

Relationship between the Glass Transition Temperature and the Interaction Parameter of Miscible Binary Polymer Blends

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ABSTRACT: An equation that relates the glass transition temperature, T_g , and a binary interaction parameter, χ , for miscible binary polymer blends was derived. The equation including no adjustable parameters was based on a thermodynamic mixing formalism using enthalpy as the thermodynamic parameter. The enthalpy of mixing was written as a van Laar expression, and the T_g was formally treated as a second-order Ehrenfest transition. The equation satisfactorily predicts T_g -composition curves for miscible binary polymer blends that exhibit either positive or negative deviation from a linear mixing rule, depending on the strength of the interaction. Good agreement was found between calculated χ and values experimentally determined by equilibrium melting point depression and inverse gas chromatography.

Introduction

Specific interactions between polymers have a profound influence on the phase behavior of binary polymer blends. To form a miscible blend, the free energy of mixing $\Delta G_m \leq 0$ and the second derivative with respect to composition $\partial^2 \Delta G_m / \partial \phi^2 > 0$, where

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (1)$$

and ΔH_m and ΔS_m are the enthalpy and entropy of mixing, respectively. For high molecular weight polymers, ΔS_m is negligibly small and the sign of ΔG_m is dominated by ΔH_m . In general, ΔH_m is negative only if there are specific associative interactions between the two polymers. Therefore, the formation of miscible polymer blends depends on the occurrence of exothermic interactions such as hydrogen bonding,¹ dipole-dipole interactions,² acid-base interactions,³ or transition metal complexation.⁴

A common method used to judge the miscibility of blends is to measure the glass transition temperature(s), T_g . Two T_g 's indicates a two-phase system, and a single composition-dependent T_g is often taken as evidence of the formation of a miscible blend. In practice, one would like to be able to predict the T_g of a miscible blend from the properties of the component polymers.

Experimental studies on the composition dependence of the glass transition temperature for a variety of binary miscible blends show both negative and positive deviations from a simple weighted average (i.e., a rule of mixtures) of the two T_g 's of the component polymers. Over the past 40 years, a number of theoretical equations have been proposed to predict the composition dependence of T_g for miscible blends. The most frequently cited equations are those proposed by Gordon and Taylor,⁵ Fox,⁶ Couchman,⁷ and Brekner et al.⁸ With the exception of the last treatment, these equations are only able to predict T_g -composition curves that exhibit negative deviation from the rule of mixtures prediction. Positive deviation occurs in systems with strong intermolecular interactions, and the failure of the predictions is due to the inability of these equations to account for strong interactions.⁹ The equation of Brekner et al.⁸ can predict positive deviation, but it contains two adjustable parameters that cannot be independently determined.

Prud'homme¹⁰ and Lin et al.¹¹ correlated qualitatively the fitting parameters K in the Gordon-Taylor equation (5) or q in Kwei's equation¹² with the strength of the interactions in binary blends. Since K and q are adjustable

empirical parameters, however, the ability to extract fundamental information by this approach is limited.

More recently, Couchman¹³ derived a T_g equation which considers the effect of the strength of interactions using the quasi-chemical approximation. Like the equation of Brekner et al.,⁸ however, Couchman's interaction term contains two adjustable parameters. Building upon Couchman's theory for the composition dependence of T_g ,¹⁴ Painter et al.¹⁵ recently incorporated the effect of hydrogen bonding on the enthalpy of mixing and the composition dependence of T_g . Knowledge of the equilibrium constants of self-association and association between unlike groups in a blend exhibiting hydrogen bonding allows one to calculate the enthalpy of mixing and T_g .

It is desirable to have a scheme for correlating T_g with a measure of the intermolecular interactions, such as the Flory-Huggins interaction parameter, χ . In this paper, we extend Couchman's theory¹⁴ to include a term involving χ . When χ is known from another independent measurement, such as from melting point depression data, this theory can be used to predict T_g . Alternatively, when the T_g -composition relationship is known, the theory can be used to calculate χ .

