Preparation of a Fine Porous Thin Film by Phase Separation induced in the Course of Drying an Immiscible Polymer Blend Solution

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Introduction

Porous polymeric films with fine pores in the range from micrometer to sub-micrometer or nano scale order have attracted much attention for various applications, such as membrane separation and purification,[1] solid supports for sensors and catalysts,[2] scaffolds for biological cells,[3] low-dielectric constant materials for microelectronic devices,[4] and battery separators in fuel cells and lithium ion batteries.[5] Recently, phase separation[6] in immiscible polymer blend solutions to prepare porous material has been of great interest due to the simplicity and cost-efficiency of the process. Phase separation in immiscible polymer blends is induced by evaporating the solvent (solvent quenching).[7] It has been known that the dispersed domain (droplet) size and its density can be changed by the coalescence of domains during the phase separation,[8] and the process often results in low domain density and large domain size.[9] Various factors for determining the dispersed domain size and the density, such as solvent type,[10] concentration,[11] molecular weight of the polymer,[12] and weight ratios of polymers[13] have been identified. However, there still remains a great challenge in controlling the pore size and pore density and clarifying the formation mechanisms of porous structures due to the versatility of polymer blends' morphologies.

In this paper, we investigate the PS/PEG/solvent systems in terms of controllability of pore size and pore density in the film. The effects of the polymer solubility in the solvents and drying rate on the porous structure were investigated by using six different solvents in the PS/PEG polymer blend as well as different casting methods were applied to the PS/PEG blend film to control the pore size. Furthermore, the formation mechanism of the structure is also discussed.

Experimental

Materials

Polystyrene (PS) and Polyethylene glycol (PEG) were purchased from Aldrich Chemical Company and Wako Pure Chemicals Ind. Ltd., Japan, respectively. The weight average molecular weight, M_w, the number average molecular weight, M_n, and polydispersity, M_w/M_n, of these polymers were measured by gel permeation chromatography (Shimadzu, model DGU-20A$_3$, Column; Shodex GPC KF-806L, Eluent; Chloroform). The retention time and molecular weight were calibrated using PS standards. Six different organic solvents, including toluene-dehydrate, tetrahydrofuran-dehydrated (THF), methyl ethyl ketone -dehydrated (MEK), chlorobenzene-dehydrated, 1,4-dioxane-dehydrated, and chloroform -dehydrated (Wako Pure Chemicals Ind. Ltd. Japan, Purity 99.5%), were used without further purification. The characteristics of the materials used in this work are listed in Table 1.

Table 1 Characteristics of PEG, PS, and various solvents used in this work

Materials	Mw	Mn	Mw/Mn	Vapor pressure [mmHg] at 20°C	δ [MPa]$^{0.5}$
Polystyrene (PS)	222,000	99,000	2.24		18.6[14]
Polyethylene glycol (PEG)	280	260	1.07		26.1[15]
Chlorobenzene				12	19.4[14]
Methyl ethyl ketone (MEK)				71	19[14]
Tetrahydrofuran (THF)				129	18.6[14]
1,4-dioxane				27	20.5[14]
Toluene				22	18.2[14]
Chloroform				159	19[14]

Film preparation

PS and PEG 200 were blended at different weight ratios and dissolved into a solvent with different polymer concentrations.   The different casting methods are applied to this study.   At first, the solution was cast by a micro-injector onto an aluminum Petri-dish, which was 2.1 cm in radius and 0.5 cm in depth.   The film thickness was controlled by changing the amount of injected solution.   The volume of solution to be injected was 100 μl in the nominal case.   The initial thickness of solution was about 300 μm.   Secondary, the solution drops onto a substrate and sequentially performing the spin casting.   Glass slides (2.5 × 2.5 cm) are used to the substrate in the spin-casting process.   The spin-casting is performed at room temperature, at a casting speed of 3000 rpm, and with 10 s of processing time.   Then, the cast samples were dried under a nitrogen purge in a temperature-controlled incubator.

