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Permeability improvement of polyethersulfone-polietylene glycol (PEG-PES) flat sheet type membranes by tripolyphosphate-crosslinked chitosan (TPP-CS) coating

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ABSTRACT

In this study, improvement of urea and creatinine permeability of polyethersulfone (PES) membrane by coating with synthesized tripolyphosphate-crosslinked chitosan (TPP-CS) has been conducted. Original and modified membranes, e.g. pristine PES, polyethersulfone-polyethylene glycol (PES-PEG) and PES-PEG/TPP-CS membranes were characterized using FTIR, DTG, SEM, AFM, water uptake, contact angles, porosity measurement, tensile strength test and permeation tests against urea and creatinine. The results show that the PES modification by TPP-CS coating has been successfully carried out. The water uptake ability, hydrophilicity and porosity of the modified membranes increase significantly to a greater degree. All modified membranes have good thermal stability and tensile strength and their permeation ability towards urea and creatinine increase with the increasing concentration of TPP-CS. PES membrane has urea clearance ability of 7.36 mg/dL and creatinine of 0.014 mg/dL; membrane PES-PEG shows urea clearance of 11.87 mg/dL and creatinine of 0.32 mg/dL; while PES-PEG/TPP-CS membrane gives urea clearance of 20.87–36.40 mg/dL and creatinine in the range of 0.52–0.78 mg/dL. These results suggest that the PES-PEG membrane coated with TPP-CS is superior and can be used as potential material for hemodialysis membrane.

1. Introduction

In recent years, there has been an increasing interest in membrane separation technology [1,2]. This is mainly because the membrane separation process is a simple, practical and small energy consumption process and has a high level of success in the separation and purification application [3,4]. Currently, membrane separation technology is growing rapidly in various industries like pharmaceutical, chemical engineering, medical, paper and dairy industries. Hemodialysis is one of the applications that utilize the membrane separation mechanism. When the concentration of uremic compounds (urea, creatinine) in the blood rises above standard levels, this indicates kidney failure, dialysis (i.e. hemodialysis) must be done to sustain life. The principle of hemodialysis is the diffusion of uremic toxin from the body into the dialysate solution through the membrane in response to differences in concentration or pressure. The main component of the hemodialysis instrument is a semi-permeable membrane which efficiently transports low-molecular toxic substances (urea, creatinine) from blood without affecting plasma proteins and cells [5,6]. Membranes for hemodialysis should not absorb protein but are permeable for toxins in the blood. The hemodialysis process is an interface problem, and thus the key point of hemodialysis is the design of membrane structures for high performance. To achieve the secretion and retention of the toxic substances and protein, respectively, the dialysis membrane needs to be inert, mechanical stability, permeable, ease of formability and biocompatibility [7–10].

The mass transfer is controlled by the chemical composition of the material and the structure of the membrane. Synthetic polymeric based membrane-like cellulose acetate (CA), polyethersulfone (PES), polylactic acid (PLA) and polysulfone (PSf) has been widely used for hemodialysis membrane [6,11,12]. PES is one of the most common materials used in the fabrication of the hemodialysis membrane due to its thermal stability, mechanical strength, and chemical resistance

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[13,14]. However, the hydrophobic nature of PES causes the protein to be adsorbed on the surface of the membrane which could lead to the fouling effect when used during hemodialysis procedure [11,15]. Membrane fouling affects the filtration system and reduces the shelf life of the membrane. This phenomenon also affects the biocompatibility of the membrane towards the user. When protein adsorption occurs, the human immune system activates the defence mechanism. Thus, develop various side effects like inflammation, thrombosis and others [16]. To overcome this problem, PES membrane needs to be more hydrophilic and biocompatible. Increasing membrane hydrophilicity has been correlated with flux improvement, separation efficiency and membrane biocompatibility [17,18]. Surface modification of membrane is respected as an effective technology to improve membrane performance. Many efforts have been made to advance the membrane surface hydrophilicity, such as adsorption, coating, surface grafting and blending of hydrophilic polymer or particles [4,11,19,20].

Chitosan is a biodegradable and renewable polymer, with great potential in enhancing the properties of synthetic-based polymeric materials [11]. It is a natural polymer compound that is non-toxic, odourless, biocompatible and degradable. Chitosan has been used as an additive to improve the hydrophilicity and compatibility properties for various membrane materials, such as cellulose acetate (CA), polysulfone (PSf), poly (vinylidene fluoride) (PVDF), poly (acrylonitrile) (PAN) [12,21,22]. It also shows structural similarity to glycosaminoglycans, which is a component of native liver extracellular matrix (ECM) and can be chemically modified due to the presence of –OH and –NH$_2$ groups [23]. In the acidic environment, chitosan, –NH$_2$ group of chitosan is protonated to be polycationic –NH$_3$, which can react with negatively charged species such as citrate, succinate, and tripolyphosphate through electrostatic bonds to produce cross-linked *network* [24]. Chitosan derivatives obtained by chemical modifications with a certain substance are proven to have better hydrophilicity properties [2,25–28]. In the previous journal reported by Lusiana et al. [2], it has been explained that the flat membrane of CS-TPP could transport the urea up to 22 mg/dL (44%) [2]. While the other study depicted that pure PES membrane and PES/PEG membrane just have pore size around 3,62 × 10^1 Å [29] and low permeation less than 15% for urea and creatinine [30]. Although, TPP-CS membrane has a better ability to transport toxic compound than PES and PE-PEG membrane, but membrane-based PES easier to manufacture than TPP-CS membrane, for example, PES membrane can be generated easily to be hollow fibre membrane. Thus, it was interesting to combine the material from PES, PEG, CS and TPP. As far as we know, there are no previous research deals with modification of PSF/PEG membrane with CS and TPP.

In this study, PES was modified using a nontoxic polyanionic polymer, tripolyphospahate-crosslinked-chitosan (TPP-CS). TPP-CS was synthesized by the crosslinking reaction between -PO$_4$ group (STTP) with chitosan -NH$_3$ group through electrostatic attraction to form ionically crosslinked polymer [7,28]. Sodium tripolyphosphate (STPP) is a polyionic crosslinking agent with three phosphate groups, that was used to change and enhance the properties of chitosan. However, the crosslinking reaction carried out with sodium tripolyphosphate does not only introduces the phosphate group in the chitosan chain but also creates a molecule chain that can also play an important role in permeation [2]. Prior to surface modification, PES blended with polyethylene glycol (PEG) flat-sheet membrane was fabricated via the dry-wet phase inversion technique. Surface modification on the membrane was done by dip coating of PEG-PES flat-sheet membrane into TPP-CS solution. The hydrophilic nature of TPP-CS (chitosan derivatives) is expected to improve the hydrophilicity properties of the membrane. Thus, it increases the permeation performance of the PEG-PES membrane. More specifically, this work aims to study the effect of adding additive compounds to the surface of PEG-PES flat sheet membranes on morphological and permeation properties of the membrane. From this study, it has been revealed that the surface modification of PEG-PES membrane with TPP-CS has significantly improved the hydrophilicity of the membrane, thus increases the permeability and biocompatibility of the modified membrane.

