Poly(vinylidene difluoride)/poly(tetrafluoroethylene-*co*-vinylpyrrolidone) blend membranes with antifouling properties

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A B S T R A C T

To inhibit fouling phenomenon in membrane process, a new amphiphilic copolymer, poly(tetrafluoroethylene-*co*-vinylpyrrolidone) (P(TFE-VP)), was blended with poly(vinylidene difluoride) (PVDF) to fabricate a series of antifouling membranes via non solvent induced phase separation (NIPS) method. The effect of copolymer blend ratios and TFE/VP ratios on membrane properties were evaluated, and the stability of P(TFE-VP) in PVDF membrane was studied. The membrane morphology was controlled by adjusting polymer concentration in dope solution, such that all membranes have similar pore size and density, as well as pure water permeability. In evaluating the effect of TFE/VP ratios, the content of VP in dope solutions was also adjusted to allow a fair comparison. We found that for P(TFE-VP) with a higher VP content, adsorption of BSA on polymer film was negligible. Higher blend ratios of this copolymer resulted in higher surface VP content and better hydrophilicity, but antifouling performance ceased to improve when blend ratio was larger than 1:9 (copolymer:PVDF). Meanwhile, a lower VP content in copolymer resulted in inferior hydrophilicity and severe fouling of the blend membranes. It was also proved that comparing with PVP homopolymer, P(TFE-VP) had satisfying stability inside PVDF membrane.

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1. Introduction

Poly(vinylidene difluoride) (PVDF) is a high-performance plastic material exhibiting satisfactory mechanical strength and stability at high temperatures and under most harsh chemical conditions [1]. Due to such advantages, PVDF is often used for fabricating filtration membranes. However, one problem that cannot be overlooked is the high hydrophobicity of PVDF membranes, which brings about serious fouling issues in some processes like wastewater treatment and drinking water production [2]. One of the main reason for membrane fouling is the hydrophobic interaction between foulants (from feed) and the membrane surface, which causes undesired consequences such as a serious decrease in trans-membrane flux and an increase in energy consumption. Removal of deposited foulants from the membrane usually requires extra costs [3].

To mitigate fouling, modification of PVDF membranes is needed. Reported approaches for modification include grafting hydrophilic monomers [4–6], surface coating [7–9], and blending with hydrophilic polymers [10–11]. Blending PVDF with hydrophilic materials is a simple and preferable choice, and there is usually no negative effect on pore size and water permeability. Among the commercially available hydrophilic polymers, there are several reports on the application of poly(vinyl pyrrolidone) (PVP) in fabricating antifouling blend membranes due to the various merits of PVP such as its non-toxicity, low cost, and excellent hydrophilicity as well as biocompatibility [12–13]. For example, Rajabzadeh et al. [14] reported the preparation of a PVDF/PVP blend hollow-fiber membrane and its use in BSA filtration. Compared to an unmodified PVDF membrane, the PVDF/PVP blend membrane exhibited improved antifouling performance. Yuan et al. [15] prepared a PVDF-thermoplastic polyurethane (TPU)/PVP blend membrane, and comprehensively studied the effect of PVP on PVDF crystallinity, membrane morphology, and water flux. At high PVP concentrations, the formation of macrovoids was suppressed. Despite the aforementioned merits, PVDF/PVP blend membranes tend to lose PVP gradually in long-term filtrations due to the leakage of PVP from the membrane. This phenomenon leads to some undesired consequences such as decay in hydrophilicity and antifouling performance, or even contamination of the filtered solution [16].

To overcome this issue, amphiphilic copolymers have been developed to replace linear hydrophilic polymers. Amphiphilic copolymers are composed of a hydrophobic part affixing the amphiphilic molecule inside the hydrophobic PVDF matrix, and a hydrophilic part providing sufficient antifouling effect. By blending PVDF with amphiphilic copolymers, long-term antifouling effects can be ensured. Nevertheless, there are relatively few reports on copolymers containing PVP segments. Qin et al. [17] and Xu et al. [18] individually reported the radiation synthesis of PVDF-g-PVP copolymer and its application in the preparation of PVDF/PVDF-g-PVP blend membrane. They observed a significant increase in pore size and decrease in water contact angle, and the blend membranes exhibited good antifouling performance against BSA. Although PVDF-g-PVP could endow PVDF membrane with high antifouling performance, synthesis of PVDF-g-PVP involved the use of radiation grafting, which is a relatively complicated method and is not suitable for industrial scale production. Ran et al. [19] synthesized a poly(vinyl pyrrolidone)-poly (methyl methacrylate)-poly(vinyl pyrrolidone) (PVP-PMMA-PVP) block copolymer and used it to blend with polyether sulfone (PES). They investigated the role of the PVP-PMMA-PVP copolymer in different conditions of membrane preparation. Evaporation of solvent caused PVP to be buried inside the membrane, and phase inversion method caused the appearance of PVP on the membrane surface. Although the authors measured the hydrophilicity, there was no assessment of antifouling properties. Besides using an amphiphilic copolymer, other interesting techniques have been employed to stabilize PVP inside PVDF membranes. Bi et al. [20] fabricated an antifouling PVDF membrane by cross-linking PVP with PVDF. The obtained hollow-fiber membrane showed an improved resistance to fouling, and the leaching of PVP from the membrane was inhibited.

