Formation of Porous Poly(ethylene-*co*-vinyl alcohol) Membrane via Thermally Induced Phase Separation

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ABSTRACT: Crystalline poly(ethylene-*co*-vinyl alcohol) (EVOH) membranes were prepared by a thermally induced phase separation (TIPS) process. The diluents used were 1,3-propanediol and 1,3-butanediol. The dynamic crystallization temperature was determined by DSC measurement. No structure was detected by an optical microscope in the temperature region higher than the crystallization temperature. This means that porous membrane structures were formed by solid–liquid phase separation (polymer crystallization) rather than by liquid–liquid phase separation. The EVOH/butanediol system showed a higher dynamic crystallization temperature and equilibrium melting temperature than those of the EVOH/propanediol system. SEM observation showed that the sizes of the crystalline particles in the membranes depended on the polymer concentration, cooling rate, and kinds of diluents. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2449–2455, 2001

Key words: poly(ethylene-*co*-vinyl alcohol) membrane; thermally induced phase separation; crystallization; porous membrane; particulate morphology

INTRODUCTION

Recently, research of biomedical materials has been accelerated, reflecting the rapidly increased needs in the medical field. In this situation, poly-(ethylene-*co*-vinyl alcohol) (EVOH) has drawn attention as a biomedical material. EVOH is a crystalline random copolymer with hydrophilic vinyl alcohol and hydrophobic ethylene segments. A porous EVOH membrane was used in various kinds of blood purification devices such as in hemodia-

lyzers and plasmapheresis. Sakurada et al. reported that hemodialyzers consisting of EVOH hollow-fiber membranes can realize nonanticoagulant hemodialysis due to excellent blood compatibility of the membrane.[1]

Young et al. widely investigated the formation of an EVOH membrane by an immersion precipitation method.[2–6] They showed that when a homogeneous EVOH dope was immersed in a harsh bath, for example, water, instant precipitation occurs initiated by the liquid–liquid demixing process. On the other hand, if precipitation took place in a soft bath containing a substantial amount of solvent, crystallization, rather than liquid–liquid demixing, started to dominate and a

skinless particulate membrane was formed.[2] An effect of the second phase inversion on the membrane structure and a membrane formation from EVOH–water (nonsolvent)–propanol (nonsolvent) system were also investigated.[3,4] Furthermore, Young et al. studied a solute rejection of dextran by an EVOH asymmetric and particulate membrane.[7] The asymmetric membrane rejected large dextran molecules and let through small molecules. In the particulate membrane, however, there existed a maximum rejection at an intermediate dextran molecular weight. They deduced that this is because small molecules tended to be trapped inside the nanopores within the EVOH particles.

In this work, porous EVOH membranes were prepared by a thermally induced phase separation (TIPS) process. The TIPS process is a valuable way of making microporous membranes.[8–17] After a polymer is dissolved in a diluent at a high temperature, phase separation is induced by cooling or quenching the solution. The TIPS process is classified mainly into two types such as solid–liquid (S–L) TIPS, where the polymer crystallizes out of the solution, and liquid–liquid (L–L) TIPS, where the solution separates into a polymer-rich continuous phase and a polymer-lean droplet phase. As far as we know, this is the first work concerning the EVOH membrane formation by the TIPS process. The object of this work was to investigate the applicability of the TIPS process to the production of the porous EVOH membrane. A solute rejection by the EVOH membrane will be discussed in the following article.[18]

EXPERIMENTAL

Materials

The EVOH polymer (Kuraray Co., Tokyo, Japan) has an ethylene content of 32 mol % and a degree of polymerization of 1500. 1,3-Propanediol, 1,3-butanediol, dimethylformamide, and cyclohexanol were used as diluents without further purification. These diluents of extrapure reagent grade were purchased from the Nacalai Tesque Co. (Kyoto, Japan). When dimethylformamide and cyclohexanol were used, the polymer–diluent samples, which were made by cooling after melt-blending, were too soft to be used as the membrane. Therefore, only 1,3-propanediol and 1,3-butanediol were used as diluents in the membrane preparation.

