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Thermodynamics of mixing estimated by equation-of-state parameters in miscible blends of polystyrene and tetramethylbisphenol-A polycarbonate

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Abstract

Mixing thermodynamics in miscible blends of polystyrene (PS) and tetramethylbisphenol-A polycarbonate (TMPC) was investigated using liquid state pressure–specific volume–temperature (P–v–T) properties of both pure components and mixtures. The equation-of-state theories used were (1) the lattice fluid model of Sanchez and Lacombe, (2) the model of Flory, Orwoll, and Vrij, and (3) the modified cell model suggested by Dee and Walsh. The composition dependence of characteristic pressure was first used to extract the interaction parameter (ΔP^*) and Flory interaction parameter expressed in the second derivative of the free energy of mixing (χ_{sc}). It was found that the sign of χ_{sc} was negative and the magnitude of it was always significantly larger than the values obtained by small-angle neutron scattering (Yang H, O'Reilly JM. Mater Res Soc Symp Proc 1987;79:129) and diffusion measurements (Kim E, Kramer EJ, Osby JO, Walsh DJ. J Polym Sci, Part B: Polym Phys 1995;33:467), indicating that the blend P–v–T properties grossly overestimate the attractive interaction. On the other hand, the χ_{sc} predicted from the characteristic temperature was also large but had a positive sign. These results were similar to what had been found in PS/PVME blends by Ougizawa and coworkers (Ougizawa T, Dee GT, Walsh DJ. Macromolecules 1991;24:3834). While the thermal expansion coefficient began to increase as temperature is raised above the lower critical solution temperature (LCST), the volume contraction upon mixing was observed above as well as below the LCST. This observation implies that two dissimilar chains are packed together to form a certain stable stereo structure. We also note that the decreased change in core volume rather than the presence of large ΔP^* causes the volume contraction upon mixing.

Keywords: Polystyrene; Tetramethylbisphenol-A polycarbonate; Blend P–v–T properties

1. Introduction

The equation-of-state (EOS) theories have been widely used to explain the thermodynamics of mixing in polymer blends. Usually in previous studies [1–3], the characteristic parameters have been obtained by fitting the EOS to P–v–T data of the pure components and the characteristic interaction parameter has been computed from the equations for equal chemical potential of the constituent chains (*binodal* condition) or from that for the phase destabilization (*spinodal* condition). Strictly speaking, under such circumstances, the thermodynamic information only along the boundary where phase separation takes place was directly reflected and it was not well verified whether the intermolecular interaction in the single phase region could also be accounted for properly. We studied how P–v–T properties of pure components and binary blends of polystyrene (PS) and tetramethylbisphenol-A polycarbonate (TMPC) predict the intermolecular interaction by applying EOS theories. The theories tested were the lattice fluid theory of Sanchez and Lacombe [4,5] (SL), Flory, Orwoll, Vrij model [6,7] (FOV), and the modified cell model [6,8] (MCM). Corresponding characteristic parameters, P^*, v^*, and T^*, were extracted and the excess property ΔP^* could be calculated from the composition dependence of the P^* and T^* by applying a conventional molecularly motivated combining rule. From these, Flory interaction parameter χ_{sc} ('sc' stands for 'scattering', i.e. the χ obtained from the second derivative of the free energy of mixing [9]) were estimated. The specific volume as functions of temperature and composition was also analyzed. From these results together with the ones previously obtained by small-angle neutron scattering (SANS) [10] and diffusion measurements [11], the nature of miscibility and its relation to P–v–T were investigated.

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Kim and Paul [2] showed from the atomic charge calculations that PS/TMPC polymer pair has a relatively weak interaction, and they evaluated the interaction parameters by fitting pure components' P–v–T behavior and LCST type phase boundary to SL. It was claimed that Flory interaction parameter was expected to have nearly no composition dependence and relatively small temperature dependence, while the values obtained at 30°C was roughly in accordance with the SANS results. On the other hand, Kim et al. [11] claimed that the significant specific interaction is needed to explain the temperature dependence of χ_{sc} for the same polymer blends from the analysis utilizing the generalized lattice–fluid model suggested by Sanchez and Balazs [1].

