry time
	(wt%)	(h)	(°C)	(min)
1	15	10	65	20
2	15	10	55	20
3	25	5	55	20
4	15	10	55	60
5	15	5	55	20
6	25	5	55	60
7	25	5	65	60
8	15	5	55	60
9	25	10	55	20
10	25	5	65	20
11	15	10	65	60
12	25	10	65	20
13	15	5	65	60
14	25	10	55	60
15	25	10	65	60
16	15	5	65	20

Table 3. Low and high level of factors setting for CCD

Factors	Low level	Central point	High level
Dry temperature (°C)	53	**55**	57
Dry time (Min)	15	**20**	25

3. RESULTS AND DISCUSSION

3.1 Factorial Analysis by 2^3 Factorial (FFD) Analysis

3.1.1 Factors and interaction factors contribution

The highest percent contribution factors and interaction factors as a model were selected. The most significant contribution was shown for drying temperature factor which was 47.86%, followed by drying time, immersion time and concentration of polymer which were 9.15, 7.72 and 0.25%, respectively. As for interaction factor, the highest contribution was by drying temperature-drying time, followed by concentration-drying time and concentration-drying temperature which 14.78, 12.26 and 3.48% respectively.

3.1.2 ANOVA and statistical analysis

The statistics with the analysis of variance (ANOVA) shows the selected effects and their coefficients. The model of F-value of 24.25 implies the model was significant shown in Table 5. There is only a 0.01% chance that this large "Model F-Value" could occur due to noise. Values of "Prob > F" less than 0.0500 indicates that model terms are significant [16]. The purpose of 2-level factorial design was to minimize the factor number. The design identifies the factors that affect the response the most. In this case B, C, D, AC, AD, and CD were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve this model.

Table 4. Experimental table for optimization using Centre Composite Design

Run	Factor 1	Factor 2
	C:Dry Temp(°C)	D:Dry Time (Min)
1	53	25
2	55	20
3	55	20
4	51	20
5	57	15
6	59	20
7	55	20
8	55	30
9	55	20
10	55	20
11	55	10
12	53	15
13	57	25

As this design was used for chemical process, in order for the design to be acceptable was when R^2 higher than 90 %, which correspond to the experimental data fit to the model. The model allowed us to obtain the R^2 of 0.9550 shown in Fig. 5. The design show that "Predicted R-Squared" of 0.8200 was in reasonable agreement with the "Adjusted R-Squared" of 0.9156. "Adeq Precision" measures the signal to noise ratio which requires to be greater than 4 so that it is desirable. The ratio of 16.536 indicates an adequate signal. This model can be used to navigate the design space.

Table 5. Analysis of variance for selected factorial model

Source	Sum of squares	Mean square	F value	p-value Prob> F	
Model	172.43	24.63	24.25	< 0.0001	significant
A-concentration	0.44	0.44	0.44	0.5274	
B-immersion time	13.94	13.94	13.72	0.0060	
C-dry temperature	86.41	86.41	85.09	< 0.0001	
D-dry time	16.52	16.52	16.27	0.0038	
AC	6.28	6.28	6.19	0.0377	
AD	22.14	22.14	21.80	0.0016	
CD	26.69	26.69	26.28	0.0009	
Residual	8.12	1.02			
Correlation total	180.55				
Standard deviation	1.01		R-Squared	0.9550	
Mean	101.47		Adjusted R^2	0.9156	
C.V. %	0.99		Predicted R^2	0.8200	
PRESS[a]	32.50		Adequate precision	16.5355	

[a]*PRESS = Predicted residual sum of squares*

The significant factors could be ranked based on F-value or p-value. It could be concluded that the significant effects were in the order of C>CD>AD>D>B>AC. Final equation in terms of actual factors by 2-level Factorial:

$$Y = 120.97 + 2.01A - 0.37B - 0.48C - 0.49D - 0.03AC - 0.01AD + 0.01\,CD \quad (1)$$

Where Y is the contact angle (°), while the A, B, C and D are representing the factors of concentration of iPP polymer (wt%), immersion time (h), drying temperature (°C), drying time (min) respectively.

