Description of Phase Behavior of Polymer Blends by Different Equation-of-State Theories. 2. Excess Volumes and Influence of Pressure on Miscibility

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ABSTRACT: In the first part of this contribution the Sanchez–Lacombe theory and the theory of Patterson were used to describe the phase behavior of various polymer blends. It turned out that the descriptions of the blends with respect to influence the free volume and enthalpy were surprisingly similar. Moreover, the PVT behavior of polymers is predicted similarly in both cases. In this paper the predictions of the two theories concerning excess volumes and influence of pressure on miscibility are investigated.

Introduction

In contrast to rigid lattice theories, equation-of-state (EOS) theories are capable of predicting volume changes during mixing (excess volumes) and, therefore, the influence of pressure on miscibility.

The phase behavior of a mixture under pressure is governed by the sign of the excess volume of mixing:

Idealized volume vs temperature curves are shown in Figure 1. The upper curve represents a system at pressure p undergoing a phase transition with a negative volume change. This transition would correspond to a mixing on heating with a negative excess volume, or to demixing with positive excess volume, i.e., UCST and LCST behavior, respectively. A transition of this type can move to lower temperatures only upon raising the pressure by dp (second curve in Figure 1). Otherwise the two isobaric curves would intersect.

On the other hand, a system with positive volume change would represent a UCST behavior with positive excess volume or an LCST behavior with negative excess volume. Such a transition can move to higher temperatures only upon raising pressure (lower two curves in Figure 1). This means that for a blend with negative excess volume an increase of pressure always enhances miscibility, whereas for a blend with positive excess volume it is lowered.

However the curves in Figure 1 are idealized. In a real system the mixing or demixing occurs continuously with varying temperature, so that the corresponding volume changes are infinitesimal for each temperature. However, the sign of this volume change should be the same as the overall excess volume.

Alternatively, the influence of pressure can be deduced by calculating the pressure coefficient $\mathrm{d}T_{\mathrm{cr}}/\mathrm{d}p$ of the critical solution temperature, which is given by:

$$\mathrm{d}T_{\mathrm{cr}}/\mathrm{d}p \simeq T\Delta V_{\mathrm{m}}/\Delta H_{\mathrm{m}} \tag{1}$$

In addition to the volume change ΔV_{m}, this method also requires the enthalpy of mixing ΔH_{m}. It yields not only the sign but also the magnitude of the pressure coefficient.

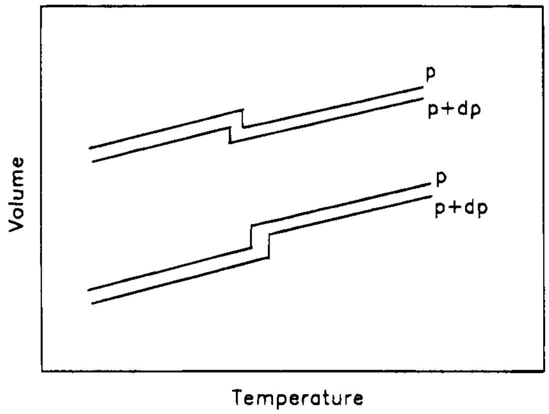

Figure 1. Idealized volume vs temperature curves of the mixing and demixing of blends.

Theory

The PF-Patterson (PFP) theory[1] has been outlined in the preceding paper.[2] However, the χ parameter was given only for vanishing pressure. For nonzero pressure, the interactional part remains unaltered, but the free-volume part acquires an additional term. For the pressure p, χ is then given by[3] (the same notation is used as in ref 2)

$$\chi = -\frac{U_1\nu^2}{RT} + \frac{C_{\mathrm{p1}}}{2R}\left[\tau + \frac{\kappa_1 p}{\alpha_1 T}\pi\right]^2 \tag{2}$$

α_1 and κ_1 are expansion coefficient and compressibility, respectively, of component 1 at pressure p. π is given by

$$-\pi = 1 - \frac{p^*_1}{p^*_2} \tag{3}$$

As in the case of vanishing pressure, eq 2 is a general expression, for which a particular model has to be applied. With the Prigogine–Flory (PF) theory[4,5] one

