Glass transition of binary systems: peculiarities at low temperature

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The present paper refers to the well known fact that the glass transition–composition curves of miscible binary systems (e.g. polymer–diluent and polymer–polymer mixtures) often exhibit a singular point when the T_g values of the two components are far apart. Two different equations apparently apply above and below the temperature of this singularity. Starting from Couchman's entropic treatment of the glass transition of mixtures, and from Angell's suggestion for the calculation of T_0 ('ideal glass transition temperature' of the component with higher T_g), it is shown that below T_0 an equation should be applicable to binary mixtures which differs considerably from the equations normally used in the literature. The new equation gives a satisfactory description of selected experimental data in the proximity of the component with lower T_g.

(Keywords: glass transition; ideal glass transition temperature; entropy of mixing; specific heat)

INTRODUCTION

For several polymer–diluent and polymer–polymer binary systems, the experimental 'T_g–composition curve', obtained by calorimetric measurements, appears to be composed of two different lines that meet at a characteristic temperature T_{cusp} (refs. 1–14). The cusp is observed in practice only when the difference between the T_g values of the two components is higher than about 70°C[12]. Unfortunately, the cusp is often found in an intermediate composition range in which the glass transition is relatively broad, and sometimes doubled. The broadening of the transition at intermediate compositions, observed in compatible polymeric blends, is a quite general phenomenon, which has been explained as an effect of the microheterogeneity of the sample, where local composition fluctuations are in excess of normal density and temperature fluctuations[15]. The situation is more complex when intermediate compositions of polymer–diluent systems are considered: from dynamic mechanical studies of mixtures it can sometimes be found that single calorimetric transitions are composed of two overlapping transitions[16], and in a few cases two different transitions are also observed calorimetrically[17–19]. Nevertheless, there is experimental evidence that in the proximity of the diluent (or near the polymer whose T_g is lower), a composition range exists within which the system is homogeneous and the experimental data cannot be described by the equations found to be applicable above T_{cusp}, that is on the side of the component with higher T_g.

A prediction of the presence of the cusp, in the framework of the free-volume theory of the glass transition, was proposed long ago by Kovacs[1–3], and the relative equations were applied successively to some systems[4,11,12,14]. The treatment is based on the hypothesis that the fractional free volume of the mixture (f) is given by the weighted sum of the fractional free volume of pure components, f_i, plus, if necessary, an interaction term, i.e.:

$$f=\phi_1 f_1+\phi_2 f_2-V_e/V \tag{1}$$

with

$$f_1=f_{g1}+\Delta\alpha_1(T-T_{g1}) \tag{2a}$$

$$f_2=f_{g2}+\Delta\alpha_2(T-T_{g2}) \tag{2b}$$

where the ϕ_i are the volume fractions, the f_{gi} are fractional free volumes of pure components at the respective glass transition temperature T_{gi}, the $\Delta\alpha_i$ are the thermal coefficients of expansion of f_{gi}, quite close to the differences between the volume expansion coefficients in the glassy and liquid state, V is the specific volume of the mixture and V_e is the excess volume. (The component with higher glass transition is denoted with the number 2, the second component with the number 1.) Another important assumption is that at the glass transition temperature of the mixture the fractional free volume is given by:

$$f_g=\phi_1 f_{g1}+\phi_2 f_{g2} \tag{3}$$

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so that one obtains:

$$T_g = \frac{\phi_1 \Delta\alpha_1 T_{g1} + \phi_2 \Delta\alpha_2 T_{g2} + V_e/V}{\phi_1 \Delta\alpha_1 + \phi_2 \Delta\alpha_2} \tag{4a}$$

or, if $V_e = 0$:

$$T_g = \frac{\phi_1 \Delta\alpha_1 T_{g1} + \phi_2 \Delta\alpha_2 T_{g2}}{\phi_1 \Delta\alpha_1 + \phi_2 \Delta\alpha_2} \tag{4b}$$

When T_g is lower than $T_{cr} = T_{g2} - f_{g2}/\Delta\alpha_2$, the critical temperature at which the fractional free volume of component 2 becomes zero, according to equation (2b), different equations are obtained:

$$T_g = T_{g1} + \left(\frac{\phi_2}{\phi_1}\right) \frac{1}{\Delta\alpha_1} \left(f_{g2} + \frac{V_e/V}{\phi_2}\right) \tag{5a}$$

or, if $V_e = 0$:

$$T_g = T_{g1} + \left(\frac{\phi_2}{\phi_1}\right) \frac{f_{g2}}{\Delta\alpha_1} \tag{5b}$$

which differ considerably from equations (4a) and (4b).

