

Preparation of asymmetric cellulose acetate membrane by phase inversion method of cellulose pulp from wood of sengon (*Paraserianthes falcataria*)

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Abstract: Cellulose acetate ultrafiltration membrane is one of kinds process of membrane which has been utilized in separation and purification processes. Cellulose acetate can be obtained from acetylation of cellulose sengon wood (*Paraserianthes falcataria*). Wood Sengon was used because it has potential as a raw material. There are three steps of cellulose diacetate manufacturing process: (1) activation of cellulose using acetic acid, (2) acetylation using acetic anhydride as reactant and sulfuric acid as catalyst, (3) hydrolysis. At each operating process was observed at 50°C. Preparation of cellulose diacetate membrane using phase inversion method by addition of cellulose diacetate as polymer; N,N-Dimethyl formamide (DMF) as solvent, water as non-solvent, and Polyethylene glycol (PEG). Membrane pore size was determined by measuring Molecular Weight Cut Off (MWCO) using Dextran and Bovin Serum Albumine (BSA) as standard solution. Membrane morphology was observed by Scanning Electron Microscope (SEM). Cellulose acetate of acetyl content of 39.66% and number average molecular weight 130,221 Da was obtained 30 minutes of activation time; one hour acetylation, and 15 hours hydrolysis. The addition of PEG produced a thickener layer and suppress the formation of macrovoid. SEM analysis shows a denser structure membrane morphology with better regularity of pore shape. The resulting membranes which were coagulated at lower temperature shows dense structure. High flux with low rejection obtained from the membrane with greater porosity and pore distribution. MWCO determination was based on the value of 80% rejection of dextran and BSA standard solution and the obtained pore size ranges obtained ≤ 67 kDa, and is still categorized as ultrafiltration membrane.

Key words: *Paraserianthes falcataria*, cellulose diacetate, inversion, cellulose diacetate membrane, ultrafiltration.

Introduction

Membrane is semipermeable barriers that separates two phases and restrict the transport of various substances in a specific way (Strathmann, 1990). In recent years, membranes and technology of membranes have grown from a laboratory scale. To day, technology of membranes are used on a large scale such as medical care/ medical industry (hemodialysis, purification of enzymes, antibiotics, etc), food industry (concentration of fruit juice, sugar purification, waste water treatment, etc), other industries (desalination and salt production, waste water treatment dan recovery of valuable, etc.) (Shibata, 2004).

Technology of membrane more efficient and economical because the processes are faster, low energy consumption, operation at mild temperatures, the non-addition of chemical products (Mulder, 1996; Countinho, 2009). In Indonesia, utilization technology of membrane is not to develop in good because the materials of membrane is very difficult to find. Cellulose acetate suitable as membrane materials because is an environmental friendly substance. Cellulose acetate can be found from acetylation process of cellulose. In Indonesia, Sengon plant is many grow and fast growing species and has potential as a raw material from its high cellulose content. Cellulose from wood pulp of Sengon (*Paraserianthes falcataria*) had be used for making membrane (Rosnelly et al., 2009, 2010).

Material and Methods.

Materials

Cellulose acetate (CA) used as the membrane forming polymer (acetyl content 39.66% with molecular weight of 130,221 Da) was produced from earlier researcher by activation, acetylation, and hydrolysis of wood sengon. The solvent used was dimethyl formamide (DMF) was procured from Merck and water as non solvent. Poroging agent used was

polyethylene glycol 1450 Da (PEG) was procured from Sigma. Both of Dextran 12 kDa and Bovin Serum Albumin 67 kDa were procured from Sigma.

Preparation of solution polymer and preparation of membrane

Solution of CA was prepared by dissolving in presence and absence of poroging agent PEG 1450 Da in a polar solvent DMF. Cellulose acetate was added in ratio 1:3; 1:4; 1:5; 1:6 respect to DMF while PEG 1450 Da was added 20% with respect to the weight of CA. Mechanical stirring was did in flask for 2 hr at room temperature until the CA and PEG were entirely dissolved to form a homogenous solution (dope solution) (Modification of Mahendran et al.. 2004; Chou et al.. 2007)