The main points necessary for obtaining the resulting equations used in the current analysis are briefly summarized. From the partition function and the Gibbs free energy expressions, the equations-of-state were derived as follows: For SL [4,5],

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \tag{1}$$

For FOV [7],

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}} \tag{2}$$

For MCM [8],

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - q\cdot\gamma} - \frac{2}{\tilde{T}}\left(\frac{A}{\tilde{v}^2} - \frac{B}{\tilde{v}^4}\right) \tag{3}$$

where $\tilde{\rho}$, $\tilde{v}$, $\tilde{P}$, $\tilde{T}$ are the reduced density, volume, pressure, and temperature ($\tilde{\rho} = \rho/\rho^* = v^*/v = 1/\tilde{v}$, $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$), respectively, r corresponds to the degree of polymerization, $A = 1.2045$, $B = 1.011$, $\gamma = (1/2)^{1/6}$ which were determined assuming that the cell lattice has a hexagonal close packed geometry, and the empirical q value used was 1.07 [8]. The EOS for mixtures are formally identical with them for pure polymers.

It has been assumed that hard-core *mer* volumes are equal for all compositions and the conventional combining rules [12,13] were used to establish the partition functions of polymer mixtures relevant to each model. For the calculation of the change in free energy upon mixing and χ_{sc}, the hard-core pressure of the mixture was approximated to be summed in such a way [3,6,13,14],

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1\theta_2\Delta P^* \tag{4}$$

where ϕ_i and θ_i are the hard-core volume fraction and the site fraction of component i respectively. θ_i was approximated to be ϕ_i. In the scattering or diffusion experiments the second concentration derivative of the free energy of mixing [9] is directly probed, which is equivalent to the inverse of the equilibrium structure factor where the wave vector approaches zero. The interaction parameter χ_{sc} can be then obtained from the following relation:

$$\frac{\chi_{\mathrm{sc}}}{V_{\mathrm{ref}}} = \frac{1}{2\mathrm{R}T}\left\{\frac{\mathrm{R}T}{V_{\mathrm{ref}}}\left(\frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2}\right) - \frac{\mathrm{d}^2\Delta G_{\mathrm{M}}}{\mathrm{d}\phi_1^2}\right\} \tag{5}$$

where ΔG_{M} is the Gibbs free energy of mixing per molar *mer* volume, r_i is the degree of polymerization of component i, and V_{ref} is the reference volume for which χ_{sc} is defined. Eq. (5) basically includes all the terms in the second concentration derivative of ΔG_{M} except for the combinatorial entropy term.

On the other hand, the second derivative of the Gibbs free energy with respect to composition can be written as

$$\frac{\mathrm{d}^2\Delta G_{\mathrm{M}}}{\mathrm{d}\phi_1^2} = \Delta G_{\mathrm{M}\phi\phi} - \frac{(\Delta G_{\mathrm{M}\tilde{\rho}\phi})^2}{\Delta G_{\mathrm{M}\tilde{\rho}\tilde{\rho}}} \tag{6}$$

where subscripts ϕ and $\tilde{\rho}$ indicate the partial derivatives with respect to ϕ_1 and $\tilde{\rho}$, respectively. As a result the expressions for χ_{sc} in SL, FOV and MCM were obtained [14], which are summarized for each theory in the following form:

$$\frac{\chi_{\mathrm{sc}}}{V_{\mathrm{ref}}} = \frac{1}{2\mathrm{R}T}\left\{a + \frac{(bT + c)^2}{d}\right\} \tag{7}$$

For SL,

$$a = 2\tilde{\rho}\Delta P^* \tag{8a}$$

$$b = \mathrm{R}\left\{\frac{1}{\tilde{\rho}}\left(\frac{1}{r_1 V_1^*} - \frac{1}{r_2 V_2^*}\right) - \left[\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\right] \times \left[\frac{1}{V_1^*} - \frac{1}{V_2^*}\right]\right\} \tag{8b}$$

$$c = P_2^* - P_1^* + (\phi_2 - \phi_1)\Delta P^* \tag{8c}$$

$$d = \frac{\mathrm{R}}{v^*}\left[\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{\left(1 - \frac{1}{r}\right)}{\tilde{\rho}^2}\right] \tag{8d}$$