One characteristic feature of the above theoretical treatment is that the free-volume parameters f_{gi} and $\Delta\alpha_i$ are somewhat arbitrary, i.e. they have to be treated as adjustable parameters. In this respect it has to be noted that the difference $(T_{g2} - T_{cr}) = f_{g2}/\Delta\alpha_2$ has been found to be ca. 150°C for polystyrene[1–3] and ca. 60°C for poly(vinyl chloride)[4].

In the present paper it is shown that an appropriate extension of Couchman's treatment is required to describe the T_g–composition curve in the proximity of the component with lower T_g.

THEORETICAL TREATMENT

In our previous work[20], the theoretical treatment proposed by Couchman[21–28] to describe the compositional dependence of T_g for binary systems has been applied to selected mixtures, for which heat capacity data were available in the literature. According to Couchman's treatment, the analytical form of the equation obtained depends directly upon the function chosen to represent the temperature dependence of the specific heat increments Δc_{pi} ($\Delta c_{pi} = c^l_{pi} - c^g_{pi}$). It was found that the most correct equation for the dependence of Δc_{pi} on the temperature gives the least satisfactory description of the experimental T_g data, a result that could be accounted for by the assumption that the entropy of mixing contains interaction terms, being not only configurational (or combinatorial), and so continuous at the glass transition temperature of the mixtures. In order to obtain the most correct equation for the dependence of Δc_{pi} on the temperature, one has to extrapolate the liquid heat capacity of the component with higher glass transition from T_{g2} down to T_{g1}. In our first approach to the problem, we have not considered a thermodynamic limit for the liquid state. However, such a limit always exists, so that, if this characteristic temperature, denoted here T_0, is greater than T_{g1}, then the extrapolation of c^l_p cannot be carried out down to T_{g1}. The method of calculation of T_0, based on Kauzmann's observation[29], has been discussed by Angell and coworkers[30,31]: at the equilibrium melting point, the difference between the entropy of the liquid and that of the crystal is the entropy of fusion, per unit weight, Δs_f, and therefore, when a supercooling process takes place down to a given low temperature, the liquid cannot lose more entropy than that lost along the thermodynamically favoured path, i.e. the entropy of fusion (Δs_f) plus the vibrational entropy of the crystal (Δs_{vib}) plus the entropies of possible solid-state transitions (Δs_{tr}). The heat capacity of the supercooled liquid must decrease to a value very close to that of the crystal at a defined temperature, indicated as T_0, so that no more entropy than that indicated above can be lost during the process of supercooling. Such a temperature T_0, at which the excess entropy ($s_{ex} = s_{liquid} - s_{crystal}$) would become zero, defined frequently as the 'ideal glass transition temperature', has to satisfy the following condition[30,31]:

$$\int_{T_0}^{T_f} [c^l_p(T) - c^c_p(T)]\, \mathrm{d} \ln T = \Delta s_f + \Delta s_{tr} \tag{6}$$

whose meaning is that the area between the liquid and the crystal c_p curves must be equal to $(\Delta s_f + \Delta s_{tr})$. Obviously the value of T_0 can be estimated only by an extrapolation of the experimental c^l_p data, obtained above T_g, and this process is open to some degree of arbitrariness when the difference $(T_g - T_0)$ is large, since there are no sound theoretical bases for such an extrapolation. As far as this problem is concerned, the most gradual possible decrease of $(c^l_p - c^c_p)$ below T_g is suggested by Angell[32], so that the entropy of the supercooled liquid remains greater than the entropy of the crystal as far as possible; as a consequence, a sharp decrease of c^l_p in the proximity of T_0 is assumed to take place[32]. As an example, it is useful to consider polyoxytrimethylene (PO3M), a polymer for which extensive amorphous and crystalline heat capacity and entropy data are available[33], and whose Δs_f and T_f are respectively 0.528 J g^{-1}K^{-1} and 308 K[34]. When Angell's procedure is followed, as shown in *Figure 1*, the calculated value of T_0 for the above polymer is 162 K. As shown in *Figure 2*, the above value of T_0 can also be obtained by extrapolation of the liquid phase entropy.

From the above considerations, it appears obvious that Couchman's treatment, rewritten in detail in our previous work[20], has to be modified when the glass transitions of the mixtures are lower than T_0 of component 2. Couchman's fundamental equation, based upon the equality of the mass-specific liquid and glassy entropies at the glass transition temperature of the mixture, is:

$$w_1 s^l_1(T_g) + w_2 s^l_2(T_g) + \Delta s^l_m = w_1 s^g_1(T_g) + w_2 s^g_2(T_g) + \Delta s^g_m \tag{7}$$

Here s^l_i and s^g_i are the mass-specific liquid and glassy entropies of pure components, w_i are the weight fractions, and Δs^l_m and Δs^g_m are the entropies of mixing of the liquid and the glass respectively.

