Peculiarities of the glass transition temperature of binary polymeric systems: entropic and enthalpic treatments

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The concentration dependence of the glass transition temperature T_g of binary polymeric systems, for the Couchman entropic and enthalpic treatments, has been described by taking into account the temperature dependence of the specific-heat increments $\Delta c_p(T)$ and the presence of a characteristic temperature T_0. It is shown that at T_0 the analytical equations undergo a sudden change. Comparison of the equations obtained with a set of experimental data on the poly(vinyl chloride)–dibutyl phthalate system appears to be satisfactory. The treatment allows one to characterize a binary system with suitable thermodynamic parameters.

(Keywords: glass transition; entropy of mixing; enthalpy of mixing)

INTRODUCTION

Recently, the composition dependence of the glass transition temperature T_g of binary polymeric systems (i.e. polymer–diluent and polymer–polymer mixtures) has been examined by the authors in the light of the entropic treatment proposed by Couchman[1,2], and the problems related to the exact form of the $\Delta c_p(T)$ function that enters Couchman's equation have been discussed in detail[3]. The influence of specific interactions has also been taken into consideration, and, moreover, the entropic treatment has been extended to low-temperature regions, where a different equation has to be applied, owing to the abrupt change of the analytical $\Delta c_p(T)$ function of the component with higher T_g at some characteristic temperature T_0 (ref. 4). The latter treatment can explain the presence of a cusp in some experimental T_g–composition curves, an argument often debated in the literature[5]. The composition dependence of T_g has been described on the basis of an enthalpic, rather than entropic, theory by Painter *et al.*[6], who investigated the effect of specific interactions, in particular of hydrogen bonds, in some polymeric blends. The problem has recently been discussed thoroughly by Couchman[7], who has treated quantitatively the influence of specific interactions, i.e. of non-random mixing, on the T_g of binary systems using an enthalpic treatment, and by Lu and Weiss[8], who have described the T_g – composition curve in terms of the Flory χ parameter.

The subject of the present paper is the comparison between the entropic and enthalpic treatments, when the temperature dependence of $\Delta c_p(T)$ is taken into account and so is the presence of the critical temperature T_0, below which different equations have to be used. Specific interactions are included in the treatment, making use of suitable parameters.

ENTROPY AND ENTHALPY OF MIXING AND THE GLASS TRANSITION TEMPERATURE

When two miscible polymeric or non-polymeric components, whose glass transition temperatures are T_{g1} and T_{g2} (with $T_{g2} > T_{g1}$), are mixed, the entropy and enthalpy of the mixture, at its glass transition temperature T_g, have identical values in the glassy and liquid phases, so that the following equations apply[1,7]:

$$w_1 s_1^l + w_2 s_2^l + \Delta s_m^l = w_1 s_1^g + w_2 s_2^g + \Delta s_m^g \qquad (1a)$$

$$w_1 h_1^l + w_2 h_2^l + \Delta h_m^l = w_1 h_1^g + w_2 h_2^g + \Delta h_m^g \qquad (1b)$$

where w_i are the weight fractions; s_i^l, s_i^g, h_i^l, h_i^g are the mass-specific liquid and glassy entropies and enthalpies of pure components; and Δs_m^l, Δs_m^g, Δh_m^l, Δh_m^g are the entropies and enthalpies of mixing of the liquid and the glass, respectively.

When strong or specific interactions are absent, i.e. when only dispersion forces are active between non-polar components, miscible binary mixtures of two polymers, or of a polymer and a diluent, are usually taken to be random. In this case Δs_m is approximately equal to the ideal combinatorial mixing entropy, in particular when

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the conformation of the macromolecules in the mixture is identical to that in the pure states. Since the combinatorial mixing entropy is dependent only on composition, at the glass transition temperature of the mixture, $\Delta s_m^l = \Delta s_m^g$.

In practice, non-weak interactions are almost always present, those active in the mixture being in general different from those of the two pure components. In a mixture or in a pure component, the number of strong or specific interactions depends on temperature and physical state, so that, as a result, the equality $\Delta s_m^l = \Delta s_m^g$ is no longer applicable. The difference $(\Delta s_m^l - \Delta s_m^g)$ can be formally used as the parameter that quantifies the effect of specific interactions on the analytical equation that describes the T_g–composition curve[3]. Analogously, in the enthalpic treatment, the difference $(\Delta h_m^l - \Delta h_m^g)$ can be used to monitor the effect of interactions between the two components. As Couchman has pointed out recently[7], the enthalpy of mixing is a function of composition, of temperature and of interaction energy, which in turn depends on the state of aggregation. Ideal athermal mixtures are rarely encountered, so that $(\Delta h_m^l - \Delta h_m^g)$ is almost always not zero.

COMPOSITION DEPENDENCE OF THE GLASS TRANSITION TEMPERATURE: THEORETICAL TREATMENT

Equations (1a) and (1b) are of general applicability, so that they can be used for whatever glass transition temperature. When the thermodynamic functions *s* and *h* have to be obtained in an explicit form, however, it should be kept in mind that the differences $(s_2^l - s_2^g)$ and $(h_2^l - h_2^g)$ will exhibit a singular point at a characteristic temperature T_{02}, when the following condition is satisfied:

$$T_{g1} < T_g < T_{02}$$

To investigate in detail the above conclusion, it is useful to start from the papers of Angell[9,10] and Gutzow and Dobreva[11,12], which deal with the thermodynamics of glassifying systems. Taking the undercooled melt as a thermodynamic system in metastable equilibrium and the crystal as a stable equilibrium phase at all the temperatures of interest, for a generic glassifying substance the 'third principle' requires that below T_g a characteristic temperature T_0 exists such that at any $T < T_0$ the following conditions apply:

$$c_p^l - c_p^c = 0 \tag{2a}$$

$$s^l - s^c = 0 \tag{2b}$$

$$g^l - g^c = h^l - h^c = \text{constant} \tag{2c}$$

where c_p is the specific heat, *g* the Gibbs free energy and *l* and *c* refer respectively to the liquid and crystal states.

