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Thin Film Composite with Hybrid Membranes: Characterization and Performance Evaluation

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Abstract – *This paper reported on the preparation of thin film composite with hybrid membrane as a barrier for a particular application in crude glycerol purification. Glycerol was incorporated as an organic additive into hybrid membrane's formulation to impart further flexibility that would compensate the rigidity structure of the membrane as a result of cross-linking reaction. A response surface methodology based on two-level full factorial central composite face centered design was selected to optimize the preparation conditions for a hybrid membrane formulated with polymer and tetraethylorthosilicate (TEOS) concentrations and a weight percentage of water added to the feed solution. The optimum conditions needed to obtain the desired responses were a 5 wt.% polymer concentration and a 4 wt.% TEOS concentration for the formulation of the hybrid membrane, with 75% w/w of additional water being added to a crude glycerol solution. Results from characterizations revealed that the fabricated hybrid membrane has better thermal and mechanical properties, and surface hydrophilicity as compared to membrane from pure polymer and hybrid without glycerol. Due to its advantages over the existing purification process that employ membrane, the use of the fabricated thin film composite is a promising pathway for crude glycerol purification process.* ***Copyright © 2015 Penerbit Akademia Baru - All rights reserved.***

Keywords: Hybrid membrane; Optimization; Characterization; Crude glycerol purification

1.0 INTRODUCTION

In biodiesel production, crude glycerol, which consists of glycerol, free fatty acids, soap, salt, MONG (matter organic nonglycerol), methanol and water, is generated. The crude glycerol can be used directly as animal feedstuff, polyglycerols and glycerol esters, but the profit is marginal, unlike purified crude glycerol, which is in high demand as a raw material in the cosmetics, food and pharmaceutical industries [1]. The conventional process of crude glycerol purification involves several unit operations, such as filtration, chemical addition and vacuum distillation. However, the drawbacks in implementation of these processes lie with the high capital cost and energy consumption, which results particularly from vacuum distillation. Furthermore, separation of glycerol from higher boiling impurities will result in loss of glycerol due to its decomposition to undesirable impurities such as acrolein and allyl alcohol upon heating at temperatures of more than 150oC at atmospheric pressure [2].

Few researchers had emerged with new purification processes by employing membrane separation as the mechanism involved in their process [1, 3, 4] due to a broad range of applications in a sustainable energy could be accomplished by using membrane separation. For the purpose of diversifying applications of hybrid membrane, this research will report on crude glycerol purification through separation using thin film composite with a hybrid membrane as the barrier layer. As compared to membranes produced from pure polymer or pure inorganic materials, a hybrid membrane possesses better mechanical and thermal properties [5]. Besides that, water permeability of the membrane increases with the increase in silica nanoprecursor (TEOS) content during membrane formulation. This situation is caused by the formation of hydrogen bonding between organic phase and inorganic phase during the sol-gel reaction [6]. This outstanding property would benefit the crude glycerol purification process as water soluble material such as glycerol, water and methanol could permeate through the membrane.

In the area of membrane separation processes, construction of mathematical models that predict the response values is a useful approach to efficient and economical design of the separation processes. To obtain better membrane performance, the optimization of membrane preparation conditions, i.e., polymer and additive concentrations and pressure applied to the membrane, are highly important [7]. In this study, hybrid membrane preparation conditions particularly organic polymer and tetraethylorthosilicate need to be optimized. Statistical methods, such as response surface methodology and artificial neural networks are widely used to optimize these systems for a wide range of applications [8].In this study, response surface methodology (RSM) was used to optimize the formulation of a hybrid membrane for purification of crude glycerol.The main advantage of RSM is a significant reduction in the number of experimental runs needed to provide sufficient information for statistically valid results; it is an approach that is faster and more informative than the classical one-variable-at-a-time approach or the use of full factorial design [7]. Central composite rotatable design, which was introduced by Box and Wilson in 1951, has recently become the most popular design for fitting the second-order model [9]. This paper describes the use of central composite design to optimize the formulation of a hybrid membrane as the barrier layer and to investigate the optimum amount of water added to the feed solution. The Design-Expert Version 6.0 (Stat-Ease Inc., 2003) software was used to generate the experimental design, perform the regression analysis on the experimental data, estimate the coefficients of the regression equation and derive the optimum parameters for the variables.

In this study, a thin film composite (TFC) membrane, which consists of polysulfone as the base support and a hybrid membrane as the barrier layer, has been prepared. Hybrid membranes were formulated from polyvinyl alcohol (PVA) and polyethylene glycol (PEG) blended polymers with the addition of glycerol as an organic additive and cross-linked with tetraethylorthosilicate (TEOS) as inorganic silica nanoprecursors. The plasticizing effect of glycerol is expected to increase the free volume of the membrane that will compensate for its rigidity of structure as a result of higher cross-linking. The incorporation of glycerol could also increase the polymer chain mobility, which would subsequently improve the permeation flux [10]. The properties of the thin film composite (TFC) membrane were characterized using contact angle analyzer, Thermogravimetric Analysis (TGA), Differential Scanning Calorimeter and tensile strength instrument. For performance evaluation of the TFC, theflux rate, percentage of glycerol and NaCl concentration were evaluated in the permeate stream resulting from separation of crude glycerol solution through the TFC.

2.0 METHODOLOGY

2.1 Materials

For the preparation of thin film composite (TFC) membranes, the materials were polyvinyl alcohol with 87-89% degree of hydrolysis (molecular weight: 85000-124000 daltons), polysulfone resin pellets (molecular weight: 44,000-53,000 daltons), polyethylene glycol (molecular weight: 400 daltons), pure glycerol, tetraethylorthosilicate (99% purity) and hydrochloric acid (37% purity) as the catalyst. All of the chemicals were obtained from Sigma Aldrich, Malaysia. The chemical 1-methyl-2-pyrrolidone (purity 99%) was obtained from Merck, Malaysia. Deionized water was used as a solvent. Crude glycerol was obtained from one of the biodiesel manufacturers in Malaysia.

2.2 Preparation of the Thin Film Composite (TFC) Membrane

The thin film composite membrane has been prepared consisting of a polysulfone membrane as the base support and a hybrid membrane as the barrier layer.

