Miscibility of Polymer Blends with Engineering Models

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The miscibility behavior of polymer blends that do not exhibit strong specific interactions is examined. Phase equilibrium calculations are presented with the van der Waals equation of state and three group-contribution models (UNIFAC, Entropic-FV, and GC-Flory). Performance of these models is also compared. The van der Waals equation of state was recently shown to accurately correlate and predict vapor–liquid and liquid–liquid equilibria for binary polymer/solvent solutions. In this work, it is demonstrated that it correlates the upper critical solution behavior of polymer blends with excellent accuracy using the usual mixing and combining rules and a single temperature- and composition-independent binary interaction parameter. This interaction parameter can be predicted via a generalized expression that uses only the pure component equation-of-state parameters. Using this generalized expression, the upper critical solution temperature can be predicted with an average error of less than 45°C. The van der Waals equation of state can correlate the lower critical solution behavior of polymer blends, using an interaction parameter that is a linear function of temperature. The UNIFAC and Entropic-FV models, in general, are able to predict qualitatively the phase behavior of polymer blends, but quantitative predictions of the critical solution temperatures are not achieved. The GC-Flory equation of state fails to predict the upper critical solution behavior in polymer blends.

Introduction

Since the work of Flory (1953), various models have been developed for describing the phase equilibria in polymer blends (Patterson and Robard, 1978; Sanchez, 1978; Koningsveld and Kleintjens, 1977; Xie et al., 1992; Sanchez and Panayiotou, 1994; Coleman et al., 1989, 1991; Song et al., 1994a,b; Lai et al., 1988; Mumby et al., 1993; Qian et al., 1990; Wakker and van Dijk, 1992; Graessley et al., 1993; Krishnamoorti et al., 1994). These models have been applied mainly to the correlation of the phase diagrams of a few polymer blends and for understanding the thermodynamics of the phase equilibria in these systems. In most cases, the predictive capabilities of the models are not investigated and their performance is not extensively analyzed. So far, none of the available models are engineering-oriented, that is, both simple to apply and reasonably accurate.

Recently, Kontogeorgis et al. (1994), Harismiadis et al. (1994a,b), Saraiva et al. (1996), and Bithas et al. (1996) have demonstrated that the van der Waals equation of state (vdW EOS) can be used for the correlation and prediction of vapor–liquid and liquid–liquid equilibria in polymer solutions. The vdW EOS has been previously applied by several investigators (Salerno et al., 1986; Watson et al., 1986; Czerwienski,

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1988; Androulakis et al., 1989; Kalospiros et al., 1991) to polar systems with low molecular weight compounds with remarkable success (using an energy parameter obtained from vapor pressures and a Peneloux-translation). Although we have elected, due to its simplicity, to extend the vdW EOS to polymer solutions and—in this work—blend, any other cubic EOS (e.g., SRK) may be used without any complexities. Recently, Kalospiros and Tassios (1995) developed an EOS/G^E model for polymer solutions by combining the Peng-Robinson EOS with the Entropic-FV activity coefficient model (Kontogeorgis et al., 1993). These results demonstrate that cubic EOSs retain their flexibility even when applied to polymer solutions. Further, Kontogeorgis et al. (1995) and Saraiva et al. (1995) have demonstrated that group-contribution models are powerful tools for semiquantitative predictions of liquid–liquid equilibria in polymer solutions.

The purpose of this work is to apply the vdW EOS and group-contribution models to liquid–liquid equilibrium calculations in polymer blends, which do not exhibit strong specific interactions. Consequently, our aim is threefold: (1) to demonstrate that cubic EOSs are suitable for all types of phase equilibrium calculations in polymeric systems; (2) to present a comprehensive comparison of the performance of the vdW EOS and various group-contribution models; and (3) to identify the strong points and the limitations of all models considered.

Clearly the aim of this work is not to develop a rigorous, theoretically sound (and possibly complex) model for polymer blends. It is rather to investigate the performance of some existing simple models (Entropic-FV, vdW EOS) and compare their results with more complex EOS (GC-Flory, PH-SCT). Both the activity coefficient models and the EOS considered in this work are among the most recently proposed models for polymers. We believe that this knowledge is useful for those aiming to apply these models for describing and predicting phase equilibria for polymer–polymer mixtures.

The UNIFAC (Fredenslund et al., 1975, 1977) and the Entropic Free-Volume (Elbro et al., 1990; Kontogeorgis et al., 1993) group-contribution activity coefficient models have been used along with the vdW and the Group-Contribution-Flory (GC-Flory: Bogdanic and Fredenslund, 1994) EOSs. In the two activity coefficient models, the UNIFAC group-interaction parameters that depend linearly on temperature have been used (Hansen et al., 1992). The UNIFAC activity coefficient model and the GC-Flory EOS require only the chemical structure of each polymer. On the other hand, the Entropic-FV activity coefficient model and the vdW EOS require knowledge of the pure polymer volumetric behavior at low pressures.

This article describes the problems of obtaining good phase equilibrium experimental data for polymer blends and the models used. Then, we demonstrate our results for a few typical systems, as well as the performance of various models used.

Experimental Data

Phase equilibria in polymer blends

A detail study of the phase behavior of polymer blends is hampered by the scarcity of accurate experimental data. The experimental study of phase equilibria is more difficult in polymer blends than in polymer solutions or mixtures of low molecular weight compounds. Particularly troublesome is the attainment of the equilibrium state after the phase separation, because the high viscosity of polymer blends leads to very slow diffusion. Traditional methods of measuring phase boundaries, free energy, and heat of mixing are not applicable to polymer blends. To overcome this difficulty, various experimental studies of the thermodynamics of oligomer–oligomer systems have been performed. However, this process may not lead to reliable results when applied to systems of higher molecular weight polymers due to steric and chain-length effects and density differences between the polymers and their oligomer analogues. Since the cohesive energy density is strongly dependent on the density, the use of low molecular weight analogues is less reliable in systems where the dispersive forces are more important than in systems where strong specific energy interactions exist (Walsh and Rostami, 1985). It is possible to measure the heats of mixing in the presence of a solvent and then deduce the heat of mixing of the polymers using Hess's law (Pedemonte et al., 1994). However, this process is not particularly successful due to the accumulation of errors in the series of experiments involved. Differential scanning calorimetry, dynamical mechanical techniques and light-scattering methods have been typically used for obtaining information regarding the compatibility of polymer blends (Olabishi et al., 1979; Koningsveld et al., 1982; Robeson, 1982). However, the data obtained by differential scanning calorimetry are not true thermodynamic data.