When the glass transition temperature of the mixture is lower than T_0 of component 2, s^l_2 becomes equal to or very close to s^c_2, as explained above and shown in the example of *Figure 2*, and therefore equation (7) can be rewritten as:

$$w_1\left(s^{0l}_1 + \int_{T_{g1}}^{T_g} c^l_{p1}(T)\, \mathrm{d}\ln T - s^{0g}_1 - \int_{T_{g1}}^{T_g} c^g_{p1}(T)\, \mathrm{d}\ln T\right) + w_2(s^c_2 - s^g_2) + (\Delta s^l_m - \Delta s^g_m) = 0 \tag{8}$$

where s^{0l}_1 and s^{0g}_1 are the entropies at T_{g1} of the pure component 1, and c^l_{p1} and c^g_{p1} are the specific heats in

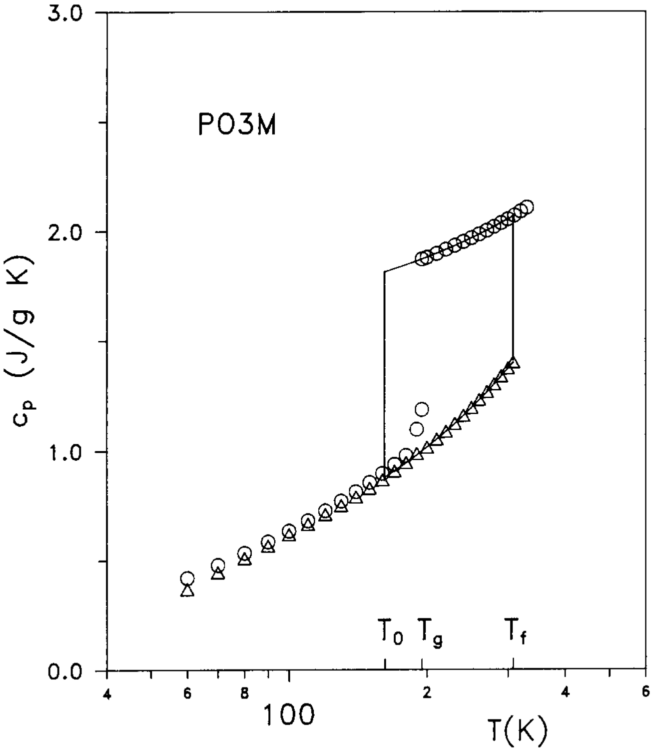

Figure 1 Example of the method proposed by Angell[30,31] to obtain the value of the 'ideal glass transition' T_0. The polymer is polyoxytrimethylene. The extrapolation of $c_p^l(T)$ from T_g to T_0 is linear on a c_p vs. T graph (not shown here). The area of the trapezoid is Δs_f. Points: (○) $c_p^l(T)$ and $c_p^g(T)$; (△) $c_p^c(T)$

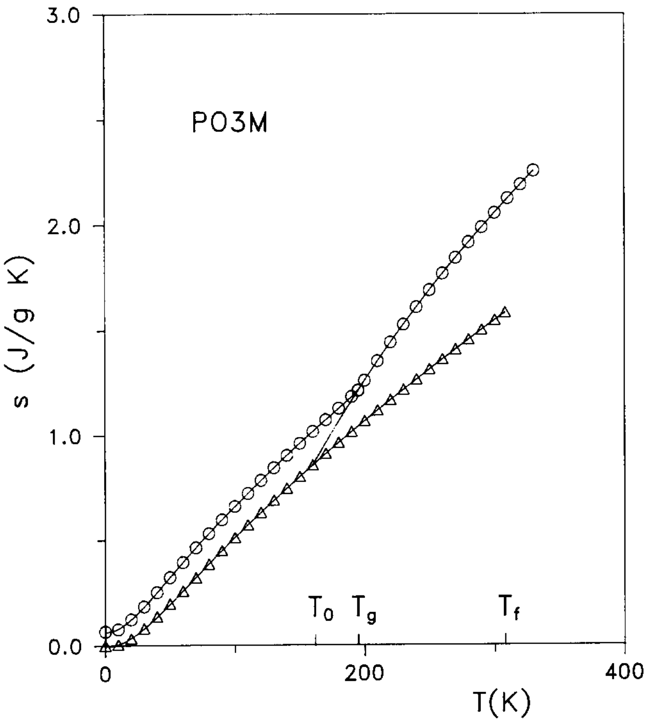

Figure 2 Entropy–temperature diagram of polyoxytrimethylene. The supercooled liquid entropy is extrapolated down to T_0. Points: (○) $s^l(T)$ and $s^g(T)$; (△) $s^c(T)$

the liquid and glassy states. Since s_1^0 is continuous at T_{g1}, the equation becomes:

$$w_1 \int_{T_{g1}}^{T_g} \Delta c_{p1}(T)\,\mathrm{d}\ln T + w_2(s_2^c - s_2^g) + (\Delta s_m^l - \Delta s_m^g) = 0 \quad (9)$$