2. Materials and method

2.1. Materials

Polyethersulfone (PES, Mw = 58,000 g/mol, Radel A-300A Resin) was purchased from Solvay Advanced Polymers; *N*-methyl-2-pyrrolidone (NMP), polyethilen glycol (PEG) (Mw = 3800 g/mol), glycerol, sodium-trypolyphosphate (STPP), acetic acid, urea (Mw = 60 g/mol), creatinine (Mw = 113 g/mol) and sulfuric acid were supplied by Merck Millipore; chitosan (Mw = 40,000 g/mol, DD = 87%) was obtained from Biotech Surindo (Indonesia).

2.2. Synthesis of tripolyphosphate crosslinked chitosan (TPP-CS)

A total of 1.5 g of chitosan dissolved in 1% acetic acid were put in 2-neck flask in a waterbath, then a certain amount of STPP was added as shown in Table 1. The mixture solution was heated at a temperature of 60–70 °C for ±4 h while stirring constantly. Furthermore, the crosslinking reaction was completed by entering the solution in the ultrasonification equipment for 30 min at 50 °C. After being cooled, the solution was ready to be used as an additive compound in the fabrication of PES derivative membranes.

2.3. Membrane PEG-PES preparation

Before being used as membrane material, Polyethersulfone (PES) was dried at 90 °C for ±1 h because it was very hygroscopic and absorbed moisture very quickly. Polyethylene glycol (PEG) 4000 was used as a mixing material and NMP as a solvent, with a composition of 15% (PES): 12.5% (PEG): 72.5% (NMP). First, PEG was dissolved in NMP at 50 °C while continuously stirring for 1–2 h. Then, PEG solution was added to the PES solution gradually and stirred continuously for 24 h at 50 °C. The obtained homogeneous solutions was cooled and printed on glass sheets to form thin sheets of film. The thin-sheet film was transferred to a water bath and soaked for 24 h to ensure that the solvent was completely evaporated, the water in the water bath container was replaced periodically. Cleaned PEG-PES membranes were dried, soaked with glycerol, dried again and finally stored and used for further experiments.

2.4. Preparation of TPP-CS modified PEG-PES membrane

PES membranes were made by phase inversion method consisting of mixing three forming materials namely PES MW 58,000, PEG MW 3800 and NMP. The mass mixing ratio of the three basic ingredients used in this study was PES 15%, PEG 12.5%, and NMP 72.5%. To evaluate the effect of TPP-CS modification on PEG-PES membrane performance, the following modification of flat sheet PEG-PES membrane through the immersion process was carried out. First, PEG-PES membrane was activated by immersing it in 60% sulfuric acid for 4 h. This immersion process was aimed to provide a negative vicinity on the surface of the

Table 1
Composition of the prepared membranes.

Membrane type	Concentration of dope solution (wt%)		Concentration of additive (wt%)	
	PES	PEG	CS	STTP
PES	15	0	0	0
PEG-PES	15	12.5	0	0
PEG-PES/TPPCS1	15	12.5	1.5	0.034
PEG-PES/TPPCS2	15	12.5	1.5	0.046
PEG-PES/TPPCS3	15	12.5	1.5	0.069
PEG-PES/TPPCS4	15	12.5	1.5	0.138

PEG-PES membrane. The electrophilic group $-SO_3H$ from sulfuric acid replaced H ions from and bound to one of the carbon atoms in benzene in the polysulfone structure which acts as an electron donor (nucleophile) [17,26,31]. After finished, it was washed with H_2O until the remaining sulfate was removed from the surface of the membrane. Then, the membrane was dipped in TPP-CS solution for 4 h followed by 30 min of ultrasonification soaking to ensure the complete reaction. The resulting PEG-PES/TPP-CS membrane was finally dried at room temperature. The addition variation of STPP-CS concentration is presented in Table 1. The success of all reaction phases was checked by analyzing the sample using FTIR. In this membrane modification experiment, four different amounts of crosslinking STPP were added to chitosan.

2.5. Characterization of membranes

2.5.1. FTIR spectroscopic analysis

The synthesized membranes were characterized by FTIR spectroscopic method to identify the types of functional groups available in the samples. For this purpose, the samples were cut to get the size of 1 × 1 cm and then placed in the analytical compartment and measured by using the Shimadzu FTIR spectroscopic instrument. The FTIR spectra of each sample was recorded in the wavenumber region of 400–4000 cm^{-1}.

2.5.2. Differential gravimetric analysis (DTG)

Thermal decomposition of membrane samples was studied by performing DTG experiment in atmospheric oxygen furnace. The temperature of the furnace was increased gradually from 30 to 900 °C with a heating rate of 10 °C/min and the thermal decomposition represented by the decrease in sample weight was automatically monitored.

2.5.3. Measurement of membrane thickness

Membrane thickness was measured by manual micrometer. To minimize the measurement errors, in this study the thickness of each membrane was measured randomly in triplicates at three different sites and the presented membrane thickness was the average result of triplicate measurements at different sites of the membrane.

2.5.4. Water uptake (WU), water contact angle (WCA) and porosity

Water absorption capability is an important character of a membrane, which describes the level of hydrophilicity or hydrophobicity of the membrane and is also associated with the degree of porosity of the membrane produced. For the determination of WU and WCA, the membranes were soaked in water for 24 h, weighed and then dried at 80 °C for 24 h and finally it was weighed again. From these two measurements, percent of water uptake and porosity can be determined by using the Eqs. (1) and (2), respectively.

$$WU = \frac{(Q_0 - Q_1)}{Q_0} \times 100 \qquad (1)$$

where Q_0 is the wet weight of the membrane (g), and Q_1 is the dry weight of the membrane (g).

Membrane hydrophilicity was measured using a sessile drop method which illustrates the membrane's ability to absorb water dripped on its surface. The smaller the contact angle formed between the water basin and the membrane, indicating the membrane is hydrophilic.

Membrane porosity was measured by soaking the membrane in water and dried with paper, then weighed. The dry membrane was determined after the wet membrane was dried in an oven at 80 °C for 24 h. From these two measurements, the percent of water absorption can be determined by Eq. (2):

$$P\,(\%) = \frac{W_0 - W1}{V \cdot \rho_w} \times 100\% \qquad (2)$$

where P is the membrane porosity (g), W_0 is the weight of the wet membrane (g), W_1 is the dry weight of the membrane (g), V is the membrane area (cm^3); and ρ_w is water density (1 g/cm^3).

2.5.5. Scanning electron microscopy (SEM)

All of the membrane morphology forms were examined with scanning electron microscopy equipment (SEM, Shimadzu). Samples were first dried in a vacuum desiccator before being attached to the sample plate (spool), the membrane was first broken off in liquid nitrogen to prevent the structural damage. Then the membrane sample was coated with Au metal for 15–30 min, followed by morphological reading using SEM.

