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Changes in the miscibility of binary and ternary blends having the same chemical components and compositions

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Abstract

The phase behavior of ternary blends of dimethylpolycarbonate (DMPC), tetramethyl polycarbonate (TMPC), styrene-acrylonitrile (SAN) copolymer has been explored. The experimental phase behavior of ternary blends was compared with that of binary blends having the same chemical components and compositions except that the DMPC and TMPC were present in the form of copolycarbonates (DMPC–TMPC). Miscible region of DMPC/TMPC/SAN ternary blends is narrower than that of DMPC–TMPC/SAN binary blends. In addition, phase separation temperature of binary blend was higher than that of corresponding ternary blend. However, the entropic and energetic terms of ternary blends were more favorable for miscibility than those of binary blends. To understand the phase behavior of blends, phase stability conditions of binary and ternary blends were analyzed. Some ternary blends that have negative interaction energy were not miscible because these blends do not satisfy stability conditions. It was revealed that the addition of component, accompanied by the asymmetry in the binary interactions, results in destabilization of blend.

Keywords: Ternary blends; Binary blends; Miscibility

1. Introduction

Successful design of polymer blend systems requires the ability to control or manipulate the phase behavior of the mixture. When homopolymer/homopolymer blend is not immiscible, a new miscible blend involving immiscible binary pair often produced via two different routes. Blending of a homopolymer with copolymer that composed of binary pair having strong intramolecular repulsion is known as a useful route to prepare a miscible blend [1–8]. The other way of preparing miscible blend is the homogenization of two immiscible polymers by adding a third polymer that is miscible with each component [9–17]. According to the binary interaction model [1–3], the former method might be a useful route in developing miscible blends. In the previous researches, various miscible blends have been developed via copolymerization [4–8]. The latter method also often used to develop a new miscible blend. However, this method was not successful in developing a new miscible blend unless the third component that is miscible with each component of blend is major component in blend [9–17].

In this study, we have explored why the latter method could not be more useful route in developing miscible blend than the former method. In the previous study [18], we examined the miscibility of binary blends containing poly(styrene-*co*-acrylonitrile) copolymer (SAN) and copolycarbonates composed of tetramethyl bisphenol-A polycarbonate (TMPC), dimethyl bisphenol-A polycarbonate (DMPC) and then characterized binary interaction energies involved in the blends. In this study, phase behavior of ternary blends composed TMPC, DMPC, and SAN was explored and then their miscibility was compared with that of binary blend. Based on the volume fluctuation thermodynamics [15,19], the phase stability of polymer mixtures was analyzed to understand the differences in the phase behavior of binary and ternary blends having the same chemical components and compositions.

2. Materials and procedures

Homopolymers and copolymers were listed in Table 1.

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Table 1
Polymers used in this study

Polymer	Copolymer composition[a]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]	Refractive index	Source
PS	–	192,400	2.16	1.593	LG chemical
SAN2	2% AN	213,000	1.72	1.591	Asahi chemical
SAN5.7	5.7% AN	210,000	1.92	1.588	Asahi chemical
SAN10	10% AN	215,000	2.03	1.583	Synthesized
SAN15	15% AN	103,500	2.03	1.579	Synthesized
SAN18	18% AN	13,500	1.95	1.577	Synthesized
SAN20	20% AN	174,500	2.21	1.575	Synthesized
SAN24	24% AN	153,000	1.83	1.572	LG chemical
DMPC	–	48,300	2.47	1.578	Synthesized
TMPC	–	46,700	2.07	1.546	Synthesized
DMPC-TMPC 41	41 wt% TMPC	40,500	2.05	1.565	Synthesized
DMPC-TMPC 50	50 wt% TMPC	30,500	1.79	1.562	Synthesized
DMPC-TMPC 60	60 wt% TMPC	23,400	1.69	1.559	Synthesized
DMPC-TMPC 74	74 wt% TMPC	29,100	1.56	1.554	Synthesized
DMPC-TMPC 83	83 wt% TMPC	28,400	1.64	1.551	Synthesized

[a] Monomer content in copolymer was determined by elemental analysis.
[b] Molecular weights were determined by GPC using polystyrene standards.

