The Equation of State Theory for Glass Transition Temperature in Miscible Polymer Blends

Ick Hwan KWON and Won Ho JO*

*Department of Textile Engineering and Center for Advanced Materials Research,
Seoul National University, Seoul, 151-742, Korea*

ABSTRACT: The lattice-fluid theory is combined with the Gibbs–DiMarzio theory to predict the compositional variation of glass transition temperatures in polymer mixtures. This approach is tested for two miscible blend systems, poly(2,6-dimethyl-1,4-phenylene ether)/polystyrene and poly(bisphenol A hydroxy ether)/poly(vinyl methyl ether). Some modification of the lattice–fluid theory is required to reduce the difference between theory and experimental data for the glass transition temperature. It reveals that the compositional variation of glass transition temperatures are mainly governed by both the interaction between the constituents and the chain flexibility change with composition.

KEY WORDS Glass Transition Temperature / Polymer Blend / Lattice Fluid Theory /

Experimental studies of the composition dependence of the glass transition temperatures (T_g) in polymer mixtures have been done for many miscible polymer mixtures. The compositional variation of T_g has been mainly interpreted with empirical expressions such as the Fox equation[1] or the Gordon–Taylor equation.[2]

Separately, a statistico-mechanical interpretation of composition effect on T_g has been given by Gibbs and DiMarzio.[3] They regards the glass formation as a result of the system's loss of configurational entropy. As the system is cooled near T_g, the number of available configurations decreases and thus the relaxation time dramatically increases. The Gibbs–DiMarzio theory assumes that a lower limit of glass transition temperature (designated T_2) exists when the system is cooled at infinitely slow rate. T_2 is defined as the temperature at which the configurational entropy of the system vanishes and the system has an infinite relaxation time. Gibbs and DiMarzio noted that T_2 varied with polymer chain length and

polymer concentration in a fashion similar to the variation of T_g. Angell and Bressel[4] have presented the evidence that T_g and T_2 have the same composition dependence for the mixture. The semi-universal rule for the correlation between T_g and T_2 was suggested by Adam and Gibbs.[5] The Gibbs–DiMarzio theory predicts a value of T_g at a given composition of the mixture but does not appear to produce an analytical equation for T_g as a function of composition such as Gordon–Taylor equation. Gordon et al.[6] proposed simple analytical expressions by combining the Gibbs–DiMarzio theory and classical thermodynamics.

Couchman and Karasz[7] considered T_2 fictive rather than actual and bypassed any consideration of molecular theory for the glass transition. They used a fundamental relation for the effect of composition on T_g, i.e., the entropy continuity condition at T_g. Although the thermodynamic basis of Couchman–Karasz equation has been disputed,[8] their equation has been proved to be quite successful in several cases.[9–11] Recently, Kwei[12] proposed an

empirical equation for the compositional variation of T_g. In his approach, the Gordon-Taylor equation was combined with the Jenckel and Heusch's empirical correction factor[13] which was employed to compensate the deviation of T_g in mixture from the weighted mean of t_g's of two pure components.

Although the above mentioned equations can be easily applied to the polymer mixtures, it is difficult to interpret the origin of the compositional variation of T_g in mixture. Panayiotou[14] combined an improved lattice–fluid model with the Gibbs–DiMarzio approach to overcome such a problem. The lattice fluid model which was introduced in the Panayiotou's approach have been proved to be quite successful in the prediction of various thermodynamic quantities of mixing such as the lower critical solution temperatures and gas solubilities at various external conditions. Nevertheless, his interpretation of the compositional variation of T_g in polymer mixture seems to be obscure and the concept of T_2 was also omitted.

In this study, a configurational entropy equation is derived based on the lattice-fluid theory and then the equation is combined with the Gibbs–DiMarzio's approach to theoretically predict the compositional variation of T_g in miscible polymer mixture. The equation is tested for two miscible polymer mixtures, poly(2,6-dimethyl-1,4-phenylene ether) (PPE)/ polystyrene (PS) and poly(bisphenol A hydroxy ether) (Phenoxy)/poly(vinyl methyl ether) (PVME).