2.2.1 Preparation of a Base Support Membrane

A phase inversion technique was employed in the preparation of the base support membrane. The polysulfone polymer solution was prepared by dissolving 11 g of polysulfone pellets into 89 g of 1-methyl-2-pyrrolidone as the solvent to yield a concentration of 11% w/w polymer solution. The mixture was stirred continuously at 60^{o}C until it became homogeneous. The mixture was subsequently left for several hours at room temperature for the removal of air bubbles. The polysulfone solution was cast onto a glass plate using a casting machine and adjustment of the thickness to 40-45 μm. The film was left at ambient temperature for 30 s before it was immersed in water as the coagulation medium for 1 h. The film was held in a large amount of water for 24 h, and the polysulfone film was subsequently cured in an oven at 45^{o}C for 1 h before preparation of the thin film composite [11].

2.2.2 Preparation of Hybrid Membranes

In the preparation of hybrid membranes, a measured amount of polyvinyl alcohol (PVA) was blended with polyethylene glycol (PEG) with a weight ratio of 9:1 [12]. A measured amount of water as the solvent was added to the mixture, and the mixture was heated at 90^{o}C until the mixture became homogeneous. Glycerol as an organic additive was added to the mixture at 10 % w/w from the total PVA/PEG blend.Then, the mixture was stirred at 90^{o}C for 15 min. The mixture was left to cool at room temperature. Using a sol-gel method, tetraethylorthosilicate (TEOS) as a nanoprecursor was added at various concentrations (1%, 2.5% and 4% w/w relative to the total polymer) to the solution.Hydrochloric acid (37 wt.%, 1 ml) was added to approximately 200 g of solution as the catalyst. The solution was then stirred continuously for 10 hat 30^{o}C.

2.2.3 Preparation of Thin Film Composites

The polysulfone membrane was placed on a glass plate. A hybrid membrane solution with a specific concentration was cast onto the polysulfone base support membrane as a thin layer by using a glass rod. The thin film composite membrane produced from this process was left for 24 h at room temperature and subsequently cured in an oven at 45^{o}C for 1 h [11].

2.3 Determination on Suitable Concentration of Organic Additive

Prior to the performance evaluation, suitable concentration of glycerol to be incorporated in hybrid membrane was determined. The selection was made due to glycerol acts as pore forming agent where high concentration of glycerol could increase the void fraction (free volume), which will subsequently reduce mechanical stability of a membrane [13]. Therefore, there is maximum concentration that could be incorporated into the hybrid formulation. To ascertain the selection, evaluation on the properties of the membranes was conducted. Three formulations had been prepared, which had varied concentrations of glycerol; 10, 20 and 30 % w/w polymer blend PVA/PEG. The formulations only contained polymer without TEOS. 10 wt.% was chosen as the minimum concentration as suggested by L. Shi et al. [14]. The details of the formulations were depicted in Table 1.

Table 1: Formulation of membranes with varied concentration of glycerol

Formulation code	**Materials**				
	PVA/PEG blend (wt.%)	Glycerol (wt.%) [w/w PVA/PEG blend]	TEOS (wt.%)	Total blended polymer (wt.%)	Water (wt.%)
F5Tg 10	4.55	0.45 [10]	0	5	95
F5Tg 20	4.17	0.83[20]	0	5	95
F5Tg 30	3.85	1.15 [30]	0	5	95

2.4 Optimization of Formulation of Hybrid Membranes and the Amount of Additional Water by Design of Experiment – Response Surface Methodology

2.4.1 Experimental Design

Three process variables were selected, i.e., the polymer concentration (A), the concentration of the silica nano-precursor (TEOS) (B) and the amount of additional water added to the feed solution (C), and these variables were optimized to yield the required level of responses. The range for each variable used in this experiment is shown in Table 2. Three responses were chosen for analysis: the permeate flux rate, the percentage glycerol permeated and the percentage salt rejection. The formulation series, which was generated by Design-Expert Version 6.0 (Stat-Ease Inc., 2003) are shown in Table 3.

Table 2: Actual levels of variables for the experimental design

Factors	Levels	
	Low	High
Hybrid membrane formulation		
(A) Polymer concentration (wt.%)	5	7
(B) TEOS concentration (wt.%)	1	4
Feed solution		
(C) Amount of additional water (%w/w)	50	100

Table 3: Experimental design

Standard run no.	Run	Block	Factors		
			Polymer conc. (%)	TEOS conc. (%)	Additional water (%)
19	1	1	6	2.50	75
5	2	1	5	1	100
2	3	1	7	1	50
6	4	1	7	1	100
1	5	1	5	1	50
11	6	1	5	2.5	75
16	7	1	6	2.5	75
9	8	1	6	4	75
13	9	1	6	2.5	50
10	10	1	7	2.5	75
17	11	1	6	2.5	75
7	12	1	5	4	100
8	13	1	7	4	100
15	14	1	6	2.5	75
18	15	1	6	2.5	75
12	16	1	6	1	75
4	17	1	7	4	50
14	18	1	6	2.5	100
3	19	1	5	4	50
20	20	1	6	2.5	75

2.4.2 Evaluation of Responses

2.4.2.1 Purification of a Crude Glycerol Mixture

Prior to the permeation test, the crude glycerol was diluted with de-ionized water at the selected percentages of 50% w/w, 75% w/w and 100% w/w. The formulations of the crude glycerol solutions are shown in Table 4.

Table 4: Formulations of crude glycerol solution

Compositions	Crude glycerol solutions		
Additional water (w/w)	50%	75%	100%
Crude glycerol (g)	200	200	200
Water (g)	100	150	200
Total solution (g)	300	350	400

The permeation test was conducted by pumping a crude glycerol solution through the thin film composite (TFC) membrane. The process was carried out using a fabricated membrane test machine, which consisted of a dead-end stirred cell resting on a magnetic stir plate. A thin-film composite (TFC) with a diameter of 4.7 cm was placed in the membrane housing. The crude glycerol solution was placed in the feed chamber, pressurized using nitrogen gas at 14 bars at room temperature and pumped through the TFC. The flow rate of the permeate stream was recorded after equilibration of the membrane and establishment of a steady-state. The volume of the permeate stream was measured after 1 h of operation, and the flux was calculated by dividing the volume by the cross-sectional area of the TFC. The compositions of the permeate stream in terms of glycerol content and sodium chloride (NaCl) concentration were determined using the glycerol content determination method and an ion meter, respectively.

The concentrations of the sodium chloride in the feed and permeate streams were determined by an ion meter (Eutech PC 2700 Meter), and the rejection rate was calculated using Eq. (1).

$$R(\%)=\left[1-\frac{C_p}{C_f}\right]x100 \tag{1}$$

where R is the rejection, and C_f and C_p are the concentrations of NaCl in the feed and permeate, respectively.