In practice, experimental c_p^l data cannot be obtained in the region from T_g to T_0, and, moreover, in principle, different extrapolated curves $c_p^l(T)$ can be devised in the above temperature region. Following Angell, one can select the most gradual decrease of $(c_p^l - c_p^c)$ below T_g, so that the entropy of the undercooled liquid remains greater than the entropy of the crystal as far as possible; as a consequence a sharp decrease of c_p^l in the proximity of T_0 is assumed to take place[10]. An identical thermodynamic c_p^l criterion is suggested, for the sake of simplicity, by Gutzow *et al.*[11,12].

Accordingly, the characteristic temperature T_0 is therefore defined in the present paper as that at which the differences $(c_p^l - c_p^c)$ and $(s^l - s^c)$ are both zero (equations (2a) and (2b)). From a physical point of view, keeping in mind the time dependence of any experimental measure of T_g, the characteristic temperature T_0 is defined as the 'ideal' glass transition temperature, or the T_g that one should observe for infinitely slow cooling rate[9–12].

To obtain in practical cases the T_0 value of a given compound, use is made of the equation[9,10]:

$$\Delta s_f = \int_{T_0}^{T_f} [c_p^l(T) - c_p^c(T)]\, \mathrm{d}\ln T \tag{3}$$

whose meaning is that the area between the liquid and crystal $c_p(T)$ curves from T_0 to the melting temperature T_f must be equal to the entropy of fusion Δs_f. To integrate equation (3), two well known approximations can be used, the first being:

$$c_p^l(T) - c_p^c(T) = \text{constant} \approx \Delta c_p(T_g) \tag{4}$$

where $\Delta c_p(T_g)$ is the value of $(c_p^l - c_p^g)$ measured at the glass transition temperature. The equation so obtained is:

$$T_0 = T_f \exp[-\Delta s_f / \Delta c_p(T_g)] \tag{5}$$

from which T_0 can be obtained when Δs_f and $\Delta c_p(T_g)$ are available.

A second, and better, approximation is[13]:

$$c_p^l(T) - c_p^c(T) = \text{constant}/T \tag{6}$$

which can be used at $T = T_g$ under the form:

$$T_g[c_p^l(T_g) - c_p^c(T_g)] = \text{constant} \approx T_g \Delta c_p(T_g) \tag{7}$$

The integrated equation is now:

$$T_0 = \frac{T_g T_f \Delta c_p(T_g)}{T_f \Delta s_f - T_g \Delta c_p(T_g)} \tag{8}$$

The values of T_0 calculated from equations (5) and (8) in some cases are found to be rather different, as seen in *Table 1* for selected polymers, whose T_g, $\Delta c_p(T_g)$, Δs_f and T_f are known from ref. 14.

Table 1 Values of T_f and T_g for selected polymers (ref. 14) and corresponding T_0 values as calculated from equations (5) and (8)

Polymer	T_f (K)	T_g (K)	T_0 (K) eq. (5)	eq. (8)
Polyethylene	415	237	161	156
Polypropylene	461	270	186	181
Poly(1-butene)	411	249	197	185
cis-Poly(1,4-butadiene)	285	171	94	100
Poly(vinyl fluoride)	503	314	217	214
Polytrifluoroethylene	495	304	244	230
Polystyrene	516	373	275	276
Polyoxyethylene	342	206	166	156
Poly(oxymethylene–oxyethylene)	348	209	157	150
Polyoxypropylene	348	198	168	153
Poly(methyl methacrylate)	450	378	234	253
Polycaprolactone	342	209	151	146
Nylon-6,6, α phase	553	323	237	226
Poly(oxy-1,4-phenylene)	535	358	270	265
Poly(oxy-2,6-dimethyl-1,4-phenylene)	580	483	420	418
Poly(ethylene terephthalate)	553	342	296	275
Poly(4,4′-isopropylidene-diphenylene carbonate)	608	418	229	251

An example is represented by diethyl phthalate (DEP), a simple substance for which extensive amorphous and crystalline heat-capacity, entropy and enthalpy data are available[15]. The c_p^l and c_p^c functions plotted in *Figure 1* for diethyl phthalate show how T_0 can be obtained on the basis of equation (3). The extrapolation of $c_p^l(T)$ is carried out from T_g to a temperature T_0 so that the area of the trapezoid is Δs_f. The obtained value of T_0 is 150 K; for comparison equations (5) and (8) give $T_0 = 151$ and 144 K respectively. As shown in *Figure 2*, the temperature T_0 can also be obtained by analytical or graphical extrapolation of the liquid-phase entropy down to the crystal entropy curve. The enthalpy curves $(h - h_0^c)$ (where h_0^c is the unknown residual crystalline enthalpy) are plotted in *Figure 3*, where a schematic representation of the undercooled liquid enthalpy is also shown, according to refs. 11 and 12. The liquid enthalpy $(h^l(T) - h_0^c)$ is extrapolated down to the T_0 value obtained from *Figures 1* or *2* (full curve). In the temperature range from T_0 down to 0 K, the liquid enthalpy curve (broken curve) is calculated according to the condition that the difference $(h^l - h^c)$, or the equivalent $((h^l - h_0^c) - (h^c - h_0^c))$, must remain constant[11,12]. It is clear from *Figure 3* that in the enthalpy curves T_0 cannot be identified easily. The important point in the above treatment is the singularity that the differences $(h^l - h^g)$ and $(s^l - s^g)$ show at the characteristic temperature T_0, as revealed in *Figures 2* and *3*.