Observation of film morphology

The porous structure of the obtained film was observed by scanning electron microscope (Tiny-SEM 1540, Technex Lab Co. Ltd.) with the treatment of gold-palladium sputter-coating under a vacuum atmosphere.   AFM (SPM-9500J3, Shimadzu, Japan) is also used to observe the morphology in the nano-scale size.   AFM images are taken in tapping mode at room temperature.   For the pore size and the density calculation, we counted the number of pores observed in a micrograph of the cross sectional area of the film and divided the number by the area of the cross section.

Results and discussion

Resulting porous structure

A mixture of polystyrene/polyethylene glycol 200 (70/30) blends and toluene solution (90 wt % solvent concentration) was prepared and cast on an aluminum Petri-dish.   Then, it was dried under nitrogen purging in a temperature-controlled incubator.   For a reference, a homogeneous solution of polystyrene alone with toluene solvent was prepared and dried with the same procedure.   Figure 1 shows SEM micrographs of surface and cross-sectional areas of the resulting PS/PEG films.   As shown in Figure 1(a), the ordered porous structure about 12 μm in pore size was formed on the surface.   The porous structure was exclusively formed on both the surface and interface between the substrate and solution.   No porous structure was observed inside the film as illustrated in Figure 1(b).   Figure 2 shows a SEM micrograph of the cross-sectional area of the resulting PS film.   As shown in Figures 1 and 2, porous structure

was well-formed in the polymer blend films but not in the film of PS alone.   Comparison of the micrographs in Figure 1 with that in Figure 2 clearly shows that the presence of PEG composition affects the morphology in the polymer blend film.   In other words, the film fabricated without PEG has no porous structure, while the films made from PS/PEG solutions showed porous structures.

(a)   (b)
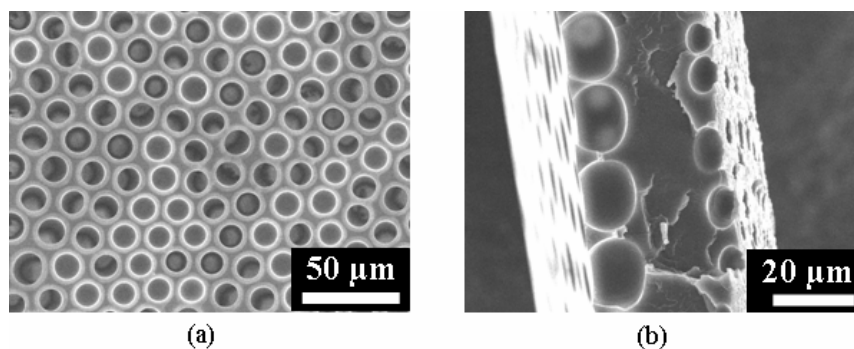
Figure 1.   SEM micrographs of PS/PEG 200 (70/30) (w/w) cast from 90 wt % toluene solution under 3 L/min N_2 flows: (a) Surface micrograph; (b) Cross-sectional micrograph.


(a)   (b)
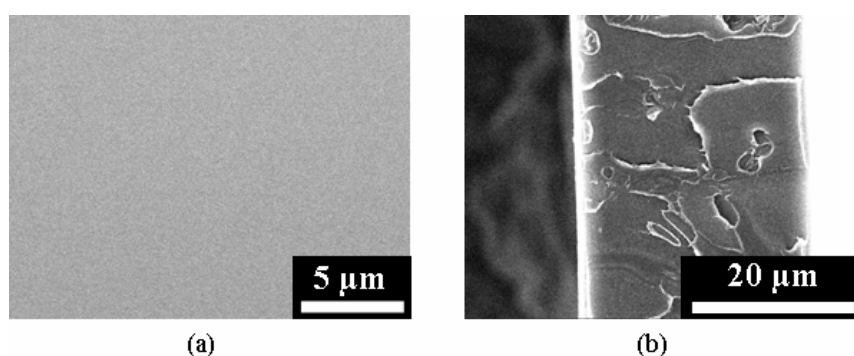
Figure 2. SEM surface and cross-sectional micrograph of PS cast from 90 wt% toluene solution under 3 L/min N_2 purging.

