

Effect of Pressure on Polymer Blend Miscibility: A Temperature–Pressure Superposition

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ABSTRACT: In this paper, we report on how interaction strength varies with pressure and temperature for several polyolefin mixtures. We find that the interaction energies that govern phase behavior in polymer blends are only a function of density for UCST polyolefin blends far from a critical point. As a result, the effects of pressure on miscibility can be predicted for such blends from knowledge of the effects of temperature on the interactions combined with *PVT* data. This remarkable simplification appears to be related to the van der Waals nature of the interactions between saturated hydrocarbons. Density dependence predicts the trends correctly for LCST polyolefin blends, but for these mixtures the interactions depend in a more complex way on *T* and *P*.

Introduction

In recent years, there has been increased interest in the effect of pressure on the miscibility of polymers.^{1–4} One reason is the need for such data to more fully understand polymer miscibility in relation to the various proposed theories and equations of state. Another is the realization that such pressure effects could be important in many situations where such blends are used, e.g., when mixing a blend in an extruder or in forming articles from a blend by injection molding. These needs have led to the development of pressure cells that can be used with both light and neutron scattering so that the phase behavior and interaction strengths of blends can be measured.^{2,5} In past work, a wide range of phase behavior at atmospheric pressure in saturated hydrocarbon blends was found.^{6–11} As several outstanding problems remain unexplained in these blends, we decided to investigate the dependence on pressure, an independent thermodynamic variable. In this paper, we point out that in certain simple cases the pressure and temperature dependence of the interaction parameter collapse as a function of density.¹²

Pressure Effects on Blend Miscibility

We start by noting some general observations about how the critical temperatures of polymer blends vary with pressure.^{13–15} For those blends that display UCST behavior (that is, phase separation upon cooling), it is nearly always found that the critical temperature, T_c , increases with pressure, i.e., the effect of increasing pressure is to decrease the range of miscibility. We have now seen this in several polyolefin blends as well as in isotopic blends. Similarly, in mixtures that display LCST behavior (phase separation upon heating), T_c also

increases with pressure. We have found this in blends of PIB with hhPP,¹¹ as have Janssen et al.¹ and Hammouda and Bauer² for PS/PVME. Thus, increasing pressure almost always reduces the miscibility range in UCST blends and increases it in LCST blends. To our knowledge, the only example of a UCST blend where miscibility was enhanced by pressure is the blend of polystyrene and poly(butyl methacrylate) studied by Hammouda and Bauer.² However, it should be noted that this blend has a negative interaction parameter that decreases algebraically with pressure (i.e., becomes more negative), indicating some specific interactions are at play. Wolf and Blaum saw a similar enhancement of miscibility in an oligomeric system when a negative heat of mixing was involved.¹⁵

These two patterns of behavior become consistent with one another if phase behavior is considered not in terms of temperature and pressure effects but rather in terms of density. In a UCST, the mixed state is favored by heating, i.e., by lowering the density of the mixture. So when pressure is applied, the density is increased, which favors phase separation. At ambient pressure and a temperature just above the UCST, the mixed state is barely stable, and as the pressure is increased the density eventually rises enough to reverse the situation and produce phase separation. The same argument applies to the LCST blends, except that here an increase in density favors the mixed state. Cooling an LCST mixture favors the mixed state by increasing the density, and increasing the pressure favors the single-phase state for the same reason. One can summarize this by saying that increasing density decreases the intermolecular separation and so increases the interactions between the polymers, whether this favors or disfavors the mixed state.

To examine the quantitative aspects of this idea, we have expressed the interaction strength for several blends in terms of density, rather than just pressure

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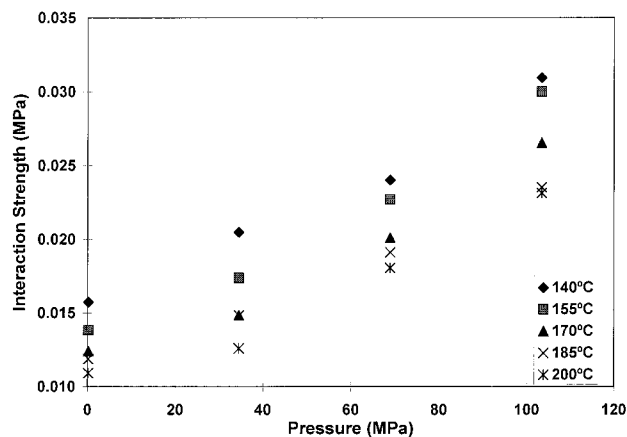


