

Polymer-polymer interactions

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Abstract - The successful development of multicomponent polymer systems generally requires careful control of polymer-polymer interactions since this is important for achieving useful mechanical properties, optically clear mixtures (miscibility), coupling of impact modifiers to a brittle matrix, compatibilization of immiscible polymers, etc. Random copolymers offer a powerful tool for achieving the desired results since they permit adjustment of both the intermolecular interactions between the mixture components and the intramolecular interactions within components. In fact, random copolymers are more often found to be miscible with other polymers than are homopolymers because of this. Recent advances in the development of theoretical frameworks and experimental techniques for evaluating polymer-polymer interactions are described. A matrix of monomer unit pair interaction energies is being constructed which is useful for making predictions about interactions and phase behavior in other blend systems.

INTRODUCTION

Physical mixtures of different types of polymers (blends or alloys) are utilized extensively to produce commercially useful materials having combinations of properties not normally found in a single polymer. Rational development of this technology has raised many interesting scientific challenges. In the area of thermodynamics, it would be useful to be able to answer a priori the questions raised in Fig. 1 since many of the properties and processing characteristics of a blend of polymers A and B depend on whether they are miscible or not, the nature of the phase diagram, or interfacial behavior in phase separated mixtures. To answer these questions requires progressively higher levels of sophistication and knowledge about the system of interest using a thermodynamic theory or model appropriate for the level of detail to be predicted. The theory will contain parameters that must be specified before prediction is possible. Some of these parameters relate only to the pure components and can be specified through appropriate characterization (e.g., composition and molecular weight information) or physical property determination (e.g., pressure-volume-temperature behavior). However, mixture parameters that characterize the polymer-polymer interactions are generally required as well. How are these parameters to be determined? In many cases, the most practical means is to reverse the prediction procedure, i.e., the parameters are deduced from observations of phase behavior. Hopefully, parameters deduced from

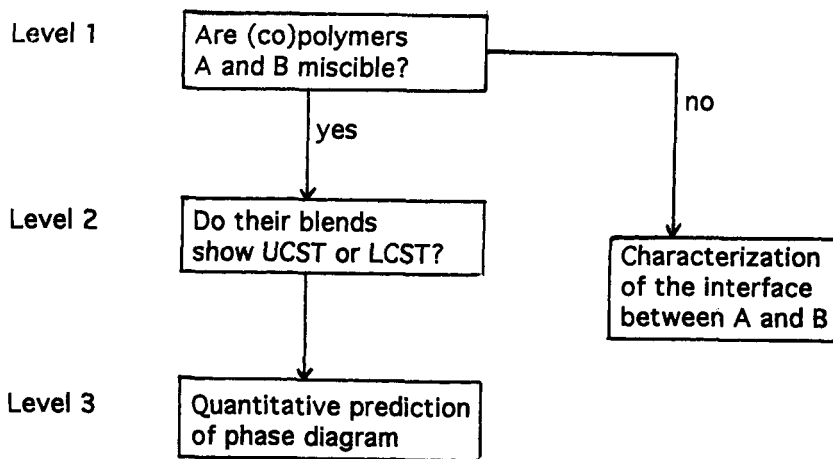


Fig.1 Questions that can be answered from proper knowledge of polymer-polymer interaction energies.

an observation for one system can be translated to other situations. The extent that this will succeed depends on the appropriateness of the theoretical framework used, the accuracy of the experimental information, and the accuracy (or level of detail) of prediction that suffices. In the best of circumstances, the parameters should be truly constants, but in reality they may be functions of blend composition or temperature. Success hinges on neglecting the complications that are not absolutely essential for meeting the predictive objectives.

Two quite divergent approaches are currently in use for describing or predicting the phase behavior of polymer blends. One uses association or quasi-chemical models (1) and is most suited for polymer mixtures where strong specific interactions, like hydrogen bonding, are involved. The other, described here, employs a mean field approach (2-8) which is appropriate when the interactions are not too specific. When only weak dispersive forces are at play, the unlike interactions are given by the geometric mean of the interactions between the two like pairs. This leads to endothermic heats of mixing and always predicts immiscibility in the limit of very high molecular weights of the components. In what follows, a framework of theory and sample experiments will be described that lead to predictive ability for mixtures of polar polymers where the geometric mean rule does not apply, heats of mixing may be exothermic, but the interactions are not so specific as to imply quasi-chemical association in the mixtures. Particular emphasis is paid to mixtures where one or both components are random copolymers.

