Synthesis of Printed Hollow Fiber Membranes Urea as a Membrane Candidate Hemodialysis

Muhammad Cholid Djunaidi[1*], Denandha Putri Ayuningrum[1], Nesti Dwi Maharani[1], Khabibi Khabibi[1], Pardoyo Pardoyo[1], Yanuardi Raharjo[2], Heru Susanto[3], and Abdullah Malik Islam Filardli[3]

[1]*Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Jl. Prof. Soedharto SH, Tembalang, Semarang 50275, Indonesia*

[2]*Department of Chemistry, Faculty of Science and Technology, Universitas Airlangga, Campus C, Mulyorejo, Surabaya 60115, Indonesia*

[3]*Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof. Soedharto SH, Tembalang, Semarang 50275, Indonesia*

* ***Corresponding author:***

email: choliddjunaidi@lecturer.undip.ac.id

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Abstract: *Chronic kidney failure is a disease that affects the world's population and an alternative solution is hemodialysis. Hemodialysis is the process of cleaning the blood from urea and creatinine through a semi-permeable membrane in the form of a hollow fiber membrane (HFM) with the following advantages: flexible and low energy requirements. The weaknesses of commercial hemodialysis membranes are that they are hydrophobic, chemical resistant, and low biocompatibility. This research uses a membrane of polysulfone combined with eugenol and polyethylene glycol (PEG) or polyethylene glycol diglycidyl ether (PEGDE). Eugenol has allyl, hydroxy, and methoxy groups which are derived from polyeugenol via allyl groups and from polyeugenol to polyeugenoxy acetic acid via hydroxyl groups. The resulting molecularly imprinted membrane (MIM) in the form of hollow fiber has better porosity, absorption, flux values and is highly selective in transport, with the order of selectivity, namely urea > creatinine > vitamin B_{12}.*

Keywords: *hollow fiber; polyeugenoxy acetate; hemodialysis; imprinted*

■ INTRODUCTION

Chronic kidney failure or chronic kidney disease (CKD) is a disease that affects one-tenth of the world's population [1]. The solution for patients with advanced-stage CKD is organ transplantation, but the chances of receiving a transplant are very low. Thus, an alternative solution for CKD patients is to run hemodialysis [2]. The number of active patients and new hemodialysis patients in Indonesia has increased from year to year. In 2007, the number of new and active patients was 4,977 and 66,433. In 2020, the number of new and active patients was 61,786 and 130,931 [3].

Hemodialysis is a treatment process for patients suffering from CKD, which involves cleaning the patient's blood from metabolic wastes and toxic substances [4]. Hemodialysis involves purifying blood through a semi-permeable membrane or based on a hollow fiber membrane (HFM), by cleaning the dirty blood from the patient's body. Then the clean blood is circulated back to the patient's body [2]. HFMs have several advantages, namely flexibility and low energy requirements [5]. Several polymeric materials widely used for commercial hemodialysis membranes are polysulfone, polyethersulfone, polyamide, cellulose triacetate, and polyacrylonitrile. This commercial membrane has the disadvantage of being hydrophobic, low chemical resistance, and low biocompatibility [6]. Polysulfone-based membranes have been increasingly used in various industrial and medical fields with the advantages of good chemical and temperature resistance as well as

good mechanical strength and stability. Polysulfone membranes in hemodialysis applications exhibit optimal biocompatibility in solute removal, good thermal stability, and mechanical properties [7].

The material used for the manufacture of hemodialysis membranes is eugenol which is derived from clove leaf oil and is used as a starting material for synthesis. Eugenol has 3 functional groups, namely allyl, hydroxy, and methoxy groups. Eugenol is degraded to polyeugenol via allyl groups and polyeugenol (PE) can be degraded to polyeugenoxy acetic acid (PA) via hydroxyl groups. Eugenol derivatives have been shown to be effective as liquid membrane carriers, with selectivity that can be changed based on the functional groups included [8]. Djunaidi and Wenten [9] made urea-selective flat membranes using eugenol for hemodialysis where eugenol was contacted with urea combined with polyethylene vinyl alcohol (PVA) and polyethylene glycol diglycidyl ether (PEGDE). The results of the research show that molecularly imprinted membrane (MIM) urea is better than non-imprinted membrane (NIM). The membrane is more selective for urea and creatinine but not for vitamin B_{12}. Djunaidi et al. [10] prepared flat membranes as candidates for hemodialysis membranes using PA-urea combined with PVA and PEGDE. The results of the study showed that MIM transports better than NIM and that the urea membrane is selective for creatinine and vitamin B_{12}, although not as great as urea. For PA-urea combined with polysulfone and polyethylene glycol (PEG), MIM was also more selective for urea than NIM, with the selectivity order of urea > creatinine > vitamin B_{12} [8].

The novelty of this study was using HFMs with polysulfone as the base membrane, variations of PEG and PEGDE cross-links, mixed transport, and characterization of the physical properties of HFMs. In this research, PA was used as an additive polymer that can provide functional groups and channels suitable for the structure and size of urea molecules. MIM synthesis was carried out using polysulfone combined with PA-urea, PEG 6000 or PEGDE, NMP, and NaOH as a catalyst. MIM printing is carried out using the phase inversion method in a coagulant bath containing water with a spinner, the dope solution passes through the spinneret and is immersed in aqua DM. NIM synthesis was carried out to compare the transport performance of MIM. This study will explain the selectivity of MIM and NIM for the transport of urea, creatinine, vitamin B_{12}, and their mixtures for hemodialysis membrane candidates.

■ EXPERIMENTAL SECTION

Materials

Eugenol p.a., polysulfone, and picric acid ($C_6H_3N_3O_7$) were purchased from Sigma Aldrich. BF_3-diethyl ether ($BF_3O(C_2H_5)_2$), methanol (CH_3OH), chloroform ($CHCl_3$) p.a., anhydrous sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), chloroacetic acid ($C_2H_3ClO_2$), hydrochloric acid (HCl) p.a., diethyl ether ($(C_2H_5)_2O$), sodium bicarbonate ($NaHCO_3$), ethanol (C_2H_5OH), *N*-methyl-2-pyrrolidone (NMP), PEG 6000, PEGDE, disodium phosphate (Na_2HPO_4), monosodium phosphate (NaH_2PO_4), 4-dimethylaminobenzaldehyde (DAB), urea, creatinine, and vitamin B_{12} were obtained from Merck, and aqua demineralized (DM) was purchased from Brataco.

Instrumentation

The instruments in this research were FTIR (Shimadzu Prestige 21 ASTM), UV-vis (B-One), SEM-EDX (JSM 6510 LA), TGA/DTA (Exstar SII 7300), HT-2402 computer universal testing machines, glassware (Pyrex and Herma), reflux apparatus, analytical balance (Ohaus), magnetic bars, stirrers, pestle and mortar, T3 Pots, pH paper (Macherey-Nagel), pH meter (Senz), Ubbelohde viscometer, fine filter paper, wrap (Kiln pack), aluminum foil (Kiln pack), caliper (digital caliper), oven (Faithful FCD-300 Serials), peristaltic pump, and hose.

Procedure

PE synthesis

Eugenol (5.8 g) was put into a two-neck flask, 0.25 mL of BF_3-diethyl ether was added every hour for 4 h and stirred. The polymerization reaction was carried out for 14–16 h at room temperature and pressure. Polymerization was stopped by adding 1 mL of methanol. The formed gel was dissolved in 30 mL of chloroform and washed with aqua DM to reach pH 7.

The solution was filtered using anhydrous Na_2SO_4 to be free from water. The solution was transferred to the mortar and evaporated at room temperature. The precipitate formed was dried, weighed, and analyzed by FTIR [8].

Synthesis of PA

An amount of 5.0 g of PE was put into a three-neck flask and then 17.5 mL of 33% NaOH was added and stirred for 30 min at 80–90 °C. Then, 50% chloroacetic acid (12.5 mL) was dropwisely added to the solution and stirred for 24 h. The precipitate formed was cooled and acidified with 6 M HCl to pH 1, extracted with 30 mL diethyl ether three times. Then separated and extracted with 30 mL 5% w/v sodium bicarbonate three times. The precipitate was acidified with 6 M HCl to pH 1 then filtered, dried, weighed, and analyzed by FTIR [10].

Contact of PA with urea

As much as 1 g of PA was contacted with 20 mL of 1000 ppm urea solution. The purpose of this contact is to incorporate the urea molecule as a template. Contact was carried out with a stirrer for 24 h, then filtered and dried to form PA-urea. The contacting solution before and after was measured using a UV-vis spectrophotometer [8].

MIM synthesis

PEG 6000 (0.833 g) or PEGDE (0.731 mL), polysulfone (3.333 g), PA-urea (0.833 g) with a weight ratio of 1:4:1 dissolved in 12 mL NMP and added 0.249 mL NaOH (0.1 M) as a catalyst. The membrane solution was stirred for 10 h at 90–100 °C. After being homogeneous, the membrane solution was printed using the phase inversion method [8]. A coagulant bath filled with water with spinnerets 30 cm apart. Dope solution is put into tube 1 and aqua DM in tube 2 which has a flowmeter installed. Tubes 1 and 2 are connected to nitrogen gas cylinders using a hose, and then the membrane solution flowmeter and nitrogen gas are opened to start the process of forming hollow fiber membranes. After the dope solution passes through the spinner and enters the coagulant bath, the aqua DM flowmeter is opened to form dense hollow fibers. After that, hollow fiber membranes are soaked in aqua DM to remove residual solvent. Membrane characterized using FTIR, SEM-EDX, and TGA.

NIM synthesis

NIM synthesis was carried out like MIM synthesis but without the urea binding step. The PA used was not in contact with urea.

