

PREPARATION OF POLY(ETHYLENE-CO-VINYL ALCOHOL) MEMBRANE VIA THERMALLY INDUCED PHASE SEPARATION

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ABSTRACT

Porous membranes were prepared via thermally induced phase separation (TIPS) of (ethylene-co-vinyl alcohol) (EVOH)/glycerol mixtures. The liquid-liquid (L-L) phase boundaries are shifted to higher temperature when the ethylene contents in EVOH increase. Moreover, the kinetic study proved that the growth of droplets formed by the general liquid-liquid (L-L) phase separation obeyed a power-law scaling relationship in the later stage of spinodal decomposition (SD). A new phase separation mechanism was presented, in which the L-L phase separation could be resulted from the crystallization. The hollow fiber membranes were prepared. The membranes showed asymmetric structures with skin layer near the outer surface, the larger pores just below the skin layer and the smaller pores near the inner surface. The effect of ethylene content (EC) in EVOH, cooling water bath temperature and take-up speed on membrane performance was investigated.

INTRODUCTION

The thermally induced phase separation (TIPS) procedure is one of the most versatile and simplest membrane preparation techniques. In this work, poly(ethylene-co-vinyl alcohol) (EVOH)/glycerol mixture was used to prepare porous membranes by TIPS. EVOH has been attracting attention in biomedical fields, especially because of its excellent compatibility.

Most of the EVOH membranes prepared by the TIPS process were particulate structure. In this work, glycerin was used as a diluent to prepare EVOH membranes induced by liquid-liquid (L-L) phase separation. The phase diagram and structure growth mechanism were investigated. Furthermore, the hollow fiber EVOH membranes were prepared by TIPS process. The effects of several preparation conditions on water permeability and solute rejection were investigated in connection with the morphologies of the membranes.

EXPERIMENTAL

Materials

Four kinds of EVOHs with different ethylene content (EC) were used. The diluent was glycerol with extra pure reagent grade.

Phase Diagram

Binodal temperature (T_{cloud}) was determined visually at a cooling rate of 1°C/min by noting the appearance of turbidity under an optical microscope. The dynamic crystallization temperature (T_c) was measured by a differential scanning calorimetry (DSC).

Light-Scattering Measurements

Light-scattering measurements were carried out to obtain the structure growth data with a polymer dynamics analyzer (Otsuka Electronics Co., DYNA-3000). For the measurement, the hot stage was located between the laser and the detector. The sample sealed with two cover slips was quenched to a desired temperature at a cooling rate of 130°C/min. The light scattering was measured with time intervals of 0.1s or 0.2s.

Hollow Fiber Membrane Preparation

Hollow fiber membranes were prepared by a batch-type extruder (Imoto Co. BA-0, Kyoto, Japan). Measured amounts of EVOH and glycerol were fed to the vessel, heated to 200 °C for EVOH44 or 140 °C for EVOH38 and EVOH32 under the nitrogen atmosphere. The polymer concentration was fixed at 25 wt%. After holding at this high temperature for 1 hour, the homogeneous polymer solution was fed to a spinneret by a gear pump under the nitrogen pressure of 0.15 MPa. The spinneret consists of outer and inner tubes, and their diameters were designed to be 1.58 mm and 0.83 mm, respectively. The hollow fiber was extruded from the spinneret and wound on a take-up winder after entering into a water bath.

RESULTS AND DISCUSSION

Figure 1 shows the phase diagrams for various EVOHs with different ethylene content (EC) from 27mol% to 44mol% (hereafter abbreviated as EVOH27, EVOH32, EVOH38 and EVOH44). These phase behaviors can be explained by the solubility parameters of EVOHs and glycerol. As EC in EVOH increases, the solubility parameter becomes far from the diluent value, which leads to the worse compatibility. The worse the compatibility is, the easier the L-L phase separation occurs in the polymer-diluent solution. Therefore, as shown in Fig.1, the liquid-liquid (L-L) phase boundaries are shifted to higher temperature when the ethylene content in EVOH increases.

Figure 2 shows the cellular pore size of various EVOH flat samples cooled at 10°C/min. The pore size decreased with increasing the polymer concentration in three EVOH cases. At

the same polymer concentration of these three kinds of EVOHs, the pore size increased with increasing EC from 32mol% to 44mol%. This result is attributable mainly to the higher binodal line shown in Fig.1, which leads to the longer time for coarsening of droplets in the polymer samples with higher EC.

Figure 3 shows a typical light scattering profiles for a 20wt% EVOH38 sample at a quench depth of 6°C, where the quench depth in this case was defined as the temperature difference between the experimental temperature and the spinodal point. The location of the maximum of I_s was shifted to the lower scattered angle region with the elapse of time, accompanying with the increase in intensity. This means that the phase-separated structure grows at the later stage of spinodal decomposition (SD).

Figure 4 shows comparison of the time-course of interphase periodic distance Λ_m between EVOH32 and EVOH38 samples. Λ_m can be related to the scattered angle θ , where intensity (I_s) shows the maximum value, by the equation (1).

$$\Lambda_m = \frac{\lambda_0}{2n_0 \sin(\theta/2)} \quad (1)$$

Here, n_0 is refractive index of the solution and λ_0 is the wavelength in vacuum (633nm). In case of EVOH38, the spinodal temperature is higher than the crystallization temperature as shown in Fig. 1, and the droplet structure grows under the normal liquid-liquid phase separation mechanism. Therefore, the domain size at each quench depth shows a clear scaling relationship with time in the whole time course as shown in Fig. 4(b). On the contrary, in case of EVOH32, it was found that the crystallization occurred prior to liquid-liquid phase separation as shown in Fig. 1. The crystalline structure formed in the initial stage did not grow so much, which corresponded to the approximate horizontal line shown in Fig.4(a). During the crystallization, the polymer concentration tends to become lower, which allows for liquid-liquid separation, and droplet is formed and Λ_m starts to grow fast. The composition change path in this case is schematically shown in Fig.5. As far as we know, this is the first finding on the L-L phase separation induced by the crystallization.