Reliable phase diagrams can be obtained by light and neutron scattering techniques when very low heating/cooling rates are used. In the latter case, some modifications of the phase behavior of the blends may be induced due to deuteration of the polymer samples (Graessly et al., 1993; Yang et al., 1983, 1986; Larbi et al., 1986; Lin and Roe, 1988). Studies of the influence of pressure on the phase behavior for polymer blends are scarce (Xie et al., 1992; Rostami and Walsh, 1985). Many researchers have tried to determine the interactions between polymer pairs, focusing on the value of the Flory–Huggins χ interaction parameter (Flory, 1941, 1942, 1953; Huggins, 1941, 1942). However, the values of the χ parameter depend significantly on the exact model and the actual values of the pure fluid parameters used. This exacerbates the possible comparison and use of these data; the obtained results can be used only as a qualitative guide (Kressler et al., 1994).

Another potential problem is the high polydispersity of the polymer samples used in the experimental studies of phase equilibria in polymer blends. Although the influence of the polymer molecular weight distribution in the cloud point curves of polymer solution is relatively well-known (Koningsveld and Kleintjens, 1970; Šolc, 1970; Saraiva et al., 1993; Hu et al., 1993, 1994), this is not the case for polymer blends. We expect that the shape of the phase diagram of polymer blends is strongly influenced by the molecular weight distribution of the polymers, especially for systems of low molecular weight polymers, but problems regarding the precipitation threshold temperatures can be overcome to some extent: from the experimental study of the cloud-point curves of polydisperse polymer systems (Nishi and Kwei, 1975; Saraiva et al., 1993), it is possible to conclude that, when the value of *weight average molecular weight* (M_w) is considered, a reasonable description of the phase behavior of polydisperse polymer systems can be accomplished even when the calculations are performed for strictly binary systems.

Having the aforementioned points in mind, the experimental data used in this article have been selected by focusing on homopolymer/homopolymer blends. The M_w and M_w/M_n of the polymers have been identified. An extended search for cloud-point experimental data for polymer blends has been performed.

Polymer volumetric data

Many experimental studies have focused on the polymer volumetric behavior. Various equations, either empirical or theoretical (Zoller, 1989; High and Danner, 1992; Rodgers, 1993; Brannock and Sanchez, 1993), have been used for describing these data with very good accuracy. Although these equations are strictly valid only over a small temperature range, extrapolation is performed in many cases. When data are not available, predictive methods must be used (Elbro et al., 1991; Tsibanogiannis et al., 1994; van Krevelen, 1990). We examined the performance of various estimation methods. A typical example is given in Figure 1 for the specific volume of polystyrene (PS). The Tait equations proposed by High and Danner (1992) and by Rodgers (1993) behave similarly in their recommended ranges with very small deviations from the experimental data. The version proposed by Rodgers seems to extrapolate more smoothly to higher and lower temperatures. The group-contribution volume model (GCVOL) method is restricted to low pressures but, in the absence of experimental data, it is to be preferred over the empirical methods proposed by van Krevelen (1990). Generally, the performance of GCVOL is better than what is shown in Figure 1 for polystyrene. A recent group-contribution method for estimating the liquid densities of polymers was proposed by Constantinou et al. (1995). Currently, this method is restricted only to 25°C, but when extended to other temperatures, it will be a powerful tool for estimating the volume of the polymer.

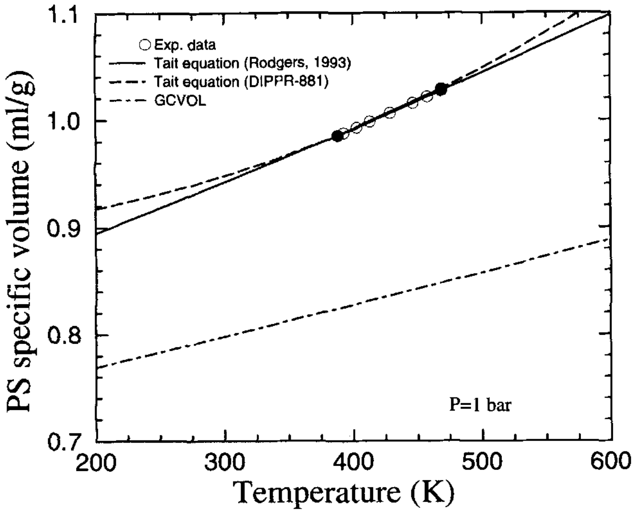

Figure 1. Specific volume of polystyrene vs. temperature.

Experimental data of Rodgers (1993) ○ are compared with model predictions. Solid circles denote the temperature limits for which the Tait equation is valid. Solid lines, Tait equation from Rodgers (1993); dashed lines, Tait equation from High and Danner (1992).

Models Used

Group-contribution models

The UNIFAC (Fredenslund et al., 1975, 1977) and the Entropic-FV (Elbro et al., 1990; Kontogeorgis et al., 1993) models distinguish two contributions to the activity coefficient:

$$\gamma_i = \gamma_i^{\text{comb}} \gamma_i^{\text{res}}, \tag{1}$$

where the superscripts *comb* and *res* imply the combinatorial and the residual (or energetic) contributions, respectively. Both models have exactly the same residual term (Hansen et al., 1992). The UNIFAC model uses the Staverman-Guggenheim combinatorial term, which is the sum of the Flory-Huggins term based on segment fractions and a shape correction term:

$$\ln \gamma_i^{\text{comb}} = \ln \frac{\varphi_i}{x_i} + 1 - \frac{\varphi_i}{x_i} - \frac{z}{2} q_i \left(\ln \frac{\varphi_i}{\theta_i} + 1 - \frac{\varphi_i}{\theta_i} \right) \tag{2}$$

where φ_i, θ_i, and q_i are the segment fraction, the surface-area fraction, and the external surface area of component i respectively; z is the coordination number, which is usually set equal to 10 (Fredenslund et al., 1975, 1977). The φ_i and θ_i fractions are defined as:

$$\varphi_i = \frac{x_i r_i}{\sum_j x_j r_j}; \qquad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j}, \tag{3}$$

where the volume and surface area parameters (r_i, q_i) are calculated from the group increments given by Bondi (1968). Values for r_i and q_i for many groups can be found in the parameter tables of UNIFAC (see, e.g., Fredenslund et al., 1977).

