Effects of the Diluent Mixing Ratio and Conditions of the Thermally Induced Phase-Separation Process on the Pore Size of Microporous Polyethylene Membranes

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ABSTRACT: Microporous polyethylene (PE) membranes having a controlled pore size were produced via the thermally induced phase separation process by manipulation of the phase boundary of the PE/diluent blend and process conditions. The phase boundary of the PE blend, caused by upper critical solution temperature type phase behavior, was controlled by the use of a diluent mixture, that is, an isoparaffin/soybean oil mixture. The phase-separation temperature of the PE/soybean oil blend was always higher than that of the PE/isoparaffin blend. In PE/(isoparaffin/soybean oil) ternary blends, the phase-separation temperature of the ternary blend rapidly increased with increasing soybean oil content in the diluent mixture. Furthermore, the phase-separation temperatures of ternary blends were always higher than that of the PE/soybean oil blend, regardless of the blend compositions, when the diluent mixture contained more than 50 wt % soybean oil. The observed phase behavior of the ternary blends was analyzed with interaction energy densities calculated with the Flory–Huggins theory and ternary stability conditions. The growth of droplets caused by both coalescence and the Oswald ripening process was observed after the onset of phase separation. As the blends became less stable, the droplet growth rate increased, and larger equilibrium droplets were formed. Microporous membranes with the desired pore structure could be prepared by control of the phase boundary and the variation of processing conditions such as the quenching depth, annealing time, and cooling rate. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3154–3162, 2008

Key words: membranes; microstructure; phase separation; polyethylene

INTRODUCTION

The thermally induced phase separation (TIPS) process has been studied extensively for the fabrication of microporous membranes.[1–14] This process gains much interest for its advantage over other conventional membrane preparation methods such as solvent casting, stretching, and track etching. In the TIPS process, a homogeneous polymer/diluent blend, prepared by melt mixing at a relatively high temperature, phase-separates into a polymer-rich phase and a polymer-lean phase upon cooling; this is caused by upper critical solution temperature (UCST) type phase behavior (liquid–liquid phase separation). The polymer-lean phase, which is composed of nearly pure diluent, forms droplets dispersed in the continuous phase. Droplets are brought up by the coarsening process during the cooling process, and then the growth of droplets finally stops when the polymer solution is solidified by further cooling under the crystallization temperature (solid–liquid phase separation). Droplets are easily extracted to form cells in the microporous membrane. Because the cells serve to construct the microporous passageways in the membrane, the size control of droplets has been the major concern in producing microporous membranes via the TIPS process.

In the TIPS process, the size of the droplets depends on the thermodynamic factors and the kinetic factors. Because of this, a clear understanding of the phase separation caused by UCST-type phase behavior (thermodynamic factors) and also the growth process of droplets caused by coarsening after the phase separation (kinetic factors) is essential to controlling the droplet size during the TIPS process.[15–19] When the process conditions for the fabrication of the membrane, that is, the kinetic factors, are fixed, the size of the droplet mainly depends on thermodynamic factors such as the polymer–diluent interaction and the molecular weight of the component. Because these factors determine the phase boundary of the polymer/diluent blend, droplet size is mainly determined by the phase-separation

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Ftemperature. The size of the droplet generally increases as the temperature gap increases between the phase-separation temperature and the crystallization temperature of the polymer. On the other hand, when the polymer/diluent system is fixed, the droplet size is mainly controlled by kinetic factors such as the cooling rate, annealing temperature, and annealing time.[9,15–19]

The TIPS process is applicable to a wide range of crystalline polymers, including polyolefins such as polyethylene (PE) and polypropylene. Polyolefin microporous membranes are widely used as separators for commercial liquid-electrolyte lithium-ion batteries.[20–27] They prevent contact between the positive and negative electrodes, that is, a short circuit, and thus have a very important insulating role in the battery. These battery separators can be divided into two major types: the polyolefin microporous membrane of a small pore diameter, which was the initial standard, and the polyolefin membrane with a large pore diameter, which has come to be used in the manufacture of prismatic mobile telephone batteries. A battery separator with a controlled pore diameter is required for use in various types of lithium-ion batteries.

In previous research, phase-separation temperatures of polymer/diluent blends were mainly manipulated by the use of different kinds of diluents.[1–19] However, the fabrication of a PE battery separator that has the desired pore size is often limited because only a few diluents are available for PE. In this study, the phase-separation temperature of PE blends was manipulated by the use of the diluent mixture, and then kinetic variables were controlled to investigate in detail the determining factors of pore size in the TIPS membranes.