3.1.3 Main factor and interaction factors contribution effect

The analysis of the experimental responses revealed that dry temperature and the dry time difference had significant interactive effects on the contact angle measurement. Out the entire factor designed, the immersion time (B) was the only factor that did not have interaction with other factors, meanwhile, the concentration (A) was not chosen to be one of the factors because of the lowest contribution percent. There were three interaction factors which were concentration and drying time (AC), concentration and time taken for drying (AD) and drying time and drying temperature (CD) considered as a model in the design.

3.1.3.1 The immersion time effect

According to the graph in Fig. 2, the contact angle decreased when immersion time increased. The longer immersion time set, poorer the membrane porosity as the methanol filled inside the pores. The pores then became swallowed that leaded to decrease of the resistant to the liquid on the membrane.

3.1.3.2 Interaction concentration /dry temperature factor and effect

Fig. 3 shows the graphs of the dry temperature at 55°C and 65°C used in the design. Upon drying, all the liquid inside the membrane namely diluent and solvent will evaporate. By applying higher temperature, the rate of evaporation of extracting methanol was faster than at lower temperature which possibly causes the pores to swelling and tends to absorb liquid quickly when contacting the distilled water onto membrane surface.

Supposedly, both pores' size and porosity decreased with the increasing of the iPP concentration in the polymer solution [15,25]. In the other words, membrane prepared by higher concentration, produces smaller pores which correspond to the better hydrophobic characteristic. Thus, for membrane prepared by concentration of 25 wt% have smaller pores' size than 15 wt%. Thus, upon evaporation of 55°C, the evaporation rates are slower and did not contribute much growing to the pore size.

As the temperature 65°C, the fastening of the rate of evaporation of methanol leaded to the pores' size to expand and lowering the contact angle measurement. At 25 wt% concentration, the contact angle measurement slightly decreased. Consider 65°C as a high temperature and rapid evaporation, there were maybe some of the methanol was unable to evaporate totally and trap inside the small pores causing the membrane tent to wet easily.

3.1.3.3 Interaction concentration /dry time factor and effect

The Fig.4 shows the dependence of drying time from the concentration. Dry time of 60 min shows gradually decreasing when the concentration increased from 15 to 25 wt%, which directly proportional to the 20 min of drying time. Upon drying, all the liquid inside the membrane namely methanol evaporated. Technically, longer time spent for drying more ensure for all the diluents and solvent exacted from the membrane.

As for membrane of 15 wt% concentration, the longer drying time was set, the higher contact angle value obtained. Drying membrane for 20 min may leave some methanol inside the pores thus more time required for total methanol extraction from pores. As for membrane of 15 wt% concentration, the longer dry time set, the higher contact angle value obtained. Drying membrane for 20 min may leave some methanol inside the pores, thus more time required for total methanol extraction from the pores. Membranes with concentration of 25 wt% have smaller pore sizes compared to 15 wt% membranes. The contact angle value for 20 min drying time was slightly higher than those for 60 min. The larger time range required for the specific observation.

3.1.3.4 Interaction dry temperature /dry time factor and effect

According to the graph shown in Fig. 5, as drying temperatures were reduced, the drying time also went down. At 60 min, the graph dropped slightly when increasing the dry temperature from 55°C

to 65°C compared to the graph of 20 min, the graph was dropped more sharply.

For 60 min drying time, the contact angle of the drying temperature of 55°C is higher than 65°C. This was because the evaporation rate of lower drying temperature is much slower. This situation allows the methanol to evaporate slowly so that the methanol molecules are not forced to exit from the pores and do not expand the pores. Even so, the longer drying time permits the methanol extracted totally from the inside of membrane's pores causing the pore volume fraction to reduce. Thus, higher temperature leads to poor porosity [26].

