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Chitosan based modified polymers designed to enhance membrane permeation capability

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Abstract. Membranes commonly used for separation processes can be made using phase inversion techniques. This study aims to determine the characteristics of the modified polyethersulfone/polyethilenglycol (PES/PEG) flat membrane using chitosan-succinate in 4 ratio mole made using phase inversion techniques. The results of SEM and BET analysis on membrane morphology prove that the membrane produced is a porous membrane. PES/PEG-CS-Succ membranes have a smaller and more uniform pore structure than PES membranes. The permeability ability of PES/PEG-CS-Succ membrane is 0,4823 mg/dL and 23,1028 mg/dL, respectively.

1. Introduction

Hemodialysis is one of application that utilizes the separation process using membranes. Hemodialysis aims to remove metabolic substances that are not needed by the body from the blood such as creatinine and urea without losing important substances in the blood such as vitamin B12 and albumin [1, 2].

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 [3]. However, the disadvantages of polyethersulfone (PES) without additives are having a dense structure, a rough surface, hydrophobic, and membrane fouling [4]. To get PES membrane with good performance, the addition of PEG and modification using cross-linked chitosan succinic acid (CS-Succ) are needed. PEG is a pore-forming agent so that the addition of PEG to PES can form PES membrane pores [5]. Modification using CS-Succ increases the permeation of PES membranes [6]. CS-Succ donates reactive groups such as -NH₂ and -OH from CS-Succ so it can increase permeation through hydrogen permeate bonds [7]. Both of them also done to reduce the hydrophobic properties of the membrane, thus providing a good influence on the process of separation and anti-fouling performance.



2. Materials and Method

2.1. Materials

Chitosan with a degree of deacetylation (DDA) 89% was purchased from PT Surindo Tech, Cirebon Indonesia. PES (polyethersulfone) (Radel A-300A Resin) was purchased from Solvay Advanced Polymers, PEG (polyethylene glycol) (molecular weight = 4000 g/mol), N-methyl-2-pyrrolidone (NMP, 99.5 %; molecular weight = 99.1 g/mol) was purchased from Acros Organics, sulphuric acid (95-97 %), acetic acid, succinic acid, urea, creatinine, phosphate buffer, picric acid, benzaldehyde dimethylamine, NaOH and HCl were obtained from Merck.

2.2. Material Synthesis

2.2.1. Synthesis of PES/PEG in NMP. The membrane was prepared in a flat sheet (sheet) with "induced phase separation nonsolvent/immersion precipitation (NIPS)" method. PES absorbs water very quickly. Therefore, PES were dried at 100 °C before the process. PEG (Poly Ethylene glycol 4000) was used as an additive and NMP as a solvent with a composition of 15% (PES): 12.5% (PEG): 72.5% (NMP). Poly Ethylene glycol 4000 were dissolved in N-Methyl Pyrrolidin (NMP) at 50 °C using a magnetic stirrer for 1-2 hours. Then Poly Ether Sulfonate (PES) was added gradually and stirred using a magnetic stirrer for 24 hours at 50 °C. The homogeneous solution was printed using film applicator on a glass substrate to form a thin sheet. Then the solution was transferred to a water bath and soaked for 24 hours in order to ensure the total evaporation of the solvent in the membrane. The PES/PEG in NMP membrane were dried.

2.2.2. Synthesis PES/PEG/CS-Succ. PES membranes were modified by the addition of CS-Succ through immersion method (soaking). PES membrane which had been printed were soaked in sulphuric acid (H₂SO₄) solution 60% for 4 hours. It provided a negative charge in the PES membrane surface [8]. PES membranes that had been soaked in 60% sulphuric acid were washed with H₂O until the rest of sulphates lost. After that, it was soaked in 15 mL of CS-Succ for 4 hours. PES/PEG/CS-Succ membranes were dried at room temperature. The composition of CS-Succ addition variations is presented in Table 1.