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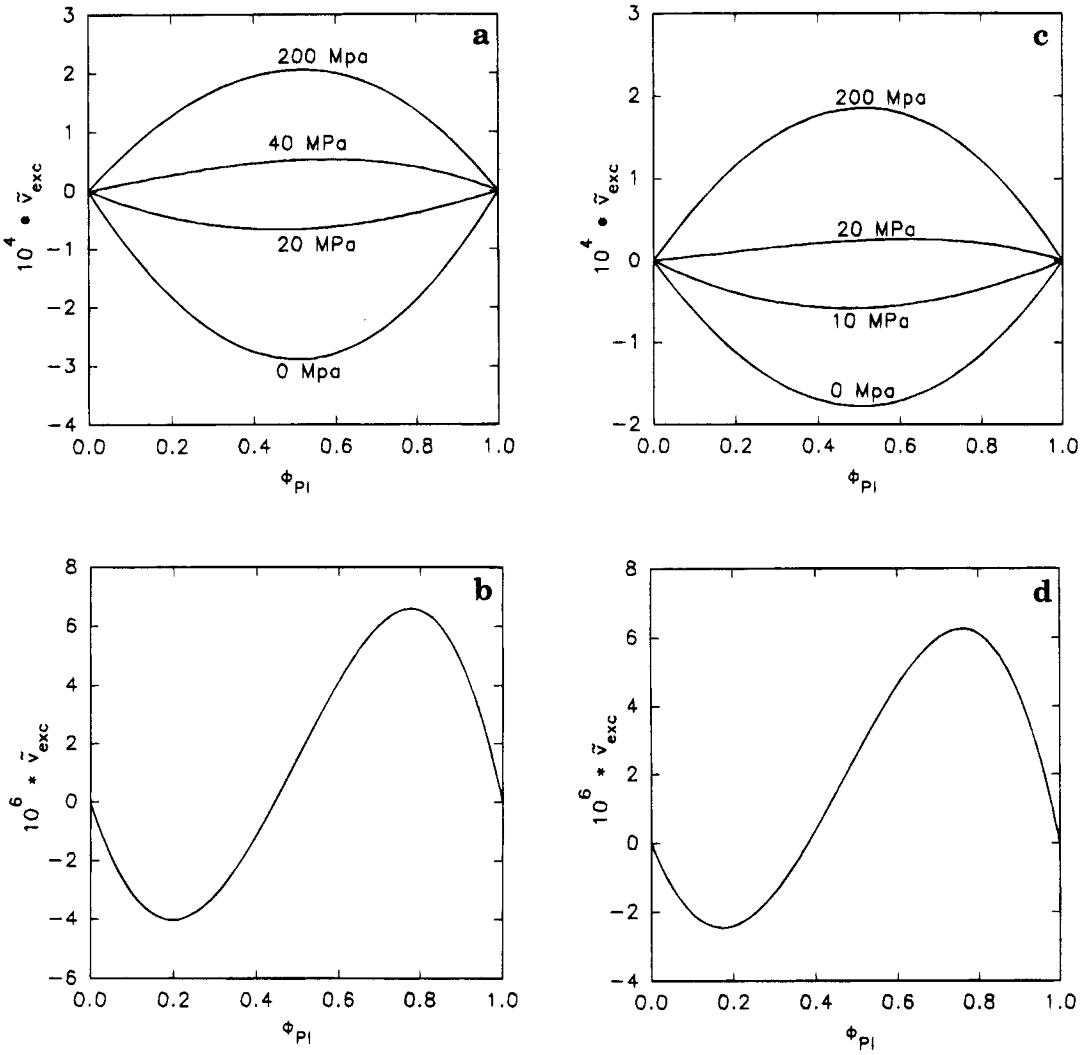

Figure 2. Reduced excess volume as a function of composition for PS/PI (at 100 °C): (a) PF theory; (b) PF theory for 30 MPa; (c) SL theory; (d) SL theory for 17 MPa.

obtains

$$\frac{\kappa_1 p}{\alpha_1 T} = \frac{\tilde{p}_1 \tilde{v}_1^{\,2}}{1 + \tilde{p}_1 \tilde{v}_1^{\,2}} \tag{4}$$