2.5.6. Surface morphology (AFM)

To study the effect of the modification on the structure of the surface morphology of PES membranes, atomic force microscopy (AFM) analysis was carried out. Membranes were cut in 1 cm^2 size, attached to a glass substrate. The analysis was carried out on the surface of the membrane with a size of 1 μm × 1 μm by the SPM-DME software.

2.6. Experiments of membrane transport performance

Characterization of transport ability of the membrane to pure water (PWP) for PES membranes and their derivatives were performed by using 4.93 cm^2 brush contact area and 0.1 atm of water pressure. The PWP was calculated by the following equation (Eq. (3)):

$$PWP = \frac{Q}{A \times \Delta t} \qquad (3)$$

where PWP describes the strength of flux (L/m^2 h), Q is the volume of the permeate solution (L), A is the membrane surface area (m^2) and Δt is the permeation time (hour). Bovine serum albumin (BSA) is used as a feed solution with a concentration of 0.5 mg/mL. BSA concentration was measured using a UV–Visible spectrophotometer at a wavelength of 280 nm.

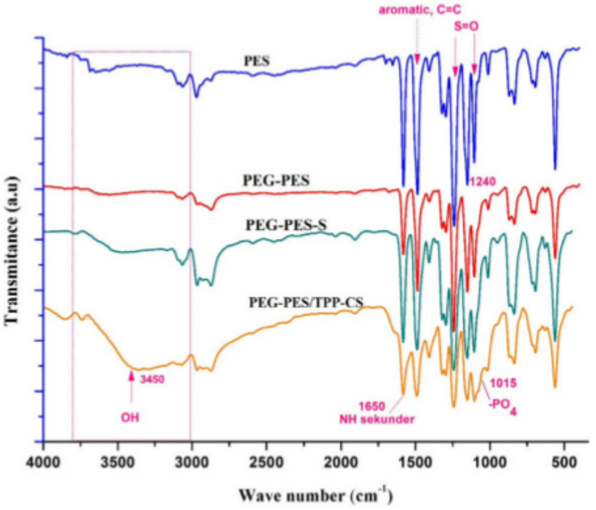
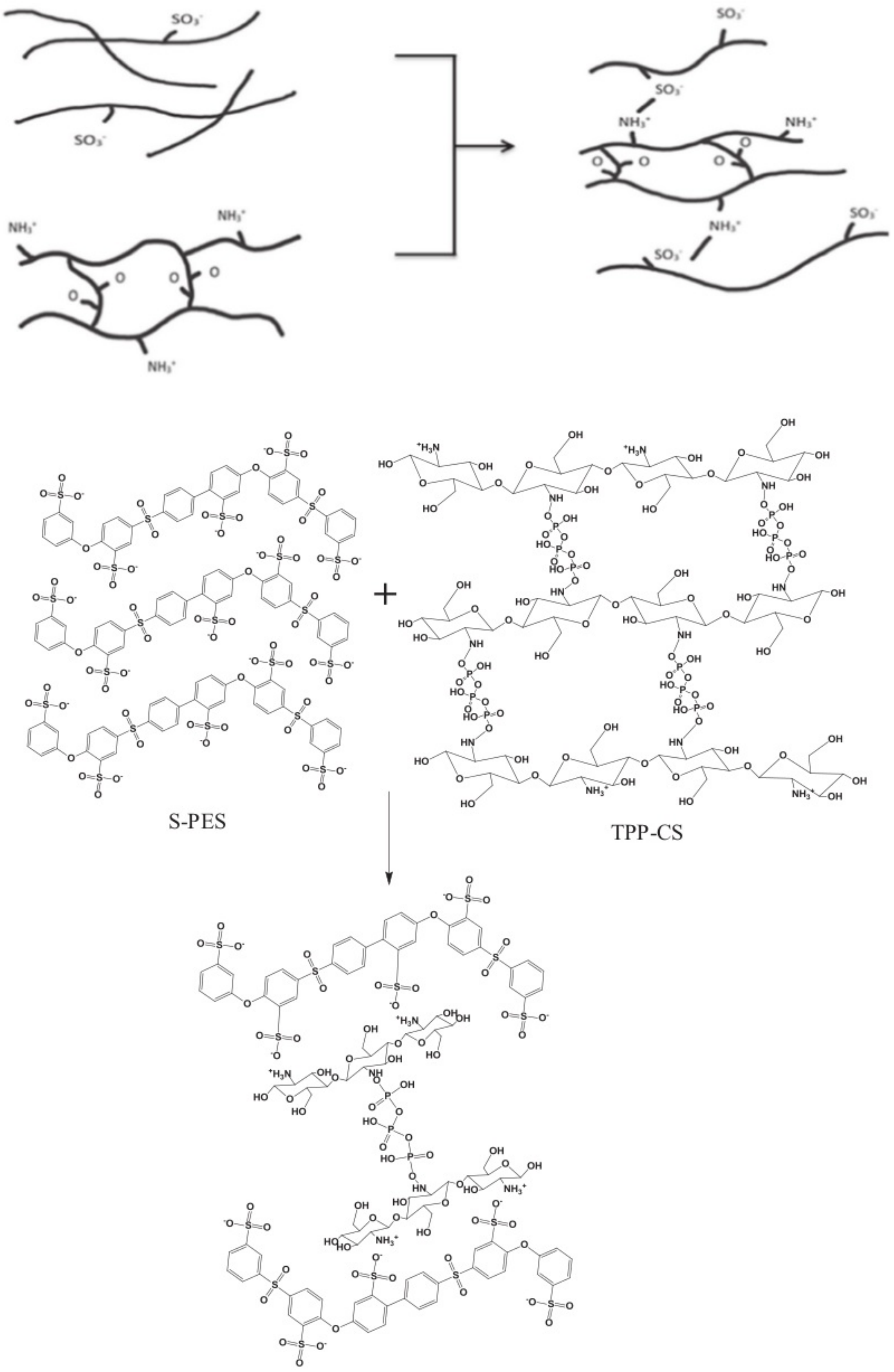


Fig. 1. FTIR spectral profiles of PES, PEG-PES, PEG-PES-sulfonated (PEG-PES-S) and PEG-PES-S/TPPCS.


SO3⁻
NH3⁺
O
S-PES
TPP-CS

The membrane sieving coefficient (SC) was also determined using the cross-flow cell. The following compounds were dissolved in deionized water with initial concentrations of 50 mg/dL urea 1.5 mg/dL creatinine, 2 mg/dL cyanocobalamin, 2 mg/dL BSA. The concentrations of feed and permeation were analyzed using UV-Visible spectrophotometer. The SC value was calculated with the Eq. (4):

$$SC = \frac{C_p}{C_f} \tag{4}$$

where C_p is the concentration of the solute in permeation and C_f is the concentration of the solute in the feed solution. SC = 1 means that the substance passed through the membranes, while SC = 0 means that the membrane rejected the substance completely.