Figure 1. Dependence of interaction strength, X , for DEB32/EH18 blend on pressure at temperatures indicated in the legend ($^{\circ}\text{C}$). The relative standard uncertainty for X in this paper is 10%.

Table 1. Polymer Characterization

polymer	chemical structure	$\bar{M}_w \times 10^{-3}$ (g/mol)	% deuterated
DEB32	ethylene-butene copolymer; 32 wt % butene	96.6	34.6
EH18	ethylene-hexene copolymer; 18.4 wt % hexene	76.6	0
PIB-I	polyisobutylene	107	0
DhhPP-B	head-to-head polypropylene	76.5	34.1

and temperature separately. The interaction strength coefficient, X , obtained from neutron scattering (using the random phase approximation⁶) is related to the Flory interaction parameter, χ ,

$$X = \frac{\chi}{\nu_0} RT$$

where R is the gas constant, T is the temperature, and ν_0 is the arbitrary reference volume used to define the value for χ . Thus, we can assume $X(P, T) = X(\rho)$ in which $\rho(P, T)$ is the mass density of a single-phase mixture at pressure P and temperature T . Relevant properties of the polymeric components in the blends considered here are given in Table 1.

UCST Blends

The variation of X with temperature and pressure for a 50/50 EH18/DEB32 blend is shown in Figure 1. These results are typical of the behavior we see for UCST blends; X decreases with temperature and increases with pressure. We have obtained PVT data on both of these polymers, and the densities of each are known at all temperatures and pressures of interest. We assume that there is negligible volume of mixing⁷ and calculate the density of the blend from the additivity of the component specific volumes. This is used in Figure 2 to show how X depends on density. The data for all of the temperatures collapse together, showing that the interaction energy density is a simple function of blend density for this case. Another case where this has worked well is the isotopic blend of hhPP-B; its interaction strength depends only on density, as shown in Figure 3.

This remarkable simplification of data has now been found for a number of UCST blends. Thus, it seems that if at two different conditions of T and P the molecules of the two components are packed together such that

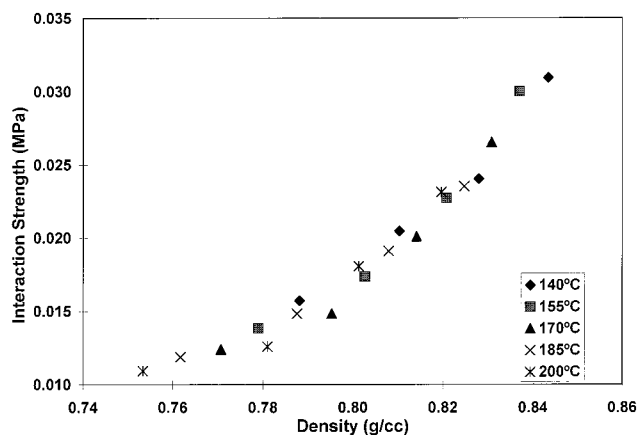


Figure 2. Dependence of interaction strength, X , for DEB32/EH18 blend on density at temperatures indicated in the legend ($^{\circ}\text{C}$).

