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Pressure–Volume–Temperature Properties and Equations of State in Polymer Blends: Characteristic Parameters in Polystyrene/Poly(vinyl methyl ether) Mixtures

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ABSTRACT: The pressure–volume–temperature (P–V–T) properties of miscible polymer blends of polystyrene (PS)/poly(vinyl methyl ether) (PVME) have been studied experimentally in the liquid state. The data for the liquid state in the one-phase region were fitted to the equations of state of Flory, Orwoll, and Vrij and to the cell model. The characteristic parameters in these equations of state at various compositions were obtained from the fitting procedure. From the composition dependence of the characteristic parameters, the interaction parameter X_{12} was obtained. In the PS/PVME blend, it was found that the value of X_{12} obtained from the characteristic pressure P^* is large and negative, but that obtained from the characteristic temperature T^* is large and positive. This discrepancy could be explained if the assumption of additive external degrees of freedom on mixing is incorrect. However, in spite of the negative X_{12}, the external degrees of freedom appear to be larger in the blends. Since this is not consistent with the observed limits of miscibility, one must look for other explanations. It was found that a moderately large temperature-dependent interaction can produce the sort of behavior observed in the P–V–T properties of the mixtures.

Introduction

Simple lattice theories do not give an adequate description of the behavior of polymers, polymer solutions, and polymer blends. Various theories have been developed, which allow for the possibility of volume changes. Well-known theories are those attributed to Simha and Somcynsky,[1] Sanchez and Lacombe,[2,3] and Flory, Orwoll, and Vrij (FOV),[4,5] and of these the last has been most extensively applied. In a recent publication we showed that a simple cell model (CM) provided a tractable and analytically simple equation of state, which described the P–V–T properties of polymer melts more accurately than the theory of Flory and co-workers.[6] We also have shown that a semiempirical modification of this equation produced a modified cell model, which described the data even better, approaching the accuracy of the data.[7]

The reduction parameters were obtained by fitting the equations of state to P–V–T data for polymer liquids. These parameters give thermodynamic information about the polymers. The characteristic parameters of the polymers are also used for the calculation of the phase diagrams of polymer blends and polymer solutions. In most cases, the characteristic parameters have been obtained for the pure components but not for the blends. According to the theory of Flory and co-workers,[5,8,9] the interaction parameter X_{12} can be obtained from the characteristic pressure P^* of both the pure components and the blends. In this paper, we describe calculations of the characteristic parameters by fitting the equations of state to P–V–T measurements of the blends. We explain the results in terms of the X_{12} value of the mixture and its temperature dependence.

Theory

There are numerous equations of state in the literature that have been proposed to describe polymer liquids. Using them, the expression for the chemical potential of mixing can be obtained and the phase diagram for mixtures can be calculated. In our previous papers[6,7] we described the basic formalism of some of the more frequently used equations of state. Here we consider only the FOV model and cell model (CM).

The equations of state are given by

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/(\tilde{T}\tilde{v}) \text{ (FOV)} \tag{1}$$

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - \gamma^{1/3}) - 2(A/\tilde{v}^2 - B/\tilde{v}^4)/\tilde{T} \text{ (CM)} \tag{2}$$

where $\tilde{P} = P/P^*$, $\tilde{v} = v/v^*$, and $\tilde{T} = T/T^*$ are the reduced pressure, volume, and temperature, P, v, and T are the actual values, and P^*, v^*, and T^* are the hard-core values (characteristic parameters). For a hexagonal close-packed geometry, $\gamma = 2^{-1/2}$, $A = 1.2045$, and $B = 1.011$ in eq 2. When calculating the free energy change on mixing of two substances to produce a homogeneous blend, one assumes that the mixture obeys the same equation of state as the pure components, that the hard-core volumes are additive, and that the interatomic interactions can be summed in such a way that the hard-core pressure of the mixture is given by

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1\theta_2 X_{12} \tag{3}$$

where ϕ_1 is a hard-core volume fraction and θ_i is a site fraction of component i, which can be approximated by a hard-core volume fraction, and X_{12} is an interaction parameter. This is a common equation to both models. Since P^* depends on the compressibility, a calculated value depends on a derivative of the P–V–T data averaged over the block of data chosen.