2.7. Ability test of membrane dialysis

Permeability or rejection test was done to determine the effectiveness of the membrane on permeate separation. Permeation tests were carried out using a permeation device attached by a tested membrane in the center. The feed phase was filled with creatinine solution of 1.5 mg/dL and urea of 50 mg/dL in 50 mL of phosphate buffer solution. The acceptor phase was filled with 50 mL of phosphate buffer. The permeation process was carried out for 6 h at room temperature. Every 1 h, 2 mL of sample was taken from the feed and acceptor phases. The samples were then complexed with picric acid for creatinine determination and with dimethylamine benzaldehyde for urea analysis, then subjected to UV–Visible spectrophotometer at a wavelength of 486 nm (creatinine) or 430 nm (urea). The permeation ability of the membrane towards the solute (clearance) is calculated by using Eq. (5):

$$\text{Clearance permeate} = C_0 - C_t \tag{5}$$

where C_0 and C_t are the concentrations of solute in the feed solution at $t = 0$ and $t = 1, 2, 3, \ldots$ h, respectively.

3. Results and discussion

3.1. Functional groups

The FTIR spectral changes due to alteration of chemical composition of PEG-PES membranes before and after modification are given in Fig. 1. Specific spectrum of PEG-PES compound is characterized by the appearance of absorption in the wavenumber of 1585 cm^{-1} regions, which belongs to the aromatic chain, C=C vibrations. The spectral bands at 1300 and 1150 cm^{-1} correspond to SO_2 groups. These FTIR absorption results are consistent with those previously reported studies [7]. The activation process of PES membranes with sulfuric acid, PEG-PES-S (PEG-PES sulfonated) gives rise to the absorption of SO_3 at 1050 cm^{-1}. An increase in absorption intensity at the wavenumber region of 830 and 1580 cm^{-1} indicates that PEG-PES has been sulfonated. The spectrum which is characteristic of chitosan absorption at 1650 is attributed to –N-H bending of secondary amide bond, resulted from the electrostatic interaction between protonated -NH_2 group and -O^- of PO_4 groups. In the presence of STPP, the NH_2 band is slightly widened and the small change of this band indicates the low values of STPP. The broad peak observed at 3700–3000 cm^{-1} is associated with the stretching O—H band. The spectra are similar to the results obtained by several researchers [3,7,28,32] (Fig. 2).

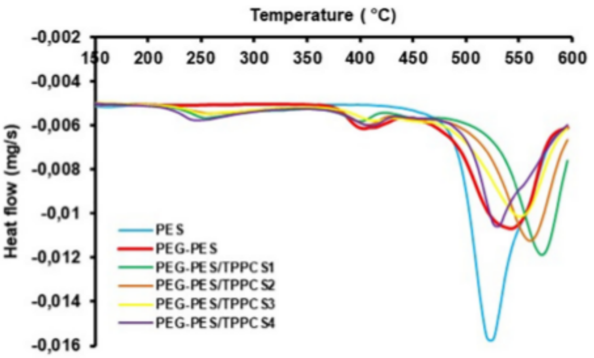


Fig. 3. DTG curve of PES and modified PES membranes.

3.2. Thermal stability

The results of TG experiment for PES polymer before and after modification are shown in Fig. 3. From the figure, it can be seen that the pure and modified sulfone polyethers have a thermal stability up to 500 °C. The polymer shows a little bit decrease in its thermal stability after being modified by using PEG and TPP-CS.

Kaleekkal et al. [15] states that PES has good thermal stability. The thermal degradation of PES membrane occurs in one stage at 475–600 °C, which is related to the decomposition of the main polymer chain [8]. Meanwhile, the incorporation of PEG in the PES membrane can affect the thermal stability of the PES membrane. This might be influenced by differences in glass transition temperatures for PES and PEG polymers. The thermal degradation of PEG-PES membranes clearly show 2 stage, the first stage occurs at temperatures of 385–425 °C which is attributed to the degradation of the PEG polymer chain and the second stage at temperatures of 475–600 °C is due to the degradation of the PES polymer chain [8].

Likewise, when the membrane is modified using the TPP-CS, its thermal stability occurs at 3 stages weight loss. The first stage occurs at 225–285 °C, shows the thermal stability of TPP-CS, the second stage occurs at 385–425 °C, indicate degradation of the PEG polymer chain [9]. The third stage of weight reduction occurs at temperatures of 480–600 °C C is due to the degradation of the PES polymer chain [12]. These results indicate that modification using PEG and TPP-CS reduce the thermal stability of the membrane.

3.3. Physical characterization of membrane

The testing results of the percentage of water uptake for various types of membranes developed indicate that the addition of PEG and TPP-CS is able to increase the percentage of water uptake and swelling of PES membranes (Table 2). The percentage of water uptake and percentage of swelling are closely correlated with physical interactions between membranes and H_2O molecules. The presence of PEG and TPP-CS increases the hydrophilic groups in the membrane. PEG donates -OH groups which can form physical interactions with H_2O, while tripolyphosphate has -PO_4 groups that can interact with H_2O through intermolecular hydrogen bonds.

The testing results also clearly show that the percentage increase in water uptake and swelling is directly proportional to the amount of tripolyphosphate monomer added to the membrane. This undoubtedly correlates with the increase in the number of hydrophilic groups in the membrane. According to Amiji [5] membrane permeability towards

Fig. 2. Illustration of crosslinked reaction mechanism of chitosan-tripolyphosphate-PES.

Table 2
The result of physical characterization of membranes.

Membrane type	Water uptake (%)	Contact angle (°)	Porosity (%)
PES	109	75	8.22
PEG-PES	150	65	52.56
PEG-PES/TPPCS1	175	48	61.20
PEG-PES/TPPCS2	235	37	62.61
PEG-PES/TPPCS3	277	25	73.51
PEG-PES/TPPCS4	354	15	76.59

creatinine and urea will increase proportionally with the increase in hydrophilic groups contained in the membrane [33].

Table 2 also summarizes the results of contact angle tests. From this table, it can be seen that pure PES membrane shows the greatest WCA value of 70°. The WCA values decrease to 65° in PES membranes added with PEG, while modification of PEG-PES membrane with TPP-CS significantly decreases WCA in the range of 50–39°. The size of the contact angle is caused by the surface tension that occurs between the membrane and water which is dropped in the sessile drop process. From WCA data it can be concluded that the PES membrane is classified as a hydrophilic membrane [34]. With the addition of PEG polymer and modifications using TPP-CS, the hydrophilic properties of the membrane increases. The similar data trend has also been reported by several previous researchers [2,7]. These WCA data are in accordance with SEM analysis data. The addition of PEG and TPP-CS causes the increase in degree of porosity of the membrane. This makes the membrane surface preferred to adsorb water and thus its adsorption capacity towards water increases.

The porosity of each membrane can be seen in Table 2. For dialysis membrane, pore size and porosity are important parameters affecting the permeation ability of membranes. From Table 2, it is obviously clear that the degree of porosity of modified membrane increases significantly as compared to pure PES membranes, with an increase in the range of 8.2 to 76.5%. Hence, it is confirmed that modification of PES membrane with hydrophilic compounds makes the membrane more porous, previous study [19] has obtained the same results when the PES membrane was modified using Tween 80. Membrane porosity refers to empty cavities between spaces in a membrane. High porosity can be interpreted that the membrane has a large empty area. With a large empty area, the ability of the membrane to hold water increases. Penetration and flow of water to the membrane will be easier by increasing membrane porosity. In general, membranes with high porosity have a higher permeate flux.