The polymers used here were the same with those used in the previous study [18]. DMPC, TMPC, and DMPC–TMPC copolycarbonates were synthesized in our laboratory by using an interfacial polymerization technique. Some of the SAN copolymers were obtained from external sources while remainder were synthesized. The detailed preparation methods were reported previously [18]. The numerical part of the code for copolymers indicates the weight percent of TMPC or that of AN. Blends were prepared via solution casting from methylene chloride. The casting solutions were at 35 °C for a day in an air circulating oven until most of the solvent had evaporated, and then the resulting films were further dried in a vacuum oven at 120 °C for a week.

Glass transition temperature (T_g) of blend was determined using a differential scanning calorimeter (DSC, TA instrument, model DSC-2010). The first scan was run up to 180 °C to erase previous thermal history during sample preparation, then the sample was quenched to 25 °C to start the second scan. The onset of the transition in the heat capacity was defined as T_g. The temperature at which phase separation caused by lower critical solution temperature, LCST, was measured by an annealing technique to access the closest true equilibrium temperature [6,18,20]. To observe approximate value of phase separation temperature, the specimen covered with a cover glass was mounted on a hot stage [Linkam THMS 600] equipped with a temperature controller [Limkam, TMS 92]. The sample was heated rapidly to a temperature about 20 °C below the expected phase separation temperature and heated 2 °C/min. Changes in the image with temperature were observed as the specimens were heated at a rate of 2 °C/min. The temperature at which the image first started to change was taken as the approximate value of phase separation temperature. To determine the true equilibrium temperature, blend specimens were annealed in the hot stage at fixed temperatures in the vicinity of the expected phase boundary for 30 min. The image was observed to determine whether a change had occurred as a result of annealing or not. The lowest temperature at which change in the image occured as a result of annealing was taken as the phase separation.

3. Results and discussion

3.1. Phase behavior of ternary blends

It was known that TMPC/PS blends and TMPC blends with SAN copolymers containing less than or equal to 18 wt% AN exhibit one-phase behavior [8]. Blends of TMPC and DMPC that were miscible did not undergo phase separation until thermal degradation [21]. However, the blends of DMPC/PS and DMPC/SAN were found to be immiscible regardless of AN content of SAN copolymers [18,20]. These results suggested that DMPC blends with PS or SAN could be miscible by adding TMPC as a third component.

Miscibility of ternary blends was confirmed with three different methods, i.e. T_g behavior of blends, optical observation, and image change by annealing. Blends appeared transparent exhibited a single glass transition temperature while blends appeared cloudy exhibited two glass transition temperatures. Fig. 1 shows the selected DSC thermograms of DMPC/TMPC/PS ternary blends containing 50 wt% PS. When the blend contains 37% or more TMPC by weight, blends with PS exhibit a single glass transition. On the other hand, blends containing 30% TMPC or less were cloudy at the casting condition and exhibited two glass transitions that were distinctly separated. The blends exhibiting a single glass transition temperature were heated at a rate of 2 °C/min in the hot stage to observe morphology change caused by LCST-type phase behavior. Fig. 2 showed image analyzer photography of DMPC/

