Enhancing the Antifouling Properties of Poly(vinylidene fluoride) (PVDF) Membrane through a Novel Blending and Surface-Grafting Modification Approach

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1. INTRODUCTION

Membrane technology has become an important treatment alternative for water and wastewater management due to its various advantages over conventional treatment technologies. Among the major types of base membrane materials, poly(vinylidene fluoride) (PVDF) and its derivatives have attracted great engineering interest in water and wastewater treatments, largely attributed to their unique properties such as excellent thermal and chemical stability in aqueous environment, good mechanical durability and engineering processability, etc., arising from the high polarity (high dielectric constant) and electron-withdrawing property of the fluorine atoms in the backbone. However, the surface of PVDF membrane is usually highly hydrophobic and hence greatly susceptible to membrane organic fouling due to favorable interaction with many hydrophobic foulant such as bacteria and protein in water and wastewater. Over the last 1 or 2 decades, numerous efforts have been made to improve the hydrophilicity and antifouling properties of the PVDF membranes.

Among the various different membrane modification methods, surface grafting has been considered to be an efficient method to improve the surface properties of membranes without destroying and altering their inside structures, which introduces and attaches polar groups or hydrophilic monomers onto the membrane surface through the formation of chemical bonds. As one of the typical surface modification methods, graft polymerization allows functional groups to be covalently attached to the membrane substrate. Some hydrophilic polymers such as sulfonyl betaine methacrylate, poly(methyl methacrylate), and poly(vinyl pyrrolidone) (PVP) have been grafted on PVDF membranes to improve their surface hydrophilic properties. Although there have been many successful stories on surface-grafting modification of PVDF membranes, the approaches generally need harsh pretreatment or even severe chemical reaction conditions, especially for the relatively inert base membrane material such as PVDF. This has, to some extent, limited its practical engineering application for membrane preparations.
Membrane surface modification may also be done through polymer blending.\(^{19−21}\) Zhu et al. reported the preparation of modified PVDF membrane with superhydrophilic and superoleophobic surface property.\(^{22,23}\) In that work, a triblock copolymer P(VDF-co-CTFE)-g-PMAA-g-fPEG with both hydrophilic and oleophobic groups was synthesized from a PVDF derivative, P(VDF-co-CTFE),\(^{24,25}\) and a fluorinated polyethylene (fPEG), and the copolymer was used as an additive polymer to blend with PVDF to prepare the desired membrane. The hydrophilic segments (poly(methyl acrylic acid), PMAA groups) can help the formation of a hydration layer on the membrane surface that may inhibit the nonspecific interaction between the foulants and the membrane surface, and the oleophobic segments (fPEG groups) with low surface free energy can reduce the adsorption or adhesion strength of the organic substances (such as protein) onto the membrane surfaces, which make them easily removable even by water flushing only. The blending method can provide a unified membrane surface that may inhibit the nonspecific interaction between the foulants and the membrane surface, and the oleophobic segments (fPEG groups) with low surface free energy can reduce the adsorption or adhesion strength of the organic substances (such as protein) onto the membrane surfaces, which make them easily removable even by water flushing only. The blending method can provide a unified membrane structure that has a PVDF backbone plus side chains containing hydrophilic internal segment (PMAA) and oleophobic terminal segment P(VDF-co-CTFE) and PVDF, which may result in a relative good compatibility.

In this study, a new approach is developed by combining the advantages and overcoming the shortcomings from the surface-grafting and polymer-blending approaches for PVDF membrane modification. Instead of first synthesizing an additive and then blending it with PVDF (as reported by Zhu), the starting polymer P(VDF-co-CTFE) was first blended with PVDF to provide active component for subsequent surface grafting of fPEG onto the prepared membrane. Compared to conventional surface-graft modification, the presence of the active component in the membrane structure made the surface-grafting reaction less demanding. The blended active component can also provide the flexibility for controlling the surface-grafting density. Compared to traditional blending approach, the use of starting polymer of P(VDF-co-CTFE) for blending with PVDF increased its compatibility and solubility with PVDF (due to smaller molecules and lack of fPEG component). The preparation conditions were examined and the obtained membranes were characterized and tested for their antifouling performance in a series of filtration experiments. Conceptually, surface-graft modification of membranes by blending active component first in the membrane structure for the attachment of other functional monomers or groups has seldom been reported.

2. RESULTS AND DISCUSSION

2.1. Chemical Structure Analysis of the Membrane Surfaces. In this study, an expected polymer structure that has a PVDF backbone plus side chains containing hydrophilic internal segment (PMAA) and oleophobic terminal segment P(VDF-co-CTFE) and PVDF, which may result in a relative good compatibility.
Table 1. Compositions of Casting Solutions for the Preparation of the Base Membranes

| membrane | PVDF (wt %) | P(VDF-co-CTFE) (wt %) | ratio of PVDF/P(VDF-co-CTFE) | PVP (wt %) | NMP (wt %) |
|----------|-------------|------------------------|-----------------------------|------------|------------|
| M1       | 19.8        | 2.2                    | 9:1                         | 0          | 78.0       |
| M2       | 17.6        | 4.4                    | 8:2                         | 0          | 78.0       |
| M3       | 15.4        | 6.6                    | 7:3                         | 0          | 78.0       |
| M4       | 13.2        | 8.8                    | 6:4                         | 0          | 78.0       |
| M5       | 19.8        | 2.2                    | 9:1                         | 5.0        | 73.0       |
| M6       | 17.6        | 4.4                    | 8:2                         | 5.0        | 73.0       |
| M7       | 15.4        | 6.6                    | 7:3                         | 5.0        | 73.0       |
| M8       | 13.2        | 8.8                    | 6:4                         | 5.0        | 73.0       |

Figure 1. Surface FT-IR spectra of the membranes M1−G1 in (a) and M5−G5 in (b).

