Membrane Formation via Phase Separation Induced by Penetration of Nonsolvent from Vapor Phase. II. Membrane Morphology

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ABSTRACT: Phase separation of poly(vinylidene fluoride) dimethylformamide solution was induced by the penetration of water vapor, and the porous membrane was formed. As the humidity in the gas phase increased, membrane morphology changed in the order of dense, porous (cellular), and lacy-like structures. At the higher humidity condition, spherical bead structure was observed, which is likely to be crystalline spherulite. With the increase of the initial polymer concentration, less pores were formed in the case of the lower humidity of 20%, whereas more distinguished spherical structures were formed in the case of higher humidity of 40%. The obtained membrane morphologies were discussed based on both the calculated composition paths during the process and the phase diagram. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 171–178, 1999

Key words: membrane formation; phase separation; crystallization; spherulitic morphology; poly(vinylidene fluoride)

INTRODUCTION

The phase separation process is one of the most widely used techniques for preparation of porous membranes. At present, most of all fabrications of commercial porous membranes by the phase separation process are attributed to the tried and error methods. Mathematical models for the membrane-forming process are essential for understanding and controlling membrane morphology and membrane performance.

Two important phenomena, that is, equilibrium thermodynamics and kinetics must be clarified for the analysis of the process. The equilibrium thermodynamics tells us the stability borders of the dope solution and the types of phase separation. The thermodynamics of a membrane forming system is usually described based on the Flory–Huggins theory.¹ The clarification of the binodal and spinodal as well as the crystallization line is the purpose of this thermodynamic study.^{2–5} On the other hand, the kinetic study reveals the composition path and the change of polymer concentration profile during the membrane forming process. The presence of skin layer and the size of pores can be deduced by this knowledge.

Phase separation of the polymer solutions for the preparation of porous membranes can be induced in several ways.^{6,7} Four main techniques

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(a) humidity = 10 %









(c) humidity = 40 %



Figure 1 Membrane structures of air-facing surface and cross-section when humidity was changed. Initial polymer concentration = 10 wt %.

have been presented, such as immersion precipitation, air-casting of the polymer solution, precipitation from the vapor phase, and thermally induced phase separation (TIPS). For the immersion precipitation, many mass transfer models have been developed,^{8–14} and the membrane morphologies obtained were discussed in relation to the calculated concentration profiles. In addition, dry-cast process have been already analyzed by mathematical models for diffusion process.^{15,16} However, as far as we know, no mass transfer model has been presented for the precipitation process by the penetration of nonsolvent vapor. In the first part of this work, mass transfer of three components during membrane formation by the precipitation from the vapor phase was analyzed.¹⁷ During this process, phase separation of the polymer solution [poly(vinylidene fluoride) (PVDF) dimethylformamide (DMF)] was induced by the penetration of water vapor. The time course of the polymer concentration profile was calculated for various cases of different humidity of the vapor phase and different initial polymer concentration.

This paper emphasizes the obtained membrane morphology. Pore size and shape are observed with scanning electron microscopy. The final membrane morphology is understood based on the calculated composition paths and phase diagram.

EXPERIMENTAL

PVDF (Aldrich Chemical Co., Metuchen, NJ, Mw: 534000) was dissolved in DMF in the concentrations of 10, 15, and 20 wt %. The polymer dope solution was cast on the glass plate with the thickness of 256 μ m and the film was put on the balance placed in the chamber, where temperature and humidity were set at 298 K and the prescribed value of 10, 20, and 40%. The humidity was controlled by a condenser and a supersonic waves humidifier (Matsushita Electric Co., Japan, FE-05KYC). The evaporation of DMF and the penetration of nonsolvent (water) into the film induced the phase separation of the polymer solution and the film becomes opaque. After obtaining the constant weight of the glass plate with the film, it was immersed in water bath at room temperature. The dried membrane was used for the scanning electron microscopy (SEM) observation.

The final sample was immersed in liquid nitrogen, fractured and coated with Au/Pd. The crosssection and the air-facing surface were viewed by using a scanning electron microscope (Hitachi Co., Ltd., Japan, S-800) under an accelerating voltage of 25 kV.

