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CHARACTERISTICS OF PVA/GO COMPOSITE MEMBRANES PREPARED USING SOLUTION CASTING TECHNIQUE FOR REDUCING METHYLENE BLUE CONCENTRATION

FAUZIAH SITI AJIZAH, NORMAN SYAKIR, AYI BAHTIAR, FITRILAWATI *

Department of Physics, Faculty of Mathematics and Natural Science, Universitas Padjadjaran
Jl. RayaBandung-Sumedang Km.21 Jatinangor 45363, Sumedang, Jawa Barat

email : fitrilawati@unpad.ac.id

Abstract.In this study, the composite films of polyvinyl alcohol (PVA) and graphene oxide (GO) that referred as PVA/GO composites were prepared with a solution casting technique to be used as a filtration membrane. PVA/GO solution was prepared by mixing PVA powder, GO dispersion and aqueous solvent, then subjected to a hydrothermal process. The PVA/GO composite solution was cast on the glass substrate, then dried overnight so the solvent evaporated and then the composites films were removed from the substrate. The PVA/GO composite that characterized by SEM indicates that the GO is evenly dispersed within the PVA matrix. The FTIR spectrum of the composite has a sharp peak at 1655 cm^{-1} that associated with C=O and C=C bonds relating to GO characteristics. The TGA measurement results show that the PVA/GO composite film has better thermal stability than the PVA film. The PVA/GO composite films have been used as filtration membranes to reduce the concentration of methylene blue (MB) solutions contained in water. The filtration experiment that performed at various pressures showed that the permeability of the PVA/GO composite membranes was relatively constant at each pressure. Membrane permeability at pressures of 20 psi, 30 psi and 45 psi for PVA membranes are 1.95×10^{-3}, 2.08×10^{-3} and 2.00×10^{-3} Darcy, while for PVA/GO composite membranes are 2.49×10^{-4}, 1.22×10^{-3} and 2.23×10^{-3} Darcy.

Keywords:PVA/GO Composite, filtraion membrane, permeability

Abstrak.Pada penelitian ini, film komposit polivinil alkohol (PVA) dan graphene oksida (GO) yang disebut sebagai komposit PVA/GO dibuat dengan teknik pengecoran larutan yang akan digunakan sebagai membran filtrasi. Larutan PVA/GO dibuat dengan mencampurkan serbuk PVA, dispersi GO, dan pelarut air, kemudian dilakukan proses hidrotermal. Larutan komposit PVA/GO dituang pada substrat kaca, kemudian dikeringkan semalaman agar pelarutnya menguap dan kemudian film komposit dilepas dari substrat. Komposit PVA/GO yang dikarakterisasi dengan SEM menunjukkan bahwa GO terdispersi secara merata di dalam matriks PVA. Spektrum FTIR dari komposit memiliki puncak tajam pada 1655 cm^{-1} yang berhubungan dengan ikatan C=O dan C=C yang berkaitan dengan karakteristik GO. Hasil pengukuran TGA menunjukkan bahwa film komposit PVA/GO memiliki stabilitas termal yang lebih baik dibandingkan dengan film PVA. Film komposit PVA/GO telah digunakan sebagai membran filtrasi untuk mengurangi konsentrasi larutan metilen biru (MB) yang terkandung di dalam air. Percobaan filtrasi yang dilakukan pada berbagai tekanan menunjukkan bahwa permeabilitas membran komposit PVA/GO relatif konstan pada setiap tekanan. Permeabilitas membran pada tekanan 20 psi, 30 psi dan 45 psi untuk membran PVA adalah $1,95\times10^{-3}$, $2,08\times10^{-3}$ dan $2,00\times10^{-3}$ Darcy, sedangkan untuk membran komposit PVA/GO adalah $2,49\times10^{-4}$, $1,22\times10^{-3}$ dan $2,23\times10^{-3}$ Darcy