The glycerol content determination was conducted according to a standard method, ISO 2879-1975. The percentage permeation of glycerol was calculated using Eq. (2), where C_f and C_p are the concentrations of glycerol in the feed and permeate, respectively.

$$P(\%)=\left[\frac{C_p}{C_f}\right]x100 \tag{2}$$

The process was repeated twice with another piece of the TFC, and the average value of the responses was calculated.

2.5 Membrane Characterization

Hybrid membrane from the optimized formulation was characterized in terms of surface hydrophilicity, thermal stability and mechanical stability. The comparisons were done with a membrane without glycerol and membrane from pure polymer. Evaluations were conducted on four types of membranes namely F1, F1*, F10 and F13. F1* is a membrane from 5 wt.% pure polymer blend of PVA/PEG with the presence of 10 w/w glycerol. The properties were analyzed through several methods as describe in the next section.

2.5.1 Contact Angle

Hydrophilicity is one of the most important factors of membrane surface and water contact angle measurement is convenient way to assess the hydrophilicity and wetting characteristic of membrane [15]. A smaller contact angle correlates with a more hydrophilic surface and less fouling by free oils and concentrated oily emulsions. The contact angle analysis was performed by using VCA Water Surface Analysis System (AST Products Inc.). A drop of distilled water (2 µL) was placed onto the surface of the membrane and the contact angle was evaluated. The contact angle was measured at five different spots of the membrane surface and the average value was obtained.

2.5.2 Thermogravimetric Analysis (TGA)

Thermal stability of membranes were analyzed using a thermogravimetric analyzer (Mettler Toledo, model Star^{e} SW). The measurements were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min from 30^{o}C to 900^{o}C.

2.5.3 Tensile strength measurement

The properties were measured in the dry state at room temperature using a tensile strength instrument (Model: Instron) with 10 N load cell. Membranes with a thickness < 100 µm were cut into rectangular shape (4 mm width and 100 mm length) for the measurements of tensile strength, elongation and elastic modulus. The test method is according to ASTM D882, which is used for the determination of tensile properties of plastics in the form of thin sheeting with less than 1 mm thickness. This includes film which has been arbitrarily defined as sheeting having nominal thickness < 0.25 mm. From the stress-strain graph generated from the analysis, the tensile strengths, elongation and elastic modulus were determined. Tensile strength is the maximum stress the film can sustain before it actually fractures or amount of force necessary to pull a material apart. Elongation refers to the amount the material will stretch before breaking. Elastic modulus is a measure of the force required to deform the film. It is a measure of the film stiffness. The cross head speed was fixed at 50 mm/min and the gauge length was set at 25 mm [16]. Five samples were tested and the average value was recorded.

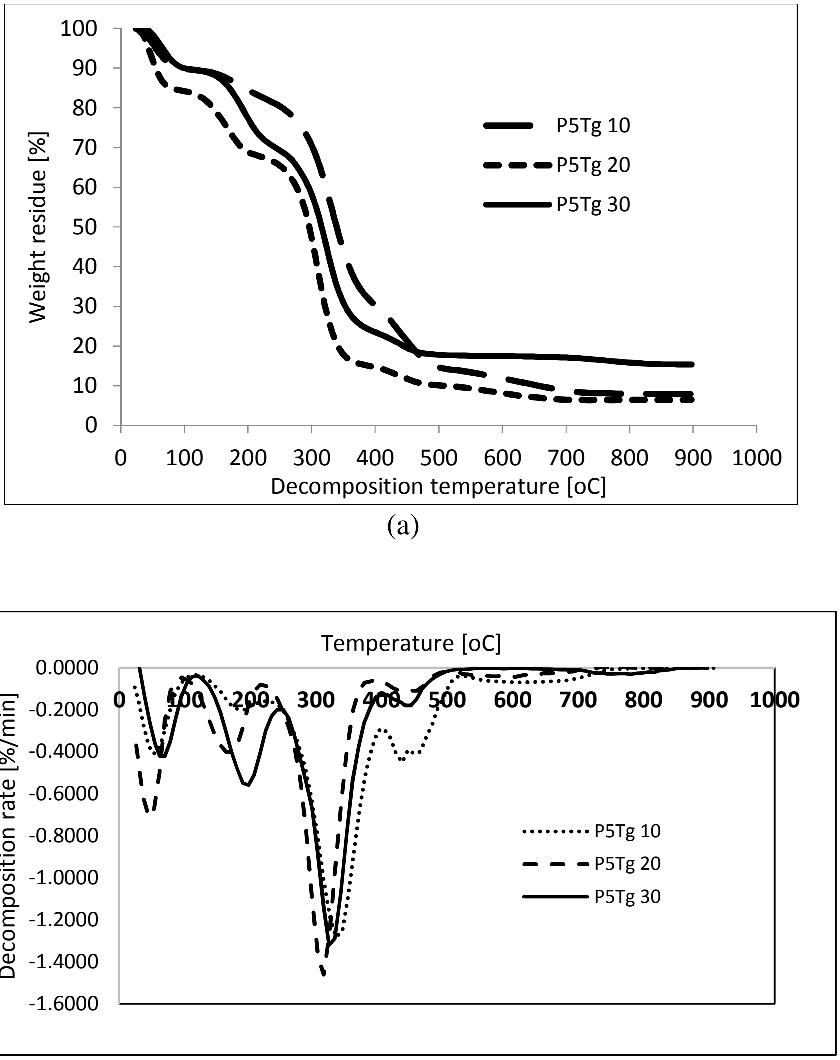
2.5.4 Measurement of Membrane's Surface Charge

The solute rejection performance of a nanofiltration membrane is normally affected by pH of a feed solution. The charged sites on nanofiltration membranes' surface for instance carboxylic group or sulfonic group are negatively charged at neutral and higher pH. Normally they lose their charge at acidic condition [17]. However, the pH dependency of each membrane should be determined as different manufacturers use their own method in the production of membrane layer. The surface charge of a hybrid membrane was measured by using a Zeta Potential Meter with Particle Sizer (Malvern). Prior to the measurement, crude glycerol solution diluted with 75% w/w water was prepared and pH of the solution was measured. Another two solutions with different pH have been prepared. pH of the solutions was adjusted by using 0.1 N sodium hydroxide. A film of hybrid membrane was cut into small pieces. Then, one piece of the film was added to each solution respectively. The film was left to settle down where the top layer of the solution was pumped out and filled into a test cell to measure its zeta potential. Then the test cell was placed into the closed container and the analysis was executed. The analysis was performed at three cycles. The result was reported in term of zeta potential value and the average value was recorded in mV unit. Zeta potential is a measure of the magnitude of electrostatic interactions between charged surfaces, where the formation is at the interface of a solid and a surrounding liquid. It represents the surface charge that occurs when functional groups dissociate on surface or when ions from the aqueous solution adsorb onto surfaces [18].