In our previous work,[12] we showed a formation mechanism of porous structures via two step phase separation in the course of drying a ternary polymer solution.   As illustrated in Table 1, the solubility parameters of PS and PEG are different, and the solubility of PS and PEG in the toluene is different as well.   The solubility parameters of polymers and solvents indicate that toluene was poor for PEG.   Thus, in the course of drying the polymer solutions, the phase separation into PEG-rich and PEG-poor (i.e., PS-rich) phases occurred.   The PEG-rich phase dispersed domain formed droplets and the PEG-poor phase became a matrix where PS and solvent coexisted as a single phase solution.   Then, secondary phase separation followed in the PEG droplets, which was induced by further solvent evaporation, and formed into solvent-rich and PEG-rich domains within the droplets.   The solvent evaporation and secondary phase separation created the pores in the film.

Effect of solvent on the formation of porous structure in PS/PEG blend film
Six homogeneous solutions of PS/PEG blends with different solvents were prepared. All solutions were made at the 70/30 PS/PEG weight ratio and 10 wt% of polymer concentration. Figure 3 shows SEM micrographs of the surface and the cross-sectional area of the resulting

films made from the six different solutions. As shown in Figure 3, the pore size and the density of pores in the film were different with the various solvents. The pore size became largest and density became smallest in the film made from the toluene solution, and the size became smallest and density became largest in the film made from the chloroform solution.
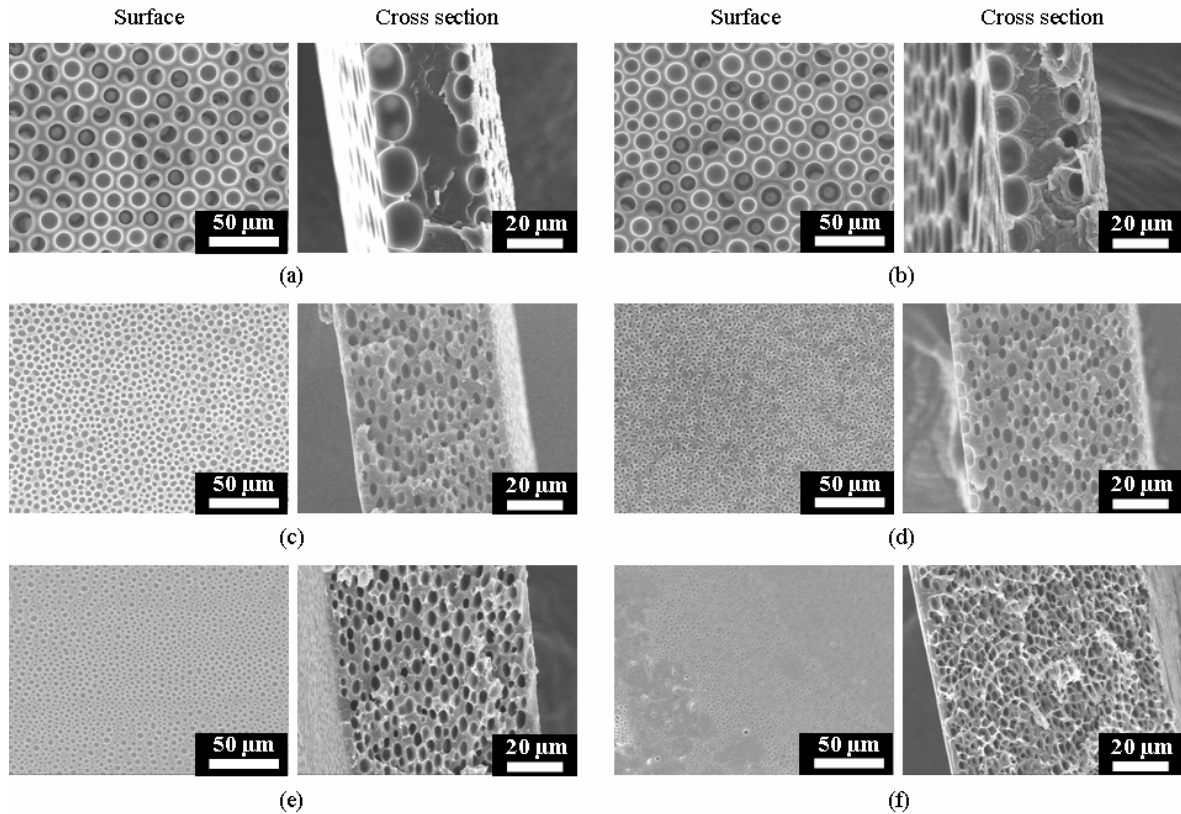
Figure 3. SEM micrographs of surface and cross sectional area in PS/PEG 200 (70/30) (w/w) cast from 90 wt% solvent under 3 L/min N_2 flows ((a) toluene; (b) chlorobenzene; (c) THF; (d) MEK; (e) 1,4-dioxane; (f) chloroform).

