Nonequilibrium Interaction and Stress Anomaly in Compatible Polymer Blends

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ABSTRACT: A lattice model is presented to depict a new concept of the nonequilibrium interaction in compatible polymer blends and to describe the effect on the anomalous yield behavior. The excess volume of mixture is analyzed and is related to the enthalpy of mixing in the nonequilibrium glassy state. Through the understanding of the nonequilibrium changes in the glassy state of miscible blends, we have derived the compositional-dependent relaxation time and obtained an expression for the yield stress. In contrast to the multiphase systems, the presence of a maximum yield stress in the miscible blend at a critical concentration is predicted as a function of the nonequilibrium interaction and the difference between the yield stresses of blending polymers. The theory is compared with experimental data on the blends of PPO/PS and PPO/P(S-pClS).

1. Introduction

Blending of polymers has received considerable attention as a useful method of improving the mechanical and rheological properties of polymers.[1-8] This increases the study of the thermodynamic and physical properties of polymer blends. The thermodynamic investigation is based on the Flory-Huggins lattice model or generalizations, such as the equation of state and the fluid-lattice theories.[9-12] When both components of a binary mixture have high molecular weights normal for commercial polymers, the entropy of mixing is negligible[1] in the free energy of mixing expression

$$\Delta G_{\mathrm{m}} \simeq \Delta H_{\mathrm{m}} = kT\chi\Phi_1\Phi_2 \tag{1}$$

where ΔH_{m} is the heat of mixing, k is the Boltzmann constant, T is the temperature, and Φ_1 and Φ_2 are the volume fractions of 1 and 2 monomers, respectively. Miscibility requires exothermic mixing, i.e., a negative enthalpy of mixing. The pair interaction between monomers of polymer 1 and polymer 2 is defined by the Flory-Huggins interaction parameter, χ, which is a negative quantity and has an inverse temperature dependence. There exists an enormous amount of literature on the interaction parameter in the liquid state.[13-19] Its effect on the melt rheology has been reported recently.[4,5]

It is apparent that our knowledge of the equilibrium interaction and the properties in the liquid state has been improving. On the contrary, there is very little development in theoretical understanding of the pair interaction between miscible polymers in the nonequilibrium glassy state and of the role of the nonequilibrium interaction on the mechanical properties of miscible blends in the solid state. This is the topic of the present paper. The material presented in this paper is organized under three headings. Section 2 outlines a theoretical analysis of the excess volume of mixture below the glass transition temperature (T_g). In section 3, we present a relationship between the nonequilibrium volume and enthalpy changes of mixing in miscible blends. We then use the theory in section 4 to discuss the presence of an interesting and desirable stress anomaly—the maximum yield (or tensile) stress at a critical concentration of the blend, which is higher than the yield stresses of both blending polymers. The theory is compared with experimental data[6-8] on blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS) and PPO and poly(styrene-*co*-*p*-chlorostyrene) (P(S-pClS)).

2. Volume of Mixing

Consider the number of lattice sites for an individual component of a binary mixture having the form[20]

$$N_j(t) = n_j(t) + x_j n_{xj} \quad j = 1, 2 \tag{2}$$

where n_j and n_{xj} are the number of holes and polymer molecules, respectively, and x_j is the number of monomer segments for the jth polymer component. It is important to mention that n consists of both equilibrium and nonequilibrium contributions in the glassy state. For temperatures above T_g, the nonequilibrium contributions to n go to zero. Each lattice site occupies a single lattice cell with volume v_j. The total volume of the mixture is given by

$$V = vN = \sum_j v_j N_j + \Delta V_{\mathrm{m}} \tag{3}$$

where v and $N = n + xn_x$ are, respectively, the lattice volume and total number of lattice sites of the blend. The summation is carried out for $j = 1$ and 2, and ΔV_{m} is the excess volume of mixing. Since the close-packed volumes should remain unchanged, the close-packed volume of the mixture is equal to the sum of the pure-component close-packed volumes:

