

Performance of Thin Film Composite in the Purification of Crude Glycerol

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Abstract—The use of membranes have been found to solve the issue of high operating cost in crude glycerol purification process due to its operation at ambient temperature and do not incorporate any chemicals. The use of a hybrid membrane in crude glycerol purification would benefit from its higher mechanical and thermal stability with enhancement in hydrophilicity for permeation of water soluble material. This paper reported on the use of thin film composites (TFCs) with a hybrid membrane as the barrier layer for the purification of crude glycerol. The TFCs were characterized by Fourier Transform Infra Red (FTIR), Thermal Gravitational Analysis (TGA), Scanning Electron Microscopy (SEM) and water contact angle. The effects of incorporating glycerol in the hybrid membrane formulation had been investigated through flux rate measurement, percentage glycerol permeated and NaCl rejection from the purification of crude glycerol. The aim of the purification process is higher NaCl rejection and higher recovery of glycerol with sufficient volume of flux. Results showed that the incorporation of glycerol in the hybrid membrane formulation had resulted in the increase of porosity and thermal stability of the barrier layer, which had subsequently increased the glycerol recovery with comparable values of flux rate and NaCl rejection as compared to that without glycerol.

Keywords- *hybrid membrane, thin film composite, characterization, performance evaluation*

I. INTRODUCTION

Crude glycerol is highly generated from biodiesel production where it consists of glycerol, free fatty acid, soap, salt, MONG (matter organic non-glycerol), methanol and water. Crude glycerol in raw form can be used directly but the value is marginal unlike purified crude glycerol, which is highly demanded in cosmetic, food and pharmaceutical industries [1]. The conventional process of crude glycerol purifications involves several steps such as filtration, chemical addition and vacuum distillation. However the drawbacks in implementing this method lie with the high capital cost and energy consumption, which is imposed by vacuum distillation. Furthermore, separating of glycerol from higher boiling point of impurities will be resulted in losses of glycerol due to decomposition to by products such as acrolein and allyl alcohol [2]. Ion exchange method on the other hand is suitable for smaller capacity plants and most importantly for salt-free crude glycerol. This method

involves passing the crude glycerol through beds of a strong cation, a weak anion and a mixed bed of strong cation-anion resins. Traces of free fatty acids, colour, odour and other mineral impurities will be eliminated by the resin beds [3]. Although the ion exchange method is simple in operation and has low energy consumption but it needs large ion exchange resin that could imposed on high cost for regeneration process. Besides that, the regeneration process produces higher amount of acidic water, which requires further treatment.

Realizing that a broad range of applications in sustainable energy could be accomplished by using membrane, several researchers had come out with a method to purify crude glycerol by employing membrane in their processes [1,4,5].

In the report by Sdrula [1], the EET Corporation had come out with one technology to purify crude glycerine obtained from biodiesel production. The process, which combines high efficiency electrodialysis and nanofiltration had been proven to provide economical solution for the purification and recovery of glycerine where it could improve efficiencies, product recovery and finished product quality. In the patented process [4], the crude glycerol obtained from transesterification process is purified through a series of two or more nanofiltration or reverse osmosis membrane where at least one of the membranes has a contact angle between 44° to 56°. As the crude glycerol contain salts such as NaCl, Na₂SO₄ or NaHCO₃, a yield about 99% purity of glycerol could be achieved. In the patent filed by Traving et al. [5], the salt free permeate stream was obtained after purification of crude glycerol through nanofiltration polymer membrane, which has pore size between 0.01 µm to 0.05 µm.

As compared to membranes produced from pure polymer or pure inorganic materials, a hybrid membrane possesses better mechanical and thermal properties [6]. 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 [7]. This outstanding property would benefit the crude glycerol purification process as water soluble material could permeate through the membrane. As reported in the previous paper [8] in the separation process of synthesized crude glycerol, higher permeation

of continuous phase of glycerol-water mixture with sufficient percentage of NaCl rejection and volume of flux had been observed through the thin film composites (TFC) with hybrid membrane as the barrier layer. For actual observation, this paper describes the application of the TFC for the purification of pure crude glycerol solution. The effect of the hybrid layer as well as the incorporation of glycerol in the formulation had been evaluated in term of the permeate flux rate, percentage glycerol permeated and NaCl rejection. The aim of the purification process is higher NaCl rejection and higher recovery of glycerol with sufficient volume of flux. Besides performance testing, the TFCs were characterized by Fourier transform infrared (FTIR) spectroscopy, thermal gravitational analysis (TGA), scanning electron microscopy (SEM) and water contact angle analysis.

