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Notes

Thermodynamic Model of the Glass Transition Behavior for Miscible Polymer Blends

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Introduction

Polymer blends have received much attention since blending is a simple, effective approach to develop new materials exhibiting combinations of properties that cannot be obtained by individual polymers.[1,2] Miscibility between two components is governed by the thermodynamics represented by the Gibbs free energy of mixing ($\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$). The mixtures are miscible when the value of ΔG_{mix} is negative, i.e., low value of ΔH_{mix} and high value of ΔS_{mix}. Immiscibility is a rule in polymer blends because both the ΔH_{mix} and the ΔS_{mix} are unfavorable. The ΔS_{mix} is unfavorable because there are few molecules of large molecular weight per unit volume. The ΔH_{mix} is also unfavorable because the van der Waals dispersion force is of the form of $-AB/r^6$ (A and B are the Hamaker constants)[3] so that compared to the reference state we have for ΔH_{mix}

$$\Delta H_{\mathrm{mix}} = -2\frac{AB}{r^6} + \frac{AA}{r^6} + \frac{BB}{r^6} = \frac{(A-B)^2}{r^6} \tag{1}$$

which is always positive. However, when the specific interactions such as hydrogen bonding, dipole−dipole interaction, or ionic interaction are established, the miscibility between two polymer mixtures can be achieved.

The glass transition temperature (T_g) reflects the molecular rearrangement rate in supercooled liquid and thus is one of the most important factors among the many transitions and relaxations in polymers. Measurement of T_g is one of the easiest determinations of whether they are miscible or immiscible in polymer mixtures.[4−6] A single T_g between individual two polymers appears for miscible blends whereas two T_gs are shown for immiscible blends. When T_g of miscible polymer blends shows the linear relationship against the polymer composition, the value of T_g is adequately expressed by the widely used Fox equation.[7−13]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{2}$$

where w_1 and w_2 are the weight fractions of components 1 and 2 with T_{g1} and T_{g2}, respectively. This equation is also used to predict the T_g of copolymers.

For some miscible polymer blends interacting with strong specific intermolecular and intramolecular forces, it has been reported that the compositional dependence of T_g shows a maximum behavior, exhibiting a positive deviation from linearity with blend composition.[14,15] This unusual behavior was ascribed to the significant hydrogen-bonding interactions between two polymers in those papers. The T_g of such polymer blends is of special interest from a practical and academic point of view.[16] In this study, we propose a simple, molecular thermodynamic model of T_g in polymer blends based on the configurational entropy model[17−20] and Flory−Huggins theory[21] to predict the glass transition behavior in polymer blends with and without specific interaction between polymers. Thus, the present T_g model encompasses not only the maximum behavior in the polymer blends with specific interactions but also the simple linear relationship against composition.

Model Development

Gibbs and DiMarzio suggested that glass formation is a result of the system's loss of configurational entropy (S_c).[17]

$$S_c = S^{\mathrm{liquid}} - S^{\mathrm{glass}} \tag{3}$$

where S^{liquid} and S^{glass} indicate the configurational entropies of the liquid and glass states, respectively.

It has been assumed that $S^{\mathrm{glass}}(n_1,0,T) = S^{\mathrm{glass}}(n_1,n_2,T) = 0$ and that ΔC_p is independent of temperature and composition.[17,19] The change in the glass transition temperature produced by blending polymer 1 and the polymer 2 can be described by[19,22,23]

$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = -\frac{1}{\Delta C_p}[S_c(n_1,n_2,T) - S_c(n_1,0,T)] \tag{4}$$

where T_{g1} and T_{g12} are the T_gs of the pure polymer 1 and of the blend of polymer 1 and polymer 2, respectively. ΔC_p is the difference in the heat capacity between the supercooled liquid and the glass. n_1 and n_2 are the numbers of molecules of polymer 1 and polymer 2, respectively.