$$vxn_x = \sum_j v_j x_j n_{xj} \tag{4}$$

The volume fraction of the jth component is

$$\Phi_j = \frac{v_j N_j}{vN} \simeq \frac{v_j x_j n_{xj}}{\sum_j v_j x_j n_{xj}} \tag{5}$$

because n_j is always much less than N_j. Subtracting eq 4 from eq 3, we have

$$vn = \sum_j v_j n_j + \Delta V_{\mathrm{m}} \tag{6}$$

The excess volume of mixture can be written in the form

$$\frac{\Delta V_{\mathrm{m}}}{vN} \simeq \frac{\Delta \bar{V}_{\mathrm{m}}}{v\bar{N}} = A\Phi_1\Phi_2 \leq 0 \tag{7}$$

where A is a nondimensional parameter that measures the strength of the volume interaction between components 1 and 2 and the "bar" refers to the equilibrium as a fully relaxed state ($\delta = 0$). In general, $A = A_{\mathrm{eq}} + A_{\mathrm{noneq}}$, consisting of both equilibrium and nonequilibrium contri-

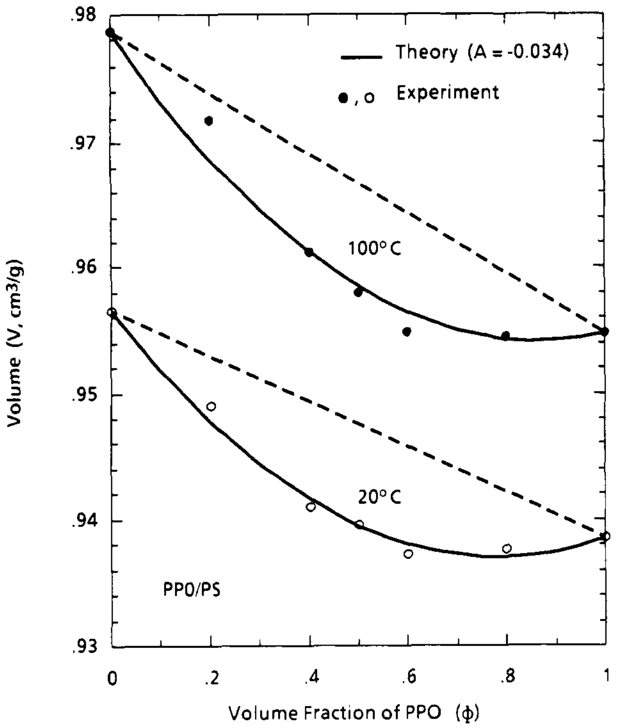

Figure 1. Comparison of the calculated and measured[22] volume of PPO/PS blends as a function of temperature and volume fraction of PPO.

butions. From eqs 5 and 7, the hole (free volume) fraction of the blend is obtained

$$f(t) = vn/vN = \sum_j \Phi_j f_j + A\Phi_1\Phi_2 \tag{8}$$

where $f_j = n_j/N_j$ is the hole fraction of the jth component of mixture. The nonequilibrium contribution to the hole fraction, $\delta(t) = f(t) - \bar{f}$, approaches to zero very slowly in the glassy state. Thus, it represents an essential ingredient to the nonequilibrium properties being explored in this paper. However, $\delta = 0$ in the molten state, and the equilibrium hole fraction ($\bar{f}$) becomes the sole contribution.