II. MATERIALS AND METHODS

A. Materials

For the preparation of thin film composite membrane, the material were polyvinyl alcohol with degree of hydrolysis of 87-89% (molecular weight: 85000-124000), polysulfone resin pellet (molecular weight: 44,000-53,000), polyethylene glycol (molecular weight: 400), pure glycerol, tetraethylorthosilicate with 99% purity as silica nano-precursor, and hydrochloric acid with 37% purity as the catalyst. All the chemicals were obtained from Sigma Aldrich, Malaysia. 1-methyl-2-pyrrolidone with purity of 99% was obtained from Merck, Malaysia and deionized water as solvent. Crude glycerol was obtained from one of the biodiesel manufacturers in Malaysia.

B. Methods

1) Preparation of a hybrid membrane

In the preparation of a hybrid membrane, sol-gel method was employed. The sol-gel reaction involves the hydrolysis of silica nanoprecursor (TEOS) and condensation of the resulting hydroxyl groups to form a nanostructure [9]. The measured amount of polyvinyl alcohol (PVA) was blended with polyethylene glycol (PEG) with a weight ratio of 9:1 [10]. A measured amount of deionized water as solvent was added to the mixture and the solution were heated at 90°C until homogeneous solution was obtained. Glycerol acted as organic additive was added to the solution, which was then stirred at 90°C for 15 minutes. The mixture was left to cool down at room temperature. By using sol-gel method, tetraethylorthosilicate (TEOS) as nano precursor at fixed concentration was added at to the solution. Then, 1 ml of hydrochloric acid (37% purity) was added as the catalyst. The solution was continuously stirred for 10 hours at 30°C. The composition of PVA, PEG, glycerol and TEOS used in the preparation of the hybrid

membrane for this study was shown in Table 1. One formulation which had given the best performance during the purification of synthetic crude glycerol had been selected for further evaluation. Another three formulations were selected for comparison purpose, which comprise of polysulfone membrane, TFC with barrier layer from pure blended polymer and TFC with barrier layer from hybrid membrane but without the incorporation of glycerol.

TABLE 1
FORMULATION OF HYBRID MEMBRANE

Materials	Formulation code		
	F1	F2	F3
Blended polymer, PVA:PEG (weight ratio)	9:1	9:1	9:1
Glycerol (wt.% blended polymer)	0	0	10
TEOS (wt. % total polymer)	0	4	4
Total polymer + TEOS (wt.%)	5	5	5
Water (wt.%)	95	95	95

2) Preparation of micro porous support membrane

In the preparation of support membrane, phase inversion technique was employed. Polysulfone polymer solution was prepared by dissolving specific amount of polysulfone pellet into 1-methyl-2-pyrrolidone as the solvent to yield 11% wt/wt concentration of polymer solution. The solution was continuously stirred at 60°C until homogeneous solution was achieved. Then, the solution was left for several hours at room temperature for the removal of air bubbles. By using the casting machine and by adjusting the thickness to 45-50 µm, the polymer solution was cast onto the glass plate. The film was left in the ambient temperature for 30 seconds before it was immersed in the water as the coagulation medium for 1 hour. Then, the film was kept in the large amount of water for 24 hours. The membrane was subsequently cured at 45°C in the oven for 1 hour [11] before preparation of the thin film composite.

3) Preparation of thin film composite

The polysulfone membrane was attached to a glass plate. A specific concentration of a hybrid membrane solution was poured onto the membrane and by using the glass rod, a thin layer of the hybrid membrane solution was coated onto the membrane. The thin film composite membrane was left for 24 hours at room temperature and subsequently cured in the oven at 45°C for one hour [11] before characterization and performance evaluation of the membrane.

4) Characterization of the thin film composites

a) Fourier transform infrared (FTIR) spectroscopy

Fourier transforms infrared (FTIR) spectrometer with model Spectrum One, manufactured by PerkinElmer had been used to determine the presence of functional groups of the membrane. The changes in the functional groups as a result from cross-linking between blended polymers and TEOS could be confirmed by using the spectrometer. The samples were taken at random from the flat sheet films and were placed in direct contact with the crystal surface and the spectrum was recorded in the range of 515-4000 cm^{-1} .

b) Thermal gravitational analysis (TGA)

Thermal stability of the hybrid membranes were analyzed by thermal gravitational analyzer (Mettler Toledo, model Star^e SW). The measurements were carried out under nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 30 to 900 $^{\circ}\text{C}$.

c) Scanning electron microscopy (SEM)

Cross sectional and surface morphologies of the porous support polysulfone membrane and thin film composites (TFC) were observed by using FESEM Supra 40 VP from Carl Zeiss SMT-Nano Technology Systems Division at 5 kV accelerating voltage. Prior to the analysis, the membranes were coated with 10 nm thickness of gold by using sputter coater (Bal-tec, Model: SCD 005) for 50 seconds.

d) Contact angle analysis

The contact angle analysis was performed by using VCA Water Surface Analysis System (AST Products Inc.). A drop of distilled water (2 μL) was dropped onto the surface of the membrane and the contact angle was evaluated. The contact angle was measured at 5 different spots of the membrane surface and the average value was derived.

