Preparation of Polypropylene/PVDF Composite Membrane by Dip-Coating Method

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Abstract. In this research, a composite membrane was prepared by dipping a hollow fiber polypropylene (PP) membrane in a polyvinylidene fluoride (PVDF) solution. A small concentration of volatile solvent (acetone and tetrahydrofuran/THF) was added to the PVDF solution to form a tight structure in the membrane surface. The influence of PVDF concentration, type of volatile solvents (acetone and THF), and the dip-coating cycle on membrane characteristics, including porosity, swelling degree, and contact angle, were investigated. The flux and rejection of the membranes were also investigated during the filtration of hexane/oil solution. The experimental results showed that low membrane porosity (3%), low swelling degree (0.1%), and high water contact angle (140°) were obtained when 8%wt PVDF was blended with 10%wt acetone and then coated on PP hollow fiber membrane surface with 3 (three) dip-coating cycles. The oil rejection was 68% after 45 minutes of filtration time with a permeate flux of 20 L.m⁻².h⁻¹. Higher membrane porosity and permeate flux can be obtained by reducing the dip-coating cycle; however, a lower oil rejection was achieved.

1. Introduction
Polypropylene (PP) has increasingly been used as membrane material since it shows excellent chemical resistance and thermal stability, and low cost [1-3]. Most commercial PP membranes are hollow fiber and have been widely used in several separation processes, including water treatment, gas separation, water-oil separation, vegetable oil membrane filtration, and other applications [4-7]. The PP membranes are generally fabricated by melt-spinning and stretching method, which forms microporous structures under controlled operating temperature [8]. Since the PP membranes are microporous, characterized by their pore size from 0.1 to 10 µm, the PP membranes have low selectivity to the soluble compounds. Therefore, modifications on the PP membrane surface have increasingly been carried out. This condition improves the selectivity and hydrophobicity or hydrophilicity, subject to the membrane application [9, 10].

There are two standard surface modification methods to improve membrane selectivity, namely interfacial polymerization (or crosslinking) [11] and physical coating methods [12]. The polymerization reaction occurs at two immiscible solvents’ interface, which contains reactive monomers and initiators/catalysts [13, 14]. Heat treatment is often used in this technique to complete the polymerization or crosslinking of the monomers on the porous membrane support [15]. This method is generally used to manufacture reverse osmosis (RO) and nanofiltration (NF) membrane. Compared to the chemically modified membrane, the physical coating is relatively more comfortable.
to be applied in large scale production with no complicated operating condition [16]. Dip-coating is one of the physical coating methods by immersing the dried PP membrane in a homogenous polymer solution for a few seconds and then lifting it vertically at a constant speed. A thin film membrane was formed on the substrate surface due to solvent evaporation from the polymer solution to the atmosphere [17].

Although it is considered a simple method for modifying PP membranes, few publications focus on the dip-coating method. Himma et al. [18] used the dip-coating method to alter the hollow fiber PP membrane surface. The dried hollow fiber PP was first immersed in a non-solvent solution (water), and then followed by immersing the membrane in the PP solution. A high hydrophobic PP membrane was obtained with a contact angle of 149°. When it was used for oil/water separation with a ratio of 1:9 v/v, the rejection of water and volatile matter were 64.35 and 67.15%, respectively. The membrane hydrophobicity was improved to 151.3° by using methyl ethyl ketone (MEK) as a non-solvent instead of water [16]. Wenten et al. [12] coated polysulfone(PSf)/PEG400/ZnO layer on the hollow fiber PP membrane surface and then used it for peat water treatment. ZnO’s presence enhanced the membrane’s hydrophilicity, which reduced organic compounds’ fouling tendency during the peat water treatment. The modified membrane removed 70% of humic substances from peat water.

In this research, the hollow fiber PP membranes were also modified by the dip-coating method. The dried hollow fiber membrane was immersed in PVDF solution and then lifted vertically at a constant speed. The influence of PVDF concentration, type of volatile solvent, and dip-coating cycle on the composite PP/PVDF membrane characteristics was investigated. The flux and rejection of the composite membrane were determined during the hexane/oil separation process.

2. Material and Methods

2.1. Materials

Polypropylene hollow fiber was supplied by GDP Filter, Indonesia, which had an inside diameter (ID) of 0.2 mm and an outside diameter (OD) of 0.4 mm. The PVDF was supplied by a local supplier (PT. KGC Saintifik) with a purity of 99.5% and a molecular weight of 600,000 Da. Meanwhile, the NN-dimethylacetamide (DMAC) was supplied by Shanghai Jingsan Jingwei Chemical CO., Ltd, with a purity of 99.0%. The tetrahydrofuran (THF, ≥99.9%) was provided by Sigma Aldrich, while a local supplier supplied the acetone. The palm oil and hexane were provided by local suppliers and then mixed with a ratio of 1:9 (v/v).