Table 1. The polymer composition for each membrane

Type membrane	PES (wt%)	PEG (wt%)	NMP (wt%)	CS (wt%)	Succ (wt%)
PES/PEG/CS-Succ30	15	12.5	72.5	1.5	3.7
PES/PEG/CS-Succ60	15	12.5	72.5	1.5	1.8
PES/PEG/CS-Succ90	15	12.5	72.5	1.5	1.2
PES/PEG/CS-Succ100	15	12.5	72.5	1.5	1.1

2.3. Membrane Characterization

2.3.1. Membrane morphology Test using SEM. PES/PEG/CS-Succ membrane morphology was examined using SEM. Images of the surface of the membrane were obtained in this characterization.

2.3.2. Thermal stability test (TGA). Thermogravimetric analysis (TGA) was used to measure the amount and the rate of weight change of the membrane as a function of temperature or time in a controlled atmosphere. TGA mainly used to determine the composition of the membrane and to predict the thermal stability of a material at temperatures up to 1200°C.

2.3.3. Surface area analyser (SAA) Test. SAA analysis was needed to determine the surface area and pore distribution of the membrane material. This analysis was used to predict the surface area and pore distribution of the membrane by the provision of nitrogen.

2.3.4. Transport of Creatinine. This test was performed to determine membrane selectivity of the separation permeate. Permeation test was conducted using a permeation tool with a membrane in it. Source phase containing 50 mL of creatinine standard solution 25 ppm in the phosphate buffer solution and the acceptor phase containing 50 mL of phosphate buffer. Permeation was conducted for 6 hours with each hour taken 2 mL sample of the source and the acceptor phase was then complexed using picric acid and analysed using UV-Vis spectrophotometer at a wavelength of 486 nm.

2.3.5. Transport of urea. Permeation test was conducted using a permeation tool with a membrane. Feed phase containing 50 mL of urea standard solution 500 ppm in the phosphate buffer solution and the acceptor phase containing 50 mL of phosphate buffer. Permeation was conducted for 6 hours and each hour was taken 2 mL sample of the source. The acceptor phase was then complexed using 4-dimethylaminobenzaldehyde (4-DAB) and analysed using UV-Vis spectrophotometer at a wavelength of 430 nm.

The percentage of transport can be calculated using the formula:

$$\% \text{ Transport} = \frac{[A]_t}{[S]_i}$$

With [A]_t = the concentration of the acceptor phase at t
[S]_t = the concentration of the source phase at t = 0

3. Results and Discussion

3.1. Synthesis of PES/PEG/CS-Succ compounds

The success of PES/PEG/CS-Succ membrane synthesis was proven by characterization using FTIR.

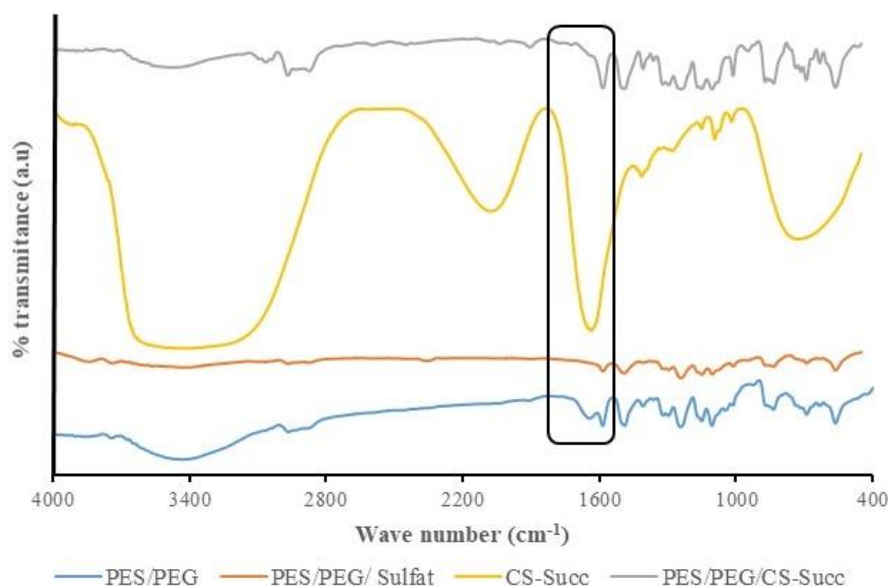


Figure 1. FTIR spectra of membranes chitosan modified.

