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Prediction of interfacial tension of immiscible polymer pairs using a square gradient theory combined with the FOV equation-of-state free energy expression

Ho Sang Lee and Won Ho Jo*
Department of Fiber and Polymer Science, Seoul National University, 151-742 Seoul, Korea

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Interfacial tension between polystyrene and polybutadiene is predicted by using a square gradient theory in conjunction with the Flory–Orwoll–Vrij equation-of-state expression for the free energy of mixing. The equation-of-state interaction parameter is determined by fitting the theory to the experimental cloud points. The square gradient coefficient is also calculated by the relation derived from a scattering function. The combined theory for interfacial tension predicts a magnitude and temperature dependence of interfacial tension although no adjustable parameter is used in calculating interfacial tension. The molecular weight dependence of interfacial tension is also predicted, and well described by a relation $\gamma = \gamma_\infty + CM_n^{-z}$ where $z = 2/3$ for low molecular weight species and $z = 1$ for higher molecular weight species. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The interfacial tension, γ, between immiscible polymer pairs has been of great theoretical and practical interest. Since the interfacial property can greatly affect the mechanical properties of polymer blends, the structure and thermodynamic state of polymers at the interface have become important issues. Particularly, interfacial tension is the most important interfacial property because it very often controls the morphology of multiphase polymers[1]. Interfacial tension is a thermodynamic property of the system which can be calculated directly from statistical thermodynamic theories. A number of thermodynamic theories have been developed for calculating the interfacial tensions of polymer blends by several workers[2–6].

Anastasiadis *et al.*[7] proposed a square gradient theory[8] in conjunction with the Flory–Huggins expression[9] for the free energy of mixing. In this approach, the magnitude of interfacial tension was strongly dependent upon the value of the interaction parameter, χ. Since it is not always easy to determine the exact value of the temperature-dependent χ-parameter, the prediction of the interfacial tension from the theory is very limited.

In formulating theories for surface tension, Poser and Sanchez[5], and Dee and Sauer[10] adopted the lattice fluid (LF) theory[11] and Flory–Orwoll–Vrij (FOV) equation-of-state theory[12], respectively. However, Poser and Sanchez[5] have not calculated the interfacial tension of the polymer–polymer interface, although they have calculated the interfacial tension between polymer and oligomer liquids using their formula. Moreover, they used the interaction parameter and the square gradient coefficient as adjustable parameters to achieve a quantitative agreement with the experimental data. The use of these fitting parameters may reduce the usefulness of such theories and sometimes makes systematic analysis difficult. Dee and Sauer[10] reported that the FOV equation might provide a better description of the molecular weight and temperature dependence of surface tension for polymer blends as compared to the LF theory. They also used the square gradient coefficient as an adjustable parameter. Moreover, they did not attempt to calculate the interfacial tension of polymer pairs, although they calculated the surface tension of polymer blends.

In this study, the square gradient coefficient is theoretically determined by following the approach of Anastasiadis *et al.*[7], and from this the interfacial tension between polystyrene (PS) and polybutadiene (PBD) is calculated using a square gradient theory combined with the FOV equation-of-state theory. The equation-of-state interaction parameter X_{AB} is determined by fitting the binodal curve from the equation-of-state theory to the experimental data[13]. The effects of temperature and molecular weight on the interfacial tension are also examined for PS–PBD systems.

THEORY

The extension of the Cahn–Hilliard (CH) theory[8] to multicomponent is well documented[14,15]. The application of the FOV equation-of-state theory to polymer solutions and blends has been studied by many workers[16–18]. However, the use of the CH theory in conjunction with the FOV equation-of-state theory to describe the interfacial tension of polymer blends has not been reported yet. Although Dee and Sauer[10] reported that they derived the equation for surface tension using the CH theory in

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* To whom correspondence should be addressed

conjunction with the FOV equation-of-state theory by following the Poser and Sanchez approach, they did not extend their theory for calculating the interfacial tensions of polymer blends.