Since the details of the formulas were described in a previous paper,[10] we indicate only the main equations. The resulting expressions for the chemical potential of the mixture are

$$\begin{aligned}\Delta\mu_1/RT = {} & \ln\phi_1 + (1 - r_1/r_2)\phi_2 + \\ & P_1^*V_1^*/RT\{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + \\ & 1/\tilde{v}_1 - 1/\tilde{v} + \tilde{P}_1(\tilde{v} - \tilde{v}_1) + \phi_2\theta_2 X_{12}/(P_1^*\tilde{v})\} \text{ (FOV)}\end{aligned} \tag{4}$$

$$\begin{aligned}\Delta\mu_1/RT = {} & \ln\phi_1 + (1 - r_1/r_2)\phi_2 + \\ & P_1^*V_1^*/RT\{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - \gamma^{1/3})/(\tilde{v}^{1/3} - \gamma^{1/3}) + \\ & \tilde{P}_1(\tilde{v}_1 - \tilde{v}) + (A/\tilde{v}_1^2 - B/\tilde{v}_1^4) - \\ & (A/\tilde{v}^2 - B/\tilde{v}^4) + \phi_2\theta_2 X_{12}/P_1^*(A/\tilde{v}^2 - B/\tilde{v}^4)\} \text{ (CM)}\end{aligned} \tag{5}$$

where r_i is the number of segments per molecule of component i. The first two terms in these equations represent the contribution of the combinatorial entropy,

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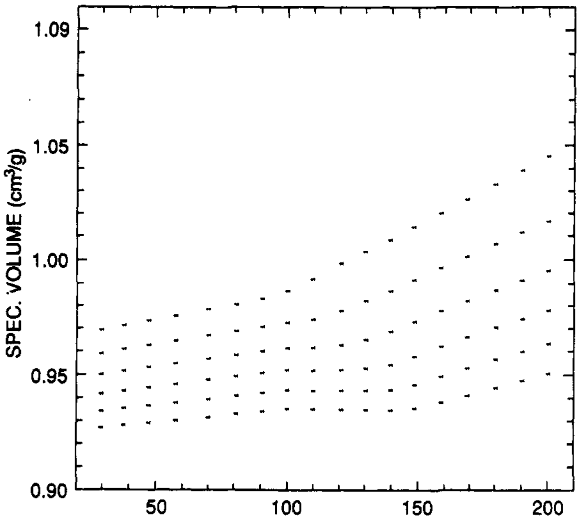

Figure 1. P–V–T data for polystyrene showing the pressure-dependent glass transition. The actual data are from 10–200 by 10 MPa, but only 0–200 by 40 MPa are shown for clarity. The 0 MPa data are an extrapolation using the Tate equation.

the last term containing X_{12} represents the contribution of the interactions to the chemical potential change, and the other terms represent the contribution of the equation of state or volume dependence.

From eqs 4 or 5 one can calculate the phase diagram for binary systems. To do this, the characteristic parameters of the pure components and X_{12} are necessary. X_{12} can, in principle, be obtained from the characteristic pressure of both pure components and blends from eq 3.

Experimental Section

Materials. The polymers used in this work were polystyrene (PS) (M_w = 114 200, M_w/M_n = 1.04) and poly(vinyl methyl ether) (PVME) (M_w = 99 000, M_w/M_n = 2.13) (Scientific Polymer Products).

Sample Preparation. The two polymers were dissolved in toluene, mixed, and then cast into films. These were then dried under vacuum at 100 °C for 2 weeks in order to remove solvent completely. The blend samples were kept in a vacuum oven before use to avoid moisture uptake. We also followed the same procedure with the pure polymers in order to ensure that sample preparation did not effect the results. The results in this case were identical with the as-received polymers.

