Thermodynamic Characterization of Polymer-Polymer Interfaces

G. D. Merfeld and D. R. Paul*

Department of Chemical Engineering and Texas Materials Institute

The University of Texas at Austin, Austin, TX 78712, U S A

SUMMARY: The properties of multiphase polymer blends are determined in part by the nature of the polymer-polymer interface. The interfacial tension, γ, influences morphology development during melt mixing while interfacial thickness, λ, is related to the adhesion between the phases in the solid blend. A quantitative relation between the thermodynamic interaction energy and these interfacial properties was first proposed in the theory of Helfand and Tagami and has since been correlated with experimental measurements with varying degrees of success. This paper demonstrates that the theory and experiment can be unified for polymer pairs of some technological importance: copolymers of styrene and acrylonitrile (SAN) with poly (2, 6-dimethyl-1, 4-phenylene oxide) (PPO) and with bisphenol-A polycarbonate (PC). For each pair, the overall interaction energy was calculated using a mean-field binary interaction model expressed in terms of the interactions between repeat unit pairs extracted from blend phase behavior. Predictions of γ and λ as a function of copolymer composition made by combining the binary interaction model with the Helfand-Tagami theory compare favorably with experimental measurements.

Introduction

The structure and properties of a blend of polymers A and B are determined in large measure by the energetic interaction between A and B. When the interaction is more favorable than a critical value, the mixture forms a single homogeneous phase; however, when the interaction is less favorable than this critical value, the mixture separates into A-rich and B-rich phases. The boundaries (in terms of temperature, molecular weight, copolymer composition, etc.) between miscibility and immiscibility, or the phase diagram, are governed by the thermodynamic energy of interaction. In addition, the nature of the interface between the A-rich and B-rich phases in immiscible mixtures is also governed by this thermodynamic interaction energy. Thus, if suitable theories exist, experimental determination of appropriate phase diagram information should allow predictions of interfacial properties. This interconnection would be useful since measurements of interfacial tension and thickness are generally more difficult than establishing the boundaries between miscibility and immiscibility. The following

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summary of recent observations demonstrates that this interrelationship can be made quite successfully, for at least two systems of some importance, using existing theories [1-3].

Theoretical Framework for Establishing Polymer-Polymer Interactions

The phase behavior of mixtures is governed by the Gibbs free energy of mixing and how it depends on concentration, temperature, and the nature of the components. The simplest such expression for mixing a unit volume of monodisperse polymers A and B is the classical result

$$\Delta g_{\mathrm{mix}} = B\phi_A\phi_B + RT\left[\frac{\rho_A\phi_A\ln\phi_A}{M_A} + \frac{\rho_B\phi_B\ln\phi_B}{M_B}\right] \tag{1}$$

where B is a binary interaction energy density, R is the gas constant, T is the absolute temperature, and ρ_i, ϕ_i, and M_i are the density, volume fraction and molecular weight of component i, respectively. This equation combines a Hildebrand-Scatchard-van Laar type heat of mixing with an expression for the combinatorial entropy of mixing given by Flory and Huggins [4,5]. In equation 1, B is an excess free energy term in which the heat of mixing plus other noncombinatorial effects are lumped. A parameter χ can be used in place of B and is related by the expression

$$\chi = \frac{B\mathrm{V}_{\mathrm{ref}}}{\mathrm{RT}} \tag{2}$$

where $\mathrm{V}_{\mathrm{ref}}$ is a reference volume which usually is taken as the molar volume of one of the repeat units in the system. However, χ is not well suited for current purposes because its value is dependent on the arbitrarily (and sometimes ambiguously) defined $\mathrm{V}_{\mathrm{ref}}$. Therefore, the use of the B parameter, which Flory identified as sometimes preferred when dealing with heterogeneous polymers [6], is strongly recommended. The relative balance between the energetic and entropic contributions to mixing determine whether the mixture forms one or two phases. The critical value of B is given by

$$B_{critical} = \frac{RT}{2}\left(\sqrt{\frac{\rho_A}{\left(\overline{M}_W\right)_A}} + \sqrt{\frac{\rho_B}{\left(\overline{M}_W\right)_B}}\right)^2 \tag{3}$$

where $\left(\overline{M}_W\right)_i$ is the weight average molecular weight of component i [7,8]. Miscibility exists when B is less than this critical value while phase separation occurs when B is larger than this value.