Membrane Preparation

Homogeneous polymer–diluent samples were prepared by a method reported by Kim and Lloyd.[14] Each solid sample was placed between a pair of microscope coverslips. A Teflon film of 100-μm thickness with a circle opening in the center was inserted between the coverslips to prevent diluent loss by evaporation. Each sample was heated on a hot stage (Linkam, LK-600PH) at 473.2 K for 1 min. Then, the sample was cooled to 298.2 K at a constant rate (usually 10 K/min) with a Linkam L-600A controller. The diluent (propanediol or butanediol) was extracted from the obtained membrane with t-butyl alcohol.

SEM Observation

For scanning electron micrograph (SEM) observation, the sample containing t-butyl alcohol was freeze-dried. The obtained microporous membrane was fractured in liquid nitrogen and mounted vertically on a sample holder. The surface of the sample was sputtered with Au/Pd in a vacuum. An SEM (Hitachi, S-2150) with an accelerating voltage of 15 kV was used to examine the membrane cross sections.

Phase Diagram and Thermal Analysis

A 3–5 mg sample was sealed in an aluminum DSC pan, melted at 473.2 K for 5 min, and then cooled at several controlled rates (usually 10 K/min) to 298.2 K by a Perkin–Elmer DSC-7. The onset of the exothermic peak during the cooling was taken as the dynamic crystallization temperature. The heat of crystallization was determined from the exothermic peak area during cooling. The equilibrium melting temperature was measured by the method of Hoffman and Weeks.[19,20] The sample was heated to 473.2 K, quenched to the desired crystallization temperature at the fastest rate possible (about 100 K/min), allowed to crystallize for 30 min at various degrees of supercooling, and then melted at a rate of 10 K/min. The time required for 50% of the crystallizable EVOH to crystallize, $t_{1/2}$, was measured as follows: After the sample was heated to 473.2 K, it was quenched to the desired temperature at the fastest rate and the thermogram was recorded. The relative crystallinity X is obtained as

$$X = Q_t/Q_0 \qquad (1)$$

where Q_t is the total heat evolved at time t and Q_0 is the total heat evolved as time approaches in-
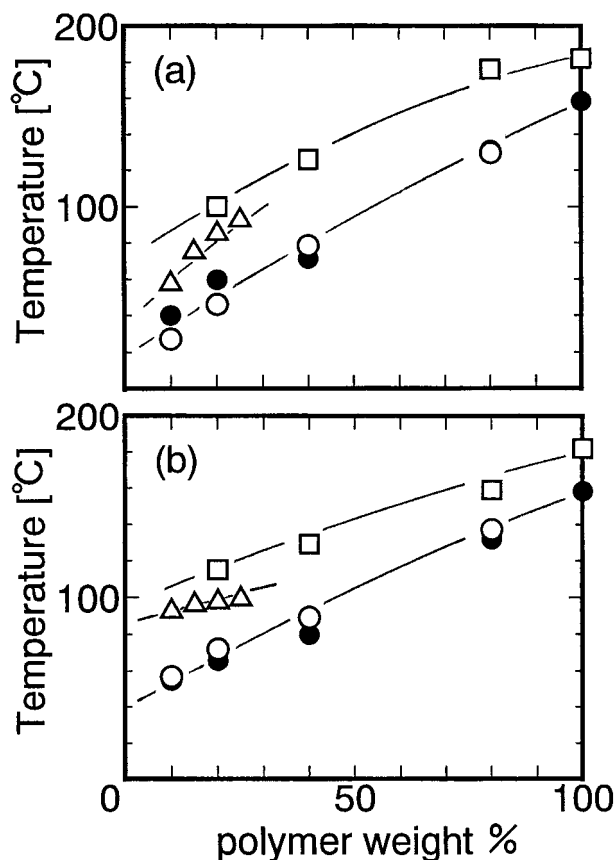
Figure 1 Phase diagram in EVOH/diluent system: (a) EVOH/1,3-propanediol system; (b) EVOH/1,3-butanediol system. (●) dynamic crystallization temperature; (○) temperature at which particles were detected by an optical microscope; (□) equilibrium melting temperature; (△) sol–gel transition temperature.

finity. The time when X becomes 0.5 corresponds to the half-time $t_{1/2}$.