***P*–*V*–*T* Measurement.** The densities of the polymers were measured at 25 °C and atmospheric pressure by using an autopycnometer (Micromeritics). The changes in density as a function of temperature and pressure were measured by using a P–V–T apparatus, which has been fully described elsewhere.[11] It consists of a sample cell containing about 1–1.5 g of sample and mercury as a confining fluid. A flexible bellows closes off one end of the cell. The movement of the bellows on changing temperature or pressure is used to calculate the volume change of the sample cell. In the isothermal mode, volume readings are obtained at fixed-pressure intervals (usually 10 MPa increases) at a constant temperature. Following measurements along an isotherm, the temperature is changed by 8–10 °C, and the process is repeated. The absolute accuracy of the device is $(1-2) \times 10^{-3}$ cm^3/g; however, volume changes as small as $(1-2) \times 10^{-4}$ cm^3/g can be resolved. A version of this P–V–T apparatus is available as a complete instrument from Gnomix Research, Boulder, CO. Plots of the P–V–T data for Polystyrene, PVME, and one example blend are shown in Figures 1–3.

Results and Discussion

Characteristic Parameters from *P*–*V*–*T* Data. Figure 4 shows the cloud-point diagram of the PS/PVME system used in this work. The P–V–T properties of the mixture were taken in the one-phase region above the glass transition temperature (and only above 30 °C) and below the cloud point for the lower critical solution temperature phase diagram. The values of the reduction parameters were obtained by fitting the equation of state to the P–V–T data of the components and blends. The goodness of fit,

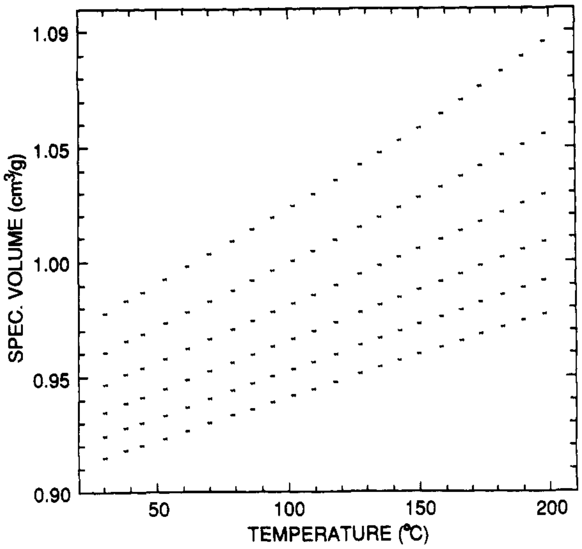

Figure 2. P–V–T data for PVME showing the volume monotonically increasing with T and decreasing with P.

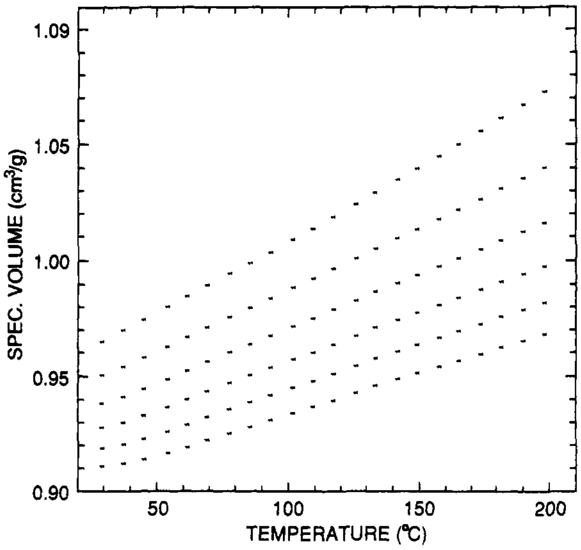

Figure 3. P–V–T data for a 50/50 polystyrene/PVME blend. The data are similar to those of pure PVME, but the effect of the pressure-dependent glass transition is apparent at low T and high P.

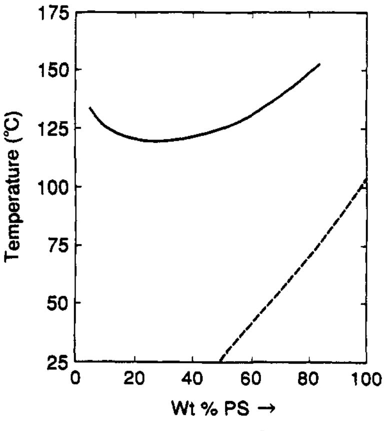

Figure 4. Approximate cloud-point diagram for polystyrene/PVME mixtures (solid line). Also shown is the glass transition temperature (dotted line).

