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Interaction Strength, Nonrandom Mixing, and the Compositional Variation of Glass Transition Temperatures

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ABSTRACT: Through the quasi-chemical approximation, I consider the effect of interaction strength and nonrandom mixing on the compositional variation of glass transition temperatures, T_g. Enthalpic relations are derived, and the reduction of these to a random-mixing relation is considered. Previous empirical random-mixing equations are shown to be approximations to this. This treatment is complemented by a volume-based theory. Conditions for the consistency of these two treatments are given.

Introduction

In a number of papers I have outlined an entropic theory of the composition dependence of the glass transition for a variety of particular aspects of the overall theme and have tested these quantitatively.[1] At the heart of this theory is the expectation that many miscible systems can reasonably be taken as more or less random, a common simplifying assumption in solution theory. When there are strong or specific interactions or when interactions between like and unlike species differ significantly, this may not be acceptable. It is this kind of situation that I address below.

Theory

In the quasi-chemical approximation, the enthalpy of mixing of a solution, ΔH_{mix}, can for polymeric materials be written approximately as

$$\Delta H_{\text{mix}} = \frac{2\phi(1-\phi)w}{1+\beta} \tag{1}$$

for a binary solution.[2] Here ϕ is (approximately) a volume fraction and

$$w = 2w_{ij} - (w_{ii} + w_{jj}) \tag{2}$$

where the w_{kl} are pair interaction energies and w is essentially a molecular level mixing parameter, usually (but not necessarily) taken as temperature-independent. Further

$$\beta = \{1 + 4\phi(1-\phi)[e^{2w/zRT} - 1]\}^{1/2} \tag{3}$$

where z is the nearest-neighbor number, T the absolute temperature, and R the gas constant. From this expression and the definition that the enthalpy, H, of the solution can be written as

$$H = \phi H_1 + (1-\phi)H_2 + \Delta H_{\text{mix}} \tag{4}$$

where the H_i are pure constituent properties (at the same temperature and pressure)

$$H = \phi H_1 + (1-\phi)H_2 + \frac{2\phi(1-\phi)w}{1+\beta} \tag{5}$$

With use of the superscripts l and g for liquid and glass, respectively, two parallel versions of eq 5 can be written

$$H^l = \phi H_1^l + (1-\phi)H_2^l + \frac{2\phi(1-\phi)w^l}{1+\beta^l} \tag{6a}$$

and

$$H^g = \phi H_1^g + (1-\phi)H_2^g + \frac{2\phi(1-\phi)w^g}{1+\beta^g} \tag{6b}$$

Taking $H^l = H^g$ at T_g of the solution and noting that $H_i^l(T_{g_i}) = H_i^g(T_{g_i})$, from eq 6 at the solution transition temperature,

$$0 = \phi\int_{T_{g_1}}^{T_g}\Delta C_{p_1}\,dT + (1-\phi)\int_{T_{g_2}}^{T_g}\Delta C_{p_2}\,dT + 2\phi(1-\phi)\left(\frac{w^l}{1+\beta^l} - \frac{w^g}{1+\beta^g}\right) \tag{7}$$

where the ΔC_{p_i} are pure-constituent transition increments of heat capacity. Subsequently, and for no other reason than simplicity and convenience, these are treated as temperature-independent.[3] When eq 7 is integrated for this simple case

$$T_g = \frac{\phi\Delta C_{p_1}T_{g_1} + (1-\phi)\Delta C_{p_2}T_{g_2} + 2\phi(1-\phi)\left(\frac{w^g}{1+\beta^g} - \frac{w^l}{1+\beta^l}\right)}{\phi\Delta C_{p_1} + (1-\phi)\Delta C_{p_2}} \tag{8}$$