3.4. Mechanical strength

The membrane tensile strength, elasticity is shown in Table 3. The PES membrane before modification has a higher elasticity and tensile strength compared to the modified PES membrane. Modifications using PEG and TPP-CS make the membrane rigid and reduce its flexibility. This might be due to the formation of a large material structure as a result of the bond between PES and the modifier. The distance between molecules becomes shorter in the same area of the membrane as a consequence of the PES modification reaction. This can make the membrane more rigid and lose its flexible properties. However, resistance to tensile stress (modulus young) increased with the modification of TPP-CS in PEG-PES membranes. Tensile resistance increases with increasing concentration from TPP-CS. However, the tensile resistance decreased again with too much TPP-CS addition (PEG-PES/TPPCS4).

3.5. Membrane morphology

The structure, porosity, selectivity and surface morphology of the membrane can be determined through the regulation of the type of polymer, solvent and non-solvent, composition and concentration of the polymer [13]. The cross section structure of the membrane is respectively shown in Fig. 4. In general, all membranes have an asymmetrical type. There is no significant difference in PEG-PES compared to PES membrane, whereas the PEG-PES membrane modified by TPP-CS shows the changes, both in the top-layer and sub-layer. Porosity in the upper layers and sub-layers increases.

The asymmetrical structure of the membrane consists of a more porous top layer with a smaller fingerlike void distance and a lower sub-layer forming a macro void with a more porous wall.

Morphological changes can be related and explained by increasing the hydrophilicity of membrane polymers and the interaction between components of the solution (NMP) and non-solvents (water) in the casting process. This can be seen from the FTIR spectra (Fig. 1), which shows absorption at 3400–3500 cm^{-1} in the PEG-PES/TPP-CS membrane, which is a characteristic band of the -OH group. This causes the affinity of the PEG-PES/TPPCS membrane for water is greater than the pure PES membrane. Greater affinity for water from the PEG-PES/TPPCS mixture results in a long time of phase exchange between the solvent and non-solvent in the polymer casting bath before formation of coagulation. Longer exchange time between the solvent and non-solvent in the coagulation process results in much pore growth and space in polymer casting. Consequently, this will result in a more porous web in the top-layer and macro void with larger pores in the sub-layer. Some researchers have also found that modification of the PES membrane makes the membrane more porous [11,14,35,36].

3.6. Surface roughness

AFM is a characterization technique, which has very high capability in microscopic observation and characterization on various material surfaces. AFM is used to study the characteristics of various membranes with different surface roughness and material insulation. In the permeation process, the membrane surface is the most accessible and reactive part of the membrane body involved in the process. Membrane morphology will show membrane ability in carrying out its functions. The effect of adding additives on the surface morphology and roughness of PES membranes was analyzed by AFM instruments. The image produced by AFM implies a low height point in an area (roughness). Brighter colored dots indicate areas with a higher surface, and darker colored spots indicate the surface of the lower area (membrane pore). From the image information, it is shown that AFM data can be used to explain the level of surface roughness of a material based on the color of the point produced.

Table 3
Assessment of mechanical properties of membranes.

Membrane type	Extension at max load (mm)	Max. load (N)	Tensile strength (MPa)	Elongation at break (%)
PES	0.13 ± 0.020	2.26 ± 0.06	3.54 ± 0.70	7.89 ± 0.57
PEG-PES	0.19 ± 0.009	2.17 ± 0.22	2.22 ± 0.12	7.83 ± 0.46
PEG-PES/TPPCS1	0.14 ± 0.010	1.57 ± 0.17	1.95 ± 0.05	3.85 ± 0.75
PEG-PES/TPPCS2	0.09 ± 0.005	0.89 ± 0.11	1.75 ± 0.36	2.42 ± 0.15
PEG-PES/TPPCS3	0.16 ± 0.000	1.39 ± 0.50	1.29 ± 0.64	2.22 ± 1.09
PEG-PES/TPPCS4	0.17 ± 0.007	1.11 ± 0.15	1.29 ± 0.22	2.22 ± 0.63

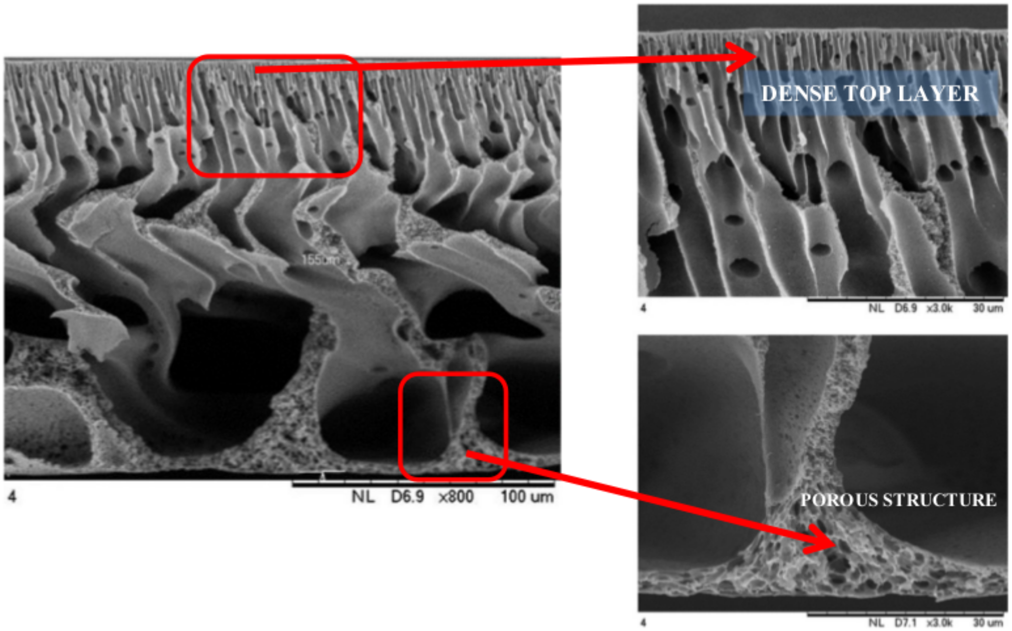


Fig. 4. Cross-sectional morphology of membranes: PEG-PES/TPPCS1 (1), PEG-PES/TPPCS2 (2), PEG-PES/TPPCS3 (3), PEG-PES/TPPCS4 (4).