Membrane hydrophilicity

HFMs were tested for hydrophilicity by measuring the contact angle (θ) of the membrane. The drop shape analysis (DSA) method is carried out by observing a sessile drop using a camera. The HFM was placed on a flat surface and dripped with 1 drop of aqua DM right above the membrane. Pictures of water droplets on the membrane are taken from a camera angle parallel to the membrane and the eye. Measurement of the water contact angle to the membrane was carried out by fittings using CorelDraw software.

Membrane porosity test

Soak the hollow fiber membrane with 10 mL of aqua DM in a petri dish for 24 h at room temperature. The membrane is dried using a tissue and weighed so that the value of W_1 (g) is obtained as the initial wet weight value of the membrane. The membrane was dried using an oven at 100 °C for 6 h until completely dry, then cooled and weighed again so that the value of W_2 (g) was obtained as the dry weight of the membrane. The resulting weight is used to determine the percent porosity of the membrane.

Water absorption test

The HFM is weighed using an analytical balance to obtain the initial weight of the membrane. The membrane was immersed in 10 mL of aqua DM for 6 h and re-weighed after immersion. The resulting weight is used to determine the percent water absorption of the membrane.

Tensile test

The HFM was subjected to a tensile test where the tensile strength and percent elongation were measured using a tensile strength tool. The membrane is pulled with a certain force until the membrane elongates and breaks. Tensile test results in the form of tensile strength data (MPa or N/mm^2) and elongation (%).

Flux test

HFMs were subjected to flux tests on 4 different solutions, namely aqua DM, urea, creatinine, and vitamin

B_{12}. Some hollow fiber membranes where each end of the membrane is glued using epoxy glue on an acrylic pipe. The membrane module that has been formed is installed on a series of pumps connected by a hose. The flux test was carried out for 1 h with 6 repetitions. The result of the flux test is the volume of the feed solution that passes through the membrane, which is then calculated for the flux value.

Urea transport

Urea transport is carried out with a hollow fiber membrane module attached to a peristaltic pump that has been installed with an adapter and hose. The feed phase (FP) in this transport is 50 ppm urea solution and the receiving phase (RP) is PBS pH 7.4, each 1000 mL. Sampling was carried out every 15 min for the first hour and every hour for up to 4 h. The samples that have been taken are added to the urea complexing solution with a ratio of 1:1 and left for 30 min. The absorbance was measured using a UV-vis spectrophotometer at a wavelength of 430 nm.

Creatinine transport

Creatinine transport is carried out with a HFM module attached to a peristaltic pump that has been installed with an adapter and hose. The FP in this transport is 50 ppm creatinine solution and the RP is PBS pH 7.4 each 1000 mL. Sampling was carried out every 15 min for the 1st hour and every hour for up to 4 h. The samples that have been taken are added to the creatinine complexing solution in a ratio of 1:1 and left for 30 min. The absorbance was measured using a UV-vis spectrophotometer at a wavelength of 486 nm.

Transport of vitamin B_{12}

The transport of vitamin B_{12} is carried out with a HFM module attached to a peristaltic pump that has been installed with an adapter and hose. The feed phase in this transport is a 50 ppm vitamin B_{12} solution and the receiving phase is PBS pH 7.4 for 1000 mL. Sampling was carried out every 15 min in the 1st hour and every hour until 4 h. Samples were measured for absorbance using a UV-vis at 361 nm.

Mixed transport

Mixed transport is carried out with a HFM module attached to a peristaltic pump that has been installed with an adapter and hose. The FP in this transport is a mixed solution (urea, creatinine, and vitamin B_{12}) and the RP is PBS pH 7.4, each 1000 mL. Sampling of the solution at the beginning (0 min) and end (4 h) for COD analysis and measurement of urea, creatinine, and vitamin B_{12}, respectively. Samples are added to a solution of urea complexing and creatinine complexing in a ratio of 1:1 and left for 30 min each. The absorbance was measured at 430 nm for urea.

■ RESULTS AND DISCUSSION

PE Synthesis

PE synthesis was carried out through eugenol polymerization by adding a BF_3-diethyl ether catalyst. The polymerization process was carried out for 16 h and was stopped using methanol. The methoxy group (CH_3O^-) bind carbonium ions so that the polymer had a methoxy end. PE in the form of a purple gel was dissolved in chloroform and washed with aqua DM until the pH was neutral. Washing with aqua DM aims to remove the catalyst and the remaining aqua DM in PE is removed by adding anhydrous Na_2SO_4. The PE obtained was allowed to stand at room temperature so that the solvent could evaporate, harden, and be crushed to get a pink powder in 95.22% yield.

The results of the PE FTIR analysis were compared with those of eugenol to determine the success of PE synthesis. The FTIR results can be seen in Fig. 1. Based on the FTIR data, PE has an absorption band at 2957.87 cm^{-1} indicating C(sp^2)–H from the aromatic ring, and absorptions at 1510 and 1601 cm^{-1} indicating C=C aromatic stretching vibrations. These aromatic compounds strengthen the aromatic groups in PE. In the eugenol spectra, there are absorption bands at 996 and 914 cm^{-1} for vinyl group but are absent in the PE spectra. When polymerization occurs, the vinyl group in eugenol will bind to other eugenols to form PE [8].

PA Synthesis

Synthesis of PA was carried out by adding NaOH and chloroacetic acid to PE. The addition of NaOH serves to form polyeugenolate salts through their hydroxy groups and chloroacetic acid reacts with polyeugenolate

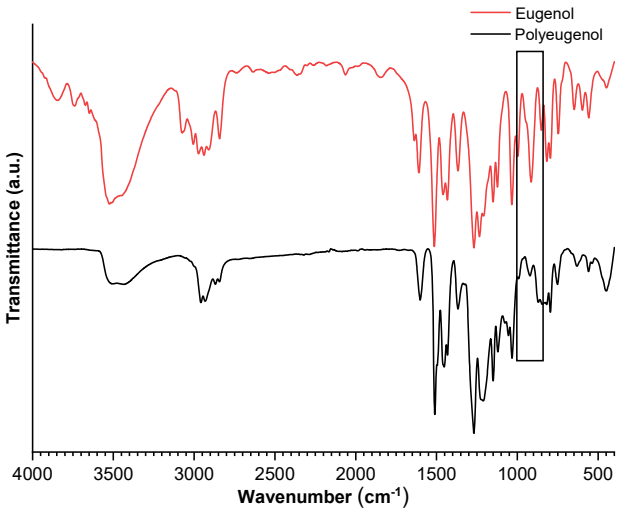


Fig 1. FTIR analysis results of eugenol and PE

sodium salts to form PA. The result obtained is in the form of a precipitate purified by extraction using diethyl ether and sodium bicarbonate. Diethyl ether and sodium bicarbonate serve to remove non-polar and polar impurities [8]. The resulting filtrate was dried at room temperature to obtain PA in 95.23% yield.

The result of FTIR analysis of PA was compared with PE to determine the success of synthesis (Fig. 2). Based on the data, PA has a hydroxyl group at an absorption band at 3390 cm^{-1} and a saturated carbonyl group ($C(sp^2)$ –H) at an absorption band of 2958 cm^{-1}. An absorption band of 1144 cm^{-1} indicates acidic CO bonds and in the PA spectra, there is an absorption band of 1731 cm^{-1} indicating an acid carbonyl group (C=O) but absent in the PE spectra indicating that PA was successfully synthesized [8]. PA has a degree of acetylation of 66.40%.

Contact of PA with Urea

Contact of PA with urea was carried out by stirring PA in 1000 ppm urea solution for 24 h. This aims to bind the urea template to PA. Urea acts as a target molecule, which aims to give the imprinted membrane the ability to recognize the target molecule when the membrane is applied. To determine the percentage of urea contacted on PA, measurement of the urea solution before contacting and the filtrate after contacting was carried out using a UV-vis spectrophotometer. The result was 696.471 ppm, which indicated that the PA was successful in binding to urea. The interaction that occurs in this contact is hydrogen bonding, PA has an OH group where the more positive hydrogen bonds to nitrogen in urea. Urea interacting with the polymer will affect the performance of the membrane when the membrane is applied in transport. The estimated interaction between PA and urea is shown in Fig. 3 [8].

The results of the FTIR analysis of PA and PA-Urea were processed using the Fityk software. The

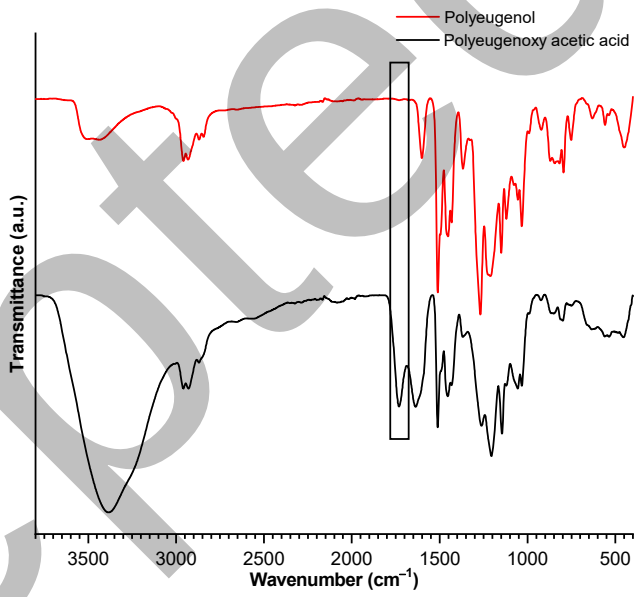


Fig 2. FTIR analysis results of PE and PA

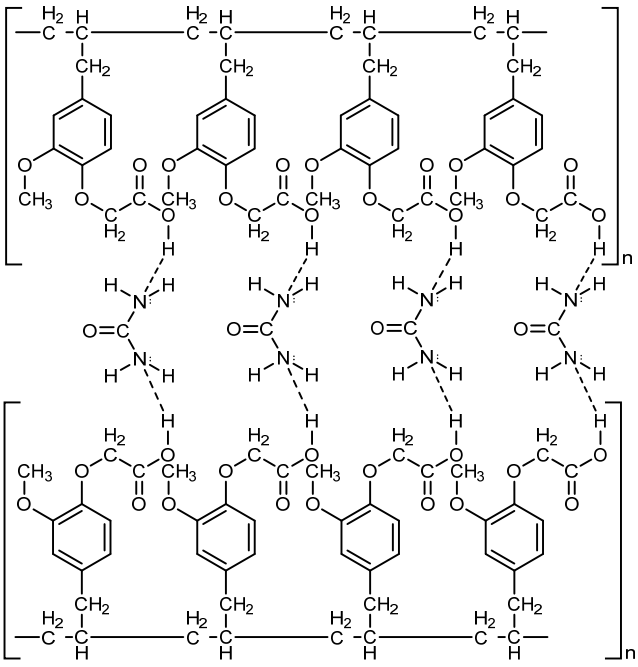


Fig 3. Approximate interaction of PA with urea [8]