THEORY

Phase diagrams for polymer-polymer mixtures are governed by the same thermodynamic principles that apply to mixtures of small molecules; however, there are some important differences in the relative magnitudes of certain terms owing to the high molecular weight of polymers and potential complications owing to polydispersity of molecular weight. The simplest theory that accounts for the issues of polymer chain size is the Flory-Huggins theory for the free energy of mixing

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} = B\phi_A\phi_B + RT \left[\frac{\rho_A\phi_A}{M_A} \ln\phi_A + \frac{\rho_B\phi_B}{M_B} \ln\phi_B \right] \quad (1)$$

where ρ_i = density, M_i = molecular weight, ϕ_i = volume fraction for component i while B = the polymer-polymer interaction energy density. For what follows, it is more useful to employ this form rather than the dimensionless χ parameter normally associated with this theory since the use of arbitrary reference volumes involved in the definition of this parameter can lead to confusion and serves no useful purpose. Values of B or χ extracted from experimental data may contain effects other than simple enthalpy contributions, so these quantities are more appropriately regarded as excess free energy parameters.

The stability of a mixed phase is assured only when the second derivative of the free energy with respect to composition is positive. For unfavorable polymer-polymer interactions (i.e., positive values of B), instability or phase separation will occur when M_A and M_B are increased to a certain critical value. In the limit $M_A, M_B \rightarrow \infty$, miscibility only exists when the polymer-polymer interactions are favorable (i.e., $B < 0$). For finite molecular weights, the combinatorial entropy is finite and always favors miscibility. The contribution of this term to the free energy becomes greater the higher the system temperature. The Flory-Huggins theory, therefore, naturally forecasts upper critical solution temperature, UCST, behavior or phase separation on cooling. However, if B is regarded as a constant, independent of temperature, this theory does not predict lower critical solution temperature, LCST, behavior which is quite common for polymer blends. The theory can be empirically modified to address this shortcoming by allowing B to be temperature dependent; the form $B(T) = B_H - TB_S$ (or the equivalent in terms of χ) is often used. However, for current purposes this increases the number of parameters to be determined so it becomes more useful to address the underlying cause via a more advanced theory.

The Flory-Huggins theory addresses phase stability in terms of constant volume. Finite compressibility adds a destabilizing influence, and often this is the origin of phase separation on heating or LCST behavior. The so-called equation of state theories account for this effect and naturally predict LCST-type phase diagrams without resorting to temperature dependent interaction energies. This class of theories retains forms similar to that of the Flory-Huggins theory for the combinatorial entropy and the interaction energy but adds free volume contributions to both the entropy and enthalpy of mixing. Here, we illustrate this class of theory by the Sanchez-Lacombe lattice fluid model (5,9). The pressure-volume-temperature relation for the components and their mixtures are represented by an equation of state that

employs characteristic parameters, denoted by asterisks, to define reduced variables, e.g., $\tilde{T} = T/T^*$, etc. These characteristic parameters may be obtained by fitting the equation of state to experimental PVT data for the components and from "mixing rules" for mixtures and copolymers. The enthalpy of mixing ΔH_m at low pressure for a binary mixture is given by

$$\frac{\Delta H_m}{V} = \tilde{\rho}^2 \Delta P^* \phi_1 \phi_2 + \tilde{\rho} [\phi_1 P_1^* (\tilde{\rho}_1 - \tilde{\rho}) + \phi_2 P_2^* (\tilde{\rho}_2 - \tilde{\rho})] \quad (2)$$

The characteristic pressure for the mixture, P^* , is related to those of the pure components, P^* , and the bare interaction energy, density, ΔP^* , by

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 \Delta P^* \quad (3)$$

where the ϕ_i are close-packed volume fractions. The reduced density $\tilde{\rho}$ refers to the mixture, whereas $\tilde{\rho}_i$ refers to the pure components. Equation (2) allows for the effects of finite compressibility on the enthalpy of mixing. The parameter ΔP^* is analogous to B in the Flory-Huggins theory (they are equal when $\tilde{\rho}_i = \tilde{\rho} = 1$) and there is a general relationship between the two (5). Expressions for other thermodynamic functions, including the free energy of mixing, have been developed (5) but are not reproduced here. This theory predicts LCST behavior even when ΔP^* is constant, independent of temperature. Thus, this theory provides a more useful framework for predicting LCST-type phase diagrams or for deducing interaction energies from such phase diagrams. Of course, the disadvantage over the Flory-Huggins theory is that PVT data for each component is required. In the case of strong enough specific interactions even ΔP^* values deduced from this framework will be temperature dependent (10).