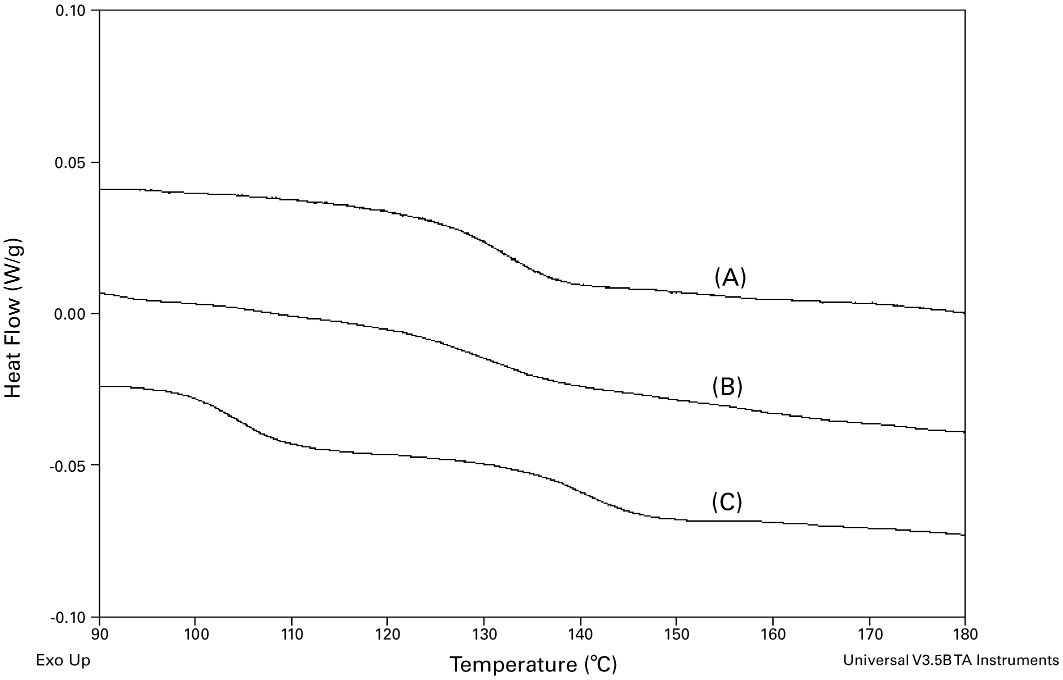

Fig. 1. The selected DSC thermograms of DMPC/TMPC/PS blends: (A) DMPC/TMPC/PS = 8.5/41.5/50; (B) DMPC/TMPC/PS = 13/37/50; (C) DMPC/TMPC/PS = 20/30/50.

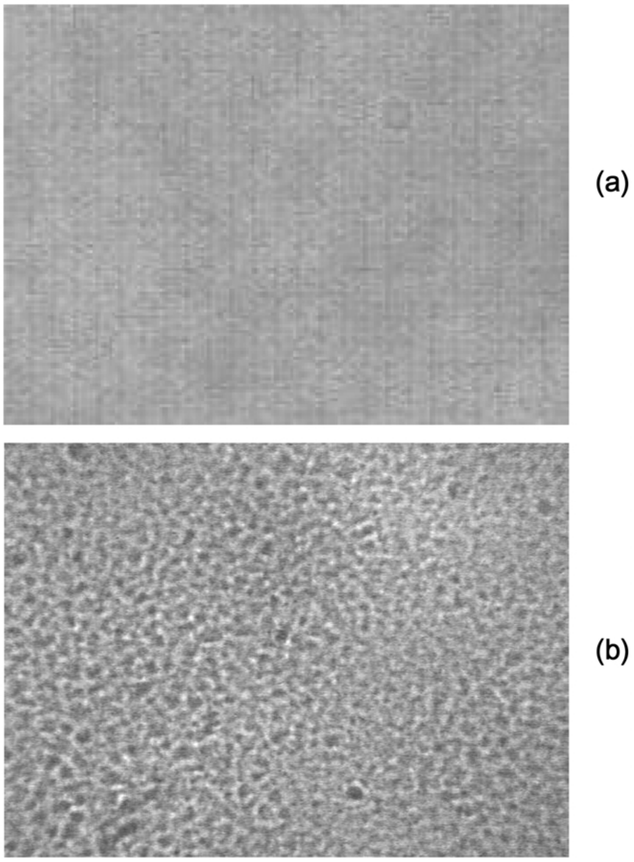

Fig. 2. The image analyzer photographies of DMPC/TMPC/PS = 13/37/50 blend observed at 160 and 175 °C, respectively: (a) observed at 160 °C; (b) observed at 175 °C.

TMPC/PS = 13/37/50 at 160 and 175 °C. Fig. 2(a) showed the image analyzer photography of blend at 160 °C and Fig. 2(b) shows the same blend at 175 °C. The blend at 160 °C was still clear and changes in the morphology of the blend were not observed while that at 175 °C was opaque and changes in the morphology were observed. Other blends exhibiting single glass transition also showed morphology change on heating. Based on these observations, it was confirmed that transparent blends exhibiting a single glass transition temperature were miscible.