deconvolution peaks are shown in the range of 1550 to 1680 cm^{-1} based on Gaussian line shapes at least square values. The results of the PA Fityk analysis are in Fig. 4(a) and (b) show that there are 6 peaks below the actual peak. This is possible because of the overlap of these peaks. Peaks I (1564 cm^{-1}), II (1586 cm^{-1}), III (1605 cm^{-1}), and IV (1637 cm^{-1}) show absorptions from C=C aromatic groups. Meanwhile, peaks V (1667 cm^{-1}) and VI (1678 cm^{-1}) indicated the carbonyl group (C=O) [8].

In Fig. 4(b), absorption from aromatic C=C can be seen in peaks I (1585 cm^{-1}) and II (1603 cm^{-1}). Peak III (1623 cm^{-1}) is indicated to the NH bending and peak IV (1643 cm^{-1}) is related to the amide group. Meanwhile, peaks V (1659 cm^{-1}) and VI (1674 cm^{-1}) indicated to the absorptions from amide carbonyl (C=O) group [8]. It can be concluded that PA has been successfully contacted with urea by the presence of peaks III, IV, V, and VI in the PA-Urea absorption analysis.

Synthesis of MIM and NIM

Synthesis of MIM and NIM was carried out using polysulfone as the basic membrane with various crosslinkers, namely PEG 6000 and PEGDE, and NaOH as a catalyst. The functional monomers used are PA which has been contacted with urea (PA-Urea) for the synthesis of MIM and PA without contacting urea for the synthesis of NIM. The resulting membrane will be applied to transport and analyzed using FTIR, SEM-EDX, and TGA. The estimated interaction between polysulfone, PEG or PEGDE, and PA-Urea is depicted in Fig. 5 [8]. NIM synthesis was carried out in the same way as MIM synthesis, but the PA used was not in contact with urea. Estimated interactions between polysulfone, PEG or PEGDE, and PA are depicted in Fig. 6 [8].

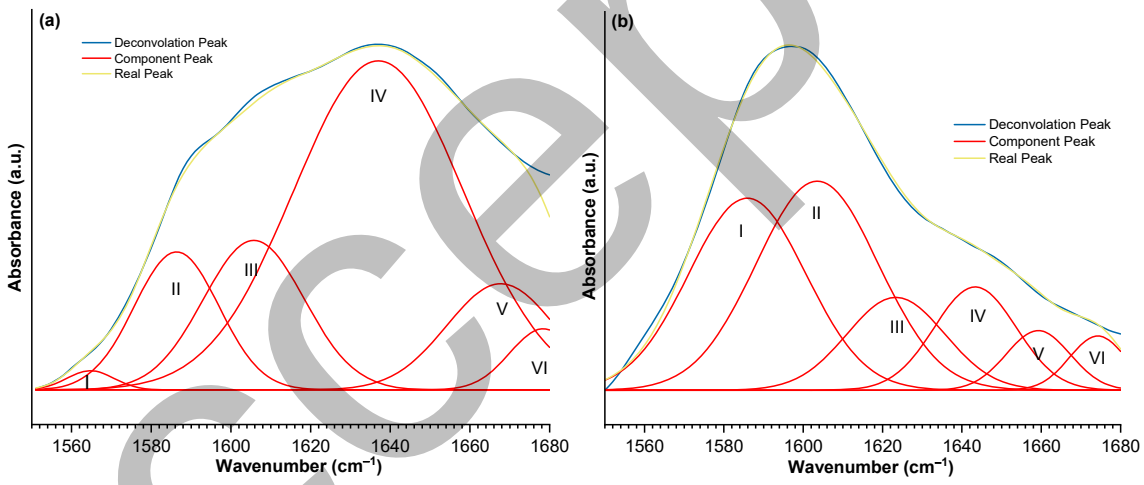
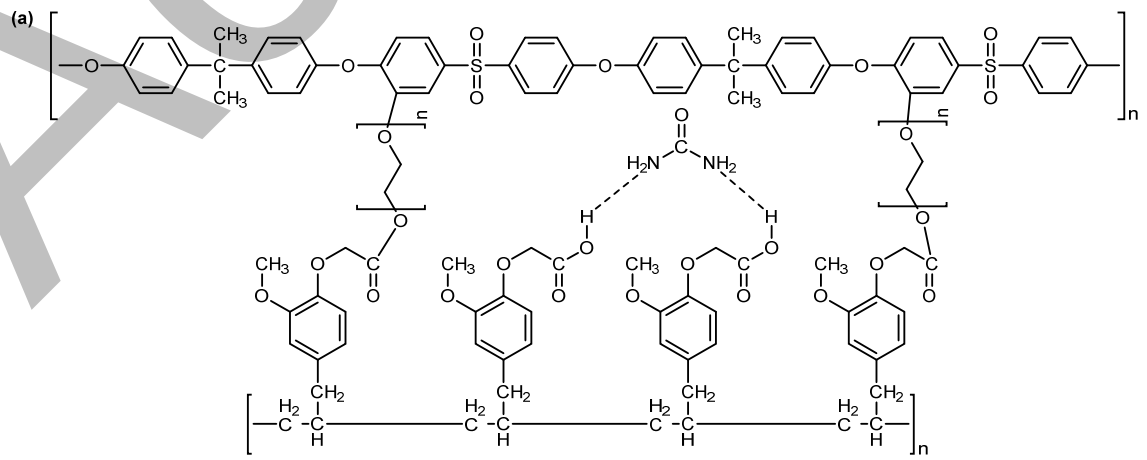


Fig 4. Fityk graph of (a) PA and (b) PA-urea



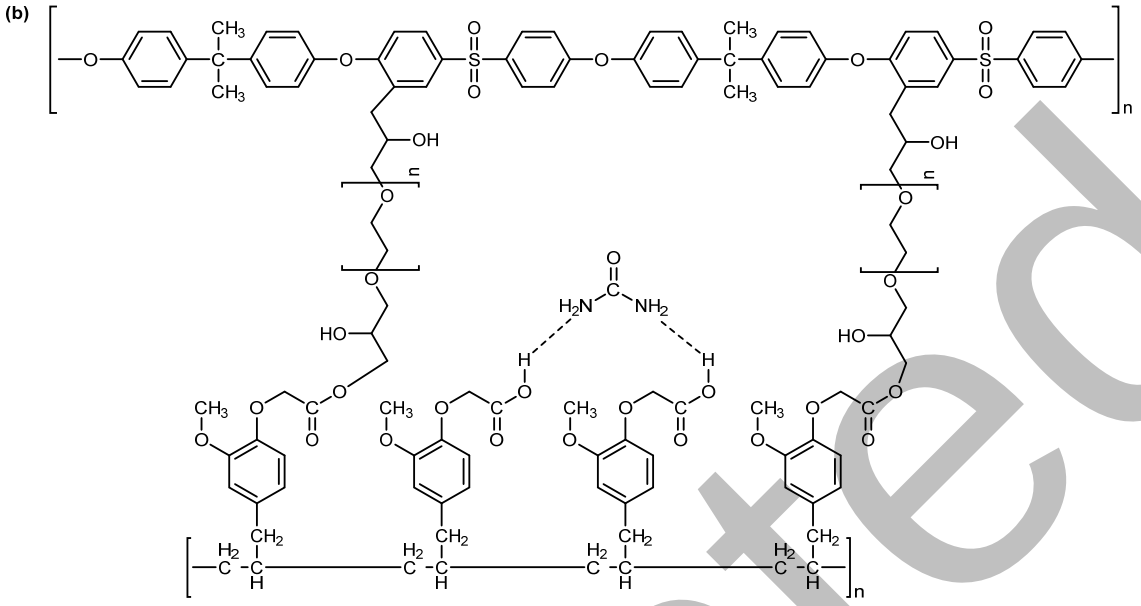


Fig 5. Estimated interactions of (a) polysulfone, PEG, and PA-Urea and (b) polysulfone, PEGDE, and PA-Urea

