Mixing Solvent’s Effect to the Characterization and Performance Cellulose Acetate/Polyethylene Glycol Membrane

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Abstract. The need for clean water continues to increase. Therefore, it is necessary to find an alternative for the get of clean water. One way is desalination process using membrane. Cellulose Acetate/Polyethylene Glycol (CA / PEG) membrane is one type of membrane that can be used for desalination process. Several studies on the manufacture of CA / PEG membranes have been performed, but have not yet produced a good performance membrane. Therefore in this research was synthesize CA/PEG/ mixing solvent membrane using Acetone – THF/ Acetone – DMF as the solvents at ratio 100-0, 90-10, 70-30, 50-50 (%volume) each and PEG as the additive vary PEG 200 and 400. CA/PEG/ mixing solvent membrane characteristics are tested. The results showed that the hydrophilicity of mixing solvent method using Acetone-DMF (50:50) increase water content up to 375.86% and Acetone-THF (50:50)’s water content increase up to 177.10% with additive PEG 200 and 400. CA/PEG/ mixing solvent membrane characteristics are tested. The results showed that the hydrophilicity of mixing solvent method using Acetone-DMF (50:50) increase water content up to 375.86% and Acetone-THF (50:50)’s water content increase up to 177.10% with additive PEG 200 and 400. CA/PEG/ mixing solvent membrane characteristics are tested. The results showed that the hydrophilicity of mixing solvent method using Acetone-DMF (50:50) increase water content up to 375.86% and Acetone-THF (50:50)’s water content increase up to 177.10% with additive PEG 200 and 400.

1. Introduction

On the earth surface consist of 2/3 sea water and 1/3 land. All water resources in the world not consumeable, just 3 % are consumeable and 97 % not consumeable such as seawater, 3 % of it consist of 2 % in glacier form and 1 % use for potable water. UNESCO at world water development report state that water in the world are used for household need, industrial need and agricultural, from All of this fact it can conclude that potable water resource for human life so crucial. Water needed in 2050 was increase till 55 %, from this prediction will be human motivation for develop and researching water purification technology and fulfill human need for fresh water [1].

One factor caused water not consumeable is total dissolve solid value exceed the limit of consumeable water. One of technology that develop for separate water from impurities as salt was membrane desalination method. Along with the different polymeric materials that are used for the preparation of phase-inversion membranes. Membranes have gained an important consign in chemical technology and have been used in a wide range of applications, such as the production of high-quality water, removal or recovery of toxic or valuable components from various industrial effluents, and applications in the food and pharmaceutical industries. With the advent of membrane technology,
separation, concentration, and purification have become industrially viable unit operations because of the high efficiency of separation, low energy of operation, simplicity of operation with modern compact modules [1].

Cellulose acetate (CA) is very widespread, with characteristics such as good toughness, high biocompatibility, good desalting, high potential flux, and relatively low cost. Thus, it has been widely used for reverse osmosis, microfiltration, and gas separation. Also, CA membranes have excellent hydrophilicity, which is very essential in the minimization of fouling [2].

2. Materials and Methods

2.1. Material

The materials used in this experiment was Cellulose acetate (CA, $M_w$ of 30,000 Da) polymers were purchased from Sigma Aldrich. The three solvents, namely, Tetrahydrofuran (THF) and acetone (both with an analytical purity of 99%); N, N-Dimethyl formamide (DMF) with 99.5% purity; polyethylene glycol 400 were all obtained from Sigma Aldrich. The coagulation bath used throughout this experiment was DI water purchased in Chemical Store klampis. NaCl with $M_w$ of 58.5 from Sigma Aldrich.

2.2. Membrane preparation

Different concentrations of CA/PEG/Acetone: THF and CA/PEG/Acetone: DMF solutions with constant ratio of CA/PEG 200 (20% wt / 80% wt) and with constant ratio of CA/PEG 200 (20% wt / 80% wt) were prepared. The compositions of all prepared membranes have been presented in Table 1.

All the membranes were prepared by the casting solution technique and the phase inversion method. For preparation of membranes, at first, homogenous solutions were prepared in Acetone: THF with different ratios (100:0, 90:10, 70:30 and 50:50) by stirrer at 3000 rpm for 12 h. The obtained homogeneous solutions were casted onto glass plates by using glass stick with constant thickness of 200 microns. Then, prepared casting films were dipped into deionized water as non-solvent for 15 minutes. In this step exchanging of solvent and non-solvent leads to membrane formation. After completing phase separation step and finishing membrane formation, the membranes were kept in two paper sheets at room temperature (25±2°C) for one day to remove water in the membrane. The preparation of the membrane adopted from [3].