S_c for polymer blends consists of the disorientation entropies of polymer 1 ($S_{\mathrm{dis}-1}$) and polymer 2 ($S_{\mathrm{dis}-2}$), the mixing entropy ($S_{\mathrm{mix}-12}$), and the specific interaction entropy ($S_{\mathrm{spe}-12}$).

$$S_c(n_1,n_2,T) = S_{\mathrm{dis}-1} + S_{\mathrm{dis}-2} + S_{\mathrm{mix}-12} + S_{\mathrm{spe}-12} \tag{5}$$

$$S_c(n_1,0,T) = S_{\mathrm{dis}-1} \tag{6}$$

Substitution of eqs 5 and 6 into eq 4 yields

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$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = -\frac{1}{\Delta C_p}[S_{dis-2} + S_{mix-12} + S_{spe-12}] \qquad (7)$$

Since the specific interactions such as hydrogen bonding, dipole−dipole interaction, or ionic interaction between two polymers reduce the overall entropy, the value of S_{spe-12} is negative. However, other entropy terms increase the overall entropy, thereby being positive values. The entropy terms are expressed as follows:[22−25]

$$S_{dis-2} = k_B n_2\left[\ln r_2 + (r_2 - 1)\ln\left(\frac{z-1}{e}\right)\right] \qquad (8)$$

$$S_{mix-12} = -k_B[n_1 \ln \phi_1 + n_2 \ln \phi_2] \qquad (9)$$

$$S_{spe-12} = \gamma_{spe} k_B \ln\left(\frac{z-1}{e}\right)\left(\frac{\phi_1}{r_1}\ln \phi_1 + \frac{\phi_2}{r_2}\ln \phi_2\right) \qquad (10)$$

where k_B is the Boltzmann constant. $\phi_1 = r_1n_1/(r_1n_1 + r_2n_2)$ and $\phi_2 = r_2n_2/(r_1n_1 + r_2n_2)$ are the volume fractions of components 1 and 2, respectively. $r_1 = \upsilon_1/\upsilon_0$ and $r_2 = \upsilon_2/\upsilon_0$, where υ_1 and υ_2 are the molar volumes of components 1 and 2, respectively, and υ_0 is the unit lattice volume. z is the lattice coordination number. γ_{spe} is a proportionality constant representing the specific interaction such as hydrogen bonding, dipole−dipole interaction, or ionic interaction between two polymers.

Combination of eqs 7−10 yields the following equation:

$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = \beta\left[\left(1 - \gamma_{spe}\ln\left(\frac{z-1}{e}\right)\right)\left(\frac{\phi_1}{r_1}\ln \phi_1 + \frac{\phi_2}{r_2}\ln \phi_2\right) - \frac{\phi_2}{r_2}\left[\ln r_2 + (r_2 - 1)\ln\left(\frac{z-1}{e}\right)\right]\right] \qquad (11)$$

where $\beta = zR/(M_{1u}\Delta C_{pp})$. R, M_{1u}, and ΔC_{pp} are the gas constant, the molecular weight of the repeat unit, and the isobaric specific heat of polymer 1, respectively.

When we limit the value of ϕ_1 to be zero, eq 11 would be expressed as follows:

$$\ln\left(\frac{T_{g2}}{T_{g1}}\right) = -\frac{\beta}{r_2}\left[\ln r_2 + (r_2 - 1)\ln\left(\frac{z-1}{e}\right)\right] \qquad (12)$$

Equations 11 and 12 can be combined to provide a configurational entropy theory for the glass transitions of binary polymer blends.

$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = \beta\left(1 - \gamma_{spe}\ln\left(\frac{z-1}{e}\right)\right)\left(\frac{\phi_1}{r_1}\ln \phi_1 + \frac{\phi_2}{r_2}\ln \phi_2\right) + \phi_2 \ln\left(\frac{T_{g2}}{T_{g1}}\right) \qquad (13)$$

From this model, we can predict T_g for the polymer blends with various compositions.