EXPERIMENTAL

The polymer and diluents used in this study are listed in Table I. High-density PE (grade 8800) was obtained from SK, Ltd. (Seoul, Korea). Isoparaffin, used as a diluent, was also supplied by SK (grade YU-8, average molecular weight = 500 g/mol). According to the supplier, an isoparaffin molecule is a long-chain normal paraffin bonded with about seven methyl side groups. Soybean oil, used also as a diluent, was supplied by CJ Corp. (Seoul, Korea). PE was dried at 80°C for about 4 days in a vacuum oven before use, whereas isoparaffin and soybean oil were used without further purification. The PE/diluent and PE/(diluent/diluent) blends were prepared by melt blending. Blends of PE and diluent were stirred in a flask at about 60°C above the melting temperature of PE for 30 min under a nitrogen purge condition.

TABLE I
Polymers and Diluents Used in This Study

Material	Molecular weight	T_m (°C)	Refractive index	Sources
High-density PE	$M_n = 115{,}000$ $M_w = 150{,}000$	135	1.491	SK, Ltd. (grade 8800)
Isoparaffin	$M_w = 500$	—	1.482	SK, Ltd. (grade YU-8)
Soybean oil	$M_w = 879$	−15	1.474	CJ Corp.

M_n, number-average molecular weight; M_w, weight-average molecular weight; T_m, melting temperature.

The temperature at which phase separation started to occur because of UCST was measured by the annealing technique to obtain, as closely as possible, the true equilibrium temperature.[28–31] To observe the approximate value of the phase-separation temperature, specimens covered with cover glasses were mounted on a hot stage (THMS 600, Linkam, Tadworth, United Kingdom) equipped with a temperature controller (TMS 92, Linkam). The edges of the bottom cover slip were sealed with Teflon tape and vacuum grease to minimize diluent loss by evaporation during the heating or cooling process and to prevent compression by the weight of a top cover slip. The samples were heated rapidly to a temperature about 20°C above the expected phase boundary. Then, the changes in optical images caused by variations in the temperature were observed with an image analyzer (I-top, Bummi Universe, Seoul, Korea) equipped with an optical microscope (Eclipse80i, Nikon, Tokyo, Japan) as the specimens were cooled at a scanning rate of 10°C/min. The temperature at which the image first started to change was taken as the approximate value of the phase-separation temperature. To determine the true equilibrium temperature, the blend specimens were annealed in a hot stage at fixed temperatures in the vicinity of the expected phase boundary for 5 min, and the change in the optical image was monitored following the annealing. The temperature at which the optical image first started to change during annealing was taken as the phase-separation temperature. The standard deviation of the phase-separation temperatures measured by this technique did not exceed ±2°C.

Melting and crystallization temperatures of the PE/diluent blends were measured with the same image analyzer equipped with a temperature control system using a cyclic heating and cooling procedure. For the measurement of the PE crystallization temperature, a sample was heated above the phase boundary by approximately 20°C and then cooled to room temperature at a scanning rate of 10°C/min. The temperature at which the first crystalline phase

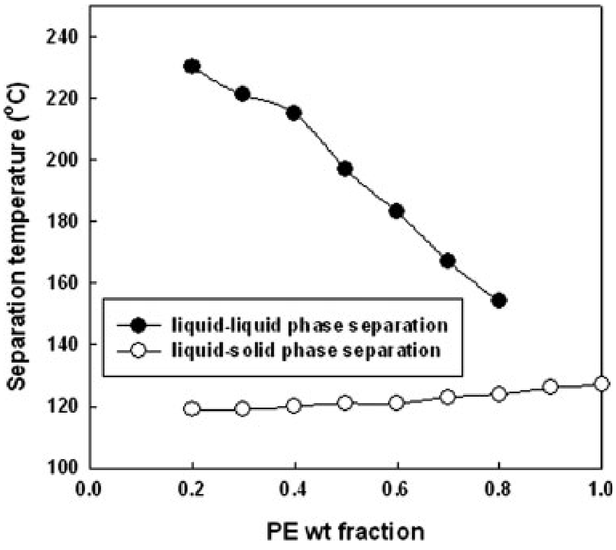

Figure 1 Phase-separation temperatures of PE blends with soybean oil of various compositions.

started to appear was taken as the crystallization temperature. The crystallized samples were reheated to measure the melting temperature of the crystalline phase that was formed during the cooling process. To minimize experimental errors and confirm the reproducibility of the thermal behavior, at least five observations for each sample were made.