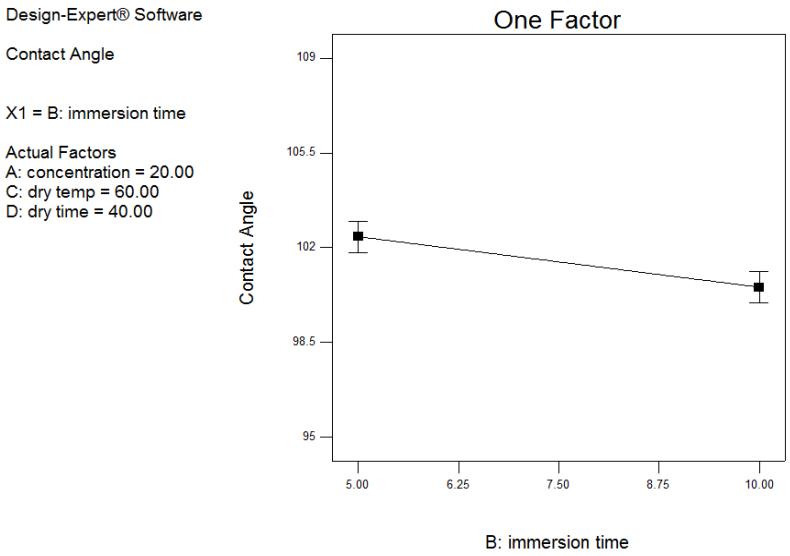

Fig. 2. The immersion time effect on the contact angle measurement

The "I-Beam" symbols on the plot describe the 95 % least significant difference (LSD) interval for the plotted points

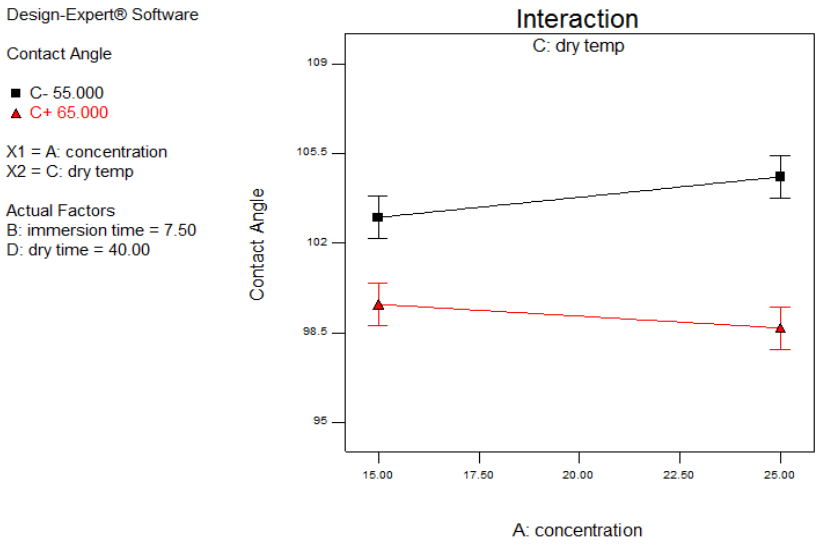

Fig. 3. The interaction effect graph between concentration and dry temperature on the contact angle measurement

The "I-Beam" symbols on the plot describe the 95 % least significant difference (LSD) interval for the plotted points

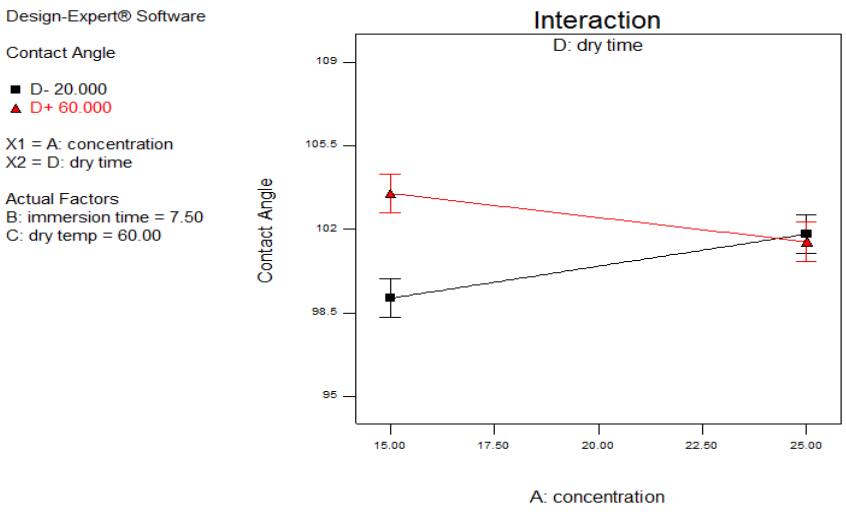

Fig. 4. The interaction effect graph between concentration and time taken for drying on the contact angle measurement

