Enhancement in Flux and Antifouling Properties of Polyvinylidene Fluoride/Polycarbonate Blend Membranes for Water Environmental Improvement

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ABSTRACT: In this work, to overcome the fouling phenomenon of hydrophobic polymer membranes, polyvinylidene fluoride (PVDF) was blended with hydrophilic polycarbonate (PC) to prepare ultrafiltration membranes via the nonsolvent-induced phase separation method. The effects of PC content on membrane morphology, pore size distribution, and surface porosity were characterized and investigated by FE-SEM and image analyzer software. Solubility parameters calculated by molecular dynamics (MD) simulation showed that PVDF and PC are compatible and the results were confirmed by differential scanning calorimetry and wide angle X-ray diffractometry. The long-term chemical stability against NaOH and mechanical property before and after the abrasion test of the prepared membranes were also characterized by dynamic thermomechanical analysis. It was found that the hydrophilicity, water flux, abrasion resistance, and antifouling properties as the performance criteria of polymeric membranes were improved because of the presence of PC, and the separation efficiency of PVDF/PC membranes is much higher than that of the pristine PVDF membrane. The exemplary water filtration performances of these polymer membranes are harnessed here in this work to purify raw water polluted by natural organic matters, addressing the key environmental issue of water contamination.

1. INTRODUCTION

Nowadays, membrane processes such as microfiltration,\textsuperscript{1,2} ultrafiltration,\textsuperscript{3−5} and nanofiltration\textsuperscript{6} are widely used in one-stage and as part of multistage purification for the improvement of a water environment.\textsuperscript{7−9} Most of the polymeric membranes, such as polyvinyl chloride (PVC), Teflon (PTFE), and polyvinylidene fluoride (PVDF), are hydrophobic or less hydrophilic. These membranes are easily contaminated by proteins and other natural organic matters (NOMs) such as sodium alginate (SA) during water filtration processes.\textsuperscript{10} The fouling is the major limitation of polymeric membranes, which leads to increased operational costs, hindering its application in the field of environmental improvement.\textsuperscript{11} Therefore, there is an urgent need for effective and efficient methods to control membrane fouling.

Many efforts have been made to overcome the fouling problem and it has been accepted that the improvement in the hydrophilicity of a membrane is confirmed as an effective and fundamental way to solve membrane fouling.\textsuperscript{12} The methods to increase membrane hydrophilicity can be classified to three main categories: surface modification, nanoparticle embedding, and polymer blending. Modification of the membrane surface, including surface coating and grafting, can increase the hydrophilicity of the membrane surface, but the instability in long-time running (elution of the coating layer)\textsuperscript{13} and unmodifiable internal pore surfaces\textsuperscript{14} hinder its working efficiency and applicability. Moreover, as post-treatment approaches, surface modification adds an extra step to the membrane manufacturing process and increases the cost.\textsuperscript{12,15}

Another method is embedding hydrophilic nanoparticles into polymer membranes, which is a bulk modification method. Compared with pristine polymer membranes, nanoparticle-embedded membranes showed better antifouling performance and enhanced water flux.\textsuperscript{16} However, nanoparticle agglomeration at higher particle contents is an obstacle for organic-inorganic hybrid membrane application.\textsuperscript{17} The third method is blending of hydrophilic and hydrophobic polymers; it is another convenient and practical bulk modification method to improve the membrane hydrophilicity. However, polymer blending is the least expensive method from an economical point of view.

PVDF, as shown in Figure 1, is one of the most widely used polymer materials to fabricate filtration membranes that benefited from its chemical stabilization, thermal properties, and corrosion resistance. However, because of the strong hydrophobicity, the usage of a PVDF membrane in water treatment processes required further increasing its hydro-
philicity. In recent years, several blending systems have been explored to prepare hydrophilic PVDF membranes with enhanced water flux and antifouling properties, such as blending with perfluoro sulfonic acid (PSFA),\textsuperscript{18} polyvinyl alcohol (PVA),\textsuperscript{19} and polymethyl methacrylate (PMMA).\textsuperscript{20} However, PVDF and water-soluble polymers are incompatible. Phase separation may lead to an interface micro void, and the mechanical properties are worse than that of the pristine PVDF membrane.\textsuperscript{21} Polycarbonate (PC), as shown in Figure 1, is a commercial polymer with a hydrophilic ester group and high glass-transition temperature ($T_g$), which is easily blended with polymers and used for filtration membranes.\textsuperscript{22} Because of the presence of PC chains, the blending of PVDF and PC may result in a hydrophilic membrane and better antifouling properties.

