# Preparasi dan Karakterisasi Blend Membran Polisulfon/Selulosa Asetat (PSF/CA)

## Preparation and Characterization of Polysulfone/Celullose Acetate (PSF/CA) Blend Membrane

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## ABSTRACT

Blend polysulfone (PSF)/cellulose acetate (CA) membranes have prepared by phase inversion method. In here, CA was prepared from bacterial cellulose by acetylation reaction. Various temperature of coagulation bath were used as variable to investigated water uptake, water flux, porosity and thermal properties of membranes. As comparison, the CA commercial (CCA) was also investigated with the same parameters. As the result, the functional group analysis by FTIR show that CA has successfully prepared from bacterial cellulose. The parameters include water uptake, water flux and porosity have the similar trend. The parameters increase with increasing of temperature of coagulation bath. The other hand, CCA membrane have similar trend to CA membranes for parameter of water water uptake, water flux and porosity. However, CCA membrane is higher than CA membranes for all parameters. Thermal analysis by Differential Scanning (DSC) showed that all blend membranes with different temperature of coagulation bath have single transition glass temperature (Tg) that indicated that molecular homogeneity.

**Keywords:** blend membrane, phase inversion, coagulation bath, water flux, porosity.

## INTRODUCTION

One of important ultrafiltration (UF) membrane materials, Cellulose Acetate (CA) offers unique advantages of good hydrophilicity, antifouling property, abundance source, and biological degradation (Pang *et al.*, 2015). Despite these advantages, CA has weaknesses in thermal and chemical stability (Saljoughi *et al.*, 2010) and low mechanical properties (Ahmad *et al.*, 2015). Many studies have been undertaken to improve CA characters. For example, introduce polyethyleneglycol (PEG) to CA solution increasing pure water flux in filtration, and improve thermal/mechanical stability of membranes due to increasing Tg by restriction of CA rotation (Shivakumar *et al.*, 2006; Saljoughi *et al.*, 2010). Another research were comparing PEG with aliphatic hyperbranch polyester to CA, resulting higher thermal and mechanical properties, instead, lower water flux (Mahdavi *et al.*, 2015).

In most studies in polymer chemistry, UF membranes were performed by synthetic CA, which is less biodegradable and environmentally friendly (Shivakumar *et al.*, 2006; Saljoughi *et al*, 2010; Peng *et al*,

2010; Mansourizadeh and Asad, 2014; Mahdavi *et al*, 2015; Ahmad *et al.*, 2015). The development of renewable resource CA has been carried out, but it remains limited to several renewable resources, such as refined fibers, deinked newspapers, bacterial cellulose, and cellulosic waste (Fei *et al*, 2015; Nedjma *et al,* 2012; Radiman and Yuliani, 2008).

In this study, bacterial cellulose (BC) was naturally produced through the fermentation of coconut water using *Acetobacter xylinum.*BC was more easily acetylated due to high purity and no delignification process (Radiman and Yuliani, 2008). This study suggests that renewable resourcederived CA gives such benefits as environmental friendliness, sustainability, and relatively low cost.

Polysulfone (PSF) is a commercially available material possessing high toughness, thermal and mechanical stability, and is used universally for the fabrication of high-performance ultrafiltration (Liu, 2017),however,it is so highly hydrophobic that it is vulnerable to fouling. The improvement of PSF characters has been done in several way such as impregnating PSF with nanoparticles such as silver, $TiO_2$, $ZrO_2,$ $SiO_2$, (Zodrow *et al*,

2009 ; Richards *et al*, 2012) or blending it with hydrophilic polymers such as nanocellulose (Zhong *et al*, 2015) and cellulose acetate (Shivakumar *et al*, 2006).

Blend membrane has been a simple processing method for blending two or more polymers in order to obtain desire characters of membranes. Blend membranes can be prepared through the phase inversion technique (Shivakumar *et al*, 2006; Saljoughi *et al*, 2010; Peng *et al*, 2010; Mansourizadeh and Asad, 2014). Membrane solution wascast into glass plate and immersed in a coagulation bath, andthen solidification began. This wet phase inversion process wasinfluenced to membranes character by condition of post-treatment after solidification (Mansourizadeh and Asad, 2014), evaporation times (Holda *et al,* 2013), and coagulation bath temperature (Saljoughi *et al*, 2010; Peng *et al*, 2010).

In the presentstudy, blend membranes of PSF/CA were prepared through the thermal/wet phase inversion technique. Acetylated bacterial cellulose from coconut water was taken as a source of CA. PEG-400 was added to the system for the formation of pore (Shivakumar *et al*, 2006; Saljoughi *et al*, 2010).The effect of coagulation bath temperature on water uptake (%), water flux, pore character and thermal properties of membranes were also investigated.