Theoretical Considerations

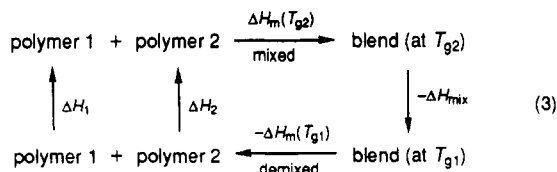
The glass transition can be treated formally as an Ehrenfest transition of second order.¹⁶ The thermodynamic functions, entropy, enthalpy, and volume, are continuous at T_g , but the first derivatives of these functions undergo discontinuities at T_g . In principle, any of these thermodynamic functions could be used to derive the relation for the compositional variation of T_g , but, in practice, the dependence of these variables on composition is not usually known. As a result, approximations of the thermodynamic functions are usually used.¹⁴ Owing to the importance of enthalpic interactions on the phase behavior of polymer blends and the relationship between enthalpy and χ , the theory described herein employed enthalpy as the thermodynamic variable.

Consider two polymers having glass transition temperatures T_{g1} and T_{g2} and respective molar enthalpies H_1 and H_2 . The molar enthalpy of a mixture of the two polymers is

$$H_{\text{mix}} = x_1 H_1 + x_2 H_2 + \Delta H_m \quad (2)$$

where x_i represents the mole fraction of polymer i in the blend and ΔH_m is the excess enthalpy of mixing. The

thermodynamic cycle for the mixing process is represented by eq 3, where ΔH_1 , ΔH_2 , and ΔH_{mix} are the changes of



enthalpies when the temperature is increased from T_{g1} to T_{g2} at constant pressure for polymer 1, polymer 2, and their blend, respectively. $\Delta H_m(T_{g1})$ and $\Delta H_m(T_{g2})$ are the excess enthalpies of mixing at T_{g1} and T_{g2} . Solving eq 3 for ΔH_{mix} yields

$$\Delta H_{\text{mix}} = x_1 \Delta H_1 + x_2 \Delta H_2 + \Delta H_m(T_{g2}) - \Delta H_m(T_{g1}) \quad (4)$$

The enthalpy changes corresponding to heating the individual components and the mixture from T_{g1} to T_{g2} are

$$\Delta H_1 = \int_{T_{g1}}^{T_{g2}} c_{p1}^l dT \quad (5)$$

$$\Delta H_2 = \int_{T_{g1}}^{T_{g2}} c_{p2}^g dT \quad (6)$$

and ΔH for the blends is

$$\Delta H_m = \int_{T_{g1}}^{T_{g2}} c_{pm}^g dT + \int_{T_{gm}}^{T_{g2}} c_{pm}^l dT \quad (7)$$

where T_{gm} is the glass transition temperature of the miscible blend and c_{pi} represents the isobaric specific heat of material i ; the superscripts l and g denote the liquid and glass states, respectively. Substitution of eqs 5–7 into eq 4 gives

$$\begin{aligned}
 \int_{T_{g1}}^{T_{g2}} c_{pm}^g dT + \int_{T_{gm}}^{T_{g2}} c_{pm}^l dT = & x_1 \int_{T_{g1}}^{T_{g2}} c_{p1}^l dT + \\
 & x_2 \int_{T_{g1}}^{T_{g2}} c_{p2}^g dT + [\Delta H_m(T_{g2}) - \Delta H_m(T_{g1})] \quad (8)
 \end{aligned}$$

Experiments have shown that the blend specific heat, c_{pm} , is not a simple weighted average of the specific heats of the pure components.¹⁷ Wolf and Wendorff¹⁸ suggested the following approximate mixing law for the blend properties:

$$c_{pm} = x_1 c_{p1} + x_2 c_{p2} + x_1 x_2 \delta c_p \quad (9)$$

where δc_p is the specific heat change due to mixing, which is usually negative for a miscible blend.¹⁷ Using eq 9 and neglecting the temperature dependence of the c_{pi} 's, one can solve eq 8 for the T_{gm}

$$T_{gm} = \frac{x_1 T_{g1} + k x_2 T_{g2}}{x_1 + k x_2} - \frac{\Delta H_m(T_{g2}) - \Delta H_m(T_{g1})}{(x_1 + k x_2)(\Delta c_{p1} - x_2 \delta c_p)} \quad (10)$$

$$k = \frac{\Delta c_{p2} - x_1 \delta c_p}{\Delta c_{p1} - x_2 \delta c_p} \quad (11)$$

$$\Delta c_{pi} = c_{pi}^l - c_{pi}^g \quad (12)$$

where Δc_{pi} is the change in the specific heat of polymer i at T_{gi} .

