On the Structure of Porous Poly(vinylidene fluoride) Membrane Prepared by Phase Inversion from Water-NMP-PVDF System

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Abstract

A PVDF membrane was prepared by isothermal immersion precipitation of a PVDF/NMP solution from pure water bath. FESEM imaging of the formed membrane revealed its porous structure, featuring tight skin, macrovoids, and cellular pores. These structural characteristics were common to membranes that were formed by precipitation of amorphous polymers from harsh nonsolvents. Evidence of crystallization in the present PVDF membrane could be observed on the surfaces of the various pores in the form of branching dendrites.

Key Words: Membrane, Poly(vinylidene fluoride), Phase Separation, Porous

1. Introduction

Poly(vinylidene fluoride) is an inert, acid resistant, mechanically strong semicrystalline polymer widely used to synthesized porous membranes for various industrial separation applications. Commercial Poly(vinylidene fluoride) membranes supplied by the Millipore Corp. were prepared by the so-called isothermal immersion-precipitation process. In this process, a dope composed of polymer, solvent and additives is immersed in a nonsolvent coagulation bath to induce precipitation by means of liquid-liquid demixing and/or crystallization [1-10]. The formed membranes often exhibit characteristics from both types of phase separations. In general, liquid-liquid demixing process engenders cellular pores whereas crystallization forms interlinked crystalline particles. Thus, by manipulating the precipitation parameters, such as dope and bath compositions, precipitation temperature, types of additives, etc., the relative rate and extents of these two phase separation processes can be adjusted to produce a wide variety of morphologies that represent different combinations of these phase separation processes. At one extreme, the formed membrane comprises a tight skin and a porous sublayer that is dominated by cellular pores and/or macrovoids. This is the case when precipitation is carried out in a harsh nonsolvent bath leading to a rapid or even immediate precipitation. At the other extreme, when precipitation is carried out in a soft nonsolvent bath, mass exchange is slow such that crystallization commences much earlier than liquid-liquid demixing. The result is a porous structure composed of arrays of interlinked crystalline particles.

In the present research, poly(vinylidene fluoride) membranes with either asymmetric or skinless structure were prepared by isothermal immersion precipitation from water/triethyl phosphase/poly(vinylidene fluoride) system. The phase diagram, including the crystallization-induced gelation line and the liquid-liquid demixing line, was determined at 25 °C. Based on the latter, bath and dope compositions were selected to prepared membranes by isothermal immersion-precipitation method. The nano-scale fine structures of the membranes were revealed by high resolution LVSEM imaging.
2. Experimental

2.1 Material

Poly(vinylidene fluoride) (Hylar 5000 HP, Ausimont U.S.A., Inc. specific gravity = 1.75, melt viscosity = 18.7 kpoise) was a semicrystalline polymer. Terpolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene (Kynar 9301, VDF/HFP/TFE = 60/20/20, intrinsic viscosity = 0.4 dL/g, Mn = 79,200 g/mole) was largely amorphous and is supplied free of charge by Elf Atochem Inc. N-methyl-2-pyrrolidone (NMP, Acros, 99 %, d = 1.028 g/ml) was used as the solvent for the polymers. Water (distilled and deionized) was used as the nonsolvent. All materials were used as received.

2.2. Gelation Boundary

The gelation phase boundary at 25 °C for the water/NMP/PVDF system was determined by the widely used ‘cloud point’ method [6,7,9]. A specific amount of PVDF (dried in a vacuum oven at 70 °C) was mixed with NMP and sealed in a Teflon-lined bottle. This mixture was then blended at elevated temperatures until the polymer was completely dissolved. To this solution was added a known quantity of water. Local precipitation could be observed. The mixture was blended at ca. 80 °C until a clear homogeneous solution was obtained. This solution was then put in a thermostatically controlled bath maintained at 25 °C over a period of 15 days. The gelation points were identified as the compositions at which homogeneous solutions started to precipitate into a gel in a series of samples with different water/NMP ratios.

2.3 Liquid-Liquid Demixing Boundary (Binodal)

The terpolymer was largely amorphous, and hence liquid-liquid demixing was observed in the cloud point measurement. A series of ternary solutions were prepared and then put in a thermostat at 25 °C, as in the aforementioned procedure. Unstable solutions underwent phase separation into two clear homogeneous liquid layers. The binodal was defined as the compositions at which homogeneous solutions started to precipitate into a gel in a series of samples with different water/NMP ratios.

2.4 Membrane Preparation and Characterization

PVDF membranes were made by the isothermal immersion-precipitation method. Dope solution was prepared by dissolving PVDF (20 wt %) in NMP (80 wt %) at an elevated temperature, as described earlier. An appropriate amount of the dope was dispersed uniformly on a glass plate (ca. 250 µm thick) and then immersed immediately into a water bath to induce phase separation. The formed membrane was washed in a series of nonsolvents and then dried under press between sheets of filter papers at 45 °C. Morphologies of the membranes were observed in cross section, top and bottom surfaces using FESEM (Leo, 1530).