A simple mean field approximation for the quantitative representation of polymer-polymer interactions [9-11] has proven to be extremely useful for blends of copolymers when the interactions are not highly specific. This binary interaction model resolves interactions down to the repeat unit or structural segment level and considers pair-wise interactions that may occur between different polymers (*inter*molecular) and within a copolymer (*intra*molecular). The model assumes that polymer interactions can be represented in terms of the interactions that exist between repeat units and that the interactions of a given segment are unaffected by the neighboring segments to which it is covalently joined. Also, since the model draws upon the statistics of a mean field approximation to determine the probability of pair-wise interactions, it naturally assumes random mixing. This requires the copolymers themselves to be relatively random with respect to the distribution of segment types along their chain structures. Strictly speaking, the use of a mean-field approximation excludes specific interactions such as hydrogen bonding that may create spatial or directional ordering which would compromise the random mixing approximation; however, many such systems have been modeled with this simple formalism. The most general form of this model for mixing two polymers A and B containing an unlimited number of repeat units is given by

$$B = \overset{\text{Inter}}{\underset{i>j}{\sum}} B_{ij}\phi_i\phi_j - \overset{\text{Intra}}{\underset{i>j}{\sum}} B_{ij}\phi_i\phi_j \tag{4}$$

This reduces to the following special case

$$B = B_{13}\phi_1 + B_{23}\phi_2 - B_{12}\phi_1\phi_2 \tag{5}$$

for mixing a copolymer of units 1 and 2 with a homopolymer comprised of 3 units where ϕ_i refers to the volume fraction of i units in the polymer.

Polymer blend phase behavior can be predicted or analyzed by inserting the binary interaction model into the thermodynamic framework of either the Flory-Huggins theory or an appropriate equation-of-state theory. The simplicity of the Flory-Huggins theory makes it useful for evaluation of isothermal phase boundaries, miscibility maps, or UCST type phase separation. To treat LCST type phase separation without resorting to empiricisms of the Flory-Huggins theory, it is necessary to employ an equation-of-state analysis. In using either of these theories, it is simplifying to assume, for experimental and computational ease, that phase observations are made at the spinodal condition. This assumption is assured for blends at or near the critical composition where the binodal and spinodal curves overlap. Typically, the blend critical composition is about 50/50 by weight for polymers of roughly similar molecular weight. But for blends whose components differ significantly in molecular weight, the critical composition shifts toward the lower molecular weight component; the adjusted critical composition can be calculated as shown elsewhere 8).

Although polymer blend phase behavior is determined predominately by the nature of the molecular interactions, it may also be influenced by many other factors including molecular weight, copolymer composition, blend ratio, temperature and pressure. Systematically changing one of these variables or a combination of them and studying the effect produced on phase behavior affords an opportunity to characterize the relevant binary interaction parameters. Of the variables mentioned, molecular weight, copolymer composition, and temperature are most commonly studied. The so-called critical molecular weight technique is useful when a change in polymer molecular weight causes a change in miscibility 12,13). A recent review (1) summarizes values of B_{ij} for many repeat unit pairs of interest determined by this strategy and other methods such as small angle neutron scattering.

Theory of Polymer-Polymer Interfaces

As discussed above, binary interaction energies play a defining role in determining the phase behavior of polymer blends. These interactions are also important in phase separated systems since they strongly influence the nature of the interface between phases which, in turn, is a factor in determining morphology (via interfacial tension) in the melt state and adhesion (via interfacial thickness) in the solid state. A quantitative relation between the thermodynamic interaction energy and interfacial properties was first proposed by Helfand and Tagami 14). The generalized theory formulated by Helfand and Sapse 15) for infinite molecular weight polymers describes the interfacial thickness, λ, as

$$\lambda = \sqrt{\frac{2RT}{B}}\left(\beta_A^2 + \beta_B^2\right)^{1/2} \tag{6}$$

In this expression, B is the interaction energy density and β_i is related to the dimension of the polymer coil by

$$\beta_i = \sqrt{\frac{\rho_i}{6}}\left(\left\langle r_i^2 \right\rangle / M_i\right)^{1/2} \tag{7}$$

where $\left\langle r_i^2 \right\rangle$ is the mean square unperturbed end-to-end chain distance and M_i is the molecular weight. Similarly, the interfacial tension, γ, is expressed in the same nomenclature as

$$\gamma = \sqrt{\frac{RTB}{2}}\left(\beta_A + \beta_B\right)\left[1 + \frac{1}{3}\frac{\left(\beta_A - \beta_B\right)^2}{\left(\beta_A + \beta_B\right)^2}\right] \tag{8}$$

Equations 7 and 8 assume infinite molecular weights of both components; more recently, Broseta *et al* 16) extended the theory to treat finite molecular weights. For blend systems that include copolymers, the appropriate form of the binary interaction model, e.g., equation 5, can be used to evaluate B provided the appropriate B_{ij} values are known.