The resulting porous structures indicated that the occurrence of phase separation alone could not explain the formation mechanism of the pore size and the density of pores. The factors controlling the process, such as drying rate and change in viscosity of the polymer solution, also affect the porous structure.

The drying rates in each solution were measured by weighing the solution over the course of drying, and the solubilities of PEG to each solvent were estimated by the Flory-Huggins interaction parameter (χ). The interaction parameters were calculated from the solubility parameters of PEG and solvents by:

$$\chi = \frac{V_i}{RT} \left(\delta_i - \delta_j \right)^2 + \beta \qquad (1)$$

where V is the molar volume of the solvent, δ is the Hildebrand solubility parameter for the solvent and polymer, R is the gas constant, and T is the absolute temperature.[16] β corresponds to the entropic component, and a value of 0.34 is used for non-polar systems. The interaction parameters in this study were calculated without an entropic component (β=0) because of the polarity of PEG.[16]

Figure 4 shows some experimental results of the drying rate.   The value of drying rate was calculated from the initial slope of the weighting curve against drying time.
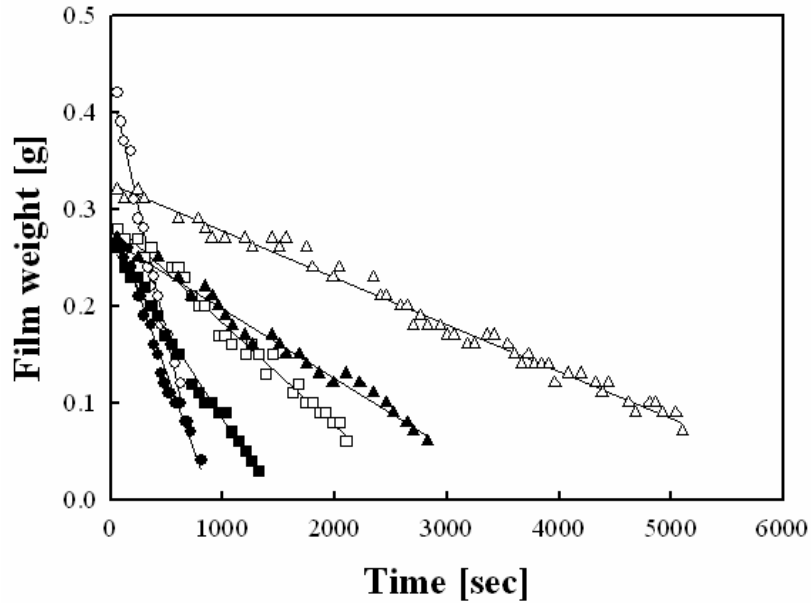

Figure 4. Drying rate for several polymer blend and solvents systems (($\circ$) Chloroform; ($\bullet$) THF; ($\square$) 1,4-dioxane; ($\blacksquare$) MEK; (Δ) Chlorobenzene; ($\blacktriangle$) Toluene).

The calculated Flory-Huggins interaction parameter is listed in Tables 2.   Figure 5 plots average pore size and density of pores in the cross-sectional area of polymer blend/solvent systems in the coordinate system of drying rate and Flory-Huggins interaction parameter (χ) between its solvent and PEG.   Figure 5 clearly shows that the higher drying rate and lower Flory-Huggins interaction parameter made porous structure in the film finer, i.e., pore size smaller and density larger.