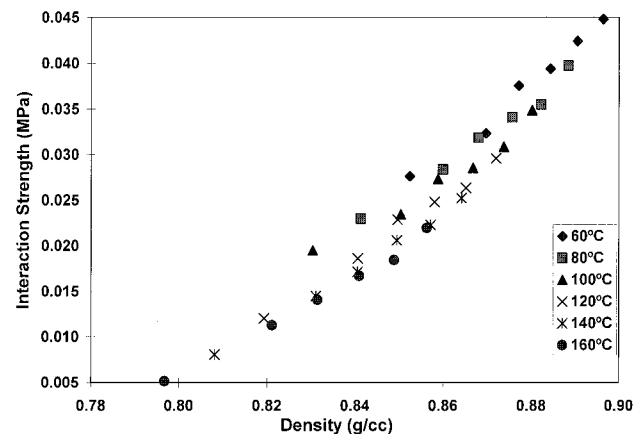


Figure 3. Dependence of interaction strength, X , for DhhPP-B/HhhPP-B blend on density at temperatures indicated in the legend ($^{\circ}\text{C}$).

the intermolecular distances are the same, then the intermolecular interactions that govern phase behavior will be the same as well. This suggests that the same van der Waals potential is acting on the molecules at all conditions, a reasonable explanation for saturated hydrocarbon molecules. Going further, if the interaction energy density is simply a function of density for such blends, one might suppose that the cohesive energy density of the components would also be a function of density alone. The cohesive energy of a polymer is of course not directly measurable, but we can derive the internal pressure from PVT data,⁹ and this is nearly identical to the cohesive energy density for saturated hydrocarbons.¹⁶ The internal pressure for EB32 is shown as a function of T and P in Figure 4 and then as a function of density in Figure 5. Although not as compelling as in Figures 2 and 3, a similar unification of data occurs here as that seen for the blends. The sort of temperature-pressure superposition of the interaction strength that we have described here was found for all of the isotopic blends we examined and for most of the other UCST blends. It only failed for blends that were near the critical temperature; the reasons for this are not clear.

LCST Blends

We have done the same analysis for a 50/50 blend of HPIB-I with hhPP-B, which is known to have an

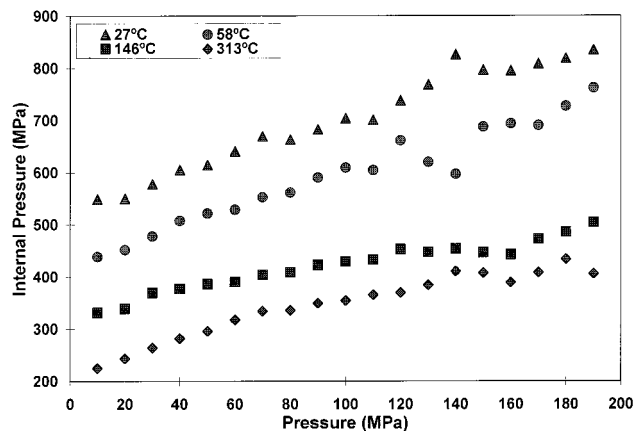


Figure 4. Dependence of internal pressure for DEB32 on pressure at temperatures indicated in the legend (°C). The relative standard uncertainty for the internal pressure in this paper is 5%.

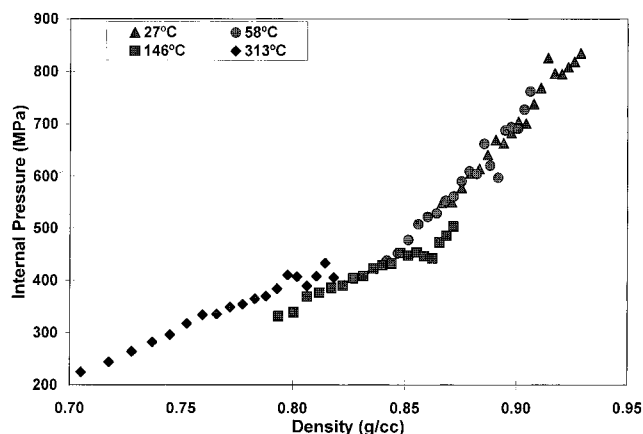


Figure 5. Dependence of internal pressure for DEB32 on density at temperatures indicated in the legend (°C).

