Blending Polymer Cellulose Acetate/Polysulfone For Resistance of Protein Fouling

Dwi Indarti*, Dana Iswara Putra, Bambang Piluharto, D. Setyawan

Dept. Chemistry, Faculty of Mathematics and Natural Sciences, University of Jember.
Jl. Kalimantan 37, Jember 68121

*Corresponding author: indartidwi.fmipa@unej.ac.id

Abstract. Blending polymer CA/PSf was prepared using N,N-dimethylacetamide (DMAc) as solvent and PEG400 as an additive in membrane fabrication. The phase inversion method using immersion precipitation process was carried out to make the membrane CA/PSf. Membrane CA/PSf characterized by measuring the contact angle of the membrane to determine the membrane hydrophilicity. Performance of membrane is measured using water flux and rejection of dextran 70 kDa and Bovine Serum Albumin (BSA) 67 kDa. The contact angle of the membrane CA/PSf which amounted to 50° until 63°, so it can be categorized as hydrophilic membranes, because the value of the contact angle is lower than 90°. The resulting water flux membranes CA/PSf from 3.8708 L.m⁻².h⁻¹ to 10.462 L.m⁻².h⁻¹. Dextran rejection generated which is equal from 40.24% to 89.53%, while the BSA rejection of membrane from 36.21% to 81.68%. Increasing the composition of PSf produces contact angle and water flux increased, but the rejection of dextran and BSA decreased. Resilience fouling membranes CA/PSf is measured by Relative water Flux Reduction (RFR) and Fouling Resistance. RFR membranes CA/PSf which amounted from 9.445% to 32.75%, while the membrane fouling resistant CA/PSf ranged from 0.6725 to 0.9055. RFR is higher when the amount of PSf increased and indicating that their membranes are prone to fouling, it also can be evidenced by the decreased value of resistance fouling when the composition of PSf increase.

1. Introduction

Cellulose acetate membrane (CA) is a hydrophilic membrane has fouling resistant but has low mechanical properties. Polysulfone membrane (PSf) is a hydrophobic membrane that has good mechanical properties but not resistant to fouling [1]. Polymer molecular weight affects the mechanical strength of the membrane. The CA in this study has a molecular weight of 30 kDa, while PSf has a molecular weight of 35 kDa, so the mechanical strength of the PSf is stronger than that of CA. The low mechanical properties of CA membranes and fouling problems on PSf membranes can be improved by blending the two polymers in the manufacture of membranes. Performed variations of CA/PSf polymer variations 95: 5, 90:10, 85:15, 80:20 and 75:25 [2]. The CA/PSf polymer blend membrane has salt rejection of 7.54% to 20.75% and 3.98% for CA membrane salt rejection without blending with PSf. CA/PSf blending polymer can increase membrane rejection value compared to membrane without blending process. The CA/PSf membrane in the [2] study, has a salt flux of 7.69 L.m⁻².h⁻¹ to 9.93 L.m⁻².h⁻¹. Salt flux increases when the CA polymer composition decreases, because the membrane pore size increases when the CA composition decreases, so that the salt flux will increases.

CA/PSf polymer blend membrane added polyethylene glycol (PEG) additive which functions as a pore forming agent on the membrane. The [3] study stated that CA / NMP membranes without PEG
produced 29.5 L.m\(^{-2}\).h\(^{-1}\) water flux and Human Serum Albumin (HSA) rejection of 87%. The addition of PEG400 was 5% and 10% resulting in water flux of 164.4 L.m\(^{-2}\).h\(^{-1}\) and 252 L.m\(^{-2}\).h\(^{-1}\) and BSA rejection of 70% and 45%. The CA/PSf blending polymer in this study aims to produce membranes with good mechanical properties and resistant to membrane fouling.

Fouling is the deposition of a dissolved particle on the membrane surface or membrane pores caused by the interaction of dissolved particles with membranes. Membrane fouling phenomenon is generally very easy to occur on hydrophobic membranes. [4] stated that PSf / PEG / DMAc membranes had a fouling resistance value of Bovine Serum Albumin (BSA) of 0.825. The fouling resistance value is <1 which indicates fouling on the membrane. Membrane fouling is also influenced by the hydrophilicity properties of membranes. Hydrophilicity of membranes can be seen from the value of membrane contact angle. Membranes with low hydrophilicity will be susceptible to membrane fouling.