Table 2 Flory-Huggins interaction parameter (χ) of solvents and polymers

Materials	Molar volume [cm^3/mol]	χ PEG-solvent at 30 ^{o}C	χ PS-solvent at 30°C
Toluene	106.8	2.64	0.35
Chlorobenzene	102.1	1.81	0.37
Chloroform	80.7	1.61	0.35
THF	81.7	1.82	0.34
MEK	90.1	1.80	0.35
1,4-dioxane	85.7	1.07	0.46
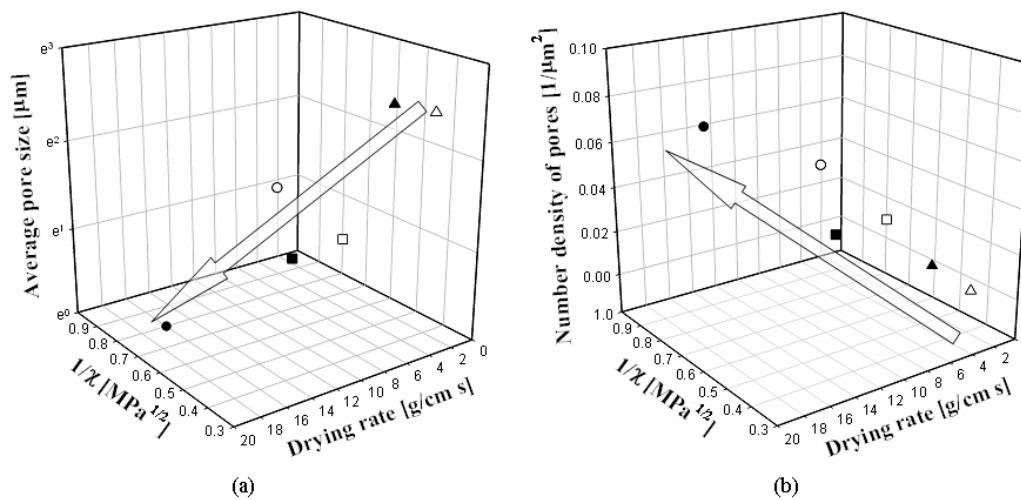
Figure 5. Average pore size (a) and number density of pores (b) in polymer blend/solvent systems on a diagram of drying rate and Flory-Huggins interaction parameter (χ) between its solvent to PEG ($(\triangle)$ Toluene, $(\blacktriangle)$ Chlorobenzene; ($\square$) MEK; ($\circ$) 1,4-dioxane; ($\blacksquare$) THF; ($\bullet$) Chloroform).

**Formation mechanism of a fine porous structure in polymer blend film**

In the course of drying a ternary composition polymer solution, solvent evaporation induces phase separation. The solvent concentration decreases from the surface and phase separation occurs from the surface. As drying proceeded, the solvent concentration profile propagated inside the solution and PEG-rich domains were created inside of the solution and coalesced. The growth rate of the PEG-rich domains was affected by drying rate and the solubility of PEG to solvent. Thus, when fast drying proceeds, the increase of drying rate increases polymer concentration as well as the viscosity of the PS-rich phase (matrix phase) quickly. High polymer concentration and high viscosity of the solution could suppress the coalescence of PEG-rich domains and made the domain size smaller and increased the density of domains in the film.

The effect of solubility of PEG to solvent on the controllability of pore size and density of pores was analyzed as follows, by means of the Flory-Huggins interaction parameter (χ). The Flory-Huggins interaction parameter corresponds to the solubility of the polymer to solvent. Grulke stated that a polymer was considered to be miscible to the solvent when χ became lower than 0.5. It is well known that the smaller the value of χ, the higher the solubility of polymer to solvent. As listed in Table 3, the solubility of PEG200 to solvent increased from 1,4-dioxane, chloroform, MEK, THF, chlorobenzene, and toluene. When the solubility of PEG to solvent increases, the polymer concentration at the onset of PEG phase separation increases. The increase in the solubility of PEG to solvent increases the polymer concentration, and the viscosity of the solutions at the onset of phase separation increases. The higher viscosity of the solution could suppress coalescence of the PEG-rich domain after the phase separation. Therefore, the pore size decreased with the increase in the solubility of PEG to solvent. Thus, the frequency of the coalescence of the PEG-rich domain was controlled by the viscosity of the matrix (PS-rich phase) at the onset of the PEG phase separation i.e., the solubility of PEG to solvent.