The basis of the CH theory is the assumption that the free energy per unit volume in a region of nonuniform composition is a function of both the local composition ϕ and the composition of the immediate environment. The total free energy for the mixture of volume V is

$$G = \int_V [G_0(\phi) + \kappa(\nabla\phi)^2 + \ldots]\, dV \tag{1}$$

where $G_0(\phi)$ is the free energy density of a uniform system of composition ϕ and $\kappa(\nabla\phi)^2$ is the additional composition contribution to the free energy arising from the local concentration gradient.

Following the development by Cahn and Hilliard[8], the interfacial tension between two coexisting phases α and β is given for a one-dimensional composition change as

$$\gamma = 2\int_{\phi_\alpha}^{\phi_\beta} (\kappa\Delta g(\phi))^{1/2}\, d\phi \tag{2}$$

where ϕ_α and ϕ_β are the volume fractions of the two coexisting phases and $\Delta g(\phi)$ is the excess free energy density of the uniform system with respect to a standard state of an equilibrium mixture α and β. The excess free energy density $\Delta g(\phi)$ is defined by

$$\Delta g(\phi) = \Delta G_0(\phi) - [n_A\Delta\mu_A(\phi_e) + n_B\Delta\mu_B(\phi_e)] \tag{3}$$

where n_A and n_B are the number density of molecules of type A and B, respectively, ϕ_e is the equilibrium composition of either of the coexisting phases, and $\Delta\mu_A$ and $\Delta\mu_B$ are the changes in chemical potentials of A and B. It is noteworthy that any mean-field fluid model can be used for determining the value of $\Delta g(\phi)$ in equation (2).

To calculate the γ, one must know the value of the coefficient of square gradient, κ, the excess free energy, $\Delta g(\phi)$, and the composition of coexisting phases α, β. First, an equation-of-state theory is employed in this paper for calculating the value of $\Delta g(\phi)$. According to Flory *et al.*[12], the reduced equation of state is given by

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 1)} - \frac{1}{\tilde{T}\tilde{v}} \tag{4}$$

where $\tilde{p} = p/p^*$, $\tilde{T} = T/T^*$ and $\tilde{v} = v/v^*$ are the reduced pressure, temperature and volume with respective to the corresponding characteristic properties, p^*, T^* and v^*, respectively.

The application of this equation-of-state to a mixture of N_A r_A-mers and N_B r_B-mers is based on the mean-field approximation. The equation-of-state for a two-component mixture has a form identical to that for the pure component if the following mixing rules are made

$$p^* = \phi_A p_A^* + \phi_B p_B^* - \theta_A\phi_B X_{AB} \tag{5}$$

$$T^* = p^*/(\phi_A p_A^*/T_A^* + \phi_B p_B^*/T_B^*) \tag{6}$$

$$\theta_B = s_B\phi_B/(s_A\phi_A + s_B\phi_B) \tag{7}$$

where ϕ_A and ϕ_B denote the segment fractions of components A and B, respectively, θ_B is the surface fraction of component B, and X_{AB} is defined as a parameter arising from the difference in interaction energy between like and unlike segmental pairs. In equation (7), s_i is the ratio of surface area per unit core volume which can be estimated by the Bondi's group contribution method[19]. In the equation-of-state theory, the chemical potential of component A in a mixture is given by

$$\Delta\mu_A/RT = \ln\phi_A + (1 - r_A/r_B)\phi_B + \frac{p_A^* V_A^*}{RT}\left\{3\tilde{T}_A \ln\left(\frac{\tilde{v}_A^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right) + \left(\frac{1}{\tilde{v}_A} - \frac{1}{\tilde{v}}\right)\right\} + \frac{V_A^* X_{AB}\theta_B^2}{\tilde{v}RT} \tag{8}$$

where V_A^* is the molar core volume of component A. When subscripts A and B are interchanged, one obtains an expression for the chemical potential of component B, $\Delta\mu_B$. Then, the excess free energy, $\Delta g(\phi)$ is calculated by substituting the value of $\Delta\mu_A$ and $\Delta\mu_B$ into equation (3). The composition, ϕ_α and ϕ_β, of the coexisting phases α and β at equilibrium are determined by equating the chemical potentials:

$$(\Delta\mu_A)_\alpha = (\Delta\mu_A)_\beta \text{ and } (\Delta\mu_B)_\alpha = (\Delta\mu_B)_\beta \tag{9}$$

