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Fabrication and properties of ultrafiltration membranes composed of polysulfone and poly(1-vinylpyrrolidone) grafted silica nanoparticles

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ABSTRACT

Membranes for ultrafiltration were prepared from polysulfone (PSf) composites with poly(1-vinylpyrrolidone) grafted silica nanoparticles (PVP-g-silica). For the synthesis of PVP-g-silica, hydroxyl terminated silica nanoparticles were reacted with (3-methacryloxypropyl)trimethoxysilane (γ-MPS) to form γ-MPS terminated silica nanoparticles (silica-MPS), which were further reacted with VP monomer. Formation of PVP-g-silica was confirmed by FT-IR, XPS, TGA, FE-SEM, and HR-TEM. PSf/PVP-g-silica membranes exhibited higher water flux than PSf membranes without any loss in solute rejection for membranes containing less than or equal to 5 wt% of PVP-g-silica. The water flux of a membrane containing 1 wt% PVP-g-silica was 2.3 times higher than that of PSf membrane. The hydrophilicity of the PSf/PVP-g-silica membrane also increased with increasing PVP-g-silica content. The hydrophilicity of the PSf/PVP membrane decreased with increasing retention time in a water bath, while the hydrophilicity of the PSf/PVP-g-silica membrane did not change with retention time. PSf/PVP-g-silica membranes exhibited enhanced fouling resistance in fouling experiments using nonionic surfactants.

1. Introduction

Polysulfone (PSf) is widely used as a component in the fabrication of ultrafiltration membranes, gas separation membranes, and the support layer of reverse osmosis membranes because of its excellent balance of chemical, thermal, and mechanical properties [1–3]. PSf membranes have a broad operating temperature and pH range, excellent chlorine tolerance, and the ability to retain their mechanical properties in hot and wet environments. However, PSf membranes exhibit drawbacks in the filtration process due mostly to their hydrophobic nature: (1) low water flux and (2) performance deterioration during filtration by fouling originating from interactions between the membrane and solute in the feed solution [1–6]. Problems exhibited by PSf membranes during filtration could be lowered by reducing the hydrophobicity of the membranes.

Intensive efforts have been made to improve the performance of PSf membranes by providing greater hydrophilicity via chemical modifications, surface coating, and blending. Structural modification and grafting of hydrophilic polymers on the surfaces of PSf membranes have been performed by oxidation, addition, substitution, and hydrolysis reactions via thermal and plasma treatment and ultraviolet irradiation [4–7]. A hydrophilic PSf membrane surface can be produced by introducing covalently bound hydrophilic functional groups or polymers to PSf using these methods. However, these approaches typically require harsh chemical conditions, which often reduce the inherent membrane flux and are practically difficult to implement. Thin film coating of the membrane with a hydrophilic polymer is the simplest way to increase the hydrophilicity of the membrane [8–10]. However, the coating layer often delaminates, and it is not easy to fabricate a defect-free ultrathin layer due to poor adhesion at the interface. In addition, the increased resistance due to the coating layer reduces water flux through the coated membrane. The post-treatment methods mentioned above require additional time-consuming processes. To develop hydrophilic membranes without the need for a post-treatment process, membranes have been fabricated from copolymers and chemically modified polymers with carboxylic acid, amine, and sulfonic acid groups [11–16]. Membranes fabricated with this method exhibited relatively high flux and improved fouling resistance. However, the surface characteristics change with pH due to negative or positive charges on the membrane surface.

Blending is another method of enhancing membrane hydrophilicity [17–24]. Poly(1-vinylpyrrolidone), PVP, a known nontoxic material used for biomedical applications, is very soluble in water. Blends of PVP with PSf have been extensively investigated for the fabrication of ultrafiltration membranes via the phase inversion method [22–24]. It is known that addition of PVP to PSf is an effective and simple method to enhance membrane hydrophilicity.

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However, most of the water-soluble PVP may be washed out during membrane formation and in the filtration process. Retention of PVP in the membrane matrix is essential for producing membranes that exhibit a performance advantage over PSf membranes with respect to water flux and fouling resistance.

In order to retain PVP in the membrane matrix, in this study, PVP-grafted silica nanoparticles (hereafter referred to as "PVP-g-silica") were synthesized and used in the fabrication of ultrafiltration membranes from casting solutions containing PSf and PVP-g-silica. The formation of PVP-g-silica was examined with FT-IR, XPS, FE-TEM, and TGA. The properties of ultrafiltration membranes fabricated from composites of PSf with PVP-g-silica were explored.

2. Materials and procedures

2.1. Materials

Bisphenol-A polysulfone (PSf, M_w=35,000 g/mol, M_n=16,000 g/mol) and poly(1-vinylpyrrolidone) (PVP, M_w=5500 g/mol) were purchased from Sigma-Aldrich Co. Silica nanoparticles with a 40 nm average diameter (grade: Aerosil OX-50) were supplied by Degussa Chem. Co. (Germany). 3-Methacryloxypropyltrimethoxysilane (γ-MPS), which was used as a silane coupling agent, 1-vinylpyrrolidone (VP), which was used as a monomer for the synthesis of PVP grafted onto the silica surface, 1-methyl-2-pyrrolidone (NMP), sodium hydroxide (NaOH), ethanol, and isopropanol were purchased from Sigma-Aldrich Co. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was used as an initiator for the radical reaction of VP and was supplied by Junsei Chemical Co. (Japan). A nonionic surfactant of polyoxyethyleneglycol alkylether, $H(CH_2)_{16}O(CH_2CH_2O)_8H$ (hereafter referred to as "$C_{16}E_8$"), was used for fouling tests and was provided by Nikko Chemicals (Japan). C and E indicate the hydrophobic methylene and hydrophilic ethylenoxy groups of the nonionic surfactant, respectively.

