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Preparation and characterization of amphiphilic copolymer PVDF-g-PMABS and its application in improving hydrophilicity and protein fouling resistance of PVDF membrane

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ABSTRACT

A facile strategy to improve the hydrophilicity and the antifouling properties of poly(vinylidene fluoride) (PVDF) membranes, a functional monomer of 4-methacrylamidobenzenesulfonic acid (MABS), was designed and synthesized through the amidation reaction between 2-methylacryloyl chloride and sulfanilic acid. Utilizing PVDF and the obtained MABS as reaction monomers, a novel amphiphilic copolymer was firstly prepared by radical polymerization method. The resulting PVDF-g-PMABS was used as a hydrophilic additive in the fabrication of PVDF porous membranes via immersion precipitation process. The surface chemical compositions and structure morphologies of as-prepared blend membranes (PVDF-g-PMABS/PVDF) were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. Contact angle measurement and cross-flow permeation test were employed to evaluate the hydrophilicity and antifouling properties of the membranes. It was found that the blend membrane with 4 wt.% PVDF-g-PMABS exhibited a noticeable pure water flux (136.34 $\mathrm{L\,m^{-2}\,h^{-1}}$) and a remarkable flux recovery ratio (FRR) of 98.60% in comparison with the pristine PVDF membrane (63.37 $\mathrm{L\,m^{-2}\,h^{-1}}$ and 38.67%, respectively). The enhanced performance was attributed to the synergetic effects of the strong hydrogen bonding force and the electrostatic repulsion of sulfonic groups against the protein foulants.

1. Introduction

PVDF membranes have been extensively applied in distillation, ion exchange, pervaporation, ultrafiltration, and microfiltration owing to its excellent chemical resistance, good thermal stability and high mechanical strength [1–4]. Nevertheless, the intrinsic hydrophobic property of PVDF membranes results in low water permeability and severe membrane fouling when treating an aqueous solution containing organic, colloidal matters, and biological substances, which are susceptible to adsorption and deposition onto the membrane surface, blocking the surface pores [5,6]. This inevitably depresses the lifetime of the membrane and subsequently leads to more operation cost of replacement [7–11].

As aforementioned drawbacks of PVDF membranes, it is generally accepted that an increase in hydrophilicity offers better membrane fouling resistance, which can prevent the adsorption and deposition of hydrophobic pollutants onto the membrane surface. Therefore, many studies of PVDF membranes have been carried out such as physical blending [12–14], surface coating and chemical grafting [15–19] to improve the hydrophilicity of PVDF membranes.

In various modification approaches, the incorporation of nanomaterials to impart the antifouling property of the membrane has attracted increasing attention because of the facile processing and predictable separation performance [20,21]. The nanomaterials used include titanium dioxide [22,23], silicon dioxide [24], aluminum oxide [25] and carbon nanotubes [26,27], etc. Unfortunately, the improvement in membrane hydrophilicity and resistance to membrane fouling is limited on account of the poor dispersibility and the entire encapsulation by polymer matrix, which significantly decreases the modification efficiency.

The antifouling performance of PVDF membranes can also be promoted by blending hydrophilic polymers, including polyvinyl pyrrolidone [28], polyethylene glycol derivatives [29], polyvinyl

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alcohol [30], polyarylonitrile [31], etc. It should be noted that these polymers are preferably water soluble, or else they will be washed out of the matrix during membrane formation and subsequent operation. More importantly, it is hard to obtain uniform blend membranes for the poor compatibility of hydrophilic polymers with hydrophobic PVDF.

To solve this problems, researchers developed amphiphilic copolymers as modifiers. The appropriate amphiphilic additives possess hydrophilic moieties and hydrophobic groups totally insoluble in water, able to interact with hydrophobic membrane polymers [32]. The hydrophobic chains guarantee the compatibility with PVDF, while the hydrophilic chains will enrich onto the membrane/pore surface during phase separation process due to segregation effect, providing a high coverage of hydrated side chains anchored by a hydrophobic backbone that is water insoluble and entangled with the PVDF bulk [3]. Zhu et al. prepared an amphiphilic PVDF-based membrane by blending hyperbranched-star Polymer, which exhibited high water flux and better fouling resistance [33]. Chen et al. reported that acryloylmorpholine-grafted PVDF, as an amphiphilic copolymer, was cast into PVDF matrix to enhance the hydrophilicity, water flux and resistance of protein adsorption of PVDF membranes [4]. Most previous reports on amphiphilic copolymer as an additive focused on the hydrophilic modification of PVDF membranes. However, few investigations have been performed regarding the incorporation of sulfonic acid-functioned amphiphilic copolymer into the PVDF membrane to improve the antifouling properties by the couping effect of enhanced hydrophilicity and negatively charged surface.