On the basis of the observed phase diagrams, the phase separation of various blends was induced by quenching below the phase-separation temperature. Samples heated above the phase boundary were cooled to a certain temperature at which they underwent the phase separation, and afterwards, the change in droplet size was monitored for a fixed time interval. The changes in droplet size of the disperse phase were analyzed as a function of time with the aid of the image analyzer. The average droplet size that did not change any more after a given time period was taken as the equilibrium droplet size. Effects of the cooling rate on the droplet size were also investigated. To produce microporous membranes, homogeneous blends were cooled below the crystallization temperature at a cooling rate of 10°C/min, and the diluent was extracted with acetone. Microporous membranes were fractured under a liquid nitrogen condition to observe the cross-sectional morphology with a scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

Phase behavior of the blends

The blends of PE with soybean oil prepared with various compositions were turbid around room temperature. However, the heterogeneous PE/soybean oil blend became homogeneous when the blend was heated above the phase boundary. The phase diagram for the PE/soybean oil blends is shown in Figure 1. These blends exhibited typical UCST-type phase behavior, which is often observed with a polymer blended with a low-molecular-weight diluent. As expected, the crystallization temperature of PE in the PE/soybean oil blends was slightly increased when the diluent content was reduced in the blend. The blends of PE with isoparaffin prepared with various compositions were also turbid at room temperature. The blends became transparent, regardless of the blend composition, when they were heated just above the melting temperature of PE. This means that PE always forms one phase mixture with isoparaffin above the melting temperature of PE. To observe the liquid–liquid phase-separation temperature of the PE/isoparaffin blend, the morphology change with temperature was observed via cooling from 200 to 100°C at a scanning rate of 10°C/min. Changes in the morphology were not observed above the crystallization temperature, and the mixture was still transparent. These results indicate that PE and isoparaffin always form homogeneous blends above the crystallization temperature, that is, the solid–liquid phase temperature.

Blends of PE with a diluent mixture (isoparaffin/soybean oil mixture) were prepared, and the phase-separation temperatures of these blends were examined. Figure 2 exhibits the phase-separation tempera-

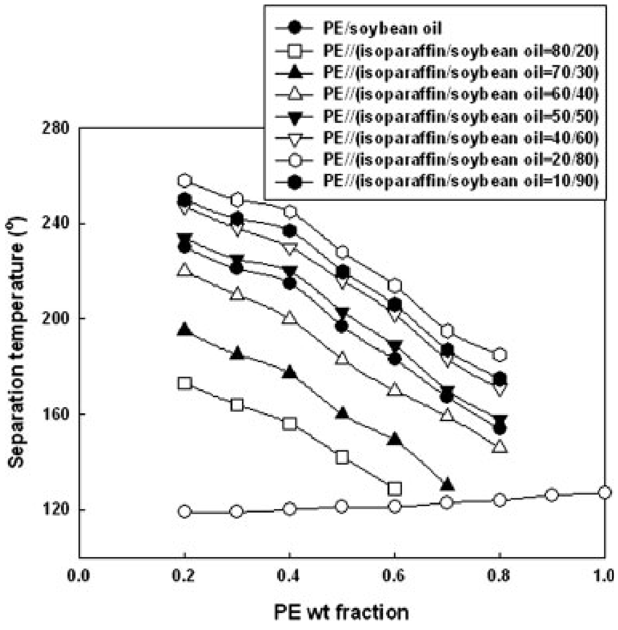

Figure 2 Phase-separation temperatures of PE/(isoparaffin/soybean oil) blends prepared by changes in the mixing ratios of the diluent and PE/soybean oil blends. Phase-separation temperatures of PE/isoparaffin blends were not observed upon cooling.

tures of the PE/(isoparaffin/soybean oil) blends as a function of the mixing ratio of the diluent. When the PE content in the blend was fixed, the phase-separation temperature of the PE/(isoparaffin/soybean oil) blend first increased with increasing soybean oil content in the diluent mixture, going through a maximum centered at about 80 wt % soybean oil before decreasing afterwards. Furthermore, the phase-separation temperatures of the PE/(isoparaffin/soybean oil) blends were always higher than that of the PE/soybean oil blend, regardless of the blend compositions, when the diluent mixture contained 50 wt % or more soybean oil. This means that the ternary blends will not often form miscible blends, even though all the binary pairs included in the ternary blends, that is, the PE/isoparaffin pair, PE/soybean oil pair, and isoparaffin/soybean oil pair, are miscible. To understand this issue, the interaction energy of each binary pair and thermodynamic ternary stability conditions are explored in the following section.

Thermodynamic analysis of the blends

For a better understanding of the phase behavior of blends, the Flory–Huggins theory[32–34] was employed to obtain the interaction energies of the binary pairs involved in the blends. The Flory–Huggins theory, neglecting the compressibility term (or excess entropy term), is only an approximation of a real system. However, quantitative information on the Van–Laar-type interaction energy density (B_{ij}) obtained by this theory is still an important element in understanding the phase behavior of a blend. The free energy of mixing per unit of volume (g) can be expressed as follows:

$$g = RT \sum_i \frac{\phi_i}{\hat{v}_i} \ln \phi_i + \sum_{i<j} \sum B_{ij} \phi_i \phi_j \tag{1}$$

where R and T indicate the gas constant and absolute temperature, ϕ_i and $\hat{v}_i$ are the volume fraction and molar volume of component i, respectively. If we assume that the measured phase-separation temperature corresponds to the binodal point, that is, the coexistence point, the interaction energy density can be calculated from the coexistence conditions:

$$\Delta\mu_i^{\alpha} = \Delta\mu_i^{\beta} \tag{2}$$

where α and β denote the different phases and subscript i indicates the individual component. The chemical potential (μ_i) is given by

$$\Delta\mu_i = RT\left[\ln \phi_i + \left(1 - \frac{\hat{v}_i}{\hat{v}}\right)\right] + \hat{v}_i \left(\sum_j \phi_j B_{ij} - \sum_{i<j} \sum \phi_i \phi_j B_{ij} \right) \tag{3}$$

where $1/\hat{v} = \sum_i \phi_i / \hat{v}_i$. The interaction energy density between PE and soybean oil was calculated from the phase boundary of PE/soybean oil blends. The remaining interaction energy densities in the ternary blends, that is, the interaction energy density between isoparaffin and soybean oil and the interaction energy density between PE and isoparaffin, were calculated from the phase boundaries of PE/(isoparaffin/soybean oil) ternary blends. The interaction energy densities obtained for different compositions with the Flory–Huggins theory were generally not constant. As described elsewhere,[28–30] the difference could have several origins, such as the difference in the compressibility of each component and specific interactions. Note that the values of the interaction energy density reported here are only the average values. The estimated interaction energy densities based on the observed phase boundaries were 0.53 cal/cm^3 for the PE/soybean oil blend, 0.21 cal/cm^3 for the PE/isoparaffin blend, and 0.28 cal/cm^3 for the soybean oil/isoparaffin blend. The positive values of the interaction energy densities indicate that the PE employed in this study is not fully miscible with the soybean oil (or isoparaffin) at room temperature, but they can form miscible blends with the diluent by an increase in the temperature.

A ternary blend that is composed of components 1 (PE), 2 (isoparaffin), and 3 (soybean oil) is miscible when the conditions given in eq. (4) are satisfied:

$$g_{11} \geq 0 \text{ and } \det \begin{vmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{vmatrix} \geq 0 \tag{4}$$

where subscripts 1 and 2 indicate partial derivatives with respect to volume fraction ϕ_1 or ϕ_2. The indicated derivatives for ternary blend are given by

$$g_{11} = -2B_{13} + RT\left(\frac{1}{\phi_1 \tilde{v}_1} + \frac{1}{\phi_3 \tilde{v}_3}\right) \tag{5}$$

$$g_{12} = g_{21} = (B_{12} - B_{13} - B_{23}) + RT\left(\frac{1}{\phi_3 \tilde{v}_3}\right) \tag{6}$$

$$g_{22} = -2B_{23} + RT\left(\frac{1}{\phi_2 \tilde{v}_2} + \frac{1}{\phi_3 \tilde{v}_3}\right) \tag{7}$$

As described in the volume fluctuation thermodynamics[35–38] and described in eq. (4), the addition of a component, that is, the additional degree of freedom accompanied by the asymmetry in the binary interactions, results in the destabilization of the mixture. When one of the binary pairs is immiscible, the corresponding region of binary immiscibility expands to include most of the ternary region until the favorable combinatorial entropy term dominates. This means that the miscibility of the ternary blend is greatly influenced by the most immiscible binary pair, that is, the PE/soybean oil pair. As a result, the

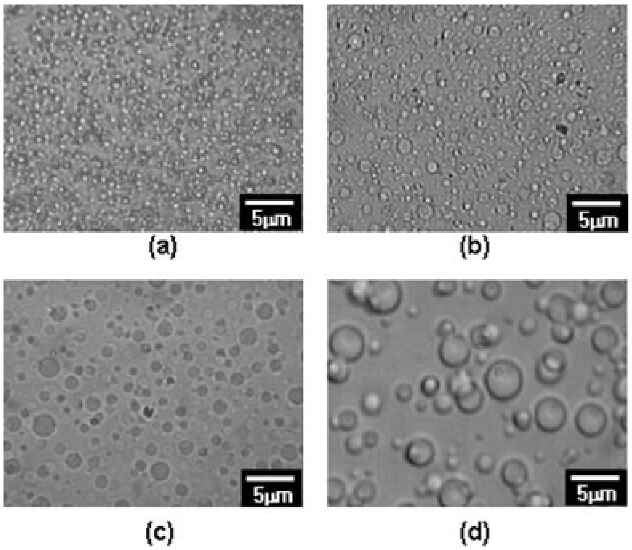

Figure 3 Optical micrographs showing changes in the droplet size and number of droplets with the annealing time after the quenching of the samples at 20°C below the observed phase temperature of the 50/50 PE/(40/60 isoparaffin/soybean oil) blend: (a) 1, (b) 5, (c) 10, and (d) 20 min.

phase-separation temperature rapidly increases with increasing soybean oil content in the ternary blend, as exhibited in Figure 2. Furthermore, phase-separation temperatures of ternary blends were always higher than those of PE/soybean oil binary blends when the diluent mixtures contained 50 wt % or more soybean oil. All binary pairs included in ternary blends are miscible when the temperature is higher than the phase-separation temperatures of the PE/soybean oil blends. This means that the ternary blends, in which the diluent mixture contains 50 wt % or more soybean oil, do not satisfy the condition for the miscible ternary blend (the 2 × 2 determinant is positive). This condition implies that the immiscibility of ternary blends could stem from asymmetry in the binary interactions, even though all the binary pairs composing the ternary blend are miscible.