Results and Discussion

Figure 1 shows the theoretical prediction of T_g calculated from eq 13 for polymer blends (polymer 1/polymer 2) with various specific interaction parameters (γ_{spe}) as a function of volume fraction of polymer 2. To simplify the system, the physical parameters for theoretical calculation are assumed to have the following values: $\beta = 1.0$, $z = 4.0$, $r_1 = 100$, $r_2 = 100$. When there is no specific interaction between two polymers ($\gamma_{spe} = 0$), the T_g shows a linear relationship against the composition of polymer blends, which is consistent with the Fox equation. As γ_{spe} values increase, the maximum behavior of T_g becomes more prominent with larger positive deviation, representing the stronger specific interaction between two polymers. When the difference of T_g between two polymers is small, the positive deviation becomes more noticeable.

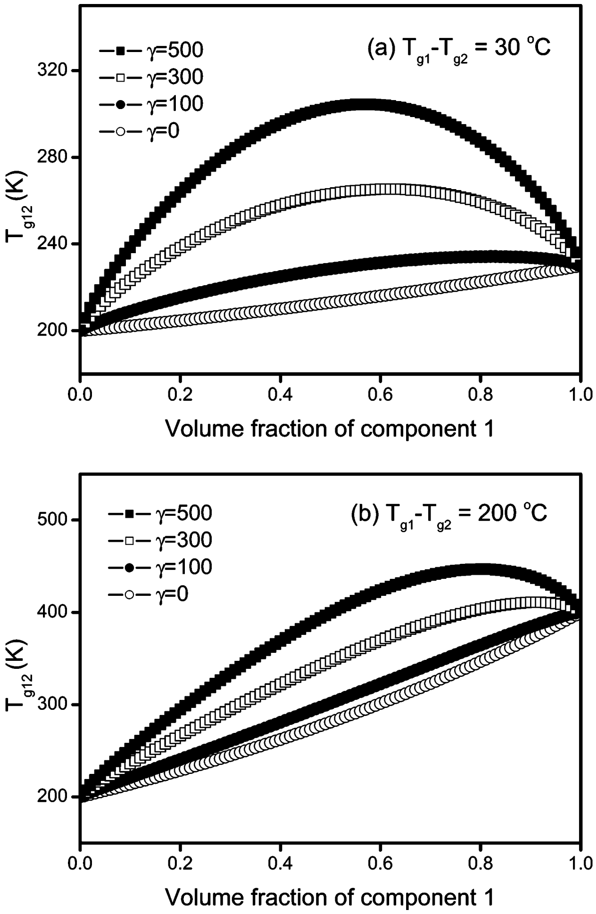

Figure 1. Theoretical prediction of T_g as a function of volume fraction of polymer 1 with varying specific interaction parameter (γ_{spe}) for blends of polymer 1 and polymer 2. The physical parameters used are at $\beta = 1.0$, $z = 4.0$, $r_1 = 100$, and $r_2 = 100$.

Figure 2 presents the comparison of the theoretical predictions with experimental glass transition temperature for blends of poly(vinylpyrrolidone) (PVP) and poly(vinylphenol) (PVPh). Kuo and Chang[14] investigated the hydrogen-bonding interaction and miscibility behavior of blends of PVP and PVPh by differential scanning calorimetry (DSC). They observed that this blend is able to form a miscible phase due to the formation of inter-hydrogen bonding between the carbonyl of PVP and the hydroxyl of PVPh. Interestingly enough, a single T_g higher than that of either individual polymer was observed, presumably due to the strong interaction between two polymers. As seen in the figure, the new model eq 13 predicts accurately the T_g values from the experimental results, but the Fox equation does not. The value of γ_{spe} of eq 13 was obtained by nonlinear regression. The higher value of γ_{spe} (= 288.1) for blends of PVP and PVPh represents the strong specific hydrogen-bonding interaction between two polymers, which is coincident with the previous experimental results of FT-IR and solid-state NMR.[14]

The new thermodynamic model of T_g was also applied to the system exhibiting a linear relationship against compositions of polymer blends. Balsamo et al.[13] prepared blends of polycarbonate (PC) and poly(ϵ-caprolactone) (PCL) in a wide