Another potential complication is that the interaction energy is dependent on blend composition (5). The crudest measure of this interaction is the Flory-Huggins parameter B . Some of the factors this theory ignores are included in the equation of state theories, so ΔP^* is generally more free of these difficulties. Beyond these effects, departures from non-random mixing (not included in any of these mean field treatments) causes composition dependent interaction terms; ultimately the specific nature of the interaction may need to be accounted for. Minor concentration dependencies can be ignored at the expense of some loss in detail of the predicted shape of the phase diagram. For the current objectives it is more important to know the range of temperature where phase separation occurs than the precise phase diagram shape. Thus, in what follows, these issues are considered to be of only secondary importance.

Until now we have ignored the fact that polymers are often polydisperse in molecular weight and the effects this has on the phase diagram. The spinodal curve, i.e., the locus of points where the second derivative of the free energy with respect to composition is zero, can be computed from theoretical expressions by using the weight average molecular weight for each component (11). The effects of polydispersity on the coexistence or binodal curve is more complex. Theories and computer software that allow for these effects are available. The binodal and spinodal become tangent at the critical point; and, except in unusual cases of polydispersity, the critical point lies at the extreme of the binodal and spinodal curves (11). Thus, prediction of critical points, or evaluation of interaction energies at the critical point, using the weight average spinodal condition is generally adequate. Again the issue of interest here is to locate the region where this occurs rather than to predict or interpret the phase diagram in fine detail.

EXTENSION TO RANDOM COPOLYMERS

About a decade ago, a mean field binary interaction model was introduced that relates the interaction energy, B , (or χ) for blends of copolymers systems in terms of the interaction energies, B_{ij} , between monomer unit pairs i and j (2-4). The general expression is

$$B = \sum_i \sum_j B_{ij} (\phi'_i - \phi''_j) (\phi''_i - \phi'_j) \quad (4)$$

where ϕ'_i and ϕ''_i are the volume fractions of i units in copolymers A and B, respectively, and $B_{ij} = 0$ with no double counting in the sum. The positive terms in this expansion stem from intermolecular interactions, i.e., i and j interactions between copolymers A and B, while the negative terms reflect intramolecular interactions within each of the copolymers. Thus, it is possible that B is negative even

though all B_{ij} are positive (4). An equivalent expression can be written for ΔP^* from the Sanchez-Lacombe theory in terms of ΔP_{ij}^* parameters for the i, j pairs. The present treatment does not consider issues of sequence distribution.

EXPERIMENTAL

The approaches for evaluating the binary interaction energies for monomer unit pairs, B_{ij} in the Flory-Huggins or ΔP_{ij}^* in the Sanchez-Lacombe frameworks, are somewhat limited. The discussion here will be limited to three approaches, viz., the critical molecular weight technique, analysis of isothermal phase maps that divide copolymer compositions forming miscible blends from those that do not, and quantitative analysis of phase diagrams, which have proved useful in our laboratory. Other techniques like small angle neutron scattering have been used by others on a more limited basis. In all cases, it is necessary to bring units i and j into intimate contact by forming a homogeneous phase in order to assess B_{ij} or ΔP_{ij}^* . This is an important point that can be addressed, when this interaction is unfavorable, by use of copolymers or the critical molecular weight approach.

Critical Molecular Weight Method

Figure 2 illustrates the concept of this method. For a polymer pair that has an unfavorable heat of mixing (or non-combinatorial free energy of mixing in more general terms), immiscible blends are formed when the components have high molecular weights; however, by decreasing the chain length of either or both components, the combinatorial entropy can be made a more and more dominant term in the free energy. The critical B_c (see Fig. 2) for miscibility increases as the molecular weights are lowered; miscibility results when $B < B_c$. Thus, B can be calculated if the critical molecular weights of the components can be determined. This approach is especially useful for polymers like polystyrene, poly(methyl methacrylate), etc. where standards of narrow polydispersity and widely varying molecular weight are readily available through anionic or other highly controlled synthesis techniques. In some cases end group effects may need to be accounted for (12,13). Figure 3 shows contours of fixed B for a given temperature and densities of the components; miscible blends are formed when the molecular weights of polymers A and B are in the region left and below the contour for a given B . Diagrams like Fig. 2 define in practice the circumstances where this technique can be useful.