Figure 2. XPS spectra of the membranes before and after modification: full XPS analysis of M5 (a) and G5 (b) and C 1s analysis of M5 (c) and G5 (d).
(PEG) was introduced for the modified membrane surface. As shown in Scheme 1, blended membranes (M1–M8, Table 1) were prepared from the mixture of PVDF/P(VDF-co-CTFE) with various ratios, and the grafted membranes (G) were obtained with a triblock copolymer of P(VDF-co-CTFE)-g-PMAA-g-PEG via the three-step reaction process.

Eight modified membranes (G1–G8) were obtained from the original eight blend membranes (M1–M8). From the Fourier-transform infrared (FT-IR) analysis, the successful grafting reactions of modification can be confirmed. Taking M1 and M5 as the examples, Figure 1 shows the surface FT-IR spectra of each membrane (M1 in Figure 1a and M5 in Figure 1b) before and after each transformation.

Compared with the spectra of the base membrane M1, a new absorption peak at 1717.00 cm⁻¹ was detected in the spectra of G1 (1.13). This peak is attributed to the carbonyl (C=O) stretching vibrations in the ester group of the grafted poly(tert-butyl methacrylate) (PtBMA). The result confirmed the successful grafting of PtBMA on the membrane surface with P(VDF-co-CTFE). On the surface of G1 (1.1), the carbonyl group peak shifted to 1709.15 cm⁻¹, indicating the occurrence of the hydrolysis reaction, and the ester was transformed to carboxylic acid, i.e., P(VDF-co-CTFE)-g-PMAA. The subsequent esterification reaction brought a newly formed carbonyl absorption peak at 1727.67 cm⁻¹, indicating that the carbonyl group in carboxylic acid PMAA was transformed to ester. Therefore, the final step of the reaction took place and generated P(VDF-co-CTFE)-g-PMAA-g-PEG. Similar FT-IR spectrum changes can be found for M5 (addition of 5 wt % PVP in the casting solution) to G5 (Figure 1b), which confirmed that the triblock copolymer P(VDF-co-CTFE)-g-PMAA-g-PEG had been successfully introduced onto the modified membrane surfaces.

Elemental analyses of the membrane surfaces before and after the modification were detected by X-ray photoelectron spectroscopy (XPS), on both the unmodified membrane M5 and modified membrane G5. Figure 2 shows the XPS spectra of M5 and G5. It can be found that the contents of elements O and C in G5 (Figure 2a) were higher than that in M5 (Figure 2b). The elemental mole percentage data are summarized in Table 2. The percentage of element O in G5 (2.83%) was higher than that of M5 (1.13%). This can be caused by the introduction of MAA and PPEG onto the membrane, where MAA has abundance of C=O and C=O bonds, and PPEG provides the C=O–C bond. Same explanation can be applied for the increasing percentage of element C from M5 (23.35%) to G5 (29.05%).

In the C 1s analysis, a C=O bond (287.75 eV) was detected for the unmodified membrane M5, as shown in Figure 2c. This can be attributed to PVP, which was added into the membrane. After surface-grafting modification, some new carbon bonds were observed for the modified membrane G5 (Figure 2d). The results confirmed again that the triblock copolymer P(VDF-co-CTFE)-g-PMAA-g-PEG was successfully formed on the PVDF surface. For example, the C-F bond (292.09 eV) comes from PPEG and the O–C=O bond (288.42 eV) is produced by MAA. It is noticed that the peak at 287.95 eV in Figure 2d was similar to that of the C=O bond (287.75 eV) in M5, but with a slight shift, and the peak area was much larger than that in M5. This can be attributed to the reacted PPEG that has repeat C–O–C group units, which might cover the original C=O peak of PVP.

2.2. Morphology of Membranes. The surface morphologies of the original base membranes (M1–M8) and the modified membranes (G1–G8, see Table 3) from the scanning electron microscope (SEM) analysis are shown in Figure 3. Compared with the membranes M1–M4 (and G1–G4), the addition of PVP in the casting mixture made the membrane structure of M5–M8 (and G5–G8) thicker, with the formation of more finger-like macrovoids. The addition of PVP did seem to significantly increase the porosity of the base membrane.

No obvious difference between the unmodified and modified membranes was observed in the cross-sectional SEMs. This is because the surface modification in this study will seldom affect the inside membrane structure. Compared with M1–M8, the surface pores of the modified membranes (G1–G8) were changed (became smaller). The growth of the triblock functional copolymer on the membrane may somehow cover or block the surface pores that are originally on the base membranes.

The higher content of P(VDF-co-CTFE) blended in the original base membranes also led to the higher porosity of the modified membranes, see Table 3. This may be attributed to the lower compatibility between P(VDF-co-CTFE) and PVDF as compared to that among PVDF itself. During the process of membrane surface modifications, the membrane pores may be easily blocked or reduced. Although no obvious pores can be found for G1–G4, with the addition of PVP, the membrane thickness and pore of G5–G8 increased to almost twice that of the membrane without PVP. For example, the thickness of the grafted membrane G4 was 65 ± 0.5 μm and that of the membrane G8 with PVP was 90 ± 0.5 μm.