Furthermore, the constant pressure heat capacity is also a function of pressure. Within the framework of the PF theory it is given by

$$C_{\mathrm{p1}} = \frac{p^*{}_1 V^*{}_1}{T^*{}_1} \tilde{C}_{\mathrm{p1}} \tag{5}$$

with

$$\tilde{C}_{\mathrm{p1}}^{\ -1} = \left(1 - \frac{2}{3} \tilde{v}_1^{\ -1/3}\right) - \frac{2(1 - \tilde{v}_1^{\ -1/3})}{1 + \tilde{p} \tilde{v}_1^{\,2}} \tag{6}$$

The Sanchez–Lacombe (SL) theory[6,7] has been presented in ref 2 as well. To allow for pressure greater than zero, an additional term has to be added to the quantity Ψ (eq 25 or ref 2). Then it reads

$$\Psi = \frac{\lambda_{12}}{\tilde{v}} - \frac{\nu}{(\Phi_1 + \nu \Phi_2)^2}\left(\frac{1}{r_1^0} - \frac{1}{r_2^0}\right) + \frac{\tilde{p}\tilde{v}}{\tilde{T}} \frac{(\nu - 1)}{(\Phi_1 + \nu \Phi_2)} \tag{7}$$

With this change, the parameter Λ introduced in the preceding paper as the analogue of the χ parameter in the stability condition retains its form. Moreover, the pressure also appears explicitly in the chemical potentials. For component 1 it reads

$$\mu_1 = kT\Bigg\{\ln \Phi_1 + \left(1 - \frac{r_1}{r_2}\right)\Phi_2 + \frac{r_1^0}{\tilde{v}}[\chi_{\mathrm{SL}} + (1 - \nu)\lambda_{12}]\Phi_2^{\,2} + r_1^0 k T^*{}_1 \left\{-\frac{1}{\tilde{v}} + \tilde{p}_1 \tilde{v} + \tilde{T}_1\left[(\tilde{v} - 1)\ln\left(1 - \frac{1}{\tilde{v}}\right) - \frac{1}{r_1^0}\ln \tilde{v}\right]\right\}\Bigg\} \tag{8}$$

Results and Discussion

The systems under investigation are the same as those in the preceding paper, i.e., polystyrene/polyisoprene (PS/PI), polystyrene/poly(methylphenylsiloxane) (PS/PMPS), and polystyrene/poly(cyclohexyl methacrylate) (PS/PCHMA). The same parameters are used for the calculations.

The phase behavior of a mixture under pressure is governed by the sign of the excess volume of mixing. Therefore we will analyse the reduced excess volume