## METHODS

### Materials
Sucrose (food grade sugar) and coconut water in this research were obtained from a traditional market.*Acetobacter xylinum*was obtained from Biology Laboratory of State University of Semarang, Indonesia. N-Methyl-2-Pyrrolidone (NMP), Polyethyleneglycol (PEG-400), Sulfuric Acid, Acetic Anhydride, and Glacial Acetic Acid were obtained from Merck. Commercial cellulose acetate and Polysulfone (PSF) (BM ~ 35.000) were obtained from Sigma Aldrich.

Synthesis of Bacterial Cellulose and Cellulose Acetate were take placed at Chemistry Laboratory of Tanjungpura University. Blend membranes PSF/CA and PSF/CCA were prepared and characterized at Chemistry Laboratory and CDAST Laboratory of University of Jember.

### Preparation of Bacterial Cellulose
Bacterial cellulose was prepared through the fermentation of coconut water by *Acetobacter xylinum*following Radiman and Yuliani (2008). Gels were pressed to reduce water and dried at 80 °C before an acetylation process began.

### Acetylation
The modification of bacterial cellulose was made through the acetylation process using acetic anhydride as aprecursor.Sulfuric acid was added in a small portion as a catalyst (Nedjma *et al*,2012; Fei *et al,* 2015). 5 grams of the bacterial cellulose was cut into small pieces and placed on three neck flasks. The glacial acetic acid with an amount of 100 mL was added to the system then stirred at 45°C for 2 hours. 16 mL of glacial acetic acid again and 0.2 mL of sulfuric acid were added to the system, stirred for an hour. The system had cooled into 18 °C. Acetic anhydride (27 mL) and sulfuric acid (0.3 mL) were added to the system and stirred at 60 °C for 6 hours. The mixture was filtered to separate undissolve part, and waterwas added to the brown solution to cease reaction. The final product was filtered and washed until neutral pH was obtained and then dried at 50 °C. Thedegree of subtitution was determined by acid base titration (Nedjma *et al*, 2012). Theacetylated bacterial cellulose was ready to use for the blend membranes.

### Functional Group Analysis by Fourier Transform Infra Red (FTIR)
The functional groups of bacterial cellulose, commerical cellulose acetate (Sigma Aldrich) and cellulose acetate from bacterial cellulosewere measured using FT-IR Bruker Alpha with RT-DLaTGS ZnSe detector. The spectra were recorded in $400 – 4000$ cm$^{-1}$.

### Preparation of Blend Membranes
Blend membranes were prepared by the themal/wet phase inversion technique at different coagulation bath temperature (CBT). PEG-400 and NMP were introduced as pore forming agent and solvent, respectively. Acetylated bacterial cellulose (CA) were used with a composition of blend membranes PSF/PEG/CA/NMP (%wt) were 17/5/5/73. The solution of the blend membranes was cast into glass plate and coagulated at 27 °C, 40 °C, and 60 °C. Then, the membranes were transferred into different fresh water to remove excess solvent. Commercial cellulose actetate was taken as a comparison of the blend membranes. Different coagulation bath temperatures were usedas a variable to study water uptake, water flux, and thermal properties of PSF/CA blend membranes.

### Determination of water uptake
Dried membranes were cut into small pieces,weighed, and defined as dry weight ($W_D$). Then, they were immersed into fresh water for 24 hours,weighed, and defined as wet weight ($W_w$). The percentage of water uptake was determined by (1).

$$w \qquad (\%) = \frac{W_w - W_D}{W_D} \qquad (1)$$

### Water Flux
Water flux wasexamined using the dead-end ultrafiltration cell with pressure at 150 kPa. The blend membranes were placed at the bottom of the

reactor with diameter 5,5 cm. Water flux was determined by pure water flux (J) (2), where V was defined as the volume of pure water passed through membranes (L); A was defined as membranes areas ($m^2$); and  t (h) was defined as sampling time for water passed through the membranes.

$$J = \frac{V}{A. \, \Delta t} \qquad (2)$$

**Membrane porosity and mean pore size**
Porosity (Ɛ) of membrane was determined by gravimetric method, using equation (3) (Golpour *et al.,*2017) .

$$\varepsilon(\%) = \frac{\omega_1 - \omega_2}{A.l.\rho_w} \qquad (3)$$

where, $_1$ and $_2$ were wet and dry membrane, respectively.  Surface area ($m^2$) of membrane was A, and thickness (m) of membrane was l.  Density of water ( $_w$) was 998 kg/$m^3$.