THEORETICAL BACKGROUND

Pure Lattice Fluid Theory

Sanchez and Lacombe[15] have determined the number of configurations, available to N_r lattice sites for N molecules, each of which occupies r sites and N_0 vacant sites.

$$\Omega = \left[\frac{N_r}{N_0}\right]^{N_0} \left[\frac{N_r}{rN} \frac{\delta r}{\sigma e^{r-1}}\right]^N \quad (1)$$

The flexibility parameter δ denotes the number of ways in which the r-mer can be arranged on the lattice after one of its mers has been fixed on a lattice site and σ is a symmetry number which is assumed to be unity in their study.

The energy of the lattice is assumed to depend only on nearest neighbor interactions and is derived based on the mean field approximation.

$$E = -N_r \left[\frac{z\varepsilon}{2}\right]\left[\frac{rN}{N_r}\right]^2 \quad (2)$$

where ε is the nonbonded mer–mer interaction and z is a bond coordination number. The partition function Z of the system can be calculated with eq 1 and 2.

$$Z(T, P) = \Omega \exp[-\beta(E + PV)] \quad (3)$$

where β is $1/kT$. The equation of state obtained from eq 3 is expressed as:

$$\hat{\rho}^2 + \hat{P} + \hat{T}[\ln(1-\hat{\rho}) + (1-1/r)\hat{\rho}] = 0 \quad (4)$$

where $\hat{\rho}$, $\hat{P}$, and $\hat{T}$ are the reduced density ($\hat{\rho} = \rho/\rho^*$), the reduced pressure ($\hat{P} = P/P^*$), and the reduced temperature ($\hat{T} = T/T^*$), respectively.

The configurational entropy of the system is obtained from eq 1, since $S = k \ln \Omega$.

$$\frac{S}{NrR} = -(\hat{v}-1)\ln(1-\hat{\rho})$$

$$-\frac{\ln(\hat{\rho})}{r} + \frac{\ln(\delta)}{r} + \frac{\ln(r)}{r} - 1 \quad (5)$$

where $\hat{v}$ is the reduced volume ($\hat{v} = 1/\hat{\rho} = v/v^*$). For freely rotating chain, $\ln(\delta)$ is expressed as eq 6.

$$\ln(\delta) = \ln(z) + (r-2)\ln(z-1) \quad (6)$$

It is assumed that only two types of conformation energy state are available for each bond. According to Flory's model for chain conformations,[16] $\ln(\delta)$ can also be expressed as eq 7.

$$\ln(\delta) = \ln(z) + fr\ln(z-2) - fr\ln(f)$$
$$-(1-f)r\ln(1-f) - fr\Delta/RT \quad (7)$$

where Δ is the potential energy difference between two energy states, and the equilibrium fraction f of higher energy state bonds is defined as:

$$f = \frac{(z-2)\exp(-\Delta/RT)}{1+(z-2)\exp(-\Delta/RT)} \quad (8)$$

The characteristic density ρ^*, the characteristic pressure P^* and the number of segments per molecule r can be calculated from the measurement of the thermal expansion coefficient α, the specific volume v, and the thermal pressure coefficient γ. The relations are given by[17]:

$$\frac{1}{T\alpha} = -\frac{\hat{\rho}^2}{(1-\hat{\rho})[\ln(1-\hat{\rho})+\hat{\rho}]} - 2 \quad (9)$$

$$\hat{T} = -\hat{\rho}^2/[\ln(1-\hat{\rho})+\hat{\rho}] \quad (10)$$

$$P^* = \gamma T \hat{\rho}^{-2} \quad (11)$$

$$r = P^*M/(RT^*\rho^*) \quad (12)$$

where M is the molecular weight of pure component.

