Approach to the composition dependence of the glass transition temperature of compatible polymer blends: 1

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Starting with the idea that, besides conformational energy barriers, surface contacts are responsible for both conformation and 'free' volume distribution, a new concept is developed to describe the glass transition in compatible polymer blends. An extended Gordon–Taylor equation results if both the effective contact probabilities of the blend components and the effect of molecular surroundings on the contact contribution to the glass transition of the blend are considered. Free volume redistribution due to surface contacts is included. The Gordon–Taylor constant K of the relation obtained is now not a fitting parameter, but is related to the ratio of the different expansion coefficients of the free volume. The relation introduces two fitting parameters, K_1 and K_2, which are related to the intensity of polymer–polymer interaction and to the effect of immediate molecular surroundings on the interaction. Data analysis suggests that these fitting parameters are not only polymer-specific, but also molecular-weight-dependent.

(Keywords: compatible polymer blends; glass transition)

INTRODUCTION

Compatible polymer blends exhibit a single glass transition temperature. Experimental studies on the composition dependence of the glass transition temperature T_g, performed on a variety of binary compatible polymer blends, have shown both negative and positive deviations, as well as S-shaped T_g vs. composition curves.

Two types of empirical equation have been used successfully to describe monotonic T_g deviations from additivity. One is the Gordon–Taylor equation[1]:

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

where K is a parameter adjusted to give the best fit, and the other is the Jenckel–Heusch[2] equation:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + b(T_{g2} - T_{g1}) w_1 w_2 \tag{2}$$

with b as a constant selected to optimize the fit. The parameter b accounts for the different heaviness of the weight fractions, w_i, of the components in the glass transition range. The quadratic term was introduced by the authors to account for specific interactions existing in the mixture. For the same reason, Kwei[3] extended the Gordon–Taylor equation by a quadratic term of the form $q w_1 w_2$. A two-parameter fitting equation was the result.

Equation (1) is the expression commonly used for glass transitions, not only of polymer mixtures, but also of random copolymers[4]. It can be derived either by applying to polymer mixtures the thermodynamic approach of continuity at T_g of both entropy and excess mixing entropy or of volume and excess mixing volume[5] or by considering the continuity and the additivity rule at T_g of the volume[6].

The problems that arise using the thermodynamic approach of continuity at T_g of the entropy or volume of the mixture are discussed by Goldstein[7] and need no further comments in the present context. The continuity and the additivity of the volume at T_g will therefore be preferred in the following.

Recently it has been shown that the Gordon–Taylor equation can be rearranged into an additivity relation, whereas the Kwei equation can be transformed into a two-term virial expression, by using volume fractions, weighted for different thermal expansion of the components[8]. It has also been demonstrated that T_g curves, especially of unsymmetrical shape, are more accurately reproduced if, beside the quadratic term, a third-power term is also used.

In the case of binary mixtures, quadratic and third-power concentration terms in virial equations are obviously related to contact probabilities of the components and thus account for the interaction between the components of the mixture.

Because of relatively small entropy contributions, interactions are considered essential for compatibilization in polymer blends. The surface contacts between components will thus contribute most to both the conformational mobility and the 'free volume' distribution, and consequently to the value of the glass transition temperature of compatible polymer blends.

Starting from these basic observations a new concept of describing the glass transition in compatible polymer blends will be presented. Contact probabilities and related specific stored energies for each type of contact between the components of the blends will be used in this approach.

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THEORETICAL APPROACH

For reasons of simplicity the following approach will not split the contact contribution into interaction-specific and component-specific parts. Such a differentiation will be presented, however, in a subsequent publication.

Assuming that 'free volume' distribution and thus also conformational mobility in polymer mixtures are dependent on the specific interactions of the components, the glass transition temperatures of compatible polymer blends depend on the frequency of both homo- and hetero-molecular contacts in the mixture. In accordance with the lattice theory of regular solutions applied to polymer systems, the overall number of contacts is constant and the number of each contact type is related to the respective volume fraction instead of to the mole fraction[9]. Considering the contribution of direct surface contacts only, the following relation will be valid for the dependence of mixture properties on composition:

$$P = E_{11}(1-\Phi)^2 + 2E_{12}(1-\Phi)\Phi + E_{22}\Phi^2 \qquad (3)$$

where Φ stands for the volume fraction of the polymer component with the higher T_g.

The parameters E associated with homo-molecular contacts, E_{11} and E_{22}, and with hetero-molecular contacts, E_{12}, account for the contribution of each contact type to the average property per contact, P. In terms of the Flory–Huggins theory[9], P is defined by the relation

$$P = P^*/\tfrac{1}{2}z(N_1 + N_2)$$

with P^* an extensive property of the system, z the lattice coordination number, i.e. the number of first neighbours to a given lattice site, and N_1 and N_2 the numbers of lattice sites occupied by the respective components: $N_1 + N_2$ then represents the total number of lattice sites.

If P is assumed to be the glass transition temperature, the physical meaning of E turns into that of a critical thermal energy stored in the respective contact. This energy is exceeded at T_g, thus allowing conformational rearrangements, accompanied by an increase of the free volume. This critical thermal energy E depends, however, not only on the enthalpic contact-specific interaction, but also on component-specific characteristics, especially on conformational energy barriers.