The combinatorial/free-volume term of the Entropic-FV model is a modification of the Flory-Huggins term, where free-volume fractions are used instead of segment, surface-area, or volume fractions:

$$\ln \gamma_i^{\text{comb}} = \ln \frac{\varphi_i^{fv}}{x_i} + 1 - \frac{\varphi_i^{fv}}{x_i}; \quad \varphi_i^{fv} = \frac{x_i V_i^{fv}}{\sum_j x_j V_j^{fv}};$$

$$V_i^{fv} = V_i - V_{wi}, \tag{4}$$

where φ_i^{fv}, V_i, and V_{wi} are, respectively, the free-volume fraction, the molar volume, and the van der Waals volume (Bondi, 1968) of component i. V_{wi} (in cm^3/mol) is equal to $15.17 r_i$.

The residual part of the activity coefficient contains the energy parameters that have been previously estimated using vapor-liquid equilibrium (VLE) data for mixtures with low molecular weight compounds. More details for the preceding models can be found in a recent publication (Kontogeorgis et al., 1995).

The group-contribution Flory (GC-Flory) EOS (Chen et al., 1990; Bogdanic and Fredenslund, 1994) is a group-contribution version of the Flory EOS (Flory et al., 1964a,b; Flory, 1970), which reproduces correctly the ideal gas limit:

$$P = \frac{RT}{V}\left(\frac{\tilde{v}+C}{\tilde{v}-1}\right) + \frac{E^{\text{res}}}{V}; \qquad \tilde{v} = \sqrt[3]{\frac{V}{V^*}}, \tag{5}$$

where T is the absolute temperature, R the universal gas constant, V the molar volume of the system, and V^* the molar hard-core volume. The C parameter is a function of temperature and the molecular structure of the mixture components. E^{res} is the residual term of the EOS that is evaluated via a UNIQUAC-type group-contribution expression.

van der Waals equation of state

The van der Waals equation of state (vdW EOS) has been recently used with remarkable success for vapor-liquid and liquid-liquid equilibrium calculations (correlation and prediction) in polymer solutions (Kontogeorgis et al., 1994; Harismiadis et al., 1994a,b; Saraiva et al., 1995a; Bithas et al., 1995). This great success may sound surprising considering the well-established theoretical deficiencies of the vdW EOS, which do not seem to affect the phase-equilibrium calculations for the systems considered. Here we will present very briefly the method for estimating the pure-polymer EOS parameters and we will give the mixing and combining rules used for phase-equilibrium calculations for polymer blends.

The vdW EOS is

$$P = \frac{RT}{V-b} - \frac{a}{V^2}, \tag{6}$$

where a and b are the energy and the covolume parameter, respectively. For estimating these EOS parameters, we first set the pressure in the EOS equal to zero. Assuming that the EOS parameters for the polymer are temperature independent, only two experimental temperature-density data at low pressure, covering as broad temperature range as possible, are required. The EOS parameters for the polymers used in this article are given in Table 1: note that they are proportional to the molecular weight of the polymer. Using these parameters, excellent correlation of polymer volume is achieved at low pressures, while the prediction of the volume at high pressures is less accurate, though still satisfactory. Details on the performance of vdW EOS for the correlation/prediction of polymer volume are given elsewhere (Kontogeorgis et al., 1994).

The classic van der Waals one-fluid mixing rules are used for estimating the EOS parameters for mixtures (a_m, b_m) of polymers:

$$a_m = \sum_i \sum_j x_i x_j a_{ij}; \qquad b_m = \sum_i \sum_j x_i x_j b_{ij}, \tag{7}$$

where x_i is the molar fraction of component i in the mixture. The cross energy (a_{ij}) and cross covolume (b_{ij}) parameters, which describe the interactions between polymers i and j, are estimated using the geometric mean and the arithmetic mean combining rules, respectively:

$$a_{ij} = \sqrt{a_i a_j}(1-k_{ij}); \qquad b_{ij} = \frac{1}{2}(b_i + b_j). \tag{8}$$

Table 1. Equation-of-State Parameters (*a/M*, *b/M*, *a/b*), and "Pseudocritical" Properties T_c and P_cM Values for the Polymers Considered in this Study*

Polymer	T (K)	a/M	b/M	a/b	T_c	P_cM
PS**	388–469	0.2349	0.8518	0.2758	982.7	11.99
BR**	277–328	0.1973	0.9586	0.2059	733.6	7.953
PMMA**	387–432	0.1893	0.7398	0.2559	912.0	12.81
PVME**	303–471	0.1967	0.8553	0.2300	819.5	9.959
PVC**	373–423	0.1605	0.6340	0.2531	902.1	14.79
PpMeS†	380–480	0.2011	0.8178	0.2459	876.4	11.14
PαMeS†	420–520	0.2378	0.8355	9.2847	1014.0	12.62
PIP†	300–450	0.1727	0.9236	0.1870	666.4	7.499

*The temperature range of the estimation of parameters is cited. Units: a/M in bar (m^3/mol)(mL/g); b/M in mL/g; a/b in bar(m^3/mol); T_c in K, P_cM in bar(kg/mol). The "pseudocritical" constants are calculated as $T_c = 8a/(27Rb)$ and $P_c = RT_c/(8b)$.

**Pure polymer volumetric data from the Tait equation (Rodgers, 1993).

†Pure polymer volumetric data from the GCVOL method (Elbro et al., 1991).

Note that for systems of compounds with large size differences and polymer solutions in particular, the Berthelot combining rule should be used for estimating the a_{ij} (Kontogeorgis et al., 1994; Harismiadis et al., 1994a):

$$a_{ij} = \sqrt{a_i a_j}\,\frac{b_{ij}}{\sqrt{b_i b_j}}(1 - L_{ij}). \tag{9}$$

The value of the correction L_{ij} to the Berthelot rule is, for polymer blends, approximately equal to that of the correction k_{ij} to the geometric-mean rule (Eq. 8).

Results and Discussion

In this section, we report the results obtained with the vdW and the GC-Flory EOSs and with the UNIFAC and the Entropic-FV activity coefficient models. First, the general picture is given. Then, a detailed description of the performance of the models considered is presented.