| Membrane with additive | Solvent (%v : %v) | Membrane with additive | Solvent (%v : %v) |
|------------------------|-------------------|------------------------|-------------------|
| PEG 200                |                   | PEG 400                |                   |
| M1                     | Acetone (100)     | M8                     | Acetone (100)     |
| M2                     | Acetone : DMF (90 : 10) | M9                 | Acetone : DMF (90 : 10) |
| M3                     | Acetone : DMF (70 : 30) | M10                | Acetone : DMF (70 : 30) |
| M4                     | Acetone : DMF (50 : 50) | M11                | Acetone : DMF (50 : 50) |
| M5                     | Acetone : THF (90 : 10) | M12               | Acetone : THF (90 : 10) |
| M6                     | Acetone : THF (70 : 30) | M13               | Acetone : THF (70 : 30) |
| M7                     | Acetone : THF (50 : 50) | M14               | Acetone : THF (50 : 50) |
2.3. Water content
Water content of the membranes was obtained after soaking membranes in water for 24 h and the membranes were weighed followed by mopping it with blotting paper. The wet membranes were placed in oven at 75 °C for 48 h and the dry weights of the membranes were determined [3]. The percent of water content (WC) was calculated using the equation:

\[ \text{water content} = \left( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100\% \]  

(1)

The term “water content” is water that can be filling in void volume of the membrane.

2.4. Scanning electron microscopy (SEM)
Membrane were snapped under liquid nitrogen using pinset to give a generally consistent and clean cut. The membranes were then sputter-coated with thin film of gold. The membranes were mounted on brass plates with double-carbon tape in a lateral position. Cross-sectional images of the membranes were obtained. SEM analysis measured by Bruker EDS made in Germany.

2.5. Fourier Transform Infrared (FTIR)
In order to know OH bonding in the various membrane with different concentration of mixing solvent and PEG as additive, FTIR spectra of all of the sample was obtained by spectrophotometer. Range for Fourier Transform Infrared test was 0 cm\(^{-1}\) until 4000 cm\(^{-1}\). The type of bonding observed in this experiment was OH bonding stretching mode, in peak between 3600 cm\(^{-1}\) till 3800 cm\(^{-1}\), peak area measured by ImageJ.

3. Results and Discussion

3.1. Scanning electron microscopy (SEM)
Miscibility or solubility parameter between solvent and nonsolvent is one of the most important parameters in membrane formation. If miscibility between solvent and non-solvent is high (difference of solubility parameter between solvent and non-solvent is low), the non-solvent is more able to diffuse in casting film and in this case, solvent leaves casting solution faster. Slower diffusion rate lead to membrane finger-like formation [4] Therefore exchanging of solvent and non-solvent in coagulation bath happens faster and consequently, instantaneous demixing happens [3]. This leads to formation of porous fracture surface. The values of solubility parameters (in this paper it define with RHSP value) of acetone/THF mixture and acetone/DMF mixture with different ratio of acetone : THF and acetone : DMF as mixing solvents and water as non-solvent have been shown in Table 2 and Table 3. SEM image of cross sectional area in Figure 1 shows that CA/PEG membrane with different mixing solvent ratio exhibits finger-like structure with different pore size.

| Component | δp (disperse) | δh (hydrogen) | δp (polar) | Ref  |
|-----------|---------------|---------------|------------|------|
| THF       | 5.45          | 8             | 6.1        | [3]  |
| Acetone   | 15.5          | 7             | 10.4       | [3]  |
| DMF       | 17.4          | 11.3          | 13.7       | [6]  |
| Cellulose | 7.9           | 3.5           | 6.3        | [6]  |
| Water     | 15.6          | 16            | 42.3       | [6]  |

The value of RHSP s-p will decrease as THF in mixing solvent ratio increase, this lead to more better interaction as THF ratio increase in the solvent, then it made longer phase separation process.
value can make this prediction because this calculation related to cohesive energy density of energy that required for electron movement from functional group of polymer to solvent [5]. The effect of DMF was opposite as DMF ratio increase RHSP (S-W) ratio was increased, this result lead to solvent diffuse more easily in water in coagulant bath, then it lead to incrase of membrane porosity. For membrane CA/PEG 200 mixing solvent acetone : THF and acetone : DMF with ratio of 70 : 30 has the same symmetric membrane morphology, it can be due to very fast phase inversion caused by very thin membrane thickness.

**Table 3. RHSP (s-p) and RHSP (s-w) of mixing solvent**

| Membrane   | RHSP (s-w) | RHSP (p-s) | Ref. |
|------------|------------|------------|------|
| M1, M8     | 34.4       | 12.7       | [6]  |
| M2, M9     | 32.7       | 16.6       | [6]  |
| M3, M10    | 31.8       | 17.7       | [6]  |
| M4, M11    | 31.06      | 18.9       | [6]  |
| M5, M12    | 33.6       | 14.1       | [6]  |
| M6, M13    | 34.8       | 10.3       | [6]  |
| M7, M14    | 36.5       | 6.8        | [6]  |