3.0 RESULTS AND DISCUSSION

3.1 Determination on Suitable Concentration of Organic Additive for Hybrid Membranes

Based on thermal characteristics evaluated through TGA, as compared with 10 wt.%, the incorporation of 20 wt.% of glycerol had reduced thermal stability of the membrane due to lower decomposition temperatures for each weight loss profile particularly at temperature less than 450ºC as depicted in Figure 1. Despite of higher weight loss observed for membrane with 30 wt.% glycerol at temperatures less than 450ºC but it is slightly more stable at temperature more than 450ºC as compared to that with 10 wt.% glycerol.



(a)

(b)

Figure 1: (a) and (b) TGA curves of membranes from 5 wt.% total polymer concentration with various concentration of glycerol

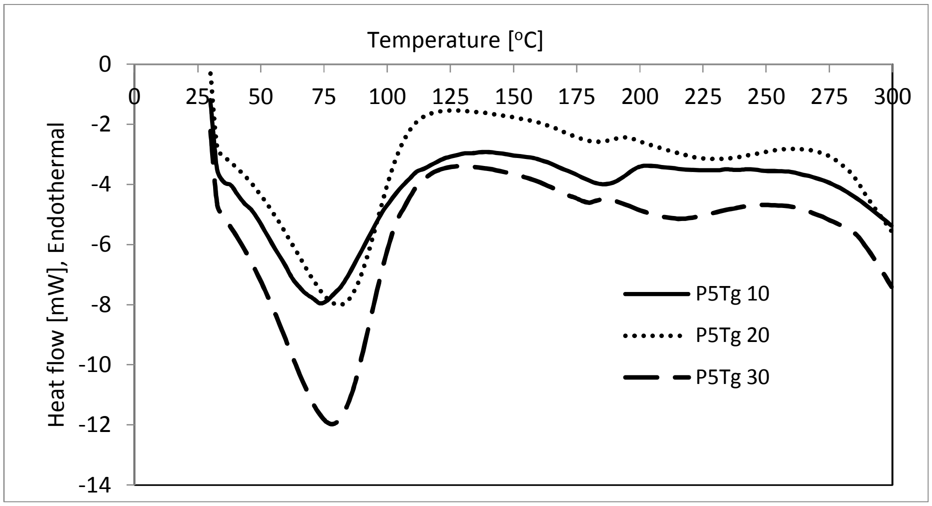


Figure 2: DSC spectra of membranes from 5 wt.% total polymer concentration with various concentration of glycerol

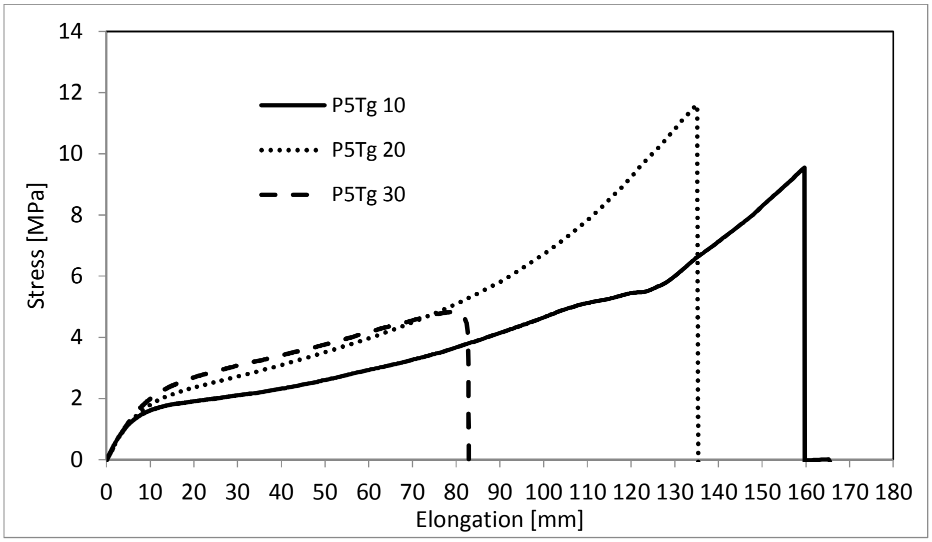


Figure 3: Stress vs elongation for membranes from 5 wt.% total polymer concentration with various concentration of glycerol

As shown in Figure 2 from thermal analysis by using DSC, by increasing the concentration of glycerol in the membrane's formulation, the first endothermic peak which corresponds to detachment of the water molecules and the hydroxyl end functional group has larger area as compared to other membranes. This situation is anticipated to happen due to a higher amount of glycerol molecules added during fabrication of membrane. In term of the plasticizing effect, a membrane with 10 wt.% glycerol has the lowest glass transition temperature (T_g) which is at 73.59 °C as compared to membranes with 20 wt.% (80.58 °C) and 30 wt.% glycerol (77.79 °C). The lowest T_g value indicated that 10 wt.% glycerol is sufficient to reduce the polymer chain stiffness as a result of cross-linking between polymer and inorganic component during hybrid membrane's formation. For the second endothermic peaks, all membranes exhibited almost the same decomposition temperatures.

Figure 3 depicts that an addition of 20 wt.% glycerol into the formulation has significantly increased the tensile strength and elastic modulus of the membrane but it suffers from lower elongation at break as compared to membrane with 10 wt.% glycerol. As shown in Table 5, further increase in its concentration (30 wt.%) has drastically reduced the membrane's mechanical stability particularly on tensile strength and elongation at break, but with higher elastic modulus. Higher elastic modulus with lower elongation at break signifies a membrane with a rigidity structure as a result of strong interaction with polymer blend.

Table 5: Mechanical properties of various membranes

Membrane	Tensile strength (MPa)	Elongation (mm)	Elastic modulus (MPa)
F5Tg 10	9.55	159.67	5.64
F5Tg 20	11.61	135.33	6.08
F5Tg 30	4.825	82.83	6.25

Therefore, based on thermal and mechanical stabilities analysis on the membranes, glycerol with 10 wt.% added to the polymer blend PVA/PEG had been selected as the optimum concentration for fabrication of hybrid membranes.

