Preparation and characterization of PVDF/alkali-treated PVDF blend membranes

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Abstract. Poly(vinylidene fluoride) (PVDF) powder was treated with aqueous sodium hydroxide to obtain partially defluorinated fluoropolymers with expected properties such as improved hydrophilicity and fouling resistance (used as membrane material). The effects of concentration of aqueous sodium hydroxide were investigated. The results showed that the membrane’s hydrophilicity increased with increase of the fraction of alkaline treated PVDF powder. The fouling potential also decreased with the increase of the fraction of alkaline treated PVDF powder.

Introduction

PVDF is one of the most widely used fluoropolymer due to its excellent mechanical/chemical properties. However, the hydrophobic property of PVDF limits its application in some fields, especially in the field of water treatment. Because the hydrophobic interactions between membrane and the particulates contained in feed water easily cause membrane fouling [1]. To improve hydrophilicity, various investigations have been carried out. Examples are plasma treatment [2], blending PVDF with hydrophilic polymers [3-5], chemical functionalization [6], and radiation induced surface grafting [7, 8].

In this study, we proposed a method that directly degrades PVDF powder with aqueous sodium hydroxide. The degradation reaction was carried out in temperature controlled conditions with adjustable stirring speed. The degradation products are expected to consist mainly of non-thoroughly degraded PVDF powder, few polar based (OH based, carbonyl based etc.,) compounds and carbon-rich compounds. These newly formed materials blended with virgin PVDF are cast to form a membrane via the phase inverse process. The effects of blending ratio on characteristics of membranes were expressed via contact angle, water uptake, mechanical properties, porosity, TGA. The permeation performance in term of pure water flux, protein rejection, fouling potential and cleaning efficiency was also investigated. The major concern in this study is to examine the process of the alkaline treatment of PVDF powder and further improve membrane hydrophilicity via blending with the PVDF powder after alkaline treatment.

Experiment

Materials

The PVDF (Solvey 6013/1001 Mw ca. 2.2×105gmol-1) powder was used in this study. NaOH, Ethyl acetate, Bovine serum albumin (BSA) and N,N-dimethylacetamide (DMAc) are extra pure grade.

Alkaline Treatment

NaOH pellets were dissolved in deionized (DI) water to prepare different aqueous solution concentrations (2 M, 7 M, and 12 M). The temperature was set to 100°C. PVDF powder were added in the NaOH solution for 2 hours treatment and then the samples were filtrated through glass microfiber filters to separate solid and liquid phases. The solid particles were rinsed with 50 ml DI water thrice and dried at 100°C for 2h in air.

Preparation of PVDF/Alkaline Treated PVDF Blend Membrane

The membranes were prepared by the phase inversion method. A casting polymer solution (80°C) composed of 15 wt.% polymer (at various fractions of PVDF/alkaline treated PVDF powder. For convenience, we termed the fraction of alkaline treated PVDF powder in blend as X in the following
context.), and 85 wt.% DMAc was cast on a glass plate to form a flat membrane by immersing in de-ionized (DI) water. The membranes were classified as type I, type II, and type III based on the added alkaline treated PVDF powder, which were obtained at three different treatment conditions (Table 1).

Table 1 Preparation of membranes with different alkaline treatment conditions and blend ratio X.

<table>
<thead>
<tr>
<th>X</th>
<th>Type I (Treated with 2 M NaOH)</th>
<th>Type II (Treated with 7 M NaOH)</th>
<th>Type III (Treated with 12 M NaOH)</th>
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<tr>
<td>10</td>
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All mechanical tests were performed using the Universal Testing Machine (UTM LF Plus, Lloyd), equipped with a 1 kN load cell. The test was conducted using a cross-head speed of 10 mm/min. Thermal degradation of the membranes was measured using TGA (TG/DSC 92) by heating the samples from 60 °C to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Membrane mean pore size distribution was measured using a Capillary Flow Porometer (Porous Materials Inc., Model CFP-1200AE). Static contact angles of the membrane surface were measured using the sessile drop method. The water uptake was measured using the method suggested by Baroña et al. [6]. A dead-end magnetically stirred cell (Amicon Co., Ltd., Type 8050) with a 43 mm diameter and volume of 50 mL was used to measure the membrane performances. The effective membrane area (A) was 13.85 cm². To evaluate the fouling potential, a filtration protocol suggested by Zhang et al. [1] was used in this study.