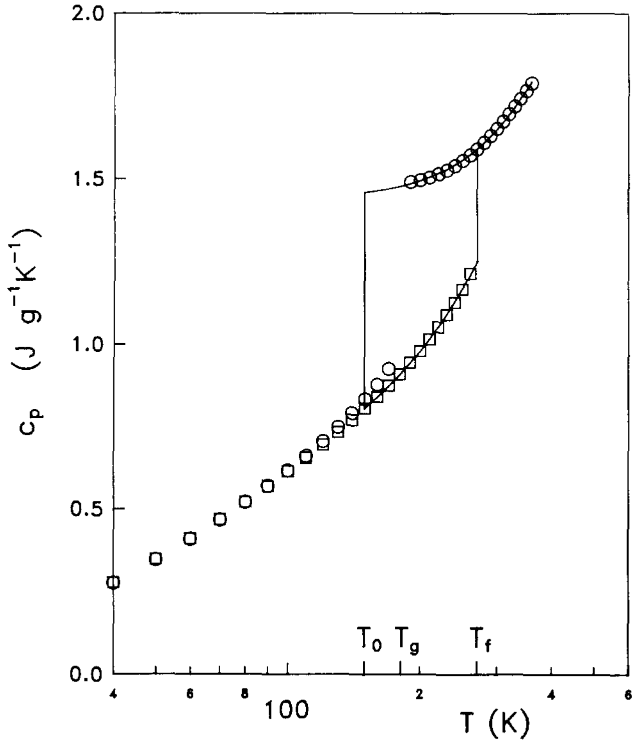

Figure 1 Specific heat–temperature diagram of diethyl phthalate. Data taken from ref. 15. The undercooled liquid specific heat is extrapolated down to T_0. The area of the trapezoid is Δs_f (see text). Points: (○) $c_p^l(T)$ and $c_p^g(T)$; (□) $c_p^c(T)$

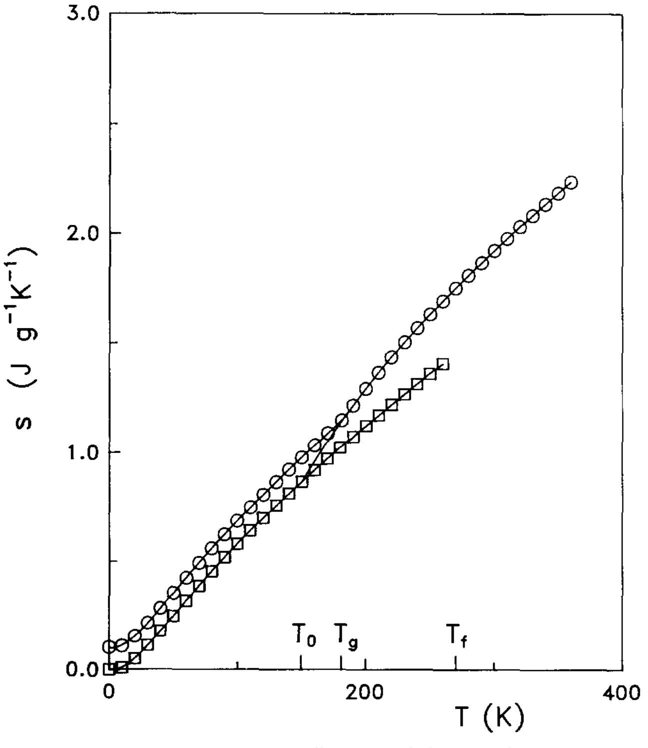

Figure 2 Entropy–temperature diagram of diethyl phthalate. Data taken from ref. 15. The undercooled liquid entropy is extrapolated down to T_0 (see text). Points: (○) $s^l(T)$ and $s^g(T)$; (□) $s^c(T)$

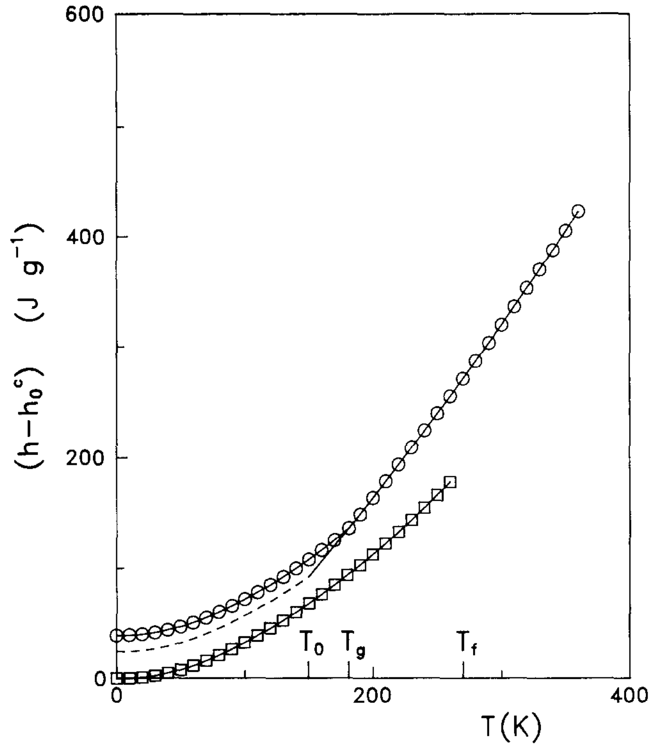

Figure 3 Enthalpy–temperature diagram of diethyl phthalate. Data taken from ref. 15. The undercooled liquid enthalpy is extrapolated down to T_0 (full curve; for broken curve, see text). Points: (○) $(h^l(T) - h_0^c)$ and $(h^g(T) - h_0^c)$; (□) $(h^c(T) - h_0^c)$

