Treatment of Palm Oil Mill Effluent by Poly(L-Lactic Acid)-Poly(Ethylene Glycol)/ Silica Membrane
(Rawatan Efluen Kilang Sawit menggunakan Membran Poli(L-Asid Laktik)-Poli(Etilena Glikol)/Silika)

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ABSTRACT

Biodegradable membrane technology has received an increasing interest in many fields of applications exclusively to preserve the earth. A renewable polymer such as poly(L-lactic acid) (PLLA) often being introduced with reinforcement material to improve the characteristics of membranes itself. Herein, this study highlights the development of membrane from poly(L-lactic acid)-poly(ethylene glycol) (PLLA-PEG) copolymer with silica (SiO_2) in the treatment of palm oil mill effluent (POME) wastewater. We hypothesized that the incorporation of SiO_2 as a nanofiller promoted PLLA-PEG/ SiO_2 membrane to have a porous and higher number of pores on the membrane surface. Therefore, the effect of silica amount added in the PLLA-PEG copolymer membrane was also investigated and examined by using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Based on FTIR analysis, the presence of the urethane (-NHCOO-) functional group indicated the formation of PLLA-PEG copolymer and SEM micrographs showed porous surface on the membranes with increasing pores size in a favor of SiO_2 amount added. Also, the surface wettability of membranes was evaluated through water contact angle which render hydrophilic characteristics. These membranes were subsequently applied for POME filtration where the test resulted in significant discolouration of POME. Furthermore, the high percentage removal efficiency of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solid (TSS) up to 99.5% empowers the treated POME wastewater to be within the range set by the Malaysian Department of the Environment.

Keywords: Copolymer; membrane; poly(ethylene glycol); poly(lactic acid); POME

ABSTRAK

Pada masa kini, teknologi membran terbiodegradasi semakin mendapat perhatian dalam pelbagai bidang aplikasi khususnya untuk menjaga kesejahteraan bumi. Polimer yang berasaskan sumber keterbaharuan seperti poli(asid laktik) selalunya ditambah baik dengan bahan penguat bagi meningkatkan ciri membran tersebut. Oleh itu, kajian ini memfokuskan kepada perkembangan membran berasaskan kopolimer poli(L-asid laktik)-poli(etilena glikol) (PLLA-PEG) dengan penambahan silika bagi rawatan air sisa buangan efluen minyak kelapa sawit. Kami menjangkakan bahawa penambahan silika sebagai pengisi di dalam membran PLLA-PEG/SiO_2 menjadikan permukaannya berliang dan mampu meningkatkan bilangan liang. Oleh itu, kesan penambaan berat silika ke dalam membran kopolimer PLLA-PEG dikaji menggunakan FTIR, SEM dan EDX. Berdasarkan analisis FTIR, pembentukan kopolimer PLLA-PEG telah dibuktikan dengan kehadiran kumpulan berfungsi uretana (-NHCOO-) dan mikrograf SEM menunjukkan permukaan berliang yang terdapat pada membran selain terdapat peningkatan dari segi saiz liang selepas penambahan berat silika. Seterusnya, kebolehbasahan permukaan membran telah dinilai melalui analisis sudut sentuhan air kerana telah memperlihatkan ciri-ciri kehidrofilikan. Kesemua membran ini telah diaplikasikan bagi rawatan POME yang telah menunjukkan perubahan penyahwarnaan yang signifikan. Tambahan lagi, kadar peratusan penyingkiran yang tinggi bagi BOD, COD dan TSS sehingga 99.5% telah membuatkan air sisa POME yang terawat berada dalam had pengeluaran yang telah dikeluarkan oleh Jabatan Alam Sekitar Malaysia.

Kata kunci: Kopolimer; membran; poli(etilena glikol); poli(L-asid laktik); POME

INTRODUCTION

Currently, Malaysia dominates global palm oil production by almost 40% and accounts for about 44% of exports across the world. Standing next to Indonesia, Malaysia is one of the biggest exporter and producer in the palm oil industry that plays a crucial role in meeting the growing global demand for its oils and fats sustainably. Despite being a significant sector behind the national economic growth, problems arise where 9.9 million tons of solids

wastes and 20 million tons of palm oil mill effluent (POME) are generated every year. In response to these issues, tremendous efforts were done to curb the thick dark brownish colour effluent that generated from mills. This dark brown effluent or POME can destroy many aquatic plants whenever dumped into the nearby river and indirectly affect human health as the river has been one of the water resource for human (Ghani et al. 2018). Other than that, this hazardous liquid waste has an unpleasant odor and highly polluted with high biochemical and chemical oxygen demand (BOD & COD).