2.2. Dip-coating of hollow fiber PP membrane

The PVDF solution was prepared by blending polymer in DMAC at room temperature until the solution was homogenous. The PVDF concentration was varied from 0 – 8% by weight. A dip coater was used to immerse the PP hollow fiber membrane in PVDF solution vertically. The PP membrane was immersed for 10 seconds and then lifted at a constant speed of 15 mm.s\(^{-1}\). The coated PP membrane was dried at room temperature for 24 hours until all solvent was evaporated. The schematic dip-coating process of the hollow fiber PP membrane is shown in Figure 1.

![Figure 1. Dip-coating process of hollow fiber PP membrane in PVDF solution.](image-url)
2.3. Determination of porosity and swelling degree of the composite PP/PVDF membrane.

The porosity of the composite PP/PVDF membrane was determined by weighing dry and wet membrane. Distilled water was flowed through the dried membrane pore using a centrifugal pump for a few minutes until all membrane pore was filled with water. The wetted membrane was drained off until there is no water on the membrane surface and then weighed. The composite membrane porosity ($\varepsilon$) was determined by the following equation:

$$\text{Porosity} = \frac{(W_w - W_d)}{(V \times \rho_w)}$$

(1)

where $W_d$ is the weight of dry membrane (g), $W_w$ is the weight of wet membrane (g), $V$ is the volume of composite hollow fiber membrane (cm$^3$), and $\rho_w$ is the density of water (0.99708 g/cm$^3$).

The membrane’s swelling degree was determined by immersing the membrane in a solvent (hexane) for 48 hours. The wet membrane was wiped to remove water on the membrane surface and then weighed. The effect of hexane on the membrane swelling degree was calculated using the following equation.

$$\text{Swelling degree} \% = \left[ \frac{(W_w - W_d)}{W_w} \right] \times 100\%$$

(2)

2.4. Determination of contact angle of the composite membrane

The water contact angle on the composite membrane surface was measured using a digital microscope (Genesys Logic Microscope 1600xUSB). A micro-syringe was used to drop and place the water droplets on the membrane surface. The contact angles were measured from a digital image of the water droplet using a graphic software (Corel Draw) program. The contact angle measurement was conducted 3 (three) times at different locations to minimize experimental errors.

2.5. Flux and oil rejection of the composite PP/PVDF membrane

The experimental set-up for the filtration of hexane/oil solution is presented in Figure 2. The hollow fiber membrane was placed in a U-shape hollow fiber membrane module and operated under dead-end mode (inside-out flow) at different operating pressure (2 and 4 bars). The permeate flux was determined by measuring the volume of permeate produced per time and membrane area, as described in the following equation.

$$J = \frac{V}{A \times t}$$

(3)

Where $J$ is the permeate flux (L.m$^{-2}$.h$^{-1}$), $V$ is the permeate volume (L), $A$ is the surface membrane area (m$^2$), and $t$ is filtration time (h).

Meanwhile, oil rejection (R, %) was calculated by the following equation:

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

(4)

$C_p$ is the concentration of oil in the feed solution, and $C_f$ is the concentration of oil in permeate solution.
3. Result and Discussion

3.1. The influence of operating parameters on the composite membrane characteristics

Figure 3 shows the influence of PVDF concentrations, solvent types, and dip-coating cycles on the composite membrane porosities. The experimental results showed that the increase of PVDF concentration reduced membrane porosity. It has been known that the concentration of polymer is related to the intrinsic viscosity of the polymer solution. The higher density of the polymer solution inhibited the membrane pore’s growth, and consequently, it reduced the pore size formed in the membrane structure (Figure 3a). Besides, the increase of polymer concentration reduced the void fraction in the membrane structure [19]. The composite membrane’s porosity was significantly decreased when 8%wt PVDF was used in the coating solution with three dip-coating cycles. Figure 3b shows that the addition of volatile solvent as an additive improves the composite membrane’s porosity (Figure 3b). The presence of a volatile solvent reduced the polymer and solvent’s miscibility. It contributed to phase separation phenomena in the membrane solution and led to the pore nuclei formation in the membrane structure [20]. Besides dip-coating cycles and polymer concentration, the membrane porosity was also influenced by the volatile solvent type (Figure 3c). It has been reported that the acetone was more volatile than THF. The delayed phase separation in THF/DMAc/PVDF solution allowed the pore nuclei to form and grow in the membrane structure. Therefore, the membrane porosity that used THF as an additive was higher than acetone. The highest membrane porosity (25%) was achieved when 4%wt PVDF was blended with 10%wt THF with 2 (two) times of dip-coating process. Meanwhile the lowest membrane porosity (3%) was resulted when 8%wt PVDF was blended with 10%wt acetone.
The influence of dip-coating cycles on composite membrane porosity at different concentrations of PVDF: (a) with acetone, (b) at various concentrations of PVDF in THF, and (c) at different types of solvents.