It should be pointed out that (3) does not account for the influence of molecular surroundings on the contacts. Thus the parameters E depend only on the type of contact.

The boundary conditions of (3) applied for the composition dependence of the glass transition temperature of the mixture are:

$$\begin{aligned} &\text{for } \Phi = 0, \quad P = T_{g1} \quad \text{i.e.} \quad E_{11} = T_{g1} \\ &\text{for } \Phi = 1, \quad P = T_{g2} \quad \text{i.e.} \quad E_{22} = T_{g2} \end{aligned} \qquad (4)$$

Rearranging, (3) transforms into:

$$\begin{aligned} (T_g - T_{g1})/(T_{g2} - T_{g1}) &= (P - E_{11})/(E_{22} - E_{11}) \\ &= (1 + K_1)\Phi - K_1\Phi^2 \end{aligned} \qquad (5)$$

with

$$\begin{aligned} K_1 &= [2E_{12} - (E_{11} + E_{22})]/(E_{22} - E_{11}) \\ &= [2E_{12} - (E_{11} + E_{22})]/(T_{g2} - T_{g1}) \end{aligned}$$

The condition of additivity:

$$T_g = (1-\Phi)T_{g1} + \Phi T_{g2} \qquad \text{i.e.} \qquad (T_g - T_{g1})/(T_{g2} - T_{g1}) = \Phi \qquad (6)$$

holds for $K_1 = 0$, i.e. the contribution of 'hetero-molecular' contacts is the mean of that of the 'homo-molecular' contacts:

$$2E_{12} = E_{11} + E_{22}$$

It is evident that K_1 accounts for deviations from additivity due to the difference between the contributions of the hetero- and the respective homo-molecular contacts to the glass transition temperature of the blend.

Conceived for the thermodynamics of polymer solutions, the Flory–Huggins theory also yields relations with only a single fitting parameter, the 'interaction parameter' χ. But it is well known that χ is influenced by the composition of the solution and both first-order[10] and second-order dependences[11,12] of χ on solution composition have been proposed. The 'equation-of-state' theory[12] predicts a quadratic dependence of Φ on the interaction parameter.

The concept of considering the effect on T_g of the binary contacts only, without accounting for the effect of the molecular surroundings on the contacts, is an idealized approach, which applies only for zero or for very small enthalpic interactions of the components of the mixture. Thus, for a more realistic model, it seems necessary to extend the Flory–Huggins theory by considering in addition at least the effect of the immediate molecular surroundings of the binary contacts.

The influence of the molecular surroundings on binary contacts is denoted as follows:

$$e_{ij\text{-}k} = e'_{ij\text{-}k}\, y_{ij} \qquad (7)$$

$$(i = j \text{ or } i \neq j \text{ and } k = i \text{ or } k = j)$$

with y_{ij} the number of possible immediate molecular neighbours of the surface contact point between the components i and j. Here e' represents the influence of an individual molecular unit of the neighbouring component k, whereas e represents the overall effect of an exclusive k neighbourhood on the ij contact interaction.

Applying this approach to a binary miscible mixture, equation (3) transforms into:

$$\begin{aligned} P = {} & (1-\Phi)^2[E_{11} + (1-\Phi)e_{11\text{-}1} + \Phi e_{11\text{-}2}] \\ & + 2\Phi(1-\Phi)[E_{12} + (1-\Phi)e_{12\text{-}1} + \Phi e_{12\text{-}2}] \\ & + \Phi^2[E_{22} + (1-\Phi)e_{22\text{-}1} + \Phi e_{22\text{-}2}] \end{aligned} \qquad (8)$$

By rearranging (8), the significance of the contact parameters E and the effect of the neighbouring characteristics e may be shown as:

$$\begin{aligned} P = {} & (1-\Phi)^2[(E_{11} + e_{11\text{-}1}) + (e_{11\text{-}2} - e_{11\text{-}1})\Phi] \\ & + \Phi(1-\Phi)\{[(E_{12} + e_{12\text{-}1}) + (e_{12\text{-}2} - e_{12\text{-}1})\Phi] \\ & + [(E_{12} + e_{12\text{-}2}) + (e_{12\text{-}1} - e_{12\text{-}2})(1-\Phi)]\} \\ & + \Phi^2[(E_{22} + e_{22\text{-}2}) + (e_{22\text{-}1} - e_{22\text{-}2})(1-\Phi)] \end{aligned} \qquad (9)$$

The sum $E_{ii-i}=E_{ii}+e_{ii-i}$ characterizes the contribution to the property P of the homo-molecular contact in its own neighbourhood, i.e. the property of the pure component i, whereas the difference $e^*_{ii-j}=e_{ii-j}-e_{ii-i}$ represents the effect on this contribution of substitution in the neighbourhood of the contact of the i units by j units. The parameter e^* includes also free volume redistribution due to surface contacts. These impact parameters are then multiplied by the respective volume fraction of the second component to account for the probability of such substitution. The hetero contacts in (8) may be considered either in the exclusive neighbourhood of the first blend component, $E_{12-1}=E_{12}+e_{12-1}$, or of the second component, $E_{12-2}=E_{12}+e_{12-2}$. For both cases the effect of substitution of one component by the other in the neighbourhood of a hetero contact is taken into account by $e^*_{12-1}=e_{12-1}-e_{12-2}$ and $e^*_{12-2}=e_{12-2}-e_{12-1}$, respectively. The probability of such substitution results by multiplying these magnitudes with the corresponding volume fraction. It is evident that $e^*_{12-1}=-e^*_{12-2}$.

