Effects of PVDF concentration on the properties of PVDF membranes

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Abstract. Polyvinylidene fluoride (PVDF) is a good polymeric material for preparing ultrafiltration and microfiltration membranes due to its high mechanical properties and chemical resistance. The objective of this work is to study the effects of PVDF concentration on the membrane properties such as mechanical strength, permeability of water and permselectivity of T-500 and T-2000 dextran solutions. These membranes were also characterized by contact angle determination and its morphology was observed by scanning electron microscopy (SEM). From the experimental data, it can be concluded that PVDF concentration affects the surface properties, permeability and permselectivity of the produced membranes. Higher PVDF concentrations results in higher hydrophobicity, mechanical properties and rejection towards T-500 and T-2000 dextrans, but lower water flux.

1. Introduction
Membrane technology has been applied for ultrafiltration (UF) and microfiltration (MF) since several decades, especially for separation process and water treatment [1-5]. Many researchers are still developing various polymeric membranes in order to improve the filtration performances and efficiency. Polyvinylidene fluoride (PVDF) is considered as a promising polymer for UF and MF applications due to its high mechanical properties and chemical resistance [6, 7].

The characteristics of PVDF membranes are affected by various factors such as preparation method, composition of polymer, solvent and additive, porogene and coagulation bath [8-10]. UF and MF membranes are usually prepared by phase inversion method which is quite simple and yields asymmetric membranes with appropriate pore dimension. The addition of additives and porogene influence the diffusion rate of solvent and non-solvent during the phase inversion [11]. Polar additives results in coarser membrane surface, while the additions of porogene in pore dimension [12, 13]. Membrane composition and coagulant temperature affect the resulting membrane structure. The addition of electrolyte or polar organic compound such as glycerol results in membranes having longer microvoid structures, while low temperature coagulant yields faster polymer crystallization [14, 15]. Other researchers found that the use of alcohols in the coagulation bath produced membranes with higher hydrophobicity [16].

In this work, PVDF membranes have been prepared by phase inversion, in which the concentration of polymer was varied. The objective of this work is to study the effects of PVDF concentration on the
membrane properties such as mechanical strength, permeability of water and permselectivity of T-500 and T-2000 dextran solutions. These membranes were also characterized by contact angle determination and its morphology was observed by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

PVDF powder (Solef® 1015, Solvay), polyethylene glycol (PEG)-400 (Merck), dimethylacetamide – DMAc (99%, Merck), H₂SO₄ (96%, Merck), phenol (99%, Merck), dextran T-500 (M₀ 500 kDa) and T-2000 (M₀ 2000 kDa) (Pharmacosmos) were used without further purification.

2.2. Membrane preparation

A mixture of PVDF and PEG 400 was put in DMAc and stirred at 60 °C until the polymer was completely dissolved and formed a dope. The concentration of PVDF used was 15, 17, 19 and 21% w/w and the PEG was kept constant at 5% w/w. The dope was cast on a glass plate and directly put in a water coagulant. The resulting membrane was then separated from the plate and washed in running water for several hours in order to remove the residual solvent. The membranes were then kept in glycerin before being characterized.

2.3. Membrane characterization

The contact angle was measured by droplet method using Tantec Contact Angle Meter. The solid membrane was cut according to the dimension of the sample holder and a droplet of water was put on it. The angle was recorded and the data was taken at different points randomly. The morphology of the membranes was observed by using SEM JEOL JSM-6360LA. The PVDF membranes were gold coated and the photos of membrane surfaces and cross-sections were taken using 2000 and 10,000 magnification. The mechanical properties of the membranes, taken as the force at break and elongation at break, were measured by using Tensolab mechanical tester. Membranes of 3 × 50 mm were cut according to ASTM D 3822-07. The data was taken for 5 to 6 samples and the average value was calculated.

2.4. Water flux and rejection towards dextran solutions

Both water flux and rejection were determined using a dead-end cell. The PVDF membranes were cut according to cell dimension and put at the bottom of it which has a diameter of 5 cm. The cell was filled with demineralized water and the applied pressure was 1 bar. Prior to measurements, all membranes were compacted for 30 minutes and the volume of the permeate was measured afterwards. Equation (1) was used for calculating the water flux.

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

where \( J \) is the water flux (L.m⁻².h⁻¹), \( V \) is the permeate volume (L), \( A \) is the membrane area (m²) and \( t \) is the filtration time (h).

For the measurement of rejection of T-500 and T-2000 dextran solutions with a concentration of 1000 ppm, the feed was changed accordingly. The compaction was again done for 30 minutes and at the end of filtration process, the samples of both permeate and retentate were taken for quantitative analysis. Into those samples, a few mL of phenol was added and the concentration of dextran was measured at 490 nm using Spectronic-20. The percentage of rejection toward dextran was calculated by equation (2)

\[ R = \left(1 - \frac{C_p}{C_R}\right) \times 100 \]
where $R$ is the rejection percentage, $C_p$ is the concentration of dextran in the permeate (M) and $C_R$ is the concentration of dextran in the retentate (M).