By assuming various functional dependences of the specific heat increments Δc_{p1} on temperature, various equations can be derived from equation (9). The zeroth-order approximation $\Delta c_{p1} = \text{constant} = \Delta c_{p1}(T_{g1})$ appears to be acceptable, if one keeps in mind the fact that, for most binary systems, for which T_g-composition data are available in the literature, the temperature range from T_{g1} to T_0, where equation (9) should be applicable, is rather narrow (typically of the order of 20–30°C). From equation (9), after integration and expansion of the logarithm, a relation is obtained that bears a strict similarity with the Kovacs equation (5a):

$$T_g = T_{g1} + \left(\frac{w_2}{w_1}\right)\frac{T_{g1}}{\Delta c_{p1}}\left((s_2^g - s_2^c) + \frac{(\Delta s_m^g - \Delta s_m^l)}{w_2}\right) \quad (10a)$$

It is interesting to note that by using either the approximation $\Delta c_{p1} = \text{constant}/T$, for T_g very close to T_{g1}, or the more correct equation $\Delta c_{p1} = a_1 + b_1 T$, one again obtains equation (10a) after integration and expansion of the logarithm.

Let us now assume $\Delta s_m^g = \Delta s_m^l$, as expected for ideal and regular solutions[21]. Equation (10a) then becomes:

$$T_g = T_{g1} + \left(\frac{w_2}{w_1}\right)\frac{T_{g1}}{\Delta c_{p1}}(s_2^g - s_2^c) \quad (10b)$$

formally similar to the Kovacs equation (5b).

Since it is invariably expected that $s_2^g > s_2^c$, equation (10b) correctly predicts that the glass transition temperature of the mixture is higher than T_{g1}.

In order to obtain a simplified equation, one has to evaluate the temperature and therefore concentration dependence of the entropy differences in equations (10a) and (10b). It has to be noted that $(s_2^g - s_2^c)$ can be taken as approximately constant (see *Figure 2*), since the range of temperature between T_{g1} and T_0 is generally narrow. With this approximation the term:

$$\left((s_2^g - s_2^c) + \frac{(\Delta s_m^g - \Delta s_m^l)}{w_2}\right)$$

also becomes constant if the difference $(\Delta s_m^g - \Delta s_m^l)$ is linearly dependent on w_2, as expected for any excess thermodynamic function in a restricted concentration range near component 1 (that is $(\Delta s_m^g - \Delta s_m^l) = w_2 q^*$ where q^* is an *a priori* unknown parameter). As a consequence, equations (10a) and (10b) can be rewritten in the following form:

$$T_g = T_{g1} + \left(\frac{w_2}{w_1}\right)\frac{T_{g1}}{\Delta c_{p1}} q \quad (11)$$

where q is a constant, characteristic of the system, or, if $\Delta s_m^l = \Delta s_m^g$, of the polymer alone.

The similarity between the new equations (10a) and (10b) and the Kovacs equations (5a) and (5b) is not simply formal. According to Miller[35,36], the glass transition occurs in pure polymers when the product $z_2^* s_{c2}$ (where z_2^* is the minimum number of monomer segments in the cooperative unit and s_{c2} is the conformational entropy referred to 1 g of repeat unit) reaches a critical value, given by:

$$z_{g2}^* s_{cg2} = 11.7 n_2/M_2\ \mathrm{J\,g^{-1}\,K^{-1}}$$

(Here z_{g2}^* and s_{cg2} are respectively the minimum size of cooperative unit and the conformational entropy referred to the glass transition temperature T_{g2}, n_2 is the number of rotatable main-chain bonds in the repeat unit and M_2 is its molecular weight.) The relationship between s_{c2} and the fractional free volume f_2 was obtained by Miller by combining the Vogel–Tamman–Fulcher equation, Adam–Gibbs equation and Doolittle equation[35]. At T_{g2} the following relation was derived:

$$s_{cg2} = \frac{11.7n_2}{M_2}\frac{f_{g2}}{\Delta\alpha_2 T_{g2}}\ \mathrm{J\,g^{-1}\,K^{-1}} \tag{12}$$

in which $\Delta\alpha_2$ is, as usual, the free-volume coefficient of expansion.