Fig. 5 shows a 2D and 3D AFM image of pure PES membrane and modified PES on a 5 × 5 μm scan size. From the pictures, it is shown that the surface morphology changes with the integration of PES with PEG in the casting solution and the addition of TPP-CS additive compounds on the PEG-PES membrane through the grafting process. The roughness of the PES membrane increases with the presence of PEG in the casting solution. This is related to the pore formation process in the process of solidification. The presence of PEG makes it easier for water to penetrate in the casting solution, which will leave a pore trace on the membrane and this results in a porous membrane with increased surface roughness. The roughness of the PES membrane also increased with the modification of the membrane using the TPP-CS additive compound. Like PEG, hydrophilicity and the number of active groups in TPP-CS compounds are suspected to be the reasons for membrane surface roughness. The increase in TPP concentration in CS as an additive produces a roughness parameter that also increases, but decreases on membrane PEG-PES/TPPCS4. It seems that the increase in molecular weight tends to produce dense aggregate nodules in the skin layer which contribute to increasing roughness parameters. In order to improve the morphology and topography, the addition of PEG and TPP-CS can also improve the chemical properties of PES membranes by producing additional reactive functions (OH from PEG and -PO_4 from TPP-CS) into the membrane structure. It can be observed that membranes with high surface roughness exhibit high flux and membranes with the smooth surfaces showing low flux. This can be seen from the results of PWP and urea and creatinine clearance values. Changes in roughness parameters are proportional to changes in pore size [4]. This can be explained because the roughness parameter depends on the deep depression that characterizes the high pores and peaks that correspond to the nodules, high roughness parameters are expected. The surface roughness parameters of PES membranes and modified PES are presented in Table 4.

3.7. Water permeation

Comparison of the ability of water permeation on all PES derivative membranes is shown in Fig. 6. Flux value is the main parameter in assessing membrane performance. Permeability is the speed of permeation, which is defined as the volume that passes through a membrane of unity in a certain unit of time with the driving force in the form of pressure. The value of the permeability coefficient of pure water indicates the ease of water molecules to pass through the membrane. The higher of the permeability coefficient in the membrane, it means water to pass through the membrane easily. Membrane permeability was seen from flux values. The value will correlate with membrane permeability to water-soluble permeate compounds such as urea and creatinine. It can be seen that the modifications made to the PES membrane increases of water permeability. It can be seen that the modifications made to the PES membrane increases of water permeability. Probably, the results related that addition additives influence to the increase in membrane porosity. The same relationship between water permeation and membrane porosity was also observed by other researcher [17].

From Fig. 7, it can be seen that the membrane has good filtering capacity for certain-size species. Urea (MW 60 g/mol) and creatinine (MW 113 g/mol) can pass through the membrane easily, while species with the medium molecular weight (Vit B_{12}, MW 1355 g/mol) and large molecules (albumin, MW 69,000 g/mol) are not able to pass through the membrane. In addition, it is observable that urea permeability is greater than creatinine. This is because the molecular size of urea is the smallest one compared to other species. The highest permeability of urea and creatinine was obtained from TPP-CS modified PEG-PES membrane, with filtering capabilities up to 0.7 and the lowest value is shown by pure PES membrane which has urea filtration ability of only 0.18.

There is always consistent data showing that the ability of membranes to filter urea is always the largest as compared to that shown for creatinine, Vit B_{12}, and albumin. Urea with a molecular weight of 60 g/mol has molecular size of 4 A, creatinine (MW 113 g/mol) sizing 5.5 A, vitamin B_{12} (MW 1355 g/mol) is 22 A and albumin (MW 69,000 g/mol) measuring 3.8 mm. It appears that urea has the smallest size compared to the others. The small size of the urea causes greater urea mobility, making it easily enters the membrane pore system. Thus, it is understandable that the amount of urea passes through the membrane is the highest among the other species.

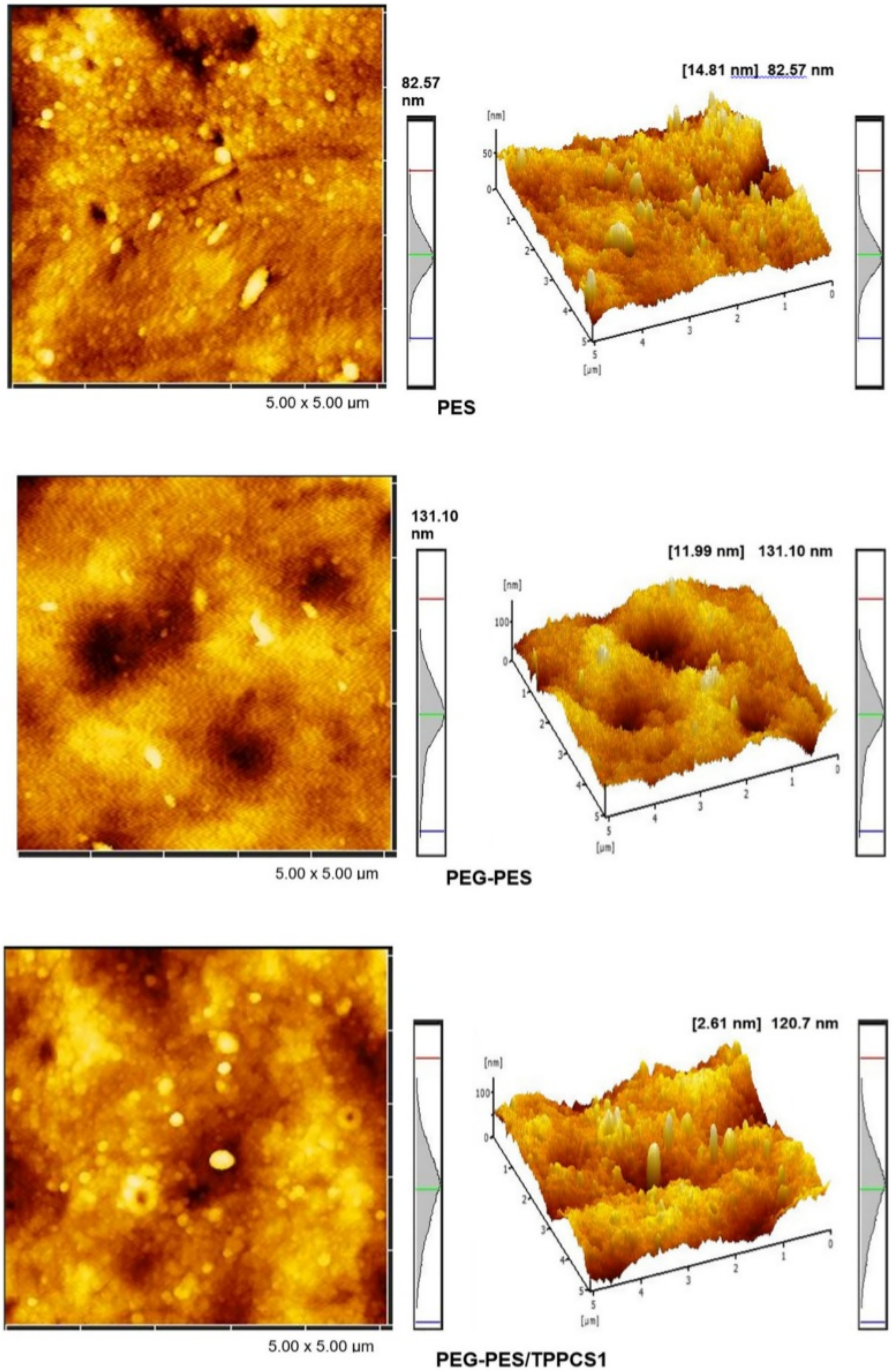
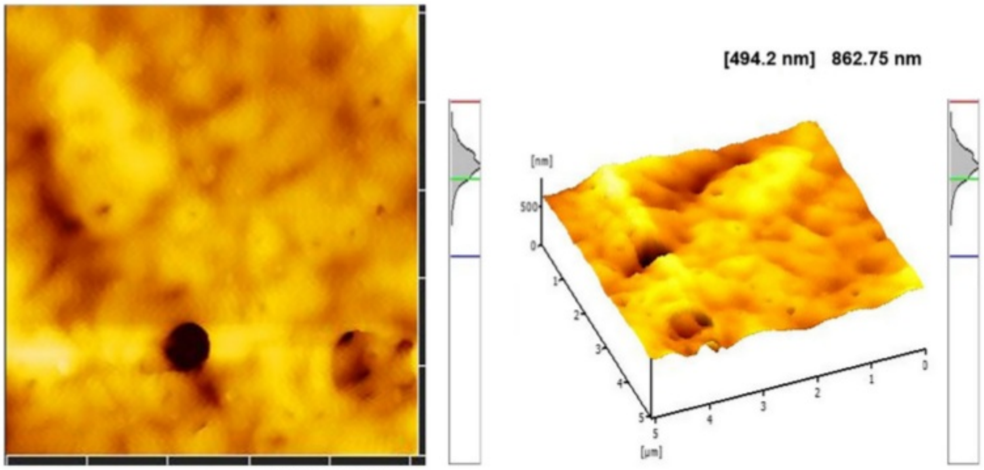
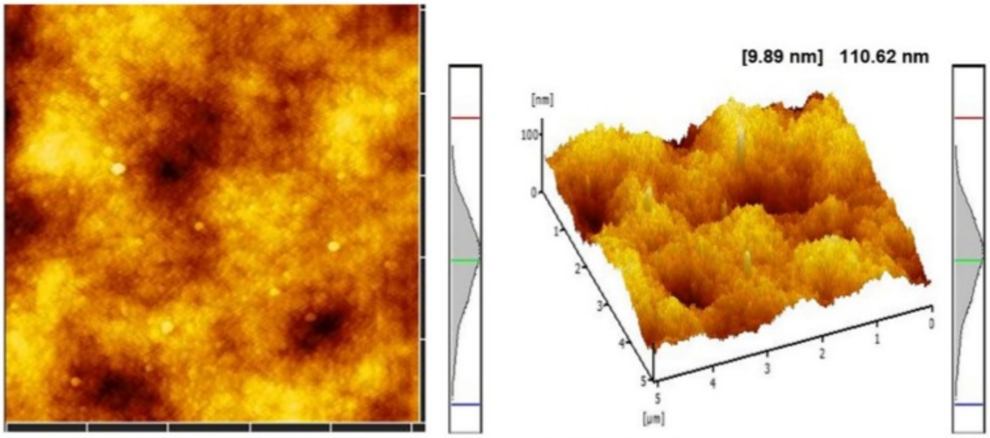