When reconsidering polymeric mixtures, it is useful to introduce the specific-heat increment $(\Delta c_p = c_p^l - c_p^g)$ of the two components into Couchman's equations (1a) and (1b), so that one obtains:

$$w_1 \int_{T_{g1}}^{T_g} \Delta c_{p1}(T)\,\mathrm{d}\ln T + w_2 \int_{T_{g2}}^{T_g} \Delta c_{p2}(T)\,\mathrm{d}\ln T + (\Delta s_m^l - \Delta s_m^g) = 0 \tag{9a}$$

$$w_1 \int_{T_{g1}}^{T_g} \Delta c_{p1}(T)\,\mathrm{d}T + w_2 \int_{T_{g2}}^{T_g} \Delta c_{p2}(T)\,\mathrm{d}T + (\Delta h_m^l - \Delta h_m^g) = 0 \tag{9b}$$

Let us consider the case in which component 2 has a characteristic temperature T_{02} lower than T_{g1}, a situation often encountered in practice. The first approximation:

$$\Delta c_{pi}(T) = \text{constant}/T = \Delta c_{pi}(T_{gi})T_{gi}/T \qquad (10)$$

applied to both components, gives, from equation (9a):

$$T_g = \frac{w_1 \Delta c_{p1} T_{g1} + w_2 \Delta c_{p2} T_{g2}}{w_1 \Delta c_{p1} + w_2 \Delta c_{p2} + (\Delta s_m^l - \Delta s_m^g)} \qquad (11a)$$

and from equation (9b):

$$\ln T_g = \frac{w_1 \Delta c_{p1} T_{g1} \ln T_{g1} + w_2 \Delta c_{p2} T_{g2} \ln T_{g2} - (\Delta h_m^l - \Delta h_m^g)}{w_1 \Delta c_{p1} T_{g1} + w_2 \Delta c_{p2} T_{g2}} \qquad (11b)$$

where the Δc_{pi} are the specific-heat increments of pure components at the respective glass transition temperature. Equations (11a) and (11b) can be applied in the range of T_g from T_{g1} to T_{g2} when $T_{g1} > T_{02}$.

When T_{g1} is lower than T_{02} (as frequently found for high-T_g polymers in low-T_g solvent), equation (10) cannot be used for component 2 in the whole temperature range. In particular, below T_{02}, i.e. below the temperature at which, on cooling at an extremely low rate, Δc_{p2} would undergo a sudden decrease to values near zero (*Figure 1*), the integration of equations (9a) and (9b) has to be carried out accordingly. Taking $\Delta c_{p2} \approx 0$ in the temperature range from T_{g1} to T_{02}, the following approximations can therefore be introduced:

$$\int_{T_{g2}}^{T_g} \Delta c_{p2}(T)\,\mathrm{d}\ln T \approx \int_{T_{g2}}^{T_{02}} \Delta c_{p2}(T)\,\mathrm{d}\ln T \qquad (12a)$$

$$\int_{T_{g2}}^{T_g} \Delta c_{p2}(T)\,\mathrm{d}T \approx \int_{T_{g2}}^{T_{02}} \Delta c_{p2}(T)\,\mathrm{d}T \qquad (12b)$$

It has to be noted that now the approximation $\Delta c_{p2}(T) = \text{constant}/T$ can be used with confidence in the temperature range from T_{02} to T_{g2}. When the approximation $\Delta c_{p1}(T) = \text{constant}/T$ is introduced without restrictions, integration of equations (9a) and (9b) gives respectively:

$$\frac{1}{T_g} = \frac{1}{T_{g1}} + \frac{1}{\Delta c_{p1} T_{g1}}\left[\Delta c_{p2}\frac{T_{02} - T_{g2}}{T_{02}} + \frac{(\Delta s_m^l - \Delta s_m^g)}{w_2}\right]\left(\frac{w_2}{w_1}\right) \qquad (13a)$$

$$\ln T_g = \ln T_{g1} + \frac{1}{\Delta c_{p1} T_{g1}}\left[\Delta c_{p2} T_{g2} \ln\left(\frac{T_{g2}}{T_{02}}\right) - \frac{(\Delta h_m^l - \Delta h_m^g)}{w_2}\right]\left(\frac{w_2}{w_1}\right) \qquad (13b)$$

They are applicable only in the temperature range from T_{g1} to T_{02}, i.e. in the concentration range close to the low-T_g component, whereas, of course, equations (11a) and (11b) are to be used above T_{02}. Thus the whole T_g–composition curve of a system whose T_{g1} is lower than T_{02} can be described by using either equations (11a) and (13a) (entropic treatment) or equations (11b) and (13b) (enthalpic treatment). The two approaches should in principle and in practice be equivalent, because either in the entropic or in the enthalpic model the considered mixing terms have a physical meaning that, as already noted, is strictly connected with the strength of intermolecular interactions.

In a previous paper[4], a linear equation rather different from equation (13a) was derived by introducing different approximations; it was formally very similar to free-volume equations[16].