The version of eq 8 that is the simplest is the random-mixing (high-temperature or large-z) form when $\beta^g \rightarrow \beta^l \rightarrow 1$, which reduces eq 8 to

$$T_g = \frac{\phi\Delta C_{p_1}T_{g_1} + (1-\phi)\Delta C_{p_2}T_{g_2} + \phi(1-\phi)\Delta w}{\phi\Delta C_{p_1} + (1-\phi)\Delta C_{p_2}} \tag{9}$$

where Δw is defined as

$$\Delta w = w^g - w^l \tag{10}$$

This relation I have given previously.[4] Two cases of eq 9 are of immediate interest, the first of these obtained when $\Delta C_{p_1} = \Delta C_{p_2} = \Delta C_p$ to give

$$T_g = \phi T_{g_1} + (1-\phi)T_{g_2} + \phi(1-\phi)\frac{\Delta w}{\Delta C_p} \tag{11}$$

Equation 11 is in form identical with an approximate version of the empirical Kwei equation[5,6] and identifies the parameter q there as $\Delta w/\Delta C_p$, a reduced transition difference of "exchange" energies. The Kwei equation results if in eq 9 the approximation $\Delta C_{p_1} = \Delta C_{p_2} = \Delta C_p$

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is used only for the term in Δw and is[5,6]

$$T_g = \frac{\phi T_{g_1} + (1-\phi)\dfrac{\Delta C_{p_2}}{\Delta C_{p_1}} T_{g_2}}{\phi + (1-\phi)\dfrac{\Delta C_{p_2}}{\Delta C_{p_1}}} + \phi(1-\phi)\frac{\Delta w}{\Delta C_p} \qquad (12)$$

This identifies k of the Kwei equation as $\Delta C_{p_2}/\Delta C_{p_1}$ and demonstrates that this relation is part of a series of random-mixing expressions for the compositional variation of T_g.

Equations 1–3 can be used to derive a convenient first-order correction to ΔH_{mix} and therefore to give a first-order correction to the mixing relation. Actually, it can of course be used to give all orders of corrections, but the first one leads to the simplest closed-form expression for T_g. For comparatively small w/zRT

$$\Delta H_{\mathrm{mix}} \simeq \phi(1-\phi)w\left[1 - \frac{2\phi(1-\phi)w}{zRT}\right] \qquad (13)$$

showing that ΔH_{mix} then lies always below the random value. Using eq 13 in eq 8, in the approximation $(1+x)^{1/2} \simeq 1 + {}^1/_2 x$ the version of eq 8 derived from the use of eq 13 is

$$T_g = \frac{\phi \Delta C_{p_1} T_{g_1} + (1-\phi)\Delta C_{p_2} T_{g_2} + \phi(1-\phi)\Delta w}{\phi \Delta C_{p_1} + (1-\phi)\Delta C_{p_2}} - \frac{2\phi^2(1-\phi)^2 \Delta w^2}{zR[\phi \Delta C_{p_1} T_{g_1} + (1-\phi)\Delta C_{p_2} T_{g_2} + \phi(1-\phi)\Delta w]} \qquad (14)$$

where

$$\Delta w^2 = (w^g)^2 - (w^l)^2 \qquad (15)$$

The derivation of eq 14 involves the solution of a quadratic equation, only one solution of which recovers the random-mixing expression. Equation 14 shows that to first order the effect of nonrandomness simply adds a term to the expression for the solution T_g. For simplicity, I shall go no further than the first correction term, although others can be added readily via, for example, a MacLaurin expansion of the ΔH_{mix} or by direct approximation. In the event $\Delta C_{p_1} \simeq \Delta C_{p_2} = \Delta C_p$, eq 14 simplifies somewhat to

$$T_g = \phi T_{g_1} + (1-\phi)T_{g_2} + \phi(1-\phi)\frac{\Delta w}{\Delta C_p} - \frac{2\phi^2(1-\phi)^2 \dfrac{\Delta w^2}{\Delta C_p}}{zR\left[\phi T_{g_1} + (1-\phi)T_{g_2} + \phi(1-\phi)\dfrac{\Delta w}{\Delta C_p}\right]} \qquad (16)$$

An order of magnitude estimate indicates that dependent on Δw^2 the nonrandom-mixing term may not always be negligible.

