Effect of Inner Non-solvent Condition on Morphology of PVDF Hollow Fiber Membranes Prepared by NIPS Spinning Process

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Abstract

Hollow fiber membranes of PVDF were prepared by isothermal wet spinning process from the water/DMF/PVDF system at 25 °C. The dope solution comprised 21 wt% PVDF in DMF, and pure water was employed both as the inner and outer coagulants. SEM imaging of the membrane indicated an unexpected interesting morphology: columnar macrovoids extended from the outer surface to the central region, while cellular pores constituted the inner half of the membrane. As water was a harsh nonsolvent, one tended to think that macrovoids shall form towards the inner surface of the hollow fiber. Absence of macrovoids in this region was explained based on the fact that DMF would accumulate rapidly in the inner extruding stream as it underwent mass-exchange with water in the inner bath. Such activity rendered effectively the coagulant became effectively a soft one. As a result, macrovoids was eliminated and the inner surface became porous.

Key Words: PVDF, Hollow Fiber, Membrane, Morphology, NIPS

1. Introduction

Porous hollow fiber membranes are used over a wide range of applications, such as reverse osmosis, and ultra-filtration, membrane distillation, etc. [1–5]. They are generally prepared by the non-solvent induced phase separation (NIPS) spinning process. In such process, a polymer solution (dope) consisting of polymer, solvent, and sometimes additives is pumped through the annulus, and a bore injection fluid is pumped through the inner needle tube of the spinneret. Together these two streams are extruded into a non-solvent bath where exchange of solvent and non-solvent across the dope/bath interfaces induces instability and subsequent phase separation of the dope solution. After appropriate washing and drying, the formed membranes are collected by means of a take-up device [1–10]. By varying the spinning parameters, e.g. the inner and outer diameters of the spinneret, the compositions of the polymer solution, non-solvent strength of the inner and outer baths, etc., porous hollow fiber membranes can be produced encompassing a wide range of morphologies.

NIPS process typically results in asymmetric or symmetric membranes (flat sheet or hollow fiber). Asymmetric membrane has a skin layer on the surface which serves as a selective barrier to differentiate incoming feeds. Underneath the skin is a porous bulk, which functions as the mechanical support to sustain the transmembrane pressure during filtration operations [11–17]. The porous bulk may be sponge-like or contain teardrop- or finger-like macrovoids, depending on the preparation conditions. Asymmetric structure is typically formed by pre-
cipitation of the dope solution in a so-called harsh nonsolvent bath, e.g. water, such that polymer can accumulate rapidly near the surface region (contacting the bath) to give a continuous gel layer that eventually develops into a skin. The pores in the bulk are derived from polymer-lean phase formed during phase separation induced by the influx of non-solvent. In contrast to asymmetric membrane, symmetric membrane is skinless and has a relatively uniform pore distribution across the membrane [18–24]. The membrane may be formed by carrying out polymer precipitation in a soft nonsolvent bath (e.g., a bath containing significant amount of solvent) such that exchange of solvent and nonsolvent is slow and polymer concentration would not build-up sharply during the phase separation process [18–24].

In the present research, porous PVDF hollow fiber membranes were prepared by isothermal NIPS process from the water/DMF/PVDF system. Morphologies of the membranes were observed by means of SEM. It is interesting to find that finger-like macrovoids on the lumen (inner) side can be eliminated simply by using spinneret with a sufficiently small inner tube. Such is the case even when a harsh nonsolvent, e.g., water, is employed as the inner coagulant. The reason for this unusual new finding is explained based on mass transfer and phase separation considerations. With a macrovoid-free lumen side, the membrane is expected to be stronger than ordinary ultra- or nano-filtration membranes that have macrovoids on both inner and outer sides of the membrane.

2. Experimental

2.1 Material

Poly(vinylidene fluoride) (PVDF) polymer (Kynar 740, Elf Atochem; intrinsic viscosity = 0.881 dL/g, Mn = 254,000 g/mole) and a terpolymer (Kynar 9301) of vinylidene fluoride (VDF), tetrafluoro ethylene (TFE), and hexafluoropropylene (HFP) with VDF/HFP/TFE = 60/20/20, intrinsic viscosity = 0.4 dl/g, and Mn = 79,200 g/mol was supplied by Elf Atochem Inc. N,N-dimethylformamide (DMF, Baker Analyzed, reagent grade) was used as the solvent for preparation of dopes for hollow fiber spinning. Distilled-deionized water was used as the non-solvent for precipitation of PVDF from the dope. All materials were used as received.