As Miller pointed out[36], the conformational entropy, that is the entropy related to the rotation of main-chain bonds, is only a fraction of the excess entropy, i.e. of the difference between the liquid and the crystal entropies. In fact, by using the 'universal' values for f_{g2} and $\Delta\alpha_2 T_{g2}$ (respectively 0.025[37] and 0.113[38]), one can find that for several polymers the conformational entropy at T_{g2}, calculated according to equation (12), is very close to the residual entropy at 0 K, $s_2(0)$, as tabulated by Wunderlich[34]. At a temperature lower than T_{g2}, the difference $(s_2^g - s_2^c)$ is generally between the residual entropy at 0 K and the excess entropy at T_{g2}, which in turn is about two or three times the residual entropy (see *Figure 2* and refs. 39 and 40). As a consequence, the difference $(s_2^g - s_2^c)$ in equations (10a) and (10b) can be approximately replaced by s_{cg2} as given by equation (12). Equation (10b) therefore becomes:

$$T_g = T_{g1} + \left(\frac{\phi_2}{\phi_1}\right)\left(\frac{\rho_2}{\rho_1}\right)\frac{T_{g1}}{\Delta c_{p1}}\frac{11.7n_2}{M_2}\frac{f_{g2}}{\Delta\alpha_2 T_{g2}} \tag{13}$$

where ϕ_i are the volume fractions and ρ_i are the densities of pure components. Assuming $\Delta\alpha_i T_{gi} = \text{constant}$[38], one obtains:

$$T_g = T_{g1} + \left(\frac{\phi_2}{\phi_1}\right)\frac{f_{g2}}{\Delta\alpha_1}\left(\frac{\rho_2}{\rho_1}\right)\frac{11.7n_2}{M_2\Delta c_{p1}} \tag{14}$$

Since $(\rho_2/\rho_1)(11.7n_2/M_2\Delta c_{p1})$ is found to be quite close to unity for a score of binary systems examined, the glass transition temperature calculated according to equation (14) is numerically similar to that obtained from equation (5b).

COMPARISON WITH EXPERIMENTAL DATA

In order to compare equation (11) with experimental data, it is interesting to examine a few binary systems, whose T_g–composition curve is known in the entire composition range, and for which the glass transition temperature of component 1 is lower than the T_0 of the second component.

Following Angell's suggestion (equation (6)), the temperature T_0 has been calculated for a few polymers. When crystalline specific heat is not available, a good approximate relation can be obtained from equation (6) taking the difference $[c_p^l(T) - c_p^c(T)]$ as constant and quite close to the specific heat increment Δc_p at T_g:

$$T_0 = T_f \exp(-\Delta s_f/\Delta c_p) \tag{15}$$

(The term Δs_{tr} has been neglected since solid–solid transitions are taken to be absent.)

By using the respective temperatures and enthalpies of fusion collected by Wunderlich[34] and the specific heat increments from our previous work[20], the values of T_0 have been calculated, according to equation (15), for polycarbonate ($T_0 = 205$ K), polystyrene ($T_0 = 280$ K), poly(2,6-dimethyl-1,4-phenylene oxide) ($T_0 = 391$ K) and poly(vinyl chloride) (193 K). The values obtained for polycarbonate (PC), polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) are close to those tabulated by Privalko[41] (respectively 220, 261 and 380 K). As far as poly(vinyl chloride) (PVC) is concerned, it has to be pointed out that very different values of the enthalpy of fusion are found in the literature[42] and that the most probable value should be lower than that given by Wunderlich; as a consequence T_0 should be larger than 193 K.

Taking into consideration the polycarbonate–tricresyl phosphate (PC–TTP) system[43], the T_g–composition curve does not show peculiarities indicative of a transition from one type of equation to a different one. In fact T_{g1} is very close to the 'ideal glass transition' of PC and perhaps higher. Again, it is understandable that no peculiarities are found for the PPO–PS system[44], even if, in this case, too few experimental data are available.

Data on several binary systems containing PVC are found in the literature[4–7,12,17,19]. From the form of the T_g *versus* w_1 curves, it appears likely that, in the composition range near the component with lower T_g, equation (11) should be applicable, at least when the mixture appears to be homogeneous.

Three binary plasticizer–PVC systems have been studied in the proximity of the diluent, and the results are reported here.

The plot of T_g *versus* w_2/w_1, according to equation (11), for the system poly(vinyl chloride)–dipropyl phthalate (PVC–DPP)[5] (*Figure 3*) shows a linear dependence up to about 210 K. From the values of T_{g1} and Δc_{p1} ($T_{g1} = 180$ K and $\Delta c_{p1}(T_{g1}) = 0.52\ \mathrm{J\,g^{-1}\,K^{-1}}$ (ref. 5)),