Nevertheless, there are several common methods employed to treat POME mainly to decrease BOD and COD values of effluent such as biological treatment. This treatment uses a combination effect of aerobic, anaerobic, and facultative ponds. However, undeniable drawbacks are still present as there is no significant reduction in POME color even after the biological treatment. The color of POME was displayed to be dark brownish due to the degradation of lignocellulosic compounds which are lignin and tannin (Ali Amat et al. 2015). Therefore, the use of biodegradable membrane technology will be a great solution in providing green chemistry that could separate the residues and eventually changes the color of effluent. A green biodegradable polymer such as poly(L-lactic acid) (PLLA) is the most prominent polymer that widely used in various applications especially in packaging, flame retardant, biomedical field and membranes (Basu et al. 2018; El-Gendy et al. 2017; Liu et al. 2004; Nasrin et al. 2017). PLLA is a versatile polymer made from renewable agricultural raw materials such as corn and potatoes that makes them great in biocompatibility, processability, and biodegradability (Feng et al. 2016; Xian et al. 2018). PLLA interestingly has high stiffness and strength, thermoplastic, transparent, and recyclable (Gui et al. 2012). However, PLLA is a hydrophobic polymer with inherent brittleness and poor toughness (Nagarajan et al. 2016). In order for PLLA based materials to possess the hydrophilic character for water surface wettability, a hydrophilic polymer such as polyethylene glycol (PEG) needs to be introduced into the PLLA surface or membrane matrix.

PEG is water-soluble and an excellent plasticizer for PLLA to form a good miscible solution (Chen et al. 2005). Besides that, PEG can increase the porosity and thickness of a membrane (Saljoughi et al. 2010). In this research, we attempted to synthesis a potentially biodegradable membrane with a combination of PLLA-PEG multiblock copolymer as the membrane matrix and silica as a pore-forming agent and filler. This multiblock copolymerization technique was chosen over polymer blending merely to improve the original physical-chemical properties of the material and provide good miscibility (Ruf et al. 2018). To date, there are significant numbers of literature on PLLA as the main material in membranes (Gaitán et al. 2018; Phaechamud et al. 2016; Wang et al. 2016). The study by Chieng et al. (2014) disclosed that even though PLA plasticized with PEG increased the flexibility of PLA, other properties such as thermal stability and mechanical strength still can be improved by the addition of reinforcement nanofiller. On the other hand, study on PLLA-PEG copolymer membrane with silica and its application in POME treatment has not yet been performed. The incorporation of silica during the PLLA-PEG membrane fabrication is particularly interesting as it can behave as an adsorbent in the membrane as well as a pore template that increases the porosity of the membrane. The amount of silica is varied at different percentages which were 0, 2, 6, and 10% and the resulting membranes were characterized to examine their physical-chemical properties and membrane performance.

MATERIALS AND METHOD

MATERIALS

PLLA was purchased from ESUN, China. PEG (M_w=10000 g/mol), tin(II) 2-ethylhexanoate (Sn(oct)$_2$, 95%), 1,6-hexamethylene diisocyanate (HMDI, 98%), dichloromethane (DCM), tetrahydrofuran (THF) and silica were purchased from Sigma-Aldrich (Malaysia) in analytical grade. All chemicals and reagents were used without further purification. Silica gel was sieved to the size of 45 μm prior to use. For further performance application of membranes, the palm oil mill effluent (POME) wastewater was taken from Labu, Negeri Sembilan (2º 47.08 N and 102º30.25 E) and collected from the final discharge pond.

METHOD

PLLA-PEG copolymer used as the membrane matrix was prepared using PLLA:PEG weight ratio of 7:3, before adding with a variable amount of silica as described in Table 1.

TABLE 1. Composition of copolymer PLLA-PEG/SiO$_2$ membranes

Copolymer membranes	Weight of PLLA	Weight of PEG	Weight of silica
0% silica membranes	7g	3g	0.0g
2% silica membranes	7g	3g	0.2g
6% silica membranes	7g	3g	0.6g
10% silica membranes	7g	3g	1.0g

PREPARATION OF PLLA-PEG/SILICA

PLLA (7 g) pellets were dissolved into 42 mL of DCM in a round bottom flask and covered with a greased flask stopper. The solution was stirred for 2 h to completely dissolve PLLA. In the meantime, silica was stirred in 42 mL of THF in a beaker. After 2 h, 3 g of PEG was added into the flask that contains PLLA solution, followed by 36 mg of Sn(Oct)$_2$ and 0.7 g of HMDI. The solution was stirred for another 2 h at 45 °C allowing PLLA-PEG multiblock copolymer to form. Then, the silica/THF mixture was added into the flask containing the PLLA-PEG copolymer solution and stirred overnight at 45 °C. This step was repeated several times with different percentages of silica as described in Table 1.

FABRICATION OF PLLA-PEG/SILICA MEMBRANE

The modified fabrication of membrane was carried out based on previous study in the phase immersion method. PLLA-PEG/silica solution was casted onto a glass plate with a thickness of 0.20 mm using a casting knife (Norfarhana 2014). After leaving for a few minutes at room temperature, the glass plate was immersed into distilled water in a basin. Then, an off-white solid membrane was formed and carefully peeled off. The samples were kept for the next characterization.