The enthalpy of mixing for a binary polymer blend can be represented by a van Laar relationship

$$\Delta H_m(T) = \chi R T \phi_1 \phi_2 \quad (13)$$

where ϕ_i is the volume fraction of component i , R is the gas constant, T is the temperature, and χ is the Flory-Huggins interaction parameter.¹⁹ Substituting eq 13 into

eq 10

$$T_{gm} = \frac{x_1 T_{g1} + k x_2 T_{g2}}{x_1 + k x_2} - \frac{\chi R (T_{g2} - T_{g1}) \phi_1 \phi_2}{(x_1 + k x_2)(\Delta c_{p1} - x_2 \delta c_p)} \quad (14)$$

In general, χ is dependent on composition,^{20–24} and in this analysis, a quadratic function of composition is assumed

$$\chi = \chi_0 + \chi_1 w_2 + \chi_2 w_2^2 \quad (15)$$

where w_2 is the weight fraction of polymer 2. Substituting eq 15 into eq 14 and redefining Δc_{pi} in terms of unit mass gives

$$T_{gm} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + \frac{A w_1 w_2}{(w_1 + k w_2)(w_1 + b w_2)(w_1 + c w_2)^2} \quad (16)$$

$$A = \frac{-\chi R (T_{g1} - T_{g2}) c}{M_1 \Delta c_{p1}} \quad (17)$$

$$k = \frac{\Delta c_{p2} - w_1 \delta c_p}{\Delta c_{p1} - w_2 \delta c_p} \quad (18)$$

where $c = \rho_1/\rho_2$, $b = M_2/M_1$, ρ_i is the density of polymer i , and M_i is the molar mass per chain segment of component i . Equations 16–18 relate the glass transition temperature of the blend to the interaction parameter. Thus, when T_{gm} is known, these equations can be used to calculate χ .

Results and Discussion

According to eqs 16–18, the T_g -composition behavior for a binary polymer blend is governed by the values of the parameters k and A . From eq 17, A is linearly dependent on χ . The stronger the intermolecular interactions, the larger is the value of A , and the larger will be the positive deviation of T_{gm} from a linearly weighted average of the component polymer T_g 's.

In eq 18, δc_p is usually small compared with Δc_{pi} ²⁵ and k can be approximated by

$$k = \frac{\Delta c_{p1}}{\Delta c_{p2}} \left[1 + w_1 \frac{\delta c_p^l}{\Delta c_{p2}} + w_2 \frac{\delta c_p^g}{\Delta c_{p1}} \right] \quad (19)$$

In general, k is slightly dependent on blend composition.

Since the parameters k and A have opposite effects on T_g , miscible blends may exhibit either positive or negative deviation from the linear mixing rule depending on the strength of the interpolymer interactions. At this point, it is useful to discuss the effect of interactions on T_g for three cases involving very weak, relatively weak, and strong interpolymer interactions.

1. Very Weak or No Specific Interactions. When the interactions are very weak, δc_p and A (or χ) are also very small. It is appropriate then to neglect their effects on T_g , and eq 11 simplifies to the following form of Couchman's equation:

$$T_g = (w_1 T_{g1} + K_0 w_2 T_{g2}) / (w_1 + K_0 w_2) \quad (20)$$

where $K_0 = \Delta c_{p2}/\Delta c_{p1}$. [Note that by definition, polymer 1 is the lower T_g component, and, therefore, $K_0 = \Delta c_{p2}/\Delta c_{p1} < 1$. Thus, eq 20 always predicts negative deviation for $(T_g)_{\text{blend}}$.] An example in this case is the blend of isotactic and syndiotactic poly(methyl methacrylate) (PMMA).²⁶ The experimental T_g 's and the predictions of eq 20 for isotactic/syndiotactic PMMA blends, shown in Figure 1, are in good agreement.