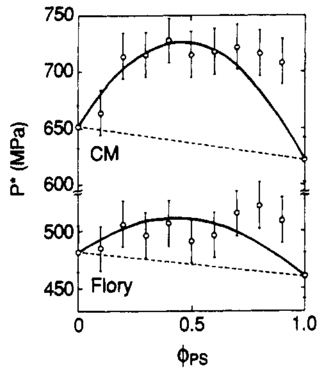

Figure 5. Characteristic pressure, P^*, of PS/PVME blends plotted against the hard-core volume fraction of PS from the two equations of state. The solid lines are the expected values for X_{12} = −150 J/cm^3 (FOV) and −300 J/cm^3 (CM).

S^2, is defined as

$$S^2 \equiv \sum_i (P_{i,\text{data}} - P_{i,\text{fit}})^2/(N-3) \qquad (6)$$

where $P_{i,\text{data}}$ is the measured pressure and $P_{i,\text{fit}}$ is the value predicted by the equation of state, and N is the number of data points. Values of S^2 in the range 0.1–0.2 correspond to errors that are the limit of experimental accuracy of the present experimental apparatus. In each case the largest temperature and pressure range was chosen for the P–V–T data; i.e., temperatures ranged from T_g + 30 °C to the phase-separation temperature of Figure 4, and pressures ranged from 10 to 200 MPa. The value of S^2 decreases if smaller blocks of data are used, and one sees changes in the values of the reduction parameters obtained. The changes are largest for those equations that do not provide a good global description of the P–V–T data, i.e., the FOV model. No qualitative differences in our results are obtained if one uses smaller subsets of the P–V–T data.

We feel that this procedure provides a fair criterion for comparing the goodness of fit of various equations of state.

Figure 5 shows the characteristic pressure, P^*, plotted against the hard-core specific volume fraction of polystyrene

$$\phi_2 = m_2 V^*_{\text{sp},2}/(m_1 V^*_{\text{sp},1} + m_2 V^*_{\text{sp},2}) \qquad (7)$$

where m_i is the mass and $V^*_{\text{sp},i}$ is the hard-core specific volume of component i. The fit of the equation to the data is least sensitive to P^* of the parameters, and this is evidenced by the scatter in this quantity. However, the composition dependence of P^* is not additive, and P^* is obviously larger in the blends, indicating that X_{12} is negative. The solid curve in Figure 5 represents the value of X_{12} = −150 J/cm^3 for the Flory model (CM; −300 J/cm^3) calculated from eq 3. The error in X_{12} would appear to be about ±50 J/cm^3 although there is also an indication that the functional form may be incorrect.

The hard-core specific volumes, V^*_{sp}, of the two polymers are nearly identical, and there is very little variation with composition. All compositions fall within 0.817 ± 0.007 cm^3 (FOV) and 0.908 ± 0.007 cm^3 (CM), which is close to experimental uncertainty. The values for the blends should be additive in weight fraction independent of the interaction. They are, however, found to be approximately 0.01 cm^3 lower than additive at intermediate compositions, which is statistically significant.

Figure 6 shows the characteristic temperature, T^*, plotted against ϕ. T^* of the blend is much lower than additive. When using eq 4, one assumes additivity of the external degrees of freedom

$$c = \phi_1 c_1 + \phi_2 c_2 \qquad (8)$$

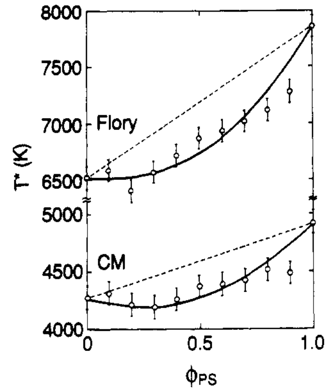

Figure 6. Characteristic temperature, T^*, of PS/PVME blends plotted against the hard-core volume fraction of PS from the two equations of state. The solid lines are the expected values for X_{12} = 100 J/cm^3 (FOV) and 200 J/cm^3 (CM).