General

The group-contribution models examined proved to be only partially successful. For most systems examined, we have been able to predict the type of the experimental phase diagram. However, the critical solution temperatures of most polymer blends examined has been predicted with an average error around 100°C, with both UNIFAC and the Entropic-FV models (see, e.g., Figures 2 and 3). This rather poor quantitative behavior is not very surprising, if one takes into account the group-contribution nature of the applied methods: no experimental information about the pure polymer has been used. Even when the polymer molar volume required in the Entropic-FV model was obtained from the Tait equation (which describes accurately the volumetric behavior of the polymer) instead of the GCVOL method (Elbro et al., 1991), we did not obtain significantly better results. The reason is the small contribution of the combinatorial and free-volume

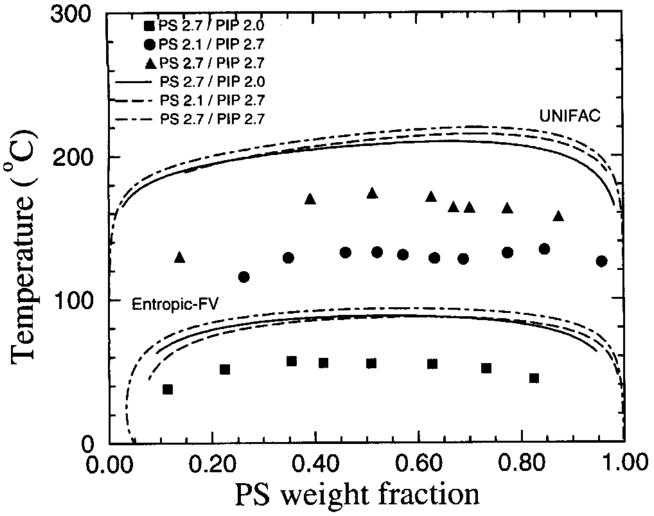

Figure 2. Experimental (symbols) and calculated (lines) cloud point curves for three polyisoprene (PIP)/polystyrene (PS) blends.

Experimental data from Šolc et al. (1984). Molecular weights of the polymers are: PS 2.1: $M_w = 2.1$ kg/mol; PS 2.7: $M_w = 2.7$ kg/mol; PIP 2.0: $M_w = 2.0$ kg/mol; PIP 2.7: $M_w = 2.7$ kg/mol.

part of the Entropic-FV model to the total value of the Gibbs free energy of mixing. In general, the Entropic-FV model proved to be more reliable than UNIFAC.

On the other hand, the GC-Flory EOS cannot predict the upper critical solution behavior for polymer blends. In the few cases where immiscibility was predicted with this model, this was of the lower critical solution type. The typical behavior of this model is shown in Figure 3. Very large errors are obtained, even when the polymer blend exhibits lower critical solution behavior. Typically, the difference between the experimental and the predicted lower critical solution temperature (LCST) is around 200°C. These results are in sharp contrast to the relative success of the GC-Flory model in predicting vapor–liquid and liquid–liquid equilibria for polymer solutions (Bogdanic and Fredenslund, 1994; Saraiva et al., 1995b). The problems of the GC-Flory EOS in predicting phase equilibria for polymer blends demonstrate the difficulties that some complex models may reveal when applied to complex systems.

Using the simple vdW EOS, it has been possible to correlate the phase diagrams of polymer blends that exhibit an upper critical solution behavior using a single temperature-independent binary-interaction parameter (Eq. 8). Typical examples are given in Figures 3, 4 and 5. The binary-interaction parameter (k_{ij}) has been correlated successfully as a function of the pure fluid equation of state parameters (Figure 6):

$$k_{ij} = 0.1530 - 1.089\zeta^3; \qquad \zeta = \frac{|d_i - d_j|}{d_i + d_j}; \qquad d_i = \frac{a_i}{b_i^2} \propto P_c. \tag{10}$$

The parameter ζ describes the differences of the critical pressures (P_c) of the molecules and was first introduced by Scott and van Konynenburg (1970) for the classification of the phase diagrams generated by the vdW EOS. The parame-

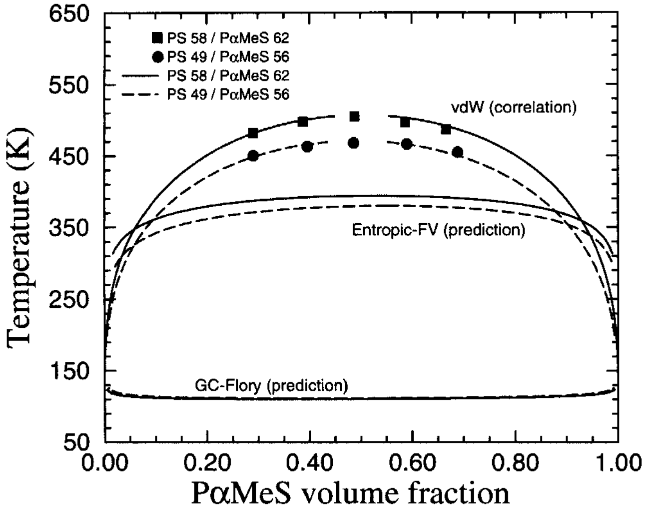

Figure 3. Experimental (symbols) and calculated (lines) cloud point curves for two polystyrene (PS)/poly(α-methyl styrene) (PαMeS) blends.

The van der Waals equation of state is used for correlating the experimental data, whereas the Entropic-FV and the GC-Flory equations of state are predictive models. Experimental data from Lin and Roe (1988). Molecular weight data of the polymers are: PS 58: $M_w = 58.4$ kg/mol; $M_w/M_n = 1.07$. PS 49: $M_w = 49.0$ kg/mol; $M_w/M_n = 1.06$. PαMeS 62: $M_w = 62.1$ kg/mol; $M_w/M_n = 1.05$. PαMeS 56: $M_w = 56.1$ kg/mol; $M_w/M_n = 1.07$.