The temperature at which particle structures started to be formed was determined by an optical microscope (Olympus, BX50). The sample was sealed with two coverslips as described above and placed on the hot stage. The hot stage was placed on the platform of the optical microscope. The sample was heated to 473.2 K for 1 min and cooled at 10 K/min. The temperature at which the particle structure started to form was recorded for various polymer concentration conditions.

A sol–gel transition temperature was measured as follows[21,22]: The solid polymer–diluent sample in a test tube was heated to 443.2 K to be melted. Then, the solution was quenched at a constant temperature. After standing for 24 h, the test tube was inverted. When the meniscus deformed under its own weight, the solution was judged still to be a sol. When the solution would no longer flow, we judged that the system had gelled.

RESULTS AND DISCUSSION

Figure 1 shows phase diagrams obtained for the EVOH/propanediol and EVOH/butanediol systems. In both systems, the dynamic crystallization temperature was approximately in agreement with the temperature at which particles were detected by the optical microscope. This indicates that particles were formed by crystallization nucleation of EVOH. Observation by the optical microscope was usually done to determine a binodal line, which is the border of the liquid–liquid phase separation.[13,14] In this case, however, no structure was observed by the microscope in the region higher than the dynamic crystallization temperature. Therefore, the apparent binodal line probably exists in the lower-temperature region. Thus, membrane structures in these two systems were formed by solid–liquid phase separation (polymer crystallization) rather than by liquid–liquid phase separation. The dynamic crystallization temperature in the EVOH/butanediol system was higher especially in the low polymer concentration region than that in the EVOH/propanediol system.

The solubility parameters of EVOH, propanediol, and butanediol are summarized in Table I. The difference in parameters is larger in the EVOH/butanediol system than in the EVOH/propanediol system. This means that the compatibility between EVOH and butanediol is lower, which leads to the high crystallization temperature in

Table I Solubility Parameters for Several Substances

Substance	Solubility Parameter $[(MPa)^{1/2}]$
1,3-Propanediol	24.0[a]
1,3-Butanediol	28.9[b]
EVOH	22.6[c]
Polyethylene	15.76[d]
Poly(vinyl alcohol)	25.78[d]

[a] Estimated by use of group contribution method by Hoy.[23]
[b] Ref. 24.
[c] Estimated from values of polyethylene and poly(vinyl alcohol) by considering the composition.
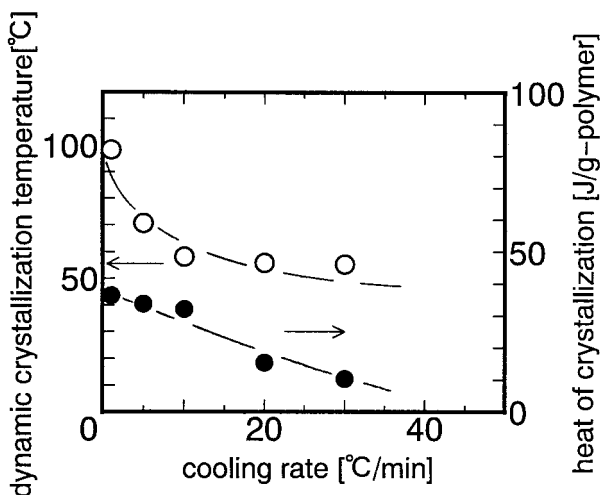[d] Ref. 25.

Figure 2 Effect of cooling rate on dynamic crystallization temperature and heat of crystallization in EVOH/1,3-propanediol system (40 wt % EVOH).

Figure 1. The equilibrium melting temperature obtained from Hoffman–Weeks plots is also shown in Figure 1. Because supercooling is necessary for actual crystallization, the dynamic crystallization temperature is much lower than the equilibrium melting temperature in both systems. The equilibrium melting temperature in the EVOH/butanediol system is higher in the low polymer concentration region than in the EVOH/propanediol system, similarly to the tendency of the dynamic crystallization temperature.

The sol–gel transition temperature in Figure 1 is located between the equilibrium melting temperature and the dynamic crystallization temperature in both systems. The gelation due to the polymer crystallization has been widely accepted. On the other hand, Paul[26] and Feke and Prins[27] suggested that the gelation can originate from liquid–liquid phase separation. In our case, the gelation is due to the polymer crystallization because the binodal temperature could not be observed. The sol–gel transition temperature was determined after standing in the constant temperature for 24 h. Thus, in this experimental condition, the polymer solution was placed at a high temperature close to the crystallization temperature for a longer time than in the condition of gradual cooling of 10 K/min, in which the dynamic crystallization temperature was measured. Therefore, a polymer is more likely to crystallize in the former case than in the latter case. This is the reason why the sol–gel transition temperature is higher than is the dynamic crystallization temperature.