Equation (9) becomes then:

$$P=(1-\Phi)^2(E_{11-1}+e^*_{11-2}\Phi)+(1-\Phi)\Phi\{(E_{12-1}+e^*_{12-2}\Phi)+[E_{12-2}+e^*_{12-1}(1-\Phi)]\}+\Phi^2[E_{22-2}+e^*_{22-1}(1-\Phi)] \qquad (10)$$

Assuming as before that P is the glass transition temperature, the only difference from the simpler formulation of (3) is the supposed composition dependence of the contact energy parameters. Accordingly the E_{ij-k} parameters of (10) ($i=i$ or $i=j$ and $k=i$ or $k=j$) represent that fraction of stored thermal energy in an ij contact located in a k neighbourhood which is overcome at the T_g of the blend. The respective e^*_{ij-l} parameters ($l=k$ and $l=i$ or $l=j$) represent the variation of this energy as a result of the substitution of the k neighbourhood by an l neighbourhood.

The boundary conditions of (8) to (10) applied for the composition dependence of the glass transition temperature of the mixture are, respectively:

$$\text{for } \Phi=0, \quad P=T_{g1} \quad \text{i.e.} \quad E_{11-1}=E_{11}+e_{11-1}=T_{g1} \qquad (11)$$
$$\text{for } \Phi=1, \quad P=T_{g2} \quad \text{i.e.} \quad E_{22-2}=E_{22}+e_{22-2}=T_{g2}$$

By rearranging (10) into the form of (4) one obtains:

$$(T_g-T_{g1})/(T_{g2}-T_{g1})=(1+K_1)\Phi-(K_1+K_2)\Phi^2+K_2\Phi^3 \qquad (12)$$

with

$$K_1=[(E_{12-1}-E_{11-1})+(E_{12-2}-E_{22-2})+(e^*_{12-1}+e^*_{11-2})]/(T_{g2}-T_{g1})$$
$$K_2=(2e^*_{12-1}+e^*_{11-2}-e^*_{22-1})/(T_{g2}-T_{g1}) \qquad (13)$$

i.e.

$$K_2=[(e^*_{12-1}+e^*_{11-2})-(e^*_{12-2}+e^*_{22-1})]/(T_{g2}-T_{g1})$$

An attempt to illustrate the physical content of the parameters included in the brackets of the constants K_1 and K_2, respectively, is shown in *Figure 1*. Accordingly, the constants K_1 and K_2 are composed of differences between extreme molecular arrangements; K_2 depends exclusively on the influences of changes in the neighbourhood of the binary contacts, whereas K_1 has a more complex meaning. K_1 depends on both the contact contributions (critical thermal energies) and the influence of changes in the neighbourhood upon the contact contribution.

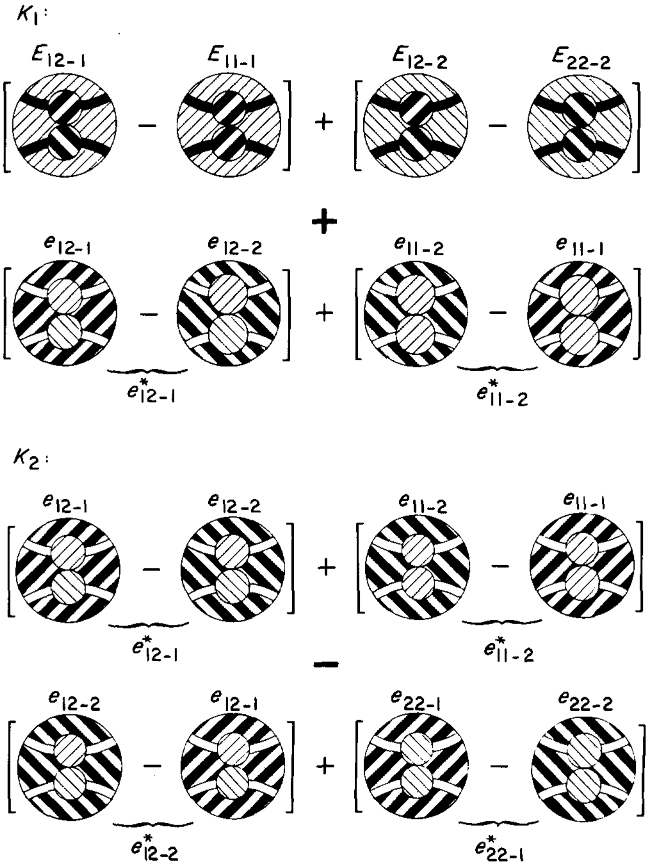

Figure 1 Illustration of the binary contact contribution and of the effects of surroundings of extreme molecular arrangements as they are included in the constants K_1 and K_2 of equation (12). Dark hatching indicates if contact contribution or surrounding effects are considered

The condition of additivity holds this time for both $K_1=0$ and $K_2=0$. The condition $K_2=0$ assumes uniform effects of the molecular surroundings for all contact interactions, i.e. all differences included in K_2 and shown in *Figure 1* become zero. $K_1=0$ can be analysed only if K_2 is already zero. Then the same condition of additivity results as for (5).