**Table 2. Element Mole Percentages for M5 and G5 Analyzed via XPS**

|     | C 1s (%) | O 1s (%) | F 1s (%) | Cl 2p (%) |
|-----|----------|----------|----------|-----------|
| M5  | 23.35    | 1.13     | 73.26    | 0.26      |
| G5  | 29.05    | 2.83     | 67.95    | 0.17      |

**Table 3. Porosity and Membrane Surface Pore Sizes of Modified Membranes**

| membrane | PVDF/P(VDF-co-CTFE), wt % of PVP | thickness (μm) | porosity ε (%) | surface pore size (μm) | water flux (L m⁻² h⁻¹) |
|----------|---------------------------------|----------------|----------------|-----------------------|------------------------|
| G1       | 9:1, 0                          | 100 ± 1.5      | 18.3 ± 1.5     | 0.1495 ± 0.025        | 364.0 ± 11.0           |
| G2       | 8:2, 0                          | 80 ± 1.0       | 19.0 ± 1.2     | 0.1286 ± 0.022        | 262.9 ± 12.3           |
| G3       | 7:3, 0                          | 70 ± 0.5       | 23.3 ± 1.0     | 0.1247 ± 0.035        | 236.7 ± 4.6            |
| G4       | 6:4, 0                          | 65 ± 0.5       | 23.8 ± 1.4     | 0.1072 ± 0.029        | 224.6 ± 6.5            |
| G5       | 9:1, 5                          | 190 ± 4.0      | 32.7 ± 1.7     | 0.1495 ± 0.025        | 364.0 ± 11.0           |
| G6       | 8:2, 5                          | 180 ± 3.0      | 34.4 ± 2.4     | 0.1286 ± 0.022        | 262.9 ± 12.3           |
| G7       | 7:3, 5                          | 175 ± 3.0      | 28.6 ± 3.8     | 0.1247 ± 0.035        | 236.7 ± 4.6            |
| G8       | 6:4, 5                          | 155 ± 2.5      | 31.8 ± 3.1     | 0.1072 ± 0.029        | 224.6 ± 6.5            |
Figure 3. Surface and cross-sectional SEM images of original membranes M1–M8 and modified membranes G1–G8.
increased to $155 \pm 2.5 \, \mu m$. The porosity of the membranes containing 5 wt % PVP (G5–G8) increased 78.4, 80.9, 22.8, and 33.5% more than those corresponding membranes without PVP (i.e., G1–G4).

Whereas no pure water flux was detected for membranes G1–G4 under the filtration conditions (transmembrane pressure, TMP of 0.15 MPa), the pure water flux of the membranes G5–G8 varied from 364.0 to 224.6 L m$^{-2}$ h$^{-1}$ with the increasing ratio of P(VDF-co-CTFE) in the base membranes. This may be due to more blocking of the membrane surface pores by more grafted products formed on the membrane. The higher the ratio of P(VDF-co-CTFE) in the blend mixture, the larger the amount of triblock copolymer obtained from the three-step reaction should be grafted onto the membrane surface; therefore, more polymer chains may extend and cover some of the membrane pores. The surface pore sizes decreased from 0.150 $\mu m$ (for G5, 9:1) to 0.107 $\mu m$ (for G8, 6:4).

The surface roughness of the base membranes (M4, M8) and the corresponding modified membranes (G4, G8) were obtained by atomic force microscopy (AFM), as shown in Figure 4. The only difference between membranes M4 and M8 was the addition of PVP that acted as a porogen in the membrane formation. It can be found in Figure 4 that no obvious difference in the roughness average ($R_a$) was observed for the two base membranes (M4: 32.2 nm, M8: 32.9 nm). In contrast, the roughness of the corresponding modified membranes were significantly different (G4: 45.6 nm, G8: 105.0 nm). This is because the modification reactions took place on the membrane surface, and more new components were grafted and introduced to the membrane surface, leading to the increase in the surface roughness.

A huge increase in roughness was observed for the modified membrane G8 from M8. The addition of PVP in the membrane M8 made it a most porous membrane structure and also more reaction sites were available on the membrane surface. So, larger amount of triblock copolymer could be grafted onto the membrane surface. The speculation may be supported by the IR comparison for G4 and G8, as shown in Figure 5. The membrane G8 had a stronger absorbance than G4 at 1729.75 cm$^{-1}$ (C=O bond), which only comes from the formation of the triblock copolymer. In addition, G8 also had a stronger C–F bond absorbance than G4. For example, the absorbance of the C–F bond at 1171.08 cm$^{-1}$ in membrane G8 is obviously higher than that of G4. This indicates that more C–F bonds (from the triblock copolymer) were introduced onto the G8 surface.

### 2.3. Mechanical Strength of the Membranes.

The mechanical strength of both unmodified and modified PVDF blend membranes was tested, as shown in Figure 6. The
mechanical properties (including tensile stress and tensile strain) of the modified membranes G1–G8 were weaker than that of unmodified membranes M1–M8, especially for the tensile stress (Figure 6a). It indicated that the surface-grafting modification did not affect their mechanical properties too much. The membrane’s mechanical strength was found to be reduced with the increasing ratio of P(VDF-co-CTFE) in the original blend membrane. This may be caused by the poor compatibility between P(VDF-co-CTFE) and PVDF. However, the membranes with addition of PVP appeared to have more significant effect on the mechanical strength, attributed to the more porous membranes formed, as discussed earlier. The results were in accordance to the observations of the SEM graphs in Figure 3, which shows that membranes M5–M8 (G5–G8) had more finger-like pores than membranes without PVP. The mechanical properties are summarized in Figure 7. Overall, the hydrophilicity and oleophobicity of the modified membranes were improved as compared to those of the original base membranes. This is because of the introduction of the triblock copolymer on the membrane surface, and the copolymer has both hydrophilic (PMAA) and oleophobic (fPEG) segments. Higher ratio of P(VDF-co-CTFE) in the original base membranes led to larger amount of the copolymer to be grafted; therefore, greater improvement in the hydrophilic and oleophobic property could be observed. The addition of PVP in the original blend mixture helped improve the membrane hydrophilicity. It caused the surface modification reaction to occur as much as possible; thus, more triblock copolymer was grafted onto the membranes as compared to the membranes without PVP. The reported WCA of pure PVDF membrane was ~96° and the OCA was ~15° (in air). In this work, the first blended PVDF with P(VDF-co-CTFE) in the ratio of 6:4 (M8) gave WCA of 81.6 ± 1.35° and underwater OCA of 114.0 ± 2.26°. Then, after surface-grafting modification, the modified membrane G8 showed the lowest WCA (63.7 ± 0.6°) and the highest underwater OCA (129.7 ± 1.81°). It means that the PVDF surface hydrophilicity and oleophobicity were greatly improved by using such blending–surface-grafting modification.