2.2. Synthesis and characterization of PVP-g-silica nanoparticles

PVP grafted silica nanoparticles (PVP-g-silica) were prepared in this work. The details of PVP-g-silica synthesis and characterization are provided in the next section. The molecular structure of PVP-g-silica was confirmed by Fourier transform infrared (FT-IR, Magna 750, Nicolet, USA) analysis and X-ray photoelectron spectroscopy (XPS, VG-microtech, ESCA2000, UK) using a Mg Kα X-ray source (1253.6 eV) and a hemispherical analyzer. FT-IR spectra were collected over 30 scans in the 4000–500 cm^{-1} region using attenuated total reflection (ATR) mode at a resolution of 4 cm^{-1}. XPS spectra were obtained in high-resolution mode with a 20 eV pass energy and 0.1 eV step size. All binding energies were calibrated to carbon (C1s) at 284.5 eV. In curve fitting, the widths of the Gaussian peaks were kept constant in each spectrum. Transmission electron microscopy (HR-TEM, model: JEM 2000EXII, JEOL, Japan) and scanning electron microscopy (FE-SEM, model: Sigma, Carl Zeiss, Germany) were employed to investigate the morphologies of pristine silica nanoparticles, PVP-g-silica, and membranes. Thermogravimetric analysis (TGA, model: TGA-2050, TA Instruments, USA) of the samples was carried out to determine the amount of PVP grafted onto silica nanoparticles. TGA analyses were performed under nitrogen at a heating rate of 10 °C/min. Specimens for TGA experiments were dried in a vacuum oven at 100 °C for one day.

2.3. Membrane preparation

Membranes for ultrafiltration were prepared by the wet phase inversion process, which is a well-known process for preparing a variety of asymmetric membranes [1–3,22]. PSf, pristine silica nanoparticles, and PVP-g-silica were dried for at least 24 h at 100 °C before being used in the casting solution. The fraction of PSf in the casting solution was held constant at 20 wt%. The compositions of the casting solutions used and their abbreviations are listed in Table 1. Note that the numerical value included as part of the abbreviations for the membranes indicates the PVP-g-silica (or pristine silica) wt% of the membrane. A casting solution composed of 20 wt% PSf and 80 wt% NMP was stirred and heated at 80 °C for 10 h until the polymers were completely dissolved, and various amounts of PVP-g-silica or pristine silica nanoparticles (1, 3, 5, 8, or 10 wt% of the PSF content) were then added to the solutions. Degassing was performed in an ultrasonic water bath for 2 h. The resulting solution reached 30 °C and was cast onto a polyester nonwoven fabric with a doctor blade at a thickness of 0.1 mm. The cast film was immersed in a water bath until most of the solvent had been removed. Note that the retention time in the water bath was one day if not otherwise specified.

2.4. Membrane characterization

An aqueous solution containing 1000 ppm of PEG (polyethyleneglycol, weight average molecular weight=40,000, polydispersity index=1.03) was used as the feed solution for the membrane performance test. As shown in Fig. 1, ultrafiltration (UF) experiments were performed in a flat-sheet cross-flow UF test cell with an active membrane area of 19.63 cm^2 (internal diameter: 50 mm, external diameter: 57 mm, and cell volume: 196 ml) at 3×10^5 Pa, 30 °C, and a flow rate of 0.7 l/min. Both the retentate and permeate were recycled to the feed tank to maintain a constant concentration of solute. Magnetic stirring was employed to minimize the concentration polarization (600 rpm). The solute concentration of the permeate was measured with a refractometer (model: RI-2031, Jasco, Japan) equipped with a constant flow rate pump (model:

Table 1
Membranes and their abbreviations used in this study.

Composition of the casting solution (wt ratio)	Membrane composition (wt%)	Membrane abbreviation
NMP/PSf=80/20	PSf	PSf
NMP/PSf/PVP=80/20/5	PSf/PVP=80/20	PSf/PVP=80/20
NMP/PSf/PVP-g-silica=79.8/20/0.2	PSf/PVP-g-silica=99/1	PSf/PVP-g-silica-1
NMP/PSf/PVP-g-silica=79.38/20/0.62	PSf/PVP-g-silica=97/3	PSf/PVP-g-silica-3
NMP/PSf/PVP-g-silica=78.9/20/1.1	PSf/PVP-g-silica=95/5	PSf/PVP-g-silica-5
NMP/PSf/PVP-g-silica=78.26/20/1.74	PSf/PVP-g-silica=92/8	PSf/PVP-g-silica-8
NMP/PSf/PVP-g-silica=77.8/20/2.2	PSf/silica=90/10	PSf/PVP-g-silica-10
NMP/PSf/silica=79.8/20/0.2	PSf/silica=99/1	PSf/silica-1
NMP/PSf/silica=79.38/20/0.62	PSf/silica=97/3	PSf/silica-3
NMP/PSf/silica=78.9/20/1.1	PSf/silica=95/5	PSf/silica-5
NMP/PSf/silica=78.26/20/1.74	PSf/silica=92/8	PSf/silica-8
NMP/PSf/silica=77.8/20/2.2	PSf/silica=90/10	PSf/silica-10