Heat of fusion of the obtained membrane was measured by a Perkin–Elmer DSC-7. Sealed aluminum DSC pans including 1.0-3.0-mg membrane sample was heated with the rate of 10° C/ min from 100° C to 200° C. The heat of fusion was obtained from the observed endothermic peak.

RESULTS AND DISCUSSION

Figure 1 shows the membrane structures of the air-facing (top) surface and the cross-section



Figure 2 Calculated composition paths in three humidity cases. (a) humidity = 10%; (b) humidity = 20%; (c) = humidity = 40%. Initial polymer concentration = 10 wt %, (\blacksquare) critical point, (\blacktriangle) initial composition. Tie lines in these figures are the lines when the binodal crosses over the crystallization line.

when the humidity was changed. The initial polymer concentration in the dope solution was fixed to 10 wt %. In the cross-section photographs, upper side corresponds to the air-facing surface. When the humidity was 10%, no porous structures are observed in the cross-section photograph, although there are a few pores in the surface photograph. Therefore, whole structure in this case is the homogeneous dense structure. The local porous structure in the membrane surface may be due to the polymer crystallization, as described below, rather than the liquid-liquid phase separation. On the other hand, at the humidity of 20%, the porous structure was formed. Pore were cellular and polymer formed the continuous matrix phase. As can be seen from the cross-section SEM photograph, the pore was fairly large and occasionally pierced through the membrane. The surface SEM photographs in Figure 1(a) and 1(b) showed the spherical bead structures. Because PVDF is crystalline, the beads are likely to be crystalline spherulites. Similar spherical bead structure was reported in PVDF microfilter.¹⁸ When the humidity was as high as 40%, the obtained structure seems to be the lace-like structure rather than the cellular structure. The spherical bead structures are again detected in this case.

The calculated composition paths are shown in Figure 2. The calculated binodal, spinodal and crystallization line are included in these figures, as well as a tie line when the binodal crosses over the crystallization line. These figures are parts of the enlarged triangular coordinates. The open squares and closed circles denote the calculated compositions at the air-facing surface and in the center inside the film, respectively. Closed squares and closed triangles are the critical point and the initial composition. Numbers in this figures denote the time in the dimension of minute, while numbers followed by character s are the time in the dimension of second. As shown in Figure 2(a), when the humidity is 10%, the compositions do not cross the binodal line. Therefore, the liquid-liquid phase separation can not occur, which leads to the dense structure as shown in Figure 1(a). When the humidity is 20%, the compositions approach to the binodal line. Since the porous structure was formed in this condition (Fig. 1(b)), the compositions must be inside the binodal line when certain time passes. There may be errors in the location of the phase diagrams or in the calculated compositions in Figure 2. The compositions both at the surface and in the center change keeping the positions close to the binodal line for long time. Probably, the actual compositions will change in the metastable region between the binodal and the spinodal. Therefore, the nucleation and growth (NG) mechanism is the promising mechanism for the porous structure. The compositions are located above the critical points (**■**) and, thus, the polymer lean phase initiates as droplets by NG mechanism. This is the reason that the pores are the isolated cellular structures in Figure 1(b). In the case of the humidity of 40%, the compositions go across both the

(a) initial polymer concentration = 10 wt%











Figure 3 Membrane structures of air-facing surface and cross-section when initial polymer concentration was changed. Humidity = 20%.

binodal and spinodal quickly and enter the unstable region (inside the spinodal line). Thus, the promising mechanism for the porous structure shown in Figure 1(c) is a spinodal decomposition (SD). The lace-like structure in Figure 1(c) is a consequence of the phase separation of SD. After about 85 min, the compositions both at the surface and in the center cross the tie line which shows the border of the crystallization. This polymer crystallization brings about the spherulitic structures in Figure 1(c).

Figure 3 shows the membrane structures when the initial polymer concentration was changed.