2.2 Phase Diagram Determination

The gelation phase boundary at 25 °C for the ternary system, water/DMF/PVDF, was determined by the widely used cloud point method [20,23]. Briefly, a specific amount of PVDF (dried in an oven at 60 °C) was mixed with DMF and sealed in a glass bottle with Teflon-lined cap. The mixture was blended at 60 °C until the polymer was completely dissolved. A known quantity of water was then added to the polymer solution. Local precipitation may be observed at the contact of water with the solution. The mixture (termed dope) was further blended at 60 °C until it became clear and homogeneous again. Then it was put in a thermostat maintained at 25 °C over the period of 30 days during which gelation might occur and the dope became a gel. The gelation points in the phase diagram were identified as the compositions at which gelation first occurred in a series of samples with increasing non-solvent/solvent ratios.

The terpolymer (Kynar 9301) is largely amorphous, and hence can be used as a model to access the liquid-liquid (L-L) demixing boundary (often termed binodal in the literature). Such is based on the fact that Kynar 9301 is chemical structurally similar to PVDF (Kynar 740) and that these two polymers have close solubility parameters, 7.2 and 7.74 (cal/cm³)½ respectively for the terpolymer and PVDF. To experimentally access the binodal, a series of solutions composed of water/DMF/Kynar 9301 were prepared and then put in a thermostat maintained at 25 °C, as in the procedure described above. Unstable solutions underwent L-L demixing into two clear homogeneous liquid layers. The binodal points were defined as the compositions of the separated liquid phases. It is also noted that the dope would not gel (still flows) even at the concentration of 50 wt.%, which may be associated with the low molecular weight of the polymer.

2.3 Membrane Preparation and SEM Observation

A schematic representation of the employed NIPS spinning process is illustrated in Figure 1. The dope solution for spinning was prepared by dissolving 21 wt% of PVDF in DMF at 60 °C. It was cooled to 25 °C and then pumped through the annulus of the spinneret. On the other hand, water was pumped through the central tube of the (ID/OD = 0.16/0.4 mm). Together these two streams entered the coagulation bath where phase sepa-
RATION occurred and polymer precipitated to form a porous hollow fiber membrane. The membrane was washed repeatedly first with distilled water, then with isopropanol, followed by hexane. Afterwards, it was dried at 50 °C in a convective oven. Flat sheet membranes were also prepared for comparison of porous structures. The membrane was prepared by immersion the 21 wt% dope cast on a glass plate into a water bath at 25 °C. The nascent membrane, as being peeled off from the glass plate, was washed and dried with the same procedure for processing hollow fiber membranes.

Morphologies of the porous membranes (both flat sheet and hollow fiber) were observed using a field emission scanning electron microscope (FESEM, Leo 1530, Carl Zeiss, Oberkochen, Germany). A piece of membrane sample was vacuum-dried and then attached to a sample holder by means of conductive copper tapes. The cross section of the membrane was obtained by fracturing in liquid nitrogen. Silver paste was applied at the edges of the sample to enhance electronic conductivity. Then, the sample was sputtered with a thin layer (~2 nm) of Pt-Pd alloy and observed under a low acceleration voltage, 2 kV, by means of an in-lens detector.

3. Results and Discussion

3.1 Phase Diagram of the Water/DMF/PVDF System

In Figure 2, the experimental phase equilibrium curves at 25 °C are presented both for the amorphous terpolymer and the crystalline PVDF in water-DMF systems. The solid circles (●) represent the cloud point compositions measured for the terpolymer in water-DMF solutions. These points mark the L-L demixing phase boundary; inside which an originally homogeneous solution will separate into two liquid phases in equilibrium. Above the gelation line is a single-phase region, in which a homogeneous dope can be prepared with a long-term stability. Below this line is a metastable zone, in which an originally homogeneous dope solution will gel upon standing at 25 °C over an extended period of time. The fact that gelation was induced by crystallization has been proven by various techniques, such as differential scanning calorimetry (DSC), polarized optical microscopy (POM),
SEM, etc. [11,25]. As the gelation region encloses the binodal, a dope inside the binodal can undergo both L-L demixing and crystallization types of phase separation.