Finally, the coefficient of square gradient, κ, is determined by following the approach of Anastasiadis *et al.*[7]. They derived the coefficient by using a linear response theory within the framework of the random phase approximation[20,21]. de Gennes[21] suggested that the chain experiences no force and remains ideal in a dense system. Therefore, an ideal single chain approximation can be employed in the calculation of the scattering function, $S(\mathbf{q})$, where $\mathbf{q}$ is the scattering vector. The scattering function is related to the volume fractions and the chain length by[21,22]

$$\frac{1}{S(\mathbf{q})} = \frac{1}{\phi_A f_D(N_A, \mathbf{q})} + \frac{1}{\phi_B f_D(N_B, \mathbf{q})} - 2\chi \tag{10}$$

where $f_D(N_A, \mathbf{q})$ is the Debye function[23], defined as

$$f_D(x) = \frac{2}{x^2}(x + \exp(-x) - 1) \tag{11}$$

with $x = N^2q^2b^2/6 = q^2 < r_0^2 > /6 = q^2R_G^2$, where b is the Kuhn statistical segment length, $< r_0^2 >$ is the mean square end-to-end distance, and R_G is the radius of gyration. From the two limiting expressions for $S(\mathbf{q})$ which can be calculated for $qR_G \gg 1$ and $qR_G \ll 1$, the square gradient coefficient can be obtained. The square gradient coefficients, κ, for the narrow interphase and the broad interphase are given as follows:

$$\frac{\kappa_{\text{narrow}}}{kT} = \frac{\langle r_0^2\rangle_A}{24\phi V_A} + \frac{\langle r_0^2\rangle_B}{24(1-\phi)V_B} \quad (qR_G \gg 1) \tag{12}$$

$$\frac{\kappa_{\text{broad}}}{kT} = \frac{\langle r_0^2\rangle_A}{36\phi V_A} + \frac{\langle r_0^2\rangle_B}{36(1-\phi)V_B} \quad (qR_G < 1) \tag{13}$$

Equation (13) and its equivalent for a symmetric system have been widely used[24,25] to model the dynamics of concentration fluctuations in binary polymer blends near the critical point, whereas equation (12) has been used to study micelle formation in homopolymer–copolymer mixtures[26]. Here we used equation (13) for calculating the square gradient coefficient.

RESULTS AND DISCUSSION

The square gradient theory (SG-FOV) combined with the FOV equation-of-state theory has been used for calculating

Table 1 Characteristic parameters for pure polymers

Polymer	p^* (J/cm^3)	T^* (K)	v^* (cm^3/g)
PS[a]	506.0	7948	0.8205
PBD[b]	488.5	6494	0.9435

[a] From Ref. 30
[b] From Ref. 31

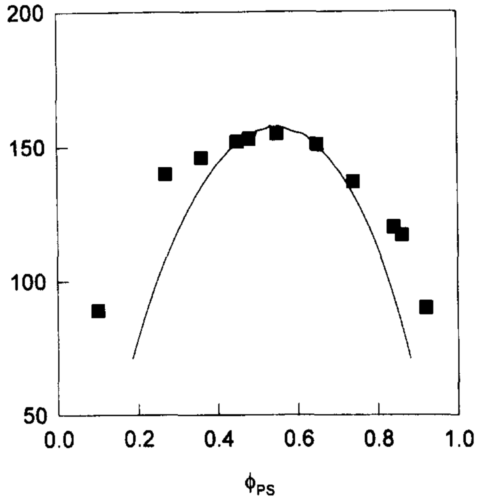

Figure 1 A comparison of a simulated binodal curve of PS–PBD blends using the FOV equation of state with experimental cloud points[13], from which an EOS interaction parameter X_{12} is determined. The experimental cloud points were determined for the blend system of PB (M_w = 2400 g/mol) and PBD (M_w = 2400 g/mol)