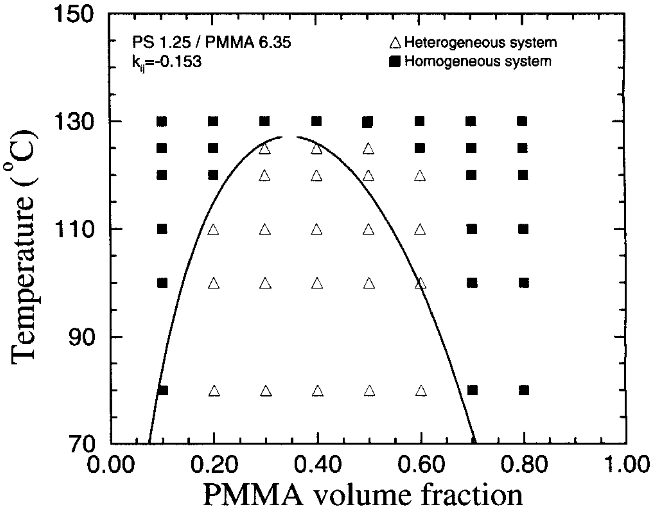

Figure 4. Experimental miscibility data and calculated cloud-point curve for the system of polystyrene (PS) with poly(methyl methacrylate) (PMMA).

Conditions for which the system is in the one-phase region (■); conditions within the two-phase region (△). The van der Waals equation of state (—) is used for correlating the phase equilibrium data ($k_{ij} = -0.153$). Experimental data from Kressler et al. (1994). Molecular weights of the polymers are: PS: $M_w = 1.25$ kg/mol; PMMA: $M_w = 6.35$ kg/mol.

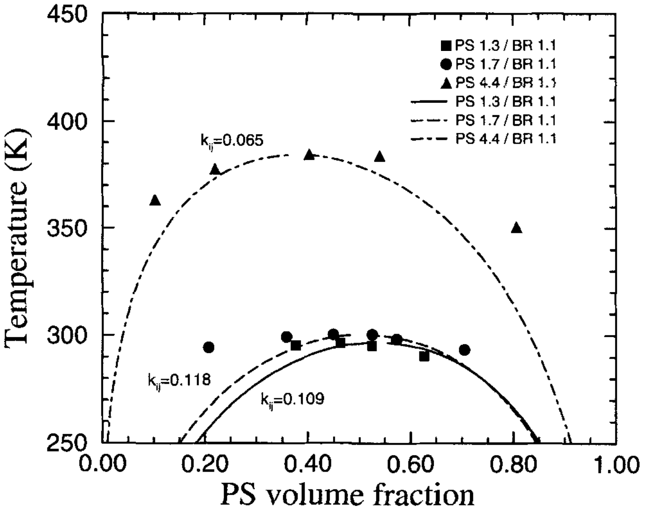

Figure 5. Experimental (symbols) and calculated (lines) cloud-point curves for three polystyrene (PS)/polybutadiene (BR) blends.

The van der Waals equation of state is used for correlating the experimental data. Required binary interaction parameters are shown in the figure. Experimental data from Rostami and Walsh (1985). Molecular weight data of the polymers are: PS 1.3: $M_w = 1.34$ kg/mol; $M_w/M_n = 1.12$. PS 1.7: $M_w = 1.67$ kg/mol; $M_w/M_n = 1.10$. PS 4.4 $M_w = 4.37$ kg/mol; $M_w/M_n = 1.12$. BR 1.1: $M_w = 1.10$ kg/mol; $M_w/M_n = 1.20$.

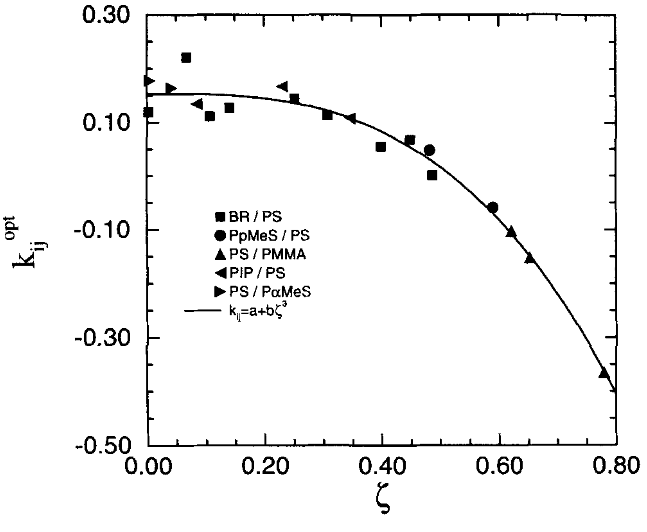

Figure 6. Optimum binary interaction parameter (k_{ij}) for the systems studied vs. the ζ parameter (points) and its prediction by Eq. 8 (solid line).

Experimental phase diagram data used are: Roe and Zin (1980), Rostami and Walsh (1985), Russel et al. (1985) for the system of polystyrene with polybutadiene; Stroeks et al. (1991) for the system of polystyrene with poly(para-methyl styrene); Kressler et al. (1994) for the system of polystyrene with poly(methyl methacrylate); Šolc et al. (1984) for the system of polystyrene with polyisoprene; Lin and Roe (1988) for the system of polystyrene with poly(α-methyl styrene).

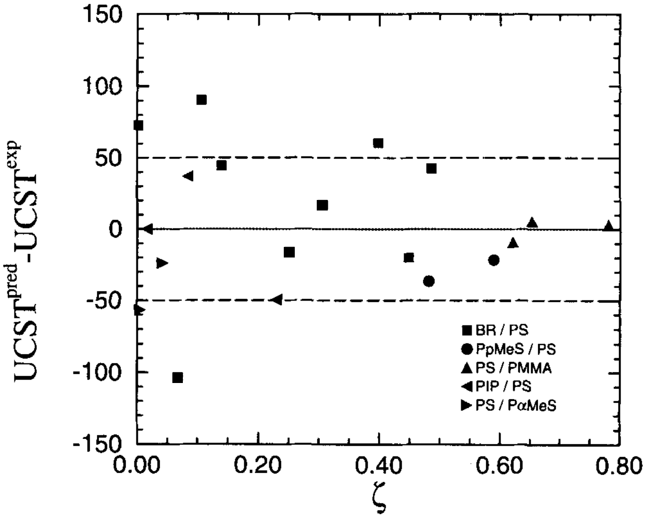

Figure 7. Predictions of the van der Waals equation of state for the upper critical temperature in polymer blends when Eq. 8 is used for estimating the binary interaction parameter.