Poly(methyl methacrylate), PMMA, does not form miscible blends with polystyrene, PS, or poly(α -methyl styrene), P α MS, when the components have ordinary molecular weights typical of commercial materials. However, by dramatically lowering the molecular weight of each polymer, miscibility can be achieved (12). The PMMA-PS system shows UCST behavior while the PMMA-P α MS system shows LCST behavior. In terms of the Sanchez-Lacombe equation of state analysis, LCST behavior is likely when the characteristic temperatures of the two components, $\Delta T^* = |T_i^* - T_j^*|$, are significantly different, the T^* for PMMA is much closer to that of PS than it is to the T^* for P α MS (12). Using experimental PVT data, the Sanchez-Lacombe theory correctly predicts that the blends with PS should show a UCST and that the blends with P α MS should show an LCST. The nature of the phase diagram is strongly influenced by both ΔP^* and ΔT^* .

In some cases, lowering the component molecular weights in discrete steps results only in an observed change from immiscibility to miscibility without producing a quantifiable phase diagram. In such cases, only upper and lower bounds on the interaction energy can be deduced. Generally the method of synthesis of polymers leads to one or both end groups with structures that differ somewhat from that of the polymer repeat unit. At quite low molecular weights these end groups can become a significant enough perturbation to the overall structure and, thus, the energy density to merit attention. Several approaches for dealing with this issue are available. The observed interaction energies can be extrapolated to the high molecular weight limit when sufficient data are available, and a form of the binary interaction model, eq. 4, can be used to aid this correction when information about the interactions between end groups and relevant monomer units is available (12,13). Finally, there are synthetic possibilities for making the end groups look more like the polymer repeat unit which can minimize or eliminate this concern.

Copolymer Composition Mapping

For homopolymer-copolymer, copolymer-copolymer, copolymer-terpolymer, etc. binary blends the applicable value of B is given by eq.4. If the molecular weights of polymers A and B are fixed, then the critical value for miscibility, given in Fig. 2, is fixed. Copolymer compositions that cause $B < B_c$ to be

negative form miscible blends while in the composition region where $B-B_c$ is positive the blends are immiscible. An experimental composition map for blends of styrene/acrylonitrile copolymers with methyl methacrylate/t-butyl methacrylate is shown in Fig. 4. The open points denote blends found to be miscible while closed points denote blends found to be immiscible at 130°C. The theory predicts these regions should be separated by a conic section; the exact shape is defined by the relative values of the B_{ij} parameters and B_c . Matching the theory to the experimental composition map has proved to be a powerful tool for deducing B_{ij} or ΔP_{ij}^* parameters (4-7,14). Of course there are both theoretical and practical limits on how many parameters can be meaningfully extracted from such fitting procedures (5,6,14).

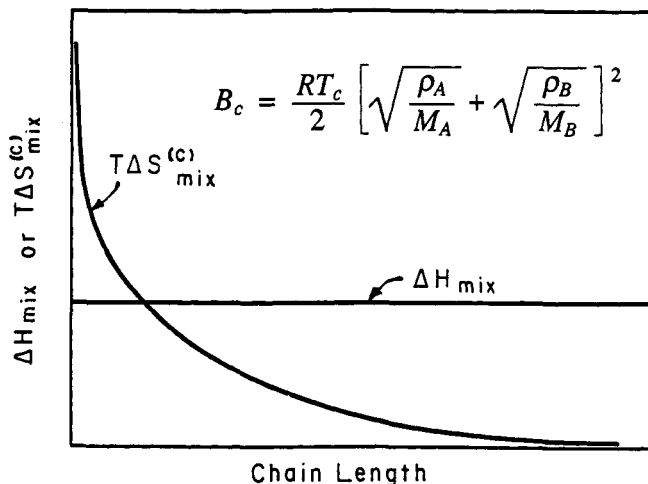


Fig.2 Thermodynamic basis of critical molecular weight method. Equation defines B_c .