Furthermore, the dynamic water contact angles of modified membranes (G1–G8) were also tested. As shown in Figure 8a, the WCAs of all the grafted membranes dropped along with the contact time. With the addition of PVP, the WCAs of membranes G5–G8 dropped more rapidly and quickly, becoming zero in less than 22 min. Especially, membrane G8, which was modified from the original blended mixture of PVDF/P(VDF-co-CTFE) in 6:4 and 5 wt % of PVP, showed the best water affinity. The WCA decreased from 63.7 to 0° within only 9 min. Because of the highest content of P(VDF-co-CTFE) added in the blend mixture of PVDF/P(VDF-co-CTFE) at 6:4 offered the most amount of starting material for the surface-grafting modification, more triblock copolymer that is both hydrophilic and oleophobic could therefore be introduced to the membrane surface.

Figure 8b shows a comparison between the unmodified base membrane M8 and the modified membrane G8. The starting WCA of G8 (63.7°) was lower than that of M8 (81.6°), and the WCA of G8 dropped much faster than that of M8. This can further indicate that the surface-grafted triblock copolymer greatly improved the membrane surface wettability.
2.5. Membrane Antifouling Performance. The antifouling performances of the four modified membranes G5–G8 were evaluated by the filtrations of bovine serum albumin (BSA) solution and oil/water emulsion under the same filtration conditions. Besides, one of the unmodified membranes, M8, which has the highest content of P(VDF-co-
CTFE) (PVDF/P(VDF-co-CTFE) = 6:4) and PVP, was also chosen to test for the filtration experiments. Figure 9 shows the relative flux decays (RFDs) of the prepared membranes during the filtration of BSA solution and oil/water emulsion. Other related data are summarized in Tables 4 and 5.

As shown in Figure 9a and Table 4, the initial pure water fluxes ($J_w$) of M8, G5–G8 membranes were at 337.7, 377.3, 268.2, 241.7, and 221.1 L m$^{-2}$ h$^{-1}$, respectively. The flux difference between the original unmodified membrane M8 and the modified membrane G8 can be explained by the surface pores blocking caused by surface grafting (the reason for the water flux decline from G5 to G8 has been discussed in previous Section 3.2).

Although the unmodified membrane M8 showed a very high water flux at the beginning, the permeation flux dropped most quickly during the 120 min filtration of the BSA solution. The performance showed that the relative flux decay (RFD) reached 83.1%, the relative flux recovery (RFR) was only 43.0%, and the BSA retention rate was very low (28.8%). After the surface modification, the modified membrane G8 showed the smallest flux decay (62.7% RFD), the highest RFR (89.3%), and a much improved BSA retention rate (at 69.4%). Among the various modified membranes, from G5 to G8, the membranes with more grafted triblock copolymer exhibited a much slower flux decay, a higher RFR, and a greater BSA retention. It indicated that the introduction of the functional triblock copolymer on the membrane surface can indeed enhance the antifouling effects to the proteins.

During the filtration of oil/water emulsions, a similar phenomenon was observed in Figure 9b. The separation efficiency of the oil/water emulsion followed the trend: G8 > G7 > G6 > G5 > M8. That is to say, the more functional copolymer on the PVDF membrane surface, the better the filtration results obtained for the membranes. As shown in Table 5, the original unmodified membrane M8 gave the smallest oil retention (30.4%), the highest RFD (78.8%), and the lowest RFR (51.8%). However, after the modification of M8 to G8, the oil/water separation property was dramatically improved. The G8 membrane gave the greatest oil retention (98.6%), the lowest RFD (58.3%), and the highest RFR (92.7%). The other modified membranes G5, G6, and G7 also had a good oil retention of 86.8, 97.8, and even 98.9%, respectively. All these results support the antifouling improvements of the modified membranes, which was grafted with the functional copolymers that had both hydrophilic and oleophobic segments within their molecular structure.

A second cycle of the oil/water filtration was also carried out for each type of membrane after a 10 min ultrasonic cleaning of the used membrane in previous run. Their oil retention rates were found to be slightly decreased, but still maintained at a good level, for example, G7 at 98.0% and G8 at 97.3%, as shown in Table 5.

The modified membranes in this paper showed a good antifouling performance, especially in the oil/water emulsion separations. Figure 10 shows the oil retention and the permeation fluxes of the membrane G8 in five repeated filtration cycles. Although the permeation flux after 2 h filtration ($J_o$) declined in each cycle, the stable pure water flux ($J_w$) was maintained at a similar level after a simple water clean up, and, the oil retention was still maintained at as high as 96.2% after the five times of reuse. The visual effect of the oil/water emulsion separation by the membrane G8 is showed in Figure 11.

### Table 5. RFD, RFR, and Retention in Oil/Water Emulsion Filtration

| membrane | $J_w$ (L m$^{-2}$ h$^{-1}$) | $J_o$ (L m$^{-2}$ h$^{-1}$) | $J_r$ (L m$^{-2}$ h$^{-1}$) | RFD (%) | RFR (%) | cycle 1 | cycle 2 |
|----------|-----------------|-----------------|-----------------|---------|---------|---------|---------|
| M8       | 343.0           | 72.6            | 177.6           | 78.8    | 51.8    | 30.4    | 22.6    |
| G5       | 380.2           | 94.3            | 262.3           | 75.2    | 69.0    | 86.8    | 83.9    |
| G6       | 266.4           | 73.0            | 215.2           | 72.6    | 80.8    | 97.8    | 95.8    |
| G7       | 244.6           | 69.0            | 218.1           | 71.8    | 89.2    | 98.9    | 98.0    |
| G8       | 219.3           | 91.4            | 203.4           | 58.3    | 92.7    | 98.6    | 97.3    |

The visual effect of the oil/water emulsion separation by the membrane G8 is showed in Figure 11.

