Permanent Antimicrobial Poly(vinylidene fluoride) Prepared by Chemical Bonding with Poly(hexamethylene guanidine)

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ABSTRACT: Biofouling is one of the major obstacles in the application of poly(vinylidene fluoride) (PVDF) membrane in water and wastewater treatment. Developing antimicrobial PVDF could kill the attached microbe in the initial stage, thus theoretically inhibiting the formation of biofilm and delaying the occurrence of biofouling. However, the leaching of the antimicrobial component and deterioration of antimicrobial properties remain a concern. In this work, an antimicrobial PVDF (PVDF-g-AGE-PHMG) was developed by chemical bonding PVDF with poly(hexamethylene guanidine hydrochloride) (PHMG). The obtained PVDF-g-AGE-PHMG was blended with pristine PVDF to prepare an antimicrobial PVDF membrane. The results of Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) confirmed that PHMG was successfully grafted into the PVDF membrane. The morphologies, membrane porosity, water contact angles, antimicrobial properties, mechanical properties, and thermostability of the as-prepared membranes were investigated. When the content of PVDF-g-AGE-PHMG reached 10.0 wt %, the inhibition rates of both antimicrobial PVDF membrane against *Escherichia coli* and *Staphylococcus aureus* were above 99.99%. Due to the increased hydrophilicity, excellent antimicrobial activity, nonleaching of antimicrobial component, good mechanical properties, and thermostability, the as-prepared PVDF membrane has promising applications in the field of water treatment.

1. INTRODUCTION

Membrane separation technology has been playing an increasingly important role in the field of ultrafiltration, microfiltration, and reverse osmosis to address the problems related to water purification.1–9 Poly(vinylidene fluoride) (PVDF) has been widely used in the field of membrane separation due to its excellent thermal stability, chemical stability, mechanical strength, and membrane-forming properties.3–7 However, membrane biofouling during filtration processes was a serious hindrance in the application of the PVDF membrane.3 Various contaminants (bacteria, protein, polysaccharides, inorganic matters, etc.) in water were adsorbed on the surface and pores of the membrane, and then a sticky biofilm is formed with the growth and colonization of bacteria, resulting in the adsorption of more pollutants and irreversible membrane pollution.3–11

Extensive efforts have been made to develop hydrophilic membranes to prevent surface adsorption and accumulation of contaminants.12–14 Surface coating, blending, or grafting with hydrophilic poly(ethylene glycol) or zwitterionic polymer were the general methods of improving the hydrophilicity of membrane material and reducing the adsorption capacity.15–18 However, the improvement in hydrophilicity could not adequately prevent bacterial adhesion, colony and biofilm formation, and further severe fouling.19

If microbes are killed at the beginning of contacting with the membrane, then the biofilm formation can be inhibited from the start, thus delaying biofilm contamination. Therefore, various bactericidal substances (nanoparticles,20,21 graphene-based materials,22 carbon nanotubes,23 chitosan,24 quaternary ammonium compounds,25,26 guanidine antibacterial compounds,27 and so on28) have been introduced into membranes by in situ or postmodification to achieve sterilized membrane. However, the continuous release of bactericidal substances resulted in the loss of antibacterial activity as well as an environmental risk.29 Therefore, it is necessary to develop stable and long-term bactericidal membranes.

Guanidine compounds like poly(hexamethylene guanidine hydrochloride) (PHMG) have attracted extensive attention...
because of their good water solubility, excellent and broad-spectrum antibacterial effect, and nontoxicity.\textsuperscript{10–32} It is generally believed that the antibacterial mechanism of PHMG is that the cationic macromolecules will be first adsorbed on the negatively charged membrane of bacterial cells, followed by damage to the plasma membrane, resulting in the leakage of the inner components, and death of bacteria.\textsuperscript{33} Importantly, this kind of physical activity will not cause drug resistance.\textsuperscript{34,35}