The method for improving fouling was done by [5], namely by blending polymers in the manufacture of membranes. Blending polymer PES / CA / PVP which has Fouling Degree (FD) and Flux Attenuation (FA) values of 21% and 30%, while FD and FA values on PES membranes without blending with CA are 38 % and 49% [5]. High FD and FA values can indicate that the membrane is susceptible to fouling. Based on the research, blending polymer CA / PES on membranes is more resistant to fouling than PES membranes without the blending process with CA.

2. Methods

2.1. Materials
Polysulfone p.a. 35 kDa, cellulose acetate (39.9 wt%, MW 30 kDa), N,N-dimethyl acetamide (DMAc) = 0.98 g / mL, NaH\(_2\)PO\(_4\).2H\(_2\)O (pa), BSA 67 kDa, and dextran 70 kDa were purchase from sigma aldrich. Phenol p.a, sulfuric acid, Comasie Brilliant Blue (CBB), ethanol 95%, 85% phosphoric acid were purchase from merck, poly(ethylene glycol) 400 (PEG400) was obtain from Brataco Chemika, aluminum foil, filter paper, electric tape and distilled water.

Membranes preparation using phase inversion techniques. Content of polymers and solvents used is 25% and 75%, respectively. The polymer solution was prepared according to Table 1. The CA/PSf polymer mixture was dissolved in a solvent until homogeneous, then PEG400 was added as much as 5% and stirred the mixture until homogeneous.

| Composition | \(w_{\text{CA}}\) (gram) | \(w_{\text{PSF}}\) (gram) | \(V_{\text{DMAc}}\) (mL) | \(V_{\text{PEG}}\) (mL) |
|-------------|------------------|-----------------|-----------------|-----------------|
| 95/5        | 2.85             | 0.15            | 9.18            | 0.53            |
| 90/10       | 2.7              | 0.3             | 9.18            | 0.53            |
| 85/15       | 2.55             | 0.45            | 9.18            | 0.53            |
| 80/20       | 2.4              | 0.6             | 9.18            | 0.53            |
| 75/25       | 2.25             | 0.75            | 9.18            | 0.53            |

Casting solution (dope solution) is left until no air bubbles in the membrane. The dope solution is poured into a glass plate membrane mold which has been given tape on the edge of the glass plate to adjust the thickness of the membrane. Next, a glass plate that immersed into a coagulation tub containing distilled water, so that a membrane will form.

2.2. Hydrophilicity and morphology of membranes
The hydrophilicity test of CA/PSf polymer blend membrane with various variations can be determined by the contact angle of membrane. A meter contact angle with the help of image J. software was used...
to measure the membrane contact angle. Membrane morphology was observed from cross-section SEM (Scanning Electron Microscopy).

2.3. Flux Test
The membrane was cut in a circle according to the diameter of the ultrafiltration dead-end device. Membrane compaction was carried out before water flux testing. Compaction was carried out by inserting approximately 50 mL of distilled water into the filtration cell and tightly closed then given a pressure of 2 bars. Distilled water that pass through the membrane every mL are noted the flow time needed to obtain a constant flux. Volume flux is determined by the equation:

\[ J_v = \frac{V}{A \times t} \]  

(1)

2.4. Rejection Coefficient
The effectiveness of the membrane can be known from the membrane rejection coefficient. Membrane rejection was measured using 70 kDa dextran solution and 67 kDa BSA at 2 bar pressure. The dextran concentrations in the retentate and permeate sections were obtained through visible spectrophotometer analysis using H\(_2\)SO\(_4\) reagents and 5% phenol, while the BSA concentrations were analyzed using the Bradford method. Rejection was determined using the equation (2) which \( C_p \) is permeate concentration, and \( C_f \) is feed concentration):

\[ R = \left( 1 - \frac{C_p}{C_f} \right) \times 100\% \]  

(2)

2.5. Fouling Test
Fouling test of ultrafiltration was carried out by measuring water flux before and after filtration using BSA solution. A foulant solution and 50 mL BSA solution were put into an ultrafiltration tool set and then BSA was filtrated for one hour. Membrane that has been filtered with BSA soaked and rinsed using distilled water and then wiped the surface of the membrane using a tissue, then measured water flux in the same way using three times repetition. Membrane fouling was determined by measuring the value of water flux before and after filtration using BSA to calculate the RFR (Relative water Flux Reduction) and fouling resistance with the equation (3) and (4) [7]. \( J_{am} \) is flux before adsorption and \( J_{ads} \) is flux after adsorption.