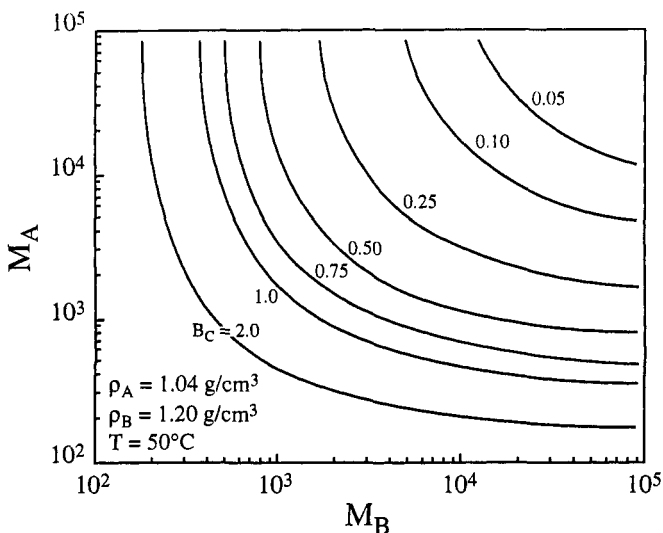


Fig.3 Contours of fixed B_c (in cal/cm³) that define the boundary between miscible and immiscible blends formed from polymers A and B of varying molecular weights for the densities and temperature shown.

Of course, the copolymer mapping and critical molecular weight approaches can be combined to advantage. Suppose a series of styrene copolymers with monomer X (e.g., acrylonitrile, maleic anhydride, methyl methacrylate, etc.) is available in different compositions all having the same high molecular weight. To evaluate the interaction of styrene with monomer unit X, one could explore the miscibility of the SX copolymers of composition ϕ_x with monodisperse PS of varying molecular weight, M. The boundary between miscible and immiscible blends at fixed T on ϕ_x versus M coordinates can be expressed as

$$\left(\frac{\rho}{M_w}\right)_{sx}^2 + \left(\frac{\rho}{M}\right)_s^2 = \phi_x \left(\frac{2B_{sx}}{RT}\right)^2 \tag{5}$$

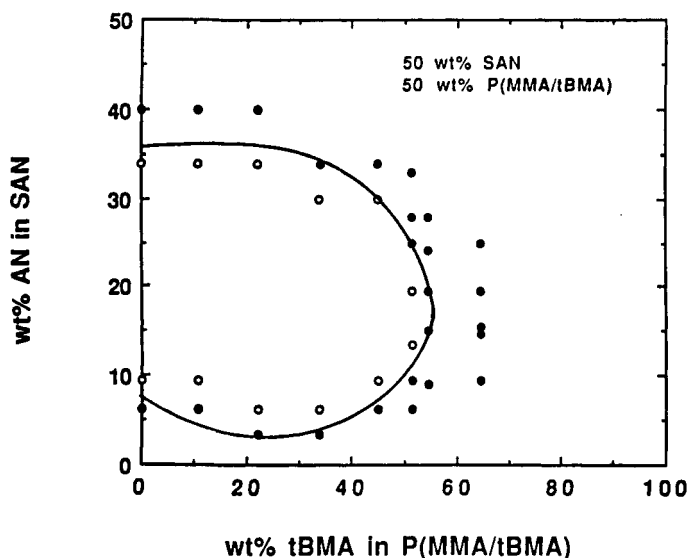


Fig.4 Example of an isothermal copolymer-copolymer miscibility map. Points denote blend determined to be miscible (open) and immiscible (closed).