Figure 2 shows the effect of the cooling rate on the dynamic crystallization temperature. The crystallization temperature clearly decreased with increase of the cooling rate. This is because cooling at any finite rate permits supercooling for the actual crystallization. The similar decrease in the crystallization temperature was reported by Lloyd et al.[13]

The heats of crystallization are shown in Figure 3. The heats of crystallization monotonously decreased as the polymer concentration in the solution decreased in both systems. This means that the degree of crystallinity decreased with decrease of the polymer concentration. Mandelkern et al. reported that crystallization from dilute and moderately dilute solutions enhances crystallinity.[21] The high crystallinity is due to the enhancement of polymer mobility in dilute solutions. The result in this work shows an opposite tendency, that is, the depression of the crystallinity in a dilute solution. A chance of contact in polymer molecules becomes lower in the dilute solution. This leads to the lower crystallinity. In our case, this effect may be more effective than is the enhancement of polymer mobility. In the EVOH/butanediol system, higher crystallinity was obtained in the same polymer concentration solution than in the EVOH/propanediol system. The dynamic crystallization temperature is higher in the EVOH/butanediol system as shown in Figure 1. Therefore, polymer mobility is higher at the beginning of the crystallization due to the high temperature and a crystallization period
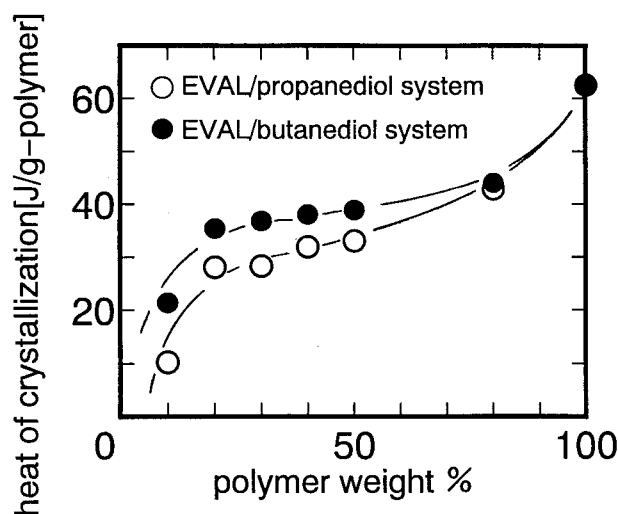

Figure 3 Relation between polymer weight percent and heat of crystallization. Cooling rate: 10 K/min.
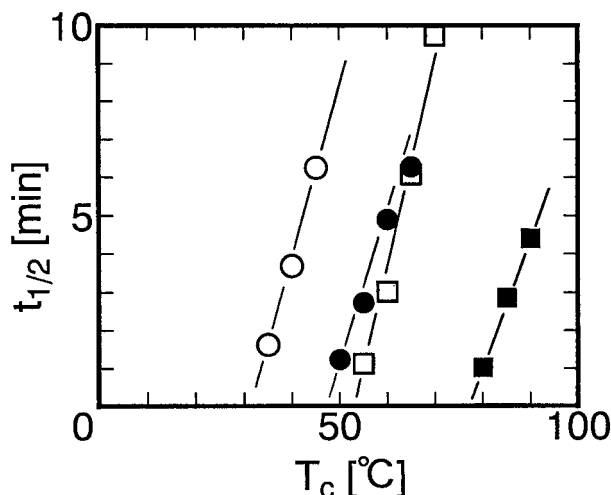
Figure 4 Relation between half-time for crystallization $t_{1/2}$ and crystallization temperature T_c. (○) EVOH/1,3-propanediol system (20 wt % EVOH); (□) EVOH/1,3-propanediol system (40 wt % EVOH); (●) EVOH/1,3-butanediol system (20 wt % EVOH); (■) EVOH/1,3-butanediol system (40 wt % EVOH).

from the onset to the cessation of the crystallization at the low temperature is longer if both systems cease crystallization at the same temperature. This may lead to the higher crystallinity in the EVOH/butanediol system. However, further study is necessary to clarify the detailed reason.