Characteristics of the PES/PEG spectra are typical absorptions in the wave number regions of 1149 cm^{-1} and 1105 cm^{-1} which are symmetrical and asymmetric strain absorption of $-\text{SO}_2$ groups. There are also absorption at 1243 cm^{-1} derived from the C-O-C strain [9]. Sulfonated PES spectra (PES/PEG-S) showed improvement $-\text{SO}_2$ absorption intensity at wave number 1149 cm^{-1} and 1105 cm^{-1} as well as emerging new absorption at wave number 1637 cm^{-1} which is an alkene absorption, the effect of $-\text{SO}_3$ group substitution in the aromatic ring of the PES. The increasing of absorption intensity at wave number 830 cm^{-1} - 1580 cm^{-1} indicates that the PES/PEG has been sulfonated. PES/PEG/CS-Succ spectra specifically is marked with the shift wavenumber of 1643 cm^{-1} , an absorption of C=O of carboxylic group. It means the modifying process of the CS-Succ was successfully carried out properly. At wave number 1410 cm^{-1} showed the absorption of $-\text{NH}$ group which is a transmutation of $-\text{NH}_2$ group. For NH_2 and OH groups of CS-Succ provides wide absorption in the wave number region 3400 cm^{-1} .

3.2. Membranes Characterization

3.2.1. Scanning electron microscopy (SEM). SEM analysis was carried out to see the effect of PES modification on the appearance of the membrane surface. SEM image of PES membrane and modification results can be seen in Fig. 2.

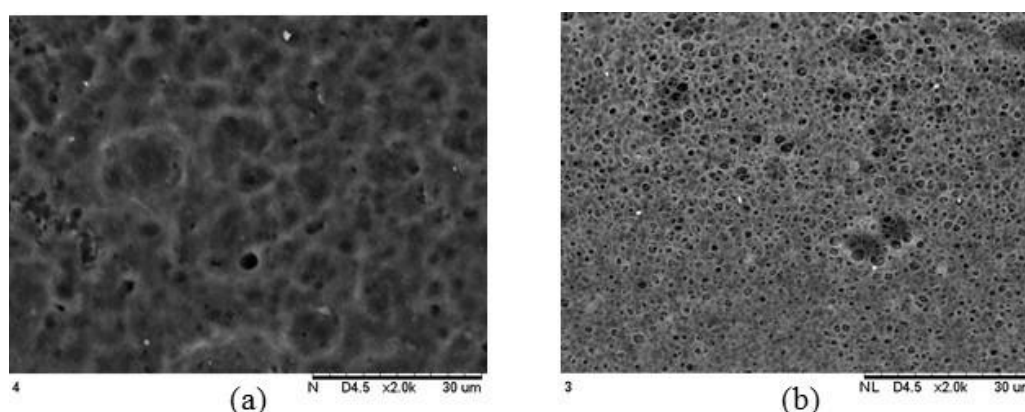


Figure 2. SEM image of PES/PEG (a) and PES/PEG/CS-Succ membranes (b).

Modification using CS-Succ were able to increase the membrane pore and the number of active sides of the permeate catcher so that the PES/PEG/CS-Succ membrane is able to diffuse more permeate compounds as reflected in Fig. 2.

3.2.2. Thermal stability test (TGA). TGA test was performed to determine the thermal stability of the PEG/PES/CS-Succ that in Fig. 3. Thermogravimetric analysis carried out at a temperature ranging between $30\text{--}900^\circ\text{C}$ with a temperature increase rate of $5^\circ\text{C}/\text{min}$. The thermogram shows the difference in the temperature range at the first stage of weight loss. PES modification causes a very significant weight loss at a temperature range of $500\text{--}600^\circ\text{C}$ with a mass loss of 3.5 mg .