The glass transition temperature is not the only property modified by the interaction strength; ΔC_p for the solution is also. From eq 6

$$\Delta C_p = \phi \Delta C_{p_1} + (1-\phi)\Delta C_{p_2} + \frac{8\phi^2(1-\phi)^2}{zRT_g^{\,2}}\left[\frac{(w^l)^2 e^{2w^l/zRT_g}}{\beta^l(1+\beta^l)^2} - \frac{(w^g)^2 e^{2w^g/zRT_g}}{\beta^g(1+\beta^g)^2}\right] \qquad (17)$$

which to first order is

$$\Delta C_p = \phi \Delta C_{p_1} + (1-\phi)\Delta C_{p_2} - \frac{2\phi^2(1-\phi)^2}{zRT_g^{\,2}}[(w^g)^2 - (w^l)^2] \qquad (18)$$

a departure from linearity in composition. To take, for example, the case of $|w^g| > |w^l|$ and both negative, this contribution to ΔC_p is negative and vice versa for the same signs but $|w^g| < |w^l|$.

Of interest in connection with the various expressions for T_g is the possible occurrence of compositional extrema in this property. Consider the simple case of random mixing and then write eq 9 as

$$T_g[\phi \Delta C_{p_1} + (1-\phi)\Delta C_{p_2}] = \phi \Delta C_{p_1} T_{g_1} + (1-\phi)\Delta C_{p_2} T_{g_2} + \phi(1-\phi)\Delta w \qquad (19)$$

At an extremum of T_g

$$T_g^*(\Delta C_{p_1} - \Delta C_{p_2}) = \Delta C_{p_1} T_{g_1} - \Delta C_{p_2} T_{g_2} + (1 - 2\phi^*)\Delta w \qquad (20)$$

From this relation and eq 9, ϕ^* *and* T_g^* can be solved for explicitly. Note that if and only if $\Delta C_{p_1} = \Delta C_{p_2}$ and $T_{g_1} = T_{g_2}$ is $\phi^* = {}^1/_2$. However, note also that for $\Delta C_{p_1} = \Delta C_{p_2}$ alone there is a simple solution for ϕ^*, namely

$$\phi^* = \frac{1}{2}\left[1 + \frac{T_{g_1} - T_{g_2}}{\Delta w/\Delta C_p}\right] \qquad (21)$$

For the simplest case

$$\left.\frac{d^2 T_g}{d\phi^2}\right|_{\phi=\phi^*} = -2\Delta w \qquad (22)$$

giving a maximum for positive Δw and a minimum for negative Δw.

The Kwei relation, eq 12, with the two parameters identified there as $\Delta C_{p_2}/\Delta C_{p_1}$ *and* $\Delta w/\Delta C_p$ taken as adjustable, has been fitted to data for a variety of blends.[5,6] Consequently, I shall not dwell on this, the main purpose of this contribution being didactic. However, it is convenient at this point to make an order of magnitude estimate for $\Delta w/\Delta C_p$. If the magnitude of Δw is more or less on the order of ${}^1/_{10}$ of that for hydrogen bonds and ΔC_p on the order of 0.1 cal^{-1} g^{-1} deg^{-1}, then $\Delta w/\Delta C_p \simeq 100$ K. This is consistent with values of q reported by Kwei.[5] The other convenient test of the theory is for random copolymerization, where in terms of monomer feed fraction f

$$T_g = \frac{f \Delta C_{p_1} T_{g_1} + (1-f)\Delta C_{p_2} T_{g_2} + f(1-f)\Delta w}{f \Delta C_{p_1} + (1-f)\Delta C_{p_2}} \qquad (23)$$

For the case of ethyl acrylate/vinylidene chloride copolymers, which exhibit a striking maximum, $T_{g_1} \simeq T_{g_2}$ to within 2 K and copolymerization is almost random.[7] Taking $\Delta C_{p_1} = \Delta C_{p_2}$, from the data $\Delta w/\Delta C_p \simeq 240$ K, which fits slightly better than the entropic relation for copolymers as quasi-binary systems of diads.[8] The overlap of the two approaches in the limit of large specific interactions, i.e., compound formation, is a sign here of conceptual consistency and suggests how the entropic theory might be modified to take into account specific interactions, by treating certain solutions as quasi-binary mixtures.