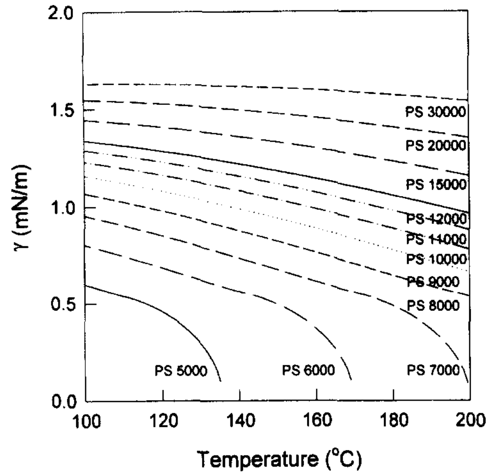

Figure 2 The calculated interfacial tension for PS–PBD blends by use of a square gradient theory combined with the FOV equation-of-state expression for the free energy of mixing. The molecular weight of PS is varied from 5000 to 3000 g/mol while the molecular weight of PBD is fixed at 1000 g/mol

the interfacial tension between polystyrene (PS) and polybutadiene (PBD). In using the SG-FOV theory, a contact interaction parameter X_{AB} in the FOV theory and characteristic parameters of pure components should be determined. One successful method to determine the value of X_{AB} is to fit the equation-of-state theory for binodal curve to the experimental data, although there are several other methods such as melting point depression[27], scattering[28], inverse gas chromatography[29], etc. The characteristic parameters for PS and PBD used in this study are taken from the literature[30,31] and are listed in *Table 1*. The parameter s_A/s_B in equation (7) for PS(A)/PBD(B) is 1.15 when the Bondi's method for estimating the van der Waals volume and surface area is used.

Table 2 Temperature dependence of interfacial tension for PS–PBD blends[a]

	$\gamma = a - bt$	
Molecular weight of PS	a (mN/m)	b [mN/(m °C)]
5000	1.229	0.0063
6000	1.397	0.0059
7000	1.507	0.0055
8000	1.597	0.0053
9000	1.662	0.0049
10000	1.717	0.0047
11000	1.749	0.0044
12000	1.765	0.0041
15000	1.785	0.0032
20000	1.789	0.0022
30000	1.796	0.0012

[a] The PBD of 1000 g/mol is used for calculating interfacial tension between various molecular weights of PS and PBD

Figure 1 shows a comparison of the simulated binodal curve with experimental cloud points[13], by which the value of X_{AB} could be determined. First, we assume that the highest cloud point on the phase diagram corresponds to the critical point of the system. Then, we simulate binodal curves according to equation (9) as varying the value of X_{AB}. By comparing the simulated curves with the experimental cloud points, we determine the X_{AB} value which gives the best-fit to the experimental data. The simulated upper critical solution temperature and its composition are very close to the experimental data, although the shape of the simulated binodal curve is not identical to the measured cloud points.