It is worth pointing out that equation (13a) has now been obtained without resorting to any approximations different from $\Delta c_{pi} = \text{constant}/T$. It can be noted that at T_{02} the transition from equations (11a) and (11b) to equations (13a) and (13b) respectively is a continuous one, the differences $(\Delta s_m^l - \Delta s_m^g)$ and $(\Delta h_m^l - \Delta h_m^g)$ being in principle continuous functions over the whole composition range. On the contrary, at the characteristic temperature T_{02} the corresponding derivatives are discontinuous. As a matter of fact, the derivatives of equations (11a), (13a), (11b) and (13b), calculated at the weight fraction w_1^0 (at which the glass transition temperature of the mixture is T_{02}), are respectively:

$$\left(\frac{\mathrm{d}T_g}{\mathrm{d}w_1}\right)_{w_1^0} = \frac{\Delta c_{p1}(T_{g1} - T_{02}) - \Delta c_{p2}(T_{g2} - T_{02}) - T_{02}[\mathrm{d}(\Delta s_m^l - \Delta s_m^g)/\mathrm{d}w_1]_{w_1^0}}{w_1^0 \Delta c_{p1} + w_2^0 \Delta c_{p2} + (\Delta s_m^l - \Delta s_m^g)_{w_1^0}} \qquad (14a)$$

$$\left(\frac{\mathrm{d}T_g}{\mathrm{d}w_1}\right)_{w_1^0} = \frac{\Delta c_{p1}(T_{g1} - T_{02}) - \Delta c_{p2}(T_{g2} - T_{02}) - T_{02}[\mathrm{d}(\Delta s_m^l - \Delta s_m^g)/\mathrm{d}w_1]_{w_1^0}}{w_1^0 \Delta c_{p1} + w_2^0 \Delta c_{p2} + (\Delta s_m^l - \Delta s_m^g)_{w_1^0} - w_2^0 \Delta c_{p2} \Delta c_{p2} T_{g2}/T_{02}} \qquad (15a)$$

$$\left(\frac{\mathrm{d}T_g}{\mathrm{d}w_1}\right)_{w_1^0} = T_{02}\frac{\Delta c_{p1} T_{g1} \ln(T_{g1}/T_{02}) - \Delta c_{p2} T_{g2} \ln(T_{g2}/T_{02}) - [\mathrm{d}(\Delta h_m^l - \Delta h_m^g)/\mathrm{d}w_1]_{w_1^0}}{w_1^0 \Delta c_{p1} T_{g1} + w_2^0 \Delta c_{p2} T_{g2}} \qquad (14b)$$

$$\left(\frac{\mathrm{d}T_g}{\mathrm{d}w_1}\right)_{w_1^0} = T_{02}\frac{\Delta c_{p1} T_{g1} \ln(T_{g1}/T_{02}) - \Delta c_{p2} T_{g2} \ln(T_{g2}/T_{02}) - [\mathrm{d}(\Delta h_m^l - \Delta h_m^g)/\mathrm{d}w_1]_{w_1^0}}{w_1^0 \Delta c_{p1} T_{g1}} \qquad (15b)$$

If the differences $(\Delta s_m^l - \Delta s_m^g)$ and $(\Delta h_m^l - \Delta h_m^g)$ are very small, and therefore negligible, from a comparison of equation (14a) with equation (15a) (entropic theory) and of equation (14b) with equation (15b) (enthalpic theory), it appears evident that the respective derivatives at w_1^0 must be discontinuous. The matter is more complex when the differences $(\Delta s_m^l - \Delta s_m^g)$ and $(\Delta h_m^l - \Delta h_m^g)$ cannot be neglected. In general, both of them will be continuous functions of composition, as previously assumed[3,4], but of course nothing can be said about their derivatives at w_1^0. However, from the analysis of experimental data for a few polymeric mixtures (see below), one can note that either $(\Delta s_m^l - \Delta s_m^g)$ or the right and left derivatives of the above differences, calculated at the singular point, are small in comparison with the other terms that appear in equations (14) and (15), so that one can deduce that really the derivatives at w_1^0 are discontinuous and that equations (11) and (13) forecast a singularity in T_g–composition curves exactly at the critical temperature T_{02}.

COMPARISON WITH EXPERIMENTAL DATA

When the T_g–composition curves are obtained by calorimetric measurements, the difficulty of defining the glass transition temperature arises. If the calorimetric curves are free of peaks due to kinetic overshoot, the point of inflection should be a good approximation to the 'equilibrium' value of T_g, i.e. to a value independent of the heating rate, according to Richardson[11]. To test the applicability of the equations obtained above, the experimental data on the poly(vinyl chloride)–dibutyl phthalate system, given in refs. 18 and 19, and referred to glass transition temperature inflection values, have been chosen as typical for analysis. Specific-heat increments of pure dibutyl phthalate (DBP) and poly(vinyl chloride) (PVC) at their glass transition temperatures are, respectively, $0.54\ \mathrm{J\,g^{-1}\,K^{-1}}$ (ref. 18) and $0.31\ \mathrm{J\,g^{-1}\,K^{-1}}$ (ref. 14). Unfortunately, the differences $(\Delta s^l_m - \Delta s^g_m)$ and $(\Delta h^l_m - \Delta h^g_m)$ and their dependence on composition are unknown for the system considered, so that they have to be determined from T_g–composition data.

