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Enhanced permeation and antifouling performance of polyvinyl chloride (PVC) blend Pluronic F127 ultrafiltration membrane by using salt coagulation bath (SCB)

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ABSTRACT

Polyvinyl chloride (PVC) has drawn much attention as an ultrafiltration (UF) membrane material. However, conventional PVC UF membranes suffer from low flux and serious fouling when applied to water treatment. In the present study, a salt coagulation bath (SCB) has been successfully employed to enhance the morphological structures and properties of PVC/Pluronic F127 (F127) UF membranes. The resultant membrane without macrovoids exhibits a high surface porosity (7.2%) and surface hydrophilicity (water contact angle of around 40°), which endows the membrane with a remarkable flux (1405 L/m^2 h/bar) and antifouling performance. Also, the surface characterization is due to an improved surface hydrophilicity that can be attributed to an increased surface oxygen composition as well as to a slightly roughened microstructure. To understand the unique structure and performance of the PVC/F127 UF membranes, hydrophilic polyethylene glycol (PEG) has also been studied under the same conditions as a comparative copolymer, where the trade-off attributes standout compared to the F127 UF membranes. This phenomenon demonstrates the unique impact of SCB on the amphipathic F127, which can be ascribed to the intensified hydrophobic-hydrophobic interaction between F127 and polymer chains. Moreover, the outstanding performance as well as simple and cost-effective preparation process indicates that SCB can be a potential technology for industrial applications.

1. Introduction

In the last decades, ultrafiltration (UF) has become an attractive alternative to the traditional process in various industrial fields, such as the food industry, water purification, and drinking water treatment where high separation efficiency is required. However, high manufacturing costs and frequent membrane fouling are the major obstacles that affect membrane selective efficiency and economic benefit [1,2]. Polyvinyl chloride (PVC) backbone polymer is one of the most marketable materials for ultrafiltration membrane fabrication due to its low price—only 10% of the price of polyvinylidene fluoride (PVDF) or polysulfone (PSF) [3]—as well as its outstanding physicochemical properties [4]. Unfortunately, PVC-based membrane has low flux and is more prone to fouling [5]. Therefore, finding easy and economical ways to increase the flux and hydrophilicity of the PVC membrane is crucial to the success of its industrial application.

Blending modification is known as a simple and effective method to improve membrane performance. Many studies have verified that membrane surface hydrophilicity improves significantly when blending hydrophilic copolymers into casting solutions [6,7]. For example, polyethylene oxide (PEO), containing a hydrophilic agent, is commonly used in membrane modification to improve membrane hydrophilicity and fouling resistance [8,9]. In addition, the amphipathic copolymer Pluronic F127 (F127), containing both hydrophilic and hydrophobic blocks, has proven more effective than the hydrophilic copolymers [10–12]. Due to this hydrophobic interaction between the polymer and hydrophobic blocks within amphipathic copolymers, the amphipathic copolymers can anchor into the polymer matrix more firmly than those hydrophilic copolymers [10,13]. Our previous work has verified the compatibility of F127 in PVC UF membrane and shown a significant improvement in membrane antifouling ability by the addition of F127 [14].

On the other hand, the composition of the coagulation bath has also had a powerful impact on membrane structures by adjusting the liquid-

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liquid demixing in nonsolvent induced phase separation (NIPS) [15]. In this type of study, one of the most common ways is to change the composition of the coagulation bath to obtain different mutual affinities with the solvent in dope solutions [16–18]. It was observed in previous work that adding solvent into the coagulation bath can delay the demixing process and suppress the formation of macrovoids, but these benefits were gained at the price of reducing membrane porosity and permeation performance [19]. Thus, due to the trade-off between pore formation (instantaneous demixing) and macrovoid suppression (delayed demixing), the studies could only focus on the kinetics of the demixing process and could not simultaneously promote the membrane mechanical property and permeation performance [20].

As is generally known, in a selective solvent, the amphipathic Pluronic copolymers can form a core-shell structure by micellization [21,22], which is strongly affected by the salinity of the solvent [23,24]. The presence of salting-out electrolytes can modify water structure and influence the hydration of polyethylene oxide (PEO) and polypropylene oxide (PPO) blocks within molecular chains, eventually leads to changes in molecular property and structure [25]. Jain et al. [26] investigated the structure of Pluronic F88 (F88) in NaCl solutions by using a small angle neutron scattering (SANS). They found that the hydrophobicity of F88 micelles increased significantly with the increasing of salt concentrations but, the hard-sphere radius of micelles was almost constant. This result indicated that a part of the PEO blocks from the side of PPO was becoming hydrophobic when the NaCl concentration was raised, implying the conformation change of PPO and PEO blocks in NaCl solutions [27]. In addition, Pandit et al. [24] also found that the solubility of propylparaben increased progressively in F127 solution containing salts, which indicated that a larger volume of hydrophobic environment is available for propylparaben to partition into when salts are present. So far, it is recognized that the occurrence and properties of the amphipathic copolymers were highly dependent on the aqueous condition, which offered us an opportunity to optimize the thermodynamics and kinetics of membrane formation by simultaneously changing the bath salinity. Unfortunately, to the best of our knowledge, the effects of bath salinity on the amphipathic copolymers and even the membrane performance has not been investigated as a part of the membrane fabrication.