Therefore, PVDF and PC were selected to prepare ultrafiltration membranes for NOM-polluted water purification. The objectives were mainly focused on the improvement of the water flux of PVDF/PC membranes and the reduction of the PVDF/PC membrane fouling phenomenon by using the hydrophilicity from PC. Meanwhile, the compatibilities of PC to PVDF were evaluated by molecular dynamics (MD) simulation and confirmed by experimental verifications.

2. RESULTS AND DISCUSSION

2.1. Miscibility and Thermal Stability. The solubility parameter ($\delta$) as one of the basic properties of polymers is an important predicted reference for evaluating the miscibility of two species. Solubility parameters of PVDF and PC can be estimated by eq 1\textsuperscript{21,22}

$$\delta^2 = \delta_{vdW}^2 + \delta_e^2 + \delta_h^2$$

where $\delta_{vdW}$, $\delta_e$ and $\delta_h$ are the van der Waals (vdW), electrostatic, and hydrogen bond components of total $\delta$, respectively. In this work, solubility parameters were calculated by MD simulations, the amorphous lattice models used for calculation are shown in Figure 2, and the results are listed in Table 1. According to solubility parameters theory, two polymers are considered to be miscible if the difference between their solubility parameters is less than 1.02 (J cm$^{-3/2}$).\textsuperscript{23} As can be seen, the calculated $\delta_{PVDF}$ [19.5 (J cm$^{-3/2}$), 300 K, 0.1 MPa] and $\delta_{PC}$ [20.0 (J cm$^{-3/2}$), 300 K, 0.1 MPa] were compared very favorably to the reported values and $|\delta_{PC} - \delta_{PVDF}| = 0.5$ (J cm$^{-3/2}$) $< 1.02$ (J cm$^{-3/2}$), indicating that PVDF and PC are miscible.

The blending of PVDF and PC in the prepared membranes was first confirmed by an energy-dispersive X-ray detector, and the results showed that fluorine (from PVDF) and oxygen (from PC) were homogeneously dispersed along the membrane surface. There was no preferential accumulation of fluorine or oxygen on blending the polymer matrix, as shown in Figure S2. Then, the DSC curves are used to test the miscibility of PVDF/PC and the thermal stability of the prepared membranes, as shown in Figure 3a. The glass-transition temperature ($T_g$) of the pristine PVDF membrane is about 44.6 °C and increased continuously up to 72.4 °C by adding PC ($T_g = 104.9$ °C) to the polymer matrix. This result indicates that the thermal stability of the prepared membranes increased with the PC content. Furthermore, single $T_g$ and the depressed melting peak ($T_m$) of the blend membranes mean that there was only one phase transition, implying that a compatible, miscible membrane without any phase separation was fabricated by blending PVDF and PC.

Meanwhile, the miscibility of PVDF and PC can also be confirmed by wide angle X-ray diffractometry (WAXD) patterns of the prepared membranes, as plotted in Figure 3b. Broader peaks in the 2$\theta$ range of 10–30$^\circ$ were observed in pristine PVDF and PVDF/PC patterns, indicating the semicrystalline nature of PVDF.\textsuperscript{26} It can be seen that peak strength decreased with the increase in PC content, indicating that PC reduced the crystallinity of the blend membranes. The maxima shifted toward smaller angles (2$\theta$), which means that the sizes or amorphous gap lengths increase.\textsuperscript{27} This phenomenon indicated that the lattice spacing of the crystalline PVDF matrix was enlarged by amorphous PC as the PC content increased in the blend system. All blend membranes have similar WAXD patterns, which confirmed the miscibility of PVDF and PC.

