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Preparation of PES/SPSf blend ultrafiltration membranes with high performance via H_2O-induced gelation phase separation

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ABSTRACT

Polyethersulphone (PES)/sulfonated polysulphone (SPSf) blend ultrafiltration membrane was prepared via non-solvent induced gelation phase separation (NIGPS) using H_2O as the non-solvent additive in the casting solution with N,N-dimethylacetamide (DMAc) as the solvent. An ultrasonic technique was employed to monitor membrane formation so as to provide the quantitative information during the phase separation. The effect of H_2O concentration in the PES/SPSf/DMAc casting system on the membrane structure and properties was investigated. Results indicated that the viscosity of the casting solution increased with the increase of H_2O content from 3 wt% to 9 wt% owing to the strong interaction between H_2O molecules and the $-SO_3^-$ group of SPSf chains, finally leading to the gelation of the system. Simultaneously, the microporous structure of the resultant membranes changed gradually into sponge-like structure from macrovoids with the increase of H_2O content in the casting solution. It was related to the changes of the phase separation behavior from instantaneous demixing to delay demixing. Specifically, the approaching ratio could be used to predict the behaviors of the instantaneous and delay demixings. Moreover, the pure water flux of PES/SPSf blend membrane obtained under the conditions of polymer concentration 18 wt%, PES: SPSf = 84:16 wt/wt and 9 wt% H_2O in the casting solution was up to 858 L/m^{2}h. The bovine serum albumin (BSA) rejection was 90.5%.

1. Introduction

Commercial polymeric ultrafiltration (UF) membranes, such as those applied in water treatment, biology science and chemical engineering, have been prepared via phase inversion method. The final structure of the membranes is the key factor that determines the property of the membrane [1,2]. Therefore, a number of studies including thermodynamics of casting solution (such as polymer concentration and additives) and kinetics of demixing process (e.g. coagulation temperature) have been carried out to obtain the desired membrane structure for various applications [3].

It is well known that the additives in the casting solution have a significant effect on the porosity of the membranes as well as the morphology. The major role of the additives is to increase the viscosity of the casting solution or make it gelation, which restrains the mutual diffusion between solvent and non-solvent due to the reduced fluidity [4]. The commonly additives in casting solutions can be divided into three basic types: hydrophilic polymers, inorganic salts and non-solvent. The hydrophilic polymer, such as poly (ethylene glycol) (PEG) or poly(*N*-vinyl-2-pyrrolidone) (PVP), have been widely used in casting solution to control the membrane structure by increasing the viscosity of the casting solution [5–7]. The reason is that the hydrophilic polymer reduces the solvation power of solvent for polymer, which induces aggregation or cross-linking in the solutions. Besides, Lee et al. [8] added LiCl to the casting solution of poly (amic acid) (PAA) and *N*-Methyl-2-pyrrolidone (NMP), changing the membrane structure into sponge-like from macrovoids. The reason was that LiCl interacted more strongly with NMP than with PAA, leading to the formation of LiCl-NMP complexes hence, a decrease in the solvency of NMP for PAA, which promoted the aggregation of entangled polymer chains in the salt-containing solutions.

In addition, it should be noticed that non-solvent additives have a more significant effect on the membrane structure than hydrophilic polymers and inorganic salts. This is because non-solvent additives usually lead to the gelation of casting solution, which exhibits a three-dimensional network in the casting solution. For instance, Wu et al. [9] investigated the effect of alcohol additives on the structure of the PES flat membrane. It was found that alcohol additive was one of the most significant factors to determine the membrane structure including macrovoids and sponge-like. Similarly, Xu et al. [10] found that the

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structure of PES hollow fiber UF membranes changed slowly into sponge-like structure from long and wide finger-like structure with the increase of ethanol concentration as non-solvent additive in the dope solution was increased from 0 to 25 wt%. At the same time, the pure water flux of the resultant membrane increased from 47 to 167 L/m^{2}h.

Further, Lin et al. [11] investigated the effect of non-solvent additive H_2O on polymethyl methacrylate (PMMA) membrane structure and demonstrated the mechanism of non-solvent H_2O induced gelation in suppressing macrovoid formation. It was found that when enough water was added in the PMMA/NMP solution, the water induced the formation of PMMA gels, which would prevent the water penetration and thus suppressed the formation of macrovoid. Moreover, Zhang et al. [12] described that the PSF flat UF membrane obtained by using ethanol and PVP together as mixed additives in PSF/DMAc/ ethanol/ PVP solution exhibited a good anti-pressure stability and high water flux. Liu et al. [13] described that PES hollow fiber membrane were fabricated using PEG 400 as weak non-solvent and water as strong non-solvent. Results demonstrated that the macrovoid formation could not be suppressed by the addition of PEG 400 alone, even at the concentration as high as 38 wt%. Only when relatively large amounts of water were added to the casting solution, macrovoids were avoided and nice spongy structure was obtained. Wang et al. [4] also found that macrovoids structure in poly (acrylonitrile-*co*-acrylic acid) membrane were suppressed by the addition of enough water or water-PEG (or glycerin) mixture if the gelation could be induced. Although a lot of work has been done, the stability of the gelation system induced by non-solvent limits its applications due to the weak interaction between non-solvent and polymer. More importantly, the resultant membrane properties including permeation, anti-fouling and mechanical strength is still not satisfactory.