The "I-Beam" symbols on the plot describe the 95 % least significant difference (LSD) interval for the plotted points

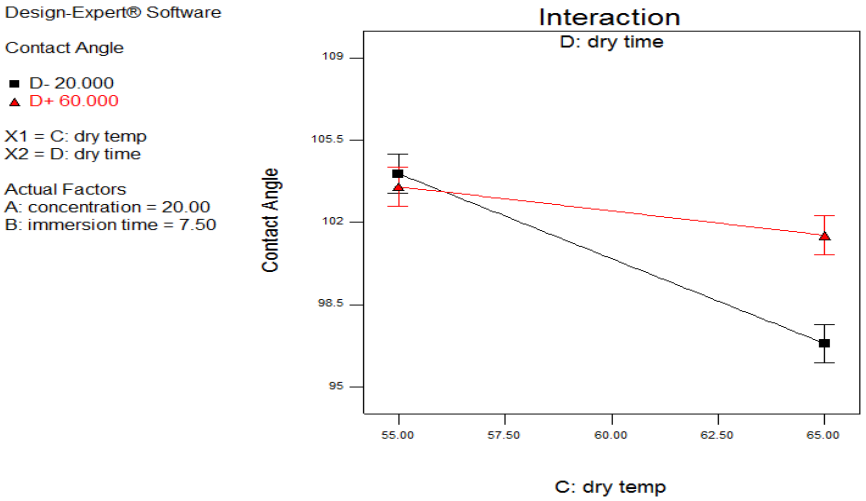

Fig. 5. The interaction effect graph between dry time and dry temperature on the contact angles measurement

The "I-Beam" symbols on the plot describe the 95 % least significant difference (LSD) interval for the plotted points

Shorter drying time of 20 min, the graph shows that lower temperatures have a better contact angle compared to higher temperature. However, a drastic changing can be observed in the graph of 20 min drying rate from 55°C to 65°C compared to 60 min of the drying temperature. A drastic changing of the temperature of 55°C was sufficient to evaporate most of solvent, but when increasing the temperature to 65°C, the possibility of the evaporation and swelling of the pores to happen were also increased.

3.1.4 The best condition and data prediction obtained from FFD

The best condition and the prediction data selected to be centre points in the central composite design (CCD) for an optimization are

shown in the Table 6. It can be seen that the best condition was at concentration 25 wt% and the immersion time of 5 h whereby the further manipulating of the data range required for drying temperature and time in order to get the optimum condition for membrane preparation. Meanwhile, the concentration and immersion time were set as constant for CCD.

3.2 Optimization by Central Composite Design (CCD)

3.2.1 Anova analysis

A good model presents a model which has a significant regression model and individual model coefficient. The ANOVA in Table 7 shows that the analysis of variable table consist of the list of source, sum of the squares, mean square, F-value and also P-value to determine either the model is significant or not.

For the validation, the experiment using best condition data were repeated .The validation also can be checking using the equations obtain from this design.

The Model F-value of 30.12 implies the model is significant. There is only a 0.01% chance that this large "Model F-Value" could occur due to noise. Values of "Prob> F" less than 0.0500 indicate model terms are significant. In this case CD, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant [27]. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table 6. The data prediction

Factor	Name	Level	Low level	High level	Std. Dev.	Coding	
A	Conc.	25	15	25	0	Actual	
B	immersion time	5	5	10	0	Actual	
C	dry temp	55	55	65	0	Actual	
D	dry time	20	20	60	0	Actual	
Response	Prediction	SE[a]Mean	95% CI[b] low	95% CI[b] high	SE[c]Pred	95% PI[d] low	95% PI[d]high
Contact angle	106.97	0.71	105.33	108.62	1.23	104.13	109.82

[a]SE Mean = Point Prediction which the standard deviation associated with the prediction of an average value at the selected factor or component levels; [b]CI = Confidence interval; [c]SE Pred = Point Prediction where the standard deviation associated with the prediction of an individual observation at the selected factor or component levels; [d]PI = Prediction interval