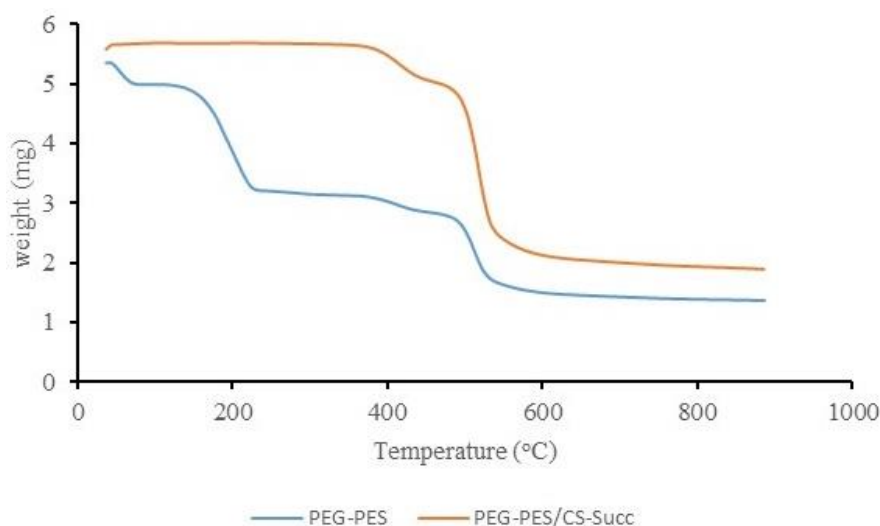


Figure 3. TGA curve of membrane chitosan modified.

3.2.3. Surface area analyser(SAA)

Determination of area and surface was carried out through the SAA test. The results obtained are presented in table 3.

Table 2. Test SAA membranes.

Type Membranes	Pore size (\AA)	Surface area ($\text{m}^2 \text{g}^{-1}$)
PES/PEG	$3,62 \times 10^1$	69.507
PES/PEG/CS	$4,61 \times 10^1$	58.259
PES/PEG/CS-Succ100	4,05	121.730

Table 2 gives information that membrane modification using CS-Succ can add the effectiveness of PES/PEG membrane. Modification of the membranes results membrane surface are increasing but the pore size PES/PEG/CS-Succ decreased compared to the other two membranes, so that it can pass the permeate selectively and hold the protein in the body.

3.2.4. *PES/PEG/CS-Succ membrane Transport of creatinine.* PES/PEG /CS-Succ Membrane transport ability shown in Fig. 4.

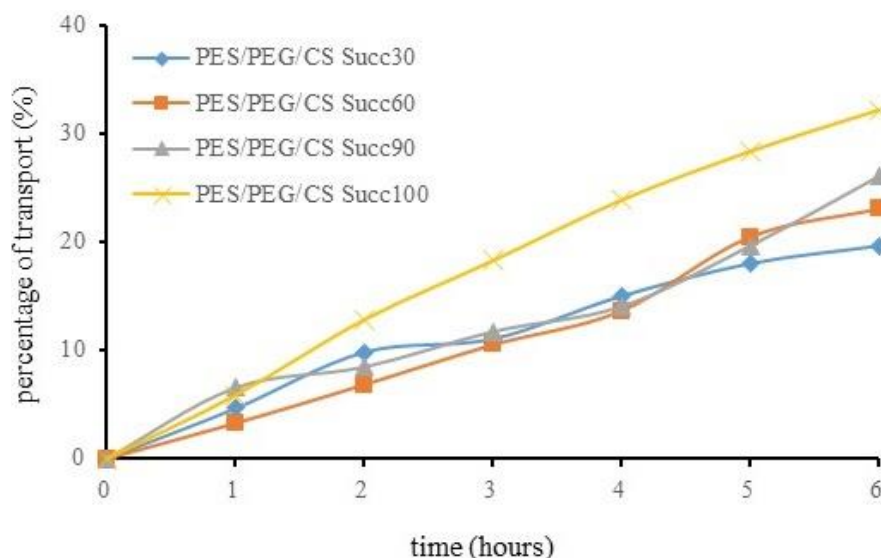


Figure 4. Transport curve of membrane chitosan modified.