For FOV,

$$a = \frac{2\frac{s_1}{s_2}\tilde{\rho}\Delta P^*}{\left(1 + \left(\frac{s_1}{s_2} - 1\right)\phi_1\right)^3} \tag{9a}$$

$$b = \left(\frac{P_1^*}{T_1^*} - \frac{P_2^*}{T_2^*}\right)\left(\frac{\tilde{\rho}^{-4/3}}{\tilde{\rho}^{-1/3} - 1}\right) \tag{9b}$$

$$c = -P_1^* + P_2^* + \left(\frac{1 - 2\phi_1 - \left(\frac{s_1}{s_2} - 1\right)\phi_1^2}{\left(1 + \left(\frac{s_1}{s_2} - 1\right)\phi_1\right)^2}\right)\Delta P^* \tag{9c}$$

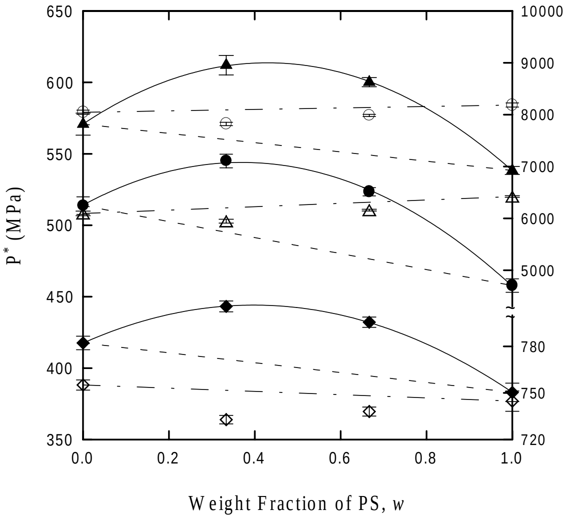

Fig. 1. Characteristic pressure and temperature, P^* and T^*, as a function of PS weight fraction, w. The symbols (◆, ●, ▲) correspond to P^* obtained from SL, FOV, and MCM, respectively, and (◇, ○, △] correspond to T^* obtained from SL, FOV, and MCM, respectively. The solid lines are fit of P^* to the data using Eq. (4) and the dotted and broken lines represent the additive values obtained using P^* and T^* of pure components, respectively. Error bars represent the standard errors evaluated assuming that the error occurs only in the fitting procedure [14].

$$d = \left(\frac{\phi_1 P_1^*}{T_1^*} + \frac{\phi_2 P_2^*}{T_2^*}\right)\left(\frac{-\tilde{\rho}^{-2/3} + \frac{4\tilde{\rho}^{-1/3}}{3}}{(\tilde{\rho}^{2/3} - \tilde{\rho})^2}\right) \tag{9d}$$

For MCM,

$$a = \frac{2\frac{s_1}{s_2}\left(A\tilde{\rho}^2 - \frac{B}{2}\tilde{\rho}^4\right)\Delta P^*}{\left(1 + \left(\frac{s_1}{s_2} - 1\right)\phi_1\right)^3} \tag{10a}$$

$$b = \left(\frac{P_1^*}{T_1^*} - \frac{P_2^*}{T_2^*}\right)\left(\frac{\tilde{\rho}^{-4/3}}{\tilde{\rho}^{-1/3} - q\gamma}\right) \tag{10b}$$

$$c = (P_2^* - P_1^*)(2A\tilde{\rho} - 2B\tilde{\rho}^3) + \left(\frac{1 - 2\phi_1 - \left(\frac{s_1}{s_2} - 1\right)\phi_1^2}{\left(1 + \left(\frac{s_1}{s_2} - 1\right)\phi_1\right)^2}\right)\Delta P^* \tag{10c}$$

$$d = \left(\frac{\phi_1 P_1^*}{T_1^*} + \frac{\phi_2 P_2^*}{T_2^*}\right)\left(\frac{-\tilde{\rho}^{-2/3} + q\gamma\frac{4\tilde{\rho}^{-1/3}}{3}}{(\tilde{\rho}^{2/3} - q\gamma\tilde{\rho})^2}\right) \tag{10d}$$

where s_i is the number of contact sites per unit core volume of species i and s_{PS}/s_{TMPC} was approximated as the ratio of surface areas of PS and TMPC per core volume using Bondi's method [15], which was 0.857 for MCM and 0.876 for FOV. In the above derivations V_{ref} in Eq. (5) was taken as V^* representing the molar hard-core *mer* volume. In FOV and MCM, χ_{sc}/V_{ref} could be directly calculated without requiring the value of V^*. In SL the molecular weight of the *mer* could be calculated from $kT^*\rho^*/P^*$, and V^* was obtained by dividing it by the density. In this case, the value of V^* ranged from 13 to 16 cm^3/mol. The hypothetical common monomer volume in SANS or diffusion experiment had been taken as a geometric mean of the volumes of structural repeating units of PS and TMPC (175 cm^3/mol) [10,11].