### 2.6. Blending and Surface-Grafting Method versus Additive-Blending Method

The modification of PVDF membrane in this study is achieved by the blending and then surface-grafting method, which is different from the method reported by Zhu et al.,$^{22}$ who prepared the triblock copolymer...
as additive first and then blended it with PVDF to obtain the blend membrane. A brief comparison between them are summarized in Table 6. The results indicated that both membranes modified in different ways showed quite similar antifouling properties. The BSA rejection of the surface-grafted membranes (69.4%) was a little smaller than that of the blend membrane (71%), but their anti-oil fouling ability was essentially the same; the oil rejection of the surface-grafted membrane in this work (∼99%) was as high as that of the blend membrane (99%). It means that the triblock copolymer prepared from P(VDF-co-CTFE) is an excellent membrane modifier, no matter it acts as a blend additive or a surface modifier candidate.

As compared with the additive-blending method, the modified PVDF membrane surfaces with greater flexibility and similar antifouling property were achieved by using the present blending and then surface-grafting method. This blending and then surface-grafting modification also avoid the possible problem in polymer solubility when additive polymer having large and complex molecular structure was prepared and blended with the base membrane materials.

3. CONCLUSIONS

A functional triblock copolymer of P(VDF-co-CTFE)-g-PMAA-g-fPEG has been found to be effective in modifying PVDF membrane for hydrophilic and oleophobic surface property. Instead of obtaining P(VDF-co-CTFE)-g-PMAA-g-fPEG first and then blending it with PVDF base material for membrane preparation, the present work blended P(VDF-co-CTFE) with PVDF first and then surface-grafted PMAA and fPEG with P(VDF-co-CTFE) on the blend membrane to obtain the desired functional polymer structure of P(VDF-co-CTFE)-g-PMAA-g-fPEG. It was found that this approach did not encounter the problem of polymer solubility for the large and complex additive of P(VDF-co-CTFE)-g-PMAA-g-fPEG in the previous approach and also provided the flexibility in controlling the density of the grafted copolymer structure. The prepared PVDF membranes showed both hydrophilic and oleophobic surface properties as well as good antifouling performance. It was found that the addition of PVP into the casting solution can further improve the property of the modified PVDF membranes due to the formation of more porous membrane surface and cross-sectional structure. In general, the higher the ratio of P(VDF-co-CTFE) in the blending mixture, more triblock copolymer should be grafted onto membrane surface, which may enhance the hydrophilicity and oleophobicity of the obtained membranes. Surface grafting can reduce the membrane’s pore size and thus lower its water flux, but the membrane showing higher rejection to organic pollutants such as protein and oil, achieved a lower relative flux decay during filtration and a higher relative flux recovery after water flushing cleaning. The modified PVDF membranes were used several times in a series tests and showed consistent performance. Therefore, the novel method by blending and then surface grafting presents an excellent alternative in PVDF membrane modification by using multifunctional and large molecular polymers.

4. MATERIALS AND METHODS

4.1. Materials. Poly(vinylidene fluoride) (PVDF, Mn ca. 534 000) was purchased from Shanghai 3F New Materials; bovine serum albumin (BSA, Mn ca. 66 000) and copper(I) chloride (CuCl, 97%) were supplied by Aladdin Industrial Corporation; n-hexadecane (98.5%) was purchased from Beijing JK-Chemical; N,N,N′,N′-pentamethylethylenediamine (PMDETA, 98%), dicyclohexyl carbodiimide (DCC, 99%), poly(vinyl pyrrolidone) (PVP, Mn ca. 58 000, k29=32), sodium dihydrogen phosphate (NaH2PO4, 99%), and disodium hydrogen phosphate (Na2HPO4, 99%) were obtained from Macklin; p-toluene sulfonic acid (TSA, 98.5%) and 4-dimethylaminopyridine (DMAP, 99%) were purchased from Alfa-Aesar; perfluoroalkyl poly(ethylene glycol) (fPEG, zonyl FSN-100) fromDupont; tert-butyl methacrylate monomer (t-BMA, 98%) from Sigma-Aldrich; methanol (99.5%) from Shanghai Chemical Reagent Company; toluene (AR) from Enox; and N-methyl pyrrolidone (NMP, AR) from Tianjin Zhiyuan Chemical Reagent. All the chemicals were used as received. Deionized (DI) water (18 MΩ), purified with a Milli-Q system from Millipore, was used to prepare all the solutions as needed in the study.

4.2. Preparation of Base PVDF/P(VDF-co-CTFE) Blend Membrane. PVDF/P(VDF-co-CTFE) blend membranes were first prepared by the immersion precipitation method. A specific amount of PVP was first dissolved in NMP and stirred for 30 min, where PVP was used to adjust the porosity of the base membrane. Then, a mixture of PVDF and P(VDF-co-CTFE) in different ratios was added into the solution and mechanically stirred at 350 rpm under 80 °C for 24 h. The obtained homogeneous casting solution was allowed to stand for deaeration at room temperature for 12 h and then cast onto a clean glass plate with a casting thickness of 250 μm. The plate was immediately immersed in a deionized water bath at 60 °C for at least 2 h to completely remove the solvent and sufficiently solidify the membrane structure. Finally, the membrane was washed repeatedly with DI water and then dried naturally. The compositions of the various PVDF/P(VDF-co-CTFE) membranes prepared in this study are given in Table 1, where M1–M4 had no PVP and M5–M8 had PVP at 5 wt % in the cast solutions.