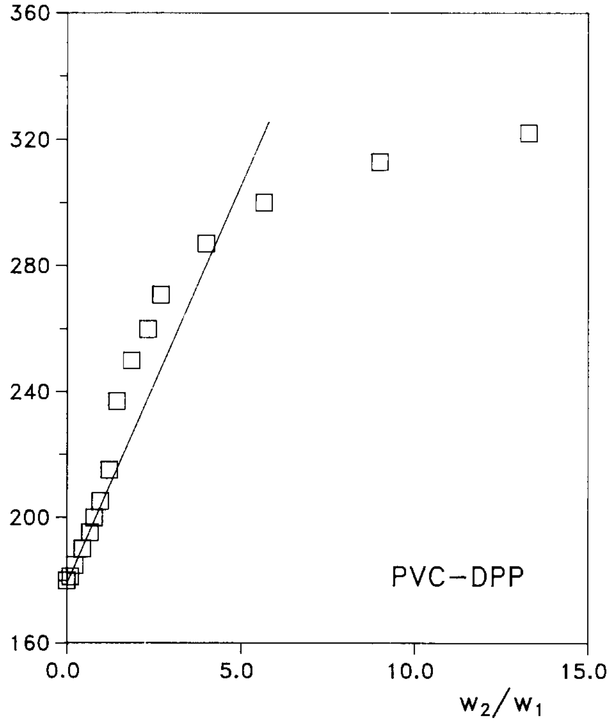

Figure 3 Glass transition temperature of PVC–DPP mixture as a function of w_2/w_1. Data taken from ref. 5. Equation (11) (full line) is used to fit experimental data

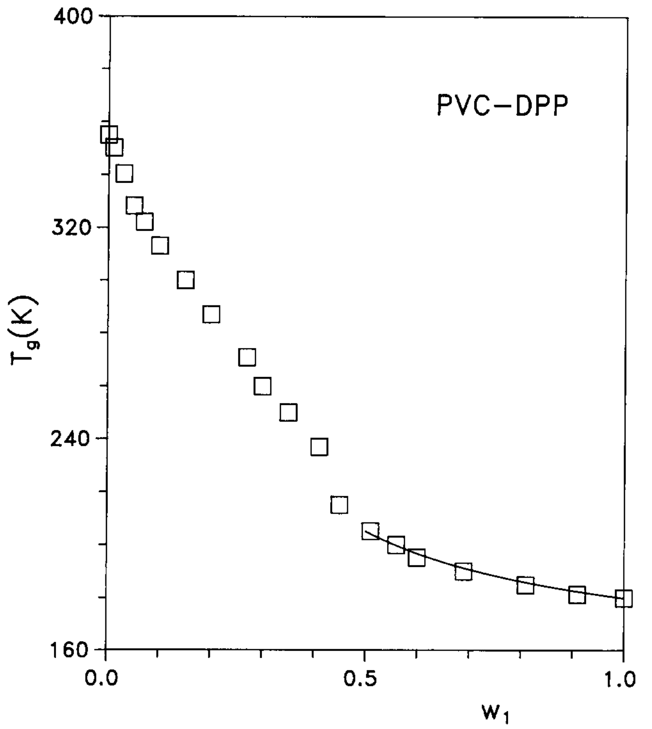

Figure 4 Glass transition temperature of PVC–DPP mixture as a function of w_1. Data taken from ref. 5. Equation (11) (full curve) is used to fit experimental data in the proximity of component 1

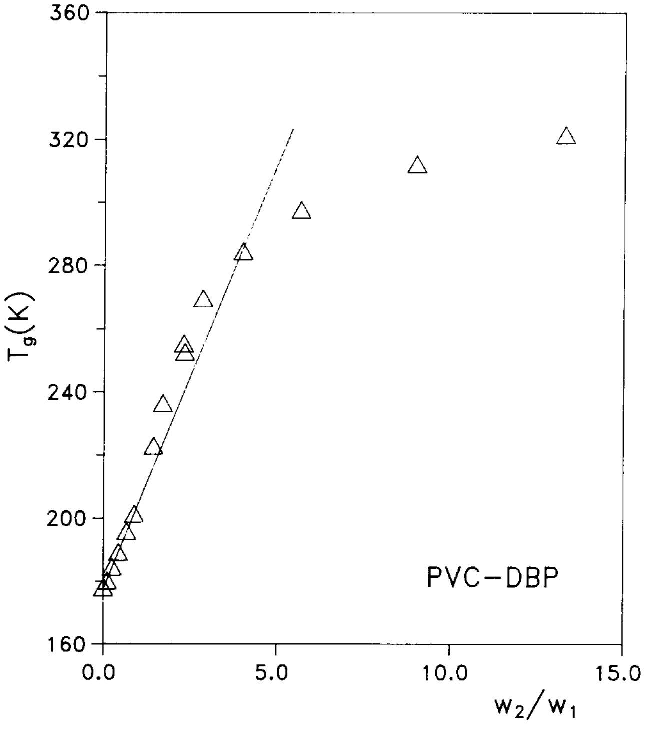

Figure 5 Glass transition temperature of PVC–DBP mixture as a function of w_2/w_1. Data taken from ref. 6. Equation (11) (full line) is used to fit experimental data

one can obtain $q=0.07$. The bottom part of the T_g–composition curve, calculated according to equation (11), with this value of q, is shown in *Figure 4*.