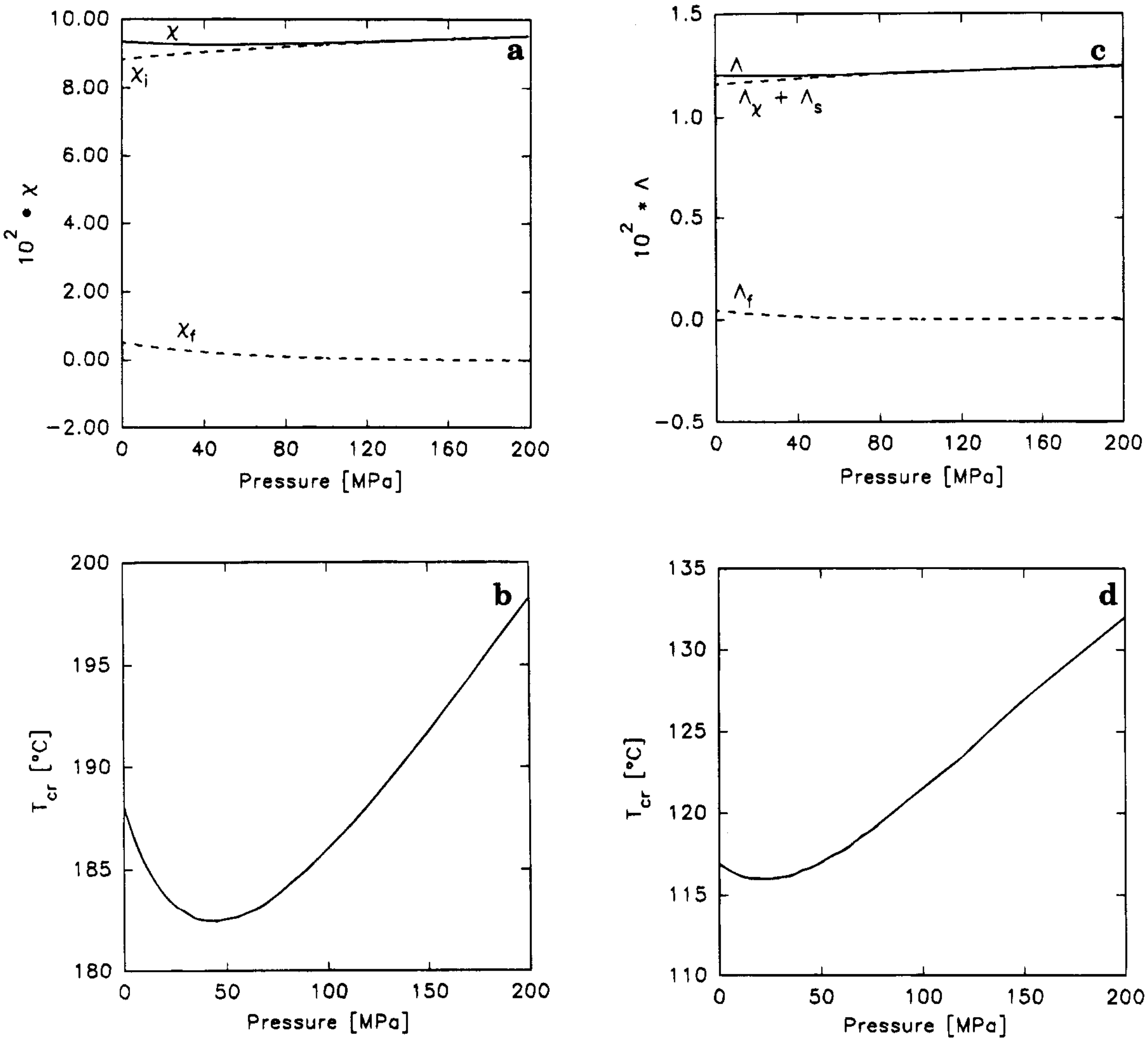

Figure 3. Pressure dependence of the various contributions of the interaction parameter (at 100 °C), and the critical temperature of PS/PI: (a) χ; (b) critical temperature calculated with PFP theory; (c) Λ; (d) critical temperature calculated with SL theory.

$\tilde{v}_{\mathrm{exc}}$ which is predicted by the two models. It is defined by

$$\tilde{v}_{\mathrm{exc}} = \tilde{v} - \Phi_1\tilde{v}_1 - \Phi_2\tilde{v}_2 \qquad (9)$$

For the SL theory this is only an approximate relation, which would be exact for the case $\nu = 1$, i.e., when the lattice site volumes for both pure components are equal. For our excess volume calculations, we will assume this to be the case.

Since the PFP theory is derived from the PF theory, its underlying EOS is the PF EOS. Figure 2a shows the reduced excess volume vs composition calculated with this theory for PS/PI at 100 °C for various pressures. For low pressures it is negative but becomes positive on raising the pressure. The change of sign occurs at about 30 MPa. At this pressure $\tilde{v}_{\mathrm{exc}}$ is still negative for high concentrations of PS, while for high PI concentrations it is already positive (Figure 2b). This means that in this pressure range the miscibility on the PS-rich side is improved by raising pressure and is lowered on the PI-rich side, i.e., the phase diagram becomes distorted. However, the magnitude of the excess volume in this transition range is about 2 orders of magnitudes smaller than for the other pressure ranges. Therefore, the shift of the temperatures of mixing and unmixing on varying the pressure is very small, so that the shape of the phase diagram hardly changes. Moreover, calculations show that the sign of the excess volume is almost independent of temperature.[8]

The reduced excess volume for the system PS/PI obtained with the SL theory is shown in Figure 2c. The results are qualitatively similar to those mentioned above, but the change of sign occurs already at about 17 MPa. Again, at this pressure the reduced excess volume is still negative for high PS concentrations and positive for high PI concentrations (Figure 2d).

