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Effect of surface properties on antifouling performance of poly(vinyl chloride-*co*-poly(ethylene glycol)methyl ether methacrylate)/PVC blend membrane

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ABSTRACT

Several membranes with low fouling properties were prepared by blending PVC with poly(vinyl chloride-*co*-poly(ethylene glycol) methyl ether methacrylate) (poly(VC-*co*-PEGMA)) copolymer via a non-solvent induced phase separation (NIPS) method. Bovine serum albumin adsorption on polymer films decreased and the membrane surface pore sizes, hydrophilicities, and antifouling properties increased on increasing the poly(VC-*co*-PEGMA)/PVC blending ratio. Membrane surface PEGMA coverage increased on increasing the poly(VC-*co*-PEGMA)/PVC blending ratio, resulting in higher hydrophilicities and lower fouling propensities. Membranes with similar water permeabilities were prepared by adjusting the dope solution composition to eliminate the effect of hydrodynamic conditions on membrane fouling performance. The effect of the membrane material on the membrane fouling propensity was much stronger than that of the membrane surface structure. Molecular dynamics simulations were performed to evaluate the surface chemical composition of the membrane matrix and results were compared with results obtained from XPS measurements.

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1. Introduction

Microfiltration (MF) membrane separation is one of the most promising separation technologies and has been widely used for the treatment of water and wastewater. Several polymers have been used for membrane preparation such as polyvinylidene difluoride (PVDF), polysulfone (PSf), polyacrylonitrile (PAN), and poly(ethersulfone) [1]. Poly(vinyl chloride) (PVC) is an alternative material for membrane preparation. Primarily, this is because of its excellent mechanical strength, high resistance to corrosion, and low cost [2–4]. However, the hydrophobic nature of PVC causes foulants to adsorb to the membrane surface as well as inside the membrane pores, resulting in a sharp decline in the water flux during filtration: this is membrane fouling [5]. Membrane fouling can be effectively inhibited by increasing the membrane surface hydrophilicity [6]. Therefore, several surface modification methods have been explored to improve the fouling resistance of PVC membranes, including blending [7–11], surface coating [12–14], and surface grafting [15–19]. Although both surface coating and grafting are effective methods to inhibit membrane fouling, they usually involve an extra step in membrane preparation and modify only the outer surface of the membrane and not the internal pore walls. Polymer blending is a convenient and versatile approach to

improve both the membrane surface and internal pore walls by giving them desirable antifouling properties. Babu et al. prepared PVC/carboxylated poly(vinyl chloride) (CPVC) [20] and PVC/polyvinyl pyrrolidone (PVP) [21] flat-sheet blended membranes and evaluated the effects of the filtration conditions on the membrane fouling performance. However, the effect of the membrane material was not assessed. Fan et al. [7] investigated PVC/polyvinyl formal (PVF) blend flat-sheet, ultrafiltration membranes and found that the segregation of the PVF component on the membrane surface increased the hydrophilicity and antifouling properties of the film. However, although blending PVC with hydrophilic copolymers is a promising approach, the compatibility of PVC/PAN [22], PVC/cellulose acetate (CA) [23], and PVC/polystyrene [24] blends is low, resulting in the formation of heterogeneous dope solution.

The blending of PVC membranes with amphiphilic copolymers has been investigated in several studies [9,25,26]. The hydrophilic segments of the amphiphilic copolymer segregate on the membrane surface, making the membrane hydrophilic with good fouling resistance. Also, the hydrophobic segment provides compatibility with the membrane matrix and improves copolymer retention in the membrane matrix. For example, copolymers containing PEG chains can easily form a hydration layer, which is resistant to foulant adsorption [9,27]. Liu et al. [9] prepared membranes with superior antifouling properties by blending a commercial poly(ethylene oxide) (PEO) based amphiphilic copolymer (Pluronic F-127) with PVC. They found that both the antifouling properties and water permeabilities of the prepared membranes improved on increasing the copolymer concentration, and this effect continued up to 8 wt%; however, further increases in the copolymer concentration led to a decrease in the water permeability. In another study, Liu et al. [25] improved the antifouling properties of a PVC/chlorinated polyvinyl chloride (CPVC) blend membrane by adding Pluronic F-127. They found that, after addition of the copolymer, the resultant membrane had higher pure water permeability. Furthermore, the membrane demonstrated almost complete flux recovery on washing after solution filtration of a 1000 ppm BSA (bovine serum albumin) solution. Jiang et al. blended poly(ether sulfone-g-poly(ethylene glycol) methyl ether methacrylate))(PES-g-PEGMA) with PVC, yielding PVC/PES-g-PEGMA blend membranes. They reported that, when the PVC/copolymer blend ratio was 7:3, the blend membrane showed considerable antifouling properties [26]. Although in these studies membranes with appropriate antifouling properties were obtained, membranes with different initial fluxes and water permeabilities were used for the comparison of the antifouling properties. Because the membrane water permeability influences the fouling properties [28,29], it is difficult to isolate the effect of the membrane material on the fouling properties.