2. Experimental

The weight-average molecular weights and polydispersity indices of PS were 253 000 and 2.0, and those of TMPC were 42 000 and 2.9, respectively. The P–v–T relation was measured for binary mixtures with PS weight fractions $w = 0, 1/3, 2/3$, and 1 as follows. First, densities were measured at 25°C at atmospheric pressure using an autopycrometer (Micrometritics). The changes in density as a function of temperature (up to ca. 280°C with 8–10°C increment) and pressure (up to 200 MPa with 10 MPa increment) were measured using a P–v–T apparatus. The absolute accuracy of the device is 10^{-3}–2×10^{-3} cm^3/g, however, volume changes as small as 10^{-4}–2×10^{-4} cm^3/g could be resolved. The details of the procedure have been fully described elsewhere [16]. Glass transition temperature (T_g) could be determined from the inflection point in the V–T

Table 1
Interaction parameters ΔP^* (MPa) obtained from blend P^* values and from the cloud point measurements. The numbers in parentheses are those obtained from blend T^* values

	Blends PVT			Cloud point measurements		
	SL	FOV	MCM	SL	FOV	CM[a]
PS/TMPC	−171 (+36)	−223 (+58)	−235 (+84)	−0.175 [2]	–	–
PS/PVME	–	−150 [6] (+100)	−300 [6] (+200)	–	−1.78 [3]	−1.76 [3]

[a] Cell model.

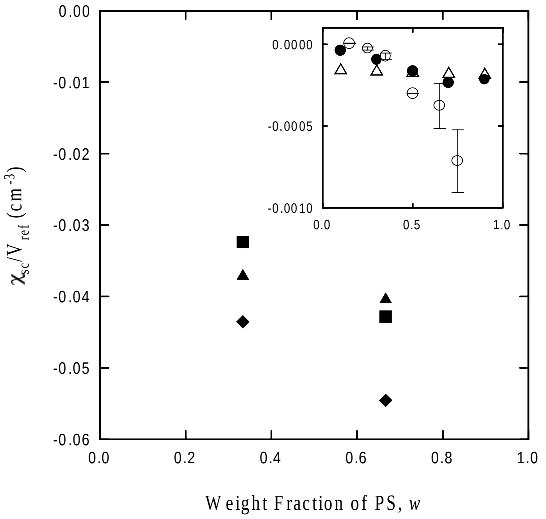

Fig. 2. The χ_{sc}/V^* values calculated as a function of PS weight fraction, w, from three EOS theories at $T_g + 45$°C. The symbols (■, ▲, ◆] correspond to the values obtained from MCM, SL, and FOV, respectively. In the inset, the values obtained from the diffusion experiment at $T_g + 45$°C [11] (○) and from the SANS [10] (●) are also represented as a function of w. Symbol △ in the inset represents the χ_{sc}/V_{ref} values at 30°C obtained by SL theory using the phase boundary condition [2]. The temperature at which SANS data were obtained was not specified [10].

curve. All the polymer mixtures as well as homopolymers had single T_gs at all pressures and the PS/TMPC blends prepared could thus be judged to be miscible. The values of T_g were, on an average, 7.7°C below the ones obtained by DSC [17]. The temperature range for fitting was from T_g to 260°C above which phase separation took place [11] at $w = 1/3$ and 2/3. The pressure range became 0–100 MPa except for pure TMPC for which all the data above 70 MPa fell into the glassy region. To obtain the characteristic parameters for each EOS, we carried out a nonlinear least-squares fit of each EOS by minimizing the following quantity:

$$S^2 = \frac{\sum_i (P_{i,\mathrm{data}} - P_{i,\mathrm{fit}})^2}{N - 3} \tag{11}$$

where $P_{i,\mathrm{data}}$ and $P_{i,\mathrm{fit}}$ are the pressure measured and predicted by the relevant EOS at a given $i(V, T)$ for the system, respectively. The corresponding characteristic parameters (P^*, ρ^*, T^*) for each EOS, S^2, and the standard errors (the size of error bar in Fig. 1) could be evaluated assuming that the error occurs only in the fitting procedure [14]. There was no apparent difference in goodness of fitting among three EOS tested in this study.

