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The effect of pH of coagulation bath on tailoring the morphology and separation performance of polysulfone/polyaniline ultrafiltration membrane

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ABSTRACT

Polysulfone/polyaniline (PSf/PANI) ultrafiltration (UF) membranes were prepared via the phase inversion method using N-methyl-2-pyrrolidone (NMP) as the solvent and PANI emeraldine base particles as the additive. It was observed that when NMP was exchanged in an aqueous bath that was non-solvent for PANI, the PANI particles re-assembled into different conformations depending on the pH of the aqueous bath. Thus, PSf/PANI UF membranes were prepared using aqueous coagulation bath with various pH values. It was expected that altering the pH of the coagulation bath could affect the surface migration of PANI particles during membrane formation and tailor the morphology as well as separation performance of the membranes. The re-assembly process of PANI particles in acid/base aqueous solution was investigated using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and ultraviolet-visible spectroscopy (UV–vis). PSf/PANI membranes were characterized by SEM and water contact measurement. The separation properties of composite membranes were investigated in terms of water permeation and protein filtration. The results showed that the porosity and surface pore size of PSf/PANI membrane increased with increasing pH values of the coagulation bath. A substantial increase in water flux was observed for PSf/PANI membranes coagulated in base aqueous bath while an obvious decrease in water flux was observed for PSf/PANI membranes coagulated in acid aqueous bath. Changes in morphology and separation performance of PSf/PANI membranes were found out to be directly related to the re-assembly process of PANI particles in aqueous bath at different pH values. The increase of membrane permeability with slightly scarifying rejection could be achieved by adjusting the pH of an aqueous bath during the preparation of PSf/PANI UF membranes.

1. Introduction

Ultrafiltration (UF) is a well-developed separation process used in water/wastewater treatment, reverse osmosis pretreatment, and separations in food, chemical and biochemical industries [1,2]. As a consequence, the improvement of UF process performance is gaining heightened attention due to increased demands. In many cases, the membrane itself plays a crucial role in membrane process. Polysulfone (PSf) is one of the most widely used membrane materials owing to its outstanding acidic and basic resistance, good thermal stability and film forming ability [3–6]. Unfortunately, the prepared PSf membranes usually exhibit low permeability and serious membrane fouling due to their hydrophobic properties [7]. Thus, intensive research efforts have focused on improving membrane permeability and fouling resistance [4,8–12].

Non-solvent induced phase separation is the most typically used technique for preparation of UF membranes [13–15]. This technique is based upon the controlled interaction of solvent and non-solvent solutions to induce a phase separation transition of polymers from a liquid dispersion to a solid state [16,17]. Phase separation by immersing the casting film in non-solvent, is generally called immersion precipitation. In this process, the polymer film solidifies, forming a membrane through the exchange between the solvent inside the casting film and the non-solvent in the coagulation bath [17]. The key factors that affect membrane morphology and properties include polymer type and concentration, additives to the polymer solution, solvent type, and non-solvent composition. Many researchers have studied the role of additives in preventing macrovoid formation, improving pore interconnectivity and increasing hydrophilicity

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[4,7,9–12,18–23]. The effects of the additives on membrane structure are complicated and closely associated to the physicochemical properties of additives, such as solubility, molecular weight, and functional group.

Water-soluble polymers such as poly(ethylene glycol) (PEG) and polyvinylpyrrolidone (PVP) have served as additives to fabricate commercial PSf UF membranes [24–27]. Due to their high solubility in both solvent and non-solvent, PVP or PEG additives are leached out of casting films during phase separation and act as pore-forming agents during membrane formation, which leads to an increase of membrane porosity and permeability. Numerous studies have reported PVP additives with varying concentration and molecular weights in attempts to improve membrane morphology and permeability [24,26]. As PVP molecular weights increased from 24 to 360 kDa, membrane sublayer structure became dense with fewer macrovoids, and the pore number and porosity of the blended membrane increased [26]. It can be concluded from previous studies that the function of pore-forming capacity has a direct relation to the physicochemistry of additives. In other words, the pore structure and permeability of the blended membrane can be tailored by altering the type, concentration, and molecular weight of these additives.