4.3. Surface-Grafting Modification on the Base Blend Membranes. The graft modification reactions on the blend PVDF membrane surface are shown in Scheme 1. The graft sites were triggered on the membrane surface through an atom transfer radical polymerization reaction from the blended P(VDF-co-CTFE) in the base membrane under a nitrogen atmosphere. For a typical modification process, the base blend membrane (M1) with a diameter of 50 mm was weighed (0.54 g) and then placed into 75 mL methanol in a 250 mL round-bottom flask. PMDETA (12.8 mg), t-BMA (55 mg), and catalytic CuCl (6.9 mg) were added into the solution and the mixture was magnetically stirred at 200 rpm under 60 °C for 4
h. After the reaction, the membrane was taken out and washed several times in methanol followed by deionized water and then vacuum dried for 24 h before the next reaction. The membranes were designated as G(1). In this reaction, poly(tert-butyl methacrylate) (P(BMA)) groups were introduced onto P(VDF-co-CTFE) in the base blend membranes M1–M8. The second step was a hydrolysis reaction for the P(BMA) groups on P(VDF-co-CTFE) to be hydrolyzed to its carboxylic acid form, i.e., poly(methyl acrylic acid) (PMAA). The G(1) membrane (0.59 g) was placed into a flask with 0.12 g TSA and 75 mL toluene. The reaction was conducted at 80 °C for 8 h. The membrane was then taken out from the flask and washed with deionized water and finally dried in vacuum. The obtained membrane was denoted as G(2). In the third step, an esterification reaction was carried out on the membrane G(2). In a flask with membrane G(2) (0.61 g) in 75 mL methanol, DCC (11 mg), DMAP (1.1 mg), and PEG (30 mg) were added. The mixture was magnetically stirred at 200 rpm at room temperature to allow the reaction to take place for 7–10 days. Finally, the membrane was washed thoroughly with deionized water and then dried in vacuum to a constant weight. The obtained membrane was the modified product in this study and used for further evaluation and filtration experiments. Therefore, correspondingly M1–M8 membranes, final membrane products G1–G8 were obtained.

4.4. Membrane Chemical Composition. An attenuated total reflection-FTIR spectrometer (ThermoFisher 6700) was used to investigate the functional groups on the membrane surface. The membrane samples were analyzed with a single high-sensitivity diamond reflection measurement crystal with a spectral range of 400–4000 cm⁻¹ and a resolution of 0.09 cm⁻¹. The surface compositions of the membranes were also analyzed by X-ray photoelectron spectroscopy (XPS) (ESCA-LAB 250xi, U.K.) using Al Kα (1486.6 eV) as the radiation source. Survey spectra were obtained over a range of 0–1201 eV.

4.5. Membrane Morphology. The morphologies of the prepared membranes were observed with a scanning electron microscope (SEM, Phenom Pro). The surfaces and cross sections of the prepared membrane samples were scanned for the SEM images with an excitation voltage of 5 kV. Atomic force microscopy (AFM, Multimode 8, Bruker) was performed using a Nanoscope V controller (Bruker) scanning probe microscope to measure the surface morphology and roughness of the membrane samples. The AFM scanning area of each membrane in this study was 20 μm x 20 μm. The porosity of the membranes was estimated from the following equation: \( \varepsilon = (m_1 - m_2)/(\rho \times A \times \delta) \times 100\% \), where \( m_1 \) and \( m_2 \) are the wet weight and dry weight (g) of the membrane sample, respectively, \( \rho \) is the density of water (g cm⁻³), \( A \) is the actual area of the membrane sample (m²), and \( \delta \) is the thickness (m) of the membrane sample.

The average surface pore sizes (\( r \)) of the prepared membrane samples were roughly estimated by the medium immersion method from the following formula:

\[
r = \sqrt{\frac{(29 - 1.75\varepsilon) \times 8\eta\delta Q}{\varepsilon \times A \times \Delta P}}
\]

where \( \varepsilon \) is the porosity (%), \( \eta \) is the viscosity of deionized water (8.9 × 10⁻⁴ Pa s), \( Q \) is the volume of water through membrane per unit time (m³ s⁻¹), and \( A \) is the actual area of membrane (m²), \( \delta \) is the membrane thickness (m), and \( \Delta P \) is the transmembrane pressure (0.1 MPa). The thicknesses of the membrane samples were determined from their corresponding SEM images, and then their cross-sectional areas were calculated.

4.6. Membrane Mechanical Strength. Tensile strengths and tensile strains at the breaks of the membrane samples were measured using an electronic tensile testing machine (Instron S944) operated at room temperature with a strain rate of 1 cm min⁻¹. For each condition used, the average value of at least three tests was reported.

4.7. Membrane Surface Wetting Properties. The surface wettability of the prepared membranes was examined with the water contact angles (WCAs) and oil contact angles (OCAs) measurements using a contact angle goniometer (ramé-hart 500). The WCAs were obtained through the static sessile drop method and OCAs of the prepared membranes were obtained by the underwater static captive bubble method. For each membrane sample, several measurements at different locations were made (at least five data for each sample were collected) and the average value of the measurements with an error less than 3° was used as the representative water or oil contact angle of the tested membranes.

4.8. Permeation and Antifouling Properties of the Membranes. The antifouling and permeation properties of the base PVDF blend membranes (M1–M8) and modified PVDF membranes (G1–G8) were tested using a dead-end filtration system with an effective filtration area of 10.18 cm². Deionized water was first passed through the membrane under a transmembrane pressure (TMP) of 0.15 MPa until a stable permeation flux was achieved over 30 min. Upon stabilization, the pressure was maintained at 0.10 MPa and the permeate flux was collected at 10 min intervals for 120 min. The collected flux was weighed to determine the average transmembrane flux of pure water \( (J_w) \) within 120 min.

Fouling tests were performed using the same equipment but a slightly different setup for flux measurement. A 1.0 L L⁻¹ BSA solution was prepared by dissolving BSA in an isotonic phosphate-buffered saline solution (formulated with sodium dihydrogen phosphate and disodium hydrogen phosphate, pH = 7.0) and pressurized at 0.10 MPa to filter through the membrane following the same procedure as above for the DI water; the flux after 120 min was recorded as \( J_{w} \). After the filtration of BSA solution was completed, the membrane was taken out and washed (ultrasonic vibration cleaning for 10 min at the vibration frequency of 40 kHz). The membrane was put back into the system and the stable pure water flux was measured again and recorded as \( J_{w} \).