Mean pore radius ($r_m$) of membrane was determined using Guerout-Elford-Ferry equation (eq.4) (Golpour *et al.,*2017).

$$r_m = \sqrt{\frac{(2.9 - 1.7 \; \varepsilon) 8\eta}{A.\varepsilon.\Delta}} \qquad (4)$$

where, Ɛ, A and l obtained from porosity data,   is viscosity of water (8,9x$10^{-4}$ Pa s), Q is the volume permeated through membrane and   P is operating pressure (1,5 bar).

**Thermal Analysis**
The thermal behaviour of samples was carried out using Differential Scanning Calorimetry (DSC 8230, Rigaku) from 30 °C tp 350 °C with heating rate 5 °C/min.

## RESULT AND DISCUSSION

The synthesis of bacterial cellulose used coconut water as medium for*Acetobacter xylinum.* The bacterial cellulose acetate was synthesized by the modification of bacterial cellulose through the acetylation process.The blend membranes of  PSF/CA were produced by the phase inversion technique at different coagulation bath temperatures.

**FTIR analysis of Bacterial Cellulose**
The bacterial cellulose (BC) was obtained during anincubation time of 6 days period resulting cellulose pellicle with a thickness of 3-4 mm (Figure1A). To illustrate the structure of  BC, spectra FTIR is shown in Figure 1B.According to spectra in Figure1B, there were characteristic peaks of cellulose structure.

Peaks at 3352.97; 2922.06; 1425.80; 1159.47 and 1030.30 cm$^{-1}$ correspond to hydroxyl groups, C-H stretching, CH$_2$ bending, C-O-C stretching and C-O stretching in cellulose respectively.  This spectra result is similar to Halib *et al.*study (2012) (Table 1), confirming that bacterial cellulose was succesfully synthesized.
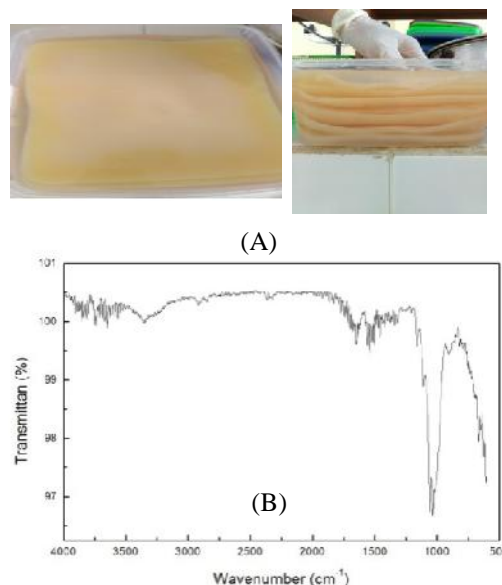


(A)



(B)

Figure 1. (A) Wet Bacterial Cellulose and (B) FTIR Spectra of Bacterial Cellulose

**FTIR analysis of cellulose acetate**
The bacterial cellulose (BC) had good purity thus, no further purification was needed before acetylation process. Physically, after the acetylation process, white powder was obtained. However, it turned to slightly brown after drying process. Figure2 shows cellulose acetate after the acetylation and drying process.
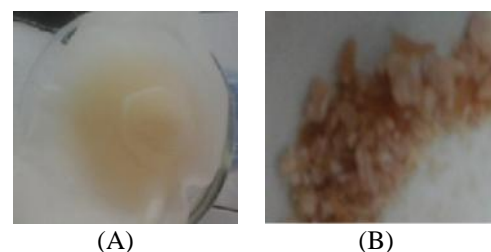


(A)                        (B)

Figure 2. Cellulose acetate, (A) after acetylation and (B) after drying.

Table 1. Infrared band assignment of cellulose materials

| Wavenumber (cm⁻¹) | | | | |
|---|---|---|---|---|
| Bacterial Cellulose (BC) (cm⁻¹) | Bacterial Cellulose* (cm⁻¹) | Cellulose Acetate (CA) (cm⁻¹) | Commercial Cellulose Acetate (CCA) (cm⁻¹) | Assignment |
| 3352.97 | 3440 | - | - | O-H Stretching |
| 2922.06 | 2926 | - | - | C-H Stretching |
| - | - | 1745.34 | 1745.40 | C=O Stretching |
| 1547.58 | - | 1540.88 | 1540.30 | Benzene ring vibrations |
| 1425.80 | 1440 | - | - | $CH_2$ Bending |
| - | 1300 | 1369,57 | 1370,35 | -C-$CH_3$ |
| - | - | 1231,10 | 1231,28 | C-O acetyl |
| 1159.47 | 1163 | - | - | C-O-C Stretching |
| 1030.30 | 1040 | 1044,31 | 1042,69 | C-O Stretching in cellulose |