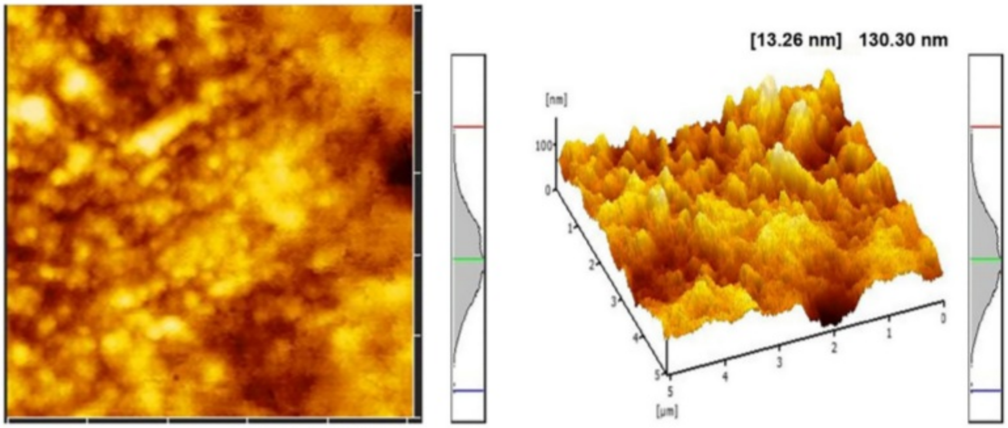
Fig. 5. Series of AFM topographic images of native PES and modified PES membrane.



PEG-PES/TPPCS2



PEG-PES/TPPCS3



PEG-PES/TPPCS4

Fig. 5. (*continued*)

Table 4
Physico-chemical characteristics of the membranes.

Membrane type	Roughness (nm)		
	R_a	R_q (RMS)	S_z (Rmax)
PES	4.1	5.1	28.1
PEG-PES	6.7	8.7	59.0
PEG-PES/TPPCS1	9.8	16.0	68.0
PEG-PES/TPPCS2	10.0	11.5	46.9
PEG-PES/TPPCS3	28.0	35.4	138.0
PEG-PES/TPPCS4	15.3	18.3	83.4

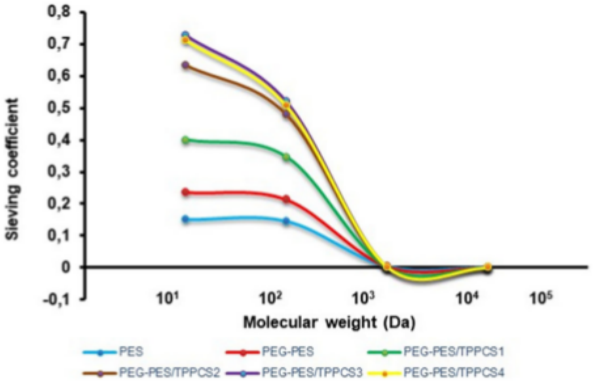


Fig. 7. Sieving coefficient of molecular weight markers for membranes. The following permeate were used: urea (60 Da), creatinine (113 Da), vitamin B_{12} (1355 Da), BSA (66 kDa).

3.8. Membrane dialysis ability

A good membrane is a membrane that has high permeability to certain components and holds other components in the function of filtration time. In this study, the transport process was carried out for 6 h and the contact area of the membrane with a permeate solution 4.96 cm^2, without pressure. The transport test was carried out in 50 mL dialysate solution with an initial creatinine concentration of 1.5 mg/dL and 50 mg/dL of urea. The concentration of transported compounds was measured using a UV–Vis spectrometer, with the absorbance measurements every hour for 6 h.