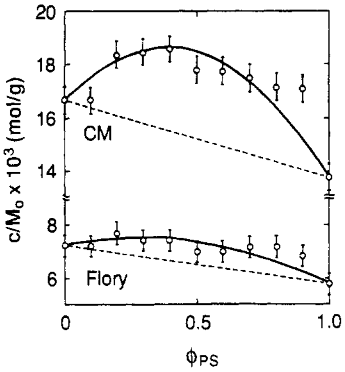

Figure 7. Values of the degrees of freedom divided by the segment molecular weight, c/M_0, plotted against the hard-core volume fraction of PS from the two equations of state.

In this case, T^* for the blend is given by

$$1/T^* = (\phi_1 P_1^*/T_1^* + \phi_2 P_2^*/T_2^*)/(\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12}) \qquad (9)$$

X_{12} can therefore be estimated by using the value of T^* in the blends and the characteristic parameters of the pure components in eq 9. The solid curve in Figure 6 is drawn for X_{12} = +100 J/cm^3 for the Flory model (CM; +200 J/cm^3). This is obviously inconsistent with the result of X_{12} obtained from P^*. Equation 9 indicates that a negative X_{12} leads to larger T^* than is predicted by the assumption of additivity.

This discrepancy could be explained if the assumption of eq 8 is incorrect. The c value of the blend can then be given by

$$c = \phi_1 c_1 + \phi_2 c_2 - \phi_1 \phi_2 c_{12} \qquad (10)$$

The relationship between T^* and c is given by

$$T^* = P^* v^*/(kc) \qquad (11)$$

and thus c/M_0 is given by

$$c/M_0 = P^* V^*_{\text{sp}}/(RT^*) \qquad (12)$$

where R is the gas constant and M_0 is the molecular weight per segment (not necessarily equivalent to a monomer). Figure 7 shows a plot of c/M_0 against ϕ. Clearly, c/M_0 calculated in this way is larger than additive, and c_{12} is calculated to be negative.

It is, however, unusual that in spite of a negative X_{12} the external degrees of freedom in the blend are predicted to be higher than additive. If X_{12} is negative and a specific interaction exists in the system, the external degrees of freedom would be expected to be restricted.

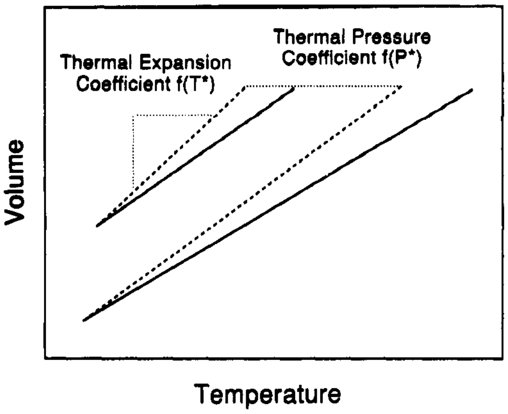

Figure 8. Hypothetical plot of volume against temperature showing two isobars (solid lines). If the cohesive energy decreased on heating, then the volumes would be larger, giving the dashed isobars. This would result in a larger expansion coefficient (and hence smaller calculated T^*) and a larger thermal pressure coefficient, $(dP/dT)v$ (and hence a larger calculated P^*).

Effect of c_{12} on the Chemical Potential. In a previous paper we simulated the phase diagram of the PS/PVME system using reduction parameters obtained for the pure polymers.[10] The values of the interaction parameter required to locate the phase diagram in the correct temperature range were approximately −2 J/cm^3 for both the FOV and CM equations. This value is obviously at variance with the values obtained from the $P-V-T$ data of the blends. The value of X_{12} used to simulate the phase diagram is probably less reliable due to possible errors and also contains all entropic and enthalpic contributions to the free energy not accounted for by the combinatorial and free volume terms. The calculations of the phase diagram also assume that $c_{12} = 0$, which the $P-V-T$ results suggest is incorrect. Taking account of c_{12}, the chemical potential is given by the following expression,[12] which includes a correction as has been pointed out previously[13] where m_i is the mass of a segment of component i.