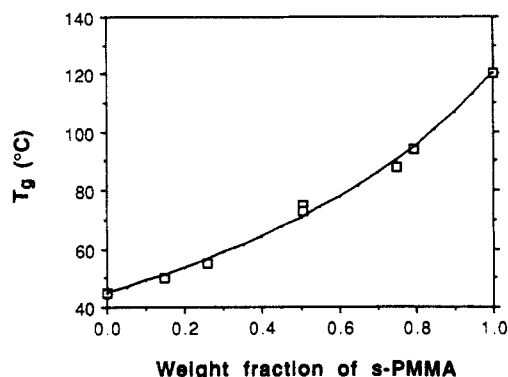


Figure 1. T_g vs composition for i-PMMA/s-PMMA blends. Curve is eq 20 with $\Delta c_{p1} = 0.41$ J/(g K) and $\Delta c_{p2} = 0.23$ J/(g K); (\square) experimental data from ref 26.

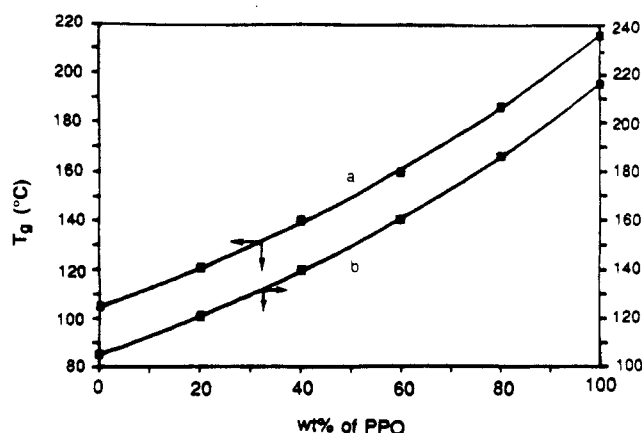


Figure 2. T_g vs composition for PS/PPO blends. Curves a and b correspond to eq 22 with $K' = 0.67$ and eq 16 with $k = 0.61$ and $A = 6$; (\square) experimental data from ref 28.

If $\Delta c_{pi}T_{gi}$ is constant,²⁷ eq 20 reduces to the Fox equation⁶

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (21)$$

Like eq 20, eq 21 predicts negative deviation of the T_g -composition curve from the rule of mixtures relationship.

2. Relatively Weak Specific Interactions. In this case, the effect of k exceeds that of A and the T_g -composition curve exhibits negative deviation from linear mixing. An approximation of eq 16 for this case is

$$T_g = (w_1T_{g1} + K'w_2T_{g2})/(w_1 + K'w_2) \quad (22)$$

$$K' = k + A/(T_{g2} - 1) \quad (23)$$

Equation 22 is identical in form to the Gordon-Taylor equation,⁵ except that in the Gordon-Taylor equation, K' is an adjustable parameter and is not defined by eq 23. The Gordon-Taylor equation can successfully describe the T_g behavior for miscible blends exhibiting negative and positive deviation if K' is treated as an adjustable parameter. Equation 22 indicates that K' increases with increasing strength of the polymer interactions. Therefore, it does represent a qualitative measure of interactions for comparison purposes, as demonstrated by the study of polyester/chlorinated polymers by Prud'homme.¹⁰

Examples of miscible binary polymer blends that are included in the category of relatively weak favorable interpolymer interaction include polystyrene/poly(2,6-dimethylphenylene oxide) (PS/PPO),²⁸ PS/poly(vinyl methyl ether) (PVME),²⁹ and PMMA/poly(ethylene oxide) (PEO).³⁰ Figure 2 compares the predictions of eq 16 and the Gordon-Taylor equation, as written in eq 22 with K' as an adjustable parameter, with experimental T_g data for PS/PPO blends. Both equations do a good job of fitting