This means that irrespective of whether the effects of molecular surroundings are considered or not, volume additivity for the glass transition temperature of compatible binary polymer mixtures is always given by (6), i.e.

$$(T_g-T_{g1})/(T_{g2}-T_{g1})=\Phi$$

The volume fraction for volume additivity condition, Φ, refers to the respective glass transition temperature of the polymer blend, T_g, and therefore will be temperature-dependent in the range of validity of (6). To define the volume fraction for the volume additivity condition the method suggested by Kovacs[6] can be used, which accounts for the different fractional free volume expansion coefficients of the blend components[13]. Taking into account the experimental difficulties encountered in volume fraction determination, generally weight fraction equations are preferred.

As Gordon and Taylor have suggested[1], weight fractions for assumed volume additivity can be introduced directly by taking into account the continuity at T_g of the specific volumes.

Applying these suppositions to the specific volume of the blend at the T_g of the blend, the following expression will be valid:

$$v_{T_g}=(w_1 v_{m,1}+w_2 v_{m,2})_{T_g}=(w_1 v_{g,1}+w_2 v_{g,2})_{T_g} \qquad (14)$$

with $v_{x,i}=1/\rho_{x,i}$ the specific volume of component i, and w_i the respective weight fraction ($x=\mathrm{m}$ or $x=\mathrm{g}$ stands for melt or glassy state).

The specific volumes of the components at the glass transition temperature of the blend can be expressed in the following manner:

$$(v_{m,i})_{T_g}=(v_{m,i})_{T_{gi}}[1+\alpha_{m,i}(T_g-T_{gi})]$$

and (15)

$$(v_{g,i})_{T_g}=(v_{g,i})_{T_{gi}}[1+\alpha_{g,i}(T_g+T_{gi})]$$

By introducing these expressions in (14) and taking into account the continuity of the specific volume at T_g, i.e.

$$(v_{m,i})_{T_{gi}}=(v_{g,i})_{T_{gi}} \qquad (16)$$

relation (17) is obtained:

$$w_1(v_1)_{T_{g1}}\Delta\alpha_1(T_g-T_{g1})=w_2(v_2)_{T_{g2}}\Delta\alpha_2(T_{g2}-T_g) \qquad (17)$$

By using the notation $K=(v_2)_{T_{g2}}\Delta\alpha_2/(v_1)_{T_{g1}}\Delta\alpha_1=\rho_1\Delta\alpha_2/\rho_2\Delta\alpha_1$ (ρ_i is the density of the component i at T_{gi}) for the ratio of the expansion coefficients of the free volume, (17) transforms into

$$(T_g-T_{g1})/(T_{g2}-T_{g1})=Kw_2/(w_1+Kw_2) \qquad (18)$$

This expression is identical with both the Gordon–Taylor equation (1) and with the additivity expression (6) for the glass transition temperature of a compatible polymer mixture.

The constant K can be expressed in terms of the T_g of the components by assuming the validity of the Simha–Boyer rule[14], $\Delta\alpha T_g=0.113$, '0.133' being a 'universal' constant:

$$K=\rho_1 T_{g1}/\rho_2 T_{g2}=K'(T_{g1}/T_{g2}) \qquad (19)$$

K' accounts for the value of the ratio of the densities, ρ_1/ρ_2, and for the possible deviations from the 'universal' value of the Simha–Boyer constant.

Introducing the above expression of the constant K, into (18), the following relation results:

$$T_g=[w_1 T_{g1}+K'(T_{g1}/T_{g2})w_2 T_{g2}]/[w_1+K'(T_{g1}/T_{g2})w_2] \qquad (20)$$

As polymers have generally very similar densities, K' will show only small deviations from unity. The most likely value of K' is assumed to be in the range of 0.8 to 1.2. An appropriate correction is recommended, however, if the polymer components have very different densities.

In the above form (20) is restricted to the volume additivity condition, the constant $K=K'(T_{g1}/T_{g2})$ no longer being a fitting parameter, in contrast to the original Gordon–Taylor relation (1).

The validity range of (20) for assumed volume additivity is illustrated in *Figure 2*. It is evident that the effective value and the range of the constant K is determined first by the value of the ratio of the densities and the validity of the Simha–Boyer rule, but depends also on the glass transition temperatures of the two components of the blend.

For $K'=1$, (20) transforms into the well known Fox relation[15]:

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

which can be considered the 'idealized' equation for the glass transition temperature of the polymer blend under the volume additivity assumption.

It is interesting to note that the same relations (20) and (21) result if one assumes the thermodynamic approaches of continuity at T_g of either the volume or of the entropy or enthalpy[16]. In the latter two cases, however, the second Simha–Boyer rule, $\Delta C_p T_g=K_{C_p}$[17] is used.