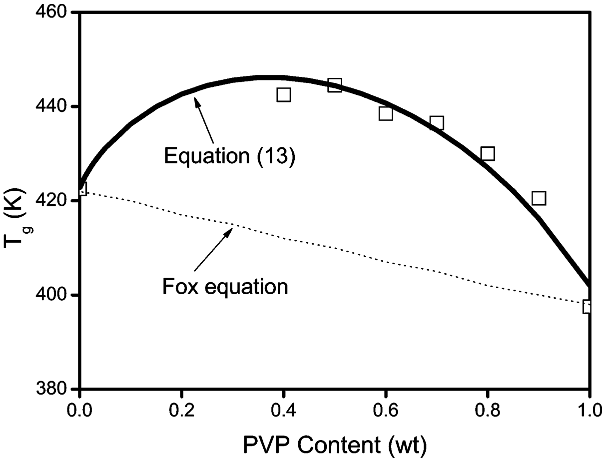

Figure 2. Comparison of the theoretical predictions with experimental glass transition temperature for blends of PVP(1)/PVPh(2). Open squares are experimental data by Kuo and Chang.[14] The solid line is calculated from eq 13, where $\gamma_{spe} = 288.1$, $r_1 = 88.8$, $r_2 = 103.4$, $z = 4$, $M_{1u} = 111$ g/mol, and $\Delta C_{pp} = 740.5$ J/(kg K).

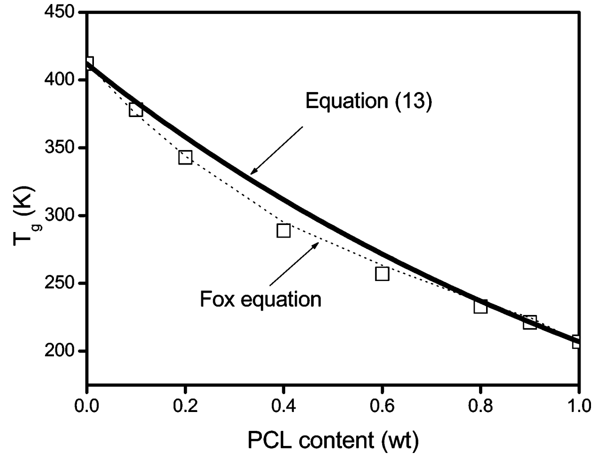

Figure 3. Comparison of the theoretical predictions with experimental glass transition temperature for blends of PC(1)/PCL(2). Open squares are experimental data by Balsamo et al.[13] New model equation is calculated from eq 13, where $\gamma_{spe} = 2.74$, $r_1 = 222.8$, $r_2 = 100.0$, $z = 4.0$, $M_{1u} = 254$ g/mol, and $\Delta C_{pp} = 388.2$ J/(kg K).

composition range and investigated the thermal behavior of the blends via DSC. The blends were miscible in the entire composition range, showing the single T_g values. The compositional variation of T_g exhibits a simple, linear relationship, which is adequately described by the Fox eq 2,[7,8] as seen in Figure 3. The new model eq 13 also predicts the experimental T_g values very accurately, comparable to the Fox equation. The lower value of γ_{spe} (=2.74) for blends of PC/PCL relative to the blends of PVP/PVPh demonstrates the weak specific interaction between two polymers in the former.

Schneider and Di Marzio[26] reported on the comparison of experimental T_g values for miscible polymer blends with an equation based on conformational entropy changes. In that study, the specific interactions were not considered, and thus they failed to predict the experimental T_g values well. This presents the importance of a physical parameter γ_{spe} in the current thermodynamic T_g model.

In conclusion, a new mathematical model was derived on the basis of configurational entropy and Flory−Huggins theory to predict the T_g of miscible polymer blends. The new model adequately predicts the T_g dependence on blend composition for the cases of (1) maximum behavior with positive deviation and (2) simple linear additivity obeying the Fox equation. More importantly, the current T_g model does not include other adjustable parameters except γ_{spe} and can be applied to any miscible binary polymer blends with hydrogen bonding, dipole−dipole interaction, or ionic interaction. From this model, we can directly compare the strength of specific interaction in each system by the value of γ_{spe}; i.e., the higher value of γ_{spe} for polymer blends represents the stronger specific interaction and vice versa.

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