Nedjma *et al* , 2012; Halib *et al*[*]., 2012; Radiman and Yuliani, 2008

To confirm cellulose acetate structure obtained, FTIR was used for functional groups analysis. FTIR spectra results are presented in Figure3.Both CA and CCA at 1745.34, 1369.57, and 1231.10 confirmed for the carboxylic groups (C=O) ;(-C-$CH_3$) and CO acetyl, respectively (Radiman and Yuliani, 2008). Table 1 shows infrared band of materials. Degree of subtitution of CA and CCA was found at 3,5 determined by acid base titration, indicating the product was cellulose triacetate.
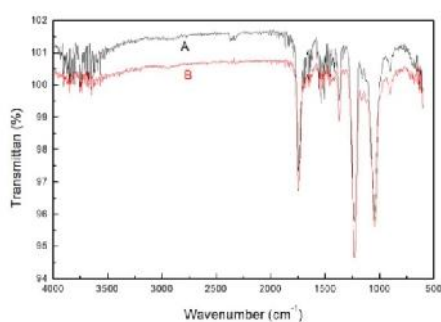


Figure 3. FTIR spectra of (A) the commercial cellulose acetate (CCA); (B) cellulose acetate from bacterial cellulose (CA)

As seen in Figure 3, there were characteristic peaksofCA structureshown in Table 1. This indicated that there was shifting peaks of bacterial cellulose (BC) to bacterial cellulose acetate (CA). Peak at 3352.97 (Figure 1B) was hydroxyl groups of cellulose, which disappeared in CA and CCA (Figure 3A and 3B).The characteristicsof celluloseacetate were confirmed by peak of carboxylic ester and acetyl group (Nedjma *et al*, 2012).

**Water Uptake,Water Flux and Porosity analysis of PSF/CA blend membranes**
Water uptake was used to analyze affinity to water of the blend membranes. As a hydrophobic polymer, polysulfone had very low affinity to water. Blending PSF with hydrophylic polymers like CA tends to lower hydrophobicity of PSF. Figure4 shows water uptake (%) of the membranes.
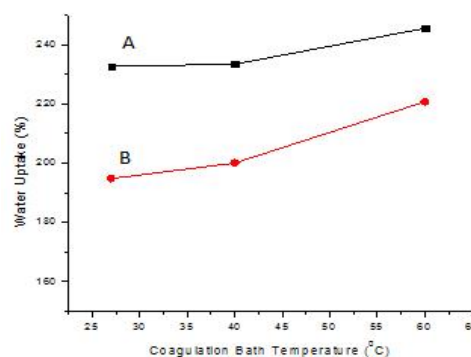


Figure 4. Water uptake (%) of the blend membranes, with (A) PSF/CCA and (B) PSF/CA

Cellulose acetate with its acetyl groups had high affinity to water.  Adding PEG-400 to the system influence pore formation of the membranes.  In the water uptake analysis, the hydrophilicity of the blend membranes greater than PSF membrane more than 10 times. Low interaction between water and PSF was possible due to high hydrophobicity of PSF. However, adding hydrophilic functional groups from CA increased interaction with water. This interaction occurred not only at the membrane surfaces, but also penetrated into pore, which formed PEG-400.The interaction water with hydrophilic functional groups in surface and pore was the major reason for high percentage water uptake of the blend membranes than PSF one.

The influence of coagulation bath temperature on water flux showed good agreement with %water uptake analysis. Figure5 indicates the changes of water flux to the coagulation bath temperature. Variation in coagulation bath temperature (CBT) showed an increase in both water uptake and water flux from room temperature (27 °C) to 60 °C.
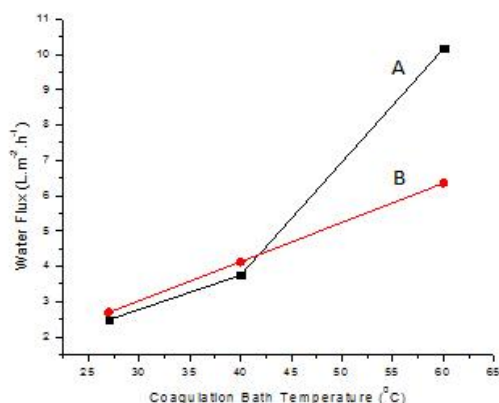


Figure 5**.** Water Flux of blend membranes,with (A)  PSF/CCA and (B) PSF/CA

CBT plays an important role in membrane formation. Room temperature (27 °C) created a normal condition for solvent-nonsolvent exchange. The hydrophilic-hydropobic interaction between CA-PSF and the presence of PEG enhanced the viscosity of dope solutions, thus introduce to delayed demixing

(Manawi, *et al.*, 2017), and produced denser skin layers, low porosity and lower water flux.