Each system is characterized by the ζ parameter. Experimental phase data used are the same as in Figure 6.

ter d_i is proportional to the square of the solubility parameter. Using Eq. 10 for predicting the binary interaction parameter, the average absolute error in predicting the upper critical solution temperature is less than 45 degrees. This is demonstrated in Figure 7, where the error in the prediction of the upper critical solution temperature is plotted vs. ζ.

Very good results are obtained, except for the low molecular weight systems of polybutadiene (PBD or BR) with polystyrene (PS). The poor predictions for BR/PS may be attributed to two reasons: (1) small uncertainties in determining the molecular weight of the polymer might shift significantly both the optimum k_{ij} and the ζ parameter, and (2) the fact that the pure polymer EOS parameters are proportional to the degree of polymerization may not hold for short chain polymers.

Note that the k_{ij} can be correlated using a more complex expression instead of the one given by Eq. 10. We have been able to predict the upper critical solution temperatures for the systems examined with an average absolute error of 35 degrees. However, in view of the limited accuracy of the experimental data and in order to avoid problems upon extrapolation to other systems, we opted for the simple Eq. 10.

A very large negative interaction parameter is required for fitting the lower critical solution temperature. This results in a very narrow phase diagram strongly skewed to one side of the phase diagram. However, if an interaction parameter that depends linearly on temperature is used, a good description of the phase diagrams is achieved, as demonstrated in Figure 8 for polystyrene with poly(vinyl methyl ether), (PVME) where only two tie-lines were used for determining the binary interaction parameter. The slightly different shape of the experimental and the calculated phase diagrams is probably due to the polydispersity of the poly(vinyl methyl ether), which is not accounted for in our calculations.

Group-contribution models

For most systems tested, both the Entropic-FV and the UNIFAC models are able to capture the qualitative aspects

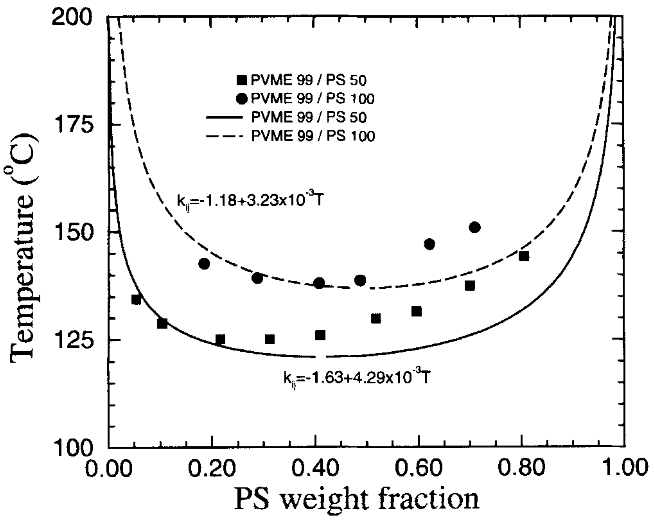

Figure 8. Experimental (symbols) and calculated (lines) cloud-point curves for two polystyrene (PS)/ poly(vinyl methyl ether) (PVME) blends.

The van der Waals equation of state is used for correlating the experimental data. The binary interaction parameters used depend linearly on temperature. Experimental data from Bae et al. (1993). Molecular weight data of the polymers are: PS 50: $M_w = 50$ kg/mol; $M_w/M_n < 1.05$. PS 100: $M_w = 100$ kg/mol; $M_w/M_n < 1.06$. PVME 99: $M_w = 99$ kg/mol; $M_w/M_n = 2.13$.

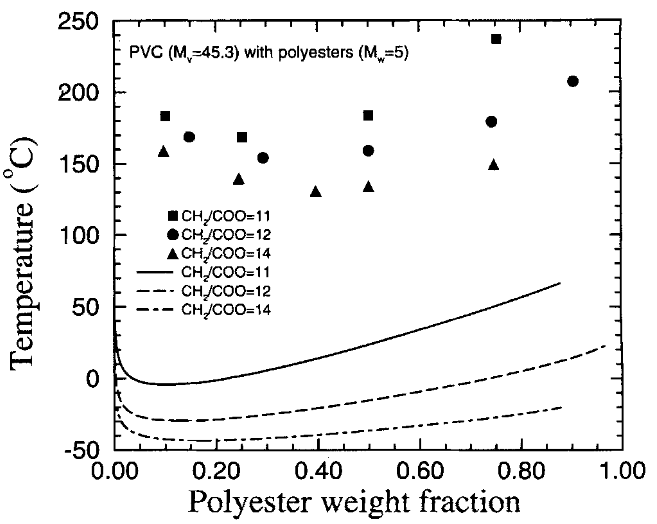

Figure 9. Experimental and calculated cloud-point curves for systems of polyesters of various CH$_2$/COO ratios with poly(vinyl chloride) (PVC).

The UNIFAC model is used. Results of the Entropic-FV model are very similar, but not given for clarity. Experimental data from Woo et al. (1985). Molecular weight data of the polymers are: PVC: $M_v = 45.3$ kg/mol; polyesters: $M_w = 5$ kg/mol.

of the phase diagrams (lower and upper critical solution behavior) of polymer blends, as can be seen in Figures 2, 3, 9 and 10. An interesting point is that UNIFAC is able to predict the lower critical solution behavior of polymer blends (Figures 9 and 10), whereas this is not usually the case for polymer/solvent solutions. The reason for this can be attributed to the different magnitude of the contribution of the combinatorial term in polymer solutions and polymer blends. In polymer solutions, the free-volume differences are quite significant, especially at high temperatures. In polymer blends, the opposite occurs: the energetic contributions (to the activity coefficient) are usually very large compared to the combinatorial ones. However, even for systems exhibiting upper critical solution behavior, the predicted critical solution temperatures (with both UNIFAC and Entropic-FV models) differ significantly from the experimental values (Figure 2). It seems that although small when compared to the energetic contributions to the Gibbs free energy of mixing, the combinatorial and free-volume contributions can have a large effect on the predicted phase diagram.