3.2 Optimization of Formulation

Results from design of experiment were tabulated in Table 6. Evaluations were made through ANOVA (analysis of variance).

3.2.1 ANOVA Analysis and Fitting of the Quadratic Model

To ensure a good model, a test was performed for the significance of the regression model and on the individual model coefficients as well as a test for lack-of-fit [19]. A summary of the effects of each variable on each response is normally represented using an ANOVA table.

Table 6: Experimental design and the results

Standard run no.	Run	Block	Factors			Responses		
			Polymer conc. (wt.%)	TEOS conc. (wt.%)	Additional water (% w/w)	Flux rate (l/day.m^2)	Glycerol permeated (%)	Salt rejection (%)
5	1	1	6	2.50	75	36.45	81.65	20.12
9	2	1	5	1	100	262.98	98.33	4.78
17	3	1	7	1	50	26	83	18.80
1	4	1	7	1	100	57.24	97.9	16
18	5	1	5	1	50	28.33	85.2	16.63
7	6	1	5	2.5	75	55.19	90.74	23.01
12	7	1	6	2.5	75	37	80	25
20	8	1	6	4	75	37.29	80	35
13	9	1	6	2.5	50	15.54	70	30
4	10	1	7	2.5	75	30	78	38
10	11	1	6	2.5	75	36	79	27
6	12	1	5	4	100	60.48	89.33	13.97
19	13	1	7	4	100	58.3	91.09	20.67
8	14	1	6	2.5	75	38	82	24
11	15	1	6	2.5	75	33.17	78	28
2	16	1	6	1	75	54.12	88	10
15	17	1	7	4	50	16	70	60
3	18	1	6	2.5	100	45	85	3.26
16	19	1	5	4	50	24	75	43.98
14	20	1	6	2.5	75	45.86	83	20

3.2.1.1 Permeate Flux Rate

As shown in Table 7, flux rate which was represented by quadratic model is significant as *P*-value is less than 0.05 [7]. The main effect and the quadratic effect of amount of water added to the feed solution and TEOS concentration, and the main effect of polymer concentration are significant model terms. The main effect of the amount of additional water are the most significant factor associated with flux rate because water is functioning as viscosity modifier [20] and the increase in viscosity of solution is normally caused by formation of aggregates [21]. The formation of aggregates will immobilize part of the matrix fluid inside them and then increase the effective solids volume fraction in the suspension [21]. The presence of water actually has reduced the interfacial tension of the crude glycerol solution which in turn could assist in the formation of small droplet particle diameter. This is due to the fact that the average size of glycerol molecules is 7 times larger than that of water molecules and the value of the energy of binary interaction in glycerol is 3 times larger than that of molecules in water [22]. Adjusted R^2-value calculated is 0.8946, which is >0.75 that indicates the appropriateness of the model [19]. This value indicates that 89.46% of the variability of the response obtained from the experiment could be explained by the model. The empirical model in term of the actual factors is shown as follows:

$$\text{Flux rate} = [1/(0.33544 + 0.017497{*}\text{polymer} + 0.068981{*}\text{TEOS} - 0.00805222{*}\text{additional water} - 0.011614{*}\text{TEOS}^2 + 4.06328\text{x}10^{-5}{*}\text{additional water}^2)]^2 \quad (3)$$

Table 7: ANOVA Table (Partial sum of squares) for response surface reduced quadratic model (response: flux rate)

Source	Sum of squares	DF	Mean Square	*F*-value	*P*-value	Prob.>*F*
Model	0.032	5	$6.468\text{x}10^{-3}$	33.25	< 0.0001	significant
A	$3.062\text{x}10^{-3}$	1	$3.062\ \text{x}10^{-3}$	15.74	0.0014	
B	$2.679\text{x}10^{-3}$	1	$2.679\ \text{x}10^{-3}$	13.77	0.0023	
C	0.024	1	0.024	123.07	< 0.0001	
B^2	$2.185\text{x}10^{-3}$	1	$2.185\ \text{x}10^{-3}$	11.23	0.0048	
C^2	$2.064\text{x}10^{-3}$	1	$2.064\ \text{x}10^{-3}$	10.61	0.0057	
Residual	$2.724\text{x}10^{-3}$	14	$1.945\text{x}10^{-4}$			
Lack of fit	$2.353\text{x}10^{-3}$	9	$2.615\text{x}10^{-4}$	3.53	0.0892	Not significant
Std. Dev.	0.014		R^2	0.9223		
Mean	0.16		Adjusted R^2	0.8946		

3.2.1.2 Percentage of Glycerol Permeated

Based on ANOVA table as shown in Table 8, the main effects of TEOS concentration and the amount of additional water, and the quadratic effects of the polymer are significant model terms. The adjusted R^2-value calculated is 0.8474, which is closed to 1 and it implied that only 15.26 % of the total variation that could not be explained by the model. This indicates the accuracy of the model [7]. The empirical model in term of the actual factors is as follow:

$$\text{Percentage glycerol permeated} = 263.115 - 64.189{*}\text{polymer} - 3.134{*}\text{TEOS} + 0.31380{*}\text{additional water} + 5.194{*}\text{polymer}^2 \quad (4)$$

3.2.1.3 NaCl Rejection

Results of response surface quadratic model for NaCl rejection in the form of analysis of variance are given in Table 9. The main effects of polymer and TEOS concentrations, and an amount of additional water, the quadratic effects of polymer concentration and the amount of additional water, and the interaction effect between TEOS concentration and the amount of additional water are significant model terms. The most significant factors affecting the salt rejection are the main effects of TEOS concentration and amount of additional water respectively. Salt rejection was significantly affected by TEOS concentration due to the increased interaction between ions in solution with the denser membrane surface [23] at higher concentration of TEOS. In contrast, higher amount of additional water would lower the interaction due to reduction on the viscosity of feed solution that will subsequently reduce the NaCl rejection.