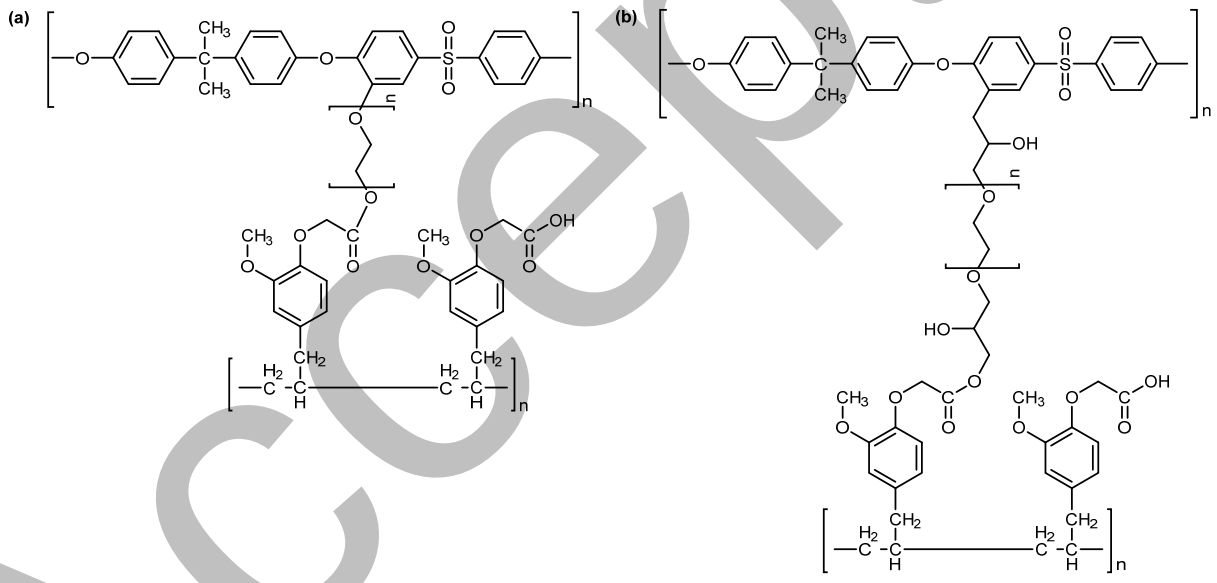


Fig 6. Estimated interactions of polysulfone and PA with (a) PEG and (b) PEGDE

Fig. 7(a) shows the results of FTIR hollow fiber MIM PEG 6000 and PEGDE. There was no absorption of the NH bending group at 1748 cm^{-1}. This indicated that the urea in MIM PEG 6000 and PEGDE had been released and was no longer contained in the membrane because it formed a template in MIM. At 1585 cm^{-1} shows C=C aromatic absorption and C–SO_2–C absorption at 1105 cm^{-1}. The signal at 3400 cm^{-1} shows the OH group, MIM PEG 6000 has a weak peak of the OH group compared to MIM PEGDE, so MIM PEGDE is more hydrophilic. Signal at 1242 cm^{-1} contains S=O groups originating from polysulfone and CO groups at 1150–1151 cm^{-1} due to cross-linking reactions between polysulfone and PEG or PEGDE [11]. Previous research shows that the strengthening of the OH intensity will indicate a weakening of the CO group [8].

Fig. 7(b) shows the results of FTIR hollow fiber NIM PEG 6000 and PEGDE, C=C aromatic (1584 cm^{-1}),

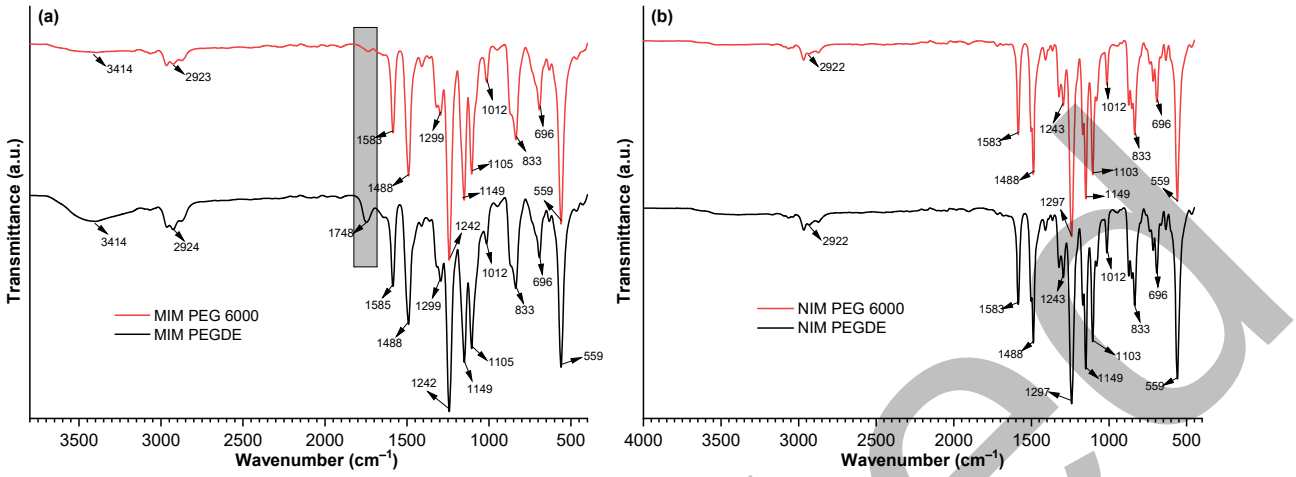
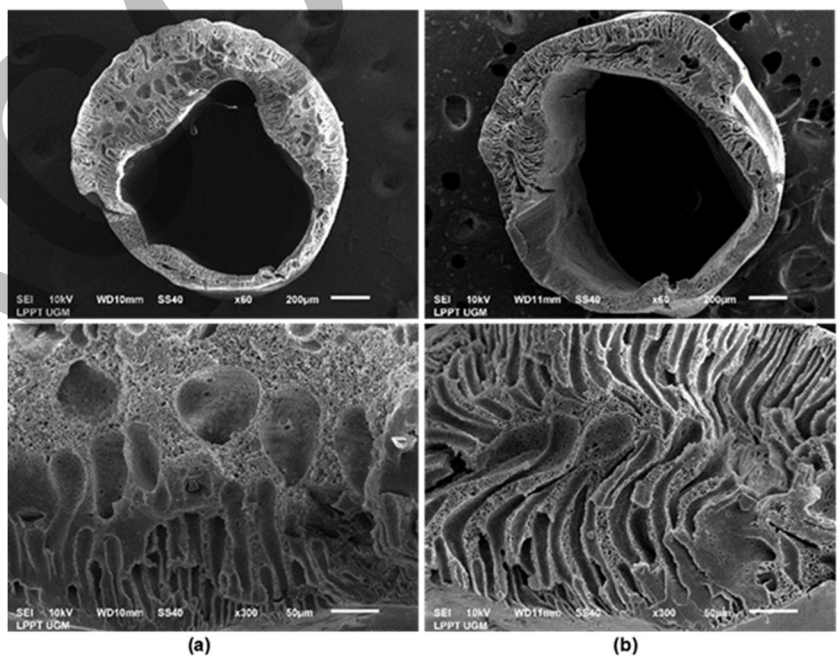


Fig 7. FTIR results of (a) MIM and (b) NIM

C–SO_2–C (1105 cm^{-1}), S=O (1240–1241 cm^{-1}), and CO absorption (1149 cm^{-1}). NIM's OH absorption appears at 3400 cm^{-1}, but it is very weak compared to MIM's OH absorption. The appearance of S=O and CO signals indicates that there is a cross-linked reaction between the polysulfone and PEG or PEGDE [11]. It can be concluded that MIM PEGDE has a high intensity of OH groups compared to MIM PEG 6000 and NIM so that MIM is more hydrophilic.

MIM and NIM analysis with SEM-EDX

Hollow fiber MIM and NIM were analyzed using SEM-EDX to determine the morphology and elemental content of HFMs. Fig. 8 shows the cross-section of the membrane using 300× magnification. Fig. 8(a–d) showed that the membrane formed a finger-like macrovoid. This happens when the printed membrane is immersed in a coagulation bath containing aqua DM. This immersion process uses a phase inversion method where the membrane will settle and pore formation occurs. The formation of membrane pores occurs due to the weak solubility of polysulfone mixed with polyeugenoxy acetic acid in water, causing the exchange of NMP solvents with water to form finger-like macrovoids more quickly. The



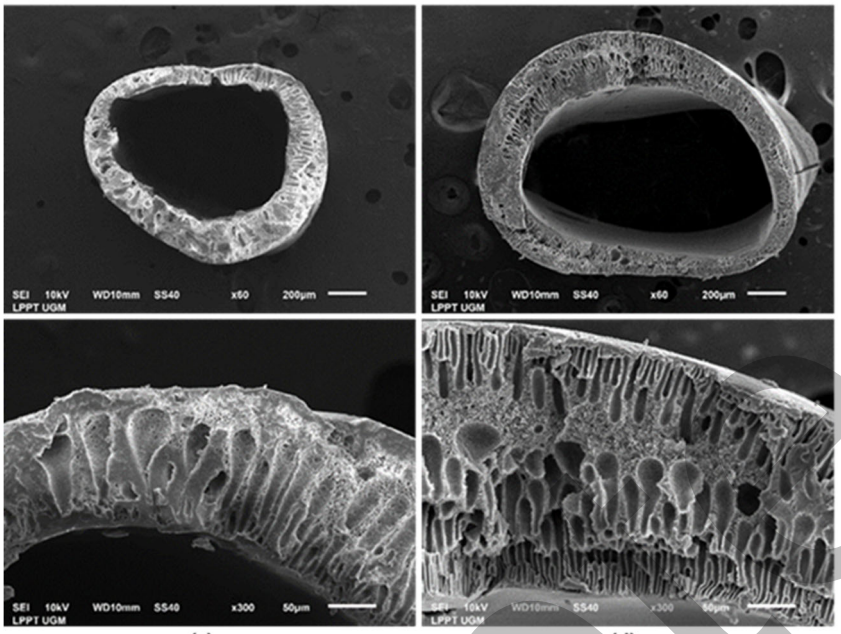


Fig 8. SEM results cross-section of (a) MIM PEG 6000, (b) MIM PEGDE, (c) NIM PEG 6000, and (d) NIM PEGDE

addition of PEG or PEGDE to the membrane will cause the bonds between polymers to weaken. PEG is hydrophilic, causing the solvent exchange process to be faster and the size of the macrovoid formation on the membrane becomes larger [11-12]. MIM PEGDE forms a denser porous structure than MIM PEG 6000 because PEGDE consists of longer PEG segments [13]. The PEGDE MIM shows a uniform shape compared to the PEG 6000 MIM, which is not uniform and not full. SEM photos show that the resulting HFM is imperfect, and the thickness of the fiber walls is irregular. Based on the results of the EDX on MIM, no N elements were found, which indicates that the MIM formed released all of the urea when the membrane was immersed in the coagulation bath. The results of the EDX analysis on MIM can be seen in Table 1.