In this work, a novel and efficient antimicrobial PVDF was developed. An antimicrobial PVDF-g-AGE-PHMG was first prepared through the alkali treatment of PVDF, the grafting of allyl glycidyl ether (AGE) to PVDF via radical reaction, and the chemical bonding of PHMG with the grafted PVDF. The obtained antimicrobial PVDF-g-AGE-PHMG was further blended with pristine PVDF to prepare the antimicrobial PVDF membrane. These PVDF membranes exhibited excellent and permanent antimicrobial activities against Escherichia coli and Staphylococcus aureus owing to the covalently bonded PHMG. Moreover, the introduction of polar PHMG also improved hydrophilicity.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Polyvinylidene fluoride (PVDF, $M_n = 6.80 \times 10^5$, FR904) was purchased from Shanghai 3F New Materials Technology Co., Ltd. Allyl glycidyl ether (AGE) was purchased from Shanghai Aladdin Chemistry Co., Ltd., China. Benzoyl peroxide (BPO, ≥ 99.9%) and potassium hydroxide (95%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Ethanol (≥ 99.5%) and methanol (≥ 99.5%) were purchased from Shanghai Taitan Chemical Co. Ltd. Poly(hexamethylene guanidine hydrochloride) (PHMG) with a number-average molecular weight ($M_n$) at 600 Da (tested by matrix-assisted laser desorption/ionization-time-of-flight-mass spectrometry (MALDI-TOF-MS)) was synthesized according to the previous procedure with minor modification.\textsuperscript{36} All reagents were used as received.

2.2. Synthesis of PVDF-g-AGE-PHMG. The synthetic scheme of PVDF-g-AGE-PHMG is shown in Figure 1. First, PVDF powder was immersed in 10 wt % potassium hydroxide and 0.5 wt % ethanol aqueous solution for 20 min at 60 °C to generate unsaturated carbon–carbon double bonds.\textsuperscript{37} The alkali-treated PVDF powder was collected by suction filtration, rinsed with deionized water several times until the filtrate was neutral, and then vacuum-dried at 60 °C for 24 h. Afterward, 10.0 g of alkali-treated PVDF powder was dissolved in 90.0 g of N,N-dimethylacetamide (DMAc) at 70 °C to form a homogeneous solution. After purging with nitrogen for 20 min, 0.90 g of allyl glycidyl ether (AGE), and 0.48 g of benzoyl peroxide (BPO) were added. The reaction was carried out at 80 °C with magnetic stirring for 6 h under nitrogen atmosphere. AGE was grafted onto PVDF via an additional polymerization initiated by BPO. The PVDF-g-AGE was precipitated by methanol, washed four times with deionized water, and then dried under vacuum at 60 °C for 24 h. PVDF-g-AGE was redissolved in DMAc and then 1.0 g of PHMG dissolved in 10 mL of ethanol was added drop by drop at 70 °C. The antibacterial PVDF (PVDF-g-AGE-PHMG) was obtained after 4 h reaction under constant magnetic stirring. Subsequently, PVDF-g-AGE-PHMG was precipitated by methanol, washed four times by deionized water, and then dried under vacuum at 60 °C for 24 h.

2.3. Membrane Preparation. The membranes were prepared by the method of nonsolvent-induced phase separation (NIPS).\textsuperscript{38} Briefly, as listed in Table 1, PVDF powder, PVDF-g-AGE, PVDF-g-AGE-PHMG, and DMAc were mixed under magnetic stirring at 60 °C to form a homogeneous solution, and then the solution was laid aside for 24 h to eliminate bubbles. Subsequently, the solution was cast on a glass plate and scraped off by a casting knife with a 200 μm gate height at room temperature. Afterward, the glass plate was immersed into a coagulation bath (distilled water) for at least 24 h at room temperature. The casting membrane transformed into a milky membrane via phase transition and then fell off the glass plate in the distilled water. Finally, the formed membrane was washed with deionized water under ultrasonication for 30 min and then dried in vacuum at 60 °C for 24 h.

2.4. Membrane Characterization. 2.4.1. Fourier Transform Infrared Spectroscopy (FT-IR). The FT-IR spectra of PHMG, PVDF, PVDF-A, and PVDF-P were recorded over the wavenumber range of 4000–400 cm$^{-1}$ by a Nicolet 5700 spectrometer.

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**Figure 1.** Schematic representation of the preparation of antimicrobial PVDF membrane.

**Table 1.** Composition of the Membrane Casting Solution

| samples     | PVDF-g-AGE-PHMG (g) | PVDF-g-AGE (g) | PVDF powder (g) | DMAc (g) | PVDF-g-AGE-PHMG (wt %)* |
|-------------|---------------------|----------------|----------------|----------|-------------------------|
| PVDF        | 5                   | 45             |                |          |                         |
| PVDF-A      | 5                   | 45             |                |          |                         |
| PVDF-P      | 0.5                 | 45             | 4.95           | 100.0    |                         |
| PVDF-1%     | 0.05                | 4.85           | 45             | 1.0      |                         |
| PVDF-3%     | 0.15                | 4.85           | 45             | 3.0      |                         |
| PVDF-5%     | 0.25                | 4.75           | 45             | 5.0      |                         |
| PVDF-10%    | 0.5                 | 4.50           | 45             | 10.0     |                         |
| PVDF-15%    | 0.75                | 4.25           | 45             | 15.0     |                         |

*Weight content of PVDF-g-AGE-PHMG in the antimicrobial membrane.
2.4.2. X-ray Photoelectron Spectroscopy (XPS) Analysis. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific) with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) was used to analyze the surface compositions of PVDF, PVDF-A, PVDF-P, and PVDF-10%. Survey XPS spectra were obtained by sweeping over 0–1350 eV electron binding energy with a step size of 1 eV.