Droplet growth mechanism

A homogeneous polymer/diluent blend that is formed at an elevated temperature undergoes phase separation when the system enters an unstable or a metastable region. The phase separation proceeds through nucleation and growth in the metastable region, whereas it occurs through spinodal decomposition in the unstable region. After the early-stage development of the microstructure, the two-phase system will continue to evolve in response to its tendency to reduce the surface energy associated with the interfacial area. It is known that this process, the so-called coarsening process, often results in a reduction in the number of droplets and an increase in the droplet size. Three different mechanisms have been taken into account to interpret the coarsening in later stages of the phase separation: Ostwald ripening, coalescence, and the hydrodynamic flow mechanism. The classical theory of Ostwald ripening is widely called the evaporation–condensation mechanism.[15] According to the theory, particles with radii larger than the critical radius grow at the expense of particles with radii smaller than the critical radius, depending on the degree of supercooling prevailing at the time. The larger particles grow by the migration of minor component molecules through the polymer matrix from smaller particles. According to the coalescence mechanism, coarsening also occurs by two or more droplets impinging on one another by translational diffusion and eventually forming a single droplet.[16,17] The third mechanism in the coarsening process is the hydrodynamic flow mechanism. According to Siggia,[19] in the cylindrical part of a bicontinuous phase-separated structure, the pressure gradient along the axis of a cylinder causes a flow of the inner fluid from a narrow region to a wide region, which results in coarsening of domains. Close observation was made to explore the growth mechanism of the dispersed droplets in the blends examined here.

Optical micrographs in Figure 3 show the changes in the droplet size with time after quenching of the sample 20°C below the observed phase temperature of the 50/50 PE/(40/60 isoparaffin/soybean oil) blend. A gradual reduction in the number of droplets and an increase in their size are observed with increasing annealing time right after the early-stage development of the domain–matrix structure. Figure 4 shows the evidence for the Ostwald ripening

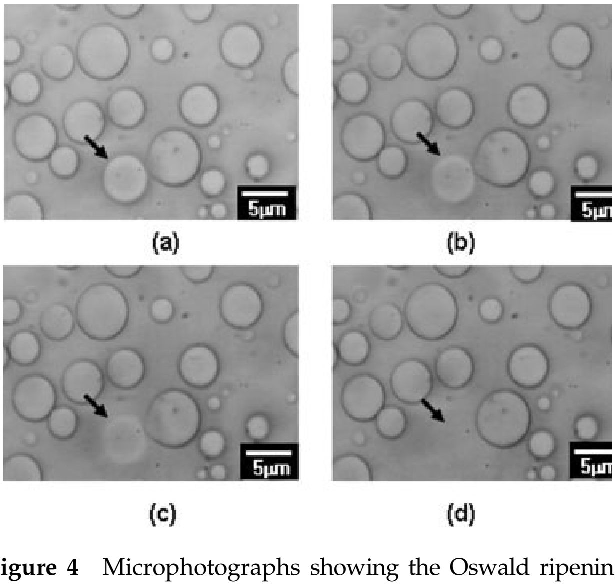

Figure 4 Microphotographs showing the Oswald ripening process of the 30/70 PE/soybean oil blend at a quenching depth of 20°C with annealing times of (a) 10 min 10.10 s, (b) 10 min 10.15 s, (c) 10 min 10.19 s, and (d) 10 min 13.21 s.