Effects of take-up speed and EC on water permeability were investigated on three kinds of hollow membranes prepared from different EVOHs with 44, 38 and 32 mol % of EC. The obtained water permeability is shown in Figure 6. The water permeability slightly increased with an increase in the take-up speed, although it was not clear for EVOH44 due to the extremely low permeability. The pores formed by phase separation were enlarged to the drawing direction during spinning. Therefore, the faster take-up speed leads to the larger pores and results in an increase in the water permeability. The permeability increased in the order of EVOH44, EVOH38 and EVOH32.

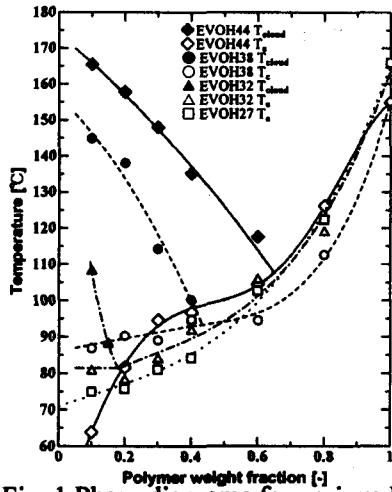


Fig. 1 Phase diagrams for various EVOHs with different ethylene content

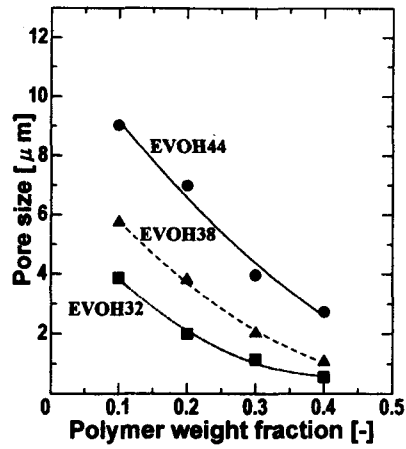


Fig. 2 Effect of polymer concentration on pore size, cooling rate: 10K/min.

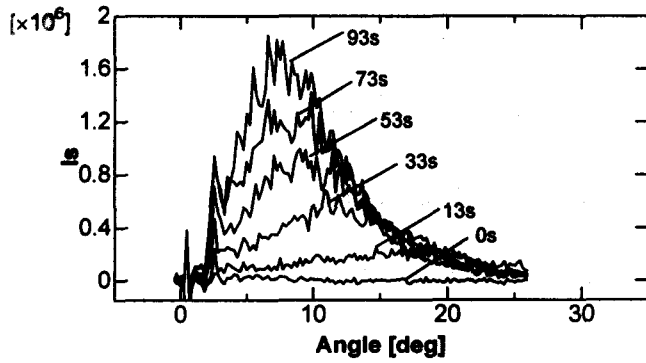


Fig. 3 Light scattering profiles for a 20wt% EVOH38 sample, quench depth 6°C.

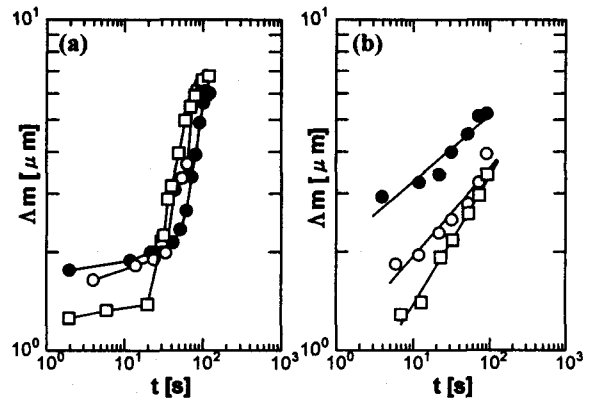


Fig. 4 Periodic distance Δm obtained from light scattering measurements, (a) 20wt% EVOH32, quench temperature: ●: 87°C; ○: 85°C; □: 83°C. (b) 20wt% EVOH38, quench depth: ●: 2°C; ○: 4°C; □: 6°C.

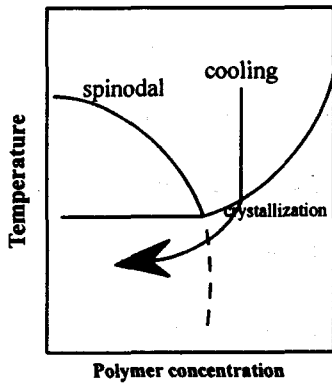


Fig. 5 Model phase diagram used to explain results in Fig. 4.

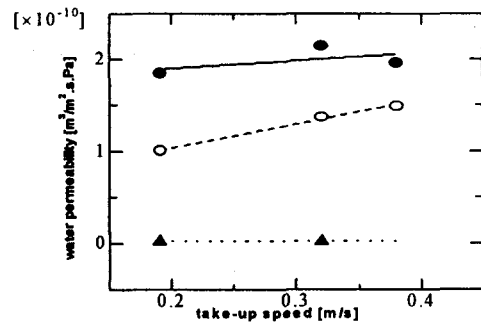


Fig. 6 Effect of EC in EVOH on water permeability. ●EVOH32, ○EVOH38, ▲EVOH44.