A reformulation of (12) in terms of weight fractions finally results in the expression:

$$\begin{aligned}(T_g-T_{g1})/(T_{g2}-T_{g1})\\ &=(1+K_1)\{[K'(T_{g1}/T_{g2})w_2]/[w_1+K'(T_{g1}/T_{g2})w_2]\}\\ &\quad-(K_1+K_2)\{[K'(T_{g1}/T_{g2})w_2]/[w_1+K'(T_{g1}/T_{g2})w_2]\}^2\\ &\quad+K_2\{[K'(T_{g1}/T_{g2})w_2]/[w_1+K'(T_{g1}/T_{g2})w_2]\}^3 \qquad (22)\end{aligned}$$

where $\{[K'(T_{g1}/T_{g2})w_2]/[w_1+K'(T_{g1}/T_{g2})w_2]\}$ represents the corrected weight fraction of the component with the higher T_g.

As (22) is applied either for $K_1 \neq 0$ and $K_2=0$ (a Kwei-like equation) or for both $K_1 \neq 0$ and $K_2 \neq 0$, volume

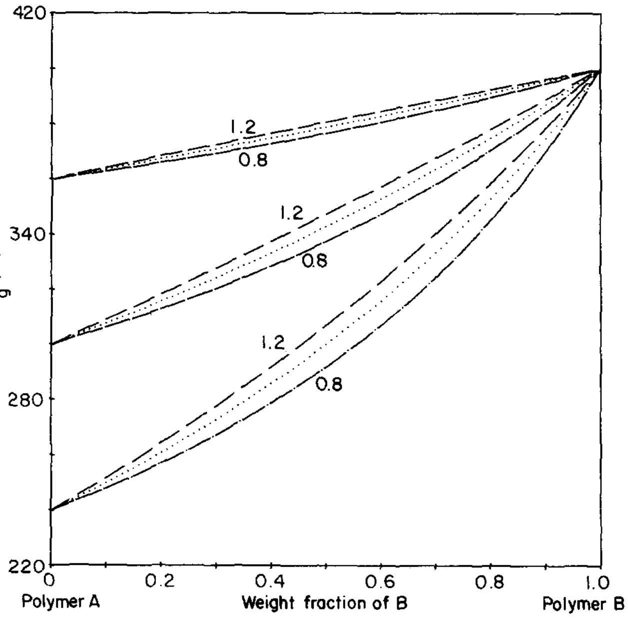

Figure 2 Representation of the validity range of the Gordon–Taylor equation (20) restricted for volume additivity condition. The most likely range of the K' value is indicated on the curves. Dotted lines represent the Fox relation (21) for $K=T_{g1}/T_{g2}$

additivity is no longer assured in this case. As mentioned the proportionality constant K' may vary in the range between 0.8 and 1.2 and as a consequence K will oscillate around the value of T_{g1}/T_{g2}. The value T_{g1}/T_{g2} is thus, however, a good approximation for K.

Subsequently our own experimental and literature T_g data for miscible polymer blends will be analysed and discussed in view of (22).

RESULTS AND DISCUSSION

The quality of equation (22) applied to experimental T_g data of compatible polymer blends results by analysing the examples illustrated in *Figures 3* to *6*. In these figures the fitting possibilities of both the original Gordon–Taylor equation (1) with K an arbitrary fitting parameter and the extended equation (22) are compared. The curves always show the computed optimum fits, in the case of (22) with the K' values ranging from 0.8 to 1.2. It is obvious that the modification of the K' value in the range mentioned does not affect the fitting quality of (22). No essential differences are observed in comparison with the 'ideal' value of $K'=1$, which means in accordance with (19) a Gordon–Taylor constant $K=(T_{g1}/T_{g2})$. The values of the parameters K_1 and K_2 depend, however, on the choice of the K' value, as will be shown below.

Excluding the PS/PPO blends, which are shown in *Figure 3*, the examples presented reveal that experimental