In our previous study, poly(vinyl chloride-co-poly(ethylene glycol)methyl ether methacrylate) (poly(VC-co-PEGMA)) blends containing different PEGMA percentages were used to prepare microfiltration membranes, and the effect of the PEGMA segment percentage on the membrane properties and, especially, the antifouling propensity was studied. Membranes with very low fouling propensities were prepared when poly(VC-co-PEGMA) with the highest available PEGMA percentage (9.8%) was used [30]. Although membranes with considerable antifouling properties were obtained, PEGMA-based copolymer membranes have low mechanical strengths, limiting their practical applications. This is especially true if we consider self-support membranes (i.e., hollow fiber membranes). Therefore, in the present study, poly(VC-co-PEGMA) with a PEGMA segment percentage of 9.8 mol% was blended with PVC by using the conventional non-solvent induced phase separation (NIPS) method to obtain membranes with an appropriate mechanical strength and antifouling performance. The

effect of the copolymer/PVC blend ratios on the surface morphology, hydrophilicity, mechanical strength, and, in particular, the fouling propensity of the prepared membranes was evaluated. To understand the mechanism of membrane fouling, molecular dynamics (MD) simulations were carried out to assess the distribution of the copolymer in the membrane matrix in the presence of water.

2. Computational Methods

Molecular dynamics simulations were carried out using Gromacs 5.0.4 program. Poly(VC-co-PEGMA) copolymer, with the structure shown in Fig. 1, and PVC molecules were constructed based on experimental information. Similar to our previous work [30,31], model building and MD simulations were carried out and details has been reported in Supplementary materials. Table S1 shows degree of polymerization, number of atoms and box size for equilibrated structure in dry condition. A representative snapshot of the poly(VC-co-PEGMA)/PVC (blend 1:2) in the presence of water is shown in Fig. 2.

3. Experimental

3.1. Materials

PVC ($M_w = 55,000$) and poly(VC-co-PEGMA) (with a PEGMA segment percentage of 9.8 mol% and M_w of 180,000) were kindly supplied by Sekisui Chemical Co., Ltd. The chemical structure of this random copolymer was shown in Fig. 1. BSA, sodium dihydrogen phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), and dimethylacetamide (DMAc) were purchased from Wako Pure Chemical Industries. The BSA solution was prepared by dissolving BSA in 0.1 mol/L phosphate buffer solution (PBS). Monodispersed polystyrene latex particles (diameter $= 50$ nm and size distribution $< 3\%$) used for the rejection measurement were purchased from Duke Scientific Corporation (Thermo Fisher Scientific, Waltham, MA). Deionized water was produced in a Millipore Milli-Q unit. All reagents were used as received.

3.2. Flat-sheet membrane fabrication

The pure PVC copolymer membrane and three blended membranes with various copolymer/PVC blend ratios were prepared by a NIPS method. The compositions of the dope solutions used for membrane casting are shown in Table 1, where the blend membranes are labeled as Blend 1:4, 1:2, and 1:1, corresponding to their copolymer/PVC blend ratios. For the prepared membranes, the dope compositions were adjusted so that they had similar pure water permeabilities to enable a better comparison of the fouling properties without the effects of different water permeabilities. To prepare flat sheet membranes, the polymers were dissolved in DMAc by stirring at 45 °C for one day to obtain homogeneous solutions and, then, degassed overnight at 25 °C. Then, the solution was cast onto a glass plate with a nonwoven support using a
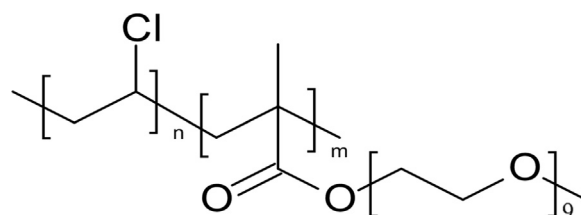

Fig. 1. Chemical structure of poly(VC-co-PEGMA).