The effect of the cooling rate on the heat of crystallization is also shown in Figure 2. The decrease in the cooling rate brought about the increase of the crystallinity. The main reason for this is that the crystallization period from the onset to the cessation of the crystallization is longer in the lower cooling rate condition.

Figure 4 shows the relation between the half-time for the crystallization $t_{1/2}$ and the crystallization temperature T_c. The half-time increased linearly with increasing T_c when the concentration of the system remained constant. The half-time decreased with increase of the polymer concentration at a constant T_c. When $t_{1/2}$ is compared in two diluent systems, the EVOH/butanediol system showed much lower $t_{1/2}$ values at the same polymer concentration and T_c condition. This is due mainly to the larger supercooling brought about by the higher crystallization temperature in the EVOH/butanediol system.

Figures 5 and 6 show SEM photomicrographs of cross sections of the membranes when the polymer concentration was changed. In both diluent systems, crystalline particles became larger as the polymer concentration increased. Moreover, increase of the polymer concentration brought about a decrease in a space volume between particles. When the EVOH membrane is used for a solute rejection experiment, a solute will trans-
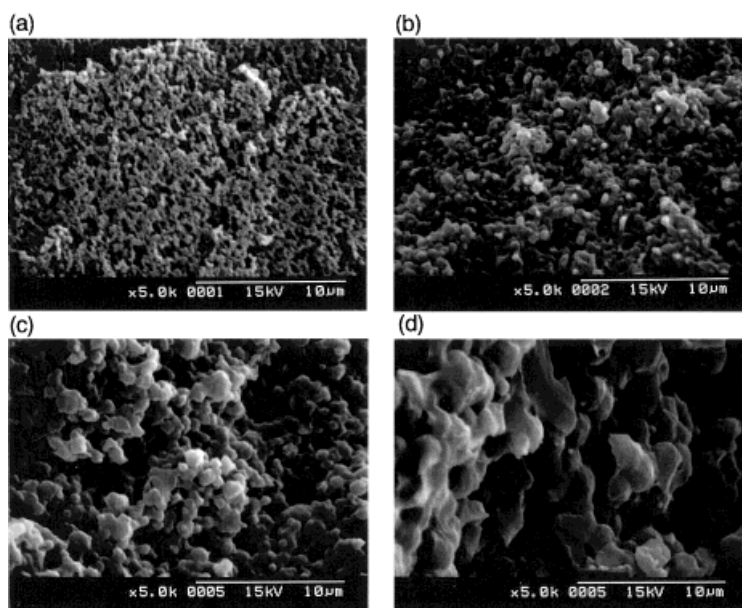

Figure 5 SEM photomicrographs of cross sections of membranes in EVOH/1,3-propanediol system. Cooling rate: 10 K/min. (a) 10 wt % EVOH; (b) 20 wt % EVOH; (c) 40 wt % EVOH; (d) 50 wt % EVOH.
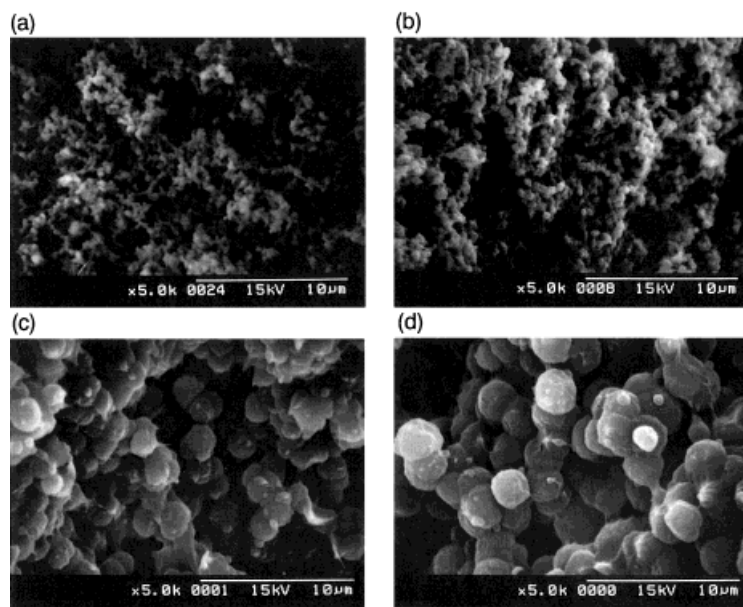
Figure 6 SEM photomicrographs of cross sections of membranes in EVOH/1,3-butanediol system. Cooling rate: 10 K/min. (a) 10 wt % EVOH; (b) 20 wt % EVOH; (c) 40 wt % EVOH; (d) 50 wt % EVOH.