For most miscible blends in the equilibrium molten state, the free volumes are found to be linearly additive[3,4]

$$\bar{f} = \sum_j \Phi_j \bar{f}_j \tag{9}$$

The melt rheological properties of PPO/PS blends[3] has been successfully described by eq 9, and the same blends in the glassy state will be used as an example in our later discussion. According to our molecular theory of glasses,[20] the temperature dependence of equilibrium free volume fraction of the jth component of mixture at temperature both above and below T_g is given by

$$\bar{f}_j(T) = \bar{f}_{rj} \exp\left[-\frac{\epsilon_{hj}}{k}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \tag{10}$$

where ϵ_{hj} is the mean hole energy of component j, and the subscript r refers to the condition at $T = T_r$, which is chosen as a fixed quantity near T_g. Subtracting eq 9 from eq 8, we obtain the departure from equilibrium of the blend

$$\delta(T,t) = f - \bar{f} = \sum_j \Phi_j \delta_j(T,t) + A\Phi_1\Phi_2 \quad \text{for } T \le T_g \tag{11}$$

The departure from equilibrium of each individual polymer component, δ_j, defines the nonequilibrium glassy state, and it can be calculated[20,21] as a function of aging time (t) and temperature. Above the glass transition, δ and δ_j, in eq 11, go to zero. This suggests that $-A \approx -A_{\text{noneq}} \gg -A_{\text{eq}}$ in the glassy state and $-A_{\text{noneq}}$ approaches zero in the equilibrium liquid state. The value of A can be determined experimentally by using the more explicit expressions of eqs 3 and 7 in the form

$$V = [V_2 + (V_1 - V_2)\Phi][1 + A\Phi(1 - \Phi)] \tag{12}$$

where $\Phi_1 = \Phi$ and $\Phi_2 = 1 - \Phi$. Equation 12 is compared with the measured specific volume of PPO/PS blends[22] in Figure 1, from which we find $A = -0.034$ at $T = 20$ and 100 °C (both temperatures are below T_g). This clearly suggests that the value of A is not sensitive to temperature in the glassy state. Within experimental errors, the $V - \Phi$ data in ref 22 (see Figure 5) also reveal that A is equal to zero at $T = 200$ and 300 °C in the liquid state. Interestingly, $A = 0$ determined here from the dilatometric data is consistent with eq 9, based on the melt rheology data[3,4] of different miscible blends including PPO/PS.

3. Nonequilibrium Interaction

In the glassy state, the departure from equilibrium for enthalpy of component j in a mixture is defined in a similar way as that for volume

$$\Delta H_j(t) = H_j(t) - \bar{H}_j \tag{13}$$

The nonequilibrium enthalpy changes are related to that of volume by[20]

$$\frac{\Delta H_j(t)}{\epsilon_{hj}\bar{N}_j} = \delta_j(t) + \frac{\epsilon_{fj}}{\epsilon_{hj}}(1 - \bar{f}_j)\theta_j(t) \tag{14}$$

The mean flex energy, ϵ_{fj}, is the conformational energy difference between high-energy gauche and low-energy trans states for polymer j and is close to $^1/_2$ of the mean hole energy, and θ_j is the conformational relaxation function. Because the conformational activation energy is between 1 and 2 orders of magnitude lower than the hole activation energy,[20] θ_j relaxes much faster than δ_j at short times and is negligible in comparison with δ_j at long times. The predicted faster conformational changes are consistent with the Fourier infrared spectroscopy data.[23] For simplicity, we shall consider the long time approximation of eq 14

$$\frac{\Delta H_j(t)}{\epsilon_{hj}\bar{N}_j} \simeq \delta_j(t) \quad j = 1, 2 \tag{15}$$

which has already been found to be a good expression for analyzing the observed effect of physical aging on the yield behavior.[21] The form of eq 15 is quite general for glass-forming polymers. In the case of compatible glassy polymer blends, we have

$$\frac{\Delta H(t)}{\epsilon_h \bar{N}} \simeq \delta(t) \quad \text{for } T \le T_g \tag{16}$$

where δ is given by eq 11. In addition to δ, ϵ_h and N of the blend are determined from the following rules of mixture

$$\bar{N} \simeq \sum_j x_j n_{xj} \simeq \sum_j \bar{N}_j \tag{17}$$

and

$$\epsilon_h \simeq \sum_j \Phi_j \epsilon_{hj} \tag{18}$$

which is derived from eqs 9 and 10 under the assumption of $(\epsilon_{hj}/k)(1/T - 1/T_g) \ll 1$. Because $\epsilon_h/kT_g = 4 \pm 0.5$ (see ref 20, p 698), eq 18 provides a reasonable approximation for $T = T_g \pm 100$ K.