2.4.3. Morphology Observations by Scanning Electron Microscopy (SEM). The surface and cross-sectional morphology of PVDF, PVDF-P, and PVDF-10% were observed by scanning electron microscopy (SEM, Hitachi S-3400 scanning electron microscope, Japan) with an accelerating voltage of 15 kV. The membranes were sprayed with gold prior to observation.

2.4.4. Membrane Porosity. The membrane porosity was measured by the dry—wet weight method. After removing the water on the surface with a piece of filter paper, the wet weight of the membrane was measured. The membrane was then dried in an oven at 60 °C until the weight reached a constant value and the dry weight of the film was measured. The average membrane weight was obtained from three repeats. The porosity (ε) of the membrane was evaluated by eq 1

$$\varepsilon = \frac{(m_0 - m_1)/\rho_w}{(m_0 - m_1)/\rho_w + m_1/\rho_p}$$  

(1)

where ε is the membrane porosity, $m_0$ is the weight of the wet membrane, $m_1$ is the weight of the dry membrane, ρw is the density of the water (0.998 g/cm³), and ρp is the density of PVDF (1.77 g/cm³).

2.4.5. Water Contact Angle. The hydrophilic property of the PVDF membranes was characterized by water contact angles measured using a contact angle instrument (Shanghai Zhongchen JC2000D3, China). Each contact angle was obtained with the average values of five measurements with a 10 µL droplet of deionized water on the membrane surface.

2.4.6. Antimicrobial Testing. The antimicrobial properties of the PVDF membranes were tested by the shaking flask method and the inhibition zone method.

The shaking flask method is a kind of quantitative test. Specifically, E. coli and S. aureus were cultured in a nutrient broth at 37 °C for 24 h and further diluted to $10^5$ CFU/mL. Then, 0.10 g of the sample was added into a glass tube with 5 mL of bacterial culture ($10^5$ CFU/mL) and shook at 250 rpm at 37 °C for 24 h. Subsequently, a series of dilutions were obtained and then 0.1 mL of each diluted solution was evenly coated on the LB agar in a Petri dish. The dishes were cultivated at 37 °C for 24 h and the number of colonies was counted. The inhibition rates of cell growth (R) were calculated from eq 2

$$R = \frac{A - B}{B} \times 100\%$$  

(2)

where A and B are the number of bacterial colonies observed in the control and membrane samples, respectively. Each sample was measured three times, and the average values of inhibition rates were calculated.

The inhibition zone method was used to characterize the leaching characteristic. Nutrient agar plates were inoculated with 0.1 mL of a solution of E. coli and S. aureus with a concentration of $10^8$ CFU/mL. Circular pieces of membranes with a diameter of 1.5 cm were placed on the agar plates. Then, these plates were cultivated at 37 °C for 24 h in an incubator before measuring the diameters of the inhibition zone.

2.4.7. Mechanical Properties. The tensile strength and elongation at the break of the PVDF membranes were measured with a Universal Electrical Testing Machine (CMT-2203, MTS) at a speed of 10 mm/min at 25 ± 2 °C. All of the samples were measured at least five times with a gauge length of 20 mm, and the average value was calculated.

2.4.8. Thermogravimetric Analysis. The thermal stabilities of PVDF, PVDF-A, and PVDF-P were studied using thermogravimetric analysis (TGA) (STA409PC, NETZSCH, Germany). All tests were conducted under a O2 atmosphere (20 mL/min) using sample weights of about 10 mg over a range of 40–600 °C at a rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. Characterization of Membrane Chemical Compositions. The FT-IR spectra of PHMG, PVDF, PVDF-A, and PVDF-P are displayed in Figure 2. The FT-IR spectra of PHMG, PVDF, PVDF-A, and PVDF-P show the typical characteristic peaks of the PVDF backbone. The asymmetric stretching, symmetric stretching, and deformation vibrations of CH$_2$ were located at 3022, 2980, and 1402 cm$^{-1}$, respectively. The peak at 1180 cm$^{-1}$ belonged to the stretching vibration of CF$_2$. In the spectrum of PHMG, the peaks at 3349 and 3182 cm$^{-1}$ were attributed to the asymmetric and symmetric stretchings of NH$_2$, respectively, 1642 cm$^{-1}$ represented the guanidine group and 2851 cm$^{-1}$ belonged to the symmetric and asymmetric
stretching vibrations of $\text{CH}_2$, respectively. Compared with PVDF, three new distinct peaks at 1642, 2851, and 2922 cm$^{-1}$ appeared on PVDF-P, which belonged to the newly bonded PHMG, indicating the successful introduction of PHMG to PVDF.

