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Comparison study of the effect of PVP and PANI nanofibers additives on membrane formation mechanism, structure and performance

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ABSTRACT

Polysulfone (PSf) ultrafiltration (UF) membranes were prepared by non-solvent induced phase separation process using two kinds of additives, i.e., polyvinylpyrrolidone (PVP) as a representation of water soluble polymers and polyaniline (PANI) nanofibers as a representation of nanomaterials. The effects of PVP and PANI nanofibers on membrane formation mechanism, structure and performance were systematically investigated, compared and analyzed. The thermodynamic and rheologic properties of the casting solutions were studied through cloud point titration measurement and viscosity measurement. Variations of the casting film during preevaporation and after immersed into the coagulation bath were observed through mass variation measurement, optical microscopy measurement and light transmission measurement. Membrane structure was characterized by X-ray photoelectron spectroscopy, scanning electron microscope and contact angle measurement. Membrane performance was evaluated by pure water flux, protein rejection, antifouling property, additive stability and mechanical property. The results demonstrated that at the same additive content, PSf/PANI nanocomposite membranes had higher protein rejections, higher antifouling property, better additive stability and larger breaking strength than PSf/PVP membranes. The correlations among membrane formation mechanism, structure and performance were also discussed in detail.

1. Introduction

Asymmetric polymer ultrafiltration (UF) membrane is not only widely used for protein separation, drug purification and waste water treatment but also appears to be the popular base membrane for fabricating composite membrane including reverse osmosis membranes, nanofiltration membranes and gas separation membranes [1]. Generally, asymmetric polymer ultrafiltration membrane is prepared by the phase inversion method, especially non-solvent induced phase separation (NIPS) process [2]. In this process, the casting solution consisted of polymer and solvent is cast into a casting film, preevaporated in an ambient atmosphere, and then immersed into a coagulation bath. Phase separation occurred by the exchange of solvent (S) and non-solvent (NS) across the interface between the casting film and atmosphere/coagulation bath. Thus, membrane formation process should be analyzed by the observation of the variation of the casting film during preevaporation and after immersed into the coagulation bath. Membrane formation mechanism during preevaporation can be investigated by measuring the mass variation of the casting film [3–5]. Two experimental techniques have been used to investigate the precipitation kinetics after immersing the casting film into the coagulation bath: optical microscopy measurement technique used by Strathmann et al. [6] and light transmittance measurement technique reported in Smolders and Mulder's works [7,8]. The former one can reflect "the pore structure during precipitation", which resembles closely the prepared membrane morphology [9,10]. The latter one can get the "demixing rate", which is defined as the time required to achieve turbidity after immersing the casting film into the coagulation bath [11].

Membrane structure and performance can be controlled by the casting solution composition, casting condition and coagulation bath composition. In order to get the membrane with excellent structure and performance, introduction of a suitable additive to the casting solution is a convenient and efficient method [12].

Recently, two kinds of additives have been widely used during the modification of polysulfone (PSf) ultrafiltration membrane. One is water soluble polymers, such as polyvinylpyrrolidone (PVP)

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and poly(ethylene glycol) (PEG) [2,12–18]. The other is hydrophilic nanomaterials, such as TiO_2 nanoparticles, polyaniline (PANI) nanofibers and carbon nanotubes [19–23].

The effects of water soluble polymer and nanomaterial additives on membrane formation, structure and performance have both similarities and differences. The similarities may be due to their non-solvent character while the differences may be due to their solubility character. Both of two kinds of additives could change thermodynamic and kinetic properties of the casting solution and enhance membrane permeability and antifouling property. Particularly, the role of water soluble polymers in the casting solution has been reported as a pore-forming agent due to their water solubility. Study of Chakrabarty et al. [12] showed that the addition of PVP increased the pore number as well as porosity of the prepared membrane. Han and Nam [17] studied the variation of thermodynamic and rheologic properties in PSf casting solution by adding PVP. The results indicated that when adding low content of PVP (below 5.0 wt%), the variation in thermodynamic property controlled the demixing process and led to the enhancement of phase separation. With further increment of PVP content, the demixing process was delayed due to the high viscosity of the casting solution. Yeo et al. [18] also found that PVP in the casting solution could accelerate phase separation and enlarge the macrovoids in the prepared membranes. It was reported that the addition of nanomaterial in the casting solution could suppress the growth of macrovoids, increase porosity and hydrophilicity, and enhance permeability, antifouling property, mechanical and thermal stabilities [19–21]. Study of Fan et al. [19] using PANI nanofibers in PSf-DMAC system indicated that PSf/PANI nanocomposite membranes had higher membrane porosity and better interconnected membrane pores than PSf membrane. Yang et al. [20] found that the addition of TiO_2 nanoparticles in PSf-DMAC-NMP system changed the rheologic properties of the casting solution from Newtonian fluid to non-Newtonian fluid. When adding appropriate content of TiO_2 nanoparticles, membrane porosity and the number of small pores increased and membrane pores became run through the cross-section structure. Bae and Tak [21] demonstrated that the addition of TiO_2 nanoparticles could induce the enlargement of membrane porosity and the improvement of antifouling property. In order to choose a suitable additive in the practical application, there is a need to carry out about the comparison of the effects of water soluble polymers and nanomaterials on membrane formation mechanism, structure and performance in detail.