C. Performance evaluation of the thin film composite

Purification of crude glycerol solution

Purification of crude glycerol solution through the thin film composites had been performed by using membrane test machine, which consists of a dead end stirred cell resting on a magnetic stir plate. The crude glycerol was obtained from one of the biodiesel manufacturer in Malaysia. Prior to the purification process, 50 wt.% of water was added to the crude glycerol to reduce the viscosity. The crude glycerol solution was then placed in the feed chamber and was pressurized by using nitrogen gas to permeate through the thin film composite (TFC). After attaining a stable flow of permeate, the permeate stream was collected for 1 hour

of operation time and the flux rate was calculated by dividing the flow rate of the permeate stream with the membrane area. The compositions of the permeate stream in terms of glycerol content and NaCl concentration was determined by glycerol content determination method and by using ion meter respectively.

Concentration of NaCl in the feed and permeate was determined by ion meter (Eutech PC 2700 Meter). The salt rejection was calculated by using (1):

$$R(\%) = \left[1 - \frac{C_p}{C_f} \right] \times 100 \quad (1)$$

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

Glycerol content determination was conducted according to standard method, ISO 2879-1975. The percentage permeation of glycerol (P) was calculated by using (2) where C_f and C_p are the concentrations of glycerol in the feed and permeate respectively. The process was repeated for three times by using another piece of the TFC and the average values were calculated.

$$P = \left[\frac{C_p}{C_f} \right] \times 100 \quad (2)$$

III. RESULTS AND DISCUSSION

A. Characterization of the thin film composites

1) FTIR

Based on Figure 1, the presence of a hybrid layer on the porous support resulted in the increase in hydrophilicity that exhibited through the existence of -OH band at 3400 cm^{-1} . Apart from that, the incorporation of TEOS (as shown by spectra C and D) resulted in the increase in the intensity of peak around 1100 cm^{-1} due to -OH of silanol underwent a reaction with -OH in the organic compound to form covalent bond Si-O-C which overlapped the original C-O bond. This cross linking reaction also resulted in a decrease in hydroxyl (-OH) group [10] but it was not too obvious as depicted in Figure 1. This situation was due to the presence of glycerol in the formulation which had increased the hydrophilicity of the hybrid membrane and it had compensated with higher concentration of TEOS incorporated into the formulation. With respect to the hybrid membrane formulation prepared through sol-gel reaction, the addition of organic additives such as glycerol to the initial phase of the sol gel reaction influenced the hydrolysis and condensation reactions, which led to the matrix modification. This process could be explained through the formation of hydrogen bonds reacted both with water and the $\equiv\text{Si-OH}$ groups and the intensity peak for hydrogen bonds appeared at 1650 cm^{-1} and 945 cm^{-1} respectively [12]. The reaction mechanism between TEOS and glycerol is shown in Figure 2 [13]. As shown by spectrum B and C, the existence of 1732 cm^{-1} band might be due to the remaining unhydrolyzed vinyl acetate group of polyvinyl alcohol [14] where the incorporation of glycerol had diminished the peak as shown by peak D.

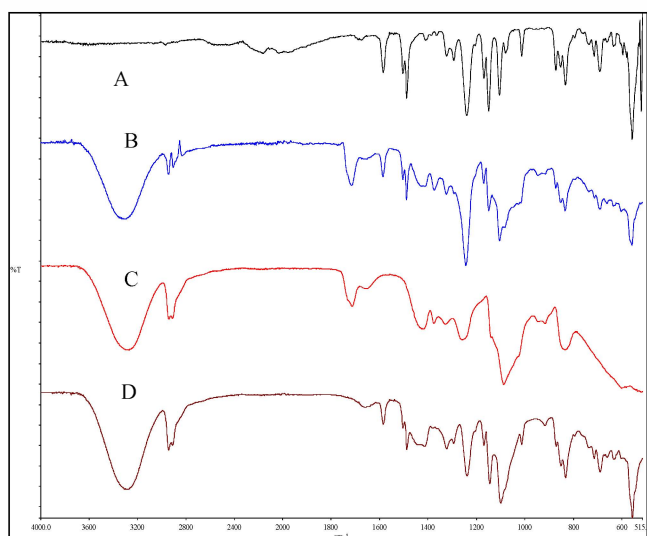


Fig. 1. FTIR spectra of membranes (A) porous support polysulfone membrane, (B) TFC with F1 as the barrier layer, (C) TFC with F2 as the barrier layer, (D) TFC with F3 as the barrier layer