Ternary blends of DMPC, TMPC and SAN having the same chemical components and compositions with DMPC–TMPC/SAN binary blends were prepared and then their miscibility was compared with that of corresponding binary blends. In the previous research [18], we examined miscibility of binary blends of DMPC–TMPC copolycarbonate and SAN copolymer. It was revealed that copolycarbonates containing equal to or more than 60 wt% of TMPC were miscible with SAN copolymers containing limit amounts of AN as shown in Fig. 3(a). The copolycarbonate (DMPC–TMPC 87) containing 87 wt% TMPC formed miscible blends with PS or SAN containing equal to or less than 15 wt% AN regardless of blend compositions. DMPC/TMPC/SAN ternary blends having the same chemical compositions with DMPC–TMPC 87/SAN blends were miscible when SAN copolymers contain equal to or less than 10 wt% AN. Both of DMPC–TMPC 74/SAN binary blends and the corresponding DMPC/TMPC/SAN ternary blends were miscible when SAN copolymers contain equal to or less than 10 wt% AN. The copolycarbonate (DMPC–TMPC 60) containing 60 wt%

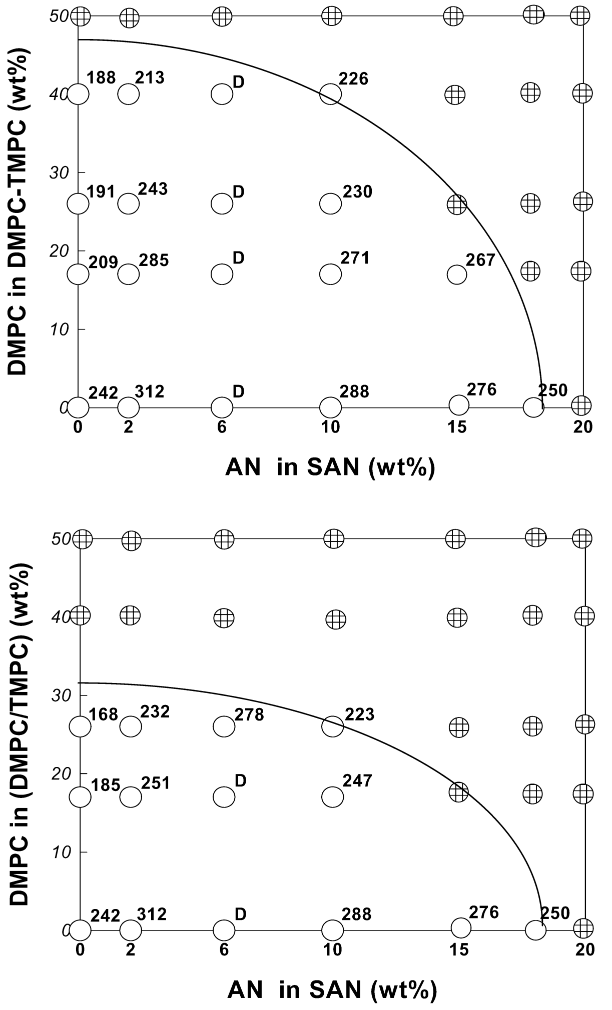

Fig. 3. Miscibility maps for (a) 50/50 = DMPC-TMPC/SAN binary blends and (b) the corresponding ternary blends. Numbers indicate phase separation temperatures of blends and 'D' means phase separation did not occurred until thermal degradation. Note that solid curves are the calculated spinodal curves.

TMPC formed miscible blends with SAN containing equal to or less than 10 wt% AN regardless of blend compositions. However, DMPC/TMPC/SAN ternary blends having the same chemical compositions with DMPC–TMPC 60/SAN blends were not miscible. As shown in Fig. 3 for binary blends (DMPC–TMPC/SAN = 5/5, Fig. 3(a)) and the corresponding ternary blends (Fig. 3(b)), the region where the ternary blends are miscible is narrower than that of binary blends. To compare the miscibility of binary with that ternary blends in more detail, phase separation temperatures caused by the LCST-type phase behavior and phase stability conditions for both blends were explored as described in the next section.