The influence of pressure on the Patterson χ parameter (at 100 °C) of the system PS/PI is shown in Figure 3a. The interactional part increases on raising the pressure, i.e., miscibility is reduced. The free-volume part however decreases, practically going to zero, thus favoring miscibility. This results in a total χ parameter that exhibits a minimum for a certain pressure. Hence miscibility is first improved on raising pressure, but on further increase of pressure it is lowered again. One would expect this behavior from the above discussion of the excess volume. The critical temperature as a function of pressure is shown in Figure 3b.

The parameter Λ of PS/PI as a function of pressure (at 100 °C, for $\Phi_{\mathrm{PI}} = 0.5$) is given in Figure 3c.

As for the corresponding Patterson χ parameter, the interactional part increases with pressure, whereas the free volume part practically goes to zero. The total

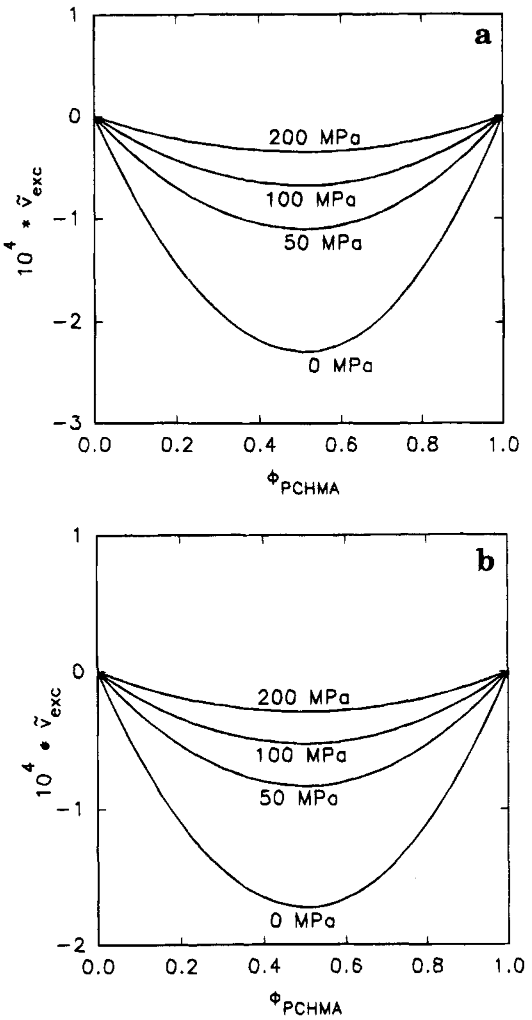

Figure 4. Reduced excess volume as a function of composition for PS/PCHMA (at 100 °C): (a) PF theory; (b) SL theory.

parameter again shows a minimum, which is located however at lower pressures than in the case of the PFP theory. This again is in agreement with the considerations of the excess volumes.

The critical temperature vs pressure is shown in Figure 3d. The influence of pressure on the critical temperature is smaller than for the PFP theory. Considering the fact, that the SL theory predicts a smaller free volume, this is not surprising.

The reduced excess volume of PS/PCHMA at 200 °C calculated with the PF theory is shown in Figure 4a. It is negative for all pressures and compositions; therefore, one expects enhanced miscibility at elevated pressures.

The corresponding result for the SL theory is shown in Figure 4b. The result again is very similar to that of the PF theory.

Figure 5a shows the influence of pressure on the χ parameter of the PFP theory (at 250 °C). Both the interactional part and the free volume part decrease with increasing pressure. However, the decrease of the free volume part is much faster, so that it dominates the behavior. For high pressures, the total χ parameter decreases to values for which one expects again complete miscibility. In fact, the critical temperature quickly goes into regions, where degradation would occur. For a pressure of about 100 MPa, it starts to increase even more rapidly, eventually going to infinity (Figure 5b). The same behavior is predicted by the SL theory. The parameter Λ (interactional terms combined) and the critical temperature are shown in Figure 5c,d, respectively.