The present work was aimed at studying the effects of water soluble polymers and nanomaterials on membrane formation, structure and performance, and clarifying their differences and similarities. PVP has been widely used as the additive during the preparation of ultrafiltration membrane while PANI represents a class of promising new materials for preparing ultrafiltration membrane [12,24]. Thus, we attempt to modify PSf membrane by adding PVP as a representation of water soluble polymers and PANI nanofibers as a representation of nanomaterials. That is, PSf/PVP membranes and PSf/PANI nanocomposite membranes were prepared via NIPS process using PVP and PANI nanofibers as the additive, respectively. The thermodynamic and rheologic properties of the casting solutions were studied through cloud point titration measurement and viscosity measurement. In order to study membrane formation mechanism in detail, a series of experiments were designed, including mass variation measurement, optical microscopy measurement and light transmission measurement. X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and contact angle measurement were used to characterize membrane surface property, morphology and hydrophilicity, respectively. Pure water flux, proteins rejection and antifouling property were measured through UF experiment to evaluate membrane performance. The effects of PVP and PANI nanofibers on membrane formation mechanism, structure and performance were analyzed and the correlations among these were also established.

2. Experimental

2.1. Materials

PSf was purchased from Dalian Polysulfone Plastic Limited Co. (Dalian, China) and used as a membrane material. Bovine serum albumin (BSA, 67 kDa) was electrophoresis pure and purchased from Zhengjiang High-technology Co. (Tianjin, China). Egg albumin (EA, 43 kDa) and trypsin (23 kDa) were supplied by Aladdin Reagent Co. (Shanghai, China). PVP and N-methyl-2-pyrrolidone (NMP) were purchased from Kewei Chemicals Co. (Tianjin, China) and used as received. PANI nanofibers were prepared by chemical oxidative polymerization in our laboratory, according to the method reported in Refs. [19,25,26]. The average diameter and length of the PANI nanofibers used in the experiment were 43 nm and 259 nm, respectively, which were determined with the aid of transmission electron microscopy (TEM, JEOL) and ImageJ software (1.38×, National Institutes of Health, USA) [26]. Pure water having a conductivity of less than 12 μs/cm was produced by a reverse osmosis system.

2.2. Membrane preparation

Membranes were prepared via immersion precipitation method. Table 1 shows the compositions of PSf/PVP/NMP casting solutions and PSf/PANI nanofibers/NMP casting solutions. PSf/PVP/NMP casting solutions were prepared by dissolving PVP and PSf into NMP. The addition contents of PVP were varied from 0.1 to 5.0 wt%. PSf/PANI nanofibers/NMP casting solutions were prepared by dispersing PANI nanofibers in NMP, and then dissolving PSf in the dispersion, according to the method reported in Ref. [19]. When the addition content of PANI nanofibers was above 1.5 wt%, it was difficult for PANI nanofibers to be well dispersed in the viscous casting solution. Thus, the addition contents of PANI nanofibers were varied from 0.01 to 1.5 wt%. For all the casting solutions, the mass content of PSf to total casting solution was 15 wt%.

The casting solutions were left still for 12 h to allow complete release of bubbles. After that, the casting solution was cast on a glass plate with a steel knife to get a casting film of 200 μm thickness, exposed to atmosphere (humidity: 28 ± 1%, temperature: 25 ± 1 °C) for 30 s, and then immersed in a coagulation bath of pure water. The prepared membranes were washed thoroughly with pure water to

Table 1
The compositions of the PSf/PVP/NMP and PSf/PANI nanofibers/NMP casting solutions.

Membranes	The casting solution compositions (wt%)			
	PSf	PVP	PANI nanofibers	NMP
PSf	15.0	–	–	85.0
PVP-0.1	15.0	0.1	–	84.9
PVP-0.5	15.0	0.5	–	84.5
PVP-1.0	15.0	1.0	–	84.0
PVP-1.5	15.0	1.5	–	83.5
PVP-2.0	15.0	2.0	–	83.0
PVP-3.0	15.0	3.0	–	82.0
PVP-5.0	15.0	5.0	–	80.0
PANI-0.01	15.0	–	0.01	84.99
PANI-0.05	15.0	–	0.05	84.95
PANI-0.1	15.0	–	0.1	84.9
PANI-0.5	15.0	–	0.5	84.5
PANI-1.0	15.0	–	1.0	84.0
PANI-1.5	15.0	–	1.5	83.5