Quantitative Analysis of Phase Diagrams

As stated earlier, polymer blends often show LCST behavior; and if the phase diagram can be accurately determined, then useful information about interaction energies can be extracted from this data within the framework of an appropriate theory. Usually the measurements consist of determining a "cloud" point, by some optical observation, or a "phase separation" temperature, by a technique like differential scanning calorimeter that monitors the glass transition behavior following annealing the blend at a series of temperatures (5). The first concern is whether such observations reflect the equilibrium phase diagram or kinetic artifacts. Extreme care must be exercised to avoid being misled by slow phase separation kinetics, solvent-induced phase separation, or fortuitous refractive index matching/mismatching as temperature is changed (5). The next issue concerns what the observed cloud point or phase separation temperatures actually correspond to on the phase diagram. Do they correspond to the binodal or spinodal curve or something in between? It would be convenient if they reflect the spinodal curve since this is easier to interpret computationally and thermodynamically due to polymer polydispersity issues. Phase separation is more rapid inside the spinodal than it is between the binodal and spinodal, so for certain kinetically limited systems closer correspondence to the spinodal may be likely. Rather elaborate scattering techniques can unequivocally determine the spinodal temperature. If there is evidence that the observations correspond to the binodal curve, then the latter can be calculated, including effects of polydispersity, and compared to the experimental results for interaction parameter determination. A useful alternative is to determine phase separation as near the critical composition as possible since here the spinodal and binodal coincide. The critical composition can be estimated a priori using the thermodynamic model. In extreme cases of polydispersity the critical point may not lie at the minimum or maximum temperature of the phase boundary, but such issues are only minor concerns for present purposes.

This approach is especially useful for copolymer systems. This is illustrated for blends of PMMA with a series of α -methyl styrene/acrylonitrile copolymers in Fig. 5. The left side shows the experimental phase separation temperatures for blends with fixed PMMA content near the critical point as a function of the wt.% AN in the copolymer. At the high molecular weights employed in this series of experiments, P α MS and PMMA are not miscible. By adding acrylonitrile to the α -methyl styrene polymer, miscibility occurs over a certain range of AN content. The phase separation temperature (LCST type) rises above the blend preparation temperature (150°C), goes through a maximum at 15-20% AN and then drops below 150°C at ~30% AN. With the available molecular weight and characteristic parameters for each blend component, the observed phase separation temperature can be used to calculate ΔP^* for each blend using the equation of state theory (14). These are the points shown in Fig. 5b. Via the equivalent of eq. 4, ΔP^* can be expressed in terms of the ΔP_{ij}^* for the three pairs MMA/ α MS, α MS/AN, and MMA/AN. Ideally, all three ΔP_{ij}^* might be deduced by fitting the model curve to the ΔP^* points. Depending on the extent and accuracy of the data points, it may be advisable to input some ΔP_{ij}^* from other observations to reduce the number of parameters extracted from the regression in order to obtain

more reliable values (14). As indicated earlier, the Flory-Huggins B can be computed from ΔP^* . This is shown in Fig. 5b along with the critical value of B (at 150°C) for these systems; the two are useful for quickly determining the region of AN composition where miscibility occurs. Note that B is considerably less "exothermic" than ΔP^* ; this reflects both the enthalpic and entropic equation of state effects lumped into this composite parameter.

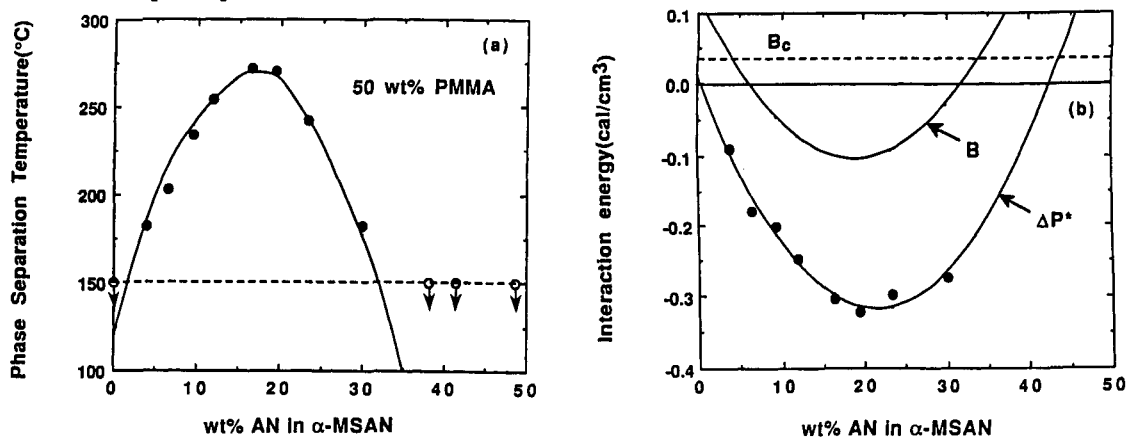


Fig. 5 An example of quantitative analysis of phase diagrams (LCST type) for homopolymer-copolymer blends

It is interesting to note that blends of PMMA with styrene/acrylonitrile copolymers, SAN, show a similar window of miscibility. However, the phase separation temperatures are much higher in the SAN case; some are above the limit of thermal decomposition of the components. The main reason for this is the smaller value of ΔT^* for the PMMA/SAN pairs compared to the PMMA/ α -MSAN systems (14).