The BSA retention (or rejection) rate was calculated by the equation \( R_{\text{BSA}} = (1 - C_{\text{BSA},p}/C_{\text{BSA},o}) \times 100\% \), where \( C_{\text{BSA},p} \) and \( C_{\text{BSA},o} \) represent the BSA concentrations in the permeate and feed, respectively, which were measured by a UV–vis spectrometer (Shimadzu UV3600, Japan) at the wavelengths of 280 nm. The same procedure was followed during the filtration experiments for the oil/water emulsion then repeated with the same membrane for up to five times. The relative flux recovery (RFR) was calculated by RFR = \((J_w - J_{w})/J_{w} \times 100\%\), and the relative flux recovery (RFR), indicating the extent of
the possible reversible fouling, was calculated by RFR = (Jf/J0) × 100%.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Ji, J.; Liu, F.; Hashim, N. A.; Abed, M. R. M.; Li, K. Poly(vinylidene fluoride) (PVDF) membranes for fluid separation. React. Funct. Polym. 2015, 86, 134–153.

(2) Grelot, A.; Grelier, P.; Vincet, C.; Brüss, U.; Grasmick, A. Fouling characterisation of a PVDF membrane. Desalination 2010, 250, 707–711.

(3) Kim, J. F.; Jung, J. T.; Wang, H. H.; Lee, S. Y.; Moore, T.; et al. Microporous PVDF membranes via thermally induced phase separation (TIPS) and stretching methods. J. Membr. Sci. 2016, 509, 94–104.

(4) Kang, G. D.; Cao, Y. M. Application and modification of poly(vinylidene fluoride) (PVDF) membranes-A review. J. Membr. Sci. 2014, 463, 145–165.

(5) Goh, P. S.; Lau, W. J.; Othman, M. H. D.; Ismail, A. F. Membrane fouling in desalination and its mitigation strategies. Desalination 2018, 425, 130–155.

(6) Zhao, G.; Chen, W. N. Design of poly(vinylidene fluoride)-g-p(hydroxyethyl methacrylate-co-N-isopropylacrylamide) membrane via surface modification for enhanced fouling resistance and release property. Appl. Surf. Sci. 2017, 398, 103–115.

(7) Lu, T.; Xu, X.; Liu, X.; Sun, T. Super hydrophilic PVDF based composite membrane for efficient separation of tetracycline. Chem. Eng. J. 2017, 308, 151–159.

(8) Wang, J.; Wu, Z.; Li, T.; Ye, J.; Shen, L.; She, Z.; Liu, F. Catalytic PVDF membrane for continuous reduction and separation of p-nitrophenol and methylene blue in emulsified oil solution. Chem. Eng. J. 2018, 334, 579–586.

(9) Sun, H.; Yang, X.; Zhang, Y.; Cheng, X.; Xu, Y.; Bai, Y.; Shao, L. Segregation-induced in situ hydrophobic modification of poly(vinylidene fluoride) ultrafiltration membranes via sticky poly(ethylene glycol) blending. J. Membr. Sci. 2018, 563, 22–30.

(10) Li, J. H.; Shao, X. S.; Zhou, Q.; Li, M. Z.; Zhang, Q. Q. The double effects of silver nanoparticles on the PVDF membrane: Surface hydrophilicity and antifouling performance. Appl. Surf. Sci. 2013, 265, 663–670.

(11) Asadollahi, M.; Bastani, D.; Musavi, S. A. Enhancement of surface properties and performance of reverse osmosis membranes after surface modification: A review. Desalination 2017, 420, 330–383.

(12) Yang, H. C.; Luo, J.; Lv, Y.; Shen, P.; Xu, Z. K. Surface engineering of polymer membranes via mussel-inspired chemistry. J. Membr. Sci. 2015, 483, 42–59.

(13) Paul, M.; Jons, S. D. Chemistry and fabrication of polymeric nanofiltration membranes: A review. Polymer 2016, 103, 417–456.

(14) Tang, Y. P.; Cai, T.; et al. Construction of antifouling lumen surface on a poly(vinylidene fluoride) hollow fiber membrane via a zwitterionic graft copolymerization strategy. Sep. Purif. Technol. 2017, 176, 294–305.

(15) Huang, X.; Wang, W.; Liu, Y.; Wang, H.; et al. Treatment of oily waste water by PVP grafted PVDF ultrafiltration membranes. Chem. Eng. J. 2015, 273, 421–429.

(16) Wang, J.; Wang, Z.; Liu, Y.; Wang, J.; Wang, S. Surface modification of NF membrane with zwitterionic polymer to improve anti-biofouling property. J. Membr. Sci. 2016, 514, 407–417.

(17) Shen, L.; Feng, S.; Li, J.; et al. Surface modification of polyvinylidene fluoride (PVDF) membrane via radiation grafting: novel mechanisms underlying the interesting enhanced membrane performance. Sci. Rep. 2017, 7, No. 2721.

(18) Venault, A.; Wei, T. C.; Shih, H. L.; et al. Antifouling pseudo-zwitterionic poly(vinylidene fluoride) membranes with efficient mixed-charge surface via glow dielectric barrier discharge plasma-induced copolymerization. J. Membr. Sci. 2016, 516, 13–25.

(19) Dizon, G. V.; Venault, A. Direct in-situ modification of PVDF membranes with a zwitterionic copolymer to form bi-continuous and fouling resistant membranes. J. Membr. Sci. 2018, 550, 45–58.