2.2. Morphology. Figure 4 shows the cross section and surface of the prepared membranes. As can be seen from the micrographs, all the membranes consist of three layers: the top layer with a very thin skin (thickness $\approx$ 100 nm), the middle layer with branch-shaped macro voids (thickness $\approx$ 10 μm), and the bottom layer with finger-like and sponge-like structures. Because the molecular weight of PC is lower than that of PVDF (PC: 203,000 g mol$^{-1}$, PVDF: 573,000 g mol$^{-1}$), the viscosity of the dope solutions decreases as the content of PC increases in the casting solution (dope viscosities were measured by a viscometer for 0.1 rpm at 25 °C, and the decreasing impact of PC content on dope viscosity is shown in Figure S3). Consequently, lower viscosity leads to faster solvent/non solvent exchanging rate, and fast phase inversion accelerates solidification of the membrane, forming a finger-

Table 1. Solubility Parameters Calculated by MD Simulation

| polymer  | $\delta_{vdW}$ | $\delta_e$ | $\delta_h$ | $\Delta$ | $\delta$ from ref |
|----------|---------------|-----------|-----------|---------|------------------|
| PVDF     | 17.7          | 7.5       | 3.4       | 19.5    | 19.4\textsuperscript{24} |
| PC       | 18.0          | 5.8       | 6.7       | 20.0    | 19.0\textsuperscript{25} |

\[\text{Equation 1}\]

\[\delta^2 = \delta_{vdW}^2 + \delta_e^2 + \delta_h^2\]

$\delta_{vdW}$, $\delta_e$, and $\delta_h$ represent the van der Waals, electrostatic, and hydrogen bond components of the total $\delta$, respectively.

Figure 1. Molecular structures of PC and PVDF.
like structure. On the other hand, slow phase inversion forms a partially solidified sponge-like structure.\(^\text{28}\) As can be seen from Figure 4, the finger-like structure became wider and the sponge-like structure decreased as the PC content increased in the dope solutions.

The calculated results from image analyzer software, which are depicted in Figure 5a–e, revealed that the pore numbers in these micrographs were 226, 766, 1251, 1358, and 1384, respectively, for PC content increase from 0 to 80 wt % (the increasing of PC content in the membrane was also confirmed by energy-dispersive X-ray diffraction, as shown in Figure S2), indicating that the number of surface pores per unit area (3.0 \(\mu\text{m} \times 2.3 \mu\text{m}\)) increased with an increase of the PC content in dope solutions. In addition, Figure 5f shows that pore size distribution curves shifted toward larger pores and the mean pore radii of the prepared membranes were 2.5, 2.8, 3.6, 4.1, and 5.8 nm, respectively. Furthermore, the statistical results from analyzer software revealed that the surface porosities (area %) were 0.7, 1.4, 2.4, 6.5, and 6.6 area % for subsequent membranes, respectively. This means that blending PVDF and PC results in membranes with not only more pores but also membranes with a larger pore radius and a higher surface porosity in comparison with the pristine PVDF membrane.

2.3. Hydrophilicity and Pure Water Flux. Figure 6a shows that the dynamic contact angles between the prepared membranes and water droplet decreased continuously with increasing PC content. The contact angle of the pristine PC membrane is in the range of 60–72\(^\text{29,30}\) and the contact angle of the pristine PVDF membrane in this work was 81.3° higher than that of pristine PC, which indicates that the reduction of contact angle is due to the presence of hydrophilic PC in the blend membranes. As mentioned, there is a C atom double-bonded to an O atom in the PC chain ester group, which bonded to an O atom in the PC chain ester group, which increases its interaction with water molecules and enhances the hydrophilicity of the blend membranes.\(^\text{3}\)

The pure water fluxes of the PVDF/PC blend membranes are represented in Figure 6b. It can be seen that the pure water fluxes increased from 154 kg m\(^{-2}\) h\(^{-1}\) for the pristine PVDF membrane to about 1180 kg m\(^{-2}\) h\(^{-1}\) for the 80 wt % PC membrane. The increase of water flux can be related to the enhancement of hydrophilicity, which is beneficial to water penetration. The increase of surface pore number and porosity also provides more paths for water penetration and leads to a higher water flux.

2.4. Abrasion, Stability, and Mechanical Properties. Solid particles widely exist in polluted water, which must be separated by polymeric membranes. Therefore, the effect of abrasive particles on the membrane durability is an important issue, and the abrasion resistance should be considered as an important property in the prepared polymeric membranes. Typical damage structures during abrasion tests are shown in Figure 7. On the surface of the PVDF/PC membrane (Figure 7a), the scratch is shallow, while on the surface of the pristine PVDF membrane (Figure 7b), the scratch is wide and deep, which reveals that PC can reduce the damage of the membrane surface caused by abrasive particles in the feed solution. Figure 8 shows the weight loss (g kg\(^{-1}\)) of the prepared membranes caused by a silicon carbide slurry. It can be observed that the weight loss of the membranes decreased with increasing PC content, which means that blending PVDF with PC resulted in a better antiabrasion property in comparison with that of the pristine PVDF membrane. The pristine PC membrane broke into pieces during the abrasion test, so there were no abrasion data in Table 2.