Rate of membrane formation affect the membrane structure. In demixing process, nuclei were growth and continue occure by solvent- non solvent exchange (Sanmugam*et al.,* 2017). The mobility of the solvent and non-solvent exchange was enhanced by increased temperature, leading to a more rapid precipitation and producing a thinner skin layer of the membranes (Peng *et al*, 2010). When casting solution immersed into coagulation bath with higher CBT,  the solvent move quickly out  and the non solvent enters into the polymer.  Nucleation occurs faster on the skin layer and retard the solvent in the sub layer to come out. It was prevent nucleation on sub layer (Farahani*et al.*, 2016). This phenomenon introduce the polymer to have macrovoids structure on sub layer.  Formation of macrovoids generally happens on quick precipitation process and precipitation is faster at higher temperature (Saljoughi*et al.*, 2010). For that reason, higher CBT produce thinner skin layer, more macrovoids, and higher porosity, thus increasing water flux.

Porosity of  PSF/CA was found smaller than PSF/CCA blend membranes, showed by Figure 6.  Mean pore radius was calculated  for the blend membrane, and show variation of pore radius from 50 nm to 180 nm with different CBT (Table 2).
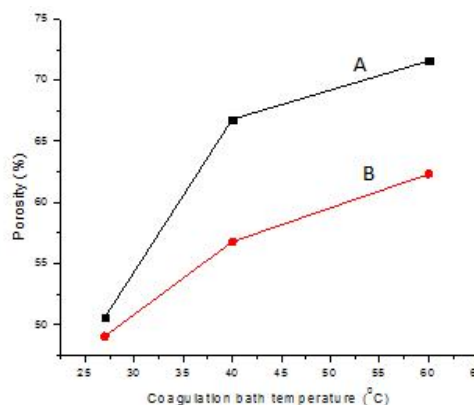


Figure 6. Porosity of  blend membranes, with (A) PSF/CCA and B)PSF/CA.

Table 2. Mean Pore Radius of Blend Membrane

| Temperature of Coagulation Bath (CBT) (°C) | Blend Membran PSF/CA (nm) | Blend Membran PSF/CCA (nm) |
|---|---|---|
| 27 | 71.6 | 46.6 |
| 40 | 99.2 | 92.3 |
| 60 | 101.1 | 119.4 |

*Thermal Properties*

Table 3. Transition Glass (Tg) and Melting Temperature (Tm) of  Blend Membrane

| Membranes* | Tg (°C) | Tm (°C) |
|---|---|---|
| PSF/CCA 27 °C | 137 | 219 |
| PSF/CA 27°C | 175 | 231 |
| PSF/CA 40°C | 195 | 264 |
| PSF/CA 60°C | 194 | 278 |

*with different CBT

The analysis of the themal properties of blend membranes using Differential Scanning Calorimetry gave information on blending properties and flexibility of the membranes. Single transition glass temperature (Tg) was found.  This showed that the blending of the membranes were homogenous.An increase in Tg indicated that the flexibility of membranes decreased.  It contributed to aggregation and contraction of polymer chains during the formation of the blend membranes in the coagulation bath (Saljoughi *et al*, 2010). Rapid movement of water as non solvent due to higher temperature and low miscibility between water and polymers in blend membran resulted in restriction in rotation molecules, thus increasing Tg.  Table 3 show Tg and Tm data of the membranes.  On another hand, the melting point (Tm) of the membranes showed a good agreement with water uptake and water flux.

**CONCLUSION**

Blend membranes PSF/CA that come from bacterial cellulose have been successfully prepared. The different CBT lead to the different properties of blends membrane, include water uptake, water flux and porosity. With increase temperature in coagulation bath increased water uptake, water flux and porosity. Compare with membrane PSF/CCA, the blend membranes PSF/CA have lower in water uptake, water flux and porosity for all CBT.  However, blend membrane based CA from bacterial cellulose have similar properties with membrane based CA from commercial one (CCA). Thermal analysis showed single transition glass temperature indicating homogeneity of the PSF/CA blend membrane.Hence, controlling in CBT would help to membranes structure formation.

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