Synthesis and characterization of composite polyethersulfone (PES) membranes with polyethylene glycol (PEG) and heparin-chitosan (Hep-CS)

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Synthesis and characterization of composite polyethersulfone (PES) membranes with polyethylene glycol (PEG) and heparin-chitosan (Hep-CS)

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Abstract. A PES-based membranes was prepared by casting a thin layer of heparin grafted PEG modified chitosan (CS) on a PES membrane. PEG addition on the process of making flat sheet PES membrane was observed through its mechanical and thermal properties. PEG concentrations were varied with PES polymer to obtain a membrane with the optimum composition. The blended membrane was characterized for its functional groups, tensile strength, and hydrophilicity. The results showed that PEG blended PES membrane gave a considerable mechanical strength. The presence of non-covalent interactions between PEG and PES played an important role on improving the mechanical and thermal properties of the membrane material. The increase amount of PEG improved the hydrophilicity property and permeability to creatinine of the membrane.

Keywords: membrane modification, mechanical strength, creatinine permeation

1. Introduction

High levels of creatinine and urea on blood are indication for the deterioration in kidney failure. The use of membrane technology to permeate urematous toxins has proven important. The membrane must function to filter and dispose of the urea and creatinine out of the blood without having to lose important compounds such as vitamins and blood proteins [1]. In recent years, many synthetic polymers in the form of PES have been used as membranes because of their high oxidative stability and high chemical, mechanical and thermal stability [2].

However the disadvantages of PES without additives are having a dense structure, a rough surface, hydrophobic, and membrane fouling which can cause protein coagulation on the surface and can cause damage to the bloods [3]. In order to get PES membrane with good performance, modification with another material that can increase hydrophilicity, permeability and antifouling properties are needed. PEG is a pore-forming agent [4]. The addition of PEG-CS to PES is expected to increase membrane pores, hydrophilicity, and permeability of membrane [5]. In the process of dialysis, heparin is used as an anticoagulant to prevent fouling on the membrane [6].

In this study heparin was reacted with chitosan in several variations of concentration [7, 8]. The presence of Hep-CS which has a sulphate group is expected to increase membrane hydrophilicity. The active groups of $-NH_3$, -OH and $-SO_3$ can bound hydrogen with creatinine, urea and H_2O [9]. Based on the above, modification of PES membrane was done by making PEG-PES membranes and immersed

with Hep-CS solution. The membrane was characterized using FTIR spectrophotometer, SEM, EDX, tensile strength, swelling test, hydrophilicity test, resistance of pH and urea and creatinine permeation.

2. Research Methodology

2.1. Materials

Chitosan (MW 40.000 Da, 87% deacety-lation degree) was obtained from PT Surindo Tech, Cirebon Indonesia. Polyethersulfone (PES), polyethylene glycol (PEG), NMP, sulphuric acid, heparin, acetic acid, urea, creatinine, phosphate buffer, poly vinyl alcohol (PVA) and picric acid were obtained from Merck.

2.2. Synthesis of Polyethersulfone/PEG membrane

The membrane was made in the flat sheets with the non-solvent induced phase separation/immersion precipitation (NIPS). The concentration ratio was 15 wt% (PES), 12.5 wt% (PEG), 72.5 wt% (NMP). PES was heated in oven (*Sigmatic*) at 100°C for 1 hour to remove the water content. Membrane solution was made by dissolving PEG in NMP at 50°C for 1-2 h, then addition of PES for 24 h at 50°C. Before membrane was printed, the solution was cultured for 30 minutes to remove air bubbles. PES/PEG solution was flattened of the glass to form a thin membrane sheet. Membrane printing was inserted into the tank of distilled water (H_2O). At this stage phase inversion occurs from liquid to solid membrane. After a few minutes, the membrane was removed from the glass and soaked in distilled water for 24 hours.