In this research, we used a type of new amphiphilic copolymer, poly(tetraflouoethylene-co-vinylpyrrolidone) (P(TFE-VP)) to blend with PVDF, fabricating a series of antifouling membranes by the conventional non-solvent induced phase separation (NIPS) method. The membranes were characterized, and used in bovine serum albumin (BSA) filtration experiments to evaluate their antifouling performance. The effect of blend ratio, as well as TFE/VP ratio of the copolymer on the antifouling performance was investigated. Leaching of P(TFE-VP) from the PVDF membrane was compared with that of PVP. Also, it is known that some parameters of the membrane process, such as permeability, surface pore size, initial flux, and operating pressure affect the fouling behavior [21–23]. In our research, we have managed to set similar water permeability and pore sizes for all the membranes evaluated, in order to minimize variations in the aforementioned parameters. This enables a discussion on the sole effect of membrane materials.

2. Materials and methods

2.1. Materials

PVDF powder (MW = 270 kg mol^{-1}) and copolymer P(TFE-VP) samples were supplied by Daikin Industries, Ltd. Table 1 lists some parameters of the copolymer samples, and the chemical structure of P(TFE-VP) is shown in Fig. 1. Henceforth, copolymers with higher and lower VP contents are abbreviated as "copolymer A" and "copolymer B" respectively. PVP powder (MW ~55 kg mol^{-1}) was purchased from Sigma-Aldrich. The molar mass of this PVP is similar to that of the copolymers. N,N-Dimethylacetamide (DMAc), sodium dihydrogen phosphate (NaH$_2$PO$_4$), disodium hydrogen phosphate (Na$_2$HPO$_4$), and BSA were

Table 1
Parameters of the copolymers.

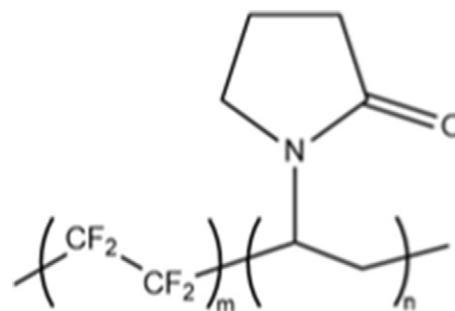| Copolymer type	Mass average molar mass (Mw, g mol^{-1})	TFE:VP ratio (mol/mol)
Copolymer A	43,000	37:63
Copolymer B	46,000	48:52

Fig. 1. Chemical structure of P(TFE-VP).

purchased from Wako Pure Chemical Industries. BSA solution was prepared by dissolving solid BSA (0.15 g) in a phosphate-buffered saline (PBS) solution containing NaH$_2$PO$_4$ (12.0 g) and Na$_2$HPO$_4$ (28.4 g) in Milli-Q water (3 L). Milli-Q water was produced in a Millipore Milli-Q water purification system (Millipore, Bedford, MA, USA). All reagents were used as received without further purification.

2.2. BSA adsorption on polymer films

The amount of BSA adsorbed on the polymer films was measured using a quartz crystal microbalance with dissipation monitoring apparatus (QCM-D; Q-Sense E1, Meiwafosis Co., Ltd., Japan). Piezoelectric quartz crystal sensors with a fundamental resonant frequency of around 5 MHz and a diameter of 14 mm (QSX 301, Q-Sense Co., Sweden) were used. The sensors were cleaned with an ultraviolet/ozone cleaner (Pro Cleaner 110; BioForce Nanosciences Co., USA) prior to QCM measurements. The cleaned sensor was then spin- coated with a 1.0 wt% polymer solution (PVDF or copolymer A/B) at 3000 rpm for 1 min, dried at 80 °C for 30 min, then set inside the QCM flow chamber, which was maintained at a fixed temperature of 25 °C during the whole measurement. PBS was then introduced into the flow chamber at a flow rate of 50 μL min^{-1}. After the frequency became constant, the PBS solution was replaced with BSA solution (1000 ppm), in order to measure the adsorption of BSA on polymer film. The change in frequency (Δf) was obtained from the apparatus, and the amount of BSA adsorbed on the film surface was calculated according to the following Sauerbrey equation [24]:

$$\Delta m = -C \frac{\Delta f}{n} \qquad (1)$$

where, Δm is the adsorption amount (ng cm^{-2}),
C is the mass sensitivity constant (17.7 ng cm^{-2} Hz^{-1} at $f = 4.95$ MHz),
Δf is the variation in frequency (Hz), and n is the overtone number ($n = 7$).

2.3. Flat-sheet membrane fabrication

The flat-sheet membranes were prepared by the conventional non-solvent induced phase separation (NIPS) method. PVDF and copolymer (or PVP) powders were mixed with DMAc, stirred at 60 °C for 8 h, and then stirred at room temperature for 16 h in order to get a homogeneous solution. In this research, no turbidity appeared in any of the casting solutions, indicating a good compatibility between PVDF and P(TFE-VP) copolymer. The solutions were allowed to stand for 8 h to release the residual gas inside. Then, the solution was spread onto a glass plate taped with a piece of non-fabric PET support material, and cast using a steel casting applicator with a gate clearance of 200 μm. The glass plate was exposed to air for 10 s and subsequently plunged into a bath of deionized water at room temperature, in which the polymer solution solidified and formed a porous membrane. All membranes