(20) Subramaniam, M. N.; Goh, P. S.; Lau, W. J.; Tan, Y. H.; Ng, B. C.; Ismail, A. F. Hydrophilic hollow fiber PVDF ultrafiltration membrane incorporated with titane nanotubes for decolorization of aerobically-treated palm oil mill effluent. Chem. Eng. J. 2017, 316, 101–110.

(21) Chen, W.; Su, Y.; Peng, J.; Zhao, X.; et al. Efficient wastewater treatment by membranes through constructing tunable antifouling membrane surfaces. Environ. Sci. Technol. 2011, 45, 6545–6552.

(22) Zhu, X.; Loo, H. E.; Bai, R. A novel membrane showing both hydrophilic and oleophobic surface properties and its non-fouling performances for potential water treatment applications. J. Membr. Sci. 2013, 436, 47–56.

(23) Bai, R. B.; Zhu, X. Y. A Highly Hydrophilic and Highly Oleophobic Membrane for Oil–Water Separation. WO Patent WO20121485920.

(24) Zheng, L.; Wang, J.; Li, J.; Zhang, Y.; Li, K.; Wei, Y. Preparation, evaluation and modification of PVDF-CTFE hydrophobic membrane for MD desalination application. Desalination 2017, 402, 162–172.

(25) Zheng, L.; Wang, J.; Yu, D.; Zhang, Y.; Wei, Y. Preparation of PVDF-CTFE hydrophobic membrane by non-solvent induced phase inversion: Relation between polymorphism and phase inversion. J. Membr. Sci. 2018, 550, 480–491.

(26) Rana, D.; Mandal, B. M.; Bhattacharyya, S. N. Analogue calorimetric studies of blends of poly(vinyl esters) and polycrylates. Macromolecules 1996, 29, 1579–1583.

(27) Rana, D.; Mandal, B. M.; Bhattacharyya, S. N. Analogue calorimetry of polymer blends: poly(styrene-co-acrylonitrile) and poly(phenyl acrylate) or poly(vinyl benzoate). Polymer 1996, 37, 2439–2443.

(28) Rana, D.; Mandal, B. M.; Bhattacharyya, S. N. Miscibility and phase diagrams of poly(phenyl acrylate) and poly(styrene-co-acrylonitrile) blends. Polymer 1993, 34, 1454–1459.

(29) Rana, D.; Bag, K.; Bhattacharyya, S. N.; Mandal, B. M. Miscibility of poly(styrene-co-buty1 acrylate) with poly(ethyl methacrylate): Existence of both UCST and LCST. J. Polym. Sci., Part B: Polym. Phys. 2000, 38, 369–375.

(30) Wang, J.; Dismer, F.; Hubbuch, J.; Ulbricht, M. Detailed analysis of membrane absorber pore structure and protein binding by advanced microscopy. J. Membr. Sci. 2008, 320, 456–467.

(31) Zheng, L.; Wang, J.; Wei, Y.; Zhang, Y.; Li, K.; Wu, Z. Interconnected PVDF-CTFE hydrophobic membranes for MD desalination: effect of PEGs on phase inversion process. RSC Adv. 2016, 6, 20926–20937.

(32) Zheng, L.; Wu, Z.; Wei, Y.; Zhang, Y.; Yuan, Y.; Wang, J. Preparation of PVDF-CTFE hydrophobic membranes for MD application: Effect of LiCl-based mixed additives. J. Membr. Sci. 2016, 506, 71–85.

(33) Thomas, R.; Guilen-Burrieza, E.; Arafat, H. A. Pore structure control of PVDF membranes using a 2-stage coagulation bath phase inversion process for application in membrane distillation (MD). J. Membr. Sci. 2014, 452, 470–480.
(34) Yoo, S. H.; Kim, J. H.; Jho, J. Y.; Won, J.; Yong, S. K. Influence of the addition of PVP on the morphology of asymmetric polyimide phase inversion membranes: effect of PVP molecular weight. *J. Membr. Sci.* **2004**, *236*, 203−207.

(35) Basri, H.; Ismail, A. F.; Aziz, M. Polyethersulfone (PES)-silver composite UF membrane: effect of silver loading and PVP molecular weight on membrane morphology and antibacterial activity. *Desalination* **2011**, *273*, 72−80.

(36) Yang, Q.; Liu, Y.; Li, Y. Control of protein (BSA) fouling in RO system by antiscalants. *J. Membr. Sci.* **2010**, *364*, 372−379.

(37) Cai, Y.; Chen, D.; Li, N.; Xu, Q.; Li, H.; He, J.; Lu, J. A smart membrane with antifouling capability and switchable oil wettability for high-efficiency oil/water emulsions separation. *J. Membr. Sci.* **2018**, *555*, 69−77.

(38) Wijmans, J. G.; Baaij, J. P. B.; Smolders, C. A. The mechanism of formation of microporous or skinned membranes produced by immersion precipitation. *J. Membrane Sci.* **1983**, *14*, 263−274.

(39) Lang, W. Z.; Zhang, X.; Shen, J. P.; Xu, H. P.; Xu, Z. L.; Guo, Y. J. The contrastive study of chemical treatment on the properties of PVDF/PFSA and PVDF/PVP ultrafiltration membranes. *Desalination* **2014**, *341*, 72−82.

(40) Chen, X.; He, Y.; Shi, C.; et al. Temperature- and pH-responsive membranes based on poly(vinylidene fluoride) functionalized with microgels. *J. Membr. Sci.* **2014**, *469*, 447−457.

(41) Yu, L. Y.; Shen, H. M.; Xu, Z. L. PVDF-TiO2 composite hollow fiber ultrafiltration membranes prepared by TiO2 Sol-Gel method and blending method. *J. Appl. Polym. Sci.* **2009**, *113*, 1763−1772.

(42) Zheng, X.; Guo, Z.; Tian, D.; Zhang, X.; Li, W.; Jiang, L. Underwater self-cleaning scaly fabric membrane for oily water separation. *Adv. Funct. Mater.* **2015**, *25*, 4336−4343.