Final Remarks

The volume also reflects the effect of specific interactions on T_g and treatment of this involves only the exchange of

$\Delta v_i \alpha_i$ for ΔC_{p_i} and v for w except in β, which remains unchanged. For example, the parallel form of eq 9 is

$$T_g = \frac{\phi \Delta(v_1 \alpha_1) T_{g_1} + (1-\phi)\Delta(v_2\alpha_2)T_{g_2} + \phi(1-\phi)\Delta v}{\phi \Delta v_1 \alpha_1 + (1-\phi)\Delta v_2 \alpha_2} \qquad (24)$$

The consistency of eqs 9 and 24 requires that

$$\frac{\Delta v}{\Delta w} = \frac{\Delta C_{p_1}}{\Delta C_{p_2}} = \frac{\Delta v_1 \alpha_1}{\Delta v_2 \alpha_2} \qquad (25)$$

The enthalpic theory does not replace the entropic theory; rather it complements the latter in its present form. Also, for all solutions except those that are athermal, the enthalpic theory contains adjustable parameters, the w. These are adjustable in that the w are not determinable a priori, although they can be fit if, for example, heats of mixing are known above and below T_g. Similarly, except in the unusual case of volume additivity, the volume-based theory has two adjustable parameters.

References and Notes

(1) See, for example: Couchman, P. R. *Macromolecules* **1987**, *20*, 1712 and references therein.

(2) Guggenheim, E. A. *Mixtures*; Oxford University Press, Oxford, U.K., 1952.

(3) Temperature-dependent ΔC_{p_i} can be included readily through eq 7 and subsequent versions thereof. For example, for $\Delta C_{p_i} T \sim$ constant, which is sometimes convenient to assume, the blend glass transition temperature is given by

$$\ln T_g = \frac{\phi \Delta C_{p_1}{}^\circ \ln T_{g_1} + (1-\phi)\Delta C_{p_2}{}^\circ \ln T_{g_2}}{\phi_1 \Delta C_{p_1}{}^\circ + (1-\phi)\Delta C_{p_2}{}^\circ}$$

where $\Delta C_{p_i}{}^\circ$ denotes $\Delta C_{p_i}(T_{g_i})$. In this case

$$\Delta C_p = \frac{1}{T_g{}^{u_1} T_g{}^{u_2} e^{\phi(1-\phi)\Delta\tilde{w}}} [\phi \Delta C_{p_1}{}^\circ T_{g_1} + (1-\phi)\Delta C_{p_2}{}^\circ T_{g_2}]$$

where u_1 denotes

$$\frac{\phi_i \Delta C_{p_i}{}^\circ}{\phi \Delta C_{p_1}{}^\circ + (1-\phi)\Delta C_{p_2}{}^\circ} \text{ and } \Delta\tilde{w} = \frac{\Delta w}{\phi \Delta C_{p_1}{}^\circ + (1-\phi)\Delta C_{p_2}{}^\circ}$$

(4) Couchman, P. R. *Proc. SPE ANTEC* **1988**, 1122.

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(6) Lin, A. A.; Kwei, T. K.; Reiser, A. *Macromolecules* **1989**, *22*, 4112.

(7) Comyn, J.; Fernandez, R. A. *Eur. Polym. J.* **1975**, *11*, 149.

(8) Couchman, P. R. *Macromolecules* **1982**, *15*, 770.