### 3.2 Morphology of PVDF Hollow Fiber and Flat Membranes

The casting dope for preparing the PVDF flat membrane consisted of 21 wt% PVDF dissolved in DMF (cf., the solid square point in Figure 2). It was a clear uniform viscous solution. When immersed in pure water (a typical harsh nonsolvent) it underwent a very rapid precipitation process to form a membrane with morphology that is characteristic of L-L demixing dominant precipitation process. The total cross section of the membrane, as shown in Figure 3(a), comprises finger-like macrovoids and cellular pores resembling those seen in common amorphous membranes. That is, L-L demixing took place first and set-in the overall porous morphology before crystallization occurred in the polymer-rich phase that surrounded the polymer-poor liquid droplets. Figure 3(b) shows the high magnification image of the upper part of Figure 3(a). A thin skin followed by parallel columnar macrovoids extending into the central region is seen. Roughened and dendritic features on the pore walls suggest occurrence of crystallization during the late stage of the phase separation process. DSC and XRD analyses of similar PVDF membranes can be found in the literature [25]. Figure 3(c) shows the enlarged view of the cross section near the bottom surface of the membrane. Cellular pores of about 3–5 μm in diameter are clearly observed. On the pore walls, spherulitic entities (e.g., central region, pointed out by an arrow) are in evidence, which were derived from spherulitic growth of PVDF crystallites. Top surface of the membrane, as shown in Figure 3(d), is dense without appreciable pores under the resolution of ca. 40 nm. Such is typical of immersing a good dope solution in a harsh non-solvent bath, such as water. Upon contact of dope and bath, a stiff gel layer forms due to a sharp upsurge of polymer concentration at the bath-dope interface, which subsequently develops into the dense skin of the membrane. The bottom surface, as shown in Figure 3(e), consists of truncated PVDF globular objects along with cellular pores. Figure 3(f) shows the high magnification of Figure 3(e), nano-granular and dendritic features are clearly demonstrated, and because the globules grow pressing-against the glass plate during precipitation, they appear flattened [23–25].

Asymmetric polymer membranes consisting of a thin...
top layer supported by a porous sublayer composed of macrovoids and cellular pores are often observed for membranes prepared by NIPS process in a harsh non-solvent bath [1,11–17,26–31]. It is well accepted that cellular pores are resulted from radial growth of polymer-poor phase during L-L demixing. As to the macrovoids, the causes of their formation have been extensively studied in the literature [26–31]. A number of mechanisms have been proposed, e.g., surface breakage due to shrinkage stress, liquid-liquid demixing and diffusional growth of cellular pores, osmosis effect during growth of cellular pores, instability caused by perturbation of the interface in steep concentration profile, etc. Based on Mulder’s proposition [1], formation of macrovoids is initiated by L-L demixing. The liquid microdrops (micelles) of the polymer-poor phase are the embryos for macrovoids developments. A schematic representation is illustrated in Figure 4 for such case. L-L demixing occurs rapidly after the binodal is crossed due to exchange of nonsolvent and solvent at the membrane-bath interface. This causes formation of first microdrops at $t = t_1$ near the top surface. Continuing influx of solvent and non-solvent into the microdrops, as driven by osmosis forces, lead to the downward-growth of macrovoids (upward growth is unlikely due to higher polymer concentration there is) cf., $t = t_2$. This activity proceeds until the polymer concentration of the polymer-rich phase enclosing the macrovoids becomes so high that gelation occurs, and further macrovoids growth becomes inhibited, cf., $t = t_3$. Finally, asymmetric membrane formed with macrovoids extending from the top surface to the central or even bottom region of the membrane.

A schematic representation of the mass transfer across the polymer solution/bath interface during immersion of a casting dope in the form of flat sheet is shown in Figure 5(a). The solvent diffuses into the non-solvent bath with flux $J_2$, whereas the non-solvent diffuse into the casting dope with flux $J_1$. As is well recognized that such mass transfer gives rise to phase separations (the dope crosses the binodal/crystallization boundaries) and lead to porous structure formation in the membrane. For the spinning of hollow fibers, a somewhat different circumstance is encountered. As shown in Figure 5(b), the polymer solution is sandwiched between a reservoir of outer non-solvent bath and an inner stream of non-solvent coagulant that flows through the center region of the system. That is, there exist two membrane/bath interfaces, across which solvent and non-solvent exchange occurs. As harsh non-solvent was employed for both the inner and outer baths in the present work, one would speculate that the morphology of the membrane shall be similar to the combination of two flat-sheet membranes arranged in the Top/Bottom/Bottom/Top order, as shown in Figure 6. That is, finger-like macrovoids dominate the regimes near the inner and outer surfaces, while cellular pores are inserted in-between the macrovoids. The real situation is quite different, however, as shown below.