Mixed Lattice Fluids

The number of configurations Ω available to N_r lattice system composed of $N_1 r_1$ mers, $N_2 r_2$ mers and N_0 empty sites is approximately given by[18]:

$$\Omega = \left[\frac{N_r}{N_0}\right]^{N_0} \left[\frac{N_r}{r_1 N_1} \frac{\delta_1 r_1}{\sigma_1 \exp(r_1-1)}\right]^{N_1}$$
$$\times \left[\frac{N_r}{r_2 N_2} \frac{\delta_2 r_2}{\sigma_2 \exp(r_2-1)}\right]^{N_2} \quad (13)$$

The configurational entropy of mixed system can be obtained from eq 13 *via* the relation $S = k \ln \Omega$.

$$\frac{S}{NrR} = -(\hat{v}-1)\ln(1-\hat{\rho}) - \frac{\ln(\hat{\rho})}{r}$$
$$- \frac{\phi_1}{r_1}\ln(\phi_1) - \frac{\phi_2}{r_2}\ln(\phi_2)$$
$$+ \frac{\phi_1}{r_1}\ln(\delta_1) + \frac{\phi_2}{r_2}\ln(\delta_2)$$

$$+ \frac{\phi_1}{r_1}\ln(r_1) + \frac{\phi_2}{r_2}\ln(r_2) - 1 \quad (14)$$

When eq 5 and 14 are compared, the mixing rule for $\ln(\delta)$ is expressed as eq 15.

$$\frac{\ln(\delta)}{r} = \frac{\phi_1}{r_1}\ln(\delta_1) + \frac{\phi_2}{r_2}\ln(\delta_2) \quad (15)$$

It is reported that the flexibility parameter δ depends on internal degrees of freedom and does not contribute to the PVT equation of state, thus to thermodynamic property changes on mixing ($\Delta G, \Delta S, \Delta H$).[15] Accordingly, it is assumed that the δ parameter does not contribute to the enthalpy change on mixing.

Extension of the lattice-fluid theory to mixtures is relatively straightforward when appropriate mixing rules are introduced. If an i molecule occupies r_i^0 sites in the pure state and has a close-packed molecular volume of $r_i^0 v_i^*$, then it will occupy r_i sites in the mixtures such that

$$r_i^0 v_i^* = r_i v^* \quad (16)$$

The characteristic parameters of mixture obey the following relations.

$$v^* = \phi_1 v_1^* + \phi_2 v_2^* \quad (17)$$

$$r = x_1 r_1 + x_2 r_2 \quad (18)$$

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 \Delta P^* \quad (19)$$

$$T^* = P^* v^*/R \quad (20)$$

$$\Delta P^* = P_1^* + P_2^* - 2P_{12}^* \quad (21)$$

$$P_{12}^* = \zeta_{12}(P_1^* P_2^*)^{1/2} \quad (22)$$

$$\phi_1^0 = r_1^0 N_1/rN = 1 - \phi_2^0 \quad (23)$$

$$\phi_1 = r_1 N_1/rN = 1 - \phi_2 \quad (24)$$

RESULTS AND DISCUSSION

Theoretical Prediction of T_g in Mixture

For two miscible blend systems PPE/PS and Phenoxy/PVME, the compositional variation of T_g is interpreted with the lattice–fluid theory. The characteristic parameters of pure polymers

Table I. Pure component properties

Polymer	$\alpha \times 10^4/\text{K}^{-1}$	$\gamma/\text{J cm}^{-3}\text{K}^{-1}$	$V_{\text{sp}}/\text{cm}^3\text{g}^{-1}$	M_n
PPE[a]	7.38	0.644	0.99	3100
PS[a]	6.10	0.620	0.93	144000
Phenoxy[b]	5.59	1.433	1.14	18000
PVME[b]	7.30	0.862	1.00	37000

[a] At 523 K, from ref 19.   [b] At 373 K, from ref 20.