Table 8: ANOVA Table (Partial sum of squares) for response surface reduced quadratic model (response: Percentage glycerol permeated)

Source	Sum of squares	DF	Mean Square	*F*-value	*P*-value	Prob.>*F*
Model	1005.96	4	251.49	27.38	<0.0001	Significant
A	34.63	1	34.63	3.77	0.0712	
B	220.99	1	220.99	24.06	0.0002	
C	615.44	1	615.44	67.00	<0.0001	
A^2	134.89	1	134.89	14.69	0.0016	
Residual	137.78	15	9.19			
Lack of fit	119.28	10	11.93	3.22	0.1042	Not significant
Pure error	18.50	5	3.70			
Std. Dev.	3.03		R^2	0.8795		
Mean	83.26		Adjusted R^2	0.8474		

Table 9: ANOVA Table (Partial sum of squares) for response surface reduced quadratic model (response: salt rejection)

Source	Sum of squares	DF	Mean Square	*F*-value	*P*-value	Prob.>*F*
Model	3209.35	6	534.89	46.57	< 0.0001	Significant
A	261.12	1	261.12	22.73	0.0004	
B	1153.69	1	1153.69	100.44	< 0.0001	
C	1226.11	1	1226.11	106.74	< 0.0001	
A^2	170.27	1	170.27	14.82	0.0020	
C^2	138.57	1	138.57	12.06	0.0041	
BC	373.87	1	373.87	32.55	< 0.0001	
Residual	149.33	13	11.49			
Lack of fit	92.27	8	11.53	1.01	0.5201	Not significant
Pure error	57.05	5	11.41			
Std. Dev.	3.39		R^2	0.9555		
Mean	23.91		Adjusted R^2	0.9350		

The adjusted R^2-value calculated is 0.9350 which is closed to 1 and it implied that only 6.50% of the total variation that could not be explained by the model. The empirical model in term of the actual factors is as follow:

Salt rejection = 177.40208 – 82.42250*Polymer + 20.83317*TEOS + 1.59218*additional water + 7.29437*Polymer^2 - 0.010529*additional water^2 - 0.18230* TEOS*additional water

(5)

The models described by Eqs. (3.1)-(3.3) could be used to predict the flux rate, the percentage of glycerol permeated and the salt (NaCl) rejection within the limits of the experiment.

3.2.2 Optimization of the Purification Process

In order to optimize the process variables for the purification of crude glycerol by numerical optimization technique, SOLVER program in Microsoft Excel has been used. The main targets are high percentage permeation of glycerol which is more than 80 % and high NaCl rejection which is more than 35 % with more than 35 L/m^2.day of flux rate. Equation (5) was used as the main target and a set of parameter, which comprises Eqns. (3) and (4) was determined. The resulted optimum conditions to obtain the main target were 5% polymer concentration, 4% TEOS and 75% additional water. Table 10 shows the percentage errors between the predicted and actual values for three responses, which was obtained from performance testing by using the resulted optimum conditions. Based on Table 10, besides high percentage error for flux rate, the regression equations generated from the response surface methodology were accurate in predicting glycerol permeated and NaCl rejection because the actual values were sufficiently close to the predicted values.

Table 10: The percentage errors between the predicted and actual experimental values

Parameters	Flux rate (L/m^2.day)	Glycerol permeated (%)	NaCl rejection (%)
Predicted value	53	83	36.52
Experimental value	43	85	36
Percentage error	23.25	2.35	1.44

3.3 Membrane Characterization

3.3.1 Contact Angle Measurement

As shown in Table 11, all thin film composites membranes showed increased in a hydrophilicity compared to the porous support membrane, which indicated through lower contact angle value. This situation is due to membranes formulated from polyvinyl alcohol are in general hydrophilic unlike polysulfone, which is hydrophobic [24]. An increase in contact angle value for hybrid membranes with the incorporation of 4 wt.% TEOS was due to cross linking reaction that led to exhaustion of hydroxyl group. However the presence of glycerol had compensated the effect, which was observed through lower contact angle of F10 as compared to F13. This situation would justify that the presence of glycerol contributes towards improving the hydrophilicity of the membrane surface.

3.3.2 Thermogravimetric Analysis (TGA)

In this study, thermogravimetric analyzer had been used to investigate thermal stability of membranes. Based on TGA analysis as shown in Figure 4, similar decomposition profiles were portrayed by F1 and F1* until ~ 350 ^{o}C but higher weight loss was portrayed by F1 at above 350 ^{o}C which revealed that a degradation temperature of membrane incorporated with glycerol is higher than that from polymer blend PVA/PEG. A strong interaction between polymer blend and glycerol through formation of hydrogen bonds would explain the improvement in thermal stability [25]. As for a hybrid membrane (F10), the presence of glycerol also has increased the thermal stability of the membrane slightly, as exhibited by the increase in the weight residue at 900 °C as compared to that without glycerol (F13). This result should confirm that glycerol is covalently bonded in the polymer matrix through a cross-linking reaction with TEOS (Figure 5) [26] that would prevent the leach-out of glycerol from the membrane during the separation process of crude glycerol.

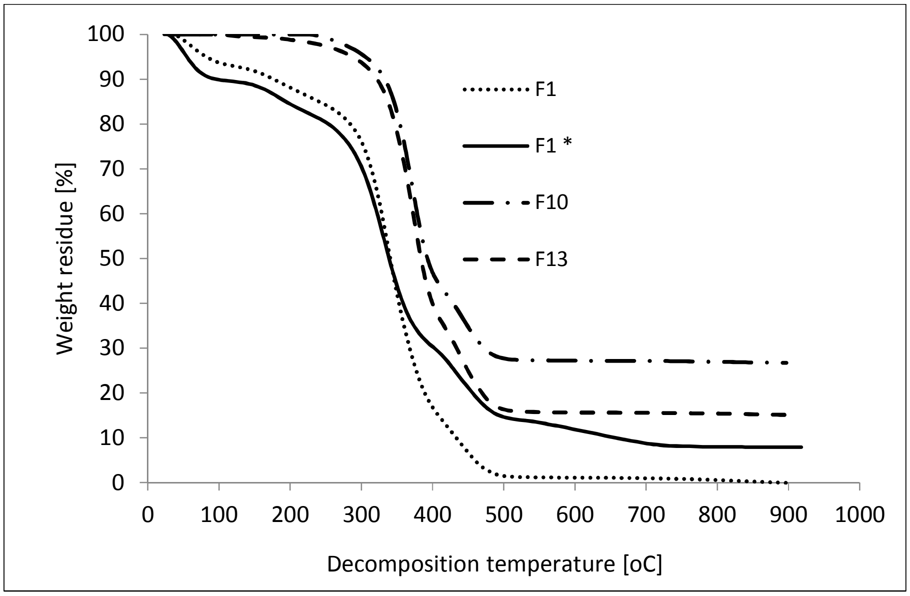
Table 11: Contact angle for porous support membrane and thin film composite membrane from various formulations

