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The influence of phase inversion process modified by chemical reaction on membrane properties and morphology

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Abstract

In this study, the chemical reaction between acetic acid (CH_3COOH) used as non-solvent additive of casting solution and sodium carbonate (Na_2CO_3) dissolved in water as coagulant was employed to modify the classical phase inversion process. By means of this method, the polyethersulphone (PES) ultrafiltration (UF) membranes were prepared. The influence of acetic acid on the properties of the polymer solution was examined by viscometry and related to the morphology of the membrane prepared from the casting solution. The membranes were characterized in terms of the pure water flux, solute transport and field emission scanning electron microscope (FESEM) observation. It was found that chemical reaction between the additive and coagulant increases membrane permeability and mean pore size while maintaining the relatively narrow pore size distribution. FESEM images also confirmed that the chemical reaction contributes to suppress the formation of macrovoid and enhance the interconnectivity of pore. Furthermore, the potential mechanism of membrane formation influenced by chemical reaction was explored tentatively.

Keywords: Polyethersulphone; Membrane preparation and structure; Coagulant bath; Additive; Chemical reaction

1. Introduction

There are several ways to prepare porous polymeric membranes, such as sintering, track etching and phase separation processes [1]. The majority of polymer membranes used for micro and ultra-filtration of liquids are prepared by the process of immersion precipitation [2], in which a film of concentrated polymer solution is cast on a suitable substrate and subsequently immersed in a non-solvent bath where the replacement of solvent by coagulant and the precipitation of polymer take place.

However, the classical procedure is not versatile enough to produce all the desirable membrane structure and properties. Modifications of the basic procedure are usually needed, including the addition of suitable additive to the casing solution or the coagulation bath, introducing additional steps, such as evaporation [3] or annealing [4], and coupling chemical reaction with phase separation process [5].

Changing the composition in the casing solution or the coagulation bath has been one of the convenient and efficient methods to prepare membranes with optimal structure and special properties. The additive may be inorganic salts [6], surfactants [7], polymer [8], mineral fillers [9] and even non-solvents for membrane materials [10]. To sum up, the role of these additives is to suppress the formation of macrovoids, enhance pore formation and improve pore interconnectivity and/or hydrophilicity.

Evaporating the volatile solvents in casting solution before immersing it in the coagulation bath is also a common treatment to improve the membrane structure [11]. For example, Mosqueda-Jimenez et al. [3] reported the mean pore size and MWCO of the membranes were decreased by increasing the solvent evaporation time. Lai et al. [10] found the evaporating step can prevent the shrinkage of membrane during the immersion step, which results in a lot of wrinkles on

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the membrane surface. In addition, evaporation is known as an efficient method to suppress the formation of macrovoids [12].

Recently, Yang and Liu [5] found the chemical reaction between the additive ($CaCl_2$) of the casting solution and the coagulation medium (aqueous solution of Na_2CO_3) plays a significant role in PAN membrane performance. That is, high reaction rate results in the fabrication of big pore size and high permeation.

In the present work, the PES membranes were prepared through the phase inversion method modified by chemical reaction. When the PES/DMF/CH_3COOH casting films were immersed in the aqueous solution of Na_2CO_3, the following chemical reaction occurred:

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + CO_2\uparrow + H_2O$$

The main objectives of this study were to present some effects of the chemical reaction on the membrane properties and morphology and explore the potential mechanism of membrane formation through the modified method tentatively.

2. Experimental

2.1. Materials

PES used as membrane material in this study was purchased from BASF. DMF, CH_3COOH and Na_2CO_3 were all obtained from Hangzhou Changqing Chemical Reagent Company. All the products were used directly without further purification.

2.2. Viscosity studies

In this study, the relative viscosities were obtained by using the method described by Lee et al. [13]. The efflux times of samples of solvent and dilute polymer solutions (less than 0.3 wt.% PES) into which different quantity of acetic acid (from 0 to 10 wt.%) was added were measured using an Ubbelohde capillary viscometer in a thermostatted water bath at $25 \pm 0.1\,^{\circ}C$. Based on these efflux times, two kinds of relative viscosities for each polymer solution were calculated in terms of the ratio of the efflux time measured for the polymer solution to the corresponding efflux times of DMF with and without presence of acetic acid, respectively.

2.3. Coagulation value measurement

A homogenous polymer solution prepared by dissolving 20 g PES in 80 g DMF solvent was placed in a thermostatted water bath ($25 \pm 0.1\,^{\circ}C$), and then the CH_3COOH was added into it with a micro-syringe. During the titration, the polymer solution was stirred. When the solution became visually turbid, the addition of CH_3COOH was stopped. Then, the required CH_3COOH amount, 16 ml measured for the system, was taken as the coagulation value of the system.

2.4. Preparation of membranes

The casing solutions consisted of 20 wt.% solution of PES in DMF into which quantity of CH_3COOH ($r = 0.5$) was added, where r is the ratio of the amount of CH_3COOH added into the system to the coagulation value of the system. Solutions were placed in sealed bottles and degassed overnight (or longer) before use. Then, a casing solution layer whose thickness is 220 μm was cast at a uniform speed and at room temperature. After 5 s evaporation in the atmosphere, the films were immersed in the water or aqueous solution of Na_2CO_3. In this paper, the Arab number in the membrane sample ID stands for the Na_2CO_3 concentration of the coagulant bath (wt.%) the membrane was prepared from, such as PES-0, PES-1, PES-5 and PES-10. Because the chemical reaction took place during the exchange between the solvent and coagulant, special care must be taken in the membrane formation process. In order to complete the formation process, the membranes were kept in the coagulation bath overnight. After that, the membranes were rinsed thoroughly with demineralized water and wet stored until used.

2.5. Flux and separation measurement

The obtained membrane sheets were cut into circle membrane species of 5.8 cm diameter before being installed into a homemade membrane permeation test apparatus. Membrane samples which were initially compacted at 400 kPa for 6 h were subjected to experiments at a trans-membrane pressure of 100 kPa. In the separation experiments, the corresponding probe solutions flowed through the test system for more than one hour before collecting permeate samples and analyzing them. Three sets of membrane samples were made for each casting condition specified in this paper and the average values were reported.

2.6. Membrane characterization based on the solute transport data

Michaels [14] reported that a straight line is yielded when solute separation (f) of an ultrafiltration membrane is plotted versus the solute diameter on a log-normal probability paper. By the use of this log-normal correlation between solute separation and solute diameter, pore size and pore size distribution can be investigated through the parameters calculated for the probe molecular which must exhibit low membrane–solute interaction. That is to say, the parameters calculated for these solutes may be considered to be the same as the parameters for the pores if the dependence of solute separation on the steric and hydrodynamic interaction between solute and pore could be ignored [15]. Hence, μ_p (the mean pore size) can be calculated as d_s (the solute diameter) corresponding to $f = 50\%$, σ_p (the geometric standard deviation) can be determined from