Starting from the solvent side, equations (13a) and (13b) (entropic and enthalpic approach respectively) can be simplified in the following form:

$$\frac{1}{T_g} = \frac{1}{T_{g1}} + \frac{q_s}{\Delta c_{p1} T_{g1}}\left(\frac{w_2}{w_1}\right) \qquad (16a)$$

$$\ln T_g = \ln T_{g1} + \frac{q_h}{\Delta c_{p1} T_{g1}}\left(\frac{w_2}{w_1}\right) \qquad (16b)$$

where q_s and q_h represent the terms in square brackets. These last parameters can be tentatively measured by plotting $1/T_g$ and $\ln T_g$ as a function of compositional ratio w_2/w_1. As shown in *Figures 4* and *5*, excellent straight lines are obtained up to $w_2/w_1 \approx 1.5$, which indicates that both analytical relations apply satisfactorily in the polymer weight fraction range from 0 to 0.6. The values of q_s and q_h are $-0.11\ \mathrm{J\,g^{-1}\,K^{-1}}$ and $23\ \mathrm{J\,g^{-1}}$ respectively. The results described above indicate that the differences $(\Delta s^l_m - \Delta s^g_m)$ and $(\Delta h^l_m - \Delta h^g_m)$ are linear functions of w_2 in the w_2 range from 0 to 0.6, since the slopes of the two equations are constant in this composition range.

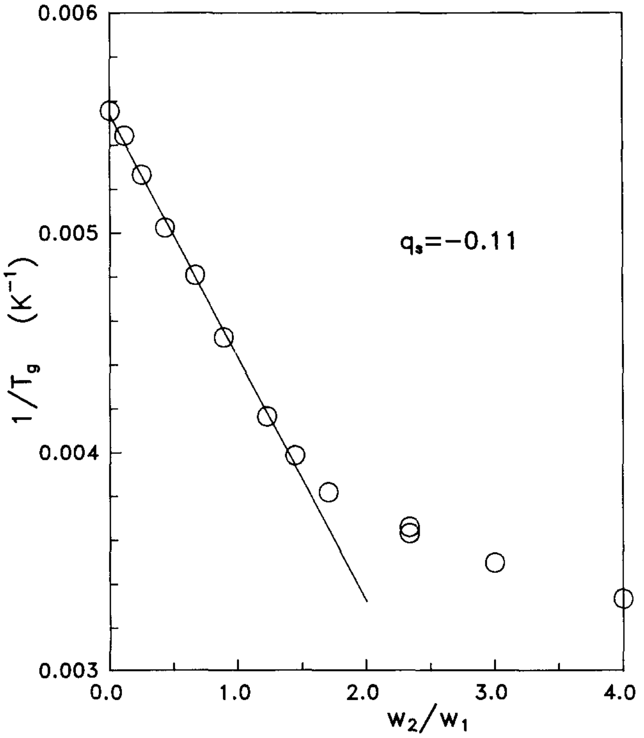

Figure 4 Dependence of $1/T_g$ on w_2/w_1 for PVC–DBP mixture. Data taken from refs. 18 and 19. Equation (16a) (entropic theory) is used to fit experimental data: $q_s = -0.11\ \mathrm{J\,g^{-1}\,K^{-1}}$ (full line)

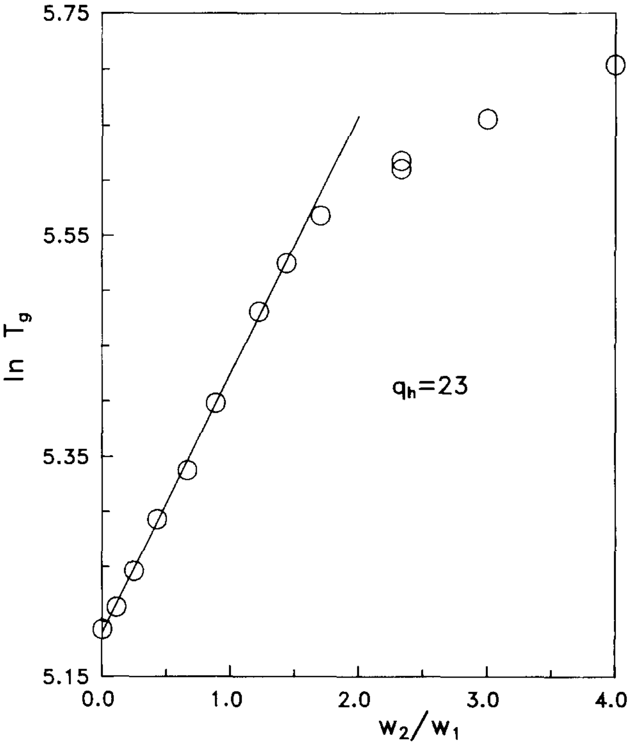

Figure 5 Dependence of $\ln T_g$ on w_2/w_1 for PVC–DBP mixture. Data taken from refs. 18 and 19. Equation (16b) (enthalpic theory) is used to fit experimental data: $q_h = 23\ \mathrm{J\,g^{-1}}$ (full line)

A different procedure was used for compositions lying in the polymer side; starting from equations (11a) and (11b), the experimental data have first been used to obtain, for all the experimental values of T_g in the range $0 < w_1 < 0.4$, the corresponding $(\Delta s^l_m - \Delta s^g_m)$ and $(\Delta h^l_m - \Delta h^g_m)$ data. Secondly, the latter have been plotted vs. different compositional parameters to minimize the squares of the deviations, which have been found to be minimized when the product $w_1 w_2$ was used as an independent variable. The best analytical functions obtained are:

$$(\Delta s^l_m - \Delta s^g_m) = Q_s w_1 w_2 \qquad (17a)$$

$$(\Delta h^l_m - \Delta h^g_m) = Q_h w_1 w_2 \qquad (17b)$$

where Q_s and Q_h have the physical meaning of parameters related to the strength of intermolecular interactions (see also ref. 7). Equations (11a) and (11b) can now be rewritten in the following form:

$$T_g = \frac{w_1 \Delta c_{p1} T_{g1} + w_2 \Delta c_{p2} T_{g2}}{w_1 \Delta c_{p1} + w_2 \Delta c_{p2} + Q_s w_1 w_2} \qquad (18a)$$

$$\ln T_g = \frac{w_1 \Delta c_{p1} T_{g1} \ln T_{g1} + w_2 \Delta c_{p2} T_{g2} \ln T_{g2} - Q_h w_1 w_2}{w_1 \Delta c_{p1} T_{g1} + w_2 \Delta c_{p2} T_{g2}} \qquad (18b)$$

For the PVC–DBP data, one obtains $Q_s = 0.055\ \mathrm{J\,g^{-1}\,K^{-1}}$ and $Q_h = 43\ \mathrm{J\,g^{-1}}$.