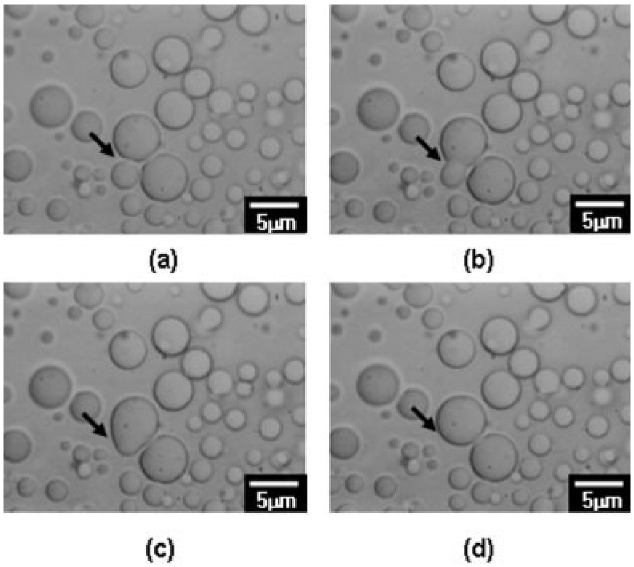

Figure 5 Microphotographs showing the coalescence process of the 30/70 PE/soybean oil blend at a quenching depth of 20°C with annealing times of (a) 12 min 2.4 s, (b) 12 min 2.5 s, (c) 12 min 2.6 s, and (d) 12 min 2.7 s.

process of 30/70 PE/soybean oil. The driving force of this process is the chemical potential, which is proportional to the curvature of the droplet. Small droplets are more apt to evaporate than large droplets because of the chemical potential difference. The evaporated diluent mixture diffuses through the polymer matrix and then is partly condensed on the surface of larger droplets. As shown in Figure 5, it was also visually confirmed that the two domains collided with each other and then coalesced into a bigger domain by the fusion at their interfaces. The coalescence of the domain was completed within 0.5 s after the initial contact, which was presumably due to the high mobility of the polymer-lean phase. Note that the growth of the droplets by the hydrodynamic flow mechanism was not observed. PE/(isoparaffin/soybean oil) blends also exhibited a coarsening process similar to that of PE/soybean oil blends. The observed results indicate that the droplet growth in the binary and ternary blends examined here occurs by both coalescence and the Ostwald ripening process.

Droplet size changes with the annealing time and quenching depth

Figure 6 show the changes in the droplet size with time after quenching of the sample 10, 20, and 30°C below the observed phase temperature of the 40/60 PE/(20/80 isoparaffin/soybean oil) blend. At a constant quenching depth, the droplets initially grow with the annealing time by the coarsening process and then level off at a fixed domain size after a certain period of annealing. The growth rate of the droplet size increases with the increase of the quenching depth, as shown in Figure 6. The collision/combination of droplets easily occurs by an increase in the quenching depth because the number of droplet increases with the quenching depth. Furthermore, because the interfacial tension and concentration difference between the two coexistence phases increase with the quenching depth, the droplet growth by the Oswald ripening process is also expected to be easily activated. However, the significant increase of the quenching depth resulting in the decrease of the diffusivity of the diluent caused by the increase of the matrix viscosity hinders the rapid growth of the droplet. Even though the growth rate of the droplet is generally determined by the competition of these two opposite factors, the results obtained in this study show that the growth rate increases by an increase in the quenching depth below the phase boundary.

The changes in the droplet size with time after quenching of the blends containing 40 wt % PE 20°C below the observed phase temperature are shown in Figure 7. The growth rate of the droplet was ranked in the order of 40/60 PE/(20/80 isoparaffin/soybean oil) > 40/60 PE/soybean oil > 40/60 PE/(80/20 isoparaffin/soybean oil), which is in the same order for the phase-separation temperatures of these blends. This means that the higher the phase-separation temperature is of the blend, the higher the growth rate is of the droplet. Because the annealing temperature of the ternary blend is higher than that of the binary blend at the same quenching depth, the diffusivity of the diluent in the ternary blend through the

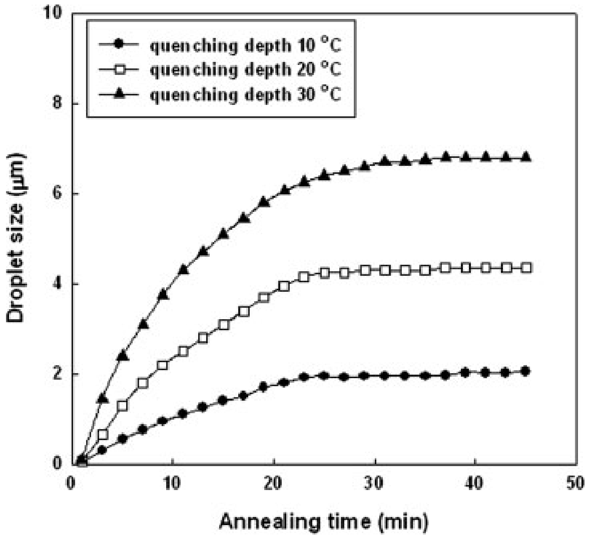

Figure 6 Changes in the droplet size with the annealing time after the quenching of the samples at 10, 20, and 30°C below the observed phase temperature of the 40/60 PE/(20/80 isoparaffin/soybean oil) blend.