Recently, our research group investigated the blend compatibility between PES and SPSf through thermodynamics of casting solution and kinetics of demixing process with water as coagulant via non-solvent-induced phase separation [14]. Results showed that the PES/SPSf blend system was completely compatible at any blend proportion, leading to the resulting membrane with sponge-like asymmetrical gradient structure as well as excellent water permeability and better antifouling ability. The objective of the present study is to further enhance the performance of the PES/SPSf blend ultrafiltration membranes by non-solvent H_2O-induced gelation phase separation. The effect of non-solvent H_2O concentration in the casting solution on the structure and properties of the blend ultrafiltration membrane was investigated. An ultrasonic technique was employed to monitor the membrane formation so as to provide the quantitative information during the phase separation. Additionally, the approaching ratio α was used to predict the behavior of instantaneous demixing and delay demixing.

2. Experimental

2.1. Materials

PES (3000 P, M_W = 62,000 g/mol) was provided by Solvay (Belgium) and SPSf (25% of sulfonation degree) was purchased from Tianjin Yanjin Technology Co. Ltd. (China). PEG (M_W = 20,000 g/mol) was purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (China). All the materials were dried in the drying oven at 70 °C for 24 h before using. DMAc was purchased from BASF (Germany) without further purification. Reverse osmosis water was used as the non-solvent additive and coagulation bath. Bovine serum albumin (BSA) (M_w = 68,000 g/mol) was purchased from Beijing Probe Bioscience Co. Ltd (China). The solubility parameter of membrane materials and solvents was listed in Table 1.

2.2. Membrane preparation

The composition of the casting solutions for membrane preparation is listed in Table 2. It is noted that the optimal ratio of PES/SPSf (PES: SPSf = 84 wt%:16 wt%) and the PEG concentration (24 wt%) obtained via plus method was obtained from our previous work [14] and used in this paper. Among them, H_2O as an additive with the concentration of 3–11 wt% was added. All the membranes were fabricated by non-solvent induced gelation phase separation. First, the mixture of polymers, DMAc and additives were stirred in a flask at 70 ± 1 °C for 8 h and then left homogenous solutions in a water bath for 12 h to remove the bubbles. Then the casting solutions were spread on a glass plate via a steel knife with the thickness of 300 μm. The nascent membrane was kept in a calorstat with the temperature of 25 ± 1 °C and the relative humidity 40 ± 1% for 10 min so as to form a gelation, and subsequently immersed in the coagulation bath of pure water (25 ± 1 °C). Finally, the resultant membrane was kept in water to remove the residual solvent and additive.

Table 1
The solubility parameter of membrane materials and solvents.

Types	PES	SPSf	DMAc	NMP	DMSO	DMF
Solubility parameter	10.73	20.67	22.7	22.9	26.6	24.8

Table 2
Composition of the casting solution.

Membranes	PES (g)	SPSf (g)	DMAc (g)	PEG (g)	H_2O (g)	H_2O (wt%)[a]
M0	7.56	1.44	41	12	0	0
M1	7.56	1.44	41	12	1.5	3
M2	7.56	1.44	41	12	2.5	5
M3	7.56	1.44	41	12	3.5	7
M4	7.56	1.44	41	12	4	8
M5	7.56	1.44	41	12	4.5	9
M6	7.56	1.44	41	12	5.5	11

[a] The concentration of water is calculated via plus method.

2.3. Ultrasonic measurements

The ultrasonic through-transmission technology was employed to monitor the membrane formation. The schematic diagram of experimental setup and the detailed experimental process can be found in the literatures published by our research group [15,16]. The time shift of ultrasonic signal owning to the mutual diffusion could be visualized so as to quantify membrane formation rate and illustrate the relationship between the phase demixing and membrane morphologies.

2.4. Falling ball experiment

Falling ball experiments were employed to determine the solution gelation. A homogenous casting solution with 18 wt% PES/SPSf and different H_2O contents was prepared in a glass tube at 70 °C. After that, the glass tube with the same volume of the casting solution (20 ml) was kept into a water bath at 25.0 ± 0.1 °C. Then, a steel ball with a diameter of 2.0 mm was placed on the surface of the casting solution and the falling time is defined as the duration in which a steel ball falls from the surface of the solution to the bottom of the tube. Finally, the gelation of casting solution could be determined according to the falling time [4,8].

2.5. Membrane characterization

The viscosity of PES/SPSf casting solutions was measured using a rotational viscometer (NDJ-8S, Hengping Instrument company, Shanghai China) connected to a temperature-control water bath. All measurements were performed at the shear rate of 10 s^{-1} with different temperatures [17].