PERFORMANCE TEST OF MEMBRANE

Raw POME is a combination wastes coming from three principal sources, which are clarification wastewater (60%), sterilizer condensate (36%) and hydrocyclone wastewater (4%). This waste is made of 95-96% water, 4-5% total solids which consist of 2-4% suspended solids as well as 0.6-0.7% oil and grease that had been discharged at 80-90 °C of temperature (Ang et al. 2018). Permeation tests for POME were done to study the flux of the membranes by using dead-end stirred cell model HP4750. The membrane was cut into a size of 50 mm in diameter and tested under nitrogen gas at constant pressure starting from 0.5 bar. Then, the reading was taken for 50 min in 5 min interval. For the quality test of POME, removal of BOD, COD and TSS as well as pH were analyzed according to methods published by American Public Health Association (APHA), American Water Works Association and Water Environment Federation. Each test was performed with different instruments and standard method which were HACH method 8000, HACH DR 3900 and ALPHA 2540 D. Table 2 displays the physicochemical parameter of POME with their respective standard discharge limit by the Malaysian Department of the Environment (DOE).

TABLE 2. Physicochemical parameter of POME by DOE standard

Parameter	POME taken in Labu	DOE standard
pH	8.39	5 - 9
BOD (mg/L)	12 300	20
COD (mg/L)	40 820	-
TSS (mg/L)	38 693	400
Oil and grease (mg/L)	2 000	50
Total nitrogen	750	150

Source: Zainal et al. (2017)

CHARACTERIZATION

The presence of structural functional groups of PLLA-PEG copolymer membranes was identified by using Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded using Spectrum 400 Perkin Elmer GX Spectrometer over the range between 4000 and 650 cm^{-1}. Membranes morphologies were investigated by using scanning electron microscopy (SEM) under the magnification at 10000× for membrane surface and 1000× and 5000× for membrane cross-sectional imaging. The presence of elements in membranes was determined by using energy dispersive X-ray (EDX) analysis. Water contact angle analysis of membranes was characterized by the Drop Shape Analyzer model DO 4010 KRUSS using the sessile drop method. Deionized water (4 μL) was dropped on the membranes and observed. A total of 5 spots for each membranes were tested and the average value was taken.

RESULTS AND DISCUSSION

PLLA AND PEG COPOLYMERIZATION

The reaction between end groups of PLLA and PEG with HMDI resulted in a polyurethane-based PLLA-PEG copolymer. Urethane functional group that serves as a linkage between the homopolymers is produced by reacting two isocyanate groups (-NCO) from HMDI with the two hydroxyl groups (-OH) from PLLA or PEG in the presence of a catalyst. As in this case, the –OH group of PLLA and PEG served as a nucleophile and attacked an electron-deficient center (N=C=O) of HMDI and when this reaction is repeated, a multiblock copolymer type is obtained. The reaction scheme of the synthesis of PLLA-PEG polyurethane copolymers can be seen in Figure 1 that results in random copolymer backbone (Sidik et al. 2018).
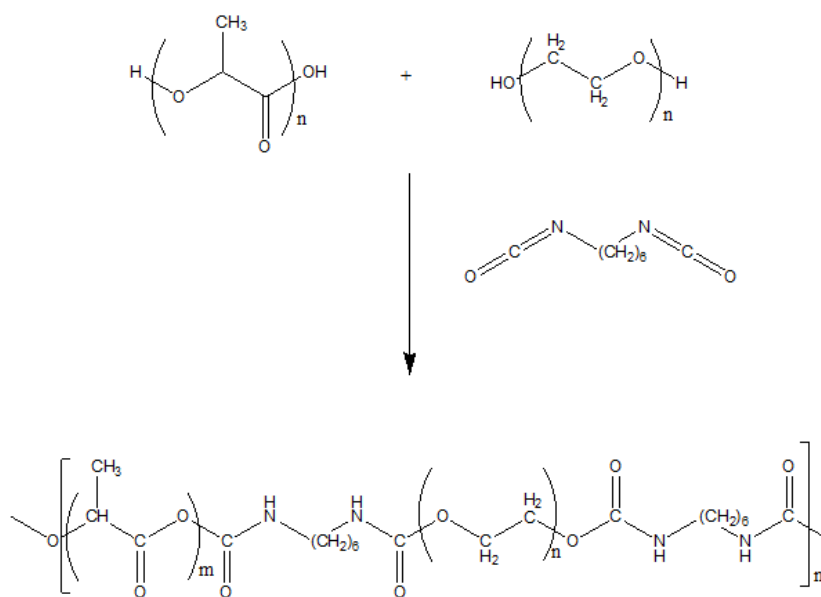

FIGURE 1. Reaction scheme between PLLA, HMDI and PEG
to produce PLLA-PEG polyurethane copolymer

FTIR ANALYSIS

The successful formation of the copolymer can be validated by the data of FTIR spectra with the presence of the urethane (-NHCOO-) functional group. This functional group is significant to prove the formation of PLLA-PEG copolymer. Furthermore, FTIR analysis was carried out to evaluate the presence of silica after the membrane fabrication process. Table 3 shows the wavenumber of functional groups for pristine PLLA, pristine PEG, PLLA-PEG copolymer membrane, and PLLA-PEG/silica membrane. The FTIR absorption bands for pristine PLLA and PEG were obtained through the previous literatures reported (Nasrin et al. 2017; Zainuddin et al. 2018).