The corresponding phase diagrams starts to close, until there is a completely closed loop. For the PFP theory, this appears for a pressure of about 109 MPa. Above 110 MPa, the loop vanishes, i.e., the system is completely miscible. This is shown in Figure 6, with the phase diagrams for 95 and 109 MPa, respectively.

For the SL theory, the pressures for which closed miscibility loops and finally complete miscibility occurs are lower. Closed loops occur for about 63 MPa, and for pressures greater than 65 MPa, complete miscibility is predicted.

For the system PS/PMPS qualitatively similar results are obtained for both, the PFP theory and the SL theory. However, the pressure coefficient $\mathrm{d}T_{cr}/\mathrm{d}p$ for the SL theory is predicted to be greater than for the PFP theory, which contradicts the statement above. The same is true for the system PS/PCHMA.

Now, it is possible to introduce into the PFP theory a parameter ζ in analogy to the SL theory, which is a measure of the deviation from the Berthelot relationship. For both theories it turns out that the pressure coefficient depends on ζ. The greater ζ, so the greater is the pressure coefficient. If the same ζ is used for the calculations for both theories, then different critical temperatures result, but the pressure coefficient obtained for the PFP theory is greater than that for the SL theory, in agreement with expectations.

For the system PS/PI, the theories predict a minimum for the critical temperature as a function of pressure. Such a behavior has in fact already been observed. Janssen et al.[9] performed pressure-dependent small-angle neutron scattering for a blend of deuterated polystyrene and poly(methylphenylsiloxane) with critical composition. The observed spinodal temperature exhibited such a pressure dependence. However, our model calculations for this system do not predict such a dependence but a monotonic decrease of the critical temperature with pressure.

The order of magnitude of the pressure coefficients is predicted reasonably only for the system PS/PI. The PFP theory yields sufficiently far away from the minimum values for the magnitude of the pressure coefficient between 0.01 and 0.013 K/bar. The SL theory predicts 0.008–0.01 K/bar. These are typical values for a UCST system. Experimentally, values between 0.011 and 0.015 K/bar have been found.[10] For PS/PMPS the models predict values which decrease with temperature. They range between 0.15 and 0.4 K/bar. For low pressures, the pressure coefficient of PS/PCHMA is predicted by both models to be approximately 0.3 K/bar. The experimentally determined values for LCST systems range between 0.012 and 0.046 K/bar.[9,11]

Conclusions

The reduced excess volumes and the influence of pressure on miscibility predicted by the PFP and the SL theory have been compared. The results of both models proved to be very similar, as in the case of their predictions at vanishing pressures, which was shown in the preceding paper. Again, not only are the results of the two models similar but so are the thermodynamic reasons they give. The influence of pressure on the interactional and the free volume part of the parameters