port through the membrane by way of the interconnected open pores between the EVOH particles. Therefore, we can expect lower permeability of the membrane prepared from the higher polymer concentration solution. The transport experiment will be discussed in the following article.[18]

Although a difference in the membrane structures in two diluent systems is not so remarkable, the EVOH/butanediol system showed a somewhat larger particle size, especially in 40 wt % sample.

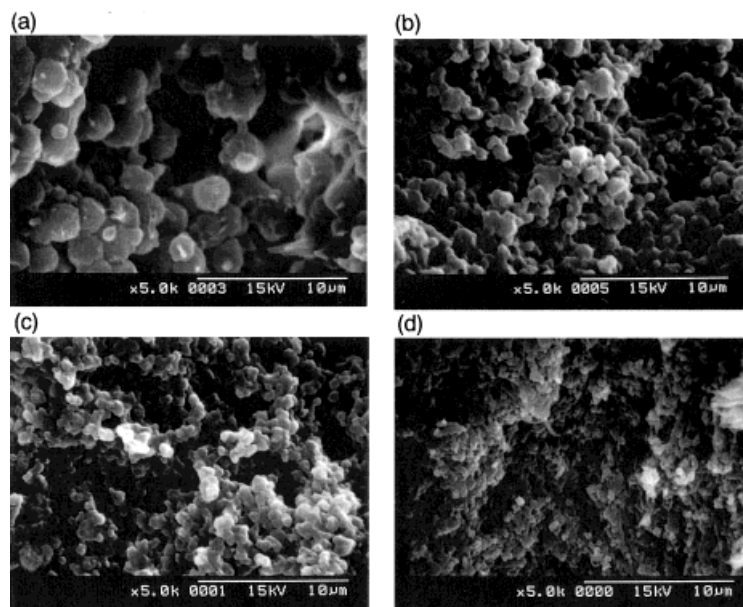The effect of the cooling rate on the membrane structures is shown in Figure 7. The faster the

Figure 7 Effect of cooling rate on membrane structures in EVOH/1,3-propanediol system (40 wt % EVOH): (a) 1 K/min; (b) 10 K/min; (c) 30 K/min; (d) 100 K/min.

cooling rate was, the smaller the particle size became. Kim and Lloyd reported similar experimental results in that the crystal size is smaller in the faster cooling condition for an isotactic polypropylene solution.[14] The result in Figure 7 means that the membrane structure, which is directly related to the membrane performance, can be controlled easily by the cooling rate. This is the characteristic of the membrane formation by the TIPS process. The volume fraction of open pores between particles is not changed so much by the change of the cooling rate because the initial polymer concentration is constant. Therefore, in the membrane with the larger particles prepared at the lower cooling rate, a channel size of open pores between the particles became large, which will bring about higher permeability and lower solute rejection.

CONCLUSIONS

Phase diagrams in EVOH/1,3-propanediol and EVOH/1,3-butanediol systems were obtained. The dynamic crystallization temperature determined by DSC measurement was approximately in agreement with temperature of particle formation determined by the optical microscope. This means that the membrane structure was formed by the solid–liquid phase separation (polymer crystallization). In the EVOH/butanediol system where the compatibility between polymer and diluent is relatively poor, the higher dynamic crystallization temperature and the higher equilibrium melting temperature were obtained, especially in the low polymer concentration region.

Structures of the EVOH membranes prepared by the TIPS process were observed. The sizes of crystalline particles increased with increasing the polymer concentration and with decreasing the cooling rate. The control of the membrane structure by the cooling rate is the characteristic of the TIPS process.

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