\[ RFR = \frac{J_{am} - J_{ads}}{J_{am}} \times 100\% \]  

(3)

\[ Fouling \ Resistance = \frac{J_{ads}}{J_{am}} \]  

(4)

3. Result and Discussion
The membrane in this study was made by mixing polymer cellulose acetate (CA) with a polysulfone (PSf) called a blending polymer. CA/PSf polymer blend membrane was made using a phase inversion technique, where the polymer which is soluble in its solvent will experience a change from liquid phase to solid through controlled conditions.
Figure 1 shows a series of processes for making CA/PSf membranes starting from the process of making dope solution (Figure 1a). CA has physical properties in the form of white powder, whereas PSf has physical properties in the form of yellowish crystals. The resulting dope solution is then printed on a glass plate followed by an immersion precipitation process in a coagulation bath (figure 1b). Polymers must dissolve in the solvent so that the liquid-liquid de-mixing process can occur. De-mixing is the initial compaction process in membrane formation due to the exchange of solvents and non-solvents on the membrane in a coagulation bath resulting in a white membrane matrix (Figure 1c) [6].

| CA/PSf Variation | Picture | Color | Thickness (mm) |
|------------------|---------|-------|----------------|
| 95/5             | White   | 0.051± 0.000577 |
| 90/10            | White   | 0.060± 0.000577 |
| 85/15            | White   | 0.065 ± 0.00116 |
| 80/20            | White   | 0.070± 0.000577 |
| 75/25            | White   | 0.078 ± 0.00116 |

Table 2 shows that the CA/PSf membrane has physical properties in the form of white solids but has different thicknesses. The difference in membrane thickness in various CA/PSf compositions in a polymer blend solution can be explained by the mechanism of membrane formation. The membrane in the coagulation bath undergoes a liquid-liquid de-mixing process that is influenced by the composition of the CA/PSf in a polymer blend solution, so that when the solution is put in the coagulation bath, it causes phase separation. In this case, the process of exchanging solvents with non-solvents namely DMAc and water (non-solvent). The speed of solvent diffusion to non-solvents affects the formation of
the top layer of the membrane. The amount increasing of PSf produces a layer of top layer on a thicker membrane. The thicker top layer causes the membrane thickness to increase.

3.1. Effect of CA/PSf composition on the contact angle (θ) and morphology of the membrane

Contact angle is an angle formed between the surface of the membrane and water droplets on the membrane. Contact angle measurements can be used to determine the hydrophilicity of the membrane. The contact angle value <90° indicates that the membrane is hydrophilic, while the contact angle > 90° indicates that the membrane is hydrophobic [8]. The effect of the composition of the CA and PSf polymers on the membrane contact angle can be seen in Table 3.

| CA/PSf Variation | Contact Angle |
|------------------|--------------|
| 95/5             | 50°          |
| 90/10            | 52°          |
| 85/15            | 59°          |
| 80/20            | 61°          |
| 75/25            | 63°          |

Table 3 shows membranes with different CA and PSf compositions will produce different membrane contact angle values. As shown in Table 3, the more the number of PSf in the composition of CA/PSf, the greater the value of contact angle membrane. The greater the contact angle of the membrane is due to the increasing number of hydrophobic polymers (PSf). The contact angle produced on the membrane shows the effect of wettability which is the result of interaction between the membrane solids and water. The more hydrophilic the membrane, the smaller the contact angle. Increased PSf causes interactions between the membrane solids with small water, so that the wettability effect on the membrane will be small and produce a high contact angle.

The membrane contact angle can be used as a reference in determining membrane hydrophilicity. Table 3 shows membranes with variations in the composition of CA/PSf have different hydrophilicity properties. The membrane hydrophilicity is inversely proportional to the membrane contact angle. A small membrane contact angle value indicates that the membrane has high hydrophilicity properties, whereas membranes with large contact angles indicate that membrane hydrophilicity properties are low. The more the amount of PSf, the lower the hydrophilicity of the membrane, because it has a high membrane contact angle value. That is caused by the increasing number of hydrophobic polymers (PSf), so that it has a high contact angle value.