Figures 5 and *6* refer to the second binary mixture examined, poly(vinyl chloride)–dibutyl phthalate (PVC–DBP)[6]. Also in this case the dependence of T_g on w_2/w_1 is linear up to about 210 K. For this system $T_{g1}=178$ K, $\Delta c_{p1}(T_{g1})=0.54$ J g^{-1} K^{-1} (ref. 6) and $q=0.08$.

Finally the data of the system poly(vinyl chloride)–n-butyl acetate (PVC–BuAc)[19] are plotted in *Figures 7* and *8*. (The full circles, compositions at which two glass transitions are observed, are not used for the fitting.) For this mixture $T_{g1}=118$ K, $\Delta c_{p1}(T_{g1})=0.84$ J g^{-1} K^{-1} (ref. 19) and $q=0.13$.

Since the parameter q is composed of two entropic terms, one relative to the polymer alone ($s_2^g-s_2^c$) and

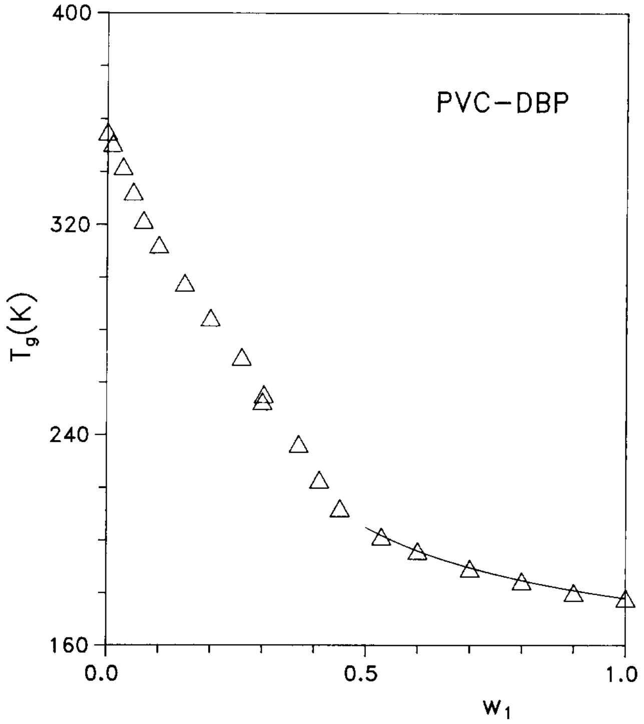

Figure 6 Glass transition temperature of PVC–DBP mixture as a function of w_1. Data taken from ref. 6. Equation (11) (full curve) is used to fit experimental data in the proximity of component 1

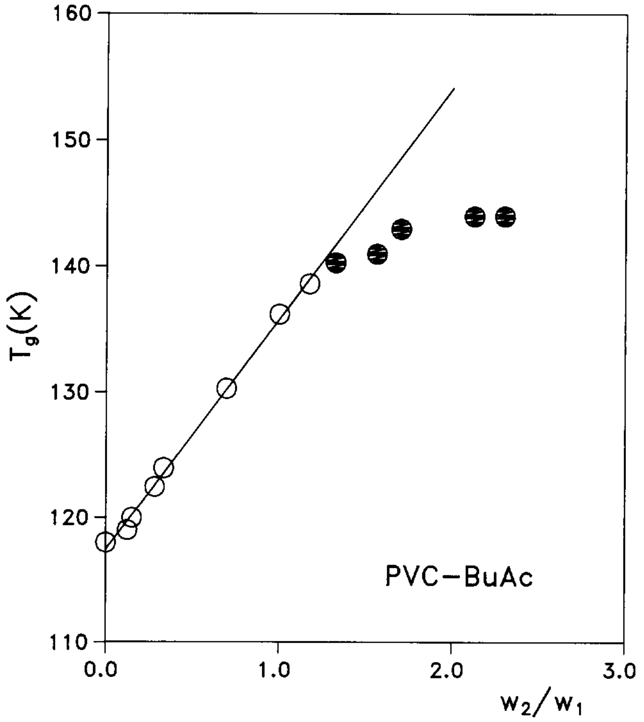

Figure 7 Glass transition temperature of PVC–BuAc mixture as a function of w_2/w_1. Data taken from ref. 19. Equation (11) (full line) is used to fit experimental data