3.2. Phase separation behavior

The temperature at which phase separation caused by LCST-type phase behavior was measured by an annealing technique to access the closest true equilibrium temperature [6,18,20]. For example DMPC/TMPC/SAN 10 = 13/37/50 blend was heated rapidly to a temperature about 200 °C and then heated at a rate of 2°C/min. Changes in the image with temperature were observed as the specimens were heated at a rate of 2°C/min. Changes in the image was observed at 230 °C. After determining the approximate temperature at which phase separation occurred, blend specimens were annealed in the hot stage at a fixed temperature for 30 min. The blend annealed at 220 °C was still clear and changes in the morphology of the blend were not observed while that annealed 230 °C was opaque and changes in the morphology were observed. The phase boundary would appear to lie between 220 and 230 °C for this blend. By successively repeating annealing process within the determined temperature range, the location of the phase boundary was determined.

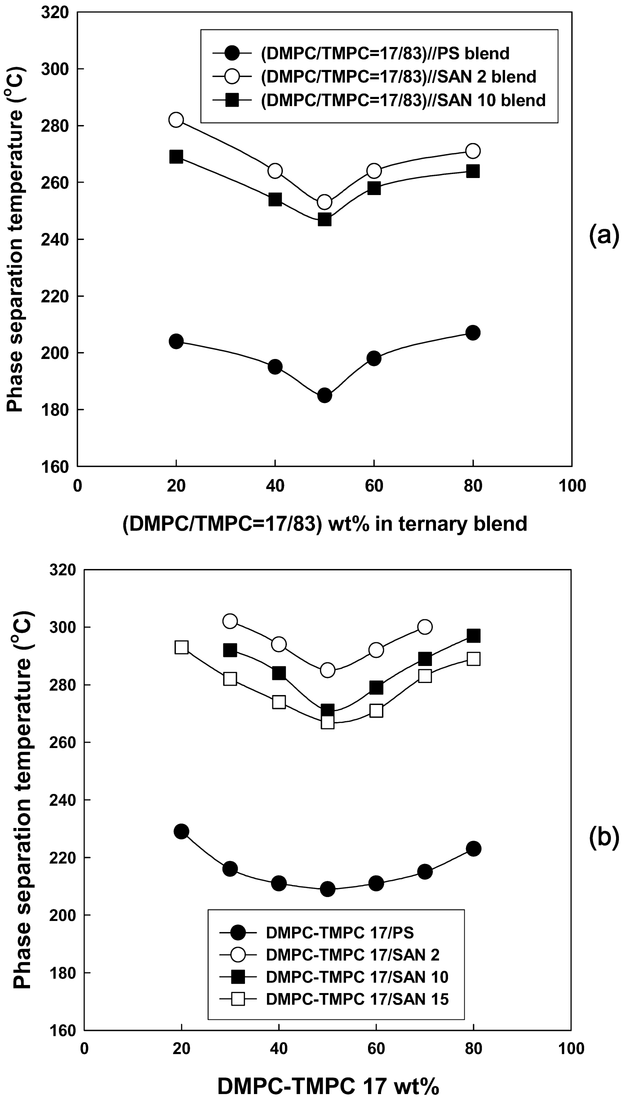

Fig. 4. Observed phase separation temperatures of DMPC-TMPC 83/SAN blends at various compositions and those of the corresponding ternary blends; (a) ternary blends; (b) binary blends.

Fig. 4 shows the observed phase separation temperatures of DMPC–TMPC 83/SAN blends at various compositions and those of the corresponding ternary blends. The phase separation temperature of binary blend was higher than that of the corresponding ternary blend. The similar trend was observed for DMPC–TMPC 74/SAN binary blends and the corresponding ternary blends as shown in Fig. 5. To compare clearly the phase behavior of binary and ternary blends, the miscibility map and experimentally determined temperatures at which 50/50 binary blends phase separate as a function of AN content in SAN copolymer and those of the corresponding ternary blend were shown in Fig. 3. Note that 'D' means phase separation did not occur on heating until thermal degradation temperature (~330 °C). The miscible region of binary blend is broader than that of ternary blend and the phase separation temperature of binary blend is higher than that of the corresponding ternary blend. The results indicate that ternary blend is always less stable than binary blend having the same chemical compositions and components. To understand the difference in the phase behavior of binary and ternary blends, phase stability conditions for binary and ternary blends were explored.