2.3. Preparation of PEG-PES/Hep-Cs Membrane

The PES membrane was modified by adding chitosan-heparin through immersion method. Modifications were made with variations in concentrations of heparin 50, 100 and 200 iu. The printed PES membrane was immersed in 60% sulphuric acid solution for 4 h. PES membranes soaked in 60% sulphuric acid then were washed with H_2O to remove the remaining sulphate solution. After that, it was soaked in 15 mL of chitosan-heparin solution for 4 h. Finally, the membranes of Chitosan-heparin were dried at room temperature.

2.4. Membrane Characterization

Functional groups were obtained with Shimadzu FTIR spectrophotometer. The mechanical strength of the blend of grafted membranes was measured using Tensometer (Shimadzu, AG-I-250 KN tester). Thickness measurements were obtained using Mitutoyo thickness meter at 3 different points of the membrane. Membrane surface image was characterized using scanning electron microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX) Shimadzu U8000.

2.5. Study of Membrane Permeation capacity for Creatinine and Urea

Permeation process experiments were done by using the following metabolites: creatinine 15 ppm and urea 500 ppm in 50 mL of dissolved phosphate buffer solution as the feed phase, and 50 mL phosphate buffer as the acceptor phase. Solute permeability passing through the membrane was determined by analysing the concentrations of each solution in the acceptor phase with a UV-Vis spectrophotometer at 0–6 h intervals. The creatinine was complexed with picric acid and NaOH to form coloured complex that absorbs a visible radiation at 486 nm (Jaffe method). Urea was complexed with 4-dimetilaminbenzaldehida (4-DAB) in acidic condition and measured at 430 nm.

2.6. Water Uptake Test

Water uptake test was carried out by soaking the membrane with known mass in 10 mL of distilled water for 6 h, and its mass changes were measured every hour.

$$water\ uptake = \frac{weight_{wet} - weight_{dry}}{weight_{dry}} x\ 100\% \quad (1)$$

2.7. Swelling Test

The test was carried out by soaking the membrane in 10 mL of distilled water system for 6h and the diameter change was measured according to procedure [10].

$$swelling = \frac{Diameter_{final} - Diameter_{initial}}{Diameter_{intial}} x\ 100\% \quad (2)$$

2.8. Contact Angle measurement

All the dry membranes with a flat surface were dropped with a drop of water from the membrane surface. Then the contact angle was determined based on the resulted image to calculate the hydrophilicity of the membrane.

3. Result and Discussion

3.1. FTIR

Fig. 1 shows FTIR spectra of PEG-PES membrane. As presented in the spectra, the PEG–PES membrane showed an absorption bands at 1149 and 1105 cm^{-1}, which could be assigned to the symmetric and asymmetric strain absorption of the $–SO_2$ groups. The absorption bands at 1243 cm^{-1} could be correlated to the strain of C-O-C groups [11]. Then the PEG-PES membrane was sulfonated with Sulphuric acid 60%. The effect of substitution of $–SO_3$ groups on the aromatic ring of PES could be indicated by an increasing intensity of absorption band of $–SO_2$ group at 1149 and 1105 cm^{-1} and a new absorption band appeared at of 1637 cm^{-1} which could be ascribed to the stretching of alkene groups. However, when The Sulfonated PEG-PES react with heparin grafted chitosan showed, the single absorption at 690 cm^{-1} wave numbers shifted to twin absorption at wave numbers of 692 and 716 cm^{-1} and also the absorption peak of the $–SO_3$ group in the aromatic ring at 1013 cm^{-1} disappears due to the interaction between PES $-SO_3$ group and heparin grafted chitosan. This interaction also causes the widening of the absorption at 1104 and 1151 cm^{-1} as the typical absorption of $-SO_2$ group.