Modification of PES/PEG membranes with CS-Succ increases membrane permeation. The highest creatinine transport was achieved in the membrane composition of PES/PEG/CS-Succ100. In this composition, there is regularity of the distance of the polymer so it increases membrane rejuvenation. In this condition, the PES/PEG/CS-Succ100 membrane was able to diffuse creatinine 32,153% out through the membrane. PES/PEG/CS-Succ30 until PES/PEG/CS-Succ100 membrane transport data are presented in table 3.

Table 3. Transport membrane Data of creatinine.

Time (hours)	PES/PEG/CS-Succ30 (%)	PES/PEG/CS-Succ60 (%)	PES/PEG/CS-Succ90 (%)	PES/PEG/CS-Succ100 (%)
0	0.000	0.000	0.000	0.000
1	4.632	3.270	6.540	5.858
2	9.809	6.812	8.447	12.807
3	11.035	10.490	11.717	18.256
4	14.986	13.624	14.033	23.842
5	17.984	20.436	19.619	28.338
6	19.619	23.025	26.022	32.153

3.2.5. PES/PEG/CS-Succ membrane Transport of urea. Study of permeation ability to urea conducted for 6 hours with absorbance measurements was conducted every hour.

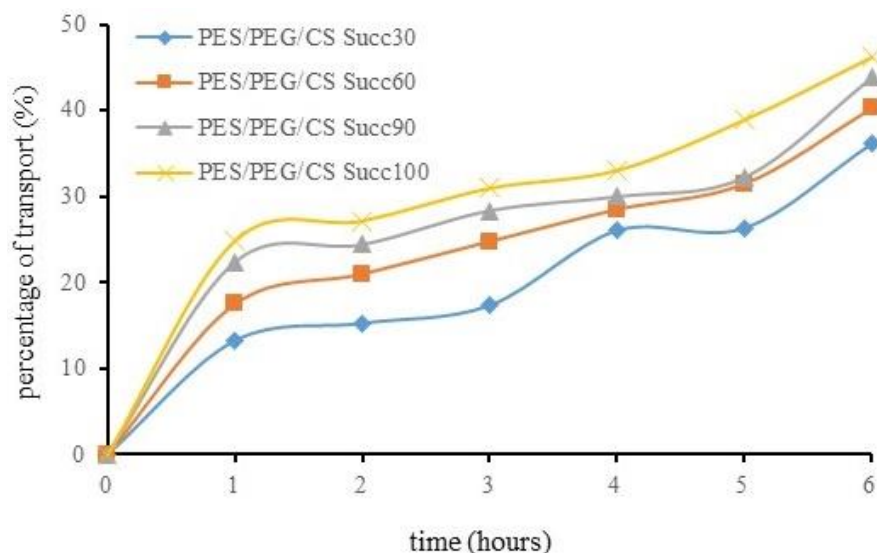


Figure 5. Transport curve of membrane chitosan modified.

Fig. 5 shows that the PES/PEG/CS-Succ membrane transport of urea has a greater percentage than the membrane transport of creatinine. It is because of the size of the smaller urea molecule of 60.07 g/mol smaller than creatinine with the BM 113 g/mol. The molecular size of a permeate affects the performance of the membrane so that the percentage of PES/PEG/CS-Succ100 membrane transport of urea at best composition is 46.205% with the ability to diffuse the urea at 23,1028 mg/dL.

Table 4. membrane transport Data of urea.

Time (hours)	PES/PEG/CS-Succ30 (%)	PES/PEG/CS-Succ60 (%)	PES/PEG/CS-Succ90 (%)	PES/PEG/CS-Succ100 (%)
0	0.000	0.000	0.000	0.000
1	13.244	17.485	22.396	24.851
2	15.253	20.982	24.405	27.158
3	17.336	24.777	28.348	30.952
4	26.042	28.497	29.985	33.036
5	26.339	31.473	32.217	38.914
6	36.161	40.253	43.824	46.205

4. Conclusion

PES/PEG membrane modification with the addition of CS-Succ can increase selectivity, porosity and membrane permeation ability. The best composition was achieved by PES/PEG/CS-Succ100 with creatinine and urea permeation abilities of 0,4823 mg/dL and 23,1028 mg/dL, respectively.

Acknowledgments

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