Results and Discussion

Mechanical Property
Tensile strength and elongation at break of the three types of membranes were shown in Fig. 1 and Fig. 2. Tensile strength slightly decreased with the increase of the X. Elongation degree sharply decreased from 270% for pure PVDF membrane to 90% for pure alkaline treated PVDF membrane. This indicates that the high content of the treated PVDF might result in raising the brittleness of materials. In comparison, type III membranes exhibited worse mechanical properties than type I and type II membranes. This is believed to be due to effects of different concentrations of alkaline treatment conditions. Higher concentration led to more thorough defluorination of PVDF.

Thermal Gravimetric Analysis
As shown in Fig. 3, the initial decomposition temperatures of all three kinds of membranes remained unchanged. This result exhibited that the blend of alkaline treated PVDF did not change membrane thermal stability.

Fig. 1. Tensile stress of three types of membrane with different X.

Fig. 2. Elongation of three types of membrane with different X.

Fig. 3. TGA curves of membranes: pure PVDF, A30, A100, B30, B100, C30, and C100.

Pore Size Distribution
Membrane pore size and pore size distribution (PSD) were reflected by bubble point pore diameter (maximum pore diameter), mean flow pore diameter, and diameter at maximal PSD. Fig. 4 showed that the mean flow pore diameter and diameter at maximal PSD did not change with the contents of
alkaline treated PVDF. No considerable differences were observed in three types of membranes. Although the bubble point pore diameter showed big fluctuation, which may be due to the individual difference of the tested membrane samples. As results, a conclusion might be drawn that the addition of alkaline treated PVDF did not affect membrane pore structures.

![Fig. 4. Variations of bubble point pore diameter (A), mean flow pore diameter (B), and diameter at maximal PSD (C) of three types of membranes with different X.](image)

**Contact Angle**

Fig. 5 shows the values of contact angle of three types of membranes. For pure PVDF membrane, the surface is highly hydrophobic, has a contact angle of 92°. The contact angle decreased with increasing alkaline treated PVDF contents. From the figure, type I and type II membranes illustrated similar behaviors, and type III membranes showed lower contact angle values. It declined considerably to 68° when the membrane was made from the pure alkaline treated PVDF powder. These results confirmed that blending with alkaline treated PVDF can improve membrane hydrophilicity.

![Fig. 5. The contact angle of three types of membranes with different X.](image)

**Water Uptake Property**

The water content of the developed membranes was studied and the values are presented in Fig. 6. The water content of pure PVDF membrane was found to be 126%. When the X was increased from 10 to 100%, the water content gradually increased from 128 to 138%, respectively. This increase in water content upon increase in treated PVDF composition confirmed the enhanced hydrophilicity and larger polymer chain segmental gap in the blend membranes.

**Membrane Performance**

The effects of alkaline treatment and blending ratio of PVDF on membrane performance were investigated by measuring the variation of pure water fluxes as a function of time. The dynamic anti-fouling properties were identified by filtration test of BSA model solution at a fixed pressure. The pure water flux J0, flux ratio Jp1/Jp2, J1/J0, and J2/J0 were shown in Fig. 7A, 7B, 7C, and 7D, respectively. The pure water flux J0 significantly increased with the increase of X. This is attributed to the improvement of membrane hydrophilicity after blending with alkaline treated PVDF powder, which reduces the permeation resistance of water through the membrane. The flux ratio of Jp1/Jp2 increased when the membrane filtered the BSA solution (Fig. 7B). This result suggests that the membranes blended with alkaline treatment powder have obviously enhanced anti-fouling ability. The flux ratio J1/J0 reflected the cleaning efficiency. From Fig. 7C, the hydraulic cleaning became more efficient with the increase of X. This is because the protein has weaker mutual attraction with the low hydrophilic membrane. The chemical cleaning efficiency improved, with a flux recovery up to 97% for type I and type II membranes, and 100% for type III membrane when the contents of the alkaline treated PVDF powder increased over 50%.
**Fig. 7.** Pure water flux (A) and flux ratio of $J_{p1}/J_{p2}$ (B), $J_1/J_0$ (C), $J_2/J_0$ (D) as a function of blending ratio of alkaline treated PVDF powder.

**Conclusions**

Treatment of PVDF powder with aqueous NaOH under certain condition results in partial defluorination. The concentration of NaOH affects the characteristics of the final products. The results confirmed the improvement of hydrophilicity of the blend membranes.

**Acknowledgements**

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