The amount increasing of PSf in addition to increasing the contact angle or hydrophilicity can also increases the membrane pore. The morphology of the membrane cross section shows the same pore shape of the three variations, namely finger like (Figure 2). Besides the larger pore size of the membrane and the shape of the finger-like pore, an increase amount of PSf causes a decrease in the uniformity of the supporting layer.
3.2. Effect of CA/PSf on water flux

Flux is the volume of feed solution that passes through the membrane per unit area of membrane and per unit time. Membranes with high flux values indicate that the membrane has good performance, conversely if the membrane has a low flux, the membrane has a poor performance. The determination of membrane flux is carried out after the membrane has compacted. At the time of compacting, the membrane flux decreases until a certain time the flux becomes constant. The membrane that has been compacted will produce membrane pores in the geometry and size that remain during the filtration process at a certain pressure. Membrane compaction was done using distilled water at 2 bar pressure.

Figure 3 shows that the more polysulfone, the shorter the compacting time. According to research by [2], the greater the amount of cellulose acetate in the membrane in the composition of CA/PSf, the smaller pores will be produced. The small pore size in the membrane makes it harder for water molecules to pass through the membrane. Water molecules that are difficult to pass through the membrane cause the rearrangement of the pore in the membrane to be longer, thus increasing the compacting time. However, when the amount of Polysulfone increases, the pore size of the membrane increases, so that water molecules will easily pass through the membrane which will reduce membrane compacting time.
Figure 3. Membrane compacting time.

Figure 4. Effect of CA/PSf on Water Flux.

Figure 4 shows that the water flux increases with the amount increasing of Polysulfone in CA/PSf. This shows that at the same time, variations in the composition of CA/PSf affect the water flux. Water flux is affected by pore size and membrane porosity where flux will increase with the increasing of the pore size or porosity of the membrane. High water flux indicates that the greater the amount of Polysulfone, the larger the pore size of the membrane.

The pore size of the membrane will affect the flux. The increasing number of polysulfone in CA/PSf polymer blending is likely to result in larger pore sizes marked by the high-water flux produced due to the CA/PSf polymer blending. Each polymer has different solubility parameters in DMAc. The difference in solubility parameter ($\Delta \delta$) CA with DMAc is 2.14 while PSf is 0.63, so that DMAc will further dissolve PSf because it has a small $\Delta \delta$. The different solubility parameters cause the polymer dissolution process is less than perfect. CA and PSf will experience interactions during the dissolution process with DMAc. The interaction between CA and PSf produces a large aggregate. The larger polymer aggregate produces a larger membrane pore. The more the amount of PSf in the composition of CA/PSf, the more PSf can interact with CA, resulting in the formation of large polymer aggregates that are also more numerous, causing the membrane pores produced to be larger.

3.3. Effect of CA/PSf on Membrane Rejection

Membrane rejection ($R$) is one of the parameters to express the selectivity of a membrane. Rejection is a measurement of membrane selectivity for passing or holding a molecule [6]. $R$ values range from
100% (when the solute in the feed solution can be held completely) and 0% (when the solute can pass completely through the membrane). Determination of rejection was done using 70 kDa dextran and 67 kDa BSA concentrating 1000 ppm at 2 bar pressure. Rejection was influenced by permeate concentration and the concentration of feed solution. The concentration of permeate and feed solution in this study were measured using a visible spectrophotometer.

Figure 5. CA/PSf membrane rejection.

Figure 5 shows the increasing amount of Polysulfone in the composition of CA/PSf produces low rejection. Rejection of the polymer blend CA/PSf membrane is higher when the amount of Polysulfone is smaller. High rejection caused by a small membrane of pore size. Smaller pore size can hold more solutes (dextran and BSA), so particles of the solute are difficult to pass through the membrane which causes high membrane rejection. The greater amount of Polysulfone can produce a larger pore size. Larger membrane pore sizes can easily pass dissolved particles in the bait. The greater amount of solute that passes through the membrane results in lower membrane rejection.

Membrane rejection and water flux have an inverse relationship, where the larger rejection membranes, the smaller water fluxes. Rejection and flux are strongly influenced by the pore size of the membrane. Membranes with large pore sizes have small rejection and high flux values, whereas membranes with small pore sizes have high rejection and low flux [9]. Large membrane pore size will easily pass the feed particles to pass through the membrane, so that membrane rejection becomes small and membrane permeability will increases.

