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Anti-fouling ultrafiltration membrane made from surface saponification of poly(vinyl acetate-co-vinyl pivalate) with enhanced syndiotacticity

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ABSTRACT

Syndiotactic poly(vinyl acetate-co-vinyl pivalate) was synthesized for the fabrication of anti-fouling membranes. The mechanical strength of the syndiotactic PVA membrane was retained by a selective surface saponification reaction and the solubility of PVA on the surface was reduced by introducing syndiotacticity. The selective saponification reaction of the membrane was monitored by FT-IR and contact angle measurements. The fouling resistance was analyzed by measuring the flux of the protein solution as well as the adsorption of humic acid and *E. coli* on the membrane surface. The surface modification of the syndiotactic polymer membrane provided good mechanical strength and better biofouling resistance.

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Introduction

Biofouling is a major problem encountered in the membrane filtration processes, such as water treatment and desalination. Membrane fouling includes inorganic fouling/scaling, organic fouling, particulate/colloidal fouling, and biofouling (or microbial/biological fouling), which occur simultaneously [1]. Biofouling is considered a major factor contributing more than 45% of all membrane fouling in ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) filtration systems [2,3]. The attachment of microbial cells to the membrane surface is the first step of membrane biofouling, leading to the formation of a biofilm layer [4]. Extracellular polymeric substances (EPSs) excreted from microorganisms are believed to play an important role in biofouling and enhanced microbial attachment to the membrane surfaces by anchoring the cells and stimulating additional colonization on the membrane surface [5]. The binding of microorganisms on the membrane surface depends on many

factors, such as the membrane material [6], roughness of the membrane surface [6,7], hydrophobicity, and surface charge [9].

The reduction of biofouling can be achieved through many methods, such as increasing the hydrophilicity of the membrane surface [10], introduction of surface charge [10], reducing the surface roughness [12,13], generating a biomimetic surface [14,15], and the incorporation of a thin film layer [16]. Among these methods, the introduction of hydrophilicity on the membrane surface has attracted considerable attentions because these processes do not affect the physical properties of the membranes and the methods are relatively simple. The hydrophilic polymers used for coating the membrane surfaces include poly(vinylpyrrolidone) [17], quaternized poly(vinyl imidazole) [18], PEO-b-PPO-b-PEO triblock copolymer [19], polysulfonamide [20], poly(vinyl alcohol) (PVA) [21], and self-assembled poly(ethylene imine) [22]. On the other hand, the high solubility of these polymers in water has limited the commercial utilization of these materials as coating materials.

Among these polymers, PVA is available in large quantities, and the intrinsic hydrophilicity of PVA makes it an attractive polymer for reducing biofouling applications to polymer-based membrane manufacturers. Despite this, the high solubility of PVA in water necessitates the physical and/or chemical crosslinking reactions of PVA. The freeze-thaw method [23,24] and heat treatment [25] of

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PVA can increase physical crosslinking, and decrease the solubility in water via the induced crystallization of PVA. This process, however, does not eliminate the dissolution of PVA in water completely. Therefore, a chemical crosslinking reaction is needed to prevent PVA from dissolution. The most popular material among chemical crosslinking agents of PVA is aldehydes, such as glutaraldehyde [26,27], formaldehyde [28,29], acrolein in the presence of sulfuric acid [30], and adipic aldehyde [31], although, there are still a few problems that need to be addressed. The crosslinked PVA swells in water. Therefore, the size of the pores in UF and NF membrane depends on the swelling ratio of surface-coated PVA [32–34]. Another problem is that the mechanical strength is also weak because the water molecules can function as a plasticizer. In addition, the use of hazardous aldehydes to crosslink PVA may not be suitable for water filtration membrane and biomedical applications.

This paper reports a new UF membrane fabrication using syndiotactic PVA made from the copolymerization of vinyl acetate and vinyl pivalate. After the fabrication of a UF membrane using the precursor polymer via precipitation in a non-solvent, only the surface of the UF membrane was hydrolyzed selectively to generate hydroxyl groups. The copolymer membrane coated with syndiotactic PVA had sufficient hydrophilicity to suppress biofouling but was insoluble and maintained its dimensional stability in water. In addition, the mechanical properties of the surface-modified UF membrane increased slightly due to the formation of H—bonding between the surface OH groups.