Table II. Characteristic parameters of pure components

Polymer	$V^*/\text{cm}^3\text{mol}^{-1}$	T^*/K	$P^*/\text{J cm}^{-3}$	r
PPE	13.48	757	467	197
PS	16.36	829	421	8272
Phenoxy	9.56	722	626	1527
PVME	13.26	638	400	2498

Table III. Glass transition temperatures, flexibility parameters, and flex energy of pure components

Polymer	T_{g}/K	$\ln\delta$	$\Delta/\text{J mol}^{-1}$
PPE[a]	452	157	1481
PS[a]	376	7485	742
Phenoxy[b]	347	1354	754
PVME[b]	232	2360	361

[a] Taken from ref 21.   [b] Taken from ref 20.

should be pre-determined to use the lattice–fluid theory. The pure component properties α, γ, and v taken from the literature[19,20] are listed in Table I. The characteristic parameters of the pure components are then calculated by use of eq 9—12 and are listed in Table II.

PPE/PS blend system has been known to be miscible and exhibits single composition dependent T_{g} over the whole range of composition.[21] Couchman[9] reported that the glass transition temperature of PPE/PS blend system shows a good agreement with the equation proposed by Couchman and Karasz.[7]

Phenoxy/PVME blend system has also reported to be miscible.[20] The stability of this mixture has been attributed to possible hydrogen bonding between the pendant hydroxy groups of Phenoxy and ether groups of PVME. The blend also exhibits a single glass transition temperature over the whole range of composition. The ratio of heat capacity change at each glass transition temperature ($\Delta Cp_2/\Delta Cp_1$) should be adjusted to 2 in order to match the Couchman–Karazs equation. However, this value is well above the experimentally determined value 1.27.[22]

Since the configurational entropy (eq 5) would become zero at T_2 according to the Gibbs–DiMarzio approach,[3] the following equation should hold at T_2.

$$\ln(\delta) = r(\hat{v}-1)\ln(1-\hat{\rho}) + \ln(\hat{\rho}) - \ln(r) + r \quad (25)$$

The linear relationship between T_2 and T_{g} is known to hold for various polymer systems.[5]

$$T_{\text{g}} = kT_2 \quad (26)$$

Adam and Gibbs[5] have determined the proportionality constant k to be $1.3 \pm 8.4\%$ from viscometric data and Bestul and Chang[23] to be $1.29 \pm 10.9\%$ from calorimetric data. Therefore it is reasonable to assume that k is equal to 1.3 by which T_2 can be determined from the experimentally determined T_{g}. When the calculated values of $\hat{\rho}$ and $\hat{v}$ at T_2 are substituted into eq 25, the flexibility parameter $\ln(\delta)$ can be determined for each pure polymers, and then the value of flex energy Δ can be evaluated from eq 7 and are listed in Table III. As the glass transition temperature increases, the rotation of segments is suppressed and the flex energy becomes higher.

When the values of $\ln(\delta_i)$ are substituted into the configurational entropy of mixture, eq 14

can be solved numerically for the composition dependent T_2. The value of binary parameter ζ_{12} is required for the calculation of the reduced volume and density of the mixture. Since the value of ζ_{12} is not available for PPE/PS blend system, we estimate the value according to the following procedure. Maconnachi et al.[19] have determined the interaction strength X_{12} for PPE/PS blend system, where X_{12} is defined in the Flory–Prigogine's equation of state theory.[24] When the value of X_{12} is known, the heat of mixing can be calculated from the Flory–Prigogine's equation of state theory. The lattice-fluid theory also gives an expression for the heat of mixing which is a function of binary interaction parameter ζ_{12}. Thus, if it is assumed that the heats of mixing from two theories are equal, the binary interaction parameter ζ_{12} is then calculated. For PPE/PS blend system, the value of ζ_{12} is evaluated to be 1.0069. The interaction strength X_{12} for Phenoxy/PVME blends is also reported by Uriarte et al.[20] By the same procedure as above, the value of ζ_{12} for Phenoxy/PVME blend system is estimated to be 1.0351. The characteristic parameters of mixture are calculated by using the mixing rules (eq 17—22) and the value of ζ_{12}. Equation 4 permitts the calculation of the reduced density or volume of mixture at any temperature. When δ_i values of pure polymers and the reduced density at each temperature are substituted into eq 14, the equation can be numerically solved for composition dependent T_2 via the relation $S=0$ at T_2. The curves in Figures 1 and 2 represent the theoretically calculated T_g with the composition. A disagreement between the experimental and theoretical values is observed in both Figures 1 and 2. Thus it seems that a modification of LF theory is necessary to overcome such a disagreement.