APPLICATIONS

Table 1 shows a brief summary of B_{ij} and ΔP_{ij}^* parameters that have been determined to date by the approaches outlined above (5,14). From these values, the interaction energy, B or ΔP^* , can be computed via eq. 4 for any pair of homopolymers, copolymers, terpolymers, etc. comprised of just these units and used to predict various levels of information about the phase behavior of the blend (see Fig. 1). The Flory-Huggins theory is useful if one only wishes to know whether miscibility occurs or not, but an equation of state theory is generally needed to answer more detailed questions about the phase diagram. For phase separated systems, interfacial tension is an important factor in determining the phase morphology formed during melt processing while the interfacial thickness determines the extent of adhesion between the two polymer phases. Both can be computed if the polymer-polymer interaction energy, B , is known (13).

TABLE 1. Typical interaction energies

Monomer unit pair	ΔP_{ij}^*	B_{ij}	at T
styrene/acrylonitrile	7.37 cal/cm ³	7.02 cal/cm ³	120°C
α -methyl styrene/acrylonitrile	8.60	7.96	150
styrene/methyl methacrylate	0.23	0.23	120
α -methyl styrene/methyl methacrylate	0.02	0.12	150
α -methyl styrene/vinyl chloride	0.26	0.37	130
methyl methacrylate/acrylonitrile	4.44	4.32	150
vinyl chloride/acrylonitrile	4.30	4.24	130

LIMITATIONS

It is important to close by pointing out the limitations of the approach described here. We have employed simple theories that are based on a mean field treatment of the polymer-polymer interactions; this is probably inherent for any scheme that attempts what amounts to a group contribution approach, i.e., deducing parameters for one system and applying them in another. A different framework is needed for strong specific interactions. An unanswered question is how far the mean field approach can be pushed

before it ceases to be useful (i.e., for which kinds of systems) for the pragmatic purposes outlined here. One aspect of this issue is that ΔP^* (but not B) has been assumed independent of temperature and composition - which will not be true when the interactions lead to sufficiently non-random mixing and have an inherent temperature dependence. For our purpose a small composition dependence of ΔP^* is not so serious since this mainly affects the shape of the phase diagram; we are more concerned about the temperature range where the phase boundary lies. Significant temperature dependence of ΔP^* is a more serious concern for this objective.

Another issue that could affect whether ΔP_{ij}^* or B_{ij} values are truly transportable from one system to another has to do with unit sequence distribution. That is, in-chain inductive effects could cause the interaction of i with j to be different depending on whether j is adjacent in the chain to k or l , etc. Formal theories have been proposed for dealing with this possibility, at the expense of additional parameters (8); but no theory of the inductive effect itself has appeared. When the i and j units are chosen to be very small (only a few atoms), especially when smaller than monomer units, this type of effect is more likely to be a problem. Unambiguous critical tests, involving units as large as typical monomer units, have not yet revealed cases where such issues pose serious limitations for current purposes.

One of the most severe known limitations of applying this scheme is that for copolymer systems eq. 4 often involves taking the difference of relatively large values of B_{ij} or ΔP_{ij}^* to compute a much smaller value of B or ΔP^* . Thus, errors in B_{ij} or ΔP_{ij}^* are amplified in importance. Furthermore, the temperature location of the phase boundary is an extremely sensitive function of the value of ΔP^* . Thus, inaccuracies in the unit pair interactions are greatly amplified in the predictions made from them. Consequently, to be of most value, the experiments and data analysis must be done very carefully. Clearly better experimental techniques and theories would be of enormous value for achieving the goals outlined here.

ACKNOWLEDGEMENT

Financial support of this work has been provided by the National Science Foundation grants Numbers DMR-89-00704 and DMR-92-15926 administered by the Division of Material Research - Polymers Program.

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