Table 7. ANOVA for response surface quadratic model

Analysis of variance table [Partial sum of squares - Type III]						
Source	**Sum of squares**	**DF[a]**	**Mean square**	**F value**	**p-value Prob> F**	
Model	174.03	5	34.81	30.12	0.0001	significant
C-Dry Temp	5.10	1	5.10	4.41	0.0739	
D-Dry Time	3.74	1	3.74	3.24	0.1150	
CD	31.14	1	31.14	26.95	0.0013	
C^2	128.56	1	128.56	111.27	< 0.0001	
D^2	29.90	1	29.90	25.88	0.0014	
Residual	8.09	7	1.16			
Lack of Fit	7.85	3	2.62	43.64	0.0016	significant
Pure Error	0.24	4	0.06			
Correlation Error	182.12	12				
Standard Deviation	1.07		R^2	0.9556		
Mean	102.91		Adjusted R^2	0.9239		
C.V. %	1.04		Predicted R^2	0.7017		
PRESS[b]	54.33		Adequate precision	14.7592		

[a]DF= Degree of Freedom; [b]PRESS = Predicted residual sum of squares

The "Lack of Fit F-value" of 43.64 implies that the lack of Fit is significant, where it is presented by a low probability value and the response predictor is neglected as mention by Montgomery [28]. There is only a 0.16% chance that a lack of this large Fit F-value could occur due to noise. Significant lack of fit is due to the sensitivity of the system. In the other word, even there is a slight change to the factor; it will lead to a large contribution to the response.

ANOVA analysis shows that the resultant quadratic polynomial models adequately represented the experimental data with the coefficients of determines (R^2) for the response is 0.9556%. This indicates that the experimental data is fit to the model as well as also describe the influence of independent variables study on the water contact angle on the membrane. As a general rule, R^2 should be closed to 1 for a good model [19].

The "Predicted R-Squared" of 0.7017 was not as close to the "Adjusted R-Squared" of 0.9239 as one might normally expect. This may indicate a large block effect or a possible problem with model and/or data. Things to consider are model reduction, response transformation, outliers, etc."Adequate Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 14.7592 indicates an adequate signal. This model can be used to navigate the design space.

The coefficient of variation (CV) is the standard deviation expressed as a percentage of the mean and was calculated by dividing the standard deviation by the mean value and multiplying by 100. It was suggested that CV should not be greater than 10% for a good fit to the selected model and these values were found to be 1.04%.

The second order regression model shows the relationship between the response (contact angle) and the operating factors C and D (drying temperature and drying time) obtained by multiple regression analysis of the experimental data. The regression equation can be use to predict the response by factor dry temperature and dry time. The regression model analysis is shown as follow.

Contact angle, Y,

$$Y = 106.15 + 0.65\ C - 0.56\ D + 2.79\ CD - 2.37C^2 - 1.14\ D^2 \quad (2)$$

3.3.2 Three-dimensional (3D) & contour plot for model graphs

The dimensional contour and surface plot are demonstrated in Fig. 6 (a) and (b) respectively. Both of the plots illustrated the effect of dry temperature from 53 to 57℃ and dry time from 15 to 25 min on the contact angle measurement of the bottom membrane prepared from 96.1 to 106.94°. The plane exhibits an optimum point of contact angle value of 106.22° by the interaction factors of dry temperature and dry time which are 54.96°C and 18.64 min respectively. The red regions in figures show the maximum contact angles values region of membranes. The desirability of this design is 0.933.

3.3.3 Confirmation runs

The regression equations obtained using the experimental data can be used to predict the contact angle at any dry temperature and dry time with the range of the levels defined. In order to validate the veracity of the model, five confirmation runs were performed. The preparation conditions are shown in Table 8. The preparation conditions for three experiments (1–3) were come from 13 experiments in Table 3, and other two experiments (4–5) were new conditions with the range of the levels defined. Eqn. (1) and (2) were applied respectively. The predicted values and the actual experimental values were compared and the percentage errors between the actual and predicted values for the flux and the selectivity were calculated. The percentage errors for the respond, contact angle are observed to vary from −0.75 to 3.92 %. According to the confirmation results, it can be concluded that the regression models were consistent with the contact angle measurement. The regression equation can be expected to apply in the preparation of iPP membranes using DPE diluents and can reasonably predict and optimize the performance of the iPP membranes.