In this work, the tensile strength (MPa) and elongation (%) before and after the abrasion test were used to determine the membranes’ antiabrasion property; the results were summarized in Table 2. It can be seen that the tensile strength and elongation of the membranes decreased as the PC content increased up to 80 wt %. This means that the mechanical properties of the PVDF/PC membranes were weakened, which can be attributed to the lower molecular weight of PC and the increasing finger-like voids, as shown in Figure 2. Finger-like macroversoids induce stress concentration and contain more fragile structures, so the mechanical properties are worse than in the sponge structure.\(^\text{28}\) Moreover, tensile strengths of the membranes decreased after the abrasion test, but the tensile reduction is more severe for the pristine PVDF membrane. In terms of tensile and elongation reduction [(original − after abrasion)/original × 100%], the pristine PVDF membrane’s tensile reduction is 80%, whereas this ratio for subsequent membranes is 67, 46, 17, and 5%, respectively. Elongation reduction of the pristine PVDF membrane is 34% but that of subsequent membranes is 23, 20, 17, and 7%, respectively. Therefore, the 80 wt % PC membrane exhibited the highest abrasion resistance. The better antiabrasion performance of the 80 wt % PC membrane may be attributed to the PC chain’s high rigidity and higher hardness than that of PVDF.

![Figure 3. (a) DSC curves and (b) XRD diffraction patterns of the prepared membranes.](https://dx.doi.org/10.1021/acsomega.0c04656)
Mechanical properties of the NaOH drip-washed membranes were used to investigate their long-term chemical stability; the results are summarized in Table 2. As can be seen, the tensile and elongation of the blend membranes after the stability test decreased as the content of PC increased. However, the mechanical properties of the pristine PVDF membrane barely changed, which can be attributed to its good chemical resistance. These results indicated that though the PVDF/PC blend membranes possess better antiabrasion performance, addition of PC to the PVDF matrix results in a low chemical stability. The thin-walled structure in the finger-like pore may be more easily affected by NaOH, resulting in a sharp decline in NaOH drip-washed membranes’ mechanical properties. Therefore, the best blend ratio should be chosen based on the feed component and cleaning conditions (Table 3).

2.5. Antifouling Properties and BSA Rejection. Figure 9 shows the filtration and antifouling performance of the prepared membranes for 0.1 g L\(^{-1}\) SA solution. It can be seen that the flux of the pristine PVDF membrane was the least and its value decreased from 104 kg m\(^{-2}\) h\(^{-1}\) to about 50 kg m\(^{-2}\) h\(^{-1}\) (reduction \(\approx 52\%\)) after 240 min. For other blend membranes, all the initial and final fluxes are higher than those of the pristine PVDF membrane. The flux reductions during SA filtration were about 26, 20, 19, and 14% for subsequent membranes, respectively, which indicates that antifouling properties increase with PC content and membrane hydrophilicity. However, the 80 wt % PC membrane had the least flux reduction (reduction \(\approx 14\%\)).

A more comprehensive understanding of antifouling phenomenon can be obtained from the fouling parameters (TFR, RFR, IFR, and RFP) which are depicted in Table 4. The first parameter, TFR (= RFR + IFR), is a degree of total flux loss due to fouling. It can be seen that all blend membranes had lower TFR, indicating that PVDF/PC membranes are more fouling-resistant than the pristine PVDF membrane. In addition, reversible fouling portion (RFP) = RFR/TFR is defined as the flux recovery degree of the contaminated membrane after cleaning. It can be observed that RFP values continuously increased and reached a maximum for the 80 wt % PC membrane. The RFP value of the 80 wt % PC membrane is 79.0 \(\pm\) 3.3%, which means that nearly 80% of the total fouling can be reversed by cleaning.

RFP in Table 4 shows that blending hydrophobic PVDF with hydrophilicity PC results in the prepared membranes with better fouling-resistant and the SA cake layers can be cleaned easily.