It has not been possible to calculate any phase separation for the systems polystyrene–poly(α-methyl styrene) (PαMeS) (Lin and Roe, 1988) and polystyrene–poly(para-methyl styrene) (PpMeS) (Stroeks et al., 1991) with UNIFAC. The reason for this is that the energetic interactions are small for these (nearly athermal) systems. Thus, the combinatorial part of the UNIFAC model is the main contribution to the Gibbs free energy of mixing, and consequently, complete miscibility is predicted. The Entropic-FV model is able to predict qualitatively the phase diagrams of the aforementioned systems. This denotes the significance of using a good approximation of the combinatorial and free-volume contributions to the Gibbs free energy of mixing. For poly(vinyl chloride) (PVC) systems, the predictions of both models are almost identical (Figures 9 and 10). The reason for this might be the low temperatures involved, which diminish the effects of the free-

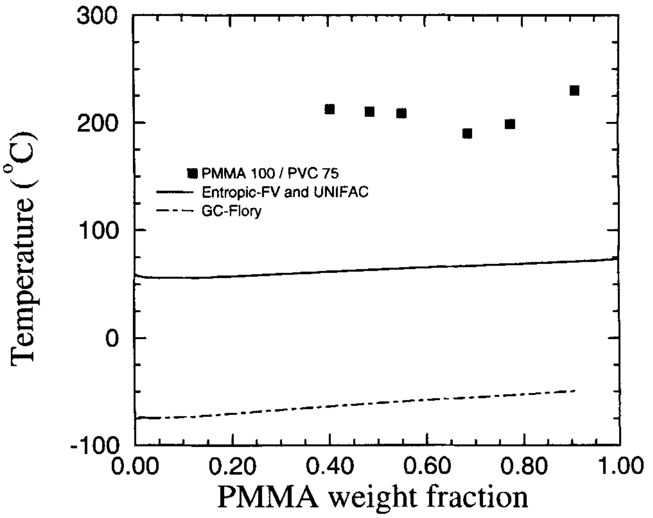

Figure 10. Experimental and calculated cloud-point curves for the system of poly(methyl methacrylate) (PMMA) with poly(vinyl chloride) (PVC).

The phase diagrams calculated with the UNIFAC and the Entropic-FV models are practically indistinguishable. Experimental data from Vorenkamp and Challa (1988). Molecular weight data of the polymers are: PMMA 100: $M_w = 100$ kg/mol; $M_w/M_n = 2.2$. PVC 75: $M_w = 75$ kg/mol; $M_w/M_n = 2.1$.

volume differences or the very large contribution of the energetic term of UNIFAC (Hansen et al., 1992) to the Gibbs free energy of mixing for the poly(vinyl chloride) systems.

The results with the GC-Flory EOS for the phase diagrams of polymer blends are unsatisfactory. In most cases complete miscibility has been predicted. For those systems where immiscibility was found, it was of the lower critical solution type (Figures 3 and 10). Thus, it seems that the GC-Flory EOS cannot predict the upper critical solution behavior for polymer blends. Although it has been proved that the GC-Flory is an excellent model for calculating vapor–liquid equilibria, and reasonably good for predicting liquid–liquid equilibria in polymer solutions (Bogdanic and Fredenslund, 1994; Saraiva et al., 1995b), the current results for polymer blends do not justify the expectations that one might have from a complex thermodynamic model.

van der Waals equation of state

From our calculations it becomes clear that the simple vdW EOS:

1. is able to correlate with good accuracy the upper critical solution behavior of polymer blends using a temperature-independent binary interaction parameter (Figures 3, 4, and 5); the actual upper critical solution temperature calculated from the EOS is a linear function of the binary interaction parameter used over a very large temperature range (100–200 K), as can be seen in Figure 11.
2. can describe the lower critical solution behavior in both polymer solutions (Saraiva et al., 1996) and polymer blends using a linear temperature-dependent binary interaction parameter (k_{ij}) (Figure 8).
3. can be used as an engineering model for predicting the upper critical solution behavior in polymer blends.

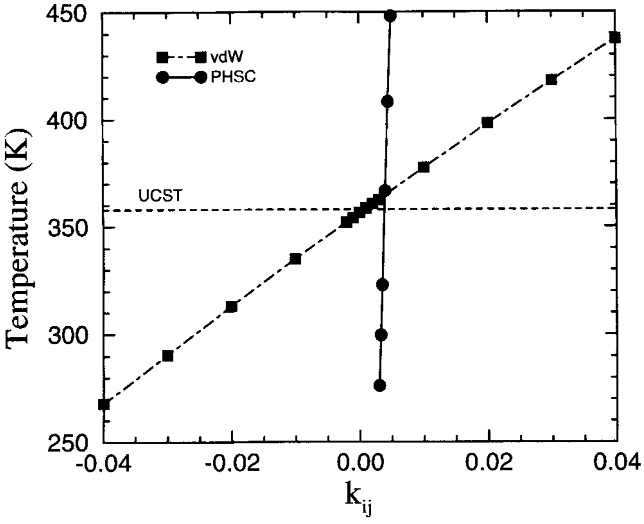

Figure 11. Calculated upper critical solution temperature vs. the interaction parameter (k_{ij}) for the system of polystyrene (PS) with polybutadiene (BR).

Squares indicate results of the van der Waals equation of state; spheres, the perturbed-hard-sphere-chain equation of state. The experimental upper critical solution temperature for this system is about 358 K (Rostami and Walsh, 1985). Lines are just a visual guide. Straight lines can fit the data excellently ($r > 0.999$) for both equations of state. Molecular weight data of the polymers are: PS: $M_w = 1.34$ kg/mol; $M_w/M_n = 1.12$. BR: $M_w = 2.35$ kg/mol; $M_w/M_n = 1.10$.

Equations of State: Simplicity vs. Accuracy

When an EOS is used, one important consideration is the correct representation of the pure fluid properties. Once this is established, and reasonable mixing and combining rules have been chosen, the next step is the correlation of the experimental data. When examining the miscibility of polymer blends, the interaction parameter that reproduces the experimental critical solution temperature has to be found. The evaluation of the performance of an EOS should focus on the following points:

1. Qualitatively correct behavior
2. Capability of correlating the different types of phase diagrams
3. The shape of the calculated phase envelopes
4. Possibility of predicting the binary interaction parameter (k_{ij})
5. The magnitude of the binary interaction parameter.