3. Results and discussion

3.1. Properties of PVDF membrane surfaces

One of the important factors determining the membrane performance is its surface properties. The polarity of membrane surface affects the interaction between membrane and components of the feed solution [17]. In this work the properties of membrane surfaces were measured as the contact angles of the membranes with water. Table 1 shows the data of contact angle of the produced PVDF membranes. It shows that higher PVDF concentration resulted in higher contact angle between membrane and water; indicating that the membranes became more hydrophobic. The 15% PVDF membranes has the lowest hydrophobicity indicated by its lowest contact angle (64°), while the 21% PVDF membrane has the highest one. It can be explained by the fact that PVDF has an intrinsic hydrophobic nature and hence, higher PVDF concentration resulted in lower interaction between membrane and water. This trend is in accordance with previous research [18].

| PVDF (%w/w) | Contact angle (°) |
|-------------|------------------|
| 15          | 64               |
| 17          | 70               |
| 19          | 72               |
| 21          | 78               |

3.2. Mechanical properties of PVDF membranes

Membrane mechanical properties determine the endurance of membranes toward the applied pressure used during its applications. The effects of PVDF membrane composition on its mechanical properties were shown at Table 2. In general, it can be concluded that higher PVDF concentration resulted in higher tensile strength and strain as well. PVDF membranes show an elastic behaviour indicated by the high value of strain which in certain composition reached more than 100%. This was also reported previously by other researchers [10, 19]. Table 2 shows that 15% PVDF has the lowest stress and strain values compared to other compositions, while the 19% PVDF has the highest strain (148%). Membrane elasticity is a good indication of long membrane life-time, since it can avoid membrane fracture during filtration processes [11].

| PVDF (%) | Stress (MPa) | Strain (%) |
|----------|--------------|------------|
| 15       | 5.73 ± 2     | 64.6 ± 21  |
| 17       | 6.83 ± 1     | 104.6 ± 12 |
| 19       | 8.29 ± 1     | 148.8 ± 6  |
| 21       | 9.08 ± 1     | 91.1 ± 41  |

3.3. Membrane permeability and permselectivity

Membrane permeability and permselectivity were determined by water flux and rejection towards T-500 and T-2000 dextran solutions. Figure 1 shows the effects of PVDF concentration on water flux and dextran rejections. It can be seen that the water flux increased with PVDF concentration. The highest water flux was shown by 15% PVDF while the lowest was reached by 21% PVDF.
membrane. Regarding the contact angle data, the 15 % PVDF membrane shows the highest polarity which explains why it has strong interactions with water and increases the water flux. This fact proves that membrane permeability and permselectivity are influenced by membrane surface and pore properties [20, 21]. Besides that, the permeability is also affected by the density of membrane pores, which the denser membrane, the smaller water fluxes [22, 23]. Figure 1 also shows that dopes with higher PVDF concentration produce denser membranes.

Membrane selectivity was measured by the rejection of dextran molecules which have a definite molecular size. Figure 1 shows that increasing PVDF concentration produced higher rejection towards dextran. The rejection of T-2000 dextran is higher than the T-500 one, because the dimension of T-2000 molecules are higher than the T-500s. As mentioned previously in the discussion of membrane permeability, membrane rejection is also influenced by surface properties as well as pore dimension [24]. The rejection data shows that the rejection percentage of the produced membranes are in the range of 50 and 85 % which means that some solutes still pass across the membranes. Since the polarity of dextran is much higher than the PVDF, one can expect that the interactions among dextran molecules and membrane surface are not optimal. Therefore, the separation of dextran molecules are predominantly determined by the membrane pores. Consequently, membranes with higher PVDF concentration have denser pores which are able to produce a better separation of dextran molecules.

![Figure 1. Effects of PVDF concentration on water flux and dextran rejections](image)

3.4. Membrane morphology

Figure 2 and 3 show the morphology of the surface and cross-sections of two types of PVDF membranes, respectively. In general it can be seen that the morphological difference between 15 % and 17 % PVDF membranes are not significant. However, the pore dimensions of the membrane surface are different; 55 to 110 nm on the 15 % PVDF membrane but the pores of the 17 % PVDF membrane could not be measured. The addition of PEG into the dope plays a role of pore former. Dopes with low PVDF have higher ratio of PEG to total polymer concentration and hence, more pores are formed. Figure 2 also shows that membranes with high PVDF concentration result in denser membranes having lower permeability but higher permselectivity.

Figure 3 reveals that all membranes are asymmetric where the pores are smaller on the top of the membrane and became gradually larger at the bottom of the membrane. Figure 3b shows that the membrane has spongy microvoid pores and finger-like macrovoids. This observation is in accordance
with the results reported by Lai et al. [10]. This structure was formed during the phase inversion where the PEG and solvent diffused into the non-solvent [25]. The PVDF crystallization occurred very fast during the coagulation process and was especially enhanced by the large temperature difference between the dope (60 °C) and coagulation bath (~22 °C). The dense microvoid structure plays an important role in the separation process of the feed solution. However, compared to the dimension of dextran molecules, some membrane pores are large enough to allow the dextran molecules to pass across the membranes.

Figure 2. SEM photos of surfaces of membranes with (a) 15% and (b) 17% PVDF concentration

Figure 3. SEM photos of cross-sections of membranes with (a) 15% and (b) 17% PVDF concentration

4. Conclusions
PVDF membranes with various PVDF concentrations have been successfully prepared by phase inversion method. From the experimental data, it can be concluded that the PVDF concentration in the dope affects the surface properties, permeability and permselectivity of the produced membranes. Higher PVDF concentrations results in higher hydrophobicity, mechanical properties and rejection towards T-500 and T-2000 dextrans, but lower water flux.

Acknowledgements
The authors thanks the LPPM of Institut Teknologi Bandung for the financial support given through the Research Program, A category, 2016.
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