3. Results and Discussion

3.1 Phase Diagrams

The experimental phase equilibrium data at 25 °C for PVDF in water/NMP solutions are presented in Figure 1. The open circles represent the gelation compositions for PVDF in water/NMP solutions. These measured data consist largely with those reported by Bottino et al. [10]. For each system, the gelation points form a phase boundary, below which gelation will take place for a dope standing at 25 °C over an extended period of time. It has been shown previously using DSC and SALS that this type of gelation was induced by polymer crystallization [8,11]. The filled circles (cloud point data) and squares (equilibrium absorption data) are measured liquid-liquid demixing compositions for the PVDF terpolymer (amorphous) in water/NMP solutions. As in other systems (e.g., water/formic acid/polyamides, 1-octanol/DMF/PVDF, water/DMF/PVDF), the binodal measured for the terpolymer was thought to approach the amorphous phase behavior of the crystalline polymer [8,11,12]. This is based on the fact that these two polymers have similar chemical structure. However, contrary to our present result, Witte pointed out that the liquid-liquid phase equilibrium boundaries of crystalline poly(L-lactide) and amorphous poly(DL-lactide) deviated significantly from each other, even though these polymers differ only in their spatial arrangements of atoms [6]. The binodal and the gelation line divided the phase diagram into three regions. Above the gelation line was a one-phase region, between the gelation line and binodal is the region where crystallization occurred exclusively, and below the binodal is where both types of phase separation could occur.

3.2. Structure of the Membranes

As a semi-crystalline polymer, PVDF may be precipitated either by liquid-liquid demixing and/or crystallization during the course of immersion-precipitation to produce membranes that
cover a wide spectrum of structures. In general, the relative weight, which depends on the sequence of these two types of precipitation events, determines whether the formed membrane will be cellular (characteristic of liquid-liquid demixing) or particulate (characteristic of crystallization) in its structure. In this article, an example was reported which represented the case where liquid-liquid demixing took place much earlier than crystallization to yield an interesting structure characterized by skin, macrovoids, cellular pores and crystal entities.

As dope "A" (cf. Figure 1) was immersed in pure water, a very rapid precipitation process (cast solution turns white instantly after immersion) was encountered. The morphologies of the formed membrane are shown in Figure 2-4. The cross section of the membrane, as shown in Figure 2(a), was highly asymmetric wherein three distinct regions could be identified. Near the top surface was a very thin dense layer, commonly termed “skin” in the literature. The top surface view, as shown in Figure 3, indicated that this layer was tight and free of sub-micron pores. Underneath the skin was a region composed of irregular columnar macrovoids that extended toward the central region of the membrane. The macrovoids were roughly parallel to each other, resembling the so-called ‘finger’ structure [1-3]. The internal surface of these macrovoids, as shown in Figure 2(b), was nonporous just like the top skin. This suggested that a very concentrated boundary layer was formed surrounding the liquid micells during phase separation, and as the micells grew downward to form macrovoids, this layer solidified by crystallization into a tight structure. Upon careful observation of Figure 2(b), one found that the surface of the wall was very rough being composed of branching crystallites whose thickness can be estimated to be 20-30 nm.

Figure 1. Phase diagram of water-TEP-PVDF system, -○− : gelation line; -●− : binodal

Figure 2. SEM micrograph of the cross section of a PVDF membrane, (a) total cross section; (b) zoom in the macrovoid

Figure 3. SEM micrograph of the top surface of a PVDF membrane
Figure 4. SEM micrograph of the cellular pores in the cross section of a PVDF membrane.

The lower half of the cross section was dominated by the cellular morphology. The pores were small (1-2 μm) and independent, as shown in Figure 4. They were, in fact, remnants of the liquid phase produced during liquid-liquid phase separation. All of the above characteristics (skin, macrovoids, cellular pores) can ordinarily be observed in amorphous membranes. Morphology typical of polymer crystallization (i.e., crystalline particles) was evident only on the wall that surrounded the pores or macrovoids; in other word, the observed membrane structure has been derived at first from liquid-liquid demixing then crystallization followed. However, the phase diagram shown in Figure 1 indicated that the casting solution should enter the miscibility phase envelopes and become metastable initially with respect to crystallization and then liquid-liquid demixing. Thus, considerations based totally on the phase behavior would predict a membrane structure controlled by crystallization, which disagreed with the observed morphology. This suggested that liquid-liquid demixing process was kinetically favored. It took place and rapidly set-in the cellular structure and subsequently crystallization follows to form the dendritic branching structure on the cell wall.

4. Conclusions

The phase equilibrium curves, binodal and crystallization line, of the membrane forming water-NMP-PVDF system were measured at 25 °C. Membranes were prepared by the isothermal immersion precipitation process to yield a structure composed of macrovoids and cellular pores, when a good dope solution was immersed in a harsh bath, water. The crystallization process, which took place in the final stage, left its imprint on the walls that surrounded the cellular pores or macrovoids.

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References


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