The BSA rejection results are also represented in Table 4. Contrary to flux, abrasion, and antifouling properties, BSA rejections decreased with PC content in the prepared membranes. The trend of rejection is in accordance with the results of pore size distribution (Figure 3) and confirms that blending of PVDF and PC results in a larger pore radius. The pore radius of the 100 wt % PC membrane was too large (average pore radius = 11.3 nm) to reject BSA molecules (rejection = 72%), as shown in Figure S4. Therefore, there is no antifouling test for the pristine PC membrane in this work because of its poor separation performance. If the membrane performance is considered in terms of rejection and flux, it is found that all PVDF/PC membranes possess 2–9 times higher water flux and only 0.8–7.9% lower BSA rejection than that of the pristine PVDF membrane. These results show that the separation efficiency of PVDF/PC membranes is much higher than that of the pristine PVDF membrane. Therefore, these ultrafiltration performances of the membranes prepared in this work are compared with reference values, and the comparisons are listed in Table S2. The BSA rejection was up to 92.4% when the pure water flux was 842 kg m\(^{-2}\) h\(^{-1}\); this ultrafiltration performance is better than that of most of other membranes reported before.

3. CONCLUSIONS

In this work, we employed a series of characterization techniques to elucidate the PVDF/PC blend membranes that were prepared for water purification. The miscibility between PVDF and PC was predicted by simulation-assisted Hansen solubility theory and confirmed by DSC and XRD analyses. Blending PVDF and PC results in membranes with a larger pore radius, a higher surface porosity, and better hydrophilicity.
in comparison with the pristine PVDF membrane. With the increase of PC content, the blend membrane’s water flux, antifouling performance, and abrasion resistance against the abrasive particle were improved and a higher tensile strength resulted after the abrasion test. However, BSA rejection and chemical stability of the membranes against the NaOH solution decreased with increasing PC content, which were attributed to the low chemical stability of PC and pore size distribution. In conclusion, blending PVDF with PC resulted in membranes with improved separation efficiency, antifouling, and antiabrasion properties. These prepared membranes are

Figure 5. Estimation of the size and the number of pores on the membrane surface by image analyzer software: (a) pristine PVDF, (b) 20 wt % PC, (c) 40 wt % PC, (d) 60 wt % PC, and (e) 80 wt % PC blend membranes. (f) Pore size distribution curves of the prepared membranes.

Figure 6. (a) Dynamic contact angles and (b) pure water flux of the prepared membranes.

Figure 7. Typical damage structures for (a) 80 wt % PC and (b) pristine PVDF membranes after the first day of the abrasion test.

Figure 8. Weight loss of the prepared membranes after 10 days of the abrasion test.
Table 2. Mechanical Properties of the Membranes before and after Abrasion and Drip-Washing Tests

| membrane         | original |                  | after abrasion test |                  | after drip-washing |
|------------------|----------|------------------|---------------------|------------------|-------------------|
|                  | tensile  | elongation (%)   | tensile  | elongation (%)   | tensile  | elongation (%)   |
| pristine PVDF    | 5.7 ± 0.1 | 62 ± 3           | 1.1 ± 0.2 | 41 ± 4           | 5.3 ± 0.2 | 60 ± 4           |
| 20 wt % PC       | 5.5 ± 0.2 | 48 ± 2           | 1.8 ± 0.2 | 37 ± 1           | 4.4 ± 0.3 | 27 ± 4           |
| 40 wt % PC       | 5.0 ± 0.1 | 44 ± 3           | 2.7 ± 0.1 | 35 ± 3           | 2.8 ± 0.3 | 24 ± 2           |
| 60 wt % PC       | 4.7 ± 0.3 | 35 ± 1           | 3.9 ± 0.3 | 30 ± 4           | 1.7 ± 0.1 | 15 ± 2           |
| 80 wt % PC       | 4.4 ± 0.2 | 28 ± 2           | 4.2 ± 0.2 | 26 ± 4           | 1.4 ± 0.2 | 7 ± 1            |
| 100 wt % PC      | 2.0 ± 0.3 | 5 ± 1            |          |                  | 1.2 ± 0.2 | 3 ± 1            |

“The pristine PC membrane broke into pieces during the abrasion test, so there were no mechanical properties after the abrasion test.

