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Characteristics of ultrafiltration membranes fabricated from polysulfone and polymer-grafted silica nanoparticles: Effects of the particle size and grafted polymer on the membrane performance

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ABSTRACT

Silica nanoparticles with a controlled size in the range of 10–100 nm were synthesized and their surface was treated with various hydrophilic polymers to produce polysulfone (PSf)/silica nanoparticles composite membranes which exhibited enhanced performance in the ultrafiltration process. PSf composite membranes containing silica nanoparticles grafted with a hydrophilic polymer exhibited a much higher water flux than the PSf membrane. Among the PSf composite membranes containing silica nanoparticles grafted with poly(vinyl alcohol) (PVA-g-silica), poly(1-vinylpyrrolidone) (PVP-g-silica), and poly(1-vinylpyrrolidone-co-acrylonitrile) (P(VP-AN)-g-silica), the solute rejection of the PSf/P(VP-AN)-g-silica membrane was the same as that of the PSf membrane, while that of PSf/PVA-g-silica was significantly lower than that of the PSf membrane. The amount of grafted polymer on the particles decreased with increasing particle size. As a result, the water flux of the membranes increased with decreasing particle size, regardless of the type of grafted polymer. The PSf/P(VP-AN)-g-silica membrane showed the best performance among the membranes examined when the particle content and size were fixed.

1. Introduction

Polysulfone (PSf), which is one of the most popular amorphous polymers, is widely used in preparing ultrafiltration membranes and as a support layer for pervaporation and reverse osmosis membranes because of its excellent balance of mechanical strength, chemical resistance, creep resistance, and thermal stability [1–4]. However, PSf membranes exhibit a low water flux compared to other membranes prepared from hydrophilic polymers because of their hydrophobic nature. Furthermore, its water flux continuously decreases during the filtration process due to fouling, originating from hydrophobic interactions between the membrane and solute in the feed solution. Therefore, modification of the PSf membrane by the incorporation of hydrophilic materials has attracted great attention.

To provide hydrophilic nature to PSf membranes, blending with hydrophilic polymers or inorganic fillers [5–14] and structure modification of PSf with hydrophilic functional groups or polymers by atomic transfer radical polymerization, plasma irradiation, and UV-assisted polymerization have been performed during the past few decades [15–25]. Since structural modifications of PSf often require complex chemical reactions and harsh chemical conditions, these approaches are difficult to implement in practical membrane fabrication. On the other hand, blending PSf with hydrophilic polymers or a filler can be an easy and effective strategy to provide a hydrophilic nature to PSf membranes. In addition, membranes with a continuous range of performance can be obtained simply by varying the blend composition. Poly(1-vinylpyrrolidone) (PVP), which is a water soluble polymer, has been widely used to enhance the hydrophilicity of PSf membranes. A hydrophilic polymer which is blended with PSf for membrane fabrication should remain in the membrane to retain the membrane hydrophilicity. However, the amount of PVP in a PSf/PVP membrane gradually decreased during the membrane preparation and filtration process [14]. To prevent PVP loss, silica nanoparticles grafted with PVP (PVP-g-silica) were incorporated into a PSf membrane. A PSf/PVP-g-silica membrane exhibited a much higher water flux than a PSf membrane with a slight loss of solute rejection [14].

The performance of PSf composite membranes containing surface-treated silica nanoparticles may be influenced by the particle size and type of grafted polymer. To evaluate these issues, nearly monodipersed silica particles with a controlled size ranging

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from 10 to 100 nm were synthesized by a sol–gel process and then, their surface was modified by grafting with poly(vinyl alcohol) (PVA), poly(1-vinylpyrrolidone) (PVP), and poly(1-vinylpyrrolidone-co-acrylonitrile) (P(VP-AN)). The characteristics of ultrafiltration membranes fabricated from a casting solution containing PSf and silica nanoparticles grafted with hydrophilic polymer were explored.

2. Materials and procedure

2.1. Materials

Bisphenol-A polysulfone (PSf, Mw=35,000 g/mol, Mn=16,000 g/mol) used for the fabrication of the ultrafiltration membranes was purchased from Aldrich Chemicals (WI, USA). Various monomers including 1-vinylpyrrolidone (VP), vinylacetate (VAc), and acylonitrile (AN), which were used for the synthesis of the polymers grafted to the silica nanoparticles, were purchased from Aldrich Chemicals. 2,2′-Azobis(2-methylpropionitrile) (AIBN) used as an initiator for the radical polymerization was supplied by Junsei Chemical Co. (Japan). Tetraethylorthosilicate (TEOS) and ammonium hydroxide (NH_4OH, 30% NH_3) used as a precursor and a catalyst, respectively, for the synthesis of silica nanoparticles, sodium hydroxide (NaOH) used for the hydrolysis of silica nanoparticles, methacryloxypropyltrimethoxysilane (γ-MPS) used as a silane coupling agent, and various solvents including 1-methyl-2-pyrrolidone (NMP), ethanol, and methanol were supplied by Junsei Chemicals. 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 surface-treated silica nanoparticles