Kata Kunci:Komposit PVA / GO, membran filtrasi, permeabilitas

1. Introduction

Membrane filtration become a technology that is widely used currently for separation process. Membranes are divided as natural membranes such as eggshell membranes and synthetic membranes that known as organic (such as polymers) and inorganic (such as ceramics, metals, zeolites, or silica) [1]. At previous work, it has been reported the application of eggshell membranes (ES) with a thickness of 210 µm as filtration membranes that can reduce dye content which is methylene blue (MB) in water by 30.6% [2]. Furthermore, it has been also reported that the ES membranes can be modified using other materials such as graphene oxide (GO) and used as a membrane filtration. The presence of GO in the ES-GO composite membrane with a thickness of 70 µm has improved its performance in reducing MB content in water by 33.53% [3]. The limited size of the ES membrane makes it difficult to be manufactured in a large scale. Therefore, synthetic membranes, especially organic polymer membranes, are chosen since it the polymer can be manufactured in large size with a porous structures.

Polyvinyl alcohol (PVA) is an alcohol-rich aliphatic polymer chain that is highly sticky, neutrally charged [4], low-cost, environmentally friendly, has good hydrophilicity,easily form as film, and is widely used in the manufacture of nanofiltration membranes [5]. PVA has good water solubility, chemical stability, thermal stability, and mechanical stability [6].The addition of other materials such as GO to the PVA membrane can also increase the membrane's ability as a filtration membrane to filter dyes. One of simple methods that can be used to perform composite membrane is a solution casting method. In the solution casting method, the formation of a composite film is started by mixing of polymers solution and nanoparticles as fillers in a suitable solvent [7]. The mixing solution was then casted on the substrate and let the solvent evaporated, after that the composite layer can be peeled off to obtain a freestanding membrane [8].

One of membrane parameters is a permeability that measure an ability of membrane to pass a molecule through the membrane. It has been reported that an ES-GO membrane with a thickness of 70 µm used as a filtration membrane to filter MB at an operating pressure of 45 psi, has a permeability of $2{,}488\times10^{-3}$ Darcy [3]. In this work, we prepared PVA/GO composite membranes using solution casting method, measured its morphology, structure, and thermal property and measured its permeability as filtration membrane.

2. Methods

2.1.Materials and experimental apparatus

The materials used in the experiment were polyvinyl alcohol powder (PVA, Mw 85,000-124,000, 99+% hydrolyzed) obtained from Sigma Aldrich, graphene oxide dispersion (GO, 4 mg/mL) obtained from Graphenea, sodium hydroxide (NaOH, Merck), sodium sulfate powder (Na_2SO_4), sulfuric acid (H_2SO_4), glutaraldehyde (GA solution in water, 25%), ethanol, isopropanol, methylene blue (MB) powder, and distilled water.

Some of experimental apparatus used in the experiment were autoclave, magnetic stirrer, and furnace for composite synthesis. In addition, some of characterization instruments used were the scanning electron microscope (SEM) (JEOL JSM 6510 LA) for morphological analysis, Fourier Transform Infrared (FTIR) spectroscopy for structure analysis, Thermogravimmetric Analyzer (TGA) (Hitachi STA7300) for thermal analysis, the UV-Vis spectrophotometer (T70+ PG Instruments Ltd) and filtration equipment for filtration tests.

2.2.Membranes Preparation and Filtration Test

PVA/GO composite membranes was started by preparing PVA-GO composite solution. 1 gram of PVA powder was slowly added into 20 mL of GO dispersion with concentration of 1 mg/mL. The mixture was then stirred for 5 hours at 70°C using a magnetic stirrer with a rotating speed of 350 rpm. The PVA/GO solution was then poured into a stainless steel autoclave, then tightly closed, and put into a furnace for a hydrothermal process at a temperature of 120°C for 1 hour. After cooling down to room temperature, the autoclave containing composite solution was taken out from the furnace. The PVA/GO membranes were prepared from a PVA/GO composite solution using the solution casting method. The PVA/GO composite solution was casted on the glass substrate, then dried overnight so the solvent was evaporated. The composites films were peeled off from the glass substrate to obtain a freestanding membrane. After that it was followed by crosslinking process since PVA is soluble in water. The freestanding membranes were put into a solution containing 4.5% Na_2SO_4%, 0.5% H_2SO_4, and 1% Glutaraldehyde for 1 hour. The PVA membranes were also prepared using a similar steps and methods.