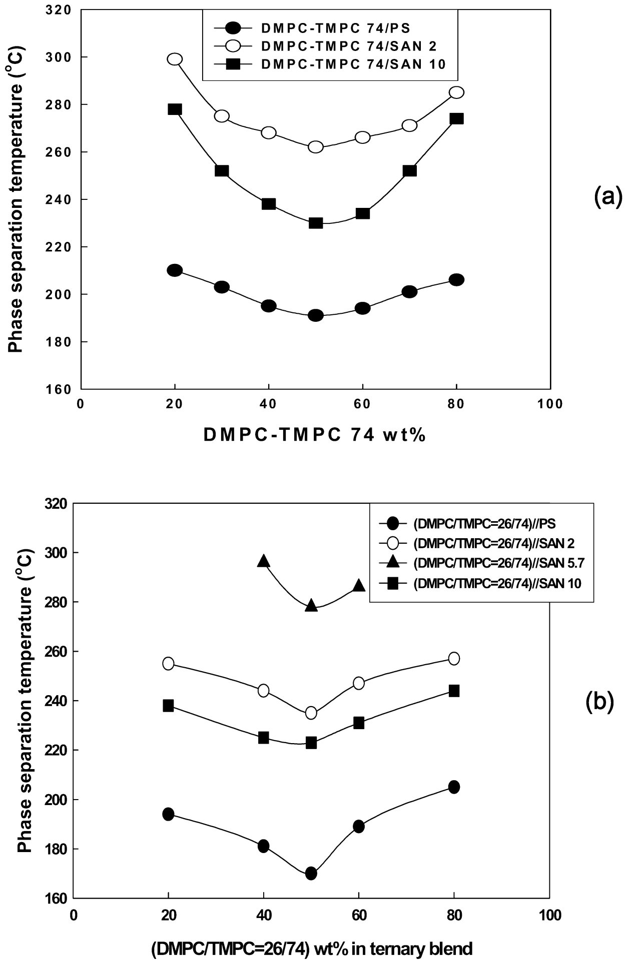

Fig. 5. Observed phase separation temperatures of DMPC-TMPC 74/SAN binary blends and those of the corresponding ternary blends; (a) binary blends; (b) ternary blends.

3.3. Phase stability

According to the volume fluctuation thermodynamics and the lattice fluid theory [15,19,22–26], the stability condition for a compressible binary mixture can be written

$$\delta^2 g = \begin{vmatrix} g_{11} & g_{\tilde{\rho}1} \\ g_{\tilde{\rho}1} & g_{\tilde{\rho}\tilde{\rho}} \end{vmatrix} = g_{11} - \frac{(g_{\tilde{\rho}1})^2}{g_{\tilde{\rho}\tilde{\rho}}} > 0 \tag{1}$$

where g is the free energy change of mixing per unit volume and the subscripts 1 and $\tilde{\rho}$ indicate partial derivatives with respect to ϕ_1 (volume fraction) or $\tilde{\rho}$ (reduced density). In terms of the Sanchez–Lacombe theory [22–26], the indicated derivatives for binary mixture are given by

$$g_{11} = -2\tilde{\rho}\Delta P^*(i,j) + RT\left(\frac{1}{\phi_1 r_1 v_1^*} + \frac{1}{\phi_2 r_2 v_2^*}\right) \tag{2}$$

$$g_{\tilde{\rho}1} = -(p_1^* - p_2^* - (1-2\phi_1)\Delta P^*(i,j)) + \frac{RT}{\tilde{\rho}} \times \left(\frac{1}{r_1 v_1^*} - \frac{1}{r_2 v_2^*}\right) - RT\left(\frac{1}{v_1^*} - \frac{1}{v_2^*}\right) \times \left(\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\right) \tag{3}$$

$$g_{\tilde{\rho}\tilde{\rho}} = \frac{RT}{v^*}\left(\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{1}{\tilde{\rho}^2}\left(1 - \frac{1}{r}\right)\right) \tag{4}$$