Finally in *Figures 6* and *7* the experimental T_g data are plotted as a function of w_1 over the full range of weight fractions, together with the curves corresponding to equations (18a) and (18b) in the left-hand part, and to equations (16a) and (16b) in the right-hand part. The critical temperature at which there is a transition from equation (18) to equation (16) for the PVC–DBP system is approximately 253 K (*Figures 6* and *7*). It should correspond to the characteristic temperature T_0 of poly(vinyl chloride), which, however, is not easily obtainable from either equation (5) or equation (8) since very different values are found in the literature for the

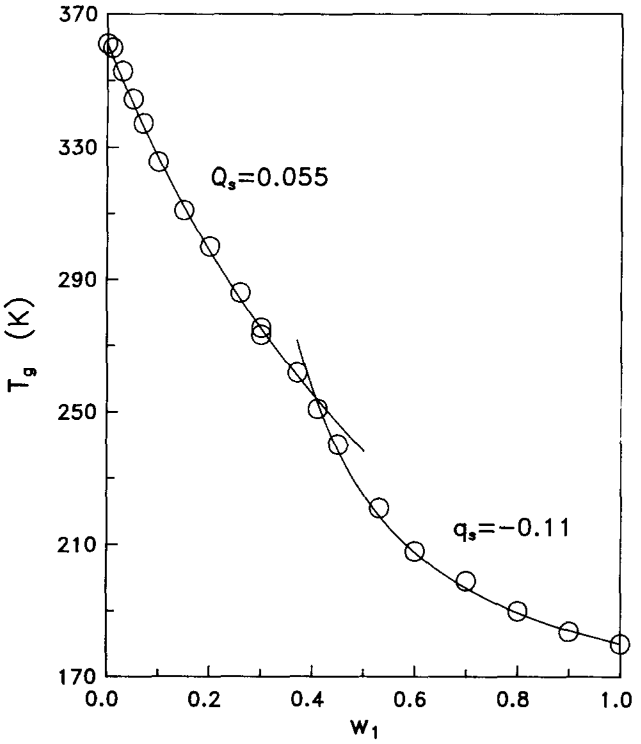

Figure 6 Glass transition temperature T_g as a function of w_1 for PVC–DBP mixture. Data taken from refs. 18 and 19. Equations (18a) and (16a) (entropic theory) are used to fit experimental data: $Q_s=0.055\ \mathrm{J\,g^{-1}\,K^{-1}}$ and $q_s=-0.11\ \mathrm{J\,g^{-1}\,K^{-1}}$ (full curves)

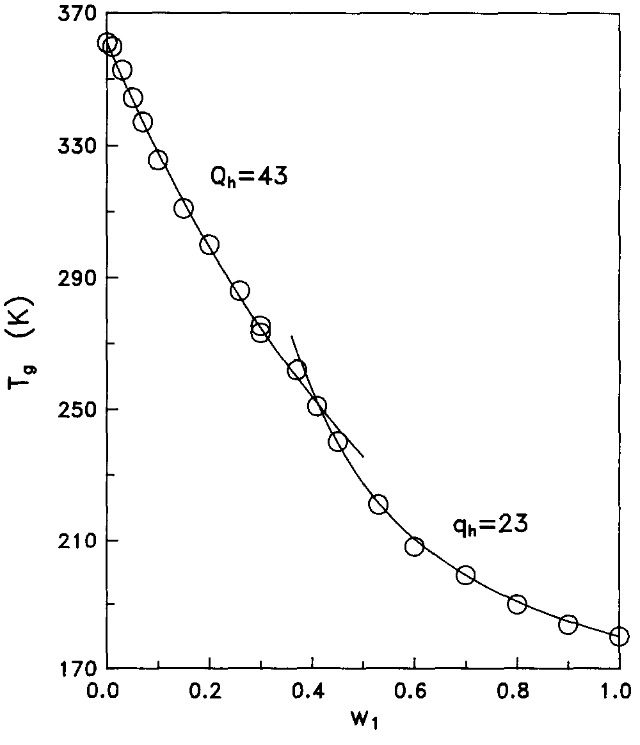

Figure 7 Glass transition temperature T_g as a function of w_1 for PVC–DBP mixture. Data taken from refs. 18 and 19. Equations (18b) and (16b) (enthalpic theory) are used to fit experimental data: $Q_h=43\ \mathrm{J\,g^{-1}}$ and $q_h=23\ \mathrm{J\,g^{-1}}$ (full curves)