We wanted to establish the usefulness of a simple EOS vs. that of a complex one. For this reason, a preliminary comparison of the performance of the van der Waals and the perturbed-hard-sphere-chain EOS has been performed. The peturbed-hard-sphere-chain EOS, recently proposed by Song et al. (1994a,b), is a complex EOS based on statistical mechanical theories. It is a fifth-degree polynomial in volume; the reference term is a modification of the Carnahan and Starling (1969) EOS, while a van der Waals-type attractive term is used.

Both EOSs behave very similarly in the description of polymer blends, although the perturbed-hard-sphere-chain EOS is more accurate than the van der Waals as far as the description of the pure polymer volumetric behavior is concerned. Both models are able to describe the upper critical solution behavior using a single binary interaction parameter, as shown in Figure 12 for the system of polystyrene (1.39 kg/mol) with poly(methyl methacrylate) (PMMA) (6.35 kg/mol). In this case the width of the phase diagram generated by the perturbed-hard-sphere-chain EOS is greater than that of the vdW EOS, but this is not always the case. The overall results seem to be equivalent. As far as the correlation of the lower critical solution behavior is concerned, both EOSs need a temperature-dependent k_{ij}; otherwise, a highly negative interaction parameter is necessary and the critical composition of the phase diagram is severely underpredicted.

The k_{ij} of the perturbed-hard-sphere-chain EOS is about an order of magnitude smaller than that of the vdW EOS. Although this could be considered to be a positive result, unfortunately the phase diagrams of the perturbed-hard-sphere-chain EOS are sensitive to small k_{ij} deviations. One might expect that a method to predict the interaction parameter for the perturbed-hard-sphere-chain EOS is indeed possible, since this has been the case for the vdW EOS. In general, one expects that the binary interaction parameter required by a complex EOS represents the true monomer–monomer interactions, is independent of the molecular weight of the two polymers, and can be predicted accurately. However, this may not always be the case.

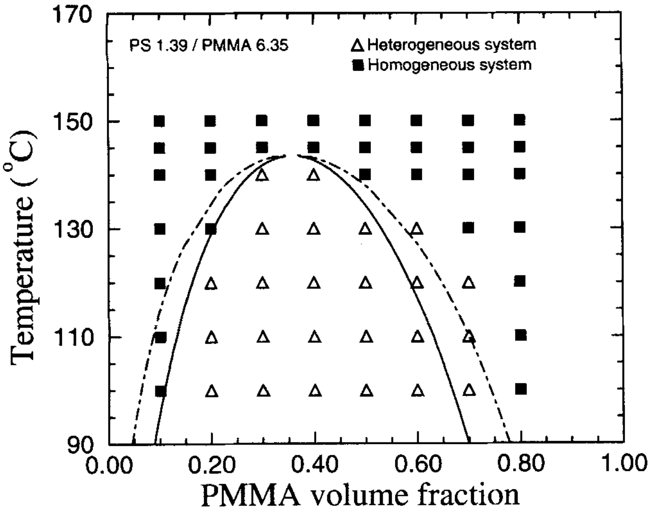

Figure 12. Experimental miscibility data and calculated cloud-point curve for the system of polystyrene (PS) with poly(methyl methacrylate) (PMMA).

Conditions for which the system is in the one-phase region (■); conditions within the two-phase region (Δ). The van der Waals (—, $k_{ij} = -0.093$) and perturbed-hard-sphere-chain (— · —, $k_{ij} = +0.0055$) equations of state are used for correlating phase equilibrium data. Experimental data from Kressler et al. (1994). Molecular weights of the polymers are: PS: $M_w = 1.39$ kg/mol; PMMA: $M_w = 6.35$ kg/mol.

In brief, the vdW EOS behaves similarly to more complex EOSs. This conclusion is expected to stand, even after an extensive comparison of the performance of the two EOSs for phase-equilibrium calculations in polymer blends. The obtained results demonstrate the flexibility and accuracy of cubic EOSs.

Conclusions

Liquid-liquid equilibrium calculations have been performed for various polymer blends with the UNIFAC and the Entropic-FV group-contribution activity coefficient models, together with the vdW and the GC-Flory EOSs. Our results can be summarized as follows:

1. The Entropic-FV and the UNIFAC models are capable of describing the qualitative aspects of the phase diagrams of polymer blends (lower/upper critical solution behavior), but the critical solution temperatures predicted by the models differ significantly from the experimental data. The Entropic-FV model is more reliable than UNIFAC, but both models predict critical solution temperatures with an error of around 100°C.
2. The GC-Flory EOS cannot predict the upper critical solution behavior of polymer blends. Even for the systems exhibiting lower critical solution behavior, and when phase split is predicted, very poor agreement with the experimental data is obtained.
3. The vdW EOS is able to correlate with good accuracy the upper critical solution behavior of polymer blends using a single *temperature and composition independent* binary interaction parameter (k_{ij}). The lower critical solution behavior in polymer blends can be accurately described if an interaction parameter that depends linearly on temperature is used.
4. Complex EOSs like, the perturbed-hard-sphere-chain equation, do not seem to have any clear advantages over the simple cubic ones as far as correlation of the upper and lower critical solution behavior in homopolymer blends is concerned.
5. The vdW EOS can be used as an engineering tool for predicting the upper critical solution behavior in both polymer solutions and blends.
6. We have shown that the lower critical solution behavior of mixtures with polymers can be described if a temperature-dependent k_{ij} is used. The generalization of the $k_{ij}(T)$ expression to both UCST and LCST will make it possible to use the vdW EOS for phase-equilibrium calculations for polymer blends (and solutions).

Notation

N = degree of polymerization
S = entropy
δ = solubility parameter
Δ = absolute difference in solubility parameters ($\Delta = |\delta_1 - \delta_2|$)
σ = standard deviation
ω = acentric factor

Subscripts and superscripts

n = number average (e.g., molecular weight)
pol = polymer
r = reduced quantity (using the critical constants)
ref = reference quantity
s = solvent
E = excess
mix = mixture

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Manuscript received Feb. 6, 1995, and revision received Jan. 4, 1996.

Correction

From the R&D note titled "Percolation in a Fractional Brownian Motion" (August 1996, p. 2392) the following note was inadvertently omitted: "In a personal communication, Sahimi (1996) pointed out that in a forthcoming article Mukhopadhyay and Sahimi (1996) also found that the percolation cluster is compact in 2-D and 3-D, although its backbone is not.