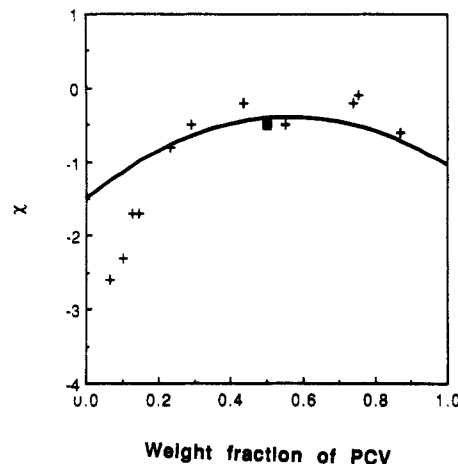
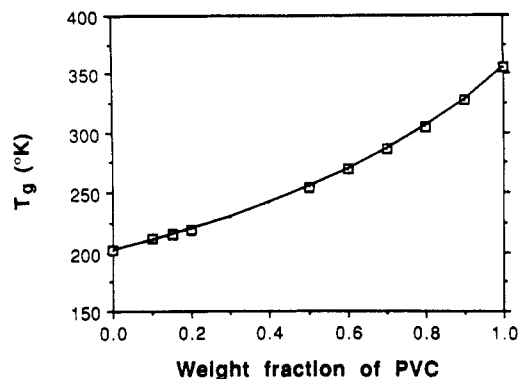


Figure 3. (a) T_g vs composition for PVC/PLC blends. Curve is eq 16 with $k = 0.35 + 0.07w_2$ and $A = 32.1(1 - w_2)^2$; experimental data (\square) taken from ref 34. (b) χ -Values calculated from eq 17; data from inverse gas chromatography³⁵ (+) and (■) melting point depression.³⁶

the data, but eq 16 provides a direct evaluation of χ , which can be calculated from A using eq 17. For the PS/PPO data shown in Figure 2, the best fit of eq 16 occurred for $A = 6$, and eq 17 gave $\chi \approx -0.2$, which agrees with the χ -values of -0.17 and -0.3 obtained respectively from melting point depressing data and heat of mixing by Plans et al.³¹ but are lower than the values of -0.02 obtained by Runt³² from melting point depression data and -0.021 to -0.085 determined from small-angle neutron scattering by Maconnachie et al.³³

Another example of a blend in this category is poly(ϵ -caprolactone) and poly(vinyl chloride) (PCL/PVC).³⁴ The best fit of eq 16 to PCL/PVC data is shown in Figure 3a, and Figure 3b compares the values of χ calculated from eq 17 with values reported from inverse gas chromatography³⁵ and melting point depression³⁶ studies. In constructing the curves in Figure 3a, k and A were allowed to vary with composition

$$k = 0.35 + 0.07w_2 \quad (24)$$

and

$$A = 32.1(1 - 2.6w_2 + 2.3w_2^2) \quad (25)$$

which yielded a composition-dependent χ . Except for the data at high PCL concentrations, i.e., $>75\%$ PCL, the χ -values calculated from eqs 16–18 were comparable to the literature values, though the theory did not do as good a job at reproducing the shape of the χ versus composition curve.

3. Strong Specific Interactions. Blends in this category exhibit positive deviation in T_g from linear additivity. In fact, positive deviation is often cited as an indication of strong interpolymer interactions in blends,

e.g., interpolymer complexes.⁹ In this case, the effect of A in eq 16 is more important, and δc_p may be neglected. Equations 16–18 become

$$T_{gm} = \frac{w_1 T_{g1} + k_0 w_2 T_{g2}}{w_1 + k_0 w_2} + \frac{A w_1 w_2}{(w_1 + k_0 w_2)(w_1 + b w_2)(w_1 + c w_2)^2} \quad (26)$$

$$A = \frac{-\chi R(T_{g1} - T_{g2})c}{M_1 \Delta c_{p1}} \quad (17)$$

$$k_0 = \Delta c_{p2} / \Delta c_{p1} \quad (27)$$

All the parameters can be measured by experiment; that is, there are no adjustable parameters in these equations.