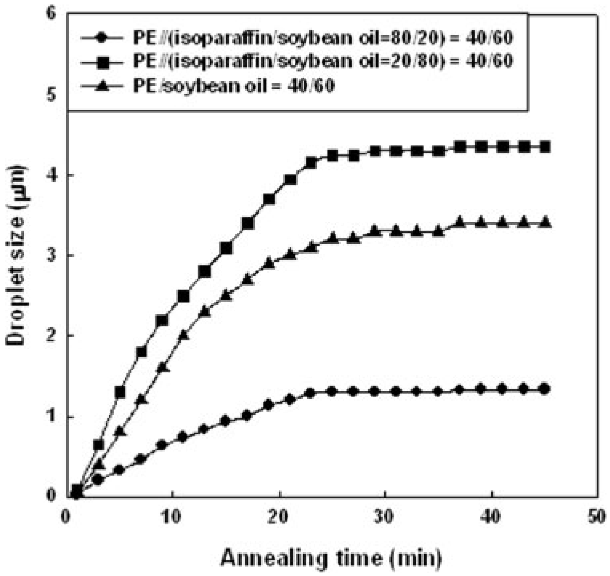

Figure 7 Changes in the droplet size of the blends containing 40 wt % PE with the annealing time after the quenching of the blend at 20°C below the observed phase temperature.

polymer matrix is higher than that in the binary blend. The increase of the diffusivity of the diluent is believed to result in the increase of the droplet growth rate. As previously mentioned, the droplets initially grow with the annealing time and then level off at a fixed domain size after a certain period of annealing. The average droplet size, which does not change any more after a given annealing time, is defined as the equilibrium droplet size. Figure 8 shows the equilibrium droplet sizes obtained with the binary PE/soybean oil blend and ternary PE/(isoparaffin/soybean oil) blends at a quenching depth of 20°C. A higher phase-separation temperature of the blend and a higher concentration of the diluent lead to a larger equilibrium droplet size.

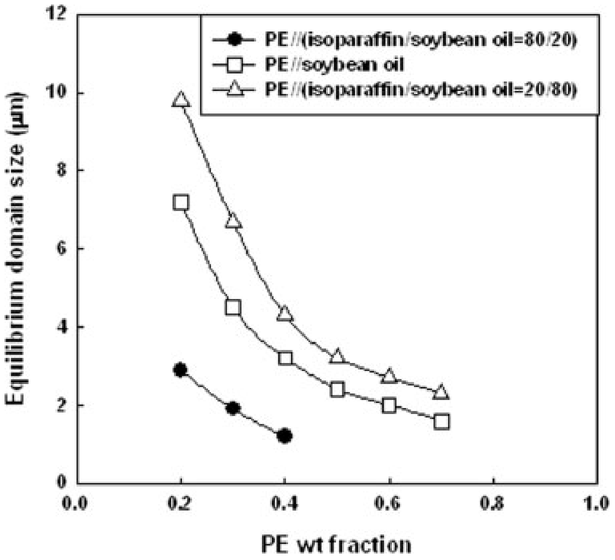

Figure 8 Equilibrium droplet sizes obtained with the PE/soybean oil binary blend and PE/(isoparaffin/soybean oil) ternary blends at a quenching depth of 20°C.

Droplet size changes at a constant cooling rate

When the homogeneous 40/60 PE/soybean oil blend was cooled at a scanning rate of 10°C/min, it underwent phase separation just below the reported phase-separation temperature, and the droplets were then further enlarged upon the cooling process. When the blends were cooled just below the crystallization temperature, the average size of droplets of the PE/soybean oil blend was 0.7 μm. Note that the small droplets formed during the crystallization process of PE were not counted for the calculation of the average size of droplets. The average droplet size of PE/isoparaffin blends, in which the solid–liquid phase separation occurs first upon cooling from one phase region, was 0.07 μm. Figure 9 shows changes in the average droplet size of the 40/60 PE/(isoparaffin/soybean oil) blends with various diluent mixing ratios. As shown in Figure 9, the average size of droplets increased with increasing soybean oil content in the diluent mixtures and went through a maximum centered at about 80 wt % soybean oil before decreasing afterwards. The changes in the droplet size showed a trend similar to the trend of the phase-separation temperatures. This means that the pore size of the membrane formed via the TIPS process can be also controlled by manipulation of the phase-separation temperature of the polymer/diluent blends. The droplet size increased up to