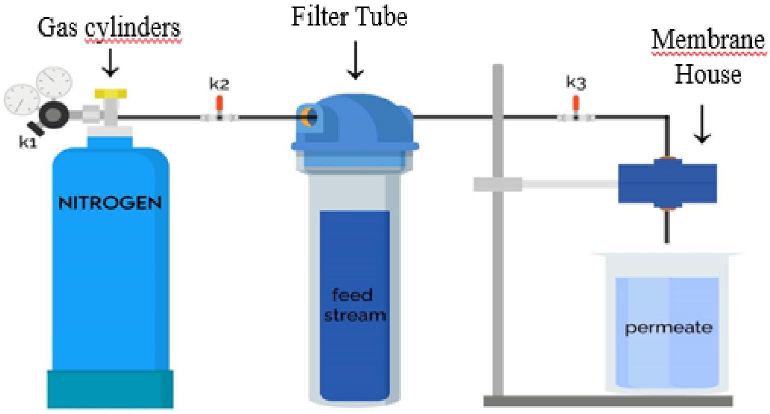


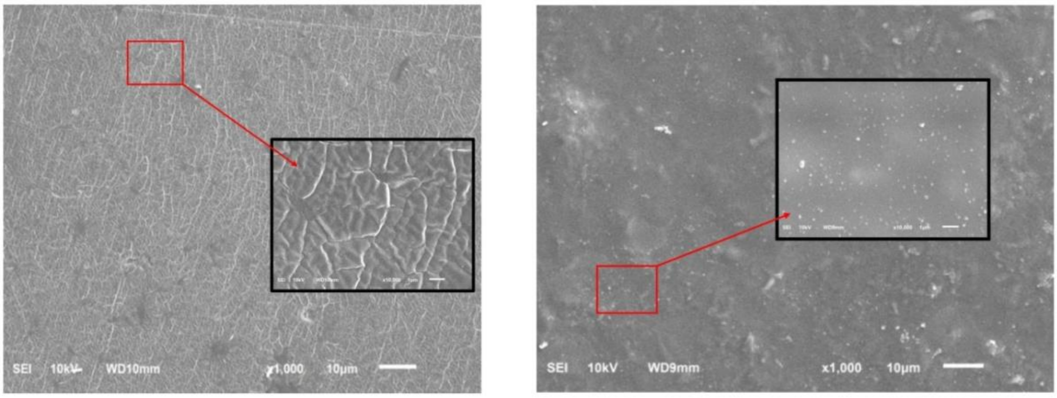
Figure 1. Schematic of filtration test equipment [3]

The prepared PVA and PVA/GO membranes were used as a membrane for filtration tests using a 5 mg/L MB solution as a test solution, using a filtration apparatus as shown in Figure 1 [3]. The filtration experiment started by inserting 1000 mL of a 5 mg/L MB solution into the filter tube, and then the PVA/GO membrane was placed on the holder membrane. The MB solution was then drained into the PVA/GO membrane assisted nitrogen pressures of 20 psi, 30 psi, and 45 psi. The permeate solution was then collected in a beaker glass and a stopwatch was used to measure an interval time of collecting a certain volume of permeate. The permeate volume was used to determine the permeability of the PVA/GO membrane that used for the filtration process. The reduction of concentration of MB permeate solutions at various time intervals were determined by measuring its absorbance using a UV-Vis spectrophotometer in the range of

500 nm to 750 nm. The concentration of MB permeate solutions was estimated using absorbance-concentration calibration curve.

3. Results and Discussion

The obtained membranes have a thickness of 30 μm. The surface morphologies of PVA membranes and PVA/GO composite membranes were observed through images of Scanning Electron Microscopy (SEM) as shown in Figure 2. The surface of the PVA membrane is homogeneous and free from defects as shown in Figure 2(a). The result is similar to the previous report which the surface of the PVA membrane was a flat surface and appears to have roughness [9, 10]. Figure 2(b) shows the surface of the PVA/GO composite membrane which was rough and uneven. There are various protrusions on the membrane indicating the presence of GO in the PVA matrix. Despite of protrusions or blotches are observed on the composite membrane, no cracks were found on the composite surface, which indicating GO was uniformly dispersed in the PVA matrix. This result is in line with previous report by Hoang et al [11].