NIM PEGDE forms more, denser, and more uniform pore structures than NIM PEG 6000 because PEGDE is a longer segment of PEG so that PEGDE forms more pores [13]. SEM photos show that the resulting HFM is imperfect and the thickness of the fiber walls is irregular. The results of the EDX analysis on NIM can be seen in Table 2. Based on Fig. 9, the results show a slightly porous and asymmetrical composite shape. Composite asymmetric membranes have a combination of a thin polymer layer in the form of a dense layer, which lies on top of a thick polymer layer in the form of a porous layer. The dense layer determines the performance of the membrane, and the porous layer determines the rate of separation [11].

MIM and NIM Analysis with TGA

Hollow fiber MIM and NIM were analyzed using the TGA function to measure changes in weight as a function of temperature. Fig. 10 and Table 3 show the results of TGA on PEG 6000 and PEGDE membranes.

Table 1. Mass percentage of elements in the MIM membrane

Element	MIM PEG 6000 (%)	MIM PEGDE (%)
C	71.04	71.84
O	25.96	21.58
S	2.88	5.79

Table 2. Mass percentage of elements in the NIM membrane

Element	NIM PEG 6000 (%)	NIM PEGDE (%)
C	69.00	72.92
O	28.20	21.21
S	2.45	5.20

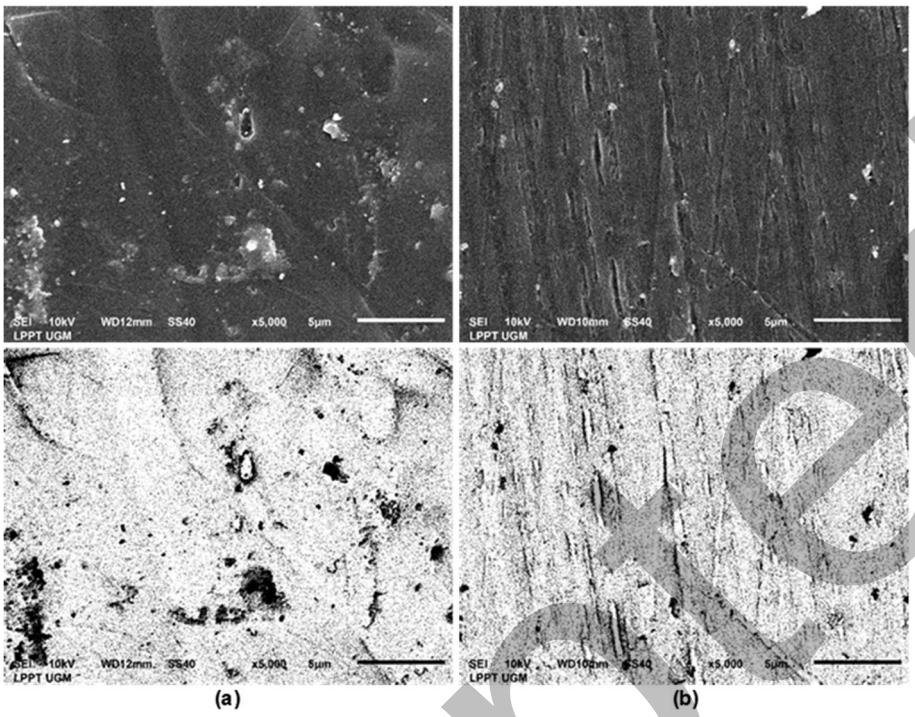


Fig 9. Surface SEM results with ImageJ of (a) NIM PEGDE and (b) MIM PEGDE

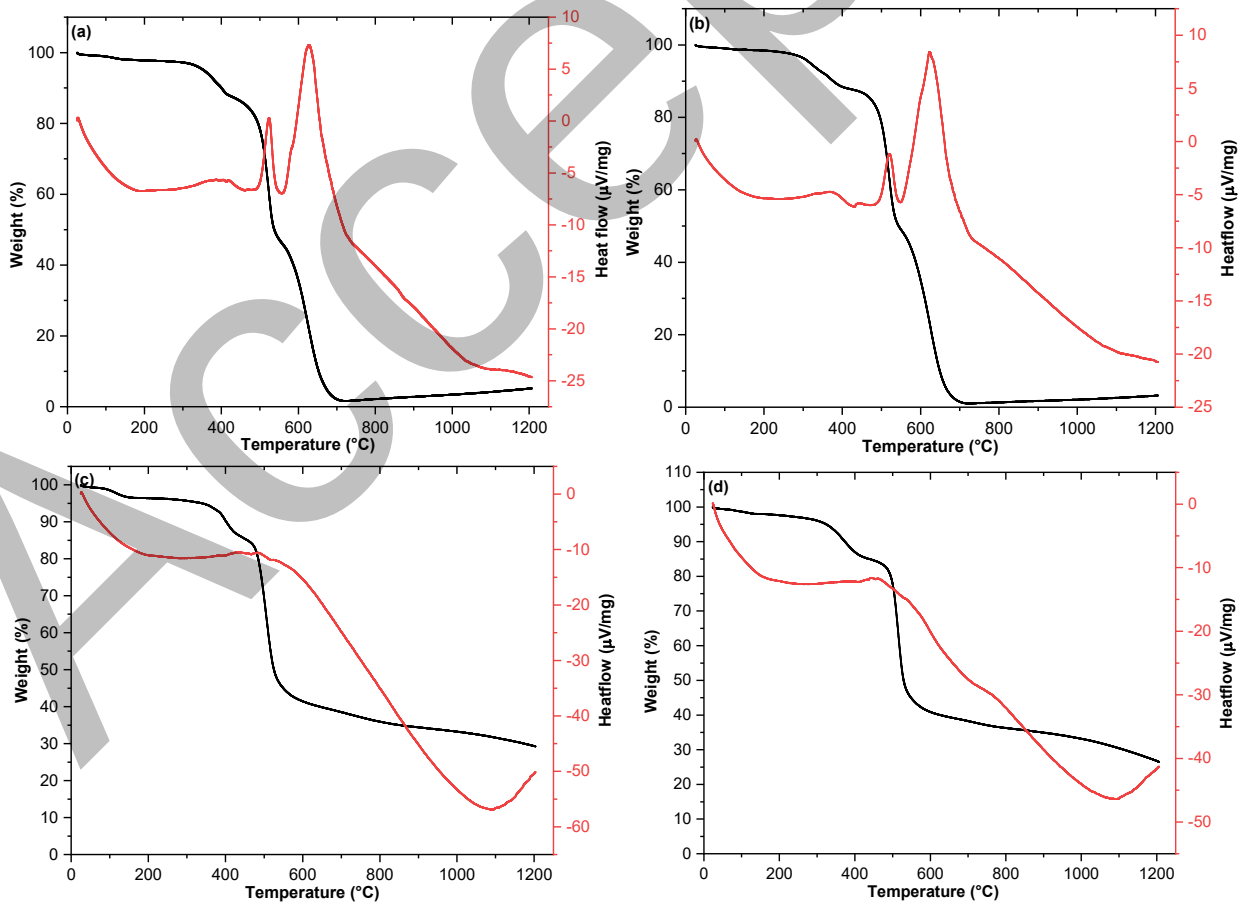


Fig 10. Thermal analysis results of (a) NIM PEG 6000, (b) NIM PEGDE, (c) MIM PEG 6000, and (d) MIM PEGDE

Table 3. MIM and NIM thermal analysis

Material	T (°C)	Decomposition (%)
	25–354	1–5
NIM PEG 6000	355–400	6–10
	401–537	11–50
	25–317	1–5
NIM PEGDE	318–376	6–10
	377–544	11–50
	25–338	1–5
MIM PEG 6000	339–402	6–10
	403–525	11–50
	23–324	1–5
MIM PEGDE	325–373	6–10
	374–529	11–50

MIM and NIM have weak exothermic peaks in the temperature range of 50–100 °C, a dehydration reaction or release of water may come from water molecules adsorbed on the membrane. The thermal process of the membrane is in the temperature range of around 412–725 °C, decreased significant mass caused by the double bond in the aromatic ring, which is broken into an aliphatic chain due to high temperature [10]. NIM has better thermal resistance compared to MIM because the presence of urea in MIM reduces the thermal resistance of the membrane, so NIM, which does not have urea, is more stable at higher temperatures. MIM, at around 500 °C has decomposed almost all of its material compared to NIM. The results of the TGA-DTA analysis showed that the presence of a urea template in the membrane affected its thermal stability.