Membrane	Contact angle (°)
Porous support polysulfone	75
TFC with F1 [TEOS 0 wt.%, glycerol 0 %]	47
TFC with F1* [TEOS 0 wt.%, glycerol 10 %]	43
TFC with F10 [TEOS 4 wt.%, glycerol 10 %]	50.98
TFC with F13 [TEOS 4 wt.%, glycerol 0 %]	53.68

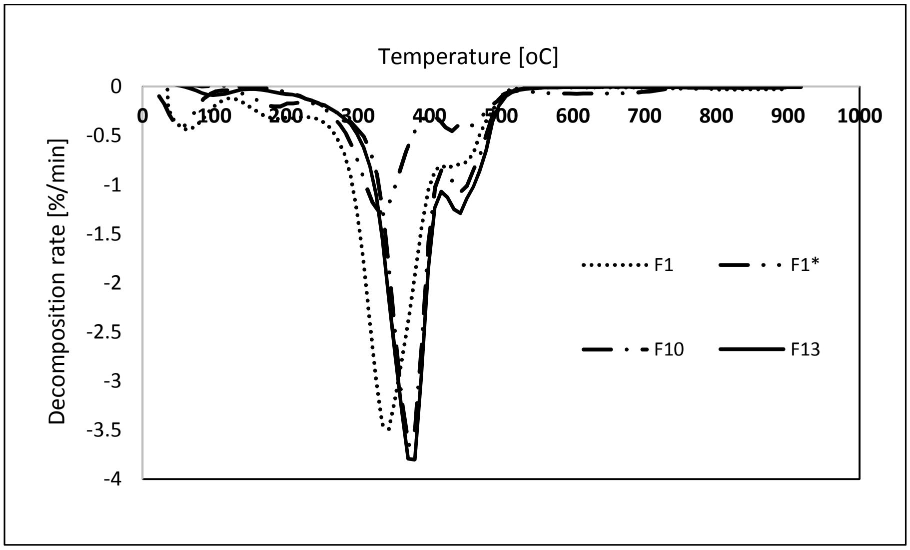
3.3.3 Mechanical Stability of Membranes

Based on Figure 6, membranes from hybrid formulations (F10, F13) exhibited higher tensile strength and elongation as compared to membrane from pure polymer blend (F1 and F1*). This result had ascertain the claim that cross-linking reaction between organic and inorganic materials resulted in better mechanical properties of the resultant hybrid membrane. It is clearly shown that the incorporation of glycerol in the pure polymer blend (F1*) has improved the tensile strength and elongation at break of the membrane. As for the hybrid membranes, the mechanical properties of membrane F10, which consists of 10 wt.% glycerol improved significantly as compared to that without glycerol (F13). Based on the figure, it was obvious that a hybrid membrane incorporated with glycerol has higher tensile strength (30.22 kPa) and elongation (154.92 mm) as compared to that without it (tensile strength 15.98 kPa, elongation 69.92 mm). However, based on the elastic modulus values as shown in Table 12 which is determined from the slope of the initial linear portion of the stress vs strain curve, F13 has higher elastic modulus (113.78 Mpa) as compared to F10 (48.82 Mpa). Elastic modulus represents the stiffness of membrane F13 which is resistance to elastic strain [16] and further confirmed through lower elongation that is attributed to the reduction in the ductibility of the membrane [27].

Generally, the presence of silica in the hybrid membrane could increase the mean distance between polymer chains which causes the increase in stiffness of the polymer structure due to restricted segmental motion [28] that leads to increase in the elastic modulus. The presence of glycerol as the plasticizer has reduced the rigidity structure of the hybrid membrane that is observed through lowering the elastic modulus [29]. Besides that, synergistic effect of glycerol with the cross-linking network portrayed by organic-inorganic materials would substantiate the enhancement in the mechanical properties of the hybrid membrane [30]. Although the incorporation of glycerol has increased the elastic modulus of F1 but the value is marginal and it has been compensated with higher elongation.

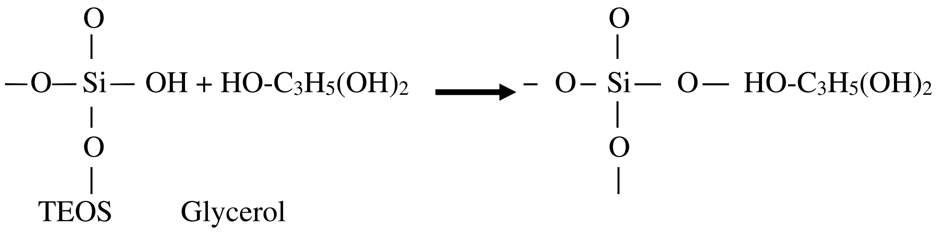


(a)



(b)

Figure 4: (a) and (b) TGA curves of membranes from various formulations with 5 wt.% total polymer concentration



$$-\text{O}-\overset{\overset{\text{O}}{|}}{\underset{\underset{\underset{|}{\text{O}}}{|}}{\text{Si}}}-\text{OH} + \text{HO-C}_3\text{H}_5(\text{OH})_2 \longrightarrow -\text{O}-\overset{\overset{\text{O}}{|}}{\underset{\underset{\underset{|}{\text{O}}}{|}}{\text{Si}}}-\text{O}-\text{HO-C}_3\text{H}_5(\text{OH})_2$$