The membrane performance was measured by calculating the clearance value. The results of pure and modified PES membrane transport are shown in Fig. 8. The results showed that PEG-PES mixture and modification with TPP-CS increased permeation of PES membranes. Moreover, PEG-PES/TPPCS1 had urea clearance value of 20.0 mg/dL, creatinine 0.52 mg/dL, PEG-PES/TPPCS2 with urea and creatinine clearance values of 31.76 mg/dL and 0.72 mg/dL, PEG-PES/TPPCS3 had urea 36.40 mg/dL clearance, creatinine 0.78 mg/dL and PEG-PES/TPPCS4 with urea clearance of 35.60 mg/dL and creatinine 0.77 mg/dL. These results were achieved in the condition of transport for 6 h with a contact area of 4.625 cm^2. PES native membranes, urea clearance value was 7.8 mg/dL, creatinine was 0.22 mg/dL and PEG-PES urea clearance was 11.87 mg/dL and creatinine clearance was 0.32 mg/dL. It was found that modification using PEG and TPP-CS increased the ability of PES membranes in the process of transport/cleaning of the urea and creatinine components.

This indicates that the active group -PO_4 from TPP-CS facilitates the membrane to bind creatinine and urea. The transport process of urematous compounds are suspected to occur through hydrogen bonds formed between the active site of the membrane and creatinine as well as urea. The presence of a phosphate group (-PO_4) increases the active site of the membrane which can form hydrogen bonds with creatinine and urea. As a result, urea and creatinine will be more transported across the membrane.

In addition, increasing porosity due to the modification process of both with PEG and TPP-CS, also plays an important role in determining the ability of membrane to transport permeate. The increase in porosity makes the number of open cavity in the membrane increases, this situation will facilitate the flow of permeate through the membrane. Likewise, the increase in pore size due to modification, as seen in the morphological analysis (Fig. 4) will certainly increase the membrane permeability to the permeate passing through the membranes.

4. Conclusion

In this study, surface modification of PES membranes with TPP-CS was successfully done. Further improvements in permeability and clearance of urea and creatinine were achieved by coating of TPP-CS on PEG-PES membrane, due to the improvement of hydrophilicity and porosity of the membrane. The presence of -PO_4 group helps to improve the permeability of the membrane by intermolecular hydrogen bonding between water and the -PO_4 group. The presence of pore former agent, PEG helps in the formation of pore thus increase the porosity of the

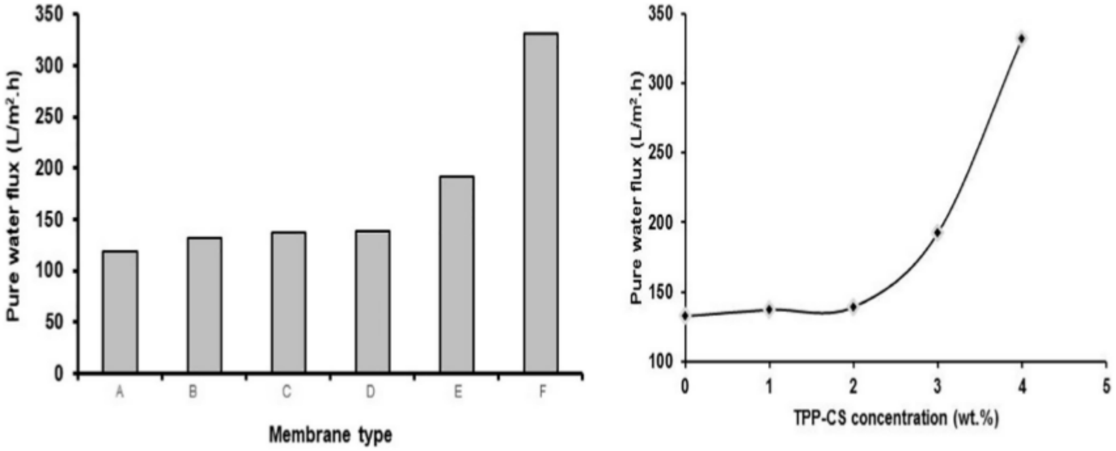


Fig. 6. Pure water permeation (PWP) of the membranes 1. PES (A), PEG-PES (B), PEG-PES/TPPCS1 (C), PEG-PES/TPPCS2 (D) PEG-PES/TPPCS3 (E), PEG-PES/TPPCS4 (F) and 2. the effect of TPPCS concentration on pure water permeability of the PES (B).

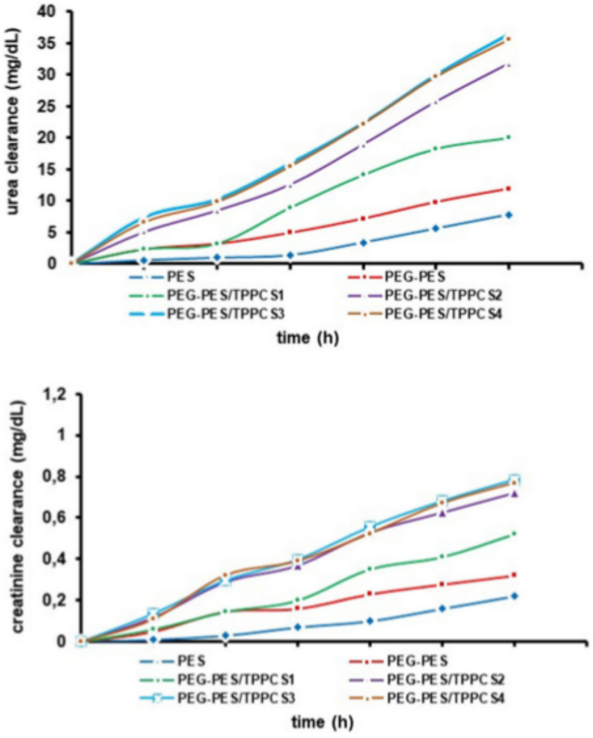


Fig. 8. Comparison of permeation ability in membranes.

membrane. Overall, the presented results show that PEG-PES membrane coated with TPP-CS cab be use as a new promising hemodialysis membrane material.

CRediT authorship contribution statement

Retno Ariadi Lusiana: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. **Vivi Dia A. Sangkota:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Writing - review & editing. **Nurwarrohman Andre Sasongko:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Visualization, Writing - review & editing. **Gunawan Gunawan:** Formal analysis, Validation, Writing - review & editing. **Anugrah Ricky Wijaya:** Formal analysis, Validation, Writing - review & editing. **Sri Juari Santosa:** Formal analysis, Validation, Writing - review & editing. **Dwi Siswanta:** Formal analysis, Validation, Writing - review & editing. **Mudasir Mudasir:** Formal analysis, Project administration, Supervision, Validation, Writing - review & editing. **Muhammad Nidzhom Zainol Abidin:** Conceptualization, Formal analysis, Investigation, Methodology, Resources, Writing - review & editing. **Sumarni Mansur:** Conceptualization, Formal analysis, Investigation, Methodology, Resources, Writing - review & editing. **Mohd Hafiz Dzarfan Othman:** Formal analysis, Project administration, Supervision, Validation, Writing - review & editing.

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Declaration of competing interest

The authors declare no conflict of interest.

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