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Forming mechanism study of unique pillar-like and defect-free PVDF ultrafiltration membranes with high flux



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ABSTRACT

An intriguing polyvinylidene fluoride (PVDF) membrane with unique pillar-like structures was synthesized. The membrane was synthesized using the phase inversion method by adding the amphiphilic graft copolymer PVDF grafted with poly(ethylene glycol) methyl ether methacrylate (PEGMA) (PVDF-g-PEGMA) to the PVDF backbone material. It had high flux and high sodium alginate rejection ratio under low transmembrane pressure. However, the mechanisms for the formation of pillar-like structures are still unknown. In this paper, we explored the formation mechanism of pillar-like structures from aspects of solvent and additive. Based on the experimental results and analysis of ternary diagram, both NMP and PVDF-g-PEGMA must coexist in casting solution to form pillar-like structures. When NMP is in the solvent, PEGMA segments have enough time to migrate to the surface and repel each other during the phase inversion process. Finally, by using the target plot method, one membrane with the best performance was chosen as the proposed membrane from all membranes that casted under different conditions. The proposed membrane has a pure water flux of 2173 L/m²/h/bar. The total organic carbon (TOC, by sodium alginate) removal efficiency is 89%. This membrane may have a good potential in water treatment applications.

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1. Introduction

Common polymers used to prepare membranes include polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyethersulfone (PES), polypropylene (PP), polyvinyl chloride (PVC), and polysulfone (PSF) [1–7]. In recent years, PVDF membranes have been used in many applications owing to their good physical and chemical resistance properties [8–11]. Several methods have been employed to increase the hydrophilicity and fouling resistance of PVDF membranes. These methods include surface coating [12], surface grafting [13,14], and blending with amphiphilic copolymers [15,16]. However, surface coating and surface grafting have several disadvantages. For instance, surface coating uses physical adsorption to coat on the membrane a thin layer of water-soluble polymers or surfactants from a solution. The coating is usually unstable and can be washed away during operation of the membrane. To introduce functional groups on the membrane surface, surface grafting requires an extra step to introduce

functional groups on the membrane surface which makes surface grafting inapplicable to large-scale industrial manufacture [17–19]. Blending amphiphilic copolymers synthesizes a hydrophilic and anti-fouling membrane in a single-step, which has potential for production at industrial scale. In this method, amphiphilic copolymers with both hydrophilic and hydrophobic segments are blended with the casting solutions during the membrane synthesis process. Hydrophobic segments in the copolymer can physically combine with the membrane backbone matrix, whereas hydrophilic segments can increase the membrane's hydrophilicity [15,20]. Several amphiphilic copolymers have been successfully applied in the casting process to improve the hydrophilicity of the membranes [12,17,21–26]. PEGylated or PEG-based functionalities incorporating poly(ethylene glycol) methyl ether methacrylate (PEGMA) have been added to PVDF membranes, and these membranes show good hydrophilicity and high resistance to fouling, as demonstrated in several previous studies [27–29]. Therefore, PEGMA was selected as the hydrophilic grafting segment in this study.

Overall, the purpose of this study is to understand the formation mechanism of pillar-like structures. It is essential to understand the reason of forming pillar-like structures since it will not only guide us

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on how to improve the performance of current prepared membrane but it will also help us to make the whole casting process more feasible for a larger-scale production. Therefore, we continued our previous research [30] on producing defect-free high-performance PVDF membranes with pillar-like structures. The outstanding characteristics of these membranes, such as high flux and sodium alginate (SA) removal efficiency, are attributed to narrow pore size distribution, high surface porosity, and the unique surface feature of approximately 200 nm between each pillar-like structure. All the pores are distributed in the spaces between pillar-like structures, which mean that surface pore diameters on membranes are less than 200 nm. The absence of large pores indicates that the membrane is defect-free. In addition, the PVDF membranes we produced had up to 15% surface porosity, much higher than other PVDF membranes described in the literature (up to 4.8%) [16]. To study formation mechanism of pillar-like structure from solvent aspect, we changed the solvent from a mixture of N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) to pure DMF and then to pure 1-methyl-2-pyrrolidinone (NMP). We also used ternary phase diagram to verify the effect of solvent. Regarding additives for membrane synthesis, we first used a copolymer solution containing impurities as an exploratory test, and then changed to a purified copolymer powder. Furthermore, we added additional NMP or PEGMA to the casting solution to simulate the use of copolymer solution in the casting process in order to reconfirm the influence of NMP and PEGMA. The cast PVDF membranes were characterized by scanning electron microscopy (SEM) for morphology, X-ray photoelectron spectroscopy (XPS) for surface composition of membrane, contact angle measurement for hydrophilicity, Fourier transform infrared attenuated reflection spectroscopy (FTIR-ATR) for the presence of PVDF-g-PEGMA, and atomic force microscopy (AFM) for roughness and adhesive force. The performance of the membranes, including permeation flux and sodium alginate (SA) rejection, was also studied. Finally, the target plot method was used to help us choose the membrane with the best performance from all casted membranes.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF, approximately 534,000 g/mol in M_w), poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n=475$ g/mol), copper (I) chloride (CuCl), 4-4'-dimethyl-2-2'-dipyridyl (DMDP), silicone oil, 1-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), hydrochloric acid (HCl), petroleum ether, methanol and sodium alginate (SA) were purchased from Sigma-Aldrich, USA. All solvents and chemicals were reagent grade, and all reagents were used as received.

