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Morphology control of polysulfone hollow fiber membranes via water vapor induced phase separation

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Abstract

Polysulfone hollow fiber membranes were fabricated by a dry/wet spinning process, with *N*-methyl pyrrolidinone (NMP) and water as solvent and coagulant, respectively. The results indicate that air-gap length and ambient humidity have dramatic effect on the membrane morphology. Macrovoids in the membranes disappeared, reappeared, and redisappeared with increasing air-gap length. Evidence was obtained showing that, because of the high affinity of NMP for water, water vapor was drawn to the dope to induce phase separation, resulting in a nascent structure in the dope before it was immersed in the coagulation bath. We proposed that, shortly after the onset of its phase separation in the air gap, the dope behaved as a transient gel, which can reasonably explain the disappearance and reappearance of macrovoids. On the other hand, when the air gap was long enough to allow phase separation of the entire dope before it reached the coagulation bath, macrovoids redisappeared. In addition, we observed that the air-gap length required for the disappearance and redisappearance of macrovoids decreased with increasing ambient humidity, which can be well reasoned by the decreasing contact time with the humid air needed to bring about phase separation of the dope in the air gap.
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1. Introduction

Membrane processes, with the advantages of easy operation and energy saving, have many applications in separation of mixtures. The applicability of a membrane technique to a separation process strongly depends on if the membrane possessing suitable separation performance can be successfully prepared. Therefore, many researches have concentrated on developing techniques to prepare membranes and to tailor their separation performance. Among the methods for preparation of polymeric membranes, the most widely used one is the phase inversion method [1]. In this method, the phase separation and subsequent solidification (gelation) of the cast polymer solution determine the final membrane morphology and the associated separation performance. There are several methods to induce phase separation during membrane forming: change in the solution temperature, the so-called thermally induced phase separation (TIPS), exchange of solvent with nonsolvent (coagulant), the so-called immersion precipitation or nonsolvent induced phase separation (NIPS), and intake of nonsolvent vapor, the so-called vapor induced phase separation (VIPS) [2,3].

With a dry stage for solvent evaporation and a wet stage for exchange of solvent with nonsolvent, the dry/wet phase inversion process produces membranes with various kinds of structure [1]. It is well known that the solvent evaporation in the dry stage affects dramatically the final membrane structure. Less attention has been paid to another phenomenon that can also occur in the dry stage: water vapor in the humid air is drawn to the cast film and thus brings about phase separation (VIPS). In particular, when the polymer solvent used possesses

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low volatility but high affinity for water, in the dry stage the intake of water vapor might prevail over the solvent evaporation. Therefore, to fully understand the forming of polymeric membranes in a dry/wet process, knowledge of VIPS is essential.

Many researches have focused on the VIPS process for preparation of flat-sheet membranes [3–10]. Han and Bhattacharyya [4] prepared polysulfone (PSf) flat-sheet membranes by simply sitting the cast film in humid air, which lead to a liquid–liquid phase separation with nucleation of the polymer-poor phase. Park et al. [3] also adopted the process to fabricate membranes and showed that phase separation only occurred when the relative humidity in air was higher than about 65%. In addition, they observed that the pore size of the resulted membrane was strongly affected by the relative humidity in air. Furthermore, Matsuyama et al. [5,6] showed that, with an increase in relative humidity, they could change the morphology of poly(vinylidenefluoride) (PVDF) membranes from dense to lacy-like, which was believed to be related to the mass increase of the cast film at higher relative humidity. Kang et al. [7,8] also obtained evidence indicating that ambient humidity is an important factor in determining the pore size of membranes. Quantitative analysis of VIPS was conducted as well. Caquineau et al. [9] measured the mass change of cast film during membrane forming and proposed a phenomenological model to explain the morphology evolution caused by VIPS. Khare et al. [10] have developed recently a mathematical model to describe the composition change in the cast film in association with the VIPS process. Another important issue about VIPS is the accompanying phase separation mechanism. Using time-resolved small angle light scattering and phase contrast optical microscopy, Lee et al. [11] were able to show that VIPS actually takes place via spinodal decomposition.