Coagulation bath composition, temperature and pH are also important parameters that influence the morphology and performance of the prepared membranes. Deshmukh and Li [28] investigated the effect of ethanol composition in coagulation bath on morphology of PVDF membrane. They observed that the presence of ethanol in the coagulation bath reduced the precipitation rate in phase inversion process and decreased the effective porosity of the blended membrane. The research group of Mohanmmadi [8,14] investigated the effect of coagulation bath temperature on the morphology and performance of asymmetric CA and PES membranes. It was found out that increasing coagulation bath temperature accelerated diffusional exchange rate of nonsolvent and the solvent during the solidification process, resulting in macrovoid formation and permeation flux enhancement. Ying et al. [29] prepared PAAc-g-PVDF and P4VP-g-PVDF microfiltration membranes in aqueous coagulation baths at various pH values. Variations in surface composition and pore size of the two types of blended membranes were observed with changing the pH of the coagulation bath, resulting from the combined effects of the interaction of hydrophilic polymer side chains with the aqueous medium of the coagulation bath.

Recently, polyaniline (PANI) has received much attention as an additive for fabricating UF membranes [30–32]. PANI is a well-known conducting polymer because of its ease of preparation, chemical durability, and acid-base doping chemistry [33–35]. PANI in emeraldine base exhibits high solubility in N-methyl-2-pyrrolidone (NMP) and poor solubility in water [28,36]. The dissolution of PANI into NMP should disentangle the polymer chains and destroy any structures that the particles may have possessed. When solutions of PANI–NMP were added to aqueous solutions, PANI was found to re-assemble into a certain shape and precipitated [33]. In our previous studies, PSf/PANI composite membranes were prepared by incorporating emeraldine base PANI in a PSf–NMP system [31]. The results suggested that a small portion of PANI was leached out of the casting film with the rapid outflow of NMP into a water bath and acted as a pore-former during phase separation. This process caused an increase of membrane pore size, porosity and flux. The pore-forming function of PANI during phase separation was associated with the additive concentration in the casting solution. Upon increasing the additive concentration in the casting solution, the absolute content of PANI diffusing into the water bath increased, while the relative content of PANI diffusing out decreased. The pure water flux of the PSf/PANI composite membrane reached a maximum when the PANI concentration in the total casting solution was 0.1 wt%. Recently, our experimental results demonstrated that PANI particles exhibited different dispersion states when a droplet of PANI/NMP solution was added into aqueous media at different pH values. Consequently, it was predicted that the pH of the aqueous bath might affect the pore-forming function of PANI during phase separation and therefore acted upon the morphology and separation performance of PSf/PANI composite membrane.

In the present work, PSf/PANI composite membranes were prepared using an aqueous coagulation bath at various pH values. The re-assembly process of PANI particles in acid/base aqueous solutions was investigated using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and ultraviolet–visible spectroscopy (UV–vis). The effects of the coagulation bath pH on the surface pore size, porosity and cross-section morphology of PSf/PANI composite membranes were also a matter investigated. Pure water flux, protein rejection and antifouling property were tested to reflect membrane performance.

2. Experimental

2.1. Materials and reagents

Polysulfone (PSf) was purchased from Dalian Polysulfone Plastic Limited Co. (Dalian, China) and used as a membrane material. Hydrochloric acid (HCl), Sodium hydroxide (NaOH), ammonia, ammonium peroxydisulfate (APS) and N-methyl-2-pyrrolidone (NMP) were purchased from Kewei Chemical Reagent Co. (Tianjin, China). 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). Pure water having a conductivity of less than 12 μs/cm was produced by a reverse osmosis system. Aniline was purified by vacuum distillation prior to be used.

2.2. Synthesis and characterization of PANI particles

PANI particles were synthesized according to a well-established procedure where chemical oxidative polymerization of aniline is conducted in aqueous HCl using APS as the oxidant [37]. The aniline was developed within an aqueous ammonia solution (3%) with stirring for 6 h. Finally, the emeraldine base PANI powders were obtained after filtration and dryness.

The following experiments were carried out to investigate the re-assembly process of PANI in acid/base aqueous solution. First, a 0.1 wt% PANI solution was prepared by dissolving PANI powders into NMP, which is a widely-used solvent for PANI. The dissolution should disentangle the polymer chains and destroy any structure that the particles may have possessed [33]. Next, a droplet of this solution was added into 10 mL of acid/base aqueous solution causing PANI to precipitate due to its immiscibility with water. Upon replacing the PANI solvent with a non-solvent, re-assembly process of PANI occurred in accordance with the surrounding chemical environment. Finally, the solution was dipped into a copper grid for TEM observation and placed into a filter membrane for SEM observation. After dryness of the samples, the morphology of re-assembled PANI particles was observed.

Ultraviolet–visible (UV–vis) spectroscopy was used to confirm the chemical composite and content of PANI in a solution. UV–vis spectrum was recorded between 250 and 1000 nm using an UV–vis spectrophotometer (TU-1810DPC, China).