Comparison of Theory and Experiment

On the whole, predictions of λ and γ have been correlated with experimental measurements with varying degrees of success. Caution must be exercised in such comparisons, however, because the measurements are difficult and require extreme care in preparing the samples, executing the experiments, and interpreting the data. Furthermore, limitations of the theory must be recognized. When these issues are carefully considered, impressive agreement between theory and experiment has been found as illustrated below for two systems of some commercial interest both involving styrene/acrylonitrile copolymers (SAN) of varying AN content.

Figure 1 shows results for interfaces formed between bisphenol-A polycarbonate (PC) and

SAN copolymers. For this system, the PC/SAN interaction energy shows a minimum, but positive, value near the azeotropic composition for SAN copolymer, i.e., ~25% wt. AN 2). Thus, the theory predicts that interfacial thickness is at a maximum at this composition while the interfacial tension is at a minimum. Mansfield 17,18) has reported an experimental value for λ measured by neutron reflectivity near this composition that is in excellent agreement with the prediction of theory, see Figure 1a. Watson and Hobbs [19] measured the interfacial tension by a capillary thread instability method for PC and a series of SAN copolymers with the results shown in Figure 1b. The agreement with theory is generally good. These trends in λ and γ also correlate very well with observations on morphology, interfacial adhesion, and mechanical properties for this system as described by Callaghan et al [2].

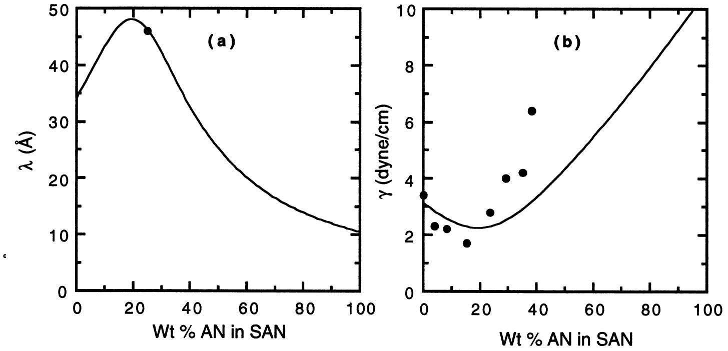

Fig. 1 Interfacial properties of PC and SAN as a function of copolymer composition (see reference 3). (a) Interfacial thickness calculated using equation 6 and binary interaction energies reported in the literature compared to a measurement made by neutron reflectivity (see reference 17). (b) Interfacial tension calculations based on equation 8 compared to measurements made by capillary thread instability (see reference 19). Calculations made at 140°C using $B_{S/PC} = 0.43$, $B_{PC/AN}=4.5$, and $B_{S/AN}=7.0$ cal/cm^3.

Figure 2 shows the interfacial thickness for PPO bilayers with SAN copolymers measured (solid points) by neutron reflectivity [3]. The solid curve is the theoretical prediction from thermodynamically measured values of B_{ij}. The agreement is quite good. For this system, PPO is miscible with polystyrene and miscibility is maintained until about 12% wt. of AN in the SAN copolymer. The PPO/SAN interaction energy is predicted to monotonically increase with AN content from negative values through the critical interaction energy and continuing to become more positive with higher AN levels. This correctly explains the trend in λ versus %AN observed by neutron reflectivity.

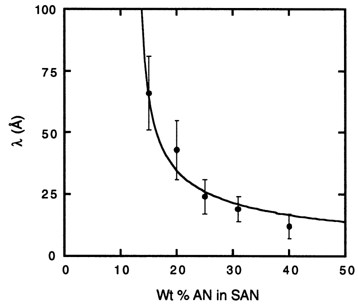

Fig. 2 Neutron reflectivity measurements and theoretical prediction of the PPO/SAN interfacial thickness as a function of SAN composition (see reference 3). The prediction is made using the interfacial theory formulated by Helfand and coworkers combined with the binary interaction model. The interface broadens exponentially as the AN content in the copolymer decreases toward the miscibility limit where SAN copolymers containing approximately 12 wt% and less re miscible with PPO. Calculations were made at 140°C using $B_{PPO/S}$=-0.34, $B_{PPO/AN}$=9.2, and $B_{S/AN}$=7.0 cal/cm^3.

Conclusion

The binary interaction approach provides a useful way of representing polymer-polymer interaction energies for copolymer systems. There is a growing body of literature on quantitative estimates of interaction energies between repeat unit pairs, B_{ij}, that can be utilized in the design and optimization of new polymer blends. This paper demonstrates that interfacial properties of immiscible blends can be predicted from this information using current theories of polymer-polymer interfaces and interactions.

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