Nearly monodispersed silica particles with a controlled size (average particle diameter=10, 25, 50, and 100 nm) were prepared by the Stober method [26,27] and then PVP, PVA, and P(VP-AN) were grafted onto the silica nanoparticles. The details of the synthesis and characterization are provided in the next section. High resolution transmission electron microscopy (HR-TEM, model: JEM 2000EXII, JEOL, Japan) and field emission scanning electron microscopy (FE-SEM, model: Sigma, Carl Zeiss, Germany) were employed to investigate the particle size and morphology of the silica nanoparticles and membranes. The average particle size was obtained from TEM and SEM images using an image analyzer (Bummi Universe, I-top, Korea). The molecular structure of the surface-treated silica nanoparticles were confirmed by Fourier transform infrared (FT-IR, Magna 750, Nicolet, USA) analyses. FT-IR spectra were collected over 32 scans in the 4000–400 cm^{-1} region using the attenuated total reflection (ATR) mode at a resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA, model: TGA-2050, TA Instruments, USA) of the samples was carried out to determine the amount of polymer grafted onto the silica nanoparticles. TGA analyses were performed under nitrogen at a heating rate of 10 °C/min. The specimens for the TGA experiments were dried in a vacuum oven at 100 °C for one day. The acrylonitrile content in the P(VP-AN) copolymer was calculated by determining the carbon, nitrogen, and oxygen contents using an element analyzer (EA, Flash 2000, CE Instrument, Italy).

2.3. Membrane preparation

Ultrafiltration membranes were prepared by the wet phase inversion process, which is a well-known process for preparing a variety of asymmetric membranes [1,28]. PSf and silica nanoparticles were dried for at least 24 h at 100 °C before use. The total fraction of PSf in the casting solution was held constant at 20 wt% in this study. A solution containing PSf and NMP was stirred at 30 °C for 24 h until the polymers were completely dissolved. Then, the surface-treated silica nanoparticles were added to the solutions. Degassing was performed in an ultrasonic water bath for 2 h. The resulting polymer solution was cast onto a non-woven polyester fabric with a doctor blade which had a thickness of 0.1 mm. The cast film was immediately immersed into a water bath and kept there for 24 h until most of the solvent was removed. The compositions of the membranes and their abbreviations are listed in Table 1. The numerical values included in the abbreviations of the membranes refer to the average diameter of the silica particles and the wt% of silica particles in the membrane, respectively.

Table 1
The membranes used in this study and their abbreviations.

Membrane composition (wt%)	Membrane abbreviation
PSf/PVA-g-silica (10 nm)=97/3	PSf/PVA-g-silica10-3
PSf/PVA-g-silica (10 nm)=95/5	PSf/PVA-g-silica10-5
PSf/PVA-g-silica (25 nm)=97/3	PSf/PVA-g-silica25-3
PSf/PVA-g-silica (50 nm)=97/3	PSf/PVA-g-silica50-3
PSf/PVA-g-silica (100 nm)=97/3	PSf/PVA-g-silica100-3
PSf/PVP-g-silica (10 nm)=97/3	PSf/PVP-g-silica10-3
PSf/PVP-g-silica (25 nm)=97/3	PSf/PVP-g-silica25-3
PSf/PVP-g-silica (50 nm)=97/3	PSf/PVP-g-silica50-3
PSf/PVP-g-silica (100 nm)=97/3	PSf/PVP-g-silica100-3
PSf/PVP-g-silica (10 nm)=95/5	PSf/PVP-g-silica10-5
PSf/PVA-g-silica (25 nm)=95/5	PSf/PVP-g-silica25-5
PSf/PVA-g-silica (50 nm)=95/5	PSf/PVP-g-silica50-5
PSf/PVA-g-silica (100 nm)=95/5	PSf/PVP-g-silica100-5
PSf/P(VP-AN)-g-silica (10 nm)=97/3	PSf/P(VP-AN)-g-silica10-3
PSf/P(VP-AN)-g-silica (25 nm)=97/3	PSf/P(VP-AN)-g-silica25-3
PSf/P(VP-AN)-g-silica (50 nm)=97/3	PSf/P(VP-AN)-g-silica50-3
PSf/P(VP-AN)-g-silica (100 nm)=97/3	PSf/P(VP-AN)-g-silica100-3
PSf/P(VP-AN)-g-silica (10 nm)=95/5	PSf/P(VP-AN)-g-silica10-5
PSf/P(VP-AN)-g-silica (25 nm)=95/5	PSf/P(VP-AN)-g-silica25-5
PSf/P(VP-AN)-g-silica (50 nm)=95/5	PSf/P(VP-AN)-g-silica50-5
PSf/P(VP-AN)-g-silica (100 nm)=95/5	PSf/P(VP-AN)-g-silica100-5

2.4. Membrane characterization

An aqueous solution containing 1000 ppm polyethyleneglycol (PEG, weight average molecular weight=30,000, polydispersity index=1.03) was used as the feed solution for the membrane performance test. 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, 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. The solute concentration of the permeated solution was measured using a refractometer (model: RI-2031, Jasco, Japan) equipped with a constant flow rate pump (model: PU-2080, Jasco, Japan). Each experiment was performed five times and the mean average was reported.

The contact angle between water and the membrane was directly measured using a contact angle goniometer (Rame-Hart, Model:100-00-(115/220)-S) to evaluate the membrane hydrophilicity. To minimize experimental error, the contact angle of each sample is an average of ten measurements. The membrane surfaces and cross-sectional morphologies were observed using FE-SEM.