The temperature dependence of the interfacial tension between PS and PBD is predicted at various molecular weights of PS as shown in *Figure 2*. The densities of PS and PBD, which are prerequisite to calculate interfacial tension, are taken from the data of Fox and Flory[32] and of Anastasiadis *et al.*[7], respectively. Interfacial tension linearly decreases with temperature in the range of 100–200°C when higher molecular weights of PS (> 9000 g/mol) are used. At a given temperature, the interfacial tension increases with the molecular weight of PS. However, in the case of lower molecular weight of PS the temperature dependence of interfacial tension deviates from linearity at close to the upper critical solution temperature. It is noteworthy that the upper critical solution temperature becomes lower as the molecular weight of the polymers decreases[33]. The temperature dependence of interfacial tension can be described by a relation $\gamma = a - bt$, where t is the temperature in degrees Centigrade, and the temperature coefficient, b, of interfacial tension corresponds to the entropy change, ΔS^σ, of interface formation per unit area at constant volume, as represented by the following equation:

$$b = \Delta S^\sigma = -\frac{d\gamma}{dT} \tag{14}$$

Table 2 lists the temperature coefficient of interfacial tension between PS with various molecular weights and PBD with a fixed molecular weight (1000 g/mol). As can be seen in *Table 2*, the temperature coefficient of relatively lower-molecular-weight PS is larger than that of higher-molecular-weight PS. This phenomenon was experimentally observed by Nam and Jo[34]. The plot of interfacial entropy *versus* the molecular weight of PS is shown in

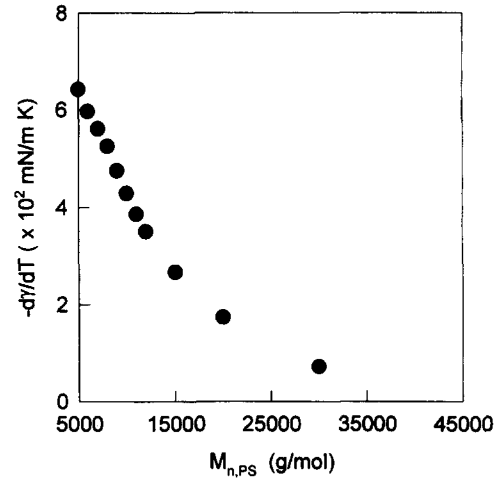

Figure 3 Molecular weight dependence of interfacial entropy of PS and PBD blends. The molecular weight of PBD is fixed at 1000 g/mol

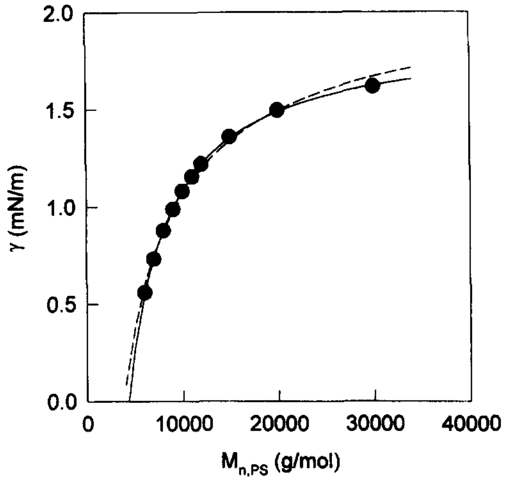

Figure 4 Molecular weight dependence of calculated interfacial tension between PS and PBD at 140°C. Solid and dashed lines are drawn by M_n^{-1} and $M_n^{-2/3}$ in equation (15), respectively

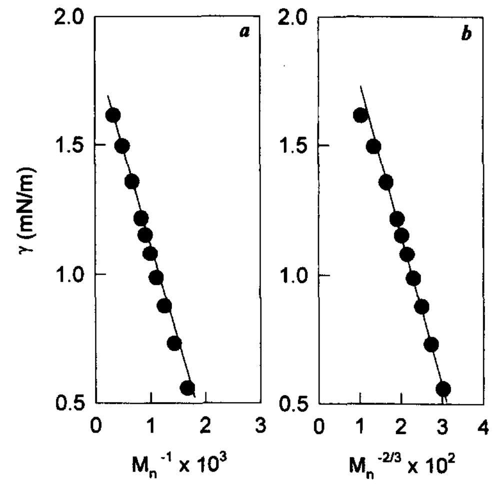

Figure 5 Plots of the interfacial tension between PS and PBD *versus* (a) M_n^{-1} of PS and (b) $M_n^{-2/3}$ of PS at 140°C

Figure 3. It is clear that the interfacial entropy increases with decreasing molecular weight of PS, which results in a lower interfacial tension.