3. Results and discussion

Fig. 1 shows that P^* values at four compositions obtained from SL, FOV and MCM, which manifest the positive deviation from the linear lines. The values of ΔP^* computed according to Eq. (4) are given in Table 1. Ougizawa and coworkers [6] have also studied the *P–v–T* properties of pure components and binary mixtures of PS and PVME by applying FOV and MCM, and their ΔP^* values are also shown together for comparison. The cloud points and pure components' *P–v–T* measurements were made for PS/TMPC system by Kim and Paul [2] and for PS/PVME system by Walsh et al. [3] Kim and Paul applied SL and Walsh et al. applied FOV and cell model. The corresponding values of ΔP^* are also listed in Table 1 for comparison. It is noted that the values obtained from the mixture *P–v–T* data are always much larger than the values obtained from the cloud point measurement by more than two orders of magnitude. The χ_{sc}/V_{ref} values at temperatures 45°C above T_gs of the mixtures were computed at each composition using Eqs. (7)–(10), which are shown in Fig. 2. The results obtained from SANS [10] (temperature not specified), diffusion experiments [11] (at temperatures 45°C above T_gs), and the cloud point measurements [2] (at 30°C) are also shown together in the inset of Fig. 2. The first thing to note is that the absolute magnitude of χ_{sc}s obtained from the characteristic pressure P^* of both pure components and binary mixtures are again much larger than the values obtained with other methods.

In the current definition of constant ΔP^*, it is assumed that there was no specific interaction and that monomers in closed-packed lattice sites are interacting randomly. The validity of this definition could be tested by analyzing T^* values of the blends [6]. Assuming the linear additivity of the extra degree of freedom,

$$T^* = \frac{\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 \Delta P^*}{(\phi_1 P_1^*/T_1^*) + (\phi_2 P_2^*/T_2^*)} \tag{12}$$

As shown in Fig. 1, T^* of the blend mixtures was lower than the linear additive line and ΔP^*s could also be estimated from T^* using Eq. (12). If the above assumption is right, T^* of the blend mixtures is expected to follow the trend manifested by P^*. The values of ΔP^* are given in parentheses in Table 1, which are approximately in the same order of magnitude as the values obtained using P^* of the mixtures, but with a *positive* sign. The external degrees of freedom per *mer* (c) is proportional to P^* and is inversely proportional to T^*, and therefore these results leads to the fact that c in the blend mixture is expected to be higher than the linear additive. However it is quite unusual that the external degrees of freedom are increased rather than restricted in the blends where the mixing process is exothermic and the volume is contracted (see discussion below). Similar incomprehensive result was also observed by Ougizawa et al. in PS/PVME blends [6].

The analysis based on the temperature dependence of χ_{sc} also predicts that the phase separation [11] cannot occur before the liquid–gas transition temperature [14]. Ougizawa et al. pointed out that the discrepancy in phase separation behavior may be partly rationalized by allowing ΔP^* to have temperature dependence [6] (ΔP^* has to become smaller as

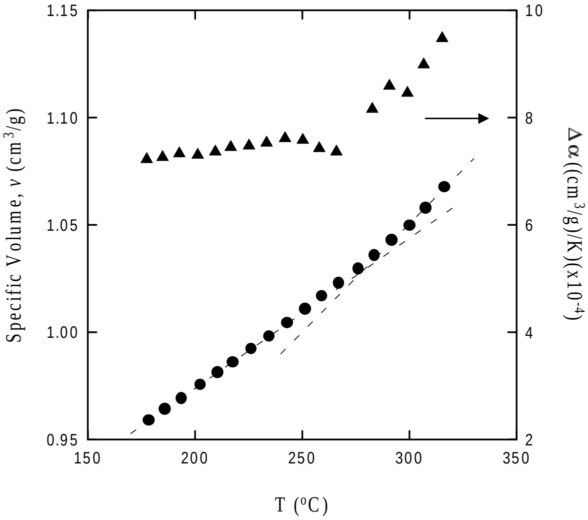

Fig. 3. Thermal expansion coefficient, $\Delta\alpha$ (▲) obtained by Eq. (13), and specific volume, v (●), as a function of temperature when $w = 1/3$. The dotted lines are the linear fits of v above and below T_{inf}.

temperature is raised). This can be due to the extra entropic effect such as specific interaction, which is caused by the spatial rearrangement of unlike chains. This type of interaction would decrease at higher temperature due to thermal agitation. However the present study shows that the magnitude of χ_{sc} predicted from the *P–v–T* data is too large at any temperature to be simply modified by introducing the temperature dependence to ΔP^*.