Membrane surface morphology is also crucial for membrane performance. Recently, a new concept was reported by Xue et al. [28], who took advantage of the high-surface-energy of hydrogel due to its rough-surface nanostructures, and eventually obtained a superhydrophilic coated steel mesh. Yuan et al. [29] also reported that the adhesion difference between solvent and membranes could be amplified by their free-standing nanowires with rough-surface morphology. The enormous surface area of the nanowires allows membrane to exhibited controlled wetting behavior ranging from superhydrophilic to superhydrophobic. Zhang et al. [30] successfully applied the salt-induced phase-inversion approach to achieve a membrane with a hierarchical micro/nanoscale structure using a poly(acrylic acid)-grafted PVDF, giving the membrane a superhydrophilic/underwater superoleophobic property.

In this paper, we reported a novel and simple way to improve the flux and surface hydrophilicity of PVC/F127 blended UF membranes. Different from the conventional process of adding a salt (such as LiCl), as a pore forming agent used to dope solutions and modify the membrane structure, we applied sodium chloride (NaCl) solutions of different concentrations as the salt coagulation bath (SCB). This SCB can influence the behaviors of amphipathic F127 during the phase inversion process. To elucidate the unique behaviors of amphipathic F127 in SCB, hydrophilic polyethylene glycol (PEG) with the same molecular weight (12,000) was employed as a comparative copolymer. The thermodynamic behaviors of both copolymers were investigated. Moreover, to test the effect of SCB on membrane properties and structures, the membrane morphology and physicochemical properties were extensively characterized.

2. Experimental

2.1. Materials

Polyvinyl chloride (PVC) with a high molecule weight, Pluronic F127 (F127), polyethylene glycol (PEG) with a molecular weight of 12,000, N-methyl-2-pyrrolidone (NMP) and sodium alginate (SA) were purchased from Sigma-Aldrich (St. Louis, MO). NaCl and $CaCl_2$ were purchased from Fisher Scientific (Pittsburgh, PA). Sodium alginate was used as the model organic foulant to test membrane retention and antifouling performance. The stock solution was prepared by adding sodium alginate to deionized (DI) water and mixing until completely dissolved. The stock solution of 1 g/L sodium alginate was stored in a sterilized glass bottle at 4 °C.

2.2. Preparation of high performance PVC UF membranes

Membranes were prepared by solution casting. The casting solution was prepared in a 250-mL conical flask by mixing PVC, F127 (or PEG) and NMP. The solution was heated to approximately 65 °C and stirred with 7.9 × 25.4 mm stir bars at 600 rpm using a digital stirring hot plate (Corning, MA). After the polymers were dissolved completely and stirred for at least 24 h, the resulting solution was degassed for at least two hours until no visible gas bubbles remained. The solution was cast on a first-surface optical grade mirror using an 8-in.–wide doctor blade (Universal blade applicator, Paul N. Gardner Company, Inc.; Pompano Beach, FL) that was set with a casting thickness of 10 mil (about 254 μm). Then, the mirror with casting solution was immersed in a DI water bath (DIB) or salt coagulation bath (NaCl aqueous solution) with different concentrations. The mirror was left in the coagulation bath for two hours until the membrane detached from the mirror, and subsequently the membrane was immersed in the deionized water bath for 24 h, after which the membrane was kept in deionized water before use. Different compositions of casting solution corresponding to different bath salinities are listed in Table 1.

2.3. Determination of phase diagram and membrane porosity

Cloud point data were measured by a titrimetric method. The solution to be titrated was prepared in a sealable bottle and kept stirring at room temperature. Non-solvent DI water or NaCl solutions with various concentrations was/were slowly added into the solution and local gelation occurred. After heating to speed up the dissolving process of gelation, the solution could cool down to room temperature. This process was repeated until the polymer solution became irreversibly turbid as detected visually [31].

Table 1
Compositions of casting solutions and their coagulation bath.

Code	Casting solution[a]	Bath[a]
MPF0	PVC/NMP/F127[b] = 12/83/5	DI water
MPF5	PVC/NMP/F127 = 12/83/5	NaCl = 5%
MPF15	PVC/NMP/F127 = 12/83/5	NaCl = 15%
MPF25	PVC/NMP/F127 = 12/83/5	NaCl = 25%
MPF35	PVC/NMP/F127 = 12/83/5	NaCl = 35%
MG0	PVC/NMP/PEG[c] = 12/83/5	DI water
MG15	PVC/NMP/PEG = 12/83/5	NaCl = 15%
MG35	PVC/NMP/PEG = 12/83/5	NaCl = 35%

[a] The composition of casting solutions and coagulation bath is calculated basing on wt%.
[b] F127 = pluronic F127.
[c] PEG = polyethylene glycol.