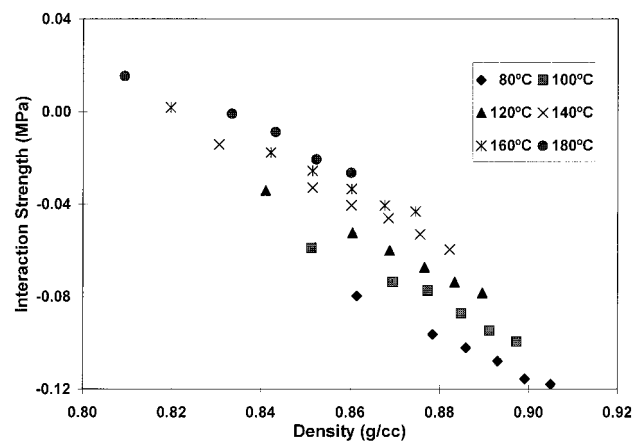


Figure 6. Dependence of interaction strength, X , for HPIB-I/DhhPP-B blend on density at temperatures indicated in the legend (°C).

LCST of 180 °C.⁷ X increases with T and decreases with P , as is typical of an LCST blend, as discussed above. It is also negative at the lower temperatures, which has been seen in many of the blends involving PIB.⁷ Again calculating the blend density and assuming no volume change on mixing, we plot interaction strength as a function of density in Figure 6. The data clearly come closer together, but do not overlap, as was the case for the EH18/EB32 blend. At constant density, those interactions that cause the net attractions in this blend

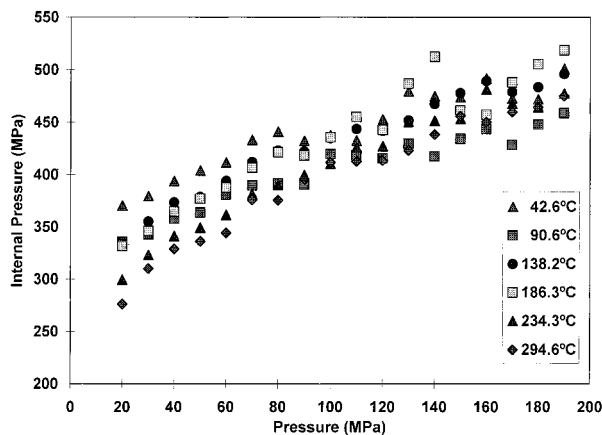


Figure 7. Dependence of internal pressure for HPIB-I on pressure at temperatures indicated in the legend (°C).

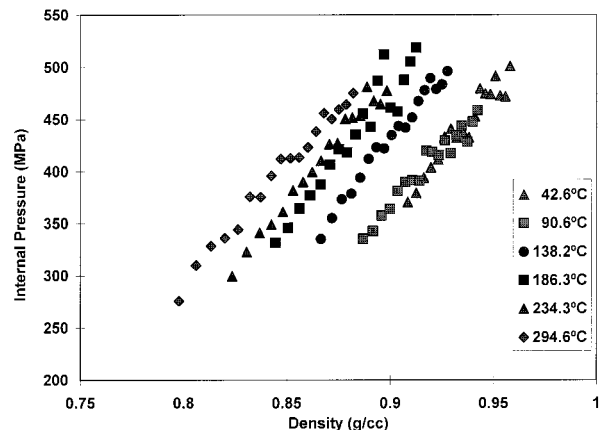


Figure 8. Dependence of internal pressure for HPIB-I on density at temperatures indicated in the legend (°C).

get smaller as temperature rises. Moreover, if one looks at the internal pressure of PIB, it is also not a simple function of density. An investigation of Figures 7 and 8 shows that in fact it is a better distillation of the PVT data to say that the internal pressure of PIB depends only on temperature and is independent of pressure. This must be related to the other unusual properties of PIB, such as its high density and low compressibility. A similar story appears to be true for PS/PVME blends.¹⁷

Conclusions

We find that the pressure and temperature dependences of interaction energies that govern phase behavior in polymer blends are only a function of density for UCST polyolefin blends far from a critical point. As a result, the effects of pressure on miscibility can be derived for such blends from PVT data and knowledge of the effects of temperature alone. This remarkable simplification appears to be related to the van der Waals nature of the interactions between saturated hydrocarbons. Density dependence predicts the trends correctly for LCST polyolefin blends, but the interactions depend in a more complex way on T and P . The causes of this complexity require further investigation.

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