The molecular weight dependence of the interfacial tension is shown in *Figure 4* where the molecular weight of PS is varied while the molecular weight of PBD is fixed. The interfacial tension increases with increasing molecular weight of PS and then approaches an asymptotic value. According to Gaines and co-workers[35,36], interfacial tension can be expressed as follows:

$$\gamma = \gamma_\infty - CM_n^{-z} \tag{15}$$

where C and z are constants, and γ_∞ is the interfacial tension at infinite molecular weight, and M_n is the number average molecular weight. The inverse two-thirds molecular weight dependence (i.e. $z = 2/3$) proposed by Gaines *et al.*[35,36] has been used empirically to describe interfacial tensions of low molecular weight materials. At a given value of z, the values of γ_∞ and C are obtained by the best fit of equation (15) to the data. The value of γ_∞ in our model is 2.23 mN/m at $z = 2/3$, which is in good agreement with experimental values ($\gamma_\infty = 2.25$ mN/m at $z = 2/3$)[34]. Close examination of *Figure 4*, however, reveals that there is a discernible deviation from the $M_n^{-2/3}$ dependence for higher molecular weight PS, although the $M_n^{-2/3}$ dependence shows good agreement with experimental data for low molecular weight PS. The value of $z = 1$ gives a better fit with experimental data for higher molecular weight PS.

In order to more clearly examine the molecular weight dependence of interfacial tension, the interfacial tension is plotted against $M_n^{-2/3}$ and M_n^{-1} as shown in *Figure 5*. A deviation from the $M_n^{-2/3}$ dependence is clearly seen for higher molecular weight PS, whereas the M_n^{-1} dependence shows a better prediction for higher molecular weight PS. In fact, the M_n^{-1} dependence of interfacial tension is well described by theory. According to Broseta *et al.*[37], the origin of molecular weight effects on the properties of polymer–polymer interfaces is purely entropic. The loss of translational entropy due to the confinement of the chains into one-half space is more severe for small molecules. As a result the interface is broader for small chains, resulting in a lower interfacial tension. They proposed the equation for the interfacial tension of monodisperse polymer mixtures by

$$\gamma = \gamma_\infty \left[1 - \frac{\pi^2}{12}\left(\frac{1}{\omega_A} + \frac{1}{\omega_B}\right) + \ldots\right] \tag{16}$$

where $\omega_A (= \chi_{AB} N_A)$ and $\omega_B (= \chi_{AB} N_B)$ are the degree of incompatibility. Equation (16) properly predicts the M_n^{-1} dependence of interfacial tension. However, it is not clear at this time why the molecular weight dependence of interfacial tension follows $z = 2/3$ at lower molecular weight, but follows $z = 1$ in equation (15) at higher molecular weight.

CONCLUSIONS

Interfacial tensions of PS–PBD blends are predicted using the square gradient theory in conjunction with the Flory–Orwoll–Vrij equation-of-state expression for the free energy of mixing. The equation-of-state interaction parameter, X_{AB}, is determined by fitting the equation-of-state theory for binodal curve to the experimental data, and other characteristic parameters of the theory are pre-determined before calculating interfacial tension. The square gradient coefficient, κ, is calculated using the equation derived from a scattering function. The dependence of interfacial tension on temperature shows linearity except for near the upper critical solution temperature. The interfacial tension between PS and PBD increases with the molecular weight of PS and then approaches to the asymptotic limit. The predicted interfacial tension follows the $M_n^{-2/3}$ dependence at lower molecular weights while it follows the M_n^{-1} dependence at high molecular weights.

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