Modification of Configurational Entropy of Mixture

Since the prediction of the thermodynamic properties of mixture is mainly governed by the choice of mixing rule, such a disagreement
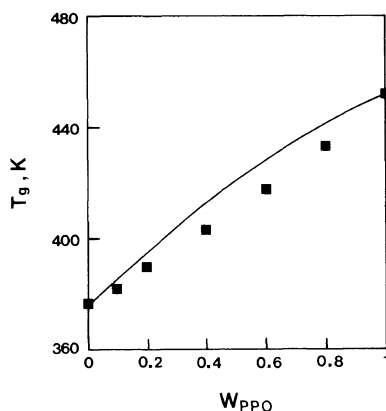

Figure 1. Glass transition temperatures of PPE/PS blends as a function of PPE weight fraction. The filled squares represent experimental values and the curves are calculated from theory ($\zeta_{12}=1.0069$).
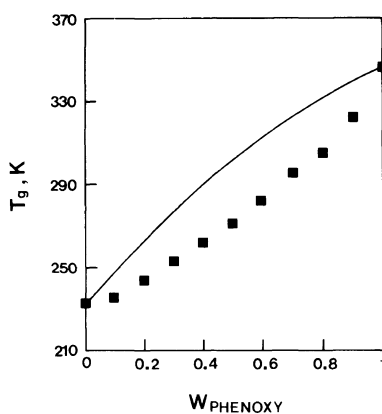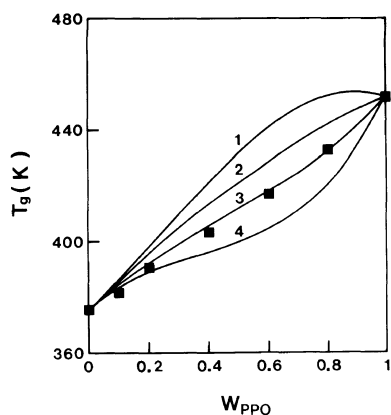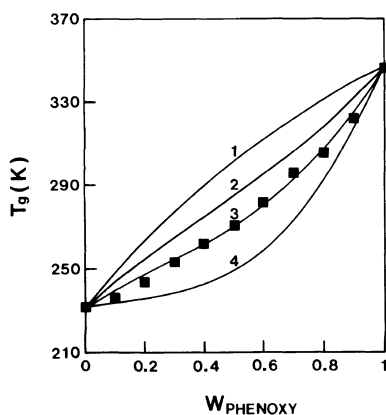

Figure 2. Glass transition temperatures of Phenoxy/ PVME blends as a function of Phenoxy weight fraction. The filled squares represent experimental values and the curves are calculated from theory ($\zeta_{12}=1.0351$).

may come from the incorrect mixing rule. The mixing rule which gives the largest effect on the configurational entropy of mixture is the rule for the flexibility parameter $\ln(\delta)$. Therefore it is attempted to modify eq 15 by introducing the flexibility correction term $K_{12}\phi_1\phi_2[\ln(\delta_1)\ln(\delta_2)]^{1/2}/r$ into eq 14 and 15.

$$\frac{\ln(\delta)}{r} = \frac{\phi_1}{r_1}\ln(\delta_1) + \frac{\phi_2}{r_2}\ln(\delta_2)$$
$$+ \frac{K_{12}\phi_1\phi_2[\ln(\delta_1)\ln(\delta_2)]^{1/2}}{r} \quad (27)$$

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Figure 3. Glass transition temperatures of PPE/PS blends as a function of PPE weight fraction. The filled squares represent experimental values and the curves are calculated from theory ($\zeta_{12} = 1.0069$): (1) $K_{12} = -0.01$, (2) $K_{12} = 0$, (3) $K_{12} = 0.009$, (4) $K_{12} = 0.02$.