(a) (b)

Figure2. Surface morphologies of (a) PVA membrane, (b) PVA/GO composite membrane

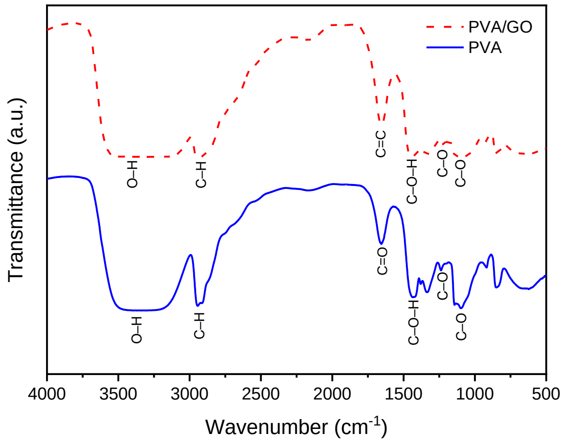


Figure3. FTIR spectra of PVA membrane and PVA/GO composite membrane

FTIR spectra of the prepared membranes are shown in Figure 3. A broad absorption peak at 3305 cm^{-1} and a peak at 2944 cm^{-1} are related to stretching vibration of the O–H and C–H group, respectively. A peak at 1655 cm^{-1} on the PVA membrane is related to C=O vibration, originated from glutaraldehyde. The sharp peak at 1650 cm^{-1} in the PVA/GO composite membrane, is identified as C=C vibration, which is a characteristic of GO. The peak at 1436 cm^{-1} is related to vibration of C–O–H, and the peak at 1099 cm^{-1} is related to vibration of C–O-C [9].

The thermal properties of the membranes were measured by using Thermogravimmetric Analysis (TGA) in a nitrogen atmosphere at the temperature range of 30^{o}C to 700^{o}C and with a heating speed of 10^{o}C/min. The TGA thermograph of PVA and PVA/GO membrane are shown in Figure 4.

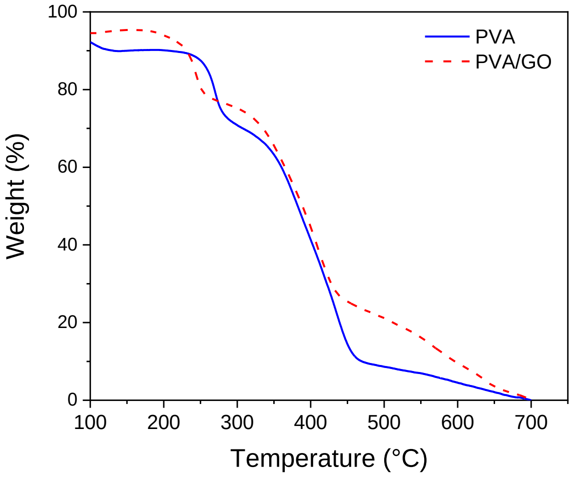


Figure4. TGA thermograph of PVA membrane compared to PVA/GO composite membrane

The TGA thermograph have a flat pattern until temperature about 200^{o}C. It is related to property of the PVA membrane and the PVA/GO composite membrane that become stronger after cross-linking process using glutaraldehyde. The initial weight loss of PVA membranes and PVA/GO composite membranes occurs at 200^{o}C – 250^{o}C, which is related with evaporation of water molecules that physically absorbed inside the membrane. The PVA and the PVA/GO composite membranes experienced a second stage of lost weight at around 350^{o}C, related to a primarily volatilization of the PVA main chain and the unstable degradation of the oxygen functional group from GO [9]. Since the amount of GO added was only small percentage concentration, no significant difference between both thermogravimetric curves is observed, as shown in Figure 4. At temperatures above 350° C, the weight of the PVA/GO membrane is slightly higher than PVA membrane that imply PVA/GO membrane has better thermal stability [9]. Besides, the second stage of weight loss of the PVA/GO composite membrane occurred at a higher temperature, which also confirmed improving thermal stability of the PVA/GO composite after and addition of GO [9].