Table 3. Fouling Parameters and BSA Rejection of the Prepared Membranes

| membrane         | TFR (%)  | RFR (%)  | IFR (%)  | RFP (%)  | rejection (%) |
|------------------|----------|----------|----------|----------|---------------|
| pristine PVDF    | 63.0 ± 3.4 | 44.2 ± 3.4 | 18.8 ± 3.4 | 70.1 ± 3.4 | 93.4 ± 3.3 |
| 20 wt % PC       | 40.7 ± 2.5 | 31.4 ± 2.5 | 9.3 ± 2.5  | 77.1 ± 2.5 | 92.6 ± 3.4 |
| 40 wt % PC       | 35.3 ± 2.6 | 27.8 ± 2.6 | 7.5 ± 2.6  | 78.8 ± 2.6 | 92.4 ± 1.7 |
| 60 wt % PC       | 30.2 ± 3.5 | 23.8 ± 3.5 | 6.4 ± 3.5  | 78.8 ± 3.5 | 86.0 ± 2.2 |
| 80 wt % PC       | 21.1 ± 3.3 | 16.7 ± 3.3 | 4.4 ± 3.3  | 79.0 ± 3.3 | 85.5 ± 2.3 |

4. EXPERIMENTAL SECTION

4.1. Materials. PVDF (Mₐ = 573,000 g mol⁻¹) was purchased from Solvay (Belgium). Tetrahydrofuran (THF, content ≥99.0%, Mₐ = 72.1 g mol⁻¹), polycarbonate (PC, Mₐ = 203,000 g mol⁻¹), and sodium hydroxide (NaOH, purities >99.9%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Sodium alginate (SA, Mₐ = 270,000 g mol⁻¹, viscosity: 200 ± 20 MPa s) was purchased from Aladdin (China). BSA (Mₐ ≈ 66 kDa, purities ≥98%) was obtained from Sigma-Aldrich (China). All chemicals were used as expected to purify raw water polluted by NOMs, lower the cleaning frequency, and address the key environmental issue of water contamination.

4.2. Preparation of Membranes. The formulations of casting solutions are given in Table 4. In this research, six casting solutions were prepared, and the total polymer concentration was set to 18 wt % in all solutions. The PC content in the total polymer (Wₚ) varied from 0 (neat PVDF) to 20, 40, 60, 80, 100 wt %. Different amounts of PVDF and PC were dissolved in THF and stirred at room temperature (26 ± 2 °C) for 48 h to ensure homogeneous mixing. The picture of dope solutions is shown in Figure S1. Then, casting solutions were degassed for 24 h. The PVDF/PC membranes were prepared via the nonsolvent-induced phase separation method.10 The polymeric casting solutions were cast on top of a glass plate using a casting knife of 100 μm and subsequently immersed in a DI water bath at 24 ± 1 °C to form the PVDF/PC membranes. The water bath was refreshed 6 times for 3 days to remove the residual organic solvent. Finally, the membranes were stored in DI water at room temperature to prevent pore collapse caused by drying.

4.3. Characterization. 4.3.1. Molecular Dynamics Simulation. In this work, solubility parameters (δ) were used to evaluate the compatibility of PVDF and PC. δ was calculated by molecular dynamics (MD) simulation as described elsewhere.10,32 Briefly, PVDF and PC molecules were packed into a cubic cell using the amorphous cell calculation modules. Polymer chains were generated in a periodic boundary box and the torsion angles of polymer backbones were sampled according to their Monte Carlo distributions.33 Then, the amorphous cell configuration underwent an extensive multi-step equilibration protocol (energy minimization, geometry optimization, and annealing)34 to relax all impracticable torsion angles. Finally, the solubility parameters (δ) of pristine PVDF and PC at 0.1 MPa and 300 K were estimated from the NPT trajectory for their amorphous cells. Molecular potential energies were calculated by polymer-consistent force field (PCFF),34 and the cutoff distance of vdW and electrostatic interactions was set at 12.5 Å.35

4.3.2. Differential Scanning Calorimetry. The compatibility between PVDF and PC and thermal behavior of blend membranes were studied via DSC measurements (DSC822, received. Deionized (DI) water was produced by a lab-equipped Millipore ultrapure water system with a conductivity of 4.8 μS cm⁻¹ and a TOC of 1.17 mg L⁻¹.
METTLER TOLEDO, Switzerland). The DSC tests were carried out in a dry nitrogen atmosphere from 25 to 250 °C. The samples of about 5 mg were placed into aluminum pans and heated to the desired temperature at a heating rate of 5 °C min⁻¹. After completing the heating process, the films were cooled at a cooling rate of 5 °C min⁻¹ to 25 °C. A vacant aluminum pan serves as a reference during the whole experiment.