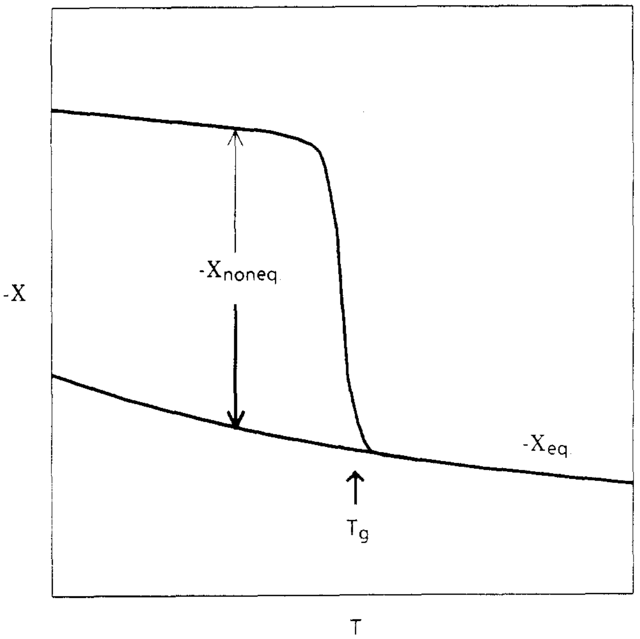

Figure 2. Schematic behavior of the nonequilibrium interaction parameter.

Therefore, the enthalpy of mixing in the glassy state is

$$\Delta H_m = \Delta H - \sum_j \Delta H_j = \epsilon_h \bar{N}[\delta - \sum_j \nu_j \delta_j \Phi_j] \tag{19}$$

where

$$\nu_j = \frac{v \epsilon_{hj}}{v_j \epsilon_h}$$

It may be worthwhile to mention that there is no comparable relationship existing between the volume and enthalpy of mixing at temperatures above T_g.[24] By substituting eq 11 into eq 19, the segmental interaction parameter for binary compatible mixtures in the glassy state is obtained

$$\chi_{noneq} = \frac{\Delta H_m}{kT\bar{N}\Phi_1\Phi_2} = \left(\frac{\epsilon_h}{kT}\right)\left[A + \sum_j \frac{(1-\nu_j)\delta_j}{1-\Phi_j}\right] \quad \text{for } T \le T_g \tag{20}$$

which approaches zero for $T > T_g$. The ratio $(1-\nu_j)\delta_j/(1-\Phi_j)$ goes to zero as $\Phi_j \rightarrow 0$. In the vicinity of the glass transition, the negative nonequilibrium interaction parameter ($-\chi_{noneq}$) is estimated to be on the order of 10^{-1} for PPO/PS blends. It is significantly larger than the negative equilibrium interaction parameter ($-\chi_{eq}$), measured[15] in accordance with eq 1 for the same system at temperatures above T_g. Therefore, we may expect a "phase transition" at T_g for the interaction parameter (χ) of compatible blends as depicted in Figure 2. The main contribution to the nonequilibrium interaction is from A, which will have a strong effect on the yield behavior of blends.

4. Yield Stress

The yield behavior of glassy polymers is closely related to the effective relaxation time (τ_j), which describes the segmental mobility of polymer j. Free volume provides a good basis for the molecular interpretation of segmental mobility. The relaxation time for polymer j is inversely proportional to the mobility of chain segments and is related to the hole fraction by[21,25]

$$\ln \tau_j = B_j/f_j \quad j = 1, 2 \tag{21}$$

where B_j is a constant and f_j includes the nonequilibrium δ_j term. Equation 21 is a generalization of the Doolittle (or WLF) equation, which is valid only for $T > T_g$, to temperatures below T_g. By including the nonequilibrium hole contribution in eq 21, we have successfully explained the transition from a WLF dependence to an Arrhenius temperature dependence of viscoelastic relaxations in the vicinity of T_g for amorphous[21] and cross-linked[26] polymers.