The parameters k_0 , b , and c in the second term in eq 26 are often between 0.7 and 1.3. In this case, the second term may be approximated by a Taylor series expansion

$$A w_1 w_2 (1 + d w_2 + \dots) \quad (28)$$

where $d = (1 - k_0) + (1 - b) + 2(1 - c)$. If $d \ll 1$, eq 26 reduces to Kwei's equation.¹² It can also be shown that transformation of eq 26 into a three-term virial expression in terms of volume fraction results in an equation similar to that of Brekner et al.⁸

Examples of strong interpolymer interactions in binary blends include hydrogen bonding of carboxylic acid and hydroxyl groups,³⁷ electron donor–acceptor complexes,⁹ ionic interactions,³ and transition metal complexes.³⁸ Figure 4a shows the glass transition temperature data taken from ref 9 for a series of electron donor–acceptor complexes, poly[*N*-(2-hydroxyethyl)carbazolyl methacrylate] (PHECM) and poly[(ω -hydroxyalkyl)-3,5-dinitrobenzoyl methacrylate] (PDNBM-*n*),⁹ and the predictions of eq 26. Satisfactory fits of the data were obtained using a composition-dependent A (i.e., χ) for each system. The χ predictions are plotted in Figure 4b; the large negative values are indicative of the very strong interchain interactions that occur in these blends. The enthalpy of mixing, ΔH_m , was also estimated from χ by using eq 13, as shown in Figure 5. The change of the calculated ΔH_m with composition of the blends is similar to the experimentally observed enthalpy change associated with decomplexation of the electron donor–acceptor complexes at 180 °C.⁹ This is expected because both quantities are measures of the strength of the intermolecular interaction.

Figure 6 compares the predictions of eq 26 with experimental T_g data for miscible blends of polyamide-6 and manganese-neutralized lightly sulfonated polystyrene (sulfonation level = 10.1 mol %). Miscibility was due to transition metal complexation of the Mn(II) cation and the amide groups.³⁸ Again, good agreement was obtained between the theory and experiment. In Figure 7, the χ -values calculated from eq 17 are compared with the values calculated from melting point depression data from ref 38. Although the χ -values determined from the T_g data were lower than those calculated from melting point depression, both approaches yielded large negative values for χ and the trends were similar.

Conclusion

The composition- T_g equation proposed in this paper directly relates T_g with the thermodynamic interaction parameter, χ , for a miscible binary blend. All parameters in this equation have well-defined physical meanings and can be determined by independent measurements. Other