Asymetric membrane are generally prepared by the phase inversion. Dope solution then cast on a glass plate at a 0,2 mm thickness and is left to evaporate time for 30 seconds. Next, the glass plate were immersed into the coagulation bath (15°C room temperature, 50°C) and left until the gelled membrane formed and preserved in pure water before characterization (Modification of Mahendran et al.. 2004; Chou et al.. 2007). The morphology of membranes was examined using a Scaning Electron Microscope (SEM) JSM – 5310 LV, Jeol Japan. The experimental setup for measuring flux and retention of standard solution (dextran and BSA) for CA membrane were carried ouat in the ultrafiltration instruments. The feed was held in a trans membrane pressure (ΔP) of 1,2 bar and was recirculated at a flow rate 34 L/hr. The flux was determined when the flow rate stabilized. The pore size distribution was determined using dentran (12 kDa) and BSA (67 kDa) with concentration in the feed solution was kept at 200 ppm for each solution. Molecular weight cut-off (MWCO) is a pore characteristics of membrane is related to rejection for a given molecular weight of a solute above 80% (Mahendran et al., 2004). The concentration of dextran and BSA were determined using UV-spectrophotometer. The flux (Jw) was calculated by the following equation (Mulder,1996):

$$J_w = V / (A \cdot \Delta t) \quad (1)$$

Where:

- Jw = water/solution flux (in L/m².hr)
- V = quantity of permeate collected (in L)
- Δt = the sampling time (hr)
- A = the membrane area (m²)

The retention R was calculated as follows (Mulder, 1996):

$$\%R = [1 - C_p/C_f] \times 100\% \quad (2)$$

Where Cf and Cp are the solute concentration in the feed and permeate.

Results and Discussion

Membranes be obtained from a homogenous solution (dope solution) in ratio1:6 of CA respect to DMF. Before characterization, compaction of all the membranes at a higher pressure than the operating pressure were did to obtain a steady state flux and need about 30 minutes for compacting. Flux of all the compacted membranes were measured after an initial stabilization period 10 minutes.

Analysis of SEM the membrane morphology shows an asymmetrical structure consisting of a dense top-layer and a porous sub-layer. The top layer formed first when the casting solution was immersed in water coagulation bath. Molecules of CA at interface aggregate rapidly so that the dense skin formed when the solvent of DMF desolvates rapidly into the water coagulation bath (Young & Chen, 1995; Javiya et al. 2008). Membrane with addition of PEG shows a denser structure of membrane morphology with better regularity of pore shape, so has a better pore density (porosity) distribution of large and visible pores. Macrovoid formed for membrane without addition of PEG. Poroging agent PEG can increase the viscosity of the solvent so that affinity solvent with non solvent more slowly. The macrovoid gradually disappeared with addition PEG (Chou et al.. 2007). At the higher of water coagulation bath temperature, the structure of membrane morphology is more

tenuous with a bigger pore size and greater number of pores so large porosity and pore distribution because diffusion of DMF into the water coagulation bath more faster. Analysis of SEM can be shown in Figure 1, Figure 2, and Figure 3.

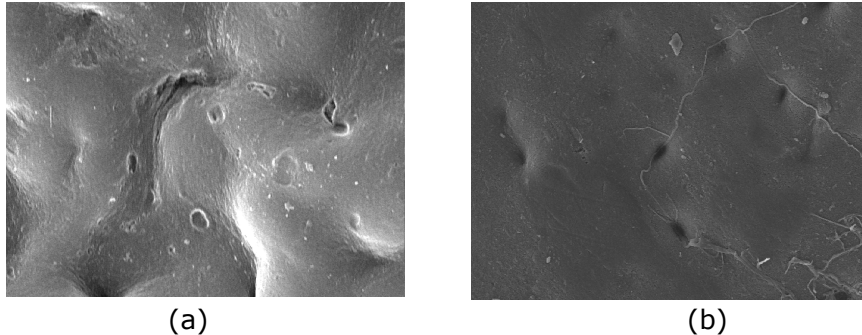


Figure 1. Asymetrical structure of membrane: (a) dense top-layer (2000x); (b) porous sub-layer (500x, room temperature of coagulation bath).

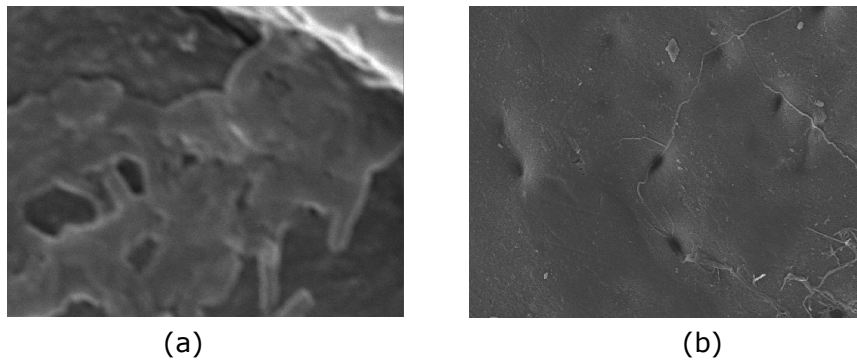


Figure 2. Structure of membrane (500x, room temperature): (a) without PEG; (b) addition PEG.