Characterization of the Physical Properties of the Membrane

Membrane hydrophilicity

The hydrophilicity of the membrane was carried out by measuring the contact angle of the membrane using the drop shape analysis (DSA) method by observing the sessile drop using a camera. Hydrophilic membranes have a contact angle of 0°–90° while hydrophobic membranes have a contact angle of 90°–120° [14]. Based on Fig. 11(a),

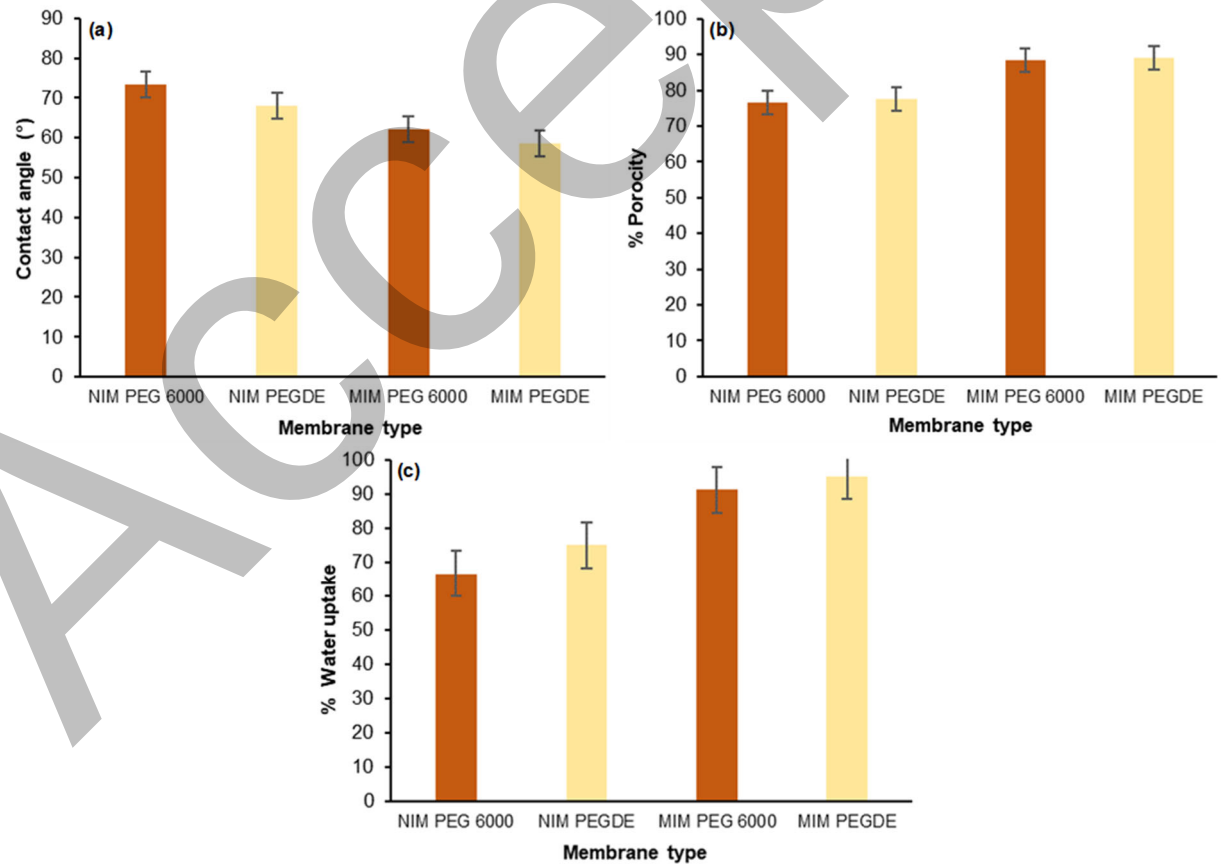


Fig 11. Results of membrane (a) hydrophilicity, (b) porosity, and (c) water absorption

the membrane using PEGDE increased the hydrophilicity of the membrane due to a decrease in the value of the contact angle. NIM PEG 6000 has a contact angle value of 73.42°, showing the lowest hydrophilicity of the membrane. Meanwhile, MIM PEGDE showing the highest hydrophilicity of the membrane (58.69°). MIM has a higher membrane hydrophilicity than NIM because MIM has OH group and may be influenced by the inclusion of a urea molecule in the OH group. Membranes that have high hydrophilicity also have high porosity values and the ability for the liquid to enter the pores faster than hydrophobic membranes, so liquids diffuse faster and increase flux [15].

Membrane porosity test

Porosity is one of the factors that affect the performance of the membrane, where the size of the pores produced will affect the performance of the membrane in determining the flux value. The membrane porosity test aims to determine the amount of substance that can be absorbed by the membrane, usually done using water. Based on Fig. 11(b) shows that MIM PEGDE has the largest percentage of porosity, 89.09%. The higher the porosity, the greater number of membrane pores, and MIM has the most pores compared to NIM. This is possible because MIM influences the inclusion of urea molecules in the OH groups so that the membrane is more hydrophilic and there is a phase inversion process in the solvent, which can then facilitate the increase in membrane porosity [16].

Water absorption test

The water absorption test on the membrane aims to determine the ability of the membrane to absorb water. The measurement of water absorption in the membrane is determined by the number of empty cavities and the ability of the membrane-forming molecules to interact with water. The percentage of water absorption in the membrane is determined by calculating the weight of the membrane before and after immersion. Based on Fig. 11(c), it can be concluded that MIM PEGDE has the largest percentage of water absorption, namely 95.24%. MIM has a higher percentage of water absorption than NIM. This is possible due to the influence of the urea inclusion in the OH group, which makes the membrane more hydrophilic and increases hydrophilicity, which causes higher water absorption. The increase in the water absorption value is directly proportional to the porosity value of the membrane, where a membrane that has small pores will make it difficult for water to pass through the membrane and vice versa; large pores will cause water to pass through the membrane easily [17].

Tensile test

The membrane tensile test was carried out to know the mechanical strength of the membrane at a certain load. The mechanical properties of the membrane include strength, hardness, stiffness, and elasticity, which can be demonstrated by measuring tensile strength, elongation, and Young's modulus [18]. Based on Fig. 12, PEGDE MIM membrane has the highest strain, but the resulting tensile stress is slightly lower. This is due to the presence of a urea template and the addition of PEGDE, which is a longer segment of PEG, so that the membrane has a tighter structure. The denser the membrane structure, the tighter the distance between the molecules in the membrane is, so it has a strong physical resistance [19]. The results of Young MIM and NIM's modulus can be seen in Fig. 13. MIM PEGDE has the lowest Young's modulus, the reduction in Young's modulus is due to the presence of large macrovoids in the membrane matrix [20]. Based on the results that have been obtained, MIM PEG 6000 has the best mechanical properties of the membrane, namely, increasing strain, tensile stress, and Young's modulus.

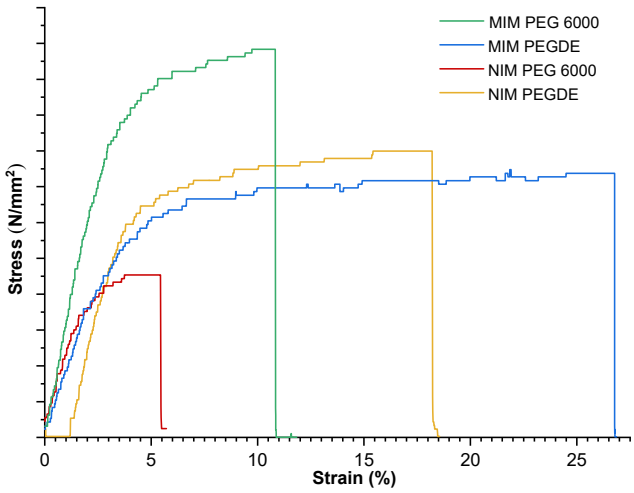


Fig 12. Stress vs strain on NIM and MIM

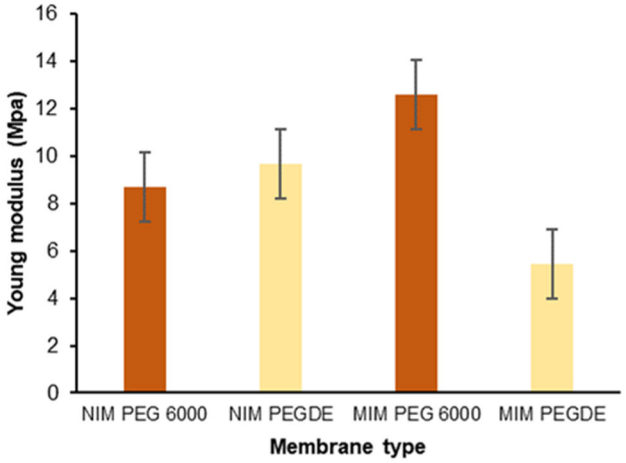


Fig 13. Young's modulus value

Flux test

The membrane flux test was carried out to determine the performance of the membrane. Flux is a measure of the speed of a particle passing through the membrane per unit of time and surface area. The factors affecting the flux are the number and size of the pores, the interaction between the membrane and the feed solution, the viscosity of the solution, and the external pressure [21]. The hollow fiber membrane to be used is measured for the thickness of the membrane, and the measurement results can be seen in Table 4. Flux measurements were carried out with 4 different solutions, namely aqua DM, urea, creatinine, and vitamin B_{12}. The molecular weight of aqua DM, urea, creatinine, and vitamin B_{12} was 18.015, 60.060, 1355.380, and 113.000 g/mol. The results of the membrane flux test are shown in Fig. 14(a) and (b). The PEG 6000 MIM membrane has the highest flux value (53.45 L/m^2.h) while PEGDE MIM membrane had the highest flux value (72.34 L/m^2.h). This is due to the presence of a urea template in MIM, which interacts with the OH groups, which causes the hydrogen bonds in MIM to be stronger so that the hydrophilic groups can interact with water molecules through hydrogen bonds. Water molecules have the smallest size compared to others, so they pass through the membrane pores more easily, causing the flux value in MIM to be the largest. This flux value is directly proportional to the value of membrane porosity and water absorption [17].