According to the binary interaction model [1–3], the interaction energy density between the pair of multicomponent polymers i and j, i.e. $\Delta P^*(i,j)$ can be expressed as

$$\Delta P^*(i,j) = \sum\sum_{k>l} \Delta P_{kl}^*(\phi_{ki} - \phi_{kj})(\phi_{lj} - \phi_{li}) \tag{5}$$

In the above, ΔP_{kl}^* is the binary interaction energy density between units k and l while ϕ_{ki} is the volume fraction of k unit in the polymer i. For a binary blend of copolymer i composed of units 1 (styrene) and 2 (AN) with another copolymer j composed of units 3 (DMPC) and 4 (TMPC), the interaction energy density between polymer i and j is given by

$$\Delta P^*(i,j) = \Delta P_{13}^*\phi_1'\phi_3'' + \Delta P_{14}^*\phi_1'\phi_4'' + \Delta P_{23}^*\phi_2'\phi_3'' + \Delta P_{24}^*\phi_2'\phi_4'' - \Delta P_{12}^*\phi_1'\phi_2' - \Delta P_{34}^*\phi_3''\phi_4'' \tag{6}$$

where ϕ_k' and ϕ_k'' denote volume fraction of unit k in copolymer i and j, respectively. In the previous research [18], the interaction energies of binary pairs involved in the DMPC–TMPC/SAN blends were calculated from the phase boundaries using the lattice-fluid theory combined with binary interaction model [1–3,22–26].

Ternary blend composed of components A (SAN), 3 (DMPC), and 4 (TMPC) is miscible when the following conditions are satisfied

$$\delta^2 g = \begin{vmatrix} g_{AA} & g_{A3} & g_{A\tilde{\rho}} \\ g_{3A} & g_{33} & g_{3\tilde{\rho}} \\ g_{4A} & g_{4\tilde{\rho}} & g_{\tilde{\rho}\tilde{\rho}} \end{vmatrix} > 0 \tag{7}$$

where the subscripts A, 3, 4 and $\tilde{\rho}$ indicate partial derivatives with respect to, ϕ_A, ϕ_3, ϕ_4, or $\tilde{\rho}$. Note that $\phi_A + \phi_3 + \phi_4 = 1$. The indicated derivatives for binary mixture are given by

$$g_{AA} = -2\tilde{\rho}\Delta P^*_{A4} + RT\left(\frac{1}{\phi_A r_A v^*_A} + \frac{1}{\phi_4 r_4 v^*_4}\right) \tag{8}$$

$$g_{A3} = g_{3A} = \tilde{\rho}(\Delta P^*_{A3} - \Delta P^*_{A4} - \Delta P^*_{34}) + RT\left(\frac{1}{\phi_4 r_4 v^*_4}\right) \tag{9}$$

$$g_{33} = -2\tilde{\rho}\Delta P^*_{34} + RT\left(\frac{1}{\phi_3 r_3 v^*_3} + \frac{1}{\phi_4 r_4 v^*_4}\right) \tag{10}$$

$$\begin{aligned} g_{A\tilde{\rho}} = g_{\tilde{\rho}A} &= -(p^*_A - p^*_4) - \phi_2(P^*_{34} - P^*_{A3} - P^*_{A4}) \\ &\quad -(1 - 2\phi_4)\Delta P^*_{A4} + \frac{RT}{\tilde{\rho}}\left(\frac{1}{r_A v^*_A} - \frac{1}{r_4 v^*_4}\right) \\ &\quad -RT\left(\frac{1}{v^*_A} - \frac{1}{v^*_4}\right)\left(\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\right) \end{aligned} \tag{11}$$

$$\begin{aligned} g_{3\tilde{\rho}} = g_{\tilde{\rho}3} &= -(p^*_3 - p^*_4) - \phi_A(P^*_{A4} - P^*_{A3} - P^*_{34}) \\ &\quad -(1 - 2\phi_4)\Delta P^*_{34} + \frac{RT}{\tilde{\rho}}\left(\frac{1}{r_3 v^*_3} - \frac{1}{r_4 v^*_4}\right) \\ &\quad -RT\left(\frac{1}{v^*_3} - \frac{1}{v^*_4}\right)\left(\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\right) \end{aligned} \tag{12}$$

$$g_{\tilde{\rho}\tilde{\rho}} = \frac{RT}{v^*}\left(\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{1}{\tilde{\rho}^2}\left(1 - \frac{1}{r}\right)\right) \tag{13}$$