The influence of operating parameters on the swelling degree of the composite PP/PVDF membrane is shown in Figure 4. Swelling of the membrane structure is attributed to the solvent’s penetration into the polymer network and leads to the polymer volume change [21]. A high concentration of solvent in membrane structure allowed the solvent to penetrate rapidly into the polymer chain. Therefore, the composite membrane with high porosity was susceptible to swelling by hexane. Otherwise, the increase of polymer concentration and dip-coating cycle reduced the swelling degree of the composite membrane. The low concentration of solvent in the membrane structure minimized the solvent’s possibility to penetrate the polymer chain. Due to the low porosity of the resulting membrane, the composite membranes that used acetone as an additive resulted in a lower swelling degree than THF.

Figure 4. The influence of dip-coating cycle on the swelling degree of the composite membrane in hexane: (a) at various PVDF concentration and (b) at the different solvent type

3.2. The influence of PVDF concentration and solvent type the composite membrane hydrophobicity

Figure 5 presents the influence of the dip-coating cycle and polymer concentration on water contact angle. The water contact angle indicates the hydrophilicity or hydrophobicity of the membrane [12]. It shows that the composite PVDF/PP membranes had a higher water contact angle than the unmodified PP membrane. A high-water contact angle between 109 and 140° was achieved by blending 4%wt PVDF and 10%wt THF in the coating solution. Meanwhile, the coating solution that used acetone as an additive produced a contact angle 121°. When the coating solution was prepared without volatile solvent as an additive, the resulted membrane had a contact angle between 102 and 106°. It was
suggested that the higher contact angle was attributed to the increased surface roughness of the membrane [16].

![Figure 5](image_url)

**Figure 5.** The influence of dip-coating cycle and solvent type on the water contact angle of the membrane

### 3.3. The influence of dip-coating cycle on permeate flux and oil rejection during the filtration of hexane/oil solution

The permeate flux the resulted composite membrane were presented in Figure 6 and 7. The experiments were conducted at two operating pressures, i.e., 2 and 4 bars. The coating polymer was prepared by blending 8%wt PVDF and 10%wt acetone. When the composite membrane was prepared by three times dip-coating cycle, the permeate flux was 20 L.m$^{-2}$.h$^{-1}$. Higher permeate flux was obtained when the dip-coating process was reduced. It has been explained that the low concentration of polymer resulted in higher membrane porosity, and as a result, the volume of permeate that passes through the membrane became larger (Figure 6a). The increase of volume fraction in the membrane structure reduced the intrinsic resistance of the membrane, and thus, the solution can more easily pass through the membrane to the permeate side. Also, the increase of operating pressure enhanced the permeate flux (Figure 6b).

![Figure 6](image_url)

**Figure 6.** Profile permeate flux during hexane/oil filtration at constant operating pressure: (a) 2 bars and (b) 4 bars
The oil rejection of the resulted composite membranes is shown in Figure 7. The figure showed high rejection of oil when the PP membrane was prepared by three times coating process. A high concentration of polymer resulted in lower membrane porosity. Therefore, the rejection of solute (oil) was improved. Higher rejection of oil was obtained when the operating pressure was raised to 4 bars. Around 50% of oil rejection was achieved when 8% PVDF and 10% acetone were blended and coated on the PP membrane with three times of the dip-coating process. The increase in operating time enhanced the oil rejection. It was attributed to the fouling formation of the membrane surface, which reduced the membrane surface layer’s sufficient pore size.

Consequently, it improved the oil rejection. Around 68% oil rejection has resulted after 45 minutes of hexane/oil filtration at an operating pressure of 4 bars. Compact fouling on the membrane surface due to a high concentration of solutes at high working pressure increased the oil rejection.

![Figure 7](image1.png)

**Figure 7.** Oil rejection during hexane/oil filtration at constant operating pressure: (a) 2 bars and (b) 4 bars

4. **Conclusion**

A composite membrane has been prepared by dipping a hollow fiber polypropylene (PP) membrane in a polyvinylidene fluoride (PVDF) solution. Two types of volatile solvents (acetone and tetrahydrofuran/THF) are added to the PVDF solution to form a tight structure in the membrane surface. The influence of PVDF concentration, type of volatile solvents (acetone and THF), and the dip-coating cycle on membrane characteristics, including porosity, swelling degree, and contact angle, are investigated. The flux and rejection of the membranes are determined during the filtration of hexane/oil solution. The increase of PVDF concentration and dip-coating cycle reduces the composite PP/PVDF membrane’s porosity and swelling degree. The lowest membrane porosity (3%) was achieved by blending 8%wt PVDF and 10%wt acetone in the coating solution and dipping the PP membrane 3 (three) times into the coating solution. The resulted membrane has a porosity of 3%, swelling degree of 0.1%, and permeate flux of 20 L.m$^{-2}$.h$^{-1}$. The oil rejection is 50% at the earlier of the filtration process and then increases to 68% after 45 minutes of hexane/oil filtration. Higher membrane porosity and permeate flux are obtained by reducing the dip-coating cycle. However, lower oil rejection has resulted.

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