The lowest flux values were PEG 6000 NIM and PEGDE NIM of 0.34 and 28.05 L/m^2.h in vitamin B_{12}

Table 4. Results of membrane thickness measurements for the flux test

Membrane type	Average thickness of the membrane (mm)			
	Aqua DM	Urea	Creatinine	Vitamin B_{12}
NIM PEG 6000	1.042	1.040	1.031	1.046
NIM PEGDE	1.260	1.270	1.258	1.249
MIM PEG 6000	1.327	1.330	1.346	1.329
MIM PEGDE	1.444	1.429	1.433	1.426

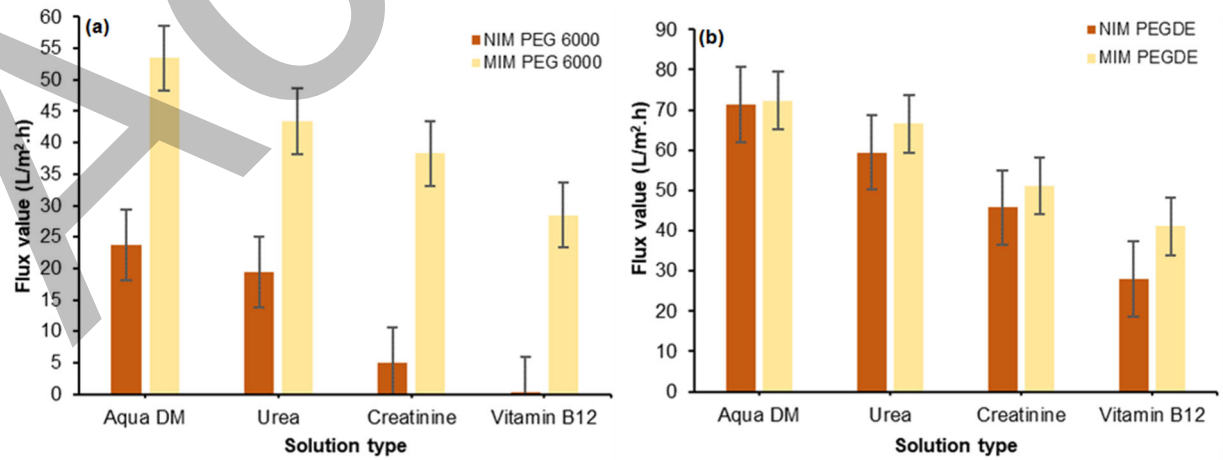


Fig 14. NIM and MIM flux values of (a) PEG 6000 and (b) PEGDE

solution for each membrane. This is due to the large molecular weight of vitamin $B_{12,}$ so it is more difficult for the membrane pores to pass vitamin B_{12} compared to the others. Based on the explanation above, it can be concluded that the greater the molecular weight, the lower the flux value, and the PEGDE membrane is better than the PEG 6000 membrane for passing a molecule. This is because the addition of PEGDE causes an increase in the number of pores and has more hydrophilic OH groups than the PEG 6000 membrane, so a molecule is easier to pass and produces a higher flux value [22].

Dry hollow fiber is used for urea transport, and then the transport data is used to calculate the membrane's selectivity to urea, which aims to determine the ability of MIM hollow fiber with a urea template in transport. The HFM to be used is measured for the thickness of the membrane, the measurement results can be seen in Table S1. Urea transport using MIM and NIM as a comparison, was carried out with 50 ppm urea solution as the feed phase and the receiving phase, namely PBS solution pH 7.4. Based on Fig. S1, it can be seen with the PEG 6000 membrane, MIM can transport 54.39% urea and NIM can transport 30.91% urea. Fig. S2. it can be seen that in the PEGDE membrane, MIM can transport 56.27% urea and NIM can transport 34.26% urea. This shows that urea transport using MIM gives better results than using NIM and MIM PEGDE is better than MIM PEG 6000, because MIM has a urea template, so it can recognize urea and transport it more optimally.

Dry hollow fiber is also used for creatinine and vitamin B_{12} transport to calculate the membrane's selectivity. The measurement results can be seen in Tables S2 and S3. Creatinine transport using MIM and NIM as a comparison was carried out with 50 ppm creatinine solution as the feed phase and the receiving phase, namely PBS solution pH 7.4. Fig. S3 shows that MIM PEG 6000 can transport 24.34% creatinine and NIM PEG 6000 can transport 20.72% creatinine. MIM PEGDE can transport 26.85% creatinine and NIM PEGDR can transport 22.48% creatinine (Fig. S4). This shows that creatinine transport using MIM gives better results than using NIM and MIM PEGDE is better than MIM PEG 6000. The ability of the membrane to transport creatinine is not optimal when compared to urea transport.

The transport of vitamin B_{12} using MIM and NIM as a comparison was carried out with a 50 ppm vitamin B_{12} solution as the feed phase and the receiving phase, namely PBS solution pH 7.4. Based on Fig. S5, it can be seen that on the PEG 6000 membrane, MIM can transport 13.78% of vitamin B_{12} and NIM can transport 9.90% of vitamin B_{12}. Based on Fig. S6, it can be seen that in the PEGDE membrane, MIM can transport 15.44% of vitamin B_{12} and NIM can transport 12% of vitamin B_{12}. It means that the transport of vitamin B_{12} using MIM gives better results than NIM, and MIM PEGDE is better than MIM PEG 6000. The membrane used is less capable of transporting vitamin B_{12} when compared to the transport of urea and creatinine.

It can be concluded that MIM hollow fiber is more capable of transporting urea than creatinine and vitamin B_{12}. This is related to MIM having a urea template and the molecular weights of urea, creatinine, and vitamin B_{12}. The molecular weight of vitamin B_{12} is greater than that of urea and creatinine, so the membrane's ability to transport vitamin B_{12} is not as good as that of urea and creatinine.

Mixed Transport on MIM and NIM

Dry hollow fiber is used to transport the mixture, and then the transport data is used to calculate the selectivity of the membrane to urea, which aims to determine the ability of MIM hollow fiber with a urea template in transport. Mixed transport using MIM and NIM as a comparison, was carried out with a mixed solution (urea, creatinine, and vitamin B_{12}) as the FP and RP, namely PBS solution pH 7.4. The %transport value is generated from 100 – %remaining transport. Based on Table 5, MIM PEG 6000 can transport 50% urea, 40.24% creatinine, 14.18% vitamin B_{12}, and NIM PEG 6000 can transport 22% urea, 18% creatinine, 5.69% vitamin B_{12}. Based on Table 6, MIM PEGDE can transport 52.31% urea, 42.59% creatinine, 16.83% vitamin B_{12}, and NIM PEGDR can transport 27.59% urea, 20.45% creatinine, 9% vitamin B_{12}. It means that mixed transport using MIM

Table 5. Percentage of mixed transport on PEG 6000 membrane

Membrane type	Urea (%)		Creatinine (%)		Vitamin B_{12} (%)	
	0 min	240 min	0 min	240 min	0 min	240 min
FP NIM	100	78.00	100	82.00	100	94.31
RP NIM	0	19.33	0	8.00	0	5.69
FP MIM	100	50.00	100	59.76	100	85.82
RP MIM	0	37.50	0	14.63	0	8.05

Table 6. Percentage of mixed transport on PEGDE membrane

Membrane type	Urea (%)		Creatinine (%)		Vitamin B_{12} (%)	
	0 min	240 min	0 min	240 min	0 min	240 min
FP NIM	100	72.41	100	79.55	100	91.00
RP NIM	0	24.14	0	10.00	0	6.75
FP MIM	100	47.69	100	57.41	100	83.17
RP MIM	0	44.62	0	17.59	0	9.39

gives better results than NIM, and MIM PEGDE is better than MIM PEG 6000. MIM hollow fiber is better able to transport urea than it is to transport creatinine and vitamin B_{12} because MIM has a urea template so that the membrane can recognize the target molecule.

Chemical oxygen demand (COD) is the amount of oxygen needed to oxidize organic matter chemically. The lower the concentration of COD in water, the lower the chemical contaminants in the water [23-24]. The mixed solution as the feed phase and the PBS solution as the receiving phase, were used for transport for COD testing. The results of the COD test can be seen in Table 7. Based on the COD test results, MIM PEGDE has the smallest COD value of 63.3 ppm in FP. This indicates that the transport using MIM PEGDE is carried out properly so that urea, creatinine, and vitamin B_{12} are in the FP more slowly than the others. PEGDE's MIM had the greatest COD value of 127.3 ppm, indicating that urea, creatinine, and vitamin B_{12} in the FP, moved to the RP.

Table 7. COD test results

Sample	COD (mg/L)
RP NIM PEG 6000	49.7
RP MIM PEG 6000	106.6
RP NIM PEGDE	124.3
RP MIM PEGDE	127.3
FP NIM PEG 6000	114.2
FP MIM PEG 6000	174.8
FP NIM PEGDE	117.2
FP MIM PEGDE	63.3

Membrane Permeability

Membrane permeability is the flow rate of the FP that passes through the HFM, which aims to determine the performance of the HFM in carrying out the transport [25]. Membrane permeability was calculated using transport data for urea, creatinine, vitamin B_{12}, and mixtures. The decrease in concentration in the feed phase is explained in Eq. (1);

$$\ln\left[\frac{C_s}{C_s^0}\right] = \left[\frac{A}{V_s}\right] P_s t \quad (1)$$

where A is the surface area of the membrane, V_s is the volume of the phase, t is time, P_s is the permeability coefficient, C_s is the concentration at 4 h, and C_s^0 is the initial concentration in the FP.