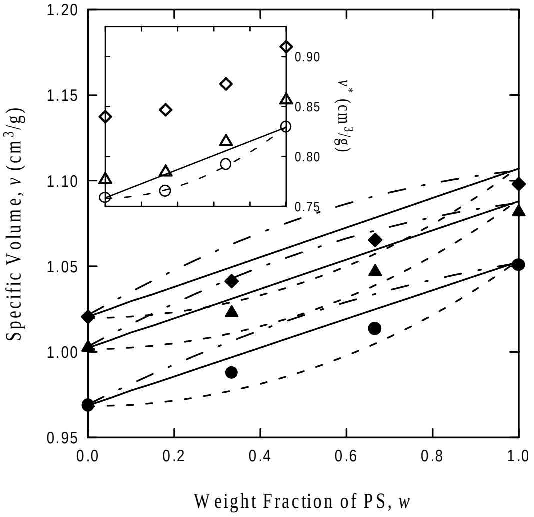

Fig. 4. Specific volume, v, at $P = 0$ MPa as a function of PS weight fraction, w, at 220°C (●), 267°C (▲) and 290°C (◆). In the inset, symbols (○, △, ◇) correspond to the characteristic specific volume, v^*, obtained using FOV, MCM and SL, respectively. The solid lines in the main figure at the corresponding temperatures represent the specific volume calculated from FOV using the additive v^* values (also solid line in the inset) when $\Delta P^* = 0$ MPa. The dotted lines in the main figure represent the ones calculated in the same way, but using the second order fit of the experimentally obtained v^* values (also dotted line in the inset) instead of the additive values. The broken-dotted lines in the main figure represent the ones calculated using the additive v^* values and the T^* values which were obtained experimentally.

It was basically assumed in the current EOS formalism that the cohesive energy density is equal to the internal pressure. It is worth pointing out that this assumption could have influenced the determination of the interaction parameter and of its temperature dependence. Cohesive energy density which is defined as the change in internal energy per unit volume of liquid associated with the vaporization process at zero pressure is a direct measure of total molecular interaction. Internal pressure ($T(\partial P/\partial T)_v - P \approx T\alpha(T)/\beta(T)$), where α is the thermal expansion coefficient and β is the isothermal compressibility), on the other hand, is a measure of the instantaneous volume derivative of cohesive energy attending an isothermal expansion, which could be evaluated from the *P–v–T* properties. A close correspondence between these two properties has been observed for various liquids with low polarity, however it was not shown to be necessarily true for liquids with polar groups [18]. Surface tension data for oligomers could be used to quantify the corrections to this assumption [19]. The study on these corrections for considering the internal pressure obtainable in *P–v–T* properties as the cohesive energy density for different polymers is in progress [19]. In addition, EOS contribution on a certain class of polyolefin blends which have no polar interaction, were shown to be insufficient to generalize the miscibility [20]. Strikingly some of them were found to have even net attraction between the components [21,22]. Packing or association of the chains would be affected by factors such as conformational entropy of the constituent chains [23] and location/size/tacticity of the side groups. It was also demonstrated by Flory [24] using his own equation-of-state theory that the phase behavior of athermal mixtures of rigid rods and random coils could be governed by entropy rather than by energetic factor. Elucidating these extra entropic contributions to miscibility is one of the focuses of future work, which may be accomplished through the use of detailed molecular modeling technique.