SEM photo micrographs of the PVDF hollow fiber membrane prepared by spinning of 21 wt% PVDF/DMF dope solution in pure water are shown in Figure 7. Pre-
Precipitation is observed to occur very rapidly to yield a morphology dictated by L-L demixing. The cross section of the hollow fiber membrane, cf., Figure 7(a), exhibits finger-like macrovoids from outer surface to the central part of the membrane followed by cellular pores all the way to the inner surface, which is similar to those shown in Figure 3(a). The outer surface, cf., Figure 7(b), forms a relatively dense skin with sporadic nm-scale dints evenly distributed on the surface. The magnified view of the inner surface can be seen from Figure 7(c). It is corrugate with identifiable pores of ~2 μm; namely, the surface is not a skin. Surprisingly, finger-like macrovoids are absent towards the lumen side of the hollow fiber, even with water being used as the inner coagulant, as opposed to what is illustrated in Figure 6. The reason can be explained based on mass transfer events that occur across the inner-interface during immersion. As DMF in the dope out flows into the inner tube, water and DMF mixed quickly to make the inner bath a soft coagulant (i.e., containing significant amount of solvent) for the polymer. Such is possible as long as the inner tube is thin enough to allow a quick build-up of DMF concentration in the inner bath. In this case, the inner gel layer would be soft.

Figure 5. Schematic representation of a polymer solution/bath interface. (a) formation of a flat membrane by NIPS method; (b) formation of a hollow fiber membrane by NIPS spinning process. $J_1$: flux of non-solvent diffusing into the dope. $J_2$: flux of solvent diffusing into the bath.

Figure 6. Schematic representation of the formation of PVDF follow fiber membrane by NIPS spinning process.
as oppose to the rigid one on the outer surface) and easily broken into pores during subsequent precipitation process [20-23]. Shieh et al. has demonstrated a similar immersion situation for the water/formic acid/Nylon-66 system. The calculated diffusion trajectory indicates clearly accumulation of solvent in the inner bath, and hence the polymer concentration at the inner-interface is much lower than that at the outer-interface. By contrast, if a large inner tube is used, the solvent-concentration built-up in the inner bath may become ineffective. In such case, the inner bath remains harsh and the formed membrane has macrovoids from both inner and outer sides of the hollow fiber, as is illustrated in Figure 8. The membrane was prepared by spinning 21% PVDF/DMF dope in water by means of a spinneret with larger inner tube (ID/OD = 0.33/0.6 mm/mm, comparing with the small tube, 0.16/0.4, shown in Figure 1). Obviously, the cross section has a macrovoids/cellular pore/macrovoids sandwich structure, being consistent with the immersion situation shown in Figure 6 where dope solution contacts harsh bath on both sides.

4. Conclusions

PVDF membranes in the forms of hollow fibers and flat sheets were prepared by nonsolvent induced phase separation at 25 °C from the water/DMF/PVDF system. SEM micrographs of the flat sheet membrane indicate an asymmetric structure featuring finger-like macro-
voids and cellular pores, typical of L-L demixing dominated phase separation process during precipitation. For the PVDF hollow fiber membrane spun by means of a spinneret with small inner tube, a similar asymmetric structure was demonstrated, in which finger-like macrovoids were absent from the inner (lumen) side contacting the harsh water bath. Such unexpected result was explained based on the fact that the out-fluxed DMF can quickly soften the small inner bath and delay the demixing process. In case that a larger inner tube was employed in the spinneret, macrovoids formed on the lumen side as usual simply because the amount of out-fluxed DMF was too small to effectively soften the inner bath.

Acknowledgement

The authors would like to thank the Ministry of Science and Technology of Taiwan for financial support. (NSC 99-2221-E-032-002-MY3).

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Manuscript Received: Mar. 9, 2017
Accepted: Jul. 30, 2017