Experimental

Materials

Vinyl pivalate (VPi) and vinyl acetate (VAc) (Sigma-Aldrich Co. USA) were purified by distillation under reduced pressure. The initiator 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) (Wako Co., Japan; 99%) was recrystallized twice in absolute methanol prior to use. PVA with a number-average molecular weight of 127,000 and a degree of saponification (DS) of 88% (Sigma-Aldrich Co. USA) was used as the suspending agent to copolymerize VPi and VAc in water. Bovine serum albumin (BSA Fraction V, Mn=67,000) was purchased from Sigma-Aldrich. Other extra-pure-grade reagents were used without further purification. Deionized water was used in all the procedures.

Suspension copolymerization of VPi and VAc

As a typical reaction, the suspending agent was dissolved in water under a nitrogen atmosphere with constant stirring in a 500 mL reactor fitted with a condenser. After degassing, the VPi and VAc monomers, along with ADMVN, were added at once at a constant polymerization temperature. After a predetermined polymerization time, the reaction mixture was cooled and kept for 1 day to precipitate the spherical poly(VPi-co-VAc) particles. To eliminate the residual VPi and VAc and the suspending agent, poly(VPi-co-VAc) was filtered off and washed with DI water. Table 1 lists the polymerization conditions [35].

The optimal mole ratio of two monomers was determined by fabricating UF membranes with various compositions in a non-solvent. As the ratio of VPi in the copolymer was 0.4, the membrane could induce a desired pore size for the UF membrane. In contrast, an increased ratio of VAc caused swelling of the final membrane in water due to the hydrophilic nature of poly(vinyl acetate).

Table 1

Reaction conditions for the suspension copolymerization of VPi and VAc.

Type of initiator	ADMVN
Type of suspending agent	PVA
Initiator concentration (mol/mol of VPi and VAc)	2×10^{-4}
Suspending agent concentration (g/dl of water)	1.5
VPi/VAc (mol/mol)	4/6
Monomer/water (v/v)	4/6
rpm	300
Polymerization temperature (°C)	50

Preparation of poly(VPi-co-VAc) membranes

Poly(VPi-co-VAc) membranes were prepared using the non-solvent induced phase separation (NIPS) method. The polymer casting solution of poly(VPi-co-VAc) was prepared by dissolving it in *N*-methyl-2-pyrrolidone at room temperature with constant stirring for at least 24 h until a homogeneous solution was obtained. The total concentration of poly(VPi-co-VAc) was kept at 8% because concentrations higher than 8% result in casting solutions with extremely high viscosity [36]. Subsequently, the solutions were cast on glass plates with a casting knife adjusted to a 250 μm thickness. The plates were then immersed in a distilled water bath at room temperature. After 24 h, the fabricated membranes were washed thoroughly with deionized water to remove the residual solvent.

Surface saponification of poly(VPi-co-VAc) membranes

Poly(VPi-co-VAc) membranes were immersed in an alkaline solution (25 wt. % NaOH solution) for a different saponification time (0H, 8H 12H, and 16H) with a constant saponification temperature (40 °C). The flask was equipped with a membrane fixing device and a magnetic stirrer. After different saponification times, the fabricated membranes were washed several times with deionized water to remove the residual sodium hydroxide [37].

Characterization of poly(VPi-co-VAc) membranes

The molecular weight of the poly(VPi-co-VAc) membranes was measured by gel permeation chromatography (GPC, Alliance e2695, Waters Co., USA) with polystyrene standards (1000–4,000,000) and a refractive index detector. The samples were prepared by dissolution in tetrahydrofuran (THF). The molecular weight of poly(VPi-co-VAc) was approximately 1.89 MDa. To determine the *S*-diad of the prepared poly(VPi-co-VAc), it was saponified completely to poly(vinyl alcohol). Poly(VPi-co-VAc) powder was dissolved in THF, and a solution of KOH in a methanol/water solution was added dropwise with constant stirring. Table 2 lists the saponification conditions.

The *S*-diad contents of the poly(VPi-co-VAc) powder was determined by 300 MHz ¹H nuclear magnetic resonance (NMR, Bruker Co., Germany) spectroscopy using dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) as the solvent, based on the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm. [38]. The syndiotacticity of saponified poly(VPi-co-VAc) was calculated from the ¹H NMR spectra using the equation in Ref. [38], which was approximately 57.3%.

The morphology of the poly(VPi-co-VAc) membranes was analyzed by scanning electron microscopy (S-4200, Hitachi Co.). The poly(VPi-co-VAc) membranes were fractured in liquid nitrogen and a cross-section of the membrane was coated with platinum by sputtering. The porosity and pore size distribution of the poly(VPi-co-VAc) and PVA membranes were calculated using a mass balance with a low surface tension (0.0151 N m⁻¹) wetting liquid (Galwick), which was provided by Porous Materials Inc. Ithaca, USA, the

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