TABLE 3. FTIR absorption bands of pristine PLLA, pristine PEG and PLLA-PEG/silica membrane

	C-H stretching	C=O stretching	O=C-N stretching	C-N stretching	C-O-C stretching	Si-O stretching	Si-O-Si
PLLA	2996, 2946	1756	-	-	-	-	
PEG	2914, 2882	-	-	-	1105	-	
PLLA-PEG	2997, 2941	1755	1619	1210	1082	-	
PLLA-PEG/ SiO$_2$	2996, 2945	1751	1621	1214	1182	960, 1100	842

Based on FTIR spectra analysis in Figure 2, PLLA-PEG/SiO$_2$ membrane exhibited almost similar peaks with PLLA-PEG copolymer membrane in their spectrum despite the added silica. These spectra showed that the urethane (-NHCOO-) functional group has positively well-formed in both membranes. C-H stretching with sp^3 character was observed at 2997 cm^{-1} and 2945 cm^{-1} in each spectrum whereas a very intense and sharp peak at 1750 -1756 cm^{-1} was represented by C=O stretching of carboxylic acid functional group. This carbonyl group peak remains unchanged as in pristine PLLA during the reaction of PLLA and HMDI. It is because only the O-H group of the polymers reacted with –NCO from HMDI. Other than that, an obvious peak was seen at 960 cm^{-1} and around 1100 cm^{-1} corresponds to the Si-O group while peak at 842 cm^{-1} was attributed to symmetry stretching of Si-O-Si as detected in Figure 2 (Chen et al. 2010). However, the peak at 1100 cm^{-1} was not clearly visible as it is overlapped by C-O-C group present in matrix membrane. Furthermore, to verify the presence of -NHCOO- functional group, a new set of peak observed at the range of 1619-1621 cm^{-1} can be assigned to the urethane C=O group and another new peak at the range of 1210-1263 cm^{-1} belongs to C-N of urethane. The presence of these two peaks was necessary to prove that the urethane -NHCOO- bond was successfully formed in this copolymerization reaction.
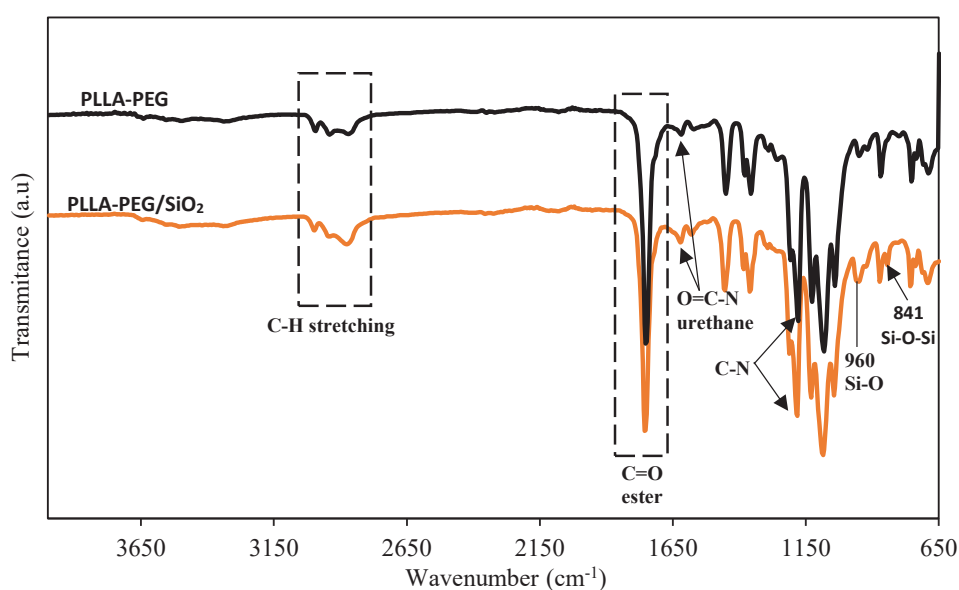

FIGURE 2. FTIR spectrum for PLLA-PEG copolymer membrane and a representative PLLA-PEG/SiO$_2$ membrane

MORPHOLOGY ANALYSIS

Surface and cross-sectional imaging on the morphology of membranes were investigated by using SEM micrograph to compare the pore size and porosity of membranes. Figure 3 illustrates the SEM micrograph on membrane surface with a variation in the percentages of silica. PLLA-PEG copolymer membrane fabricated without silica (Figure 3(a)) showed smooth surface with the presence of well-distributed pores. In comparison to Figure 3(a), PLLA-PEG copolymer membranes with 2, 6, and 10% of silica (Figure 3(b)-3(c)) also displayed well distributed pores, but higher surface porosity and larger pores. After the inclusion of 2% of silica, the average pore size decreased from 1.89 μm in 0% membrane to 0.97 μm. Then, further addition of silica at 6% increased the average pore size to 1.24 μm. This trend was similar with the literature reported by Feifel and Lisdat (2011) and Mahatmanti et al. (2018) where pore distribution was found increasing with the addition of silica. This phenomena could be related to the properties of silica and size exclusion effect. The hydrophilic nature of silica made them acted as a pore-forming agent that attributed to the formation of more pores and larger pore sizes.