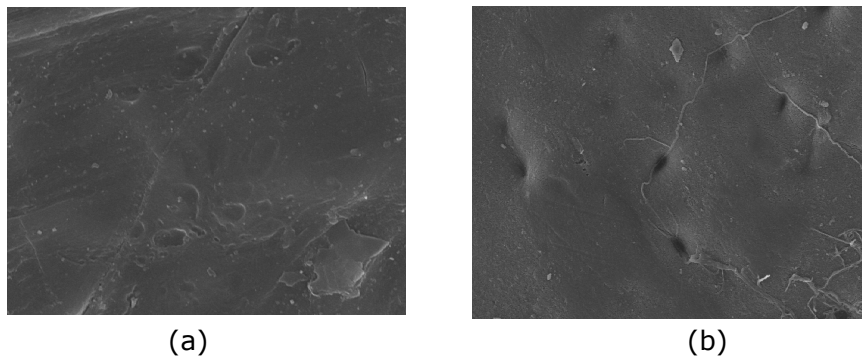


Figure 3. Structure of membrane respect to temperature of water coagulation bath (500x): (a) 15°C; (b) room temperature.

Higher temperature would strongly affect the flux performance of CA membrane because affinity between solvent of DMF and nonsolvent of water very strong. Higher PEG content would lead to higher flux because PEG is a pore-forming that creates pore in the polymer matrix of CA so that size of micropores increased. Conservally, rejection of all membranes would lead to lower with increased the content of PEG (Chou et al., 2007). High flux with low rejection obtained from the membrane with greater porosity and pore distribution. The result of flux and rejection for all membranes as shown in Table 1.

Characterization of membrane can be obtained by the pore size or molecular weight cut-off (MWCO) value which is obtained by measuring the retention of macromolecules with

molecular weight. Cellulose acetate membranes in presence and absence PEG had the MWCO of 67 kDa although there was found the different of the rejection value. While the MWCO is based on 80% of solute rejection, so that all the membranes had the same MWCO and still categorized as ultrafiltration membrane.

Table 1. Effect of various content on the membrane performance

PEG (MW)	Coagulation bath temperature (°C)	Flux of water (L/m ² .jam)	Flux of Dekstran (L/m ² .jam)	Flux of BSA (L/m ² .jam)	Rejection of Dextran (12.000 Da) (%)	Rejection of BSA (67.000 Da) (%)
Murni SA	15	53 ± 4	49 ± 4	43 ± 2	56.54 ± 4,3	84.2 ± 6.4
	30	74 ± 6	59 ± 4	58 ± 4	54.8 ± 4.1	78.7 ± 5.9
	50	96 ± 7	81 ± 6	65 ± 5	53.5 ± 4,04	74.7 ± 5.6
1450 Da	15	96 ± 10	83 ± 6	74 ± 6	60,9 ± 4.6	85.6 ± 6.5
	30	121 ± 13	95 ± 7	83 ± 6	55.9 ± 4.2	79.9 ± 5.8
	50	129 ± 14	119 ± 9	103 ± 8	50.9 ± 3.9	75.7 ± 5.7

Conclusions

Cellulose acetate of acetyl content of 39.66% and number average molecular weight 130,221 Da used for preparing of membranes with ratio of CA respect to DMF is 1:6. Membranes with the addition of PEG produced a thicker layer and suppress the formation of macrovoid. SEM analysis shows a denser structure of membrane morphology with better regularity of pore shape, so has a better pore density (porosity) distribution of large and visible pores. Coagulation at higher temperatures produced a thinner layer. The structure of membrane morphology is more tenuous with a bigger pore size and greater number of pores so large porosity and pore distribution. High flux with low rejection obtained from the membrane with greater porosity and pore distribution. MWCO determination was based on the value of 80% rejection of dextran and BSA standard solution and the obtained pore size ranges obtained ≤ 67 kDa, and is still categorized as ultrafiltration membrane.

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