3.4 Characterization the Optimum Condition of Membrane

The most optimum membranes were found at concentration 25 wt% using DPE, immersion time of 5 h, dry temperature of 54.96°C and dry time in 18.64 min, which were chemically and physically tested by SEM and FTIR.

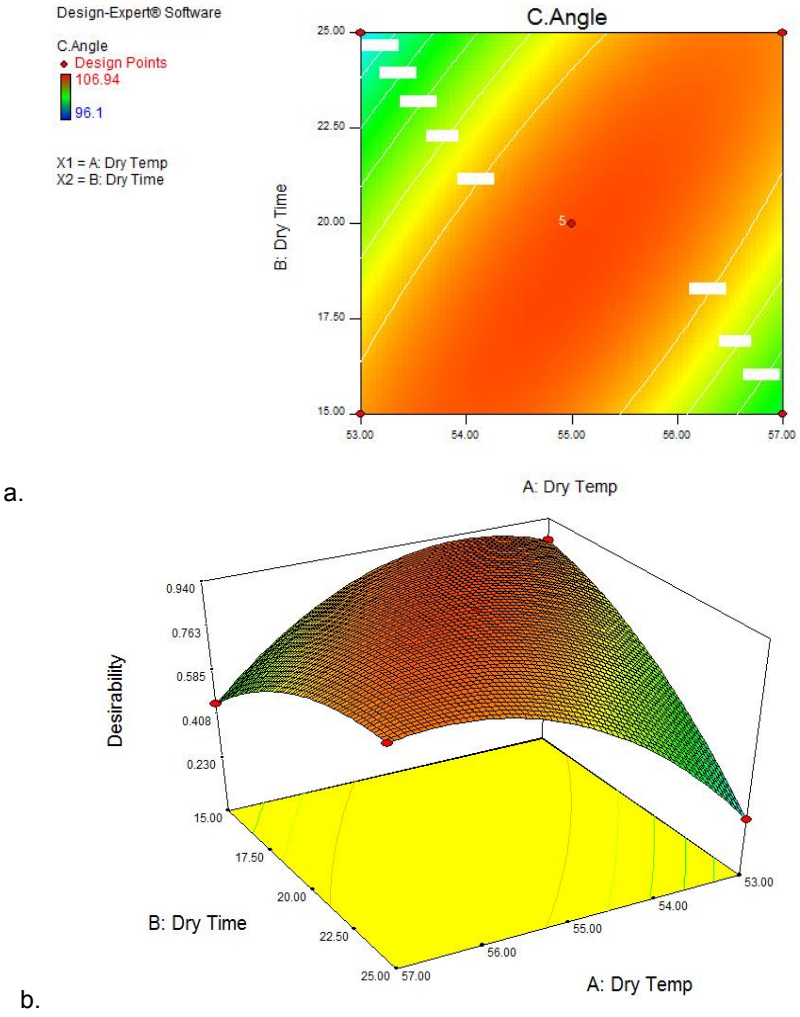

Fig. 6. Contour Plot (a) and 3D plot (b) for model graph

Table 8. Confirmation runs

Runs	Dry Temp. (°C)	Dry time (Min.)	Contact angle (°)		
			Actual	Predicted	Error (%)
1	55	20	106.73	106.1658	-0.531
2	57	15	100.03	101.0747	1.034
3	51	20	96.1	95.3858	-0.749
4	55	20	105.01	106.1658	1.089
5	55	10	98.69	102.7109	3.915

3.4.1 Structure and morphology

The cross section of the optimum membrane shown in Fig. 7 presents the spherical pores with 5000x magnification, indicating that membranes were formed via liquid-liquid TIPS [11,14]. The internal pore sizes could be estimated being between 0.64~1.27µm.