When the higher drying rate with the higher solubility of PEG to solvent system was conducted, the PEG-rich domains created inside of the film could not easily coalesce due to the higher viscosity of the matrix at the onset of phase separation. Therefore, the PEG-rich domains remained in the interior of the film, and a fine porous structure could be created in the PEG droplets by the secondary phase separation in the film.

Effect of solvent on the formation of porous structure in PS/PEG blend film
A single phase solution of PS and PEG200 at ratios of 90/10, 80/20, 70/30 in a 1 wt% benzene solvent is cast on a glass slide. Figure 6 shows AFM images of the surface of the resulting PS/PEG films.
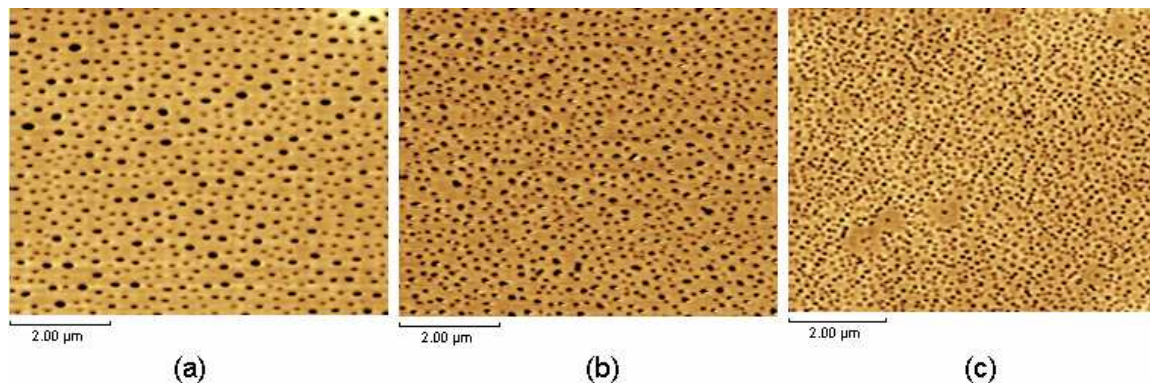
Figure 6. AFM height images of PS/PEG200 film from benzene solution: (a) 70/30, (b) 80/20, (c) 90/10 of PS/PEG

As shown in Figure 6, pores appear uniformly on the entire surface of the films and when compared to drop casting, pore size drastically decreases from micron-size to sub-micron or nano-scale order. During spin casting, at the initial stage, the solution flows on the substrate in radial direction, and actually a few amounts of the solution remains on the substrate. It caused short drying time in the solution. The growth of PEG domains is induced by coalescence, but due to short drying time, the concentration of PS solution which forms the matrix phase increases fast and suppresses the coalescence of PEG domains. Therefore, there is not enough time for phase-separated PEG domains to grow and then very small pores are created on the film surface.

Conclusions

A polymeric film with a fine porous structure was prepared by dry-casting polystyrene (PS) and polyethylene glycol (PEG) and solvent solutions. By changing the solvent to PS/PEG blend, the pore size and density as well as the porous structure were drastically changed with the different solvent types and the casting methods. The increase of drying rate and high solubility of PEG to solvent increased the polymer concentration of the PS-rich phase at the onset of phase separation of PEG. The higher concentration and higher viscosity of PS at the onset of the PEG phase separation may have suppressed the growth of the PEG-rich domain, and phase-separated PEG domains were left in the inside of the film. Moreover, the short drying time due to spin casting increased fast the concentration of the polymer solution and suppressed the coalescence of phase-separated PEG domains. It caused the very small sized domains. Then pores were created in the PEG-rich domain by secondary phase separation. Finally, a fine porous structure could be formed in the film.

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