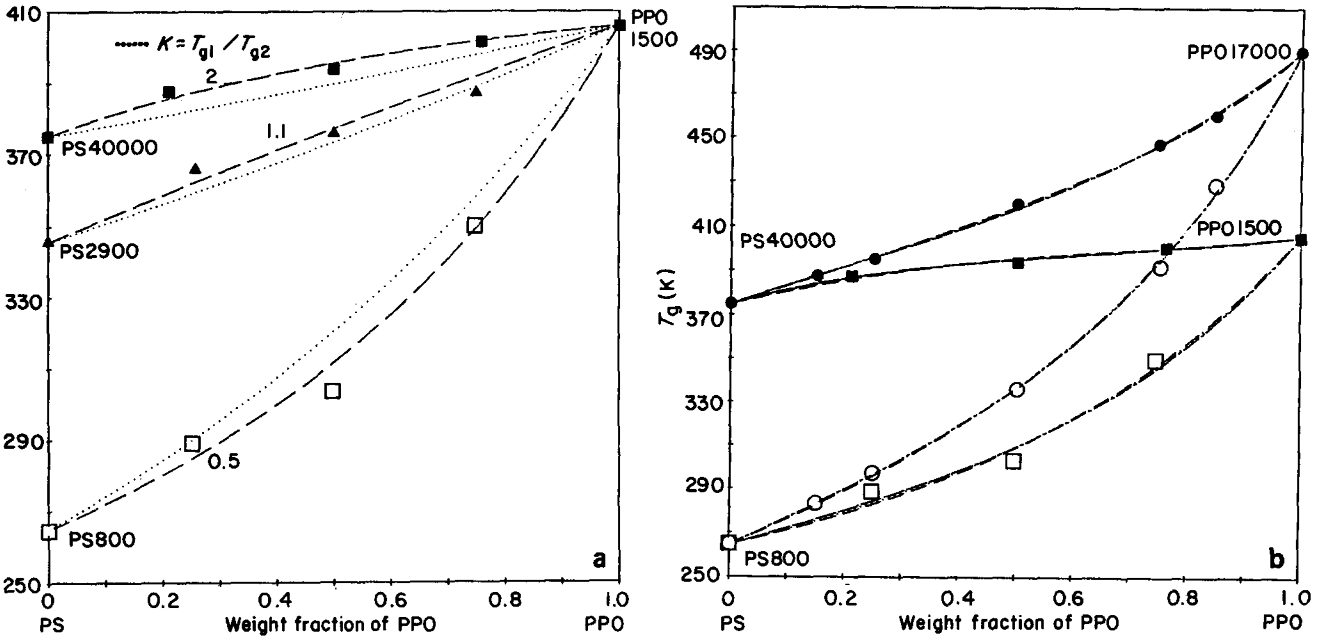

Figure 3 Composition dependence of the glass transition temperature of blends of polystyrene (PS) and poly(2,6-dimethylphenylene oxide) (PPO). Molecular weights are indicated. (Data of Gräter[18].) (a) Gordon–Taylor equation (1). Fitting parameter K indicated on the respective curves. Dotted curves represent the Fox relation (21). (b) Equation (22) with K' ranging from 0.8 to 1.2. Dotted curves correspond to the value $K'=1$

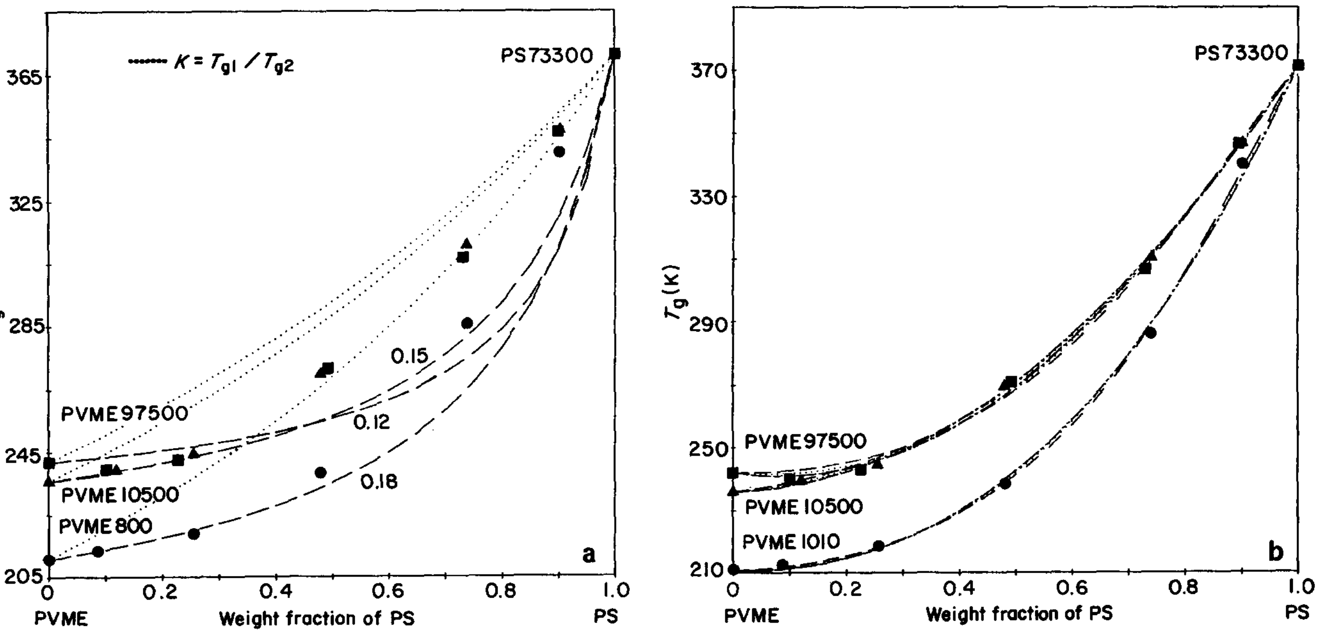

Figure 4 Composition dependence of the glass transition temperature of blends of poly(vinyl methyl ether) (PVME) and PS. (Data of Schneider and Leikauf[8].) See *Figure 3*