Although the role of VIPS in the forming of flat-sheet membranes was widely studied, as discussed in the preceding paragraph, few articles identified the importance of VIPS in the preparation of hollow fiber membranes. A wet spinning process with an air gap is actually a dry/wet process since both evaporation of solvent and intake of water vapor can occur in the air gap. Therefore, it is reasonable to expect that VIPS occur in the air gap and affect the final morphology of hollow fibers, especially when the polymer solvent has low volatility but high water affinity. However, the role of VIPS in determining the morphology of hollow fibers has yet been investigated. Only some reports [12–15] pointed out that ambient humidity might have influences on membrane morphology. Investigation on the interplay between VIPS and membrane morphology is still needed, to get insight into the morphology control of hollow fibers.

In the present work, we fabricated polysulfone hollow fiber membranes via the dry/wet spinning process, changing the length of air gap and the ambient humidity to demonstrate the effect of VIPS on membrane morphology. Our focus is on how VIPS affects the forming of macrovoids near the outer surface of hollow fibers. A special feature of this work is to lock up the nascent fiber morphology formed in the air gap, by injecting the dope into a bath of liquid nitrogen immediately after the end of the air gap zone. With this method we can compare the morphology formed in the VIPS stage with the final one, to shed light on the interplay between VIPS and the final morphology of hollow fibers.

2. Experimental

2.1. Materials

Polysulfone (PSf) (Udel P-3500) was purchased from the AMOCO Performance Products Inc. (Ridgefield, CT, USA). *N*-methyl pyrrolidinone (NMP) of reagent grade, without further purification, was used as the solvent for PSf, and distilled water was used as its coagulant. In addition, methanol of reagent grade was used to extract the frozen NMP after the dope was injected into liquid nitrogen to luck up the nascent morphology.

2.2. Spinning of PSf hollow fiber membranes

PSf chips and NMP were mixed in a flask under agitation to form a homogenous polymer solution with 26 wt.% of PSf, which was then sit still for at least one day. Next, the homogenous polymer solution was poured into a dope tank and kept there overnight for eliminating the air bubbles formed during the stages of agitation and pouring.

The degassed homogeneous solution was used to fabricate PSf hollow fiber membranes with the dry/wet spinning process. Subject to a pressure of 2 atm, the polymer solution was extruded through a spinneret, with an outside diameter of 0.83 mm and an inside one of 0.25 mm, to a coagulation bath of water with an adjustable air gap between the spinneret and the water bath. The whole spinning line, from the spinneret to the coagulation bath, was placed in a humidity-and-temperature controlled cabinet (Jwo Ruey Technical Co., Ltd., Taiwan, Model TH-1000), so that the humidity and temperature in the air gap were fixed and could be adjusted during the spinning process. The bore liquid (70/30 NMP/water) was delivered using a syringe pump (500D from ISCO Inc., USA), and there was no external elongation stress except gravity applied to the nascent hollow fiber membranes. After solidification, the fibers were removed from the coagulation bath and put in distilled water for at least three days and then in methanol for 2 h to remove the residual solvent, which was followed by an air drying stage of about 24 h at room temperature.

For some experiments, a bath of liquid nitrogen was used instead of the water bath to lock up the nascent morphology that was formed in the air gap due to VIPS. The dope was injected into the liquid nitrogen bath immediately after it passed through the air gap, so that the formed structure in the air gap could be fixed because of fast quenching. In order to examine the lock-up morphology by SEM, the NMP contained in the quenched dope had been removed to prevent it from redissolving PSf and destructing the quenched structure when the samples were taken out for drying from the bath of liquid nitrogen. The quenched dope was immersed in methanol at −90 °C for 9 h, −85 °C for 0.5 h, −60 °C for 0.5 h, and −30 °C for another 0.5 h to extract out the frozen NMP. After which, the resulted membrane was air dried for further examination of the structure by SEM.

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