However, it can be observed that for the outer surfaces, the pores are hardly detected for both top surfaces and bottom surfaces. An anisotropic pore structure was formed as near to the membrane surfaces cooling rate was faster than inside the membrane. Increasing the cooling rate lead the porosity to decrease as the growth rate period was lower [22]. The white mark on the bottom surface is possibly because of the

crystallization due to the shift from the cloud point to dynamic crystallization curves when quench in water bath and may also because of the interface with the stainless steel mold.

A study by Yave, found that the porosity decreased as the initial concentration of polymer solution increased [22]. The results observed in the SEM micrographs confirm the assumption that lower porosity of the polymer solution concentrated of 25 wt% corresponds to the smaller pores and thus increased the hydrophobic than the lower concentration studied.

3.4.2 Chemicals composition study

The chemical composition of iPP did not change through the TIPS process, as shown in Fig. 8. The wavelengths of the raw iPP which was before undergoing the TIPS process show similarity with the membrane samples. The wavelengths of 2954.33 and 2917.58 show as indicated a strong intensity of C-H bond in the membrane sample. While, the frequencies detected for the raw iPP are 2953.73 and 2920.71 cm^{-1} denotes same intensity. The spectrum ranges correspond to the CH_3, CH_2 and CH consisting of 2 or 3 bands. There was another peak at the wavelength of 1456.89 and 1456.44 cm^{-1} for iPP membrane and raw iPP respectively, picturing the deformation of CH_2 and CH_3 with medium intensity. The wavelength of 1376.59 cm^{-1} may indicate for medium intensity deformation between C-H bond, but there was also possibility that medium intensity of the O-H bond due to the alcohol present in the sample. The similar wavelength obtained by raw iPP which 1376.31 cm^{-1}. There is also the spectrum at 688.19 in the membrane sample which picturing the intensity of the O-H bond, which is variable or weak.