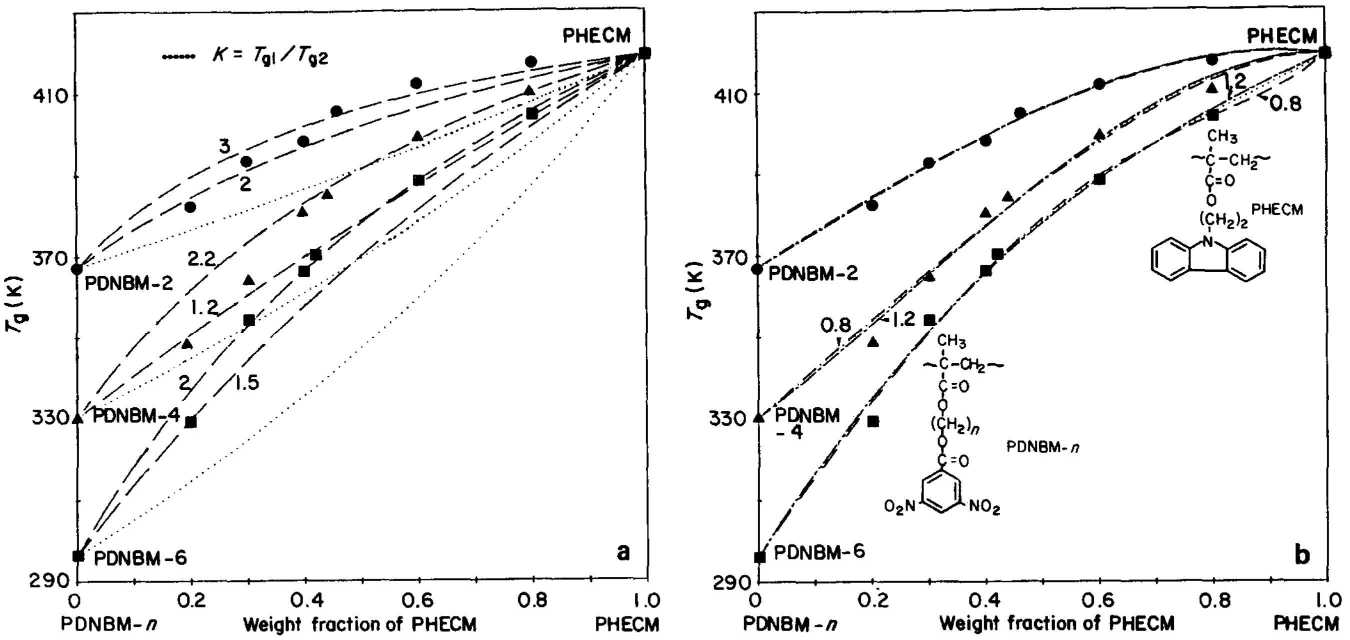

Figure 5 Composition dependence of the glass transition temperature of blends of polydonor (*N*-2 hydroxyethylcarbazolyl methacrylate) (PHECM) and of polyacceptor (ω-hydroxylalkyl-3,5-dinitrobenzoyl methacrylates) (PDNBM-*n*). Chemical structures shown on the figure. (Data of Rodriguez-Parada and Percec[19].) See *Figure 3*