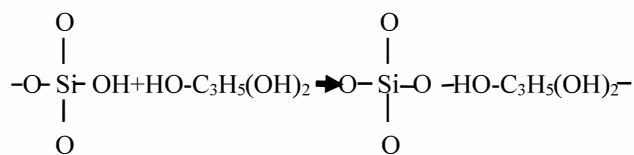


Fig. 2. Reaction mechanism between TEOS and glycerol

2) Thermogravimetric analysis (TGA)

As observed from thermal analysis via TGA in Figure 3, the spectra show four main steps of weight loss. The first step occurs at temperature less than 150°C , which was associated with the loss of absorbed water. The second step is occurred at temperature between 150 to 260°C due to degradation of polyethylene glycol moiety. The third step is associated with the removal of hydroxyl groups on polyvinyl alcohol which occurred at temperature between 260 to 430°C . The last step occurs at temperature higher than 430°C , which is due to decomposition process of polymer backbones [15].

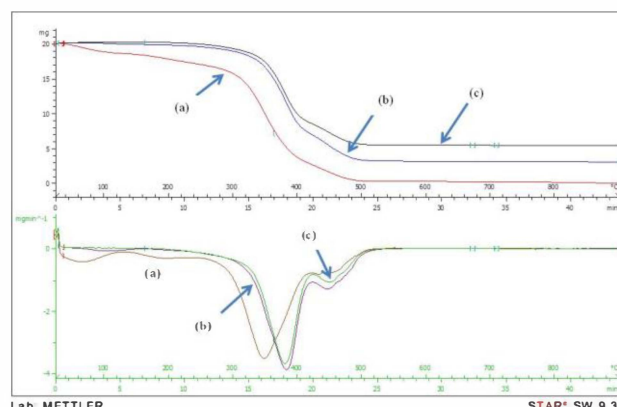


Fig. 3. TGA curves of barrier layers from formulation (a) F1, (b) F2, (c) F3

Based on the figure, the presence of TEOS as displayed by spectrum F2 and F3 had resulted in the increase in the decomposition temperature for the removal of hydroxyl group of PVA as well as the decomposition of polymer backbone. This situation could be explained through the introduction of strong interactions between the silica network and the polymer matrix which could increase the rigidity structure of the polymer [6]. By comparing between hybrid membranes F2 and F3, the presence of glycerol had significantly increased the thermal stability of the membrane. This situation was exhibited through the increase in weight residue at 900°C for hybrid membrane F3 [15].

3) Scanning electron microscopy (SEM)

Based on the surface microstructure of the membrane as depicted in Figure 4, the inorganic component and the organic component (polymer) had undergone a complete cross-linking reaction to form a homogeneous phase even at 4% TEOS where no phase separation was observed

[10]. Based on the results on the cross sectional morphologies, the presence of barrier layers on the base support polysulfone membrane has resulted in much denser pore morphology as compared to that without it. By comparing between the thin film composites (TFCs) with F2 and F3, F3 has bigger pore size. This situation was attributed to the incorporation of glycerol that had increased the porosity of the membrane surface, where glycerol acted as pore forming agent [16].