The chemical compositions on the surfaces of PVDF, PVDF-A, PVDF-P, and PVDF-10% were measured by XPS, and the results are shown in Figure 3 and Table 2. PVDF should only contain C and F elements, AGE has O element and PHMG has N element. As shown in Figure 3 and Table 2, PVDF contains F, C, and trace amounts of O and N. The O and N may be attributed to adventitious O and N elements during the XPS analysis. The signal of N could be clearly found in membranes PVDF-P and PVDF-10% (the content of N was from 0.4 to 2.2 and 2.1 atom %), which was due to the successful introduction of PHMG in these membranes. Compared to that in PVDF, the increasing content of O in PVDF-A from 2.71 to 3.25 atom % was attributed to the grafting of AGE. Combined with the results obtained by FT-IR, the successful modification of the PVDF-based membranes was demonstrated. Based on the elemental contents, the calculated content of PHMG on the surfaces of PVDF-P and PVDF-10% was about 8.75 and 7.94 wt %, respectively. During phase separation, hydrophilic substances tend to be distributed at the interface. As a result, PVDF-g-AGE-PHMG tends to be enriched on the surface. Therefore, although PVDF-10% contained only 10% PVDF-g-AGE-PHMG, the content on the PHMG surface approached that of the PVDF-P surface.

### 3.2. Morphology of Membranes

The surface and cross-sectional morphologies of PVDF, PVDF-P, and PVDF-10% are shown in Figure 4. The relatively dense surface structure could be observed on PVDF and PVDF-10%, while plenty of micropores were formed on the surface of PVDF-P. In

| elements (atom %) | sample | C  | F  | O  | N  |
|-------------------|--------|----|----|----|----|
|                  | PVDF   | 48.7| 47.0| 2.7| 0.4|
|                  | PVDF-A | 49.3| 46.9| 3.3| 0.4|
|                  | PVDF-P | 51.2| 41.1| 4.4| 2.2|
|                  | PVDF-10%| 49.4| 44.0| 3.9| 2.1|

| sample          | AGE (wt %) | PHMG (wt %) |
|-----------------|------------|-------------|
| PVDF            | 2.74       | 0.4         |
| PVDF-A          | 3.25       | 0.4         |
| PVDF-P          | 6.25       | 8.75        |
| PVDF-10%        | 4.32       | 7.94        |

Figure 4. SEM images of the surface and cross section of the samples.

Figure 5. Membrane porosity of the samples.

Figure 6. Water contact angles of the samples.
addition, these membranes exhibited a typical asymmetric cross-sectional structure, consisting of a skin layer as a selective barrier, a layer of pores, and a discrete spongy structure. The formation of this cross-sectional structure was mainly due to the high mutual diffusivity of water and DMAc. The average diameters of pores in PVDF and PVDF-P were, respectively, 33.7 and 48.2 μm. Compared to the surfaces of PVDF, there were larger pores in the cross-sectional images of PVDF-P and PVDF-10%. The membrane porosity is shown in Figure 5. The porosity of PVDF-P (75.93 ± 0.43%) was significantly higher than that of PVDF (66.04 ± 0.75%). In addition, with an increase of the PVDF-g-AGE-PHMG content, the porosity of the antibacterial PVDF membrane increased gradually. The introduction of polar PHMG groups increased the dissimilarity between PVDF-g-AGE-PHMG and PVDF, resulting in the formation of more larger pores during phase separation.

Water contact angle is an important parameter to evaluate the hydrophilicity of membranes. The contact angles data at 1 min are shown in Figure 6. Compared with that of PVDF (93.5 ± 3.8°), the water contact angle of PVDF-A (92.3 ± 4.0°) did not obviously change, while that of PVDF-P (67.4 ± 1.2°) significantly decreased. In addition, with the increase of the PVDF-g-AGE-PHMG component, the water contact angles gradually decreased. This phenomenon indicated that the improvement of hydrophilicity was due to the increase in the content of hydrophilic PHMG.