4.3.3. Wide Angle X-Ray Diffractometry. Wide angle X-ray diffractometry (WAXD) of polymer films was carried out by D8 ADVANCE, (Bruker BioSpin, Germany) with a Cu Kα radiation wavelength of 1.54 Å. Dried membranes were mounted on zero background plates and scanned over a 2θ range of 5–90° with a step size of 0.02° and a count time of 4 s per step.

4.3.4. Morphology. Cross-sectional and surface morphologies of membranes were examined by a field emission scanning electron microscope (JSM-7800F, JEOL Ltd., Japan) with an accelerating voltage of 15 kV. Cross-sectional samples were fractured in liquid nitrogen to get a nondeformed image. All samples were sputter-coated by Pt (E-1030 ion Sputter, Hitachi Science Systems, Ltd., Japan) under a vacuum atmosphere before the FE-SEM test. The membrane surface atmosphere before the FE-SEM test. The membrane surface was gently removed by 1 wt % NaOH solution and the membranes were back-washed by DI water. Subsequently, cleaned membranes were loaded in DI water again to record the pure water flux after cleaning (J₀, kg m⁻² h⁻¹) at 0.1 MPa. Fouling properties of the membranes were evaluated using the following equations:

\[ TFR = \frac{I_0 - I_1}{I_0} \]  
\[ RFR = \frac{I_2 - I_1}{I_0} \]  
\[ IFR = \frac{I_0 - I_2}{I_0} \]  
\[ REP = \frac{RFR}{TFR} \]

where TFR, RFR, IFR, and REP are the total fouling ratio, reversible fouling ratio, irreversible fouling ratio, and reversible fouling portion, respectively.

4.3.7. Mechanical Strength, Abrasion Resistance, and Stability. The mechanical strength of the prepared membranes was evaluated using a dynamic thermomechanical analysis equipment (DMA Q800, TA Instruments Inc., USA). Fully dried membranes were precut into a rectangular shape with width = 2.5 ± 0.2 mm and length = 25.0 ± 3.2 mm. The thickness (averaged: 75 ± 7.2 μm) for membranes were measured by a micrometer. Samples were fixed on a clamp for the tension test; the distance between two clamping apparatuses was in the range of 9.5 ± 0.3 mm. The temperature in the analysis chamber was controlled at 25.0 ± 0.8 °C. Test mode was set in controlled force with a procedure of ramping force of 0.5 N min⁻¹ to 17 N. Tensile (MPa) and elongation (%) were recorded by DMA equipment. The abrasion resistance of the membranes was examined by following steps: 1) permeate side of membranes were secured by low viscosity tape (MT601, MR. HOBBY, Japan) and immersed into 10 wt % silicon carbide (particle size: 75 μm, Mohs hardness: 9) slurry. The slurry is then stirred for at least 10 days to bring the membranes into full contact with abrasive silicon carbide particles. The mechanical strength of the membranes after the abrasion test was evaluated following a method similar to the DMA method to characterize the anti-abrasion property. The long-term stability of the prepared membranes was determined by submerging the unprotected membranes in 5 wt % NaOH solution for 5 days at room temperature (when the concentration of NaOH < 20 wt %, PC can remain stable without a severe effect). Then, the mechanical strength of dip-washed membranes was determined by a DMA tensile test to investigate the effect of NaOH solution on the chemical stability of the membranes. Before tensile tests, all the membranes were washed by DI water and vacuum dried at 40 °C for 24 h. The influence of vacuum drying on the membrane pore structure was tested by water
flux and BSA rejection before and after vacuum drying and after solvent exchange; the results showed that the pore structure was not affected by vacuum drying at 40 °C for 24 h. The test protocol and results are depicted in Table S1.

- **ASSOCIATED CONTENT**

  Supporting Information

  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04656.

  Pictorial representation of dope solutions, flux and BSA rejection of the PVDF membrane, energy-dispersive X-ray diffraction, viscosity curve, FE-SEM pictorial representation, and reference values (PDF)

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  Notes

  The authors declare no competing financial interest.

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