**Figure 1.** SEM Cross sectional image of membrane
3.2. Water content
The Water Content is related to the membrane hydrophilicity property. Water content of each membrane is calculated using Eq. (1). As Table 4 shows, Water Content for membrane by using pure acetone is equal to 113.18 %, whereas it for the membrane with solvent ratio acetone : DMF (50 : 50) is equal to 375.86 %. It is obvious that water content is increased by increasing the weight percent of DMF amount in Ratio solvent, it is due to increasing finger – like pore size of membrane, as DMF solvent ratio increase. This result can increase porosity of membrane, the caused is phase inversion between bimodal and spinodal curve and result regular pore in membrane selection [7]. The result of membrane with PEG 400 additive has the same pattern as membrane with PEG 200 additive. But membrane with PEG 400 as additive has more porous than membrane that use PEG 200 as additive its due to PEG 400 has more glycol content than PEG 200 glycol can be use for cutter the chain C-C in cellulose [8].

Table 4. Showed The Water Content Value of Mixing Solvent Membrane

| Membrane with additive PEG 200 | Water content (%) | Membrane with additive PEG 400 | Water content (%) |
|--------------------------------|-------------------|--------------------------------|-------------------|
| M1                             | 113.1             | M8                             | 198.7             |
| M2                             | 142.8             | M9                             | 190.6             |
| M3                             | 269.4             | M10                            | 380.6             |
| M4                             | 375.8             | M11                            | 468.6             |
| M5                             | 75.34             | M12                            | 173.2             |
| M6                             | 90.3              | M13                            | 162.5             |
| M7                             | 177.1             | M14                            | 119.2             |

3.3. FTIR
FTIR result shows the increasing of –OH group with the addition of THF and DMF up to 30 % volume for membrane with PEG 400 as additive and the increasing of it contents as shown by the increasing of area in the wavenumber of 3300 cm⁻¹ as shown in the Figure 2 and Figure 3. The increasing of –OH group up to 30% volume and decrease at 50 % volume of DMF as well as THF due to . This result shows that hydroxyl group increases up to the addition of THF and DMF content up to 30% volume solvent. The increasing of hydroxyl group in addition is caused by auto-oxidation of THF in the air [9], this reaction can lead to enrichment of O-H bonding in membrane and for DMF, the functional group in DMF have possibility in forming hydrogen bond with another DMF ring. And O-H in different chain in Cellulose acetate. Figure 2 show the result of FTIR test. The trend of hydroxyl grup in mixing solvent between THF : Acetone has similar result both PEG 200 and PEG 400 as additive. But for PEG 400 the increment not as wide as PEG 400, this can be due to formation of new hydrogen bonds between O–H groups of CA and the C=O groups of PEG [6], this can make PEG 400 has better interaction than PEG 200. The most abundant amount of hydroxyl grup in PEG 200 addition was membrane with 30 % volume, this is due to formation of hydroxyl group in THF vapour phase with oxygen. The values of OH area of FTIR image are shown in Table 5. The product contain superoxide, and have free radical properties. In final solution, the product has condense and reacted in free branch of cellulose acetate [9].

Table 5. The OH Area Value of Mixing Solvent Membrane

| Membrane with additive PEG 200 | OH Area (cm²) | Membrane with additive PEG 400 | OH Area (cm²) |
|--------------------------------|--------------|--------------------------------|--------------|
| M1                             | 1.46         | M8                             | 1.86         |
| M2                             | 1.66         | M9                             | 1.45         |
| M3  | 1.29 | M10 | 1.37 |
|-----|------|-----|------|
| M4  | 1.67 | M11 | 1.23 |
| M5  | 1.32 | M12 | 1.50 |
| M6  | 2.02 | M13 | 1.85 |
| M7  | 1.32 | M14 | 1.25 |

**Figure 2**. FTiR graph for CA/PEG200/Acetone : DMF and Acetone : THF

**Figure 3**. FTiR graph for CA/PEG400/Acetone : DMF and Acetone : THF

**4. Conclusion**
In this paper, CA nanofiltration membrane with low concentration of polymer (20% v: 80% v solvent) was prepared with pure acetone and different ratios of Acetone : THF and acetone : DMF as mixing
solvents (90:10, 70:30 and 50:50) to investigate the effect of addition of THF with low micibility to non-solvent (deionized water as coagulation bath). The results of experiments confirm that addition of THF to casting solution leads to decreasing of water content and porosity of the membrane due to decreasing of RHSP (p-s) and lead to increasing phase separation time of casting film in coagulation bath. The optimum ratio of Acetone :THF was found to be 50:50 for additive PEG 200 and 90 : 10 for PEG 400 in terms of water content. Then optimum ratio of Acetone :DMF was found to be 50:50 for both additive PEG 200 and 400 in terms of water content. For optimum hydroxyl group based FTiR The optimum ratio of Acetone :THF was found to be 70:30, Acetone : DMF 50:50 for additive PEG 200 and Acetone : DMF 50 : 50 and Acetone : THF 70 :30 for PEG 400

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