The term $(\delta^2 g)$ is composed of energetic term, compressibility term, and combinatorial entropy term for binary and ternary mixtures. Among these terms, the term related to the compressibility $(g_{\tilde{\rho}\tilde{\rho}})$ is the same for binary and ternary mixtures. The differences in the binary and ternary mixture exist in the terms related to the combinatorial entropy and energy. The difference in the combinatorial entropy is given by

$$\begin{aligned} &(\Delta s_{\mathrm{m}})_{\mathrm{ternary}} - (\Delta s_{\mathrm{m}})_{\mathrm{binary}} \\ &\quad = -R\left(\frac{\phi_3}{r_3 v^*_3}\ln\frac{\phi_3}{\phi_3 + \phi_4} + \frac{\phi_4}{r_4 v^*_4}\ln\frac{\phi_4}{\phi_3 + \phi_4}\right) > 0 \end{aligned} \tag{14}$$

where Δs_{m} is the combinatorial entropy change of mixing per unit volume. This result indicates that the combinatorial entropy of such a ternary blend is always greater than that of the corresponding binary blend. It means that ternary blend is more favorable for miscibility than the corresponding binary blend in terms of combinatorial entropy. The energetic terms differ approximately as follows

$$\begin{aligned} &(\Delta\varepsilon_{\mathrm{m}})_{\mathrm{ternary}} - (\Delta\varepsilon_{\mathrm{m}})_{\mathrm{binary}} \\ &\quad = \Delta P^*_{34}\phi_3[\phi_4 + \phi''_4(\phi_1 + \phi_2)] \end{aligned} \tag{15}$$

Since the interaction energy for the binary pair 3 and 4 ($\Delta P^*_{34} = \Delta P^*_{\mathrm{DMPC-TMPC}} = -0.09$ cal/cm^3) is negative [18], the energetic term for ternary blend is always smaller than that of binary blend. Although the terms for ternary blend related to the combinatorial entropy and energy are more favorable for the miscibility than those for binary blend, the region where ternary blends are miscible is narrower than that for binary blends and phase separation temperatures of the miscible ternary blends are lower than those of the miscible binary blends. It may be explained with stability conditions for binary blend (Eq. (1)) and ternary blend (Eq. (7)). The solid curves in Fig. 3 are the calculated spinodal curves for binary blends (Fig. 3(a)) and ternary blends (Fig. 3(b)). The spinodal curve satisfies $\delta^2 g = 0$. The miscible region of binary blends that satisfies $\delta^2 g > 0$ in Eq. (1) broader than that of ternary blends that satisfies $\delta^2 g > 0$ in Eq. (7). Binary blend is always miscible when its interaction energy is negative. However, some ternary blends that have negative interaction energy, i.e. the negative value of Gibbs free energy of mixing, are immiscible because these blends do not satisfy stability condition of Eq. (7). As described in the volume fluctuation thermodynamics [15,19], the addition of component, i.e. the additional degree of freedom accompanied by the asymmetry in the binary interactions, for ternary blends results in the destabilization even though entropy and energetic terms for the ternary are more favorable for miscibility than those of binary mixture.

4. Summary

The phase behavior of DMPC/TMPC/SAN ternary blends has been explored theoretically and experimentally and then compared with that of DMPC–TMPC/SAN binary blends having the same chemical compositions and components. The miscible region of ternary blends was much narrower than that of binary blends. In addition, the phase-separation temperatures of miscible ternary blends are always lower than those of the corresponding binary blends. To explain the difference in the phase diagram of binary blends and ternary blends, phase stability conditions based on the volume fluctuation thermodynamics were explored with interaction energies of binary pairs obtained previously. In the blends containing TMPC, DMPC, and SAN, even though the interaction energy and combinatorial entropy of ternary blend are always more favorable for miscibility than that of the corresponding binary blend, the mixture was destabilized by adding the degree of freedom to the system, i.e. increase of the number of component.

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