While the characteristic parameters are described by functions of the first derivatives of the *P–v–T* properties, it is also interesting to note how the specific volume itself change with composition. In Fig. 3, the specific volume, v, and the corresponding thermal expansion coefficient, $\Delta\alpha$, are shown as a function of temperature for $w = 1/3$ at an atmospheric pressure.

$$\Delta\alpha = \frac{v - v_{\mathrm{inf}}}{T - T_{\mathrm{inf}}} \tag{13}$$

where T_{inf} and v_{inf} are the temperature and the volume, respectively, above which $\Delta\alpha$ began to increase. Two dotted linear lines in Fig. 3 clearly reveal the point of inflection as the temperature is raised above T_{inf}. This temperature was determined to be 267°C which is close to the temperature where phase separation took place [11]. Similar observation was also obtained for $w = 2/3$. The fact that volume of the mixture expands more rapidly above T_{inf} is also plausible because two phase-separated phases rapidly becomes rich in one of the components [11] and the intermolecular interaction inside the two coexisting phases should be fairly small. Moreover the appearance of interfaces with increasing heterogeneity may cause volume expansion. Seemingly gradual increase in $\Delta\alpha$ rather than discontinuity around the phase separation temperature may be due to the insufficient equilibration time of the phase separation during the measurements. On the other hand, the composition dependence of v is shown in Fig. 4 at various temperatures: well below, near, and well above LCST (220, 267, and 290°C, respectively). It is expected that the volume contraction caused by mixing would be reduced after the temperature is increased after T_{inf}. After the phase separation, the negative excess volume of mixing is still observed. This observation could also be a reflection of the local packing effect between the dissimilar molecules in each phase-separated phase or at the interfaces.

Compressibility effect, in principle, arises from the difference in compressibility of the two pure components—the phase is more destabilized as the mixture becomes more compressible, and the net volume contraction is not directly related to the compressibility. The presence of the extra entropic contribution associated with the volume contraction, aside from the existence of the enthalpic attraction, may be evidenced by the following consideration.

We attempted to estimate v of the mixtures using FOV at the atmospheric pressure as follows, and compared the results with the experimental data in order to see whether it may reconcile with the presence of large value of ΔP^*. P^* and T^* are functions of the thermal expansion coefficient and the thermal pressure coefficient [6,12], which can be allowed to be affected by ΔP^* via Eqs. (4) and (12), respectively. As a matter of fact the left side of Eq. (2) vanishes at zero pressure leaving no term associated with P^*, which combines with Eq. (12) to give

$$\frac{\tilde{v}^{1/3}-1}{\tilde{v}^{4/3}} = T\frac{(\phi_1 P_1^*/T_1^*) + (\phi_2 P_2^*/T_2^*)}{\phi_1 P_1^* + \phi_2 P_2^* - \phi_1\phi_2\Delta P^*} \tag{14}$$

The reduced volume $\tilde{v}$, and thus v, for blends can be evaluated using P^* and T^* of pure components, v^*, and ΔP^* as a function of composition at the above three temperatures. The v^* values as a function of composition for three models are also shown in the inset of Fig. 4, where the lowest data are those obtained from FOV. It is noted that the decrease in v^* in the intermediate compositions is not directly originated from the internal pressure[1]. First, we assumed that v^* values were additive (the solid line in inset) and that ΔP^* were 0. As expected, almost linearly additive values of v are shown (the solid line in Fig. 4). If the experimentally determined T^* values as shown in Fig. 1 (i.e. the values obtained from Eq. (12) using $\Delta P^* = +58$ MPa) were used instead, the volume expansion is seen (the broken-dotted line), which is due to the repulsive interaction. Next, we used the experimentally determined v^* values (the dotted line in inset) and assumed that ΔP^* were 0. The dotted line in Fig. 4 is the result of this calculation, showing that the theory predicts even more excess volume contraction on mixing than the experimental observations. The above considerations demonstrate that it is the composition dependence of v^* rather than the presence of ΔP^* reflected in the composition dependence of T^* that derives the volume contraction in the present EOS formalism.

4. Conclusions

P–v–T properties of pure components and binary mixtures of PS and TMPC were measured and various EOS theories (SL, FOV, and MCM) were applied to extract the characteristic parameters, P^*, T^*, and ρ^* (or v^*). ΔP^* was estimated from the composition dependence of P^* or T^*, from which the scattering Flory interaction parameter χ_{sc} could be calculated. The sign of χ_{sc} obtained from P^* and T^* were negative and positive, respectively, and the magnitudes of these were significantly larger than those independently measured by other techniques, as similar results have also been previously reported for PS/PVME blends. Consequently, the blend P–v–T data considering only random-mixing-based compressibility effect could not predict the measured thermodynamic state of mixing properly. Significant volume contraction upon mixing was also observed before and even after the phase separation, which manifests that two dissimilar chains are packed in a certain way.

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