### 3.3. Antimicrobial Performance.

The typical antimicrobial photographs (10^5 CFU/mL) of PVDF, PVDF-1%, PVDF-3%, PVDF-5%, PVDF-10%, and PVDF-15% against E. coli and S. aureus are shown in Figure 7 using the shaking flask method. The pristine PVDF membrane had no capability to deactivate against E. coli and S. aureus. With the increase of PVDF-g-AGE-PHMG, the number of bacterial colonies reduced significantly. When the content of PVDF-g-AGE-PHMG reached 10 wt %, no visible colonies were observed. As shown in Table 3, the inhibition rates of PVDF-10% and PVDF-15% against E. coli and S. aureus were higher than 99.99%. To further investigate the durability of antimicrobial activity, four copies of PVDF-10% were immersed in water (80 °C), HCl solution (pH 1), KOH solution (pH 14), and NaClO solution (active chlorine ≥ 1%) for 4 h and rinsed in deionized water. As shown in Figure 8, they still exhibited excellent antibacterial properties.

| sample  | E. coli  | S. aureus |
|---------|----------|-----------|
| PVDF    | 21.50    | 22.20     |
| PVDF-1% | 16.50    | 11.00     |
| PVDF-3% | 7.40     | 4.10      |
| PVDF-5% | 2.02     | 5.70      |
| PVDF-10%| 0        | 0         |
| PVDF-15%| 0        | 0         |

3%, PVDF-5%, PVDF-10%, and PVDF-15% against E. coli and S. aureus are shown in Figure 7 using the shaking flask method. The pristine PVDF membrane had no capability to deactivate against E. coli and S. aureus. With the increase of PVDF-g-AGE-PHMG, the number of bacterial colonies reduced significantly. When the content of PVDF-g-AGE-PHMG reached 10 wt %, no visible colonies were observed. As shown in Table 3, the inhibition rates of PVDF-10% and PVDF-15% against E. coli and S. aureus were higher than 99.99%. To further investigate the durability of antimicrobial activity, four copies of PVDF-10% were immersed in water (80 °C), HCl solution (pH 1), KOH solution (pH 14), and NaClO solution (active chlorine ≥ 1%) for 4 h and rinsed in deionized water. As shown in Figure 8, they still exhibited excellent antibacterial properties.
Moreover, the results of the inhibition zone method (Figure 9) displayed that no inhibition zone was observed for these membranes. The results indicate that PHMG was firmly fixed on PVDF. Therefore, PVDF with nonleaching, long-term, and excellent antimicrobial properties will be expected to be applied in the field of water treatment without the risk of introducing an antibacterial agent into the water.

### 3.4. Mechanical Properties and Thermostability

The mechanical properties of the membranes are shown in Figure 10. The tensile strength of PVDF was 7.9 ± 0.3 MPa, while the tensile strengths of PVDF-A and PVDF-P were 4.6 ± 0.3 and 2.0 ± 0.2 MPa, respectively. The elongation at the break of PVDF-P was also decreased from 208.8 ± 22.3% (PVDF) to 59.4 ± 13.3%. The significant decrease of the tensile strengths of PVDF-A and PVDF-P was caused by the influence of alkali treatment and the increase of porosity. When PVDF-g-AGE-PHMG was blended with PVDF, the tensile strength and elongation at the break of the composite membranes gradually decreased as the ratio of PVDF-g-AGE-PHMG increased. The thermal stability was also examined. As shown in Figure 11, there was little difference among antimicrobial modified samples (PVDF-A and PVDF-P) and pure PVDF. Therefore, the introduction of PHMG has little impact on the thermostability of PVDF.

### 4. CONCLUSIONS

In this work, the synthesis of antimicrobial PVDF and its application in PVDF membranes were systematically investigated. FT-IR and XPS spectra results confirmed that PHMG was successfully grafted onto PVDF macromolecular chains. When the content of PVDF-g-AGE-PHMG reached 10.0 wt %, the inhibition rates of antimicrobial PVDF membrane against *E. coli* and *S. aureus* were both above 99.99%. Due to the increased hydrophilicity, excellent antimicrobial activity, non-leaching of antimicrobial component, good mechanical properties, and thermostability, the as-prepared PVDF membrane has promising applications in the field of water treatment.

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**Figure 10.** Tensile strength and elongation at the break of PVDF, PVDF-A, PVDF-P, PVDF-1%, PVDF-3%, PVDF-5%, PVDF-10%, and PVDF-15%.

**Figure 11.** TG (a) and derivative TG (DTG) (b) curves of PVDF, PVDF-A, and PVDF-P.
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Notes
The authors declare no competing financial interest.

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