Equations 11 and 21 give

$$\ln\left(\frac{\tau}{\tau_2}\right) = \frac{B}{f} - \frac{B_2}{f_2} = \frac{(B-B_2) - B_2(f_1/f_2 - 1)\Phi}{f} \tag{22}$$

where f of the blends is given by eq 8 and depends on A. When $\Phi \rightarrow 0$, τ/τ_2 approaches 1, which requires $B = B_2$. By introducing $C = B/2.303f_2$ and the intrinsic hole fraction

$$[f] = \frac{f - f_2}{f_2\Phi} = \left(\frac{f_1}{f_2} - 1\right) + \frac{A}{f_2}(1-\Phi) \tag{23}$$

eq 22 becomes

$$\log\left(\frac{\tau}{\tau_2}\right) = -\frac{C[f]\Phi}{1 + [f]\Phi} \tag{24}$$

The above equation describes the relaxation phenomenon in the linear viscoelastic range.

At high stress levels, the contribution from the external work done on a hole lattice site (Δw) has to be included in eq 24. The nonlinear relaxation time takes the form

$$\tau(T,\delta,\Phi) \exp\left(-\frac{\Delta w}{2\beta kT}\right) \tag{25}$$

where $\beta \le 1$ defines the shape of the hole energy spectrum.[20,21] Consider a uniaxial yield stress (σ_y) in tension or compression applied to the system. By taking into account the long-range cooperative interaction, the work done by σ_y on a hole lattice site during the plastic yield is given by

$$\Delta w = -\sigma_y \Omega_{11} \frac{N}{n} = -\frac{\sigma_y \Omega_{11}}{f} \tag{26}$$

where Ω_{11} is the activation volume. The activation volume in uniaxial compression is smaller than that in tension.[27] The ratio Ω_{11}/f in eq 26 represents the volume of polymer segments under deformation.

The yield occurs when the product of the nonlinear relaxation time and the applied strain rate ($\dot{e} = \dot{e}_{11}$) reaches a constant value.[28] From eqs 25 and 26, we get

$$\sigma_y = K + D\left(\log \dot{e} - \frac{C[f]\Phi}{1 + [f]\Phi}\right) \tag{27}$$

where K is a constant and $D = 4.606f\beta RT/\Omega_{11}$. For a fixed strain rate, the compositional-dependent yield stress is written in the form

$$\sigma_y = \sigma_{y2} - \frac{CD[f]\Phi}{1 + [f]\Phi} \tag{28}$$

The yield stresses (σ_{y1} and σ_{y2}) of blending polymers are usually known quantities. By assuming $\sigma_{y1} > \sigma_{y2}$ and defining