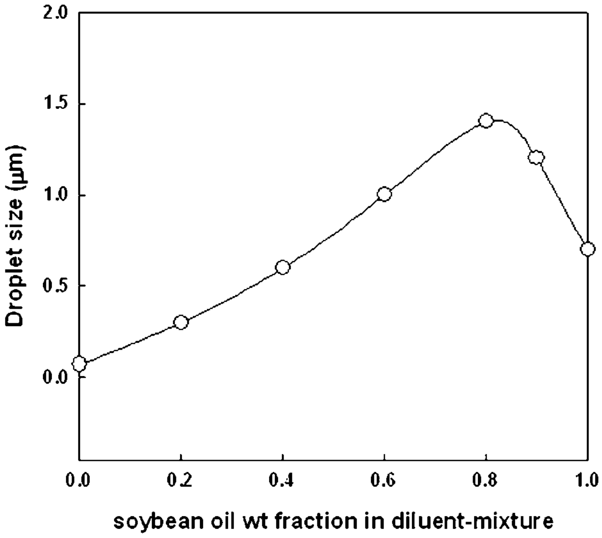

Figure 9 Changes in the average droplet size of the 40/60 PE/(isoparaffin/soybean oil) blends with various diluent mixing ratios. The samples were cooled at a scanning rate of 10°C/min.

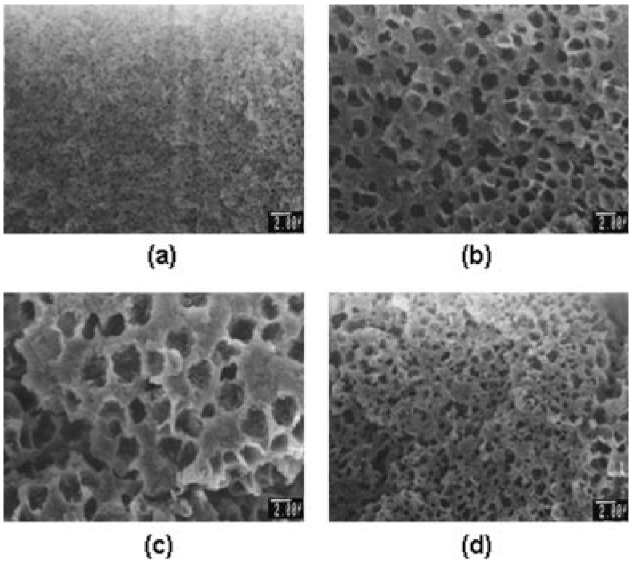

Figure 10 Cross-sectional morphologies of membranes fabricated from PE/(isoparaffin/soybean oil) blends: (a) 40/60 PE/(80/20 isoparaffin/soybean oil), (b) 40/60 PE/(40/60 isoparaffin/soybean oil), (c) 40/60 PE/(80/20 isoparaffin/soybean oil), and (d) 40/60 PE/soybean oil. The samples were cooled at a scanning rate of 10°C/min, and the diluent was extracted with acetone.

about 1.4 μm with isoparaffin and soybean oil as a diluent mixture. Figure 10 shows cross-sectional images of microporous membranes observed with scanning electron microscopy. These images also illustrate that the pore size formed by the use of a diluent mixture (20/80 isoparaffin/soybean oil) is larger than that formed by the use of soybean oil. In summary, the pore size of a battery separator can be manipulated by the adjustment of the thermodynamic factors (phase boundary) and kinetic factors (TIPS process conditions such as the quenching depth, annealing time, and cooling rate). When a microporous membrane is produced commercially, a homogeneous mixture containing a polymer and a diluent is formed in an extruder and is forced through a sheet-shaping die in a continuous stream. Because control of the kinetic factors is difficult in the extrusion process, the thermodynamic factors are more important than the kinetic factors in producing microporous membranes commercially.

CONCLUSIONS

The diluent mixing ratio and process conditions were varied to control the pore size of microporous PE membranes through TIPS. PE/soybean oil binary blends and PE/(isoparaffin/soybean oil) ternary blends exhibited typical UCST-type phase behavior, whereas PE/isoparaffin binary blends were miscible above the crystallization temperature of PE. The phase-separation temperature of the ternary blends first rapidly increased with increasing soybean oil content in the diluent mixture, went through a maximum centered at 80 wt % soybean oil, and then decreased. As a result, the phase-separation temperatures of the ternary blends were always higher than that of the PE/soybean oil blend when the diluent mixture contained more than 50 wt % soybean oil. The interaction energy densities of binary pairs calculated from the observed phase boundaries with the Flory–Huggins theory were 0.53 cal/cm^3 for the PE/soybean oil pair, 0.21 cal/cm^3 for the PE/isoparaffin pair, and 0.28 cal/cm^3 for the soybean oil/isoparaffin pair. The immiscibility of the ternary blend in the region in which all binary pairs involved in the ternary blend were miscible stemmed from asymmetry in the binary interactions. It was also confirmed that the droplets grew by both coalescence and the Ostwald ripening process after the onset of phase separation. As the blends had higher phase-separation temperatures, larger droplets were formed at a constant cooling rate, and the droplet growth rate increased at a constant quenching depth. Moreover, the droplet growth rate increased with increasing quenching depth. In summary, microporous membranes with the desired pore structure were produced by control of the phase boundary with a diluent mixture and by variation of the processing conditions in the TIPS process.

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