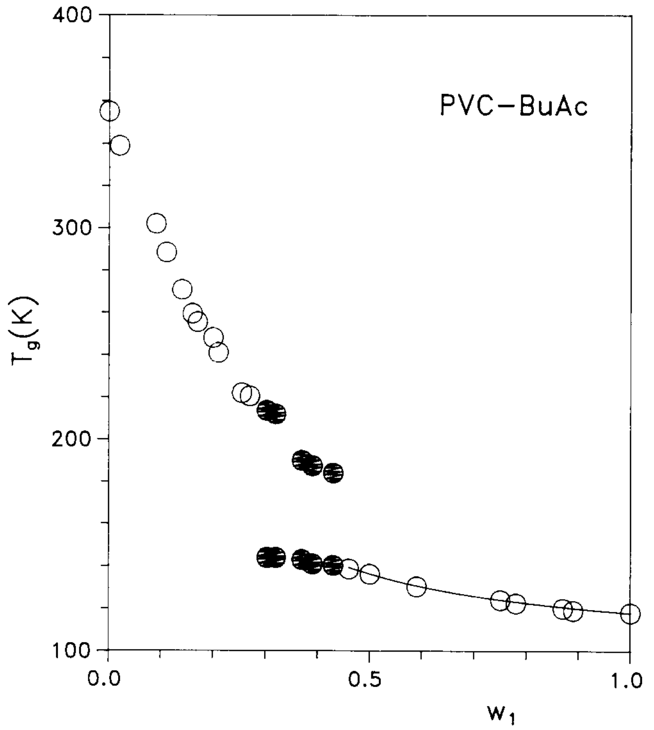

Figure 8 Glass transition temperature of PVC–BuAc mixture as a function of w_1. Data taken from ref. 19. Equation (11) (full curve) is used to fit experimental data in the proximity of component 1

the second to a difference of mixing entropies, the doubling of q observed in the passage from PVC–DPP and PVC–DBP systems to the PVC–BuAc system appears to be indicative of the fact that, probably in all these cases, the difference $(\Delta s^l_m - \Delta s^g_m)$ has a non-zero value. Unfortunately, such a difference cannot be calculated exactly from the experimental values of q, since $(s^g_2 - s^c_2)$ for PVC has not been determined as a function of temperature. Nevertheless, we know that the difference $(s^g_2 - s^c_2)$, at temperatures far from 0 K, is two or three times $s_2(0)$. Moreover, according to Wunderlich, a relatively constant contribution per 'bead', or mobile unit of the backbone chain, to the residual entropy at 0 K has been observed for many macromolecules[45]. The contribution of every 'bead', which seems to be size-independent, is about 2.5–4 J mol^{-1} K^{-1}. Taking the mean value among those tabulated in ref. 45 (3.1 J mol^{-1} K^{-1}), one obtains for PVC, whose repeat unit has two 'beads', a residual entropy close to 6 J mol^{-1} K^{-1}, or 0.1 J g^{-1} K^{-1}. If $(s^g_2 - s^c_2)$, in the range from T_0 down to about 100 K, is taken as approximately equal to twice the residual entropy, from the experimental values of q one can obtain the difference $(\Delta s^l_m - \Delta s^g_m)$ as a function of the composition. At $w_1 = 0.7$, for example, $(\Delta s^l_m - \Delta s^g_m)$ is about 4×10^{-2} J g^{-1} K^{-1} for the PVC–DPP system, 3.5×10^{-2} J g^{-1} K^{-1} for the PVC-DBP system and 2×10^{-2} J g^{-1} K^{-1} for the PVC–BuAc system. It is very interesting to note that the order of magnitude of such a difference is equal to that obtained in our previous work for the system poly(vinyl chloride)–dimethyl phthalate, whose T_g–composition curve, in the proximity of the polymer, i.e. for T_g higher than T_0, we have already studied[20]. Such a mixture is very similar to the systems investigated here, in particular to PVC–DPP and PVC–DBP systems, concerning the chemical structure of the diluent and, as a consequence, the mode of interaction between the two components.

CONCLUSIONS

For a binary miscible system, whose pure component glass transition temperatures are T_{g1} and T_{g2} (with $T_{g2} > T_{g1}$), the entropic treatment due to Couchman has to be modified when T_g of the mixture is lower than the 'ideal glass transition' T_0 of component 2. A new equation is proposed to describe the composition dependence of T_g between T_0 and T_g. It is formally similar, and, within reasonable approximations, substantially equivalent to an equation proposed by Kovacs based on the free-volume model (equation (5)). Equation (11) contains a parameter q, given by two entropic terms: the first is related to the entropy difference between glass and crystal phases of component 2, and the second contains the entropies of mixing in the liquid and glassy phases. The new equation correctly describes experimental data and can give an estimate of the above thermodynamic terms.

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