2.2. Model foulant

SA was purchased from Sigma-Aldrich (USA) for use as a model compound for extracellular polymeric substances (EPS) [31]. The SA stock solution was prepared in a flask by adding SA to deionized water and mixing until completely dissolved. The SA stock solution of 2 g/L was stored at 4 °C for future use. In all fouling experiments, the SA concentrations were determined using a Shimadzu total organic carbon (TOC) analyzer (Shimadzu Co., Japan).

2.3. Synthesis of graft copolymer PVDF-g-PEGMA

The steps used to synthesize the copolymer PVDF-g-PEGMA were similar to those previously published [22,25]. First, 5 g of PVDF was dissolved in 40 mL of NMP in a conical flask at 50 °C for

24 h and stirred using a magnetic stirrer. PEGMA (50 mL), the catalyst CuCl (0.04 g), and the initiator DMDP (0.23 g) were added to the flask after the solution was cooled to room temperature. A rubber septum was used to seal the flask, and nitrogen gas was bubbled through the solution for 30 min and stirred using a magnetic stirrer. Then the flask was put in a silicon oil bath at 90 °C for 19 h and stirred using a magnetic stirrer. The copolymer mixture was at that point ready to use for the exploratory test. The copolymer mixture contained NMP, unreacted PEGMA, CuCl, and the initiator DMDP. The amount of copolymer present in the mixture was calculated on the basis of 20% PEGMA conversion ratio [22,25,32]. To purify the copolymer mixture for the second set of synthesis, a mixture of 0.1 mL of HCl, 1 part petroleum ether, and 1 part methanol was used to precipitate the graft copolymer followed by a filtration process. The recovered polymer was redissolved in NMP and reprecipitated in petroleum ether/methanol repetitively for three times. Finally, the polymer was dried under vacuum for 12 h at 25 °C for future use [25]. Detailed characterizations of PVDF-g-PEGMA can be found in other studies [12,25]. The copolymer mixture and the purified polymer were both used as additives in this research.

2.4. Preparation of PVDF membranes

The casting solutions were prepared in 125 mL conical flasks while heating at 60 °C and stirring at 500 rpm (Corning, USA). After 24 h of heating and mixing, the casting solutions were degassed without mixing for at least 2 h until no gas bubbles were observed. A doctor blade (Universal blade applicator, Paul N. Gardner Company, Inc., Pompano Beach, FL) with a gate height of 200 μ m was used to cast the solution on a first-grade surface optical mirror. The mirror was left in air for 10 s before it was immersed for 48 h in a 25 °C coagulation bath that contained deionized water. The cast membranes were then air dried for 24 h. Membranes were prepared from casting solutions according to the compositions listed in Table 1.

2.5. Membrane characterization

2.5.1. Membrane morphology

The morphology of the membrane surface was examined with SEM (Zeiss Ultra 60; Carl Zeiss NTS, USA). Membranes were positioned on stubs with carbon dots and then sputter coated with \sim 2 nm gold layer before imaging. An acceleration voltage of 5 kV was used to examine coated samples at different magnifications. Average pore diameter ($D_{average}$), maximum observed pore diameter (D_{max}), pore density, and surface porosity (ϵ) were obtained from SEM images using the Image-Pro Plus 7.0 (Media Cybernetics, USA). The surface porosity was defined as the ratio between the total area enclosed by pores and that of the entire area.

2.5.2. Determination of the cloud point

Cloud point data were measured by the titration method. The solution to be titrated was prepared in a sealable bottle and kept stirring at 60 °C. Non-solvent (DI water) was slowly added into the solution until the polymer solution became irreversibly turbid as detected visually [33].

2.5.3. X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha XPS system) was used to study the near-surface compositions of PVDF membrane to a depth of less than 5 nm. Survey spectra were collected over 0–1350 eV, and high-resolution scan with a resolution of 0.1 eV was also collected.

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