Figure 5: Reaction mechanism between TEOS and glycerol

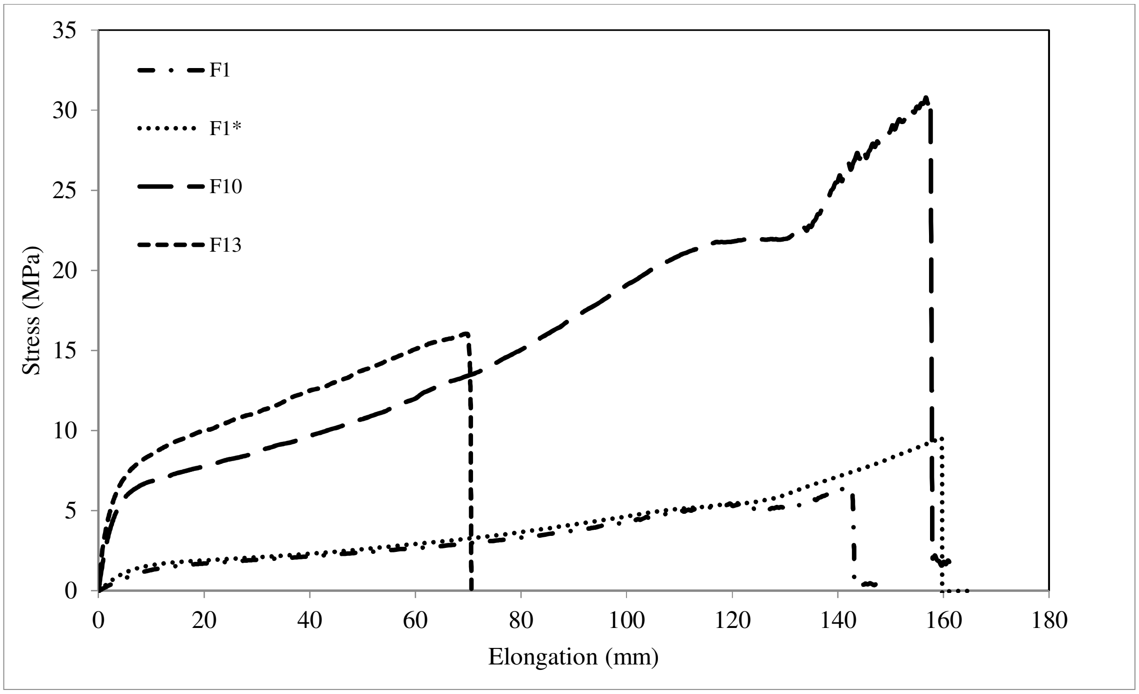


Figure 6: Stress vs elongation for membranes from various formulations with 5 wt.% total polymer concentration

Table 12: Mechanical properties of various membranes

Membrane	Tensile strength (MPa)	Elongation (mm)	Elastic modulus (MPa)
F1	6.456	141.8	3.925
F1*	9.55	159.67	5.6381
F10	30.22	154.92	48.82
F13	15.98	69.92	113.78

3.5 Mechanism of Crude Glycerol Purification Process via Membrane

Based on the above result, the thin film composite showing the nanofiltration behaviour due to rejection of NaCl is between 20 to 50% [17]. There are two mechanisms that best describe the separation performance of nanofiltration membranes namely solution-diffusion and pore flow models. The transition between pore flow and solution diffusion transport seems to occur with membranes having very small pore size. Ultrafiltration membrane that rejects sucrose and raffinose but allowing the passage of all micro-ions are following pore flow model, whereas the reverse osmosis membrane that is good in rejecting the sodium chloride clearly follows the solution-diffusion model. The transition between these two models is in the nanofiltration range where the membranes are good in rejecting divalent ions and most organic solutes but rejecting monovalent ions in the range of 20 to 70%. The performance of this type of membrane, which is a family of nanofiltration membranes are shown in Table 13. Table 13 shows the rejection performance of three types of nanofiltration membranes on micro solutes. The FT-30 is clearly exhibited a good reverse osmosis behaviour whereas the XP-20 is a very small pore flow ultrafiltration membrane. The XP-45 is in the intermediate between these two behaviours [31].

Based on the performance of the resultant TFCs with barrier layer from formulated hybrid membrane during purification process of crude glycerol, TFCs exhibit a transition type of membrane which has similar characteristic as XP-20 with a pore flow model as the transport mechanism through a membrane. Furthermore, the combination of extraordinarily high permeability with very high free volume hints at a pore flow contribution. It is anticipated that glycerol as uncharged solute would permeate through the membrane based on the pore size. The transportation of uncharged solute through nanofiltration, ultrafiltration and microfiltration membranes is through sieving or steric exclusion where a separation between two different uncharged solutes is based on their size and shape [17]. As described through pore models, the molecular width is a useful parameter rather than the molecular length to estimate the rejection of uncharged solutes, even though the solutes permeation includes both effects from diffusive and convective transport [32]. Therefore, glycerol from the crude glycerol solution with a molecular length of 0.8283 nm and molecular width of 0.2788 nm could permeate through the fabricated thin film composite membrane without much resistance. This mechanism would justify the significant higher percentage of glycerol permeated through the thin film composite with hybrid membrane as a barrier layer. High free volume of the hybrid membranes was resulted from the incorporation of glycerol in its formulation.

Based on results obtained from zeta potential analysis as shown in Table 14, the surface of the fabricated hybrid membrane is negatively charged at pH 6.52, which is the actual pH of feed solution without undergoing the neutralization process by using 0.1 N NaOH. Even at higher pH for instance 7.82, there is a slight increase in the negative charge of the membrane that is represented by an increase in the negative value of zeta potential. This analysis has ascertained the claim made in this report that the rejection of sodium chloride salt from a crude glycerol solution is due to negative charge of a hybrid membrane layer. Apart from affecting the electrostatic repulsion between the charged molecules and the membrane surface, pH of a feed solution could affect the openness of a membrane due to dissociation of membrane functional groups [33].

Table 13: Rejection of microsolutes by nanofiltration membranes

Solute	**Solute rejection (%)**			
	FT-30	XP-45	XP-20	Fabricated membranes
NaCl	99.5	50	20	30-50
$MgCl_2$	>99.5	83	-	-
$MgSO_4$	>99.5	97.5	85	-
$NaNO_3$	90	< 20	0	-
Ethylene glycol	70	24	11	-
Glycerol	96	44	15	15-20
Glucose	99	95	60	-
Sucrose	100	100	89	-

Table 14: Zeta potential values of membrane at various pH of feed solutions

pH of solution	**Zeta potential (mV)**	
	Solution without membrane	**Solution with membrane**
6.52	-3.50	-3.91
7.07	-3.14	-4.22
7.82	-2.42	-4.35

4.0 CONCLUSION

Based on the characterization results, it was obvious that hybrid membranes have better thermal and mechanical stabilities, and higher surface hydrophilicity than porous support and membrane from pure polymer. The incorporation of 10 wt.% glycerol in the polymer blend had resulted in the enhanced flexibility of membrane's matrix as well as good thermal and mechanical properties especially in term of elongation. These properties had overcome the rigidity structure and brittleness of ordinary hybrid membranes. The optimum formulation of hybrid membrane was obtained at 5% polymer and 4% TEOS, with 75% additional water for feed solution. Results from performance evaluation show that the regression equations generated from the response surface methodology were accurate in predicting percentage glycerol permeated and NaCl rejection because the actual values were sufficiently close to the predicted values. However, high percentage error was observed for flux rate (23.25%). The fabricated thin film composite, which exhibits a nanofiltration behaviour with pore flow model characteristics is a promising pathway for crude glycerol purification as it offers few advantages over the other processes that employ membranes such as operation at low pressure and at room temperature.

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