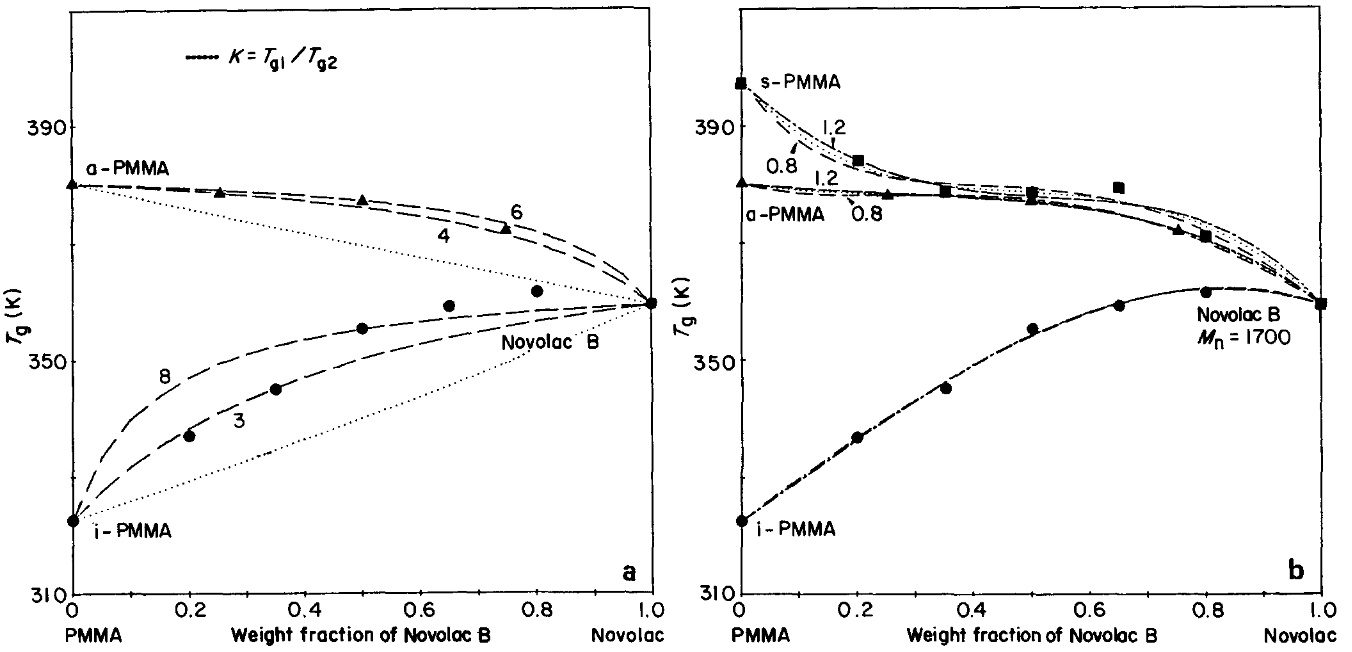

Figure 6 Composition dependence of the glass transition temperature of blends of Novolac and poly(methyl methacrylates) (PMMA) of different tacticity. (Data of Kwei[3].) See *Figure 3*

T_g data of miscible polymer blends can generally not be fitted by using the original Gordon–Taylor equation in a satisfactory manner, even if extreme K parameters are used which differ widely from the T_{g1}/T_{g2} value. The failure of the Gordon–Taylor equation is thus obvious.

The fitting quality is much improved by using the extended equation (22) which introduces two supplementary parameters, K_1 and K_2. Unfortunately the number of T_g vs. composition data for a given polymer blend is too small to discern an optimum K' value.

The impact of the K' variation on K_1 and K_2 is evidenced in a K_1 vs. K_2 representation in *Figure 7*. The arrows indicate the sense of variation of the fitting parameters K_1 and K_2 for values of K' ranging from 0.8 to 1.2. The points correspond to the ideal value of $K' = 1$. Indifferent to the chosen K' value, the general tendency of the K_1 vs. K_2 plot is preserved and thus for simplicity *Figure 8* includes only the data for $K' = 1$.

The analysis of these tendencies on the background of the contributions illustrated in *Figure 1* suggests that the K_1 parameter correlates predominantly with the intensity of the hetero-molecular contact interaction of the components of the blend. Correspondingly the respective values for the charge-transfer interaction between the electron-donor and electron-acceptor polymers PHECM /PDNBM are much higher than for the less intensive interacting PVME/PS blends. High K_1 values are obtained also for Novolac/PMMA blends which are

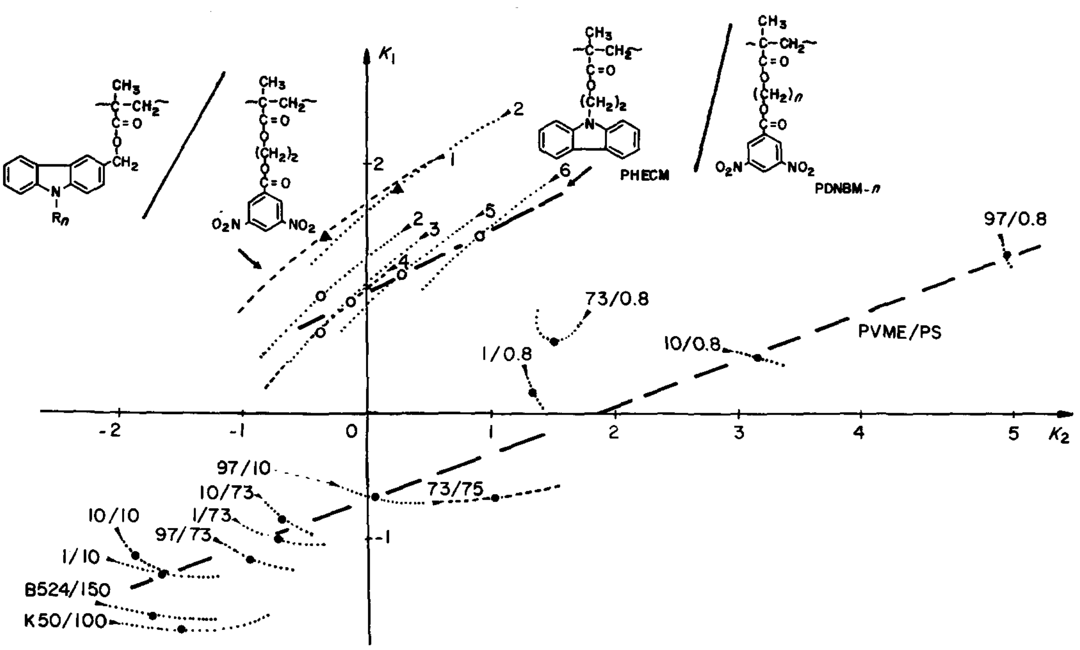

Figure 7 K_1 vs. K_2 representation of the fitting parameters of equation (22). Ranges of variation of K_1 and K_2 depending on the K' value. The notations represent the molecular weights of PVME/PS blend components in thousandths. The letters B indicate T_g data of Bank *et al.*[20] and K of Kwei *et al.*[21] The notations on the PHECM/PDNBM-*n* blends[19] indicate the number of C atoms in the hydroxyalkyl sequence of PDNBM