The characteristics of permeability of the membrane was determined through a filtration process using MB as test solutions at various pressures. The permeate produced in the filtration process was measured using a UV-Vis spectrophotometer and the peak of absorbance spectra was used to estimate aconcentration of the permeate. Then, the concentrations of the permeate were determined using calibration curve as shown in equation (1), where y = absorbance (a.u) and x = concentration (mg/L).

$$y = 0{,}18643x + 0{,}02572 \qquad (1)$$

The concentration of permeate as function of time that measured at various pressuresare shown in Figure 5(a) and 5(b). The figure show that the concentration of MB permeate did not decrease significantly. This means that the MB filtration capability of the resulting PVA membrane and PVA/GO composite membrane is not satisfied. This result might be caused by the thickness of membrane. The thickness of the PVA and the PVA/GO composite membranes obtained in this study was about 30 μm, which was a smaller compared to the thickness of the eggshell membrane (L = 70 μm) that used in the previous study in reducing MB concentration using filtration process[2].

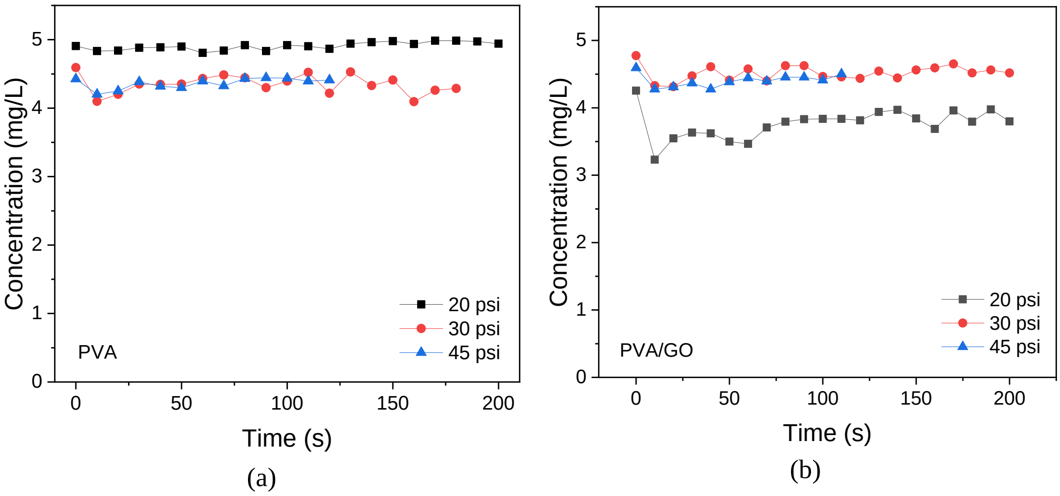


Figure 5. Concentration of MB permeate filtered at various pressures using PVA membranes (a) and PVA/GO membranes (b)

Besides, the weight composition between PVA and GO in this work has not yet varied in order to increase a membrane capability in reducing MB concentration. In previous work it has been shown that GO can act as a good adsorbent for MB molecules [12]. Therefore it is expected that when the content of GO is increases, the role of GO as an adsorbent in the composite membrane will improve its performance in filtration.

Furthermore, the membrane preparation process can also be improved to produce a better PVA/GO composite membrane as a filtration membrane. During the preparation PVA/GO solution, GO dispersion was mixed with PVA in the hydrothermal process at a temperature of 120°C. At that temperature, the oxygen group in GO can be reduced so that GO turns into rGO as reported previously [13]. Mixing of GO dispersion with PVA during the hydrothermal can cause a decreasing performance of GO as an adsorbent of MB, due to reducing of oxygen functional group in GO. Thus, in preparation PVA/GO solution a mixing of PVA and GO should not be done during hydrothermal process, but it should be done after the obtaining PVA solution. Using the PVA solution, the composite PVA/GO solution can be prepared only by mixing the PVA solution with GO dispersion using magnetic stirring at room temperature.