3.4. Resistant Fouling Membrane Polymer Blend CA/PSf

The fouling resistance of the CA/PSf polymer blend membrane can be measured based on the fouling and RFR resistance values of the membrane. Fouling resistance and RFR (relative water flux reduction) are indicators for evaluating membrane performance. RFR is the amount of reduction of water flux in the membrane that has undergone fouling with BSA. RFR can also be used to evaluate fouling resistance of membranes. A large RFR value indicates that a decrease in the value of water flux is getting bigger. A membrane with a small RFR value indicates that the membrane has good fouling resistance, whereas a membrane with a high RFR value indicates a lower membrane fouling resistance. A membrane with a fouling resistance value equal to or greater than 1 indicates that the membrane is resistant to fouling [7].
This research tested fouling resistance on membranes that had been carried out with protein filtration namely BSA 67 kDa.

![Figure 6. RFR and Fouling Resistance.](image)

Figure 6 shows the effect of variations in the composition of CA/PSf on membrane fouling resistance based on RFR values and fouling resistance. As shown in Figure 5, the higher the amount of Polysulfone in the composition of the CA/PSf, the RFR value also increases. The increased RFR value indicates that the membrane has experienced a large decrease in flux after being filtered with BSA. Membrane that has been filtered with BSA is carried out on soaking process in distilled water, so that the protein fouling on the membrane surface can be minimized. However, after measuring the water flux, the flux membrane has decreased. A decrease in flux indicates that the membrane fouled inside the pores of the membrane. Fouling that occurs in the CA/PSf polymer blend membrane happened because the membrane contains Polysulfone material, which is hydrophobic, so that the possibility for fouling of the membrane can occur. Polysulfone is a hydrophobic material, the material can adsorb protein strongly, so that during the filtration process there will be a large decrease in flux. Hydrophobic interactions between proteins and membrane surfaces can cause irreversible fouling, which can reduce the efficiency of the filtration process [8]. The decrease in water flux is caused by fouling of the membrane, so that the membrane pores are covered by feed particles, which are proteins that cause water difficult to pass through the membrane, so the flux decreases. As the amount of Polysulfone in the composition of CA/PSf increases, the RFR value also increases. An increase in RFR value indicates a membrane with a large amount of Polysulfone is more susceptible to fouling.

The fouling resistance of the membrane can also be seen from the value of the fouling resistance. Membranes with high fouling resistance values indicate that the membrane is more resistant to fouling and vice versa. As the amount of Polysulfone increases, the fouling resistance value decreases. This shows that membranes with more polysulfone are more prone to fouling, which can be measured by the high RFR value and low resistance value of membrane fouling. The membrane fouling resistance is also influenced by the membrane hydrophilicity which is determined based on the membrane contact angle values. Membranes with high hydrophilicity properties will be more resistant to fouling compared to membranes that have low hydrophilicity properties. The amount of polysulfone produces a high membrane contact angle, so that the membrane's hydrophilicity decreases causing susceptibility to be fouling as evidenced by the low resistance value of membrane fouling.

4. Conclusion
The results of the study showed the contact angle of the membrane increases with increasing number of PSf in the composition of CA/PSf, so that the hydrophilicity of the membrane is lower. The value of water flux and membrane rejection is influenced by the composition of CA/PSf in the membrane. The
amount of PSf increases resulting in a greater value of water flux and rejection (dextran 70 kDa and BSA 67 kDa) getting smaller and vice versa. Increasing the amount of PSf in the membrane results in high RFR and low fouling resistance, making it vulnerable to fouling and vice versa. Membrane that is resistant to fouling has a low RFR value and high fouling resistance.

Reference

[1] Cheryan M 1998 *Ultrafiltration and Microfiltration Handbook* 2nd edition (United States America: CRC Press)
[2] Munirah N, Mazira M A, Ramlah T M and Sharifah A 2014 *Trans Tech Publications* 594-595 281- 5.
[3] Saljoughi E. Amirilargini M and Mohammadi T 2010. *Desalination*. 262 72-8.
[4] Karlina. 2014. *Karakterisasi Fouling Protein Pada Membran Polisulfon Tersulfonasi (SPSf)*. (Jember: Universitas Jember)
[5] Sun Z and Chen F 2016. *Int. J. Biological Macromolecules*. 13 21-7.
[6] Mulder M 1996 *Basic Prinsiple of Membran Technology*. 2nd edition (Dordrecht: Kluwer Academic Publisher)
[7] Susanto H, Balakhirshnan M and Ulbricht M 2006. *J. Membrane Sci* 288 157-67.
[8] Yuan Y and Lee T R 2015 *Surface Science Technology* (USA: University of Houston)
[9] Velu S, Muruganandam L and Arthanareeswaran G 2015 *Brazilian J. Chem. Eng*. 32 179-89.