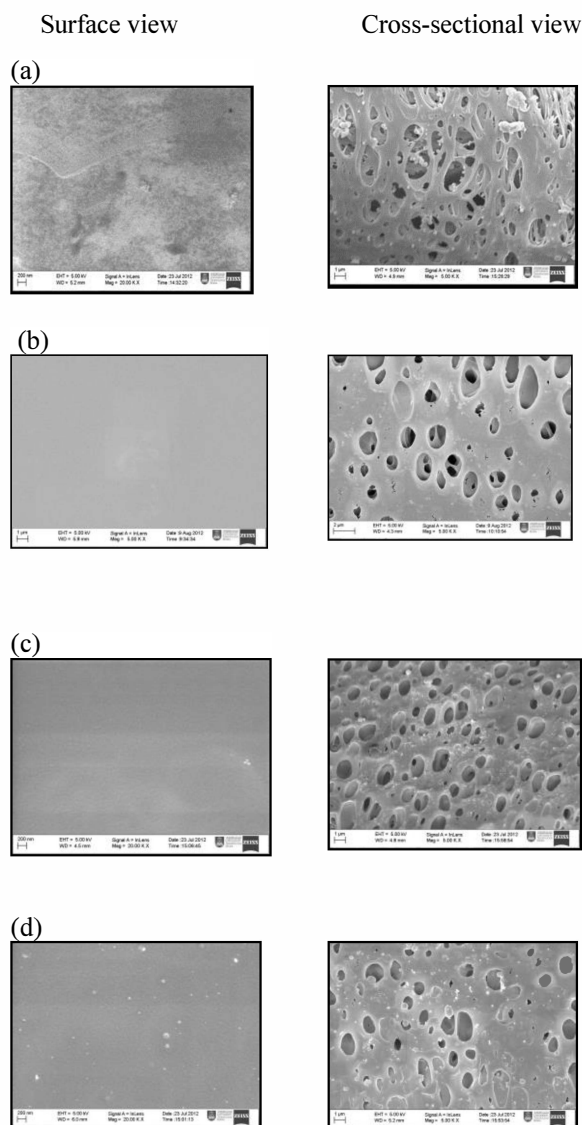


Fig. 4. SEM images of surface and cross-sectional view of (a) polysulfone, (b) TFC with F1, (c) TFC with F2, and (d) TFC with F3 at 5000x magnification

4) Contact angle measurement

The hydrophilicity of the thin film composites was further evaluated by contact angle analysis. Hydrophilicity is one of the most important factors of membrane surface and water contact angle measurement

is a convenient way to assess the hydrophilicity and wetting characteristic of the membranes [17]. As shown in Table 2, the presence of a hybrid layer had increased the hydrophilicity of the TFC as compared to the porous support membrane, where the polysulfone membrane had the highest contact angle value. This situation is due to membranes formulated from polyvinyl alcohol are in general hydrophilic unlike polysulfone, which is hydrophobic [14]. Although the rapid cross-linking reaction between the polymer and silica nanoprecursor had reduced the amount of unreacted hydroxyl group in the hybrid membrane but the difference is minimal. The decrement in the contact angle for TFC with F3 would justify the FTIR spectra shown in Figure 1 where the presence of glycerol contributes towards improving the hydrophilicity of the membrane surface.

TABLE 2
CONTACT ANGLE FOR POROUS SUPPORT MEMBRANE AND THIN FILM COMPOSITE MEMBRANE FROM VARIOUS FORMULATIONS

Membrane	Contact angle (°)
Porous support polysulfone	75
TFC with F1	47
TFC with F2	53.68
TFC with F3	50.98

B. Purification of crude glycerol solution

As shown in Table 3, although polysulfone membrane yields the highest flux rate and recovery of glycerol but it allows the highest percentage permeation of NaCl. This situation could be correlated with its bigger pore size as shown in Figure 4. Although comparable flux rate was exhibited by all thin film composite (TFC), TFCs with hybrid membrane layer had better salt rejection performance. The enhancement in the salt rejection was due to higher interaction between the ions in the solution with the hydroxyl groups on the denser membrane surface [14] as a result of rapid cross-linking reaction. Although comparable rejection of salt was performed through TFCs with membrane F2 and F3, F2 suffers from low permeation of glycerol. The incorporation of glycerol in the hybrid formulation F3 had resulted in higher recovery of glycerol due to its plasticizing effect which had increased the polymer chain mobility that would subsequently increase the free volume of the membrane [18]. As compared to the previous researches [4 to 5], by using one-stage purification of crude glycerol through the TFC (with F3 as the barrier layer), > 40% monovalent salt (NaCl) could be removed with high recovery of glycerol (> 70%).

TABLE 3
PROPERTIES OF PRODUCTS OBTAINED FROM PURIFICATION OF CRUDE GLYCEROL SOLUTION

Properties	Formulation code			
	Polysulfone membrane (porous support)	TFC with F1 as the barrier layer	TFC with F2 as the barrier layer	TFC with F3 as the barrier layer
Flux rate (L/m ³ .day)	367.90	25.82	21.82	23.54
Glycerol permeated (%)	99	83.49	61.61	74.35
NaCl rejection (%)	0.72	25.16	48.02	43.98

IV. CONCLUSION

As a conclusion, the incorporation of glycerol in the hybrid membrane formulation had been found to significantly improve the performance of the TFC in crude glycerol purification. Further development will be focusing on finding the optimum formulation for the hybrid membrane.

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