From the filtration process, the volume of permeate was also obtained and can be used to determine the flow discharge using equation (2), where Q = permeate flow discharge (mL/s), V = permeate volume (mL) and t = time (s).

$$Q = \frac{V}{t} \tag{2}$$

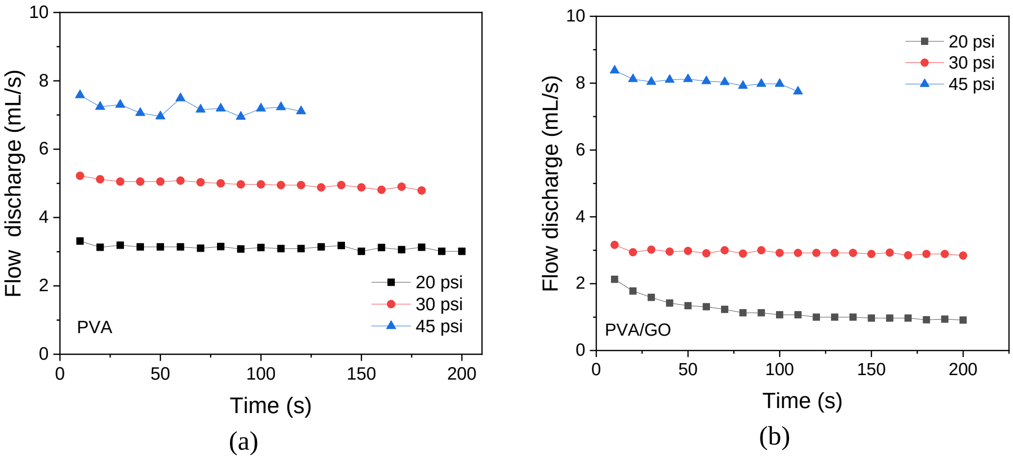


Figure 6. Flow discharge of MB permeate filtered at various pressures using PVA membranes (a) and PVA/GO membranes (b)

The flow discharge of permeate are shown in Figure 6. The flow discharge increases as the pressure rises. This happens because if the operating pressure is increased, then the thrust force received by the MB solution to exit through the membrane is higher, so the MB permeate flow discharge is rise as the operating pressure increases. At 45 psi, flow discharge was increased significantly. Since the thickness of the membrane was thin, it could not withstand the pressure applied so the membrane might leak and caused high flow discharge.

In the filtration process, when the MB solution flows through the membrane, a number of MB molecules were filtered by the membrane. The equation (3) is used to calculate the number of MB filtered into the membrane each time, where $m_{MB(m)}$ = MB mass inmembrane (mg), C_0 = MB feed concentration (mg/L), C_n = MB permeate concentration (mg/L), and V = permeate volume in a certain time (mL).

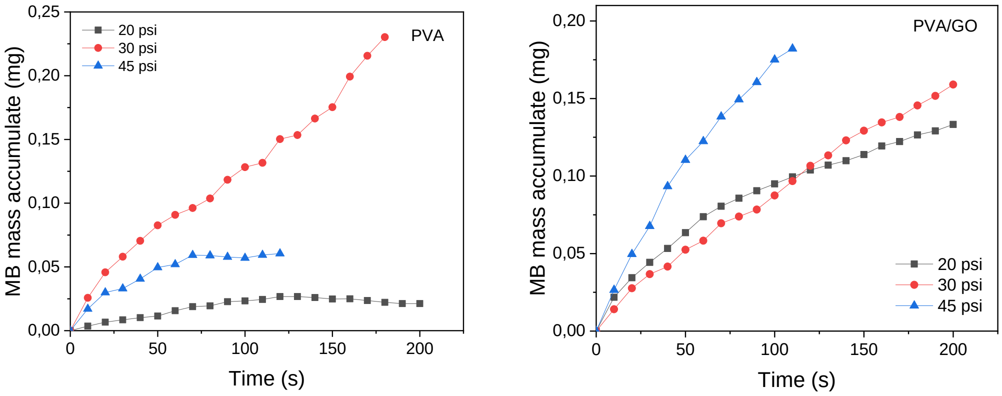
$$m_{MB(m)} = \frac{(C_0 - C_n) \times V}{1000} \tag{3}$$

The amount of MB filtered through the membrane is constant value. However, as time passes, the mass of MB filtered inside the membrane increases, as shown in Figure 7.

Some of the data obtained from the filtration process is used to determine the permeability values of PVA membranes and PVA/GO composite membranes.