Figure 4. Glass transition temperatures of Phenoxy/PVME blends as a function of Phenoxy weight fraction. The filled squares represent experimental values and the curves are calculated from theory ($\zeta_{12} = 1.0351$): (1) $K_{12} = 0$, (2) $K_{12} = 0.05$, (3) $K_{12} = 0.093$, (4) $K_{12} = 0.15$.

Figures 3 and 4 show the effect of flexibility correction factor on the compsition dependence of T_g. When the positive value of K_{12} is used, chain flexibility increases and the glass transition temperature decreases, and vice versa. The correction factor should be introduced to fit the theoretical T_g to the experimental data for both PPE/PS blends ($K_{12} = 0.009$) and Phenoxy/PVME ($K_{12} = 0.093$). Especially, a large correction factor is necessary
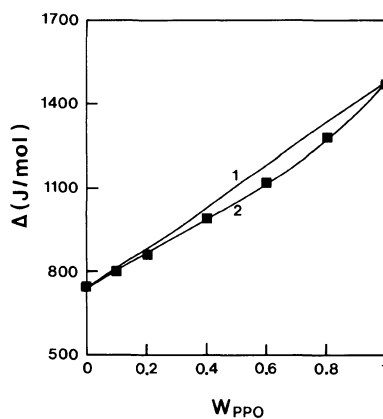

Figure 5. Flex energy of PPE/PS blends vs. PPE weight fraction. The filled squares represent the values calculated from the experimental T_g and the curves are calculated from theory ($\zeta_{12} = 1.0069$): (1) $K_{12} = 0$, (2) $K_{12} = 0.009$.

for Phenoxy/PVME blends for which the Couchman-Karasz's approach fails to fit the experimental T_g data.

The compositional dependence of flexibility parameter seems to come from the composition dependence of the coordination number z, chain length r and flex energy Δ in the mixture as can be seen in eq 6 and 7. However the compositional variation of the coordination number violates the basic assumption of the lattice-fluid theory,[15] and the chain length of mixture changes linearly with composition as shown in eq 18. For this reason, the composition dependence of $\ln(\delta)$ can be interpreted only in terms of the dependence of flex energy while z is treated as a constant value (in this study, $z = 4$).

The combination of eq 7 and 27 gives the theoretical flex energy Δ at each theoretically predicted T_2 as a function of composition as shown in Figures 5 and 6. When $\hat{v}$, r, and T_2 calculated from the experimentally determined glass transition temperatures of mixture are substituted into eq 5, the flexibility δ of the mixture can be calculated at each blend composition. The flex energy Δ can then be estimated from the value of $\ln(\delta)$ using eq 7. The flex energy calculated from the experimental T_g deviates from the unmodified
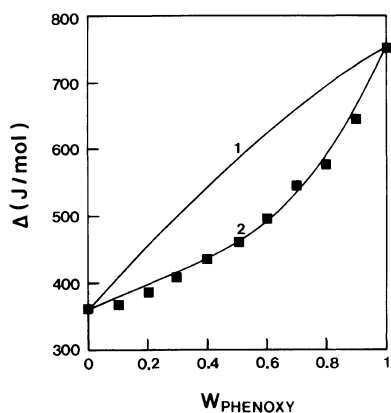
Figure 6. Flex energy of Phenoxy/PVME blends *vs.* Phenoxy weight fraction. The filled squares represent the values calculated from the experimental T_g and the curves are calculated from theory ($\zeta_{12} = 1.0351$): (1) $K_{12} = 0$, (2) $K_{12} = 0.093$.