Based on Fig. 15(a) and (b), the highest permeability value was 63.405 m/s (MIM PEGDE) and the lowest value was 7.049 m/s (NIM PEG 6000 in vitamin B_{12}). The highest value is 81.473 m/s for urea using MIM PEGDE and the lowest value (3.985 m/s) for vitamin B_{12} using NIM PEG 6000. The results of membrane permeability show that MIM has the best membrane performance in transporting. MIM has a urea template so it can recognize the target molecules, which causes the permeability value for urea transport to be high, and the greater the molecular weight, the lower

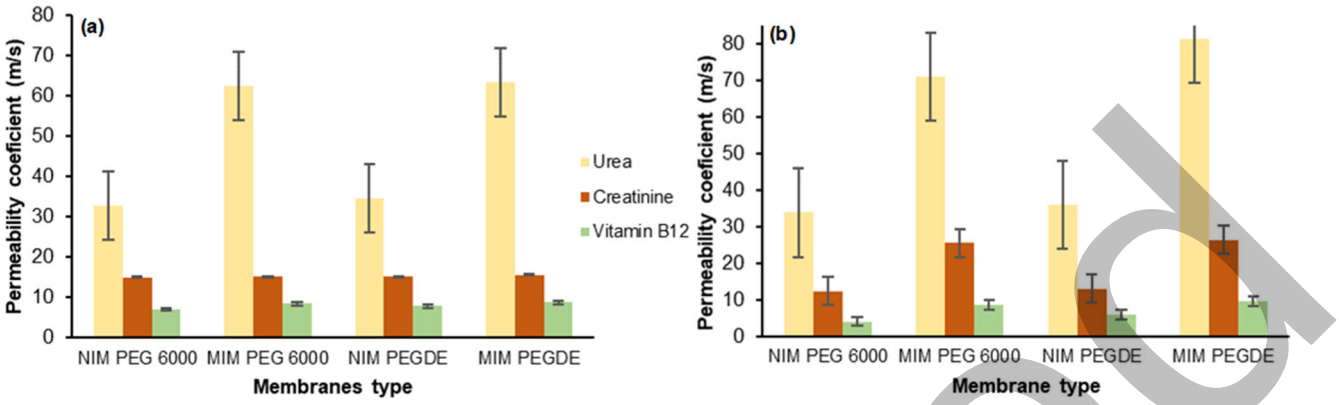


Fig 15. Permeability of (a) transport urea, creatinine, and vitamin B_{12} and (b) mixed transport

the membrane permeability value.

Urea Selectivity to Creatinine on MIM and NIM

Urea selectivity on MIM and NIM was carried out by comparing the data on the results of urea transport to the data on the results of creatinine transport. Transport was carried out for 4 h with 50 ppm urea solution and/or 50 ppm creatinine solution as the FP and PBS pH 7.4 solution as the RP. Absorbance data were obtained from samples that were measured using a UV-vis spectrophotometer at 430 (urea) and 486 nm (creatinine). The absorbance obtained is used to calculate the transport percent data and selectivity value of urea to creatinine (Fig. 16(a) and (b)).

The selectivity of urea on MIM has a higher value than the selectivity of urea on NIM. The PEGDE membrane also shows that the selectivity of urea in MIM is higher than NIM. MIM PEGDE has a higher selectivity value compared to MIM PEG 6000. This is related to MIM having a urea template so that the membrane can recognize urea molecules or be more selective towards urea molecules than creatinine. In contrast, NIM does not have a urea template [8].

Urea Selectivity to Vitamin B_{12} on MIM and NIM

Urea selectivity on MIM and NIM was carried out by comparing urea transport results to vitamin B_{12} transport results. Transport was carried out for 4 h with 50 ppm urea solution and/or 50 ppm vitamin B_{12} solution as the FP and PBS pH 7.4 solution as the RP. Absorbance data were obtained from samples measured using a UV-vis spectrophotometer at 430 and 361 nm for urea and vitamin B_{12}. Based on Fig. 17, the selectivity of urea on MIM has a higher value than the selectivity of urea on NIM. The PEGDE membrane also shows that the selectivity of urea in MIM has a higher value than the selectivity of urea in NIM. MIM PEGDE has a higher selectivity value compared to MIM PEG 6000. This is

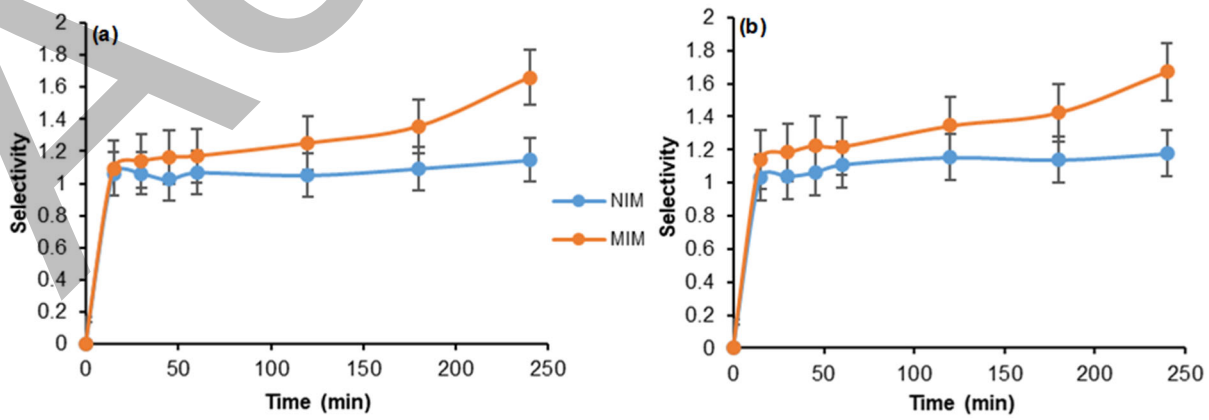


Fig 16. (a) PEG 6000 and (b) PEGDE membrane selectivity on urea vs creatinine

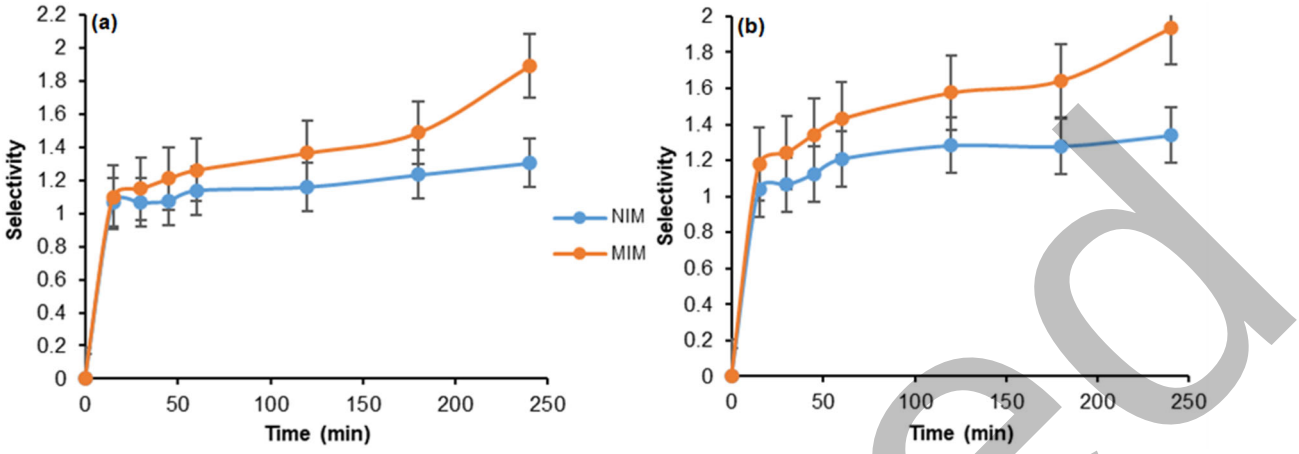


Fig 17. (a) PEG 6000 and (b) PEGDE membrane selectivity on urea vs vitamin B_{12}

related to MIM having a urea template so that the membrane can recognize urea molecules or be more selective towards urea molecules compared to vitamin B_{12}. In contrast, NIM does not have a urea template [8]. The selectivity of urea vs vitamin B_{12} shows that MIM hollow fiber is better at transporting urea than vitamin B_{12}, so the order of selectivity is urea > creatinine > vitamin B_{12}.

Urea Selectivity on Mixed Transport

Urea selectivity on MIM and NIM was carried out by comparing the data on the results of urea transport to the data on the results of creatinine and vitamin B_{12} transport. Transport was carried out for 4 h with a mixed solution (urea, creatinine, and vitamin B_{12}) as the FP and PBS solution pH 7.4 as the RP. Absorbance data were obtained from samples measured at 430 (urea), 486 (creatinine), and 361 nm (vitamin B_{12}). Table 8 shows that the selectivity of urea on MIM has a higher value than NIM. MIM PEGDE has a higher selectivity value compared to MIM PEG 6000. This is related to MIM having a urea template so that the membrane can recognize urea or be more selective towards urea compared to creatinine and vitamin B_{12}. The selectivity of urea for creatinine and vitamin B_{12} shows that MIM hollow fiber is better at transporting urea than creatinine and vitamin B_{12}, so the order of selectivity is urea > creatinine > vitamin B_{12}.

Table 8. Selectivity results in mixed transport

Membrane type	Selectivity	
	Urea vs Creatinine	Urea vs Vitamin B_{12}
NIM PEG 6000	1.051	1.209
MIM PEG 6000	1.195	1.716
NIM PEGDE	1.099	1.257
MIM PEGDE	1.204	1.744

■ CONCLUSION

PE and PA have been successfully synthesized in 95.22% and 95.23%. Molecular weight of PE and PA is 6186.29 and 4279.76 g/mol. HFM MIM produces PEGDE 6000 and PEGDE membranes while NIM synthesis produces PEG 6000 and PEGDE membranes. The sequence of selectivity of MIM is urea > creatinine > vitamin B_{12}.

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■ CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

■ AUTHOR CONTRIBUTIONS

Conceptualization, methodology, validation, resources, Muhammad Cholid Djunaidi and Yanuardi Raharjo; investigation, Khabibi; writing—original draft preparation, Denandha Putri Ayuningrum; review, and editing, Nesti Dwi Maharani and Pardoyo; supervision, Heru Susanto and Abdullah Malik Islam Filardli. All authors have read and agreed to the published version of the manuscript.

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