$$\Delta\mu_1/RT = \ln\phi_1 + (1 - r_1/r_2)\phi_2 + P_1^*V_1^*/RT\{3\tilde{T}_1 \ln[(\tilde{v}^{1/3} - 1)/(\tilde{v}^{1/3} - 1) + (1/\tilde{v}_1 - 1/\tilde{v}) + \tilde{P}_1(\tilde{v} - \tilde{v}_1) + (\phi_2\theta_2X_{12}/P_1^*\tilde{v}) + 3\phi_2{}^2\tilde{T}_1/c_1 \ln[(2\pi m_2kT)^{1/2}/hx(\gamma v^*)^{1/3}(\tilde{v}^{1/3} - 1)] + 3\phi_2{}^2\tilde{T}_1(c_1 - c_2 + 2\phi_1c_{12})/c_1 \ln(m_1/m_2)\} \quad (13)$$

This equation includes the kinetic energy term as introduced by McMaster.[12] It should be noted that, if this term is omitted, then one introduces an inconsistency in that a negative c_{12} corresponds to an entropy gain that is unfavorable for mixing. Equation 13 is identical with eq 4 except for the last two terms and indicates that a negative c_{12} is favorable for mixing. However, if X_{12} and c_{12} are both large and negative, the equation predicts that the critical point (LCST) must occur at very high temperatures. We cannot explain the observed position of the phase diagram if X_{12} and c_{12} are both large and negative.

Effect of a Temperature-Dependent Interaction. We realized that a temperature-dependent interaction could explain the large disparate values of the interaction parameter from $P-V-T$ measurements. Qualitatively this is demonstrated in Figure 8. If the interaction becomes less favorable at higher temperatures, then the intermolecular forces are by definition weaker in the blend at higher temperature than would be expected if X_{12} had been constant. Thus, the expansion coefficient will be greater in the blend than expected. T^* scales inversely with the expansion coefficient and thus will be smaller than expected. P^*, however, scales with the thermal pressure coefficient $(dP/dT)v$, and this will be higher than expected since the horizontal distance between the isobars in the graph is smaller. We should also point out that a temperature-dependent interaction is also consistent with scattering experiments[14] though this is only available above 100 °C and includes entropy components in the parameter.

One can estimate the size of this effect by generating an imaginary set of $P-V-T$ data. If we assume for the sake of argument that X_{12} falls from −14 J/cm^3 at 50 °C to −4 J/cm^3 at 100 °C in a linear fashion for a PS/PVME blend, then we can calculate the volume as a function of pressure at each independent temperature. One can then combine these volumes into one data set and fit this data set to the equations of state, obtaining values of P^* and T^* for the mixture. P^* is found to be much higher than the mean of the pure components and T^* much lower than the mean. The calculated constant interaction parameter would be −82 J/cm^3 from the P^* value and +222 J/cm^3 from the T^* value in the case of the FOV equation. It should be noted that this only assumes a linear temperature dependence, which is not necessarily true. Also a strongly temperature-dependent interaction may be associated with nonrandom mixing, which would suggest that extra entropy components should also be present. Since we have no way of estimating the form of the temperature dependence, we do not consider it worthwhile to do any more complicated fitting. However, this calculation does show that a temperature-dependent interaction parameter can lead to anomalous values of the parameter when calculated as if it were constant.

It is also worth commenting that the Flory–Huggins interaction parameter, χ, is often considered to depend on the reciprocal of absolute temperature. While this is in the same direction as the trend in X_{12}, the size of the effect is much less than envisioned so that one would have to invoke a specific interaction that dissociates with increasing temperature to explain these results.

Conclusion

$P-V-T$ measurements on PS/PVME blends suggest very large anomalous values of the interaction parameter. These could be explained by a change in the degrees of freedom on mixing, but the sign of this change is incompatible with the observed phase diagram. A more reasonable explanation is a possible temperature dependence of the interaction parameter, which has been shown to lead to a false interpretation of $P-V-T$ data.

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