$$d = (\sigma_{y1} - \sigma_{y2})/CD \tag{29}$$

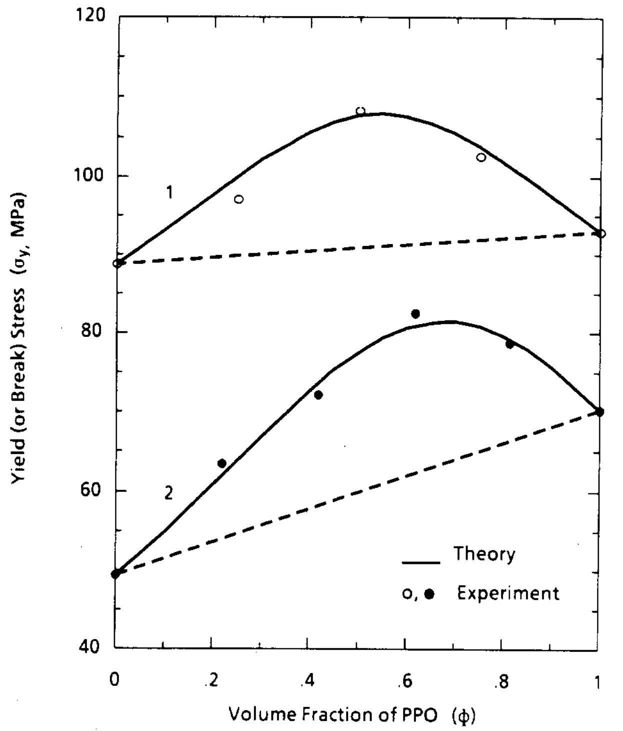

Figure 3. Comparison of the calculated and measured yield stress. Curve 1 is for PPO/PS blends under uniaxial compression,[6] and curve 2 is for PPO/P(S–pClS) blends under uniaxial tension.[7]

Table I
Physical Parameters of Polymer Blends

parameter	(1) PPO/PS in compressn	(2) PPO/P(S–pClS)[a] in tension
A	−0.034	
A/f_2	−1.40	−1.00
f_1/f_2	0.87	0.64
CD, MPa	26.7	37.2

[a] The blend of PPO and a random copolymer with 58.6 mol % of pClS (p-chlorostyrene).

the free volume ratio can be expressed as

$$f_1/f_2 = 1/(1 + d) \qquad (30)$$

There are three parameters: f_1/f_2, CD, and A/f_2 in eqs 23 and 28, which can be determined easily from eqs 28–30. In addition to σ_{y1} and σ_{y2}, all we need is another measured σ_y at a given Φ. A comparison of eq 28 and experimental data[6,7] of miscible blends is shown in Figure 3. Curves 1 and 2 represent, respectively, the PPO/PS blends in compression and the PPO/P(S–pClS) blends in tension. Table I lists the parameters used in curves 1 and 2. The unique feature here is the presence of a maximum yield (or strength) for $0 < \Phi < 1$. It is a result of the negative nonequilibrium interaction ($A < 0$). Such a phenomenon does not occur in incompatible blends or composite systems.[27,29,30] Table I also reveals that the frozen-in free volume fractions, $f_j = \bar{f}_j + \delta_j$, are equal to 0.0243 and 0.0211 for polystyrene and for PPO, respectively. These are reasonable values for polymers in the glassy state.

The critical volume fraction (Φ_c) is determined from the condition

$$\partial\sigma_y/\partial\varphi = 0 \qquad (31)$$

and is expressed as

$$\Phi_c = \frac{1}{2}\left(1 - \frac{f_2}{A}\frac{d}{1 + d}\right) \qquad (32)$$

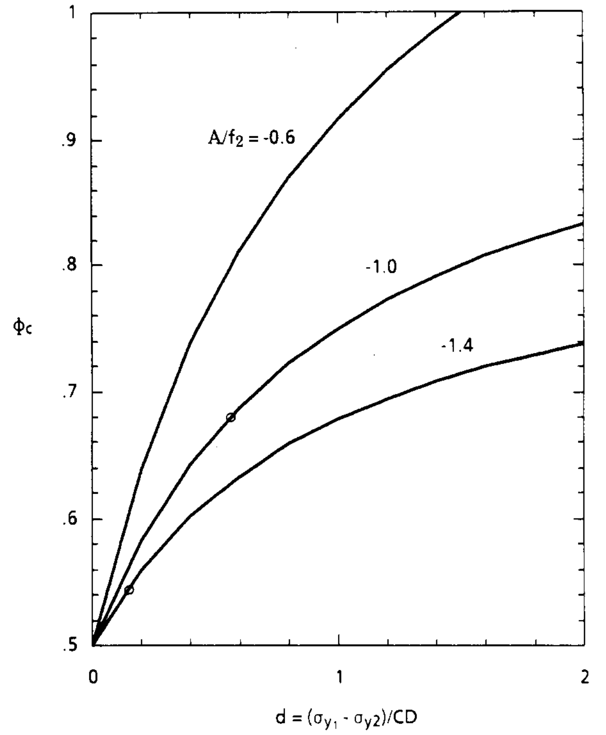

Figure 4. Parameters affecting the critical volume fraction.