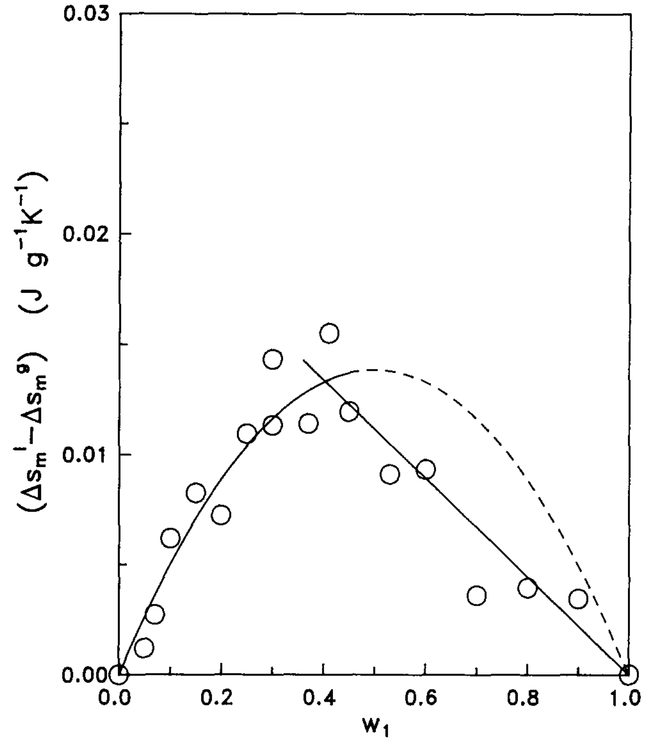

Figure 8 Difference $(\Delta s_m^l-\Delta s_m^g)$ calculated at the experimental glass transition temperature of PVC–DBP mixtures, as a function of w_1 ($0<w_1<0.4$, from equation (11a); $0.4<w_1<1$, from equation (13a)) (for full and broken curves, see text)

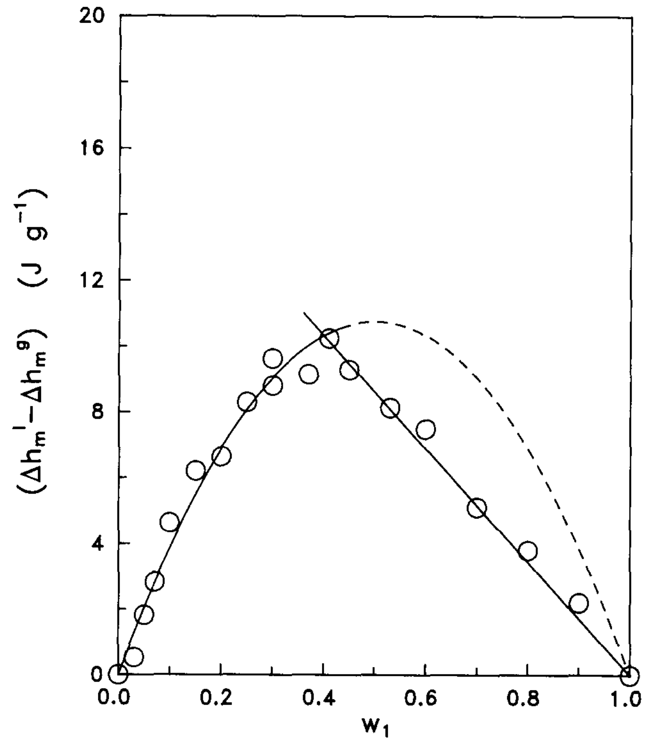

Figure 9 Difference $(\Delta h_m^l-\Delta h_m^g)$ calculated at the experimental glass transition temperature of PVC–DBP mixtures, as a function of w_1 ($0<w_1<0.4$, from equation (11b); $0.4<w_1<1$, from equation (13b)) (for full and broken curves, see text)

enthalpy of fusion of this polymer[14,20]. If T_{02} is taken to be 253 K, the corresponding enthalpy of fusion ΔH_f^0 should be approximately 8 kJ mol^{-1}, which is lower than that given by Wunderlich[14] (11 kJ mol^{-1}).

In *Figures 8* and *9* the apparent differences $(\Delta s_m^l - \Delta s_m^g)$ and $(\Delta h_m^l - \Delta h_m^g)$ at the glass transition temperature of the PVC–DBP mixtures are shown as a function of the weight fraction w_1. The excess thermodynamic functions, which can be calculated from equations (11a), (11b), (13a) and (13b), are called 'apparent' because their values are dependent on the approximation used for the temperature dependence of Δc_{pi}. In the present case they have been obtained in the concentration range $0.4 < w_1 < 1$ from equations (13a) and (13b) by using experimental T_g data and by taking $T_{02} = 253$ K. The left part of each curve is described by equations (17a) and (17b) respectively, with $Q_s = 0.055$ J g^{-1} K^{-1} and $Q_h = 43$ J g^{-1} (full curve up to $w_1 = 0.4$; in the proximity of the diluent, the curves calculated with these Q_s and Q_h values are indicated as broken curves). On the contrary, the straight full lines have been obtained from equations (13a) and (13b) by taking $q_s = -0.11$ J g^{-1} K^{-1} and $q_h = 23$ J g^{-1}.

CONCLUSIONS

For a binary miscible system, whose pure-component glass transition temperatures are T_{g1} and T_{g2} (with $T_{g2} > T_{g1}$), equations relating the T_g of the mixture to the composition, based on either an entropic or an enthalpic approach, have to be modified when the glass transition of the mixture is lower than the 'ideal glass transition' T_{02} of component 2. New equations are proposed to describe the composition dependence between T_{g1} and T_{02}; the equations derived from the enthalpic approach can be used for either athermal and non-athermal solutions, the difference $(\Delta h_m^l - \Delta h_m^g)$ appearing as an adjustable parameter. The equations proposed fit well the experimental data of the PVC–DBP system, which exhibits a cusp in the T_g–composition curve. The results show that the system is neither ideal from the entropic point of view, nor athermal, specific interactions between the α-hydrogens of PVC and the carbonyl groups of DBP being present, as already pointed out by Benedetti *et al.*[21].

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