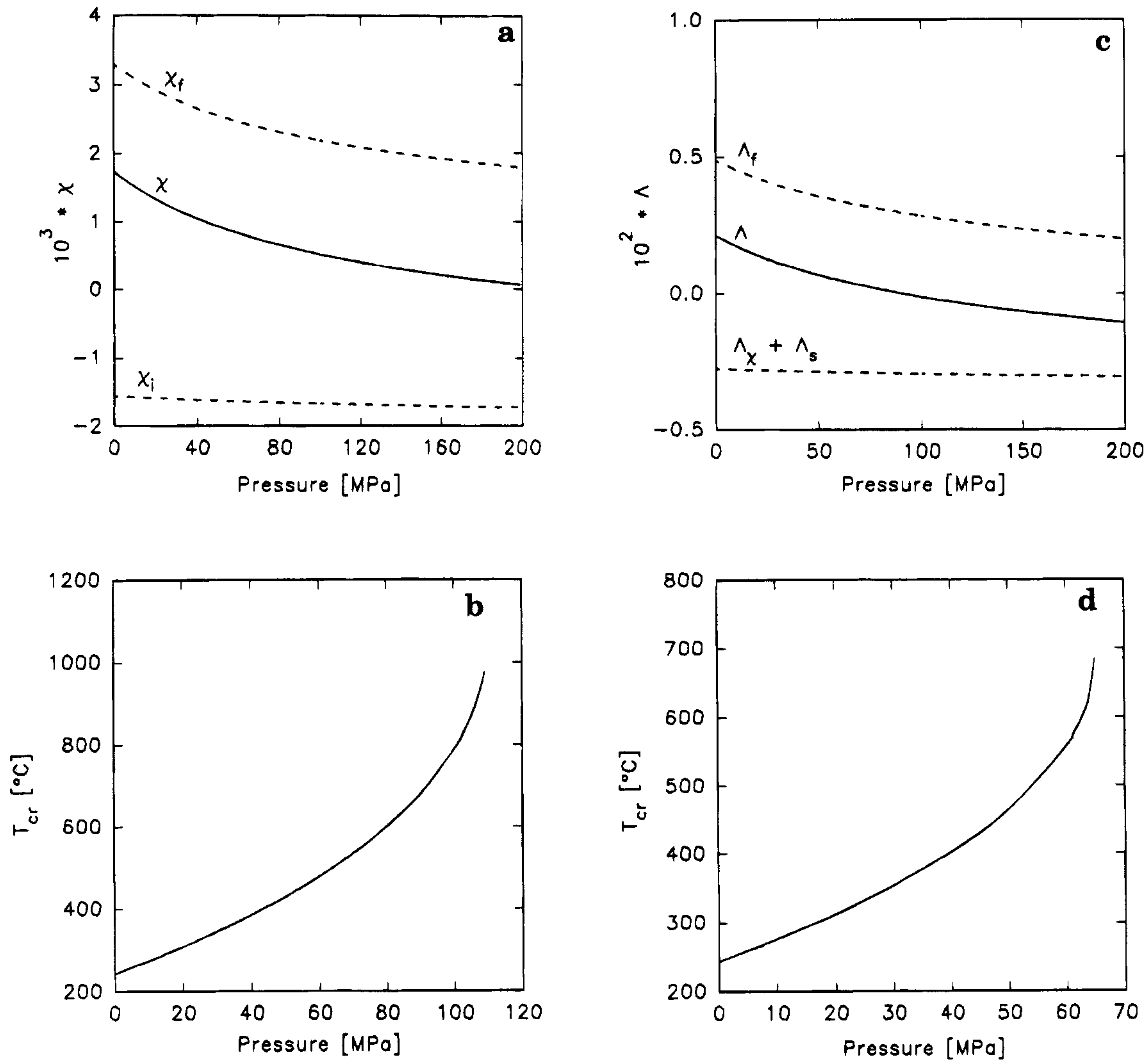

Figure 5. Pressure dependence of the various contributions of the interaction parameter (at 250 °C), and the critical temperature of PS/PCHMA: (a) χ; (b) critical temperature calculated with PFP theory; (c) Λ; (d) critical temperature calculated with SL theory.

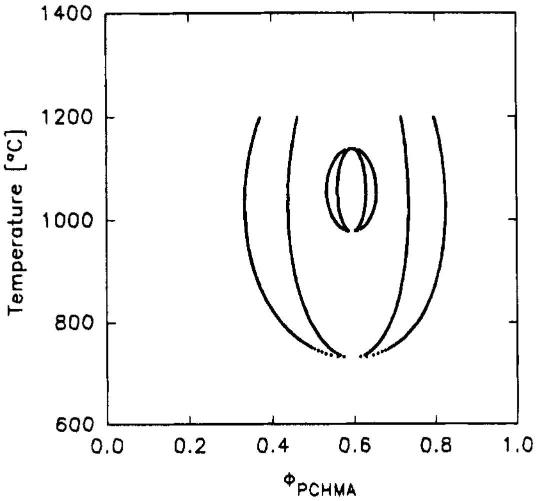

Figure 6. Phase diagrams for the system PS/PCHMA calculated with the PFP theory for 95 and 109 MPa, respectively.

χ and Λ, respectively, are the same. Moreover, the excess volumes predicted by the two models are in good qualitative agreement.

References and Notes

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