Figure 4 Calculated composition paths in three polymer concentration cases. (a) Initial polymer concentration = 10%; (b) initial polymer concentration = 15%; (c) initial polymer concentration = 20%. Humidity = 20%, (\blacksquare) critical point, (\blacktriangle) initial composition. The lines in these figures are the lines when the binodal crosses over the crystallization line.

The humidity was fixed to 20%. There were less pores in Figure 3(b) and 3(c) compared to Figure 3(a) especially as shown in the cross-section photographs. The distinguished difference between Figure 3(b) and 3(c) can not be recognized. The calculated composition paths in the conditions of Figure 3 are shown in Figure 4. The composition paths are more detached from the binodal line with the increase of the initial polymer concentration. This can explain the less pores

(a) initial polymer concentration = 10 wt%



(b) initial polymer concentration = 15 wt%



(c) initial polymer concentration = 20 wt%



Figure 5 Membrane structures of air-facing surface and cross-section when initial polymer concentration was changed. Humidity = 40%.

in the higher polymer concentration in Figure 3, because the phase separation can not occur if the composition is outside the binodal line.

The membrane structures are shown in Figure 5 when the initial polymer concentration was changed under the condition of the constant humidity of 40%. With the increase of the polymer concentration, more distinguished spherulitic structures are observed in the surface and the cross section photographs. The size of the spherulite becomes larger at the higher polymer concentration of 20 wt %, as can be clearly seen in the surface photographs. As described in the first part

of this study, the polymer concentration at the air-facing surface was not so high compared with the initial concentration even at the initial stage of the process.¹⁷ This means that the polymer concentration profiles is not so sharp and the isotropic structure is expected from this calculation result. The observed isotropic structures in Figures 1, 3, and 5 agree with this expectation.

As shown in Figure 6, the calculated composition paths are similar for three conditions. In all cases, composition paths enter in the unstable region quickly. Thus, the spinodal decomposition is the promising mechanism of the phase separation in all cases. The polymer concentration crossing the tie lines which show the border of the crystallization increases with the increase of the initial polymer concentration. Therefore, it can be speculated that the volume fraction of the polymer-rich phase increases with the increase of the initial polymer concentration. Although this may be the reason of the difference in the spherulite sizes, further study is necessary to understand the difference in the spherulite sizes in more detail.

The heat of fusions of the membranes prepared by the various conditions are summarized in Table I. The heat of fusion increases with the increase of the humidity. This means that polymer is more likely to crystallize at the higher humidity condition. This tendency agrees with the observation that the spherulitic structure becomes more distinguished in the surface photographs of Figure 1. In addition, the higher initial polymer concentration leads to the higher heat of fusion. This is also in agreement with the observation of the more distinguished spherulite in the higher polymer concentration in Fig. 5.

CONCLUSIONS

Membrane formation via phase separation induced by the penetration of water vapor was investigated. Membrane morphology changed in the order of dense, porous (cellular), and lace-like structures, as the humidity increased. These morphology change could be explained by the calculated composition paths. At the higher humidity, the spherical bead structures was observed. This is likely to be crystalline spherulite.

With the increase of the initial polymer concentration, less pores were formed in the case of



Figure 6 Calculated composition paths in three polymer concentration cases. (a) Initial polymer concentration = 10%; (b) initial polymer concentration = 15%; (c) initial polymer concentration = 20%. Humidity = 40%, (\blacksquare) critical point, (\blacktriangle) initial composition. The lines in these figures are the lines when the binodal crosses over the crystallization line.

the lower humidity of 20%, whereas more distinguished spherical structures were formed in the case of the higher humidity of 40%.

From the DSC measurement, it was found that the heat of fusion of the prepared membranes increased with the increase of the humidity and with the increase of the initial polymer concentration. This tendency agreed with that in amounts of spherulitic structures observed by SEM.

Membrane Preparation Condition ^a	Heat of Fusion [J/g]
P10H10 P10H20	$34.4 \\ 35.5$
P10H40	37.4
P15H40	45.1
P20H40	47.1

Table I Heat of Fusion of Several Membranes

^a The initial polymer concentration in dope solution and the humidity are abbreviated as P and H, respectively.

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