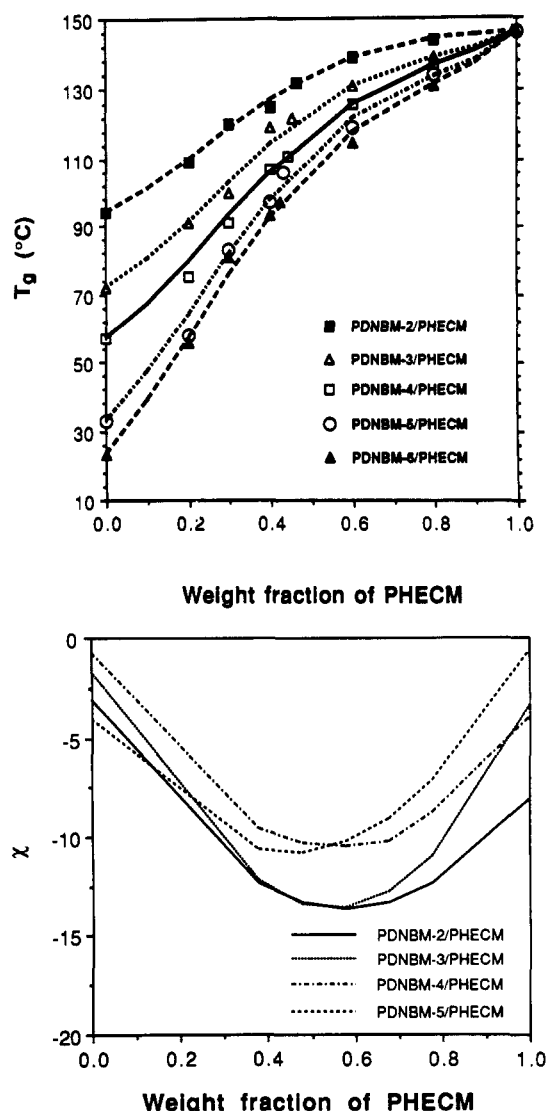


Figure 4. (a) T_g vs composition for donor (*N*-(2-hydroxyethyl)-carbazolyl methacrylate) (PHECM) and acceptor [(ω -hydroxyalkyl)-3,5-dinitrobenzoyl methacrylates] (PDNBM-*n*) blends. Curves were calculated from eq 26. Δc_{p1} was estimated by the Simha-Boyer rule.²⁷ Data were from ref 9. (b) χ -Values calculated from eq 17.

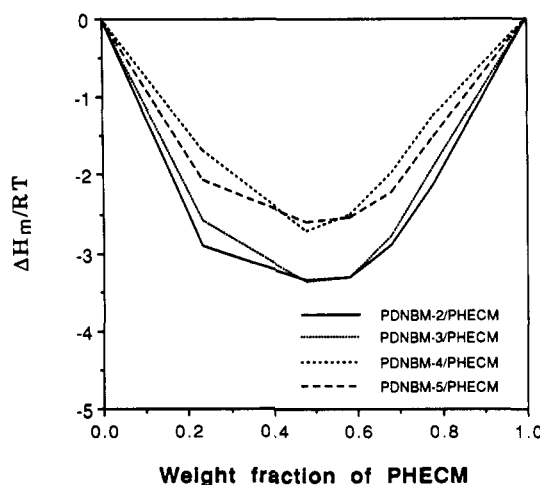


Figure 5. Enthalpy of mixing for blends in Figure 4 calculated from the interaction parameters in Figure 4b.

popularly used equations for T_g , e.g., those proposed by Fox,⁶ Gordon and Taylor,⁵ Couchman,⁷ Brekner et al.,⁸ and Kwei,¹² were shown to be special cases of the present theory. This equation offers a convenient method for evaluating χ from measurements of T_g .

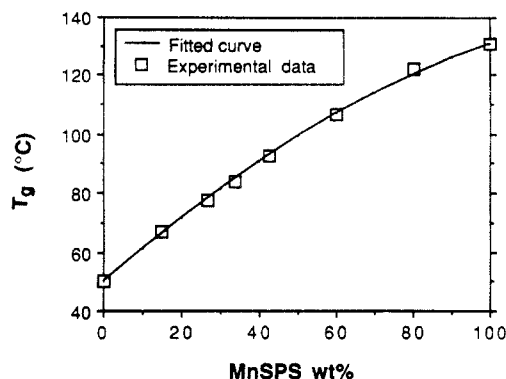


Figure 6. T_g vs composition for PA6/Mn-SPS blends. Curve is eq 26; data are from ref 38.

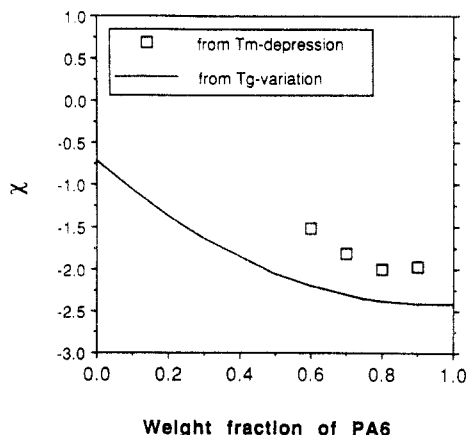


Figure 7. χ -Values for PA6/Mn-SPS blends calculated from the T_g data and eq 17 and (\square) from melting point depression data.

The effect of the strength of the interpolymer interactions on the T_g was discussed for three different classes of polymer blends: (1) with very weak, (2) with relatively weak, and (3) with strong interactions. T_g of a miscible blend may exhibit either positive or negative deviation from the weight-average values depending on the strength of the interpolymer interactions. The proposed theory adequately described the T_g behavior of all three categories of blends, and the values of χ calculated by this method agreed qualitatively with those obtained by other more classical techniques.

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