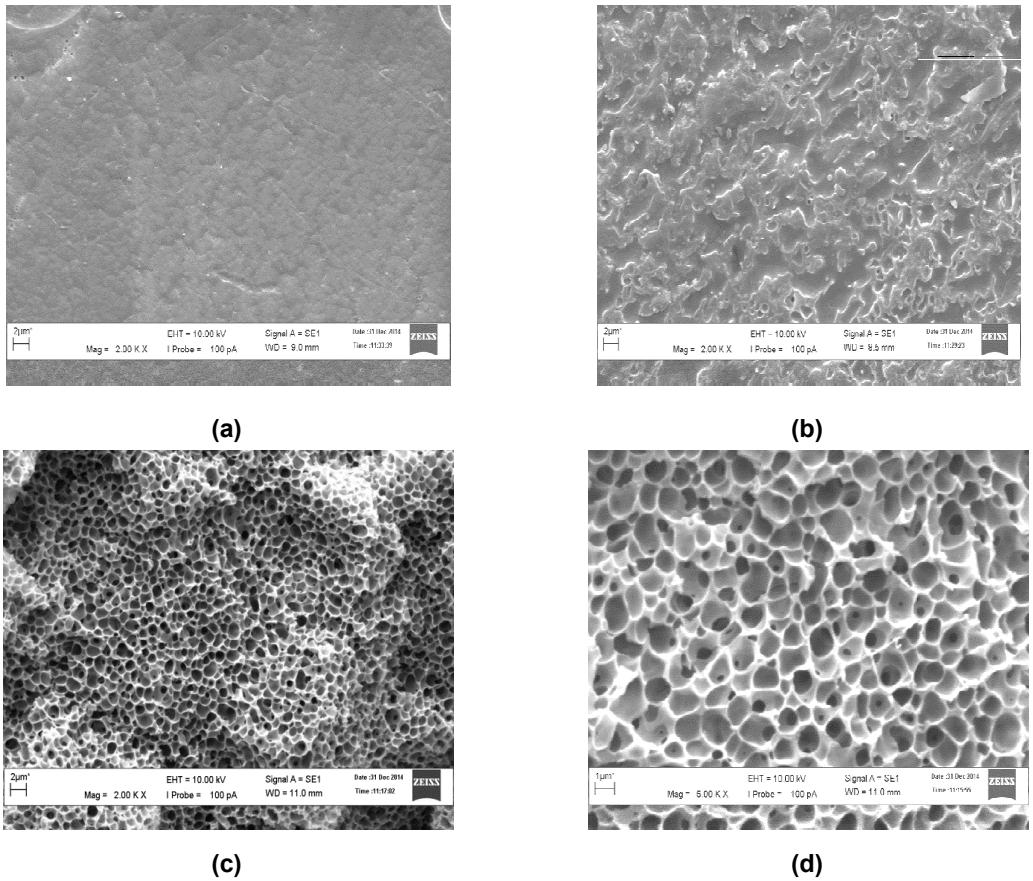

Fig. 7. Final morphologies and structure of PP-DPE membranes. Where a: top surface; b: bottom surface, c: cross section, magnification of 2.00kx and d: cross section, magnification of 5.00kx

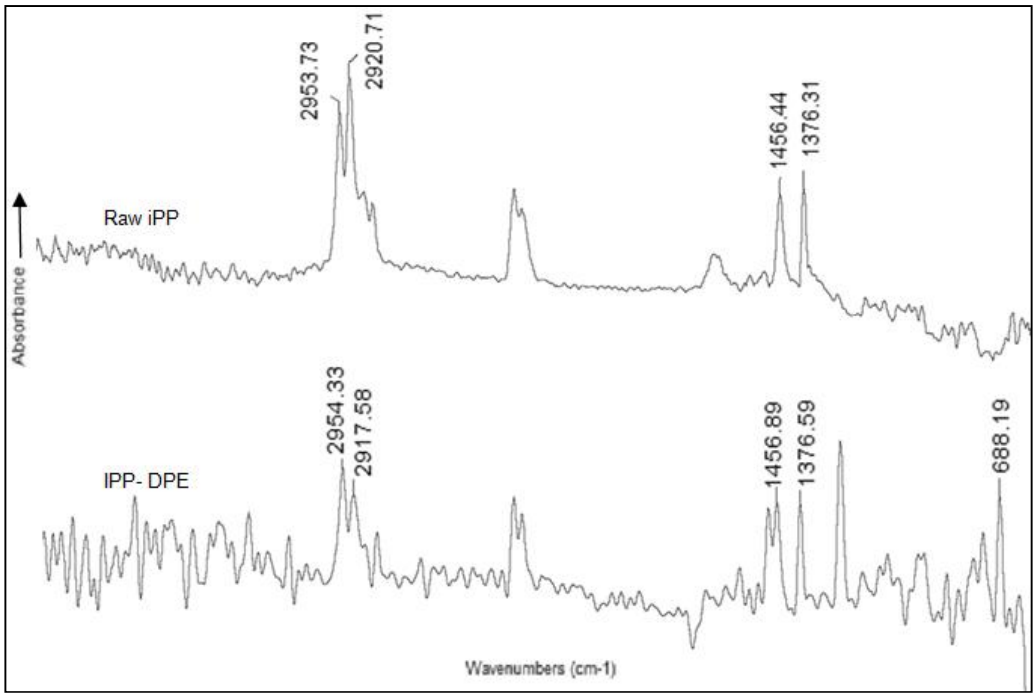

Fig. 8. FTIR spectrum of membrane with concentration 25 wt% using DPE diluents, immersion time of 5 h, dry temperature of 54.96 °C and dry time in 18.64 min

4. CONCLUSION

According to the 2-Level factorial design, the most significant contributions into characteristics of membranes made are drying temperature followed by drying time, immersion time and the concentration of polymer. The R^2 obtained in the model was 0.9550. The best conditions of PP-membrane were obtained at the concentration of 25 wt% and the immersion time of 5 h where these factors were constant for CCD. Meanwhile, temperature and drying time were the main factors chosen for CCD design. The CCD design exemplify a quadratic polynomial models with the coefficients of determines (R^2) for the response was 0.955%. However, the model has shown that lack of Fit was significant where the design was very sensitive and the response easily affected when there was changing on the variables. The most optimum membranes prepared in this experiment were those with the contact angle value of 106.22° by the interaction factors of drying temperature and drying time which are 54.96°C and 18.64 min respectively. The regression equation obtained from the 2-Level Factorial and Central Composite Design can be expected to apply in the preparation of iPP membranes using DPE diluents and can reasonably predict and optimize the performance of the iPP membranes.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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