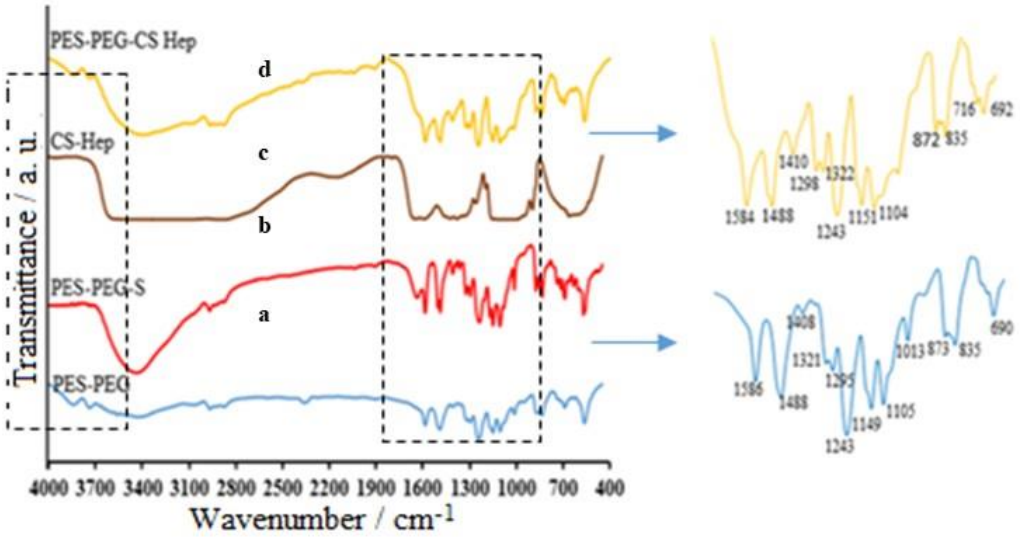

Figure 1. FTIR spectra of PEG-PES membrane (a), sulfonated PEG-PES membrane (b), Hep-CS solution (c), PEG-PES/Hep-CS membrane (d).

3.2. SEM-EDX Analysis

Fig. 2 shows the characterization of SEM of material before and after permeation. The result of membrane surface characteristics using SEM shows that the membrane after permeation has larger pores than the initial membrane. This is because the membrane is passed by a stranded compound so that the membrane pores become larger.

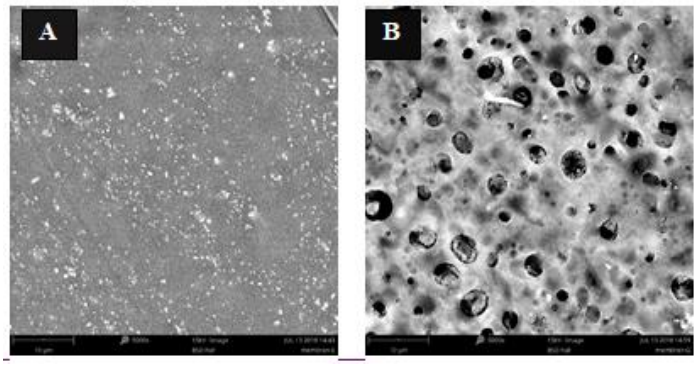

Figure 2. Characterization of SEM before (A) and after permeation (B).

SEM EDX is used to determine the components contained in the membrane. The composition contained in the Hep PES-Cs membrane can be seen in table 1.

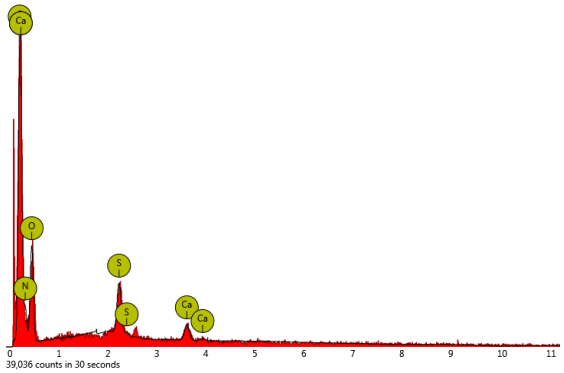

Figure 3. Composition of Hep PES-Cs membrane elements.

Fig. 3 shows the results of the PES- Hep-Cs membrane composition. The main ingredient is PES (polyether sulfone) which contains elements of C (carbon), O (oxygen), and S (sulphur) and supporting materials namely chitosan, PEG and heparin which contain elements of C (carbon), O (oxygen), N (nitrogen), S (sulphate) and H (hydrogen) [1]. The detected peaks can be attributed to the chemical ingredients of Hep PES-Cs membrane.