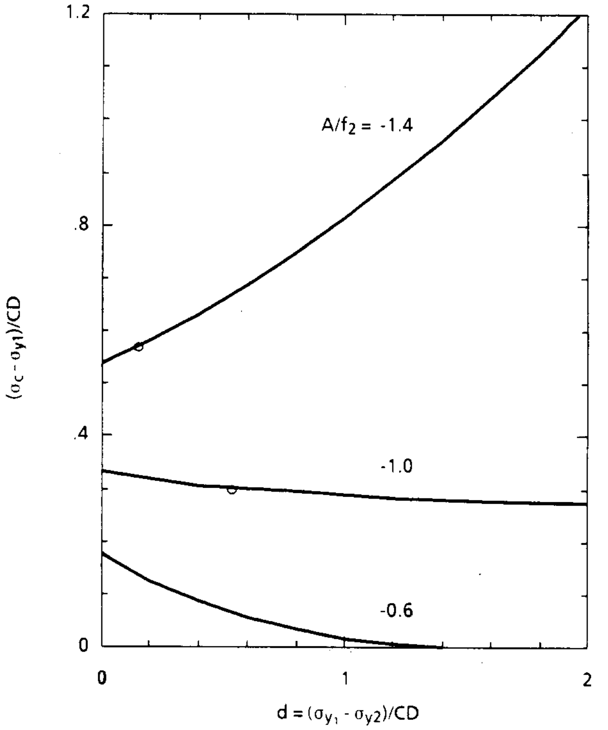

Figure 5. Parameters affecting the stress anomaly.

The stress anomaly at which the maximum yield occurs is characterized by

$$\frac{\sigma_c - \sigma_{y1}}{CD} = -\left(d + \frac{\Phi_c^{\,2}}{f_2/A + \Phi_c^{\,2}}\right) \geq 0 \qquad (33)$$

The two independent parameters in eqs 32 and 33 are d and A/f_2. Their effects on the critical concentration and stress anomaly are, respectively, shown in Figures 4 and 5. The circles in these figures correspond to the critical and anomalous values for the PPO/PS and PPO/P(S–pClS) blends. In order to make a significant improvement of the plastic yield and tensile strength of miscible blends, Figure 5 reveals that it is preferable to have $-A/f_2 \geq 1$.

5. Conclusions

The nonequilibrium structure–property relationships for miscible polymer blends in the glassy state are developed. We have (1) analyzed the excess volume of mixture, (2) related it to the nonequilibrium enthalpy of mixing, and (3) showed the strong dependence of the yield stress on the nonequilibrium interaction. The new microscopic theory is then compared with the published volume and yield stress data on the PPO/PS and PPO/P(S–pClS) blends.

In the study of the long time behavior in the glassy state, the nonequilibrium interaction parameter (χ_{noneq}) between segments of polymer 1 and polymer 2 comes essentially from the volume changes in the glassy state: the excess volume of mixing expressed in terms of A and the departures from equilibrium (δ_j) of polymer components. Among them, A is a dominant factor, which goes to zero for $T > T_g$, and plays a key role in defining the anomalous yield behavior of compatible blends.

In the solid-state deformation, the segmental mobility and the nonlinear viscoelastic relaxation are most clearly shown in the yield behavior. We have derived the compositional-dependent relaxation time by analyzing the nonequilibrium changes in the glassy state of miscible blends and obtained an expression for the yield stress. In contrast to the multiphase systems, the unique feature of compatible blends is the presence of a maximum yield stress at a critical concentration. The magnitude of these quantities depends on the values of A/f_2 and d. In the search of strong blends, we prefer to have $-A/f_2 \geq 1$ and a larger difference between the yield stresses of blending polymers.

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