In this work, a novel amphiphilic copolymer PVDF-g-PMABS was firstly synthesized by radical polymerization method and analyzed by Fourier transform infrared (FT-IR) spectroscopy and nuclear magnetic resonance (^{1}H NMR) spectroscopy. The resulting PVDF-g-PMABS as a hydrophilic additive was introduced in PVDF matrix to fabricate porous PVDF-g-PMABS/PVDF bolend membranes via phase inversion process. The permeation and antifouling properties of the PVDF-g-PMABS/PVDF blend membranes were evaluated using bovine serum albumin (BSA) as a model protein. Owing to the existence of sulfonate groups in the side chains of copolymer PVDF-g-PMABS, the blend membranes were endowed the enhanced hydrophilicity and negatively charged surface, which results in reduced fouling along with high water flux. The highly effective antifouling property imparts the amphiphilic PVDF-based membranes with potential application in protein separation and medical purification.

2. Materials and methods

2.1. Materials

PVDF powder (solef 1015) was purchased from Solvey Company of Belgium. Bovine serum albumin (BSA, Mn = 68,000 Da), 2-methylacryloyl chloride, sulfanilic acid and 2,2′-azobisisobutyronitrile (AIBN, 99%) were supplied from Aladdin (China). *N*,*N*-dimethylacetamide (DMAc) and 1-Methyl-2-pyrrolidinone (NMP) were provided by Tianjin Yongda Chemical Co., Ltd. The phosphate-buffered saline (PBS, 0.1 mol L^{-1}, pH = 7.4) was prepared by the addition of prepackaged buffer salts (Aldrich) to deionized water. All other chemicals were analytic reagent and used as received. Water used in all experiments was deionized water.

2.2. Synthesis of MABS monomer and PVDF-g-PMABS copolymer

4-Methacrylamidobenzenesulfonic acid was synthesized according to the procedure previously reported in the literature [34]. Firstly, sulfanilic acid (0.05 mol) was dissolved in a 50 mL sodium bicarbonate aqueous solution (2 mol L^{-1}), and then an equivalent amount of 2-methylacryloyl chloride was added dropwise during 15 min with vigorous stirring in an ice bath. The reaction was further kept at room temperature for another 12 h. After washing with hot water to remove traces of carboxylic acid created during the reaction, the corresponding product (MABS) was obtained by the usual acidic workup from the sodium salt.

Table 1
Composition of casting solution.

Membrane	PVDF (wt%)	PVDF-g-PMABS (wt%)	DMAC (wt%)
M0	15.0	0	85
M1	14.5	0.5	85
M2	13.5	1.5	85
M3	12.5	2.5	85
M4	11.5	3.5	85

Amphiphilic copolymer PVDF-g-PMABS was prepared by radical polymerization process. PVDF powder was first treated with 10 wt.% KOH aqueous solution for 10 min at 60 °C. The resultant precipitate was collected by filtration and then washed with deionized water until the pH became neutral. After dissolving 6.0 g the alkaline-treated PVDF into 100 mL distilled NMP under magnetic stirring at 70 °C, MABS (3.0 g) and AIBN (0.1 g) were subsequently added under N_2 atmosphere. Continuing to keep the solution at 70 °C for 12 h, the copolymer was precipitated in methanol, which was collected by filtration and washing with deionized water.

The chemical structure of the copolymer was analyzed by Fourier transform infrared (FT-IR) spectroscopy (Nicolet Avatar 370, American). To inspect the chemical composition of the copolymer, nuclear magnetic resonance (^{1}H NMR) proton spectroscopy was performed on a NMR spectrometer (400 MHz, Bruker Avance III, Germany) with deuterated dimethyl sulfoxide (DMSO) as the solvent.

2.3. Preparation of membranes

The PVDF-g-PMABS/PVDF blend membranes were fabricated via the immersed phase inversion method, and the compositions of the casting solution were illustrated in Table 1. The typical fabrication process is as follows. To begin with, corresponding amounts of PVDF and PVDF-g-PMABS were dissolved into DMAc to form a homogeneous solution at 60 °C. After releasing the bubbles in reduced pressure, the homogeneous solution was uniformly cast onto a polyethylene terephthalate (PET, NSR-80) non-woven fabric support that was fixed on a glass plate. The thickness of membranes was controlled at 150 μm by an automatic film applicator cast-knife. Subsequently, it was immediately immersed into a deionized water bath with a temperature of 35 °C. The nascent membrane was washed until the residual solvent was completely removed. Membranes prepared with different PVDF-g-PMABS contents of 0.0, 0.5, 1.5, 2.5 and 3.5 wt.% hereinafter are referred to as M0, M1, M2, M3 and M4, respectively.

2.4. Characterizations of membranes

The chemical compositions of membrane surface were investigated using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet Avatar 370, USA) and X-ray photoelectron spectroscopy (XPS, VG K-Alpha instrument, with a Al Kα X–ray source (1486.6 eV) and pass energy of 50 eV operating at a pressure of 7×10^{-10} Torr, England). Field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800, Japan) was employed to characterize membrane morphological structure. The cross-section samples were prepared by membrane fractured in