However, Figure 3(d) presented a micrograph of 10% silica membrane with average pore size of 5.70 μm that is remarkably different from other membranes. Irregular and non-uniform large pores are observed and this can be due to the agglomeration of silica at relatively high concentration during copolymer-filler-solvent mixing.

Another factor that contributed to this was the leaching of silica from membrane film during phase inversion process in water, since silica is hydrophilic and the interaction between silica particles with membrane matrix is merely physical.
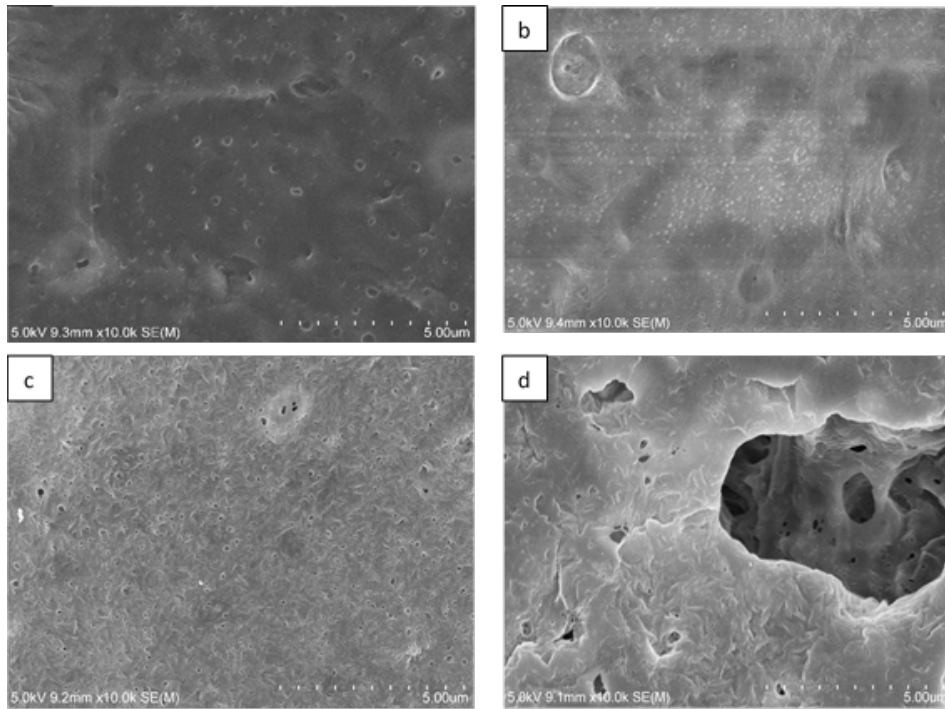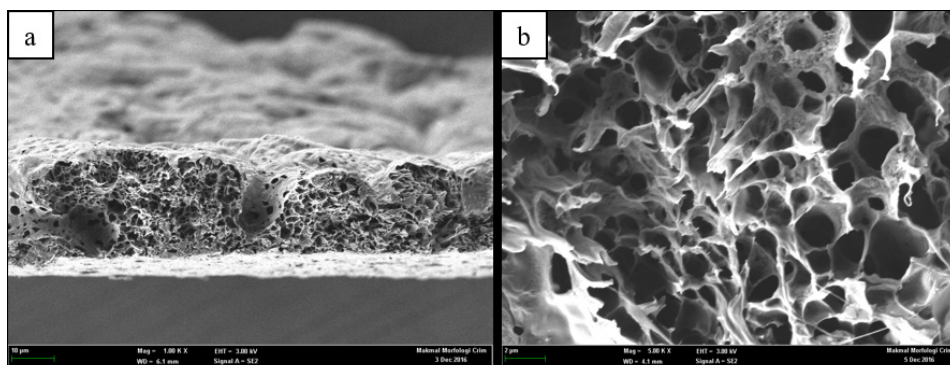

FIGURE 3. RSEM micrograph for membrane surfaces
fabricated with (a) 0%, (b) 2%, (c) 6%, and (d) 10% silica at
10 000 magnification

Meanwhile, Figure 4 shows the cross-sectional imaging of the membranes at 1000 and 5000 magnification. Overall, SEM analysis of membranes fabricated with 0, 2, 6, and 10% silica indicated high compatibility between PLLA and PEG segments of the PLLA-PEG copolymer and silica with no occurrence of phase separation. Their topographies were also similar to each other. The pore sizes for each membrane was measured and the average sizes for membrane with 0% of silica was found to be 2.16 μm and 2% of silica was measured at the average of 1.56 μm. The average pore sizes of 6 and 10% membrane were found to be 1.62 and 2.80 μm, respectively. However, in Figure 4(h), an agglomerated silica has been observed inside the matrix membrane. This phenomenon occurred due to excess of the addition of silica into the PLLA-PEG copolymer membrane.
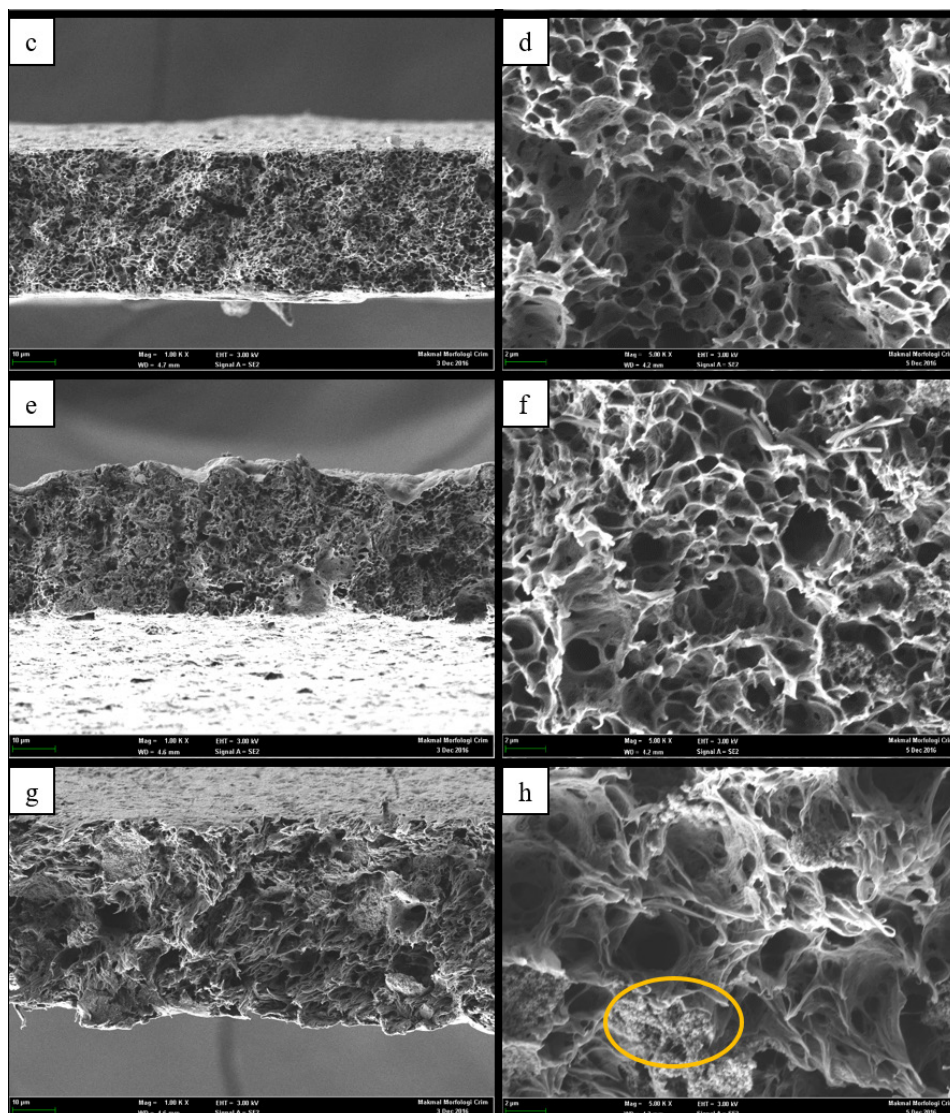
FIGURE 4. Cross sectional surface membranes fabricated
with (a,b) 0%, (c,d) 2%, (e,f) 6% and (g,h) 10% silica at
1000 (left), and 5000 (right) magnification

The chemical composition of the silicon atom after phase inversion process was determined using the energy dispersive X-ray analysis (EDX) coupled to SEM. This analysis can provide more insight on the formation of large pores in the PLLA-PEG membrane fabricated with 10% of silica as observed from the SEM micrograph. EDX results are shown in Table 4. Interestingly, lower percentages of silicon were recorded for membrane fabricated with 6 and 10% of silica in comparison to that of 2% of silica, with values of 0.74, 0.99 and 1.17%, respectively. The amount of silicon in 6 and 10% silica membrane was unexpected to be lower than the 2% silica membrane, since theoretically, the trend should correspond to the increasing amount of concentration of silica added during membrane preparation. This data supports the observation of large pores in membrane fabricated with 10% of silica due to the agglomeration of silica during mixing followed by the leaching of some silica particles during phase inversion. Membrane fabrication via phase inversion retained a fraction of the silica added where it acted as pore-forming agent in the membrane and leached the rest which acted like a pore template for the membrane.

Even though there was no agglomeration process happened in the 6% silica membrane, the amount of silicon in the membrane showed the lowest amount due to high leaching process occurred. This resulted to the increase of pore distribution on the surface of membranes as can be seen in Figure 3(c).

TABLE 4. Silicon composition in PLLA-PEG copolymer membranes

% of silica added during membrane fabrication	0	2	6	10
% of silicon from EDX analysis	0	1.17	0.74	0.99

WATER CONTACT ANGLE ANALYSIS

Water contact angle (WCA) analysis was used to determine the hydrophilic/hydrophobic property of membranes with respect to the concentration of silica during membrane preparation. The membrane matrix comprises of 70 weight-% of PLLA (hydrophobic polymer) and 30 weight-% of PEG (hydrophilic polymer). Regardless of the greater amount of PLLA present, all of the membranes showed hydrophilic property which PEG as a hydrophilic polymer played an important role in enhancing the hydrophilicity of the membranes (Akbari et al. 2016; Yunos et al. 2014). Nevertheless, the increase in hydrophilicity of membranes were also being achieved due to the amount of silica added. Silica as an inorganic filler can alter the filler-polymer interfacial interaction by increasing the number of particle-matrix interactions when dispersed in a polymer and ultimately improved the overall material (Chen et al. 2010). The initial WCA of the PLLA-PEG copolymer membrane was 82% without the presence of hydrophilic silica on the surface of membranes.

Reduction of contact angle values was observed upon the addition of silica, indicating highly hydrophilic character as water molecules have a great affinity and low resistance to wet the surface layer of membranes (Ali Amat et al. 2015). After the addition of 2% of silica, the WCA of membrane was reduced to 57% followed by 55 and 49% for PLLA-PEG copolymer membrane with addition of 6 and 10%, respectively. This phenomenon was occurred due to formation of hydrogen bond between the hydrophilic groups present in silica (Si-OH) with water (Mohd Nizar et al. 2018). Another factor that could contributed to the decrease of WCA of membrane was the surface morphology of the membrane that could be seen in SEM micrograph. As can be seen in SEM micrograph, membranes with 2, 6, and 10% of silica presented a better pore distribution and porosity compared to PLLA-PEG copolymer, that helps in lowering the water contact angle. This findings was consistent with the study of Jose et al. (2016) and Zhu et al. (2015) that showed the pores and chemical structures of the surface of membrane can affect its WCA and adhesion behavior.

PERFORMANCE TEST OF MEMBRANE
PERMEATION OF POME

Figure 5 displays the permeation flux of membranes in the treatment of POME with a constant pressure of 3 bar as a function of time. Membrane fabricated with 6% silica showed the highest value of total mean flux at 42.27 Lhr^{-1}m^{-2}, followed by 2% silica at 27.12 Lhr^{-1}m^{-2}. It was expected that the membrane with better pore
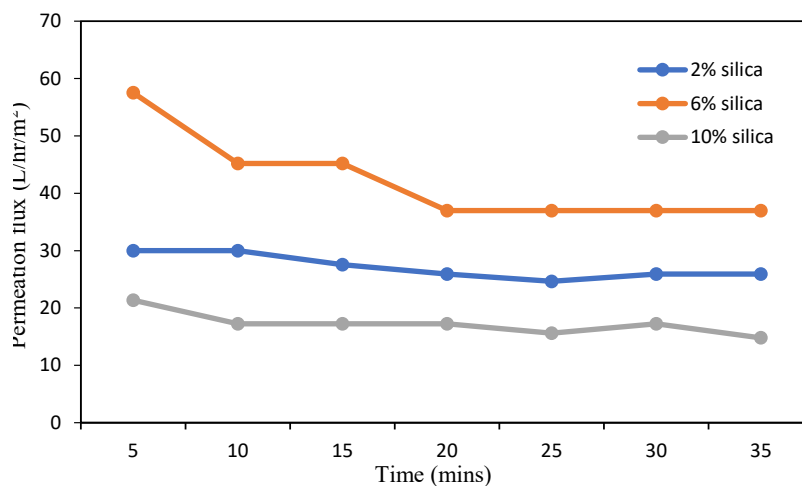

FIGURE 5. Permeation flux of POME for membranes
fabricated with 2, 6, and 10% silica

distribution presented superior POME flux than a smaller pore membrane. This could be supported by studies of Ahmed et al. (2015) and Sidik et al. (2018) that stated the bigger contribution to enhancing pure water flux and reducing solute rejection were the number of pores on the membrane surface and the better interconnectivity inside the membrane. Meanwhile, membrane fabricated with 10% silica has the lowest total mean flux at 14.79 Lhr^{-1}m^{-2}. Despite having a large pore size, this membrane demonstrated a lowest permeation flux due to the water retention of agglomerated silica present inside the matrix membrane. This agglomeration can undoubtedly seen in the cross-sectional SEM micrographs. In addition, another author also relates that the improved hydrophilicity and water permeability of membranes were attributed by the surface opening pores and highly hydrophilic PEG (Kim & Lee 1998).

DISCOLORATION OF POME

The color changes of POME after treatment indicate the color removal efficiency of the PLLA-PEG copolymer membrane influenced by silica. The initial color of POME before the filtration treatment was dark brown. As shown in Figure 6, filtration treatment using PLLA-PEG copolymer membranes with and without silica significantly improves the color of POME from dark brown to light brown. The trend in color removal efficiency precisely followed the pore size of the membrane. The greater the pore size, the clearer the color of POME. As can be observed in the results, untreated POME appeared to be in dark brown color (Figure 6(a)) while POME treated with membrane fabricated without silica which was PLLA-PEG copolymer membrane (Figure 6(b)) and 2% silica membrane (Figure 6(c)) appeared as a brown solution. Meanwhile, 6% silica membrane (Figure 6(d)) did show a changed of color that has turn into a lighter brown. Copolymer membrane fabricated with 10% of silica achieved the highest removal efficiency with the lightest brown and nearly yellow color, but this observation took longer time and higher pressure in order for the color to be achieved. Visual observation showed that the addition of silica gives a better appearance in the discoloration of the treated POME.
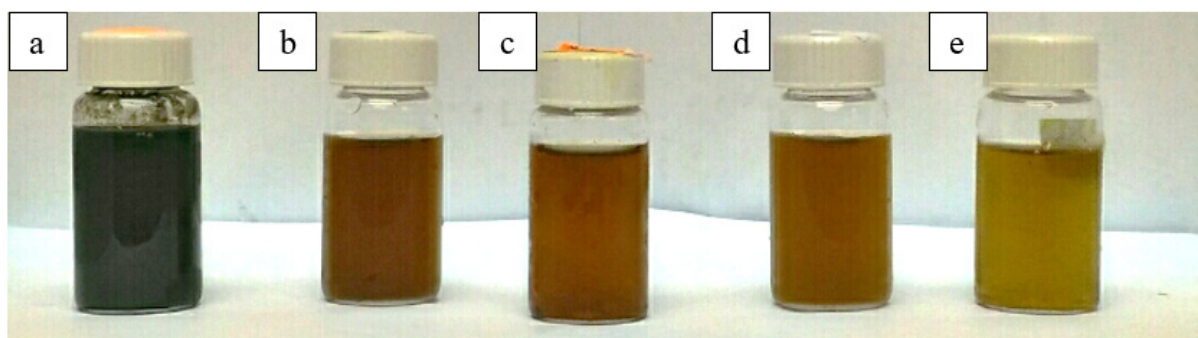
QUALITY OF POME

FIGURE 6. Discolouration of POME for (a) untreated POME, and membranes fabricated with (b) 0% (PLLA-PEG copolymer) (c) 2%, (d) 6% and (e) 10% silica

The critical concern about raw POME was the high concentration of its physicochemical parameters which included biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), and pH. They reflect the high contents of organic material such as a vigorous amount of amino acids and inorganic material like nutrients in the POME. These organic and inorganic materials have an adverse effect on the environment (Xiong et al. 2017). Table 5 summarizes the BOD, COD, TSS, and pH of POME before and after treatment using PLLA-PEG copolymer membranes with the percentage of removal efficiency. In general, PLLA-PEG copolymer membranes with silica as filler successfully reduced the level of BOD, COD and TSS with percentage removal efficiency up to 99.58%. BOD is the measure of oxygen required to oxidize inorganic material and degradation of organic material. Our finding showed that 2% and 6% silica membranes plays a significant role in reducing the amount of BOD in treated POME that gave the almost similar value of removal efficiencies which were 98.3 and 98.1%, respectively. Apart from it, the performance of COD after the treatment disclosed a

similar trend to the performance of BOD. The major reduction of BOD and COD values suggested a decrease in organic and inorganic material present after the treatment. These values of BOD and COD were relatable to the removal efficiency of total suspended solid (TSS). A well distributed and high porosity of pores in the PLLA-PEG/silica membranes was effective in trapping the suspended solid onto the membrane and allowing only clean water to pass through the membranes. Likewise, the successful separation of organic and inorganic material lead to major removal efficiencies of BOD, COD, and TSS in treated POME. As for the pH, the pH of POME remains unchanged throughout the treatment. These final readings enabled the treated POME to achieve DOE standards within the discharge limit. Furthermore, this membrane system showed unique characteristic as many studies found that membrane technology is effective in reducing the concentrated color of POME (Adeleke et al. 2017).

TABLE 5. BOD, COD, TSS, and pH of POME before and after treatment with PLLA-PEG copolymer membranes

Percentage of silica	BOD		COD		TSS		pH
	Initial = 12 300		Initial = 40 820		Initial = 38 693		Initial = 8.39
	Final	Removal efficiency	Final	Removal efficiency	Final	Removal efficiency	Final
0%	350	97.2%	1468	96.5%	200	99.48%	8.62
2%	210	98.3%	1443	96.4%	190	99.58%	8.72
6%	230	98.1%	1283	96.9%	250	99.50%	8.54
10%	380	96.9%	1898	95.4%	160	99.355	8.65

CONCLUSION

The important conclusion drawn from this work include membrane fabrication via phase inversion retained a fraction of the silica added where it acted as pore-forming agent in the membrane and leached the rest which acted like a pore-template for the membrane. The presence of urethane and silica peaks in FTIR analysis was suggested the successful functionalization of PLLA-PEG copolymer membrane consist of silica. Moreover, SEM-EDX analysis shown that the porosity and amount of silica retained in the membrane clearly affected by the percentage of silica added. Unfortunately, a 10% silica membrane did show unexpected behavior as the silica had agglomerated and left a non-uniform size of pores, while 6% silica membrane seemed evident to be the most suitable candidate that could be implemented in managing POME wastewater. As for the application of POME treatment, PLLA-PEG copolymer membrane with addition of silica did show a significant reduction in discoloration test and quality test such as BOD, COD, and TSS.

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