Figure 7. The curves are theoretically calculated glass transition temperatures of PPE/PS blends for a range of ζ_{12} values: (1) $\zeta_{12} = 1.0069$, (2) $\zeta_{12} = 1.03$, (3) $\zeta_{12} = 1.06$. The filled squares represent experimental values.

Figure 8. The curves are theoretically calculated glass transition temperatures of Phenoxy/PVME blends for a range of ζ_{12} values: (1) $\zeta_{12} = 1.0351$, (2) $\zeta_{12} = 1.06$, (3) $\zeta_{12} = 1.09$. The filled squares represent experimental values.

theoretical flex energy ($K_{12} = 0$), but shows a good agreement with the modified theory when $K_{12} = 0.009$ and 0.093 were used for PPE/PS blends and Phenoxy/PVME blends, respectively. This means that the correct compositional variation of flex energy should be taken into account to predict properly the glass transition temperature of mixture.

The Effect of Interaction Strength on T_g

In previous section, the effect of chain flexibility of T_g is discussed. The strong attractive interaction between constituents usually leads to the negative volume change on mixing and hindrance of segmental motion, and thus increases T_g. Interaction strength in mixture may be another factor which influences the composition dependence of T_g. Figures 7 and 8 illustrate that the stronger intermolecular interaction (higher value of ζ_{12}) between the constituents of the mixture, the higher the glass transition temperature. The Couchman–Karasz's approach can not explain such phenomenon since they do not use any molecular theory. Lim *et al.*[25] explained that the excess stabilization of backbone causes the deviation of T_g of mixture from the temperature of weighted mean of each component T_g
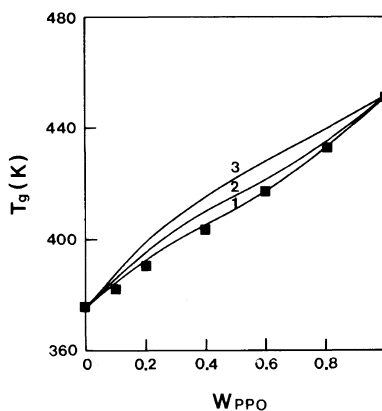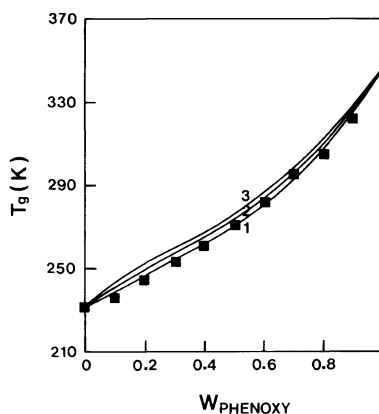
and that the sources of excess backbone stabilization can be expressed as the contact energy difference. But, excess backbone stabilization is confused with the definition for the Flory–Huggins interaction parameter. For the negative deviation of the glass transition temperatures in mixture, backbone stabilization in mixture may be lower than that in pure state. They suggested an ambiguous explanation which seemed to be only acceptable for the branched polymer blends, *i.e.*, "Although

the side chains are close together in the blend, the backbone can be less well packed than in the pure state." How explanation can be done in case of linear polymer blend? With the aid of lattice–fluid theory, the variation of the glass transition temperatures in mixture arises from two sources: one is the composition dependence of flex energy and another the interaction between the constituents.

CONCLUSIONS

Configurational entropy of mixture is derived from lattice-fluid theory. We adopt the Gibbs–DiMarzio's hypothesis in which the configurational entropy vanishes at T_2. T_2 can be converted to T_g according to the Adam–Gibbs relation. For two miscible blends, PPE/PS and Phenoxy/PVME, a disagreement between the experimental T_g and theoretically predicted T_g is observed when the theory is directly used. Thus the correction term is added to the mixing rule for chain flexibility of mixture. The modified theory explains that the variation of glass transition temperatures in mixture arises from both the composition dependence of flex energy and the interaction between the constituents.

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