Membrane permeability can be calculated using equation (4),where κ = membrane permeability (Darcy), Q = flow discharge (cm^3/s), η = fluid viscosity (cP), L = membrane thickness (cm), A = membrane surface area (cm^2) and P = pressure (atm).

$$\kappa = Q\left(\frac{\eta . L}{A . P}\right) \tag{4}$$



(a) (b)

Figure 7. MB mass accumulate in(a) PVA, (b) PVA/GO membraneduring the filtration process at various pressures

The permeability of PVA membranes and PVA/GO composite membranes during filtration processes with different pressures can be seen through the graph in Figure 8. From the figure it can be shown that the permeability values of PVA membranes and PVA/GO composite membranes during the filtration process at various pressures (20 psi, 30 psi, 45 psi) tend to be constant. The permeability values of PVA membranes and PVA/GO composite membranes can also be shown in Table 1.

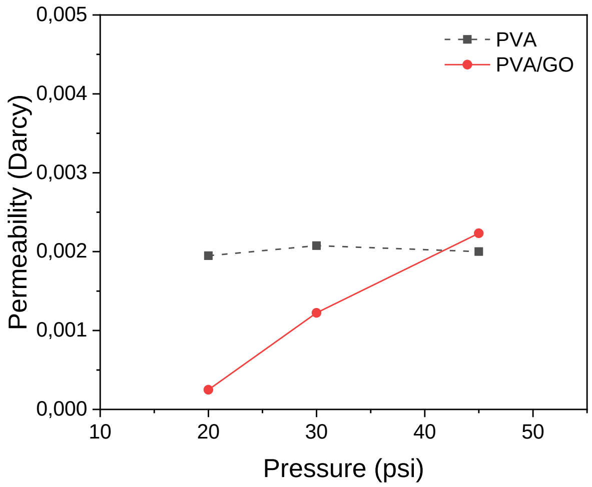


Figure 8. Permeability of PVA membrane and PVA/GO composite membrane during the filtration process at various pressures

From the information in Table 1, the permeability of the PVA membrane is relatively constant at a pressure of 20 psi, 30 psi, or 45 psi. This happens because the operating pressure on the filtration process is proportional to the permitted flow discharge. When the operating pressure increases, the permeate flow discharge will increase, so the permeability of the membrane will have a fixed value even if the membrane is operated at different pressures.

Table 1. Permeability of PVA membrane and PVA/GO composite membrane

Membrane	Permeability (Darcy) at Pressure (psi)		
	20	30	45
PVA	1.95×10^{-3} (l = 30 μm)	2.08×10^{-3} (l = 30 μm)	2.00×10^{-3} (l = 30 μm)
PVA/GO	2.49×10^{-4} (l = 60 μm)	1.22×10^{-3} (l = 30 μm)	2.23×10^{-3} (l = 30 μm)

When compared with the results of previous studies, the permeability value of the PVA/GO composite membrane produced in this study and operated at 45 psi was 2.23×10^{-3} Darcy, while the ES-GO permeability of membrane previously studied at pressure of 45 psi was $2{,}488\times10^{-3}$ Darcy [3]. The PVA/GO composite membrane produced in this study has the same permeability as ES-GO membrane, but in thickness are different. Therefore, their ability to filter MB is also different. This happened because the PVA/GO membrane produced in this study experienced a leak during the filtration process due to the fact that it was not strong enough to withstand the given operating pressure. Although the two membranes have the same permeability, their ability to filter MB is different.

4. Conclusions

PVA and PVA/GO composite membranes with thicknesses of 30 μm were prepared using the solution casting method on a glass substrate. SEM images shows that GO is uniformly dispersed into the PVA matrix and forms a PVA/GO composite. FTIR spectra show that peaks at 1655 $\text{cm}^{-1}$of PVA/GO composite membranes sharper than PVA membranes, which related to the presence of C=O vibrations from glutaraldehyde and C=C of GO. In addition, the TGA results showed PVA/GO composite has better thermal stability compare to PVA membrane. The obtained PVA membranes have permeability of 1.95×10^{-3}, 2.08×10^{-3} and 2.00×10^{-3} Darcy, while the obtained PVA/GO composite membranes have permeability of 2.49×10^{-4}, 1.22×10^{-3} and 2.23×10^{-3} Darcy respectively at pressures of 20 psi, 30 psi, and 45 psi.

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