3.3. Tensile Strength Analysis

Table 1. Tensile strength test.

Membrane	Tensile Strength (Mpa)	Strain (%)	Modulus young
PEG-PES	1.30	5.13	0.27
PEG-PES-S	3.04	6.10	0.50
PEG-PES-Cs Hep	4.13	7.02	0.59

Tensile strength tests were carried out to determine the tensile strength and flexibility of the membrane when given a tensile force from the outside, which could damage the membrane structure. The more organized the membrane structure, the membrane will have a high tensile strength and stretch. The three

membranes above have a similar modulus young. There was no significant increase when PES membrane was immersed with chitosan, heparin.

3.4. Water uptake and Swelling

The ability of the membrane to interact with water is shown through water uptake. Percentage of the membrane water uptake was determined by calculating the weight of the dry membrane and the wet membrane after immersed in water for 6 h. Water uptake is closely related to % swelling. Swelling shows the power of developing membranes when interacting with water. Swelling tests are carried out the same as water absorption tests. The difference in swelling measured is the increase in the length of the membrane diameter. Water uptake results of various types of membranes can be seen in table 2 and the % development test is shown in the table below.

Table 2. Percentage of water uptake and swelling test.

Sample	Swelling (%)	Water uptake (%)
PES	100.575	108.966
PEG-PES (sulphate 60%)	103.636	210.811
PEG-PES/Hep-CS		
✓ 50 iu	103.030	285.393
✓ 100 iu	101.724	302.609
✓ 200 iu	101.724	350.345

Based on table 2, water uptake and swelling of PES membranes increase with the modification of the membrane surface. PEG-PES has the lowest water uptake and the lowest swelling given the very hydrophobic nature of the PES membrane. The sulfonated PEG-PES membrane (PEG-PES-S) has water uptake and swelling higher than PEG-PES. The presence of the -SO_3 group on the membrane, increases the hydrophilicity of the PEG-PES membrane. The modification of the membrane surface with chitosan hydrophilic polymer grafted with heparin increases the water uptake up to 3 times. This is due to the large number of hydrophilic groups in chitosan such as -COOH and –SO_3 groups in heparin, and NH_2 chitosan groups that are able to form hydrogen bonds with water. The percentage of water uptake increases with the increase in heparin concentration added. This is related to the availability of more –SO_3 groups in membranes.

3.5. Hydrophilicity

The contact angle becomes a parameter for determining a membrane to be hydrophilic or hydrophobic. Hydrophilicity is an important parameter for a dialysis membrane because it can affect membrane permeability. The hydrophobicity test was carried out using the sessile drops method. The results of the membrane contact angle measurements are shown in Fig. 4 and the table 3.

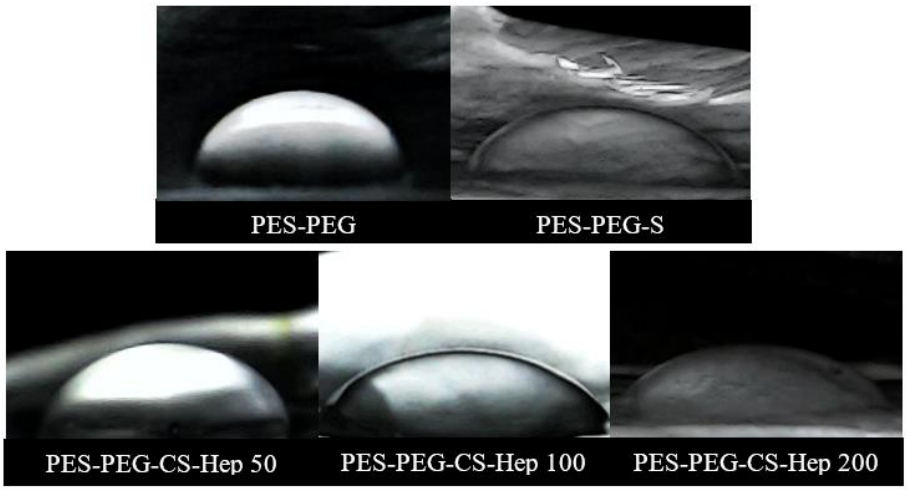

Figure 4. Drops of water of membranes.

Table 3. Water contact angle on various types of membrane.

Membrane Type	Contact Angel
PEG-PES	95.35°
PEG-PES-S	59.90°
PEG-PES-Hep-CS 50	59.35°
PEG-PES-Hep-CS 100	57.36°
PEG-PES-Hep-CS 200	51.20°

These results indicate that the PEG-PES membrane is hydrophobic because it has a contact angle>90°. PEG-PES-S membrane and PEG-PES/Hep-CS are classified as hydrophilic because they have contact angles below 90°. Hydrophilicity increases with decreasing contact angle. So that it can be concluded that the hydrophilicity membrane of PEG-PES-Hep-CS>PEG-PES>PEG-PES-Hep-CS membrane. The increase in hydrophilicity occurs because of the addition of hydrophilic groups that are able to form hydrogen bonds between the membrane and H_2O. The hydrophilicity of PEG-PES-S membrane increased with the substitution of $-SO_3$ group on PES aromatic rings. While the increase in hydrophilicity of PEG-PES-CS Hep increases with increasing levels of heparin. The presence of chitosan and heparin increases the hydrophilicity membrane of PES. -OH, $-NH_2$ and $-SO_3$ in chitosan are grafted with heparin which can form hydrogen bonds with H_2O. Increased hydrophilicity can increase membrane permeability; it also can improve membrane performance in urea and creatinine permeations.

3.6. Permeation Studies

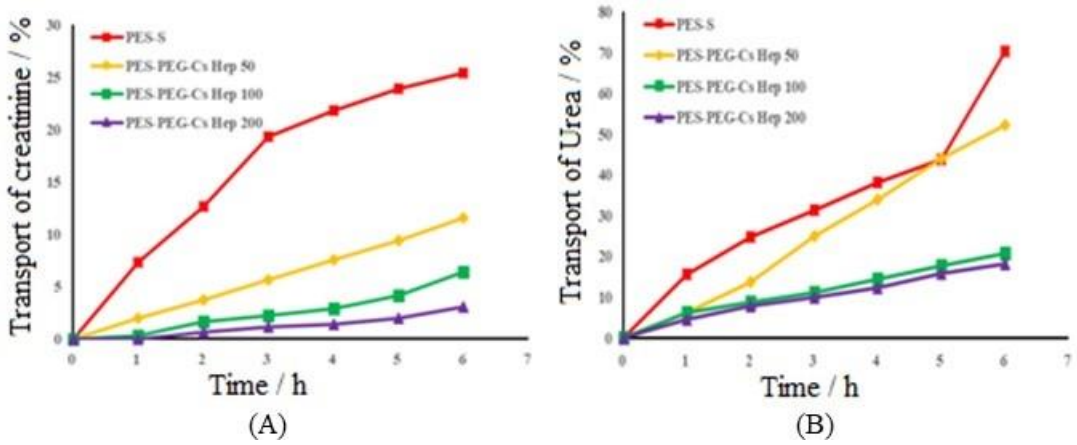

Figure 5. Permeation of creatinine (A) and urea (B).

The permeation results in Fig. 5 showed at 6 hours the percentage of creatinine permeation using PEG-PES-S membrane was 25.36% and urea was 70.25%. While the results of urea permeation using CS-S membrane was 70.25%, PEG-PES/Hep-CS 50 membrane was 52.36%, PEG-PES/Hep-CS 100 membrane was 20.67% and PEG-PES/Hep-CS 200 membrane was 18.14%. It is seen that the increase in heparin concentration decreases the permeation ability of PES membranes. This might be caused by increasingly making compounds in the membrane making the space used to bind to the permeate to be incorrect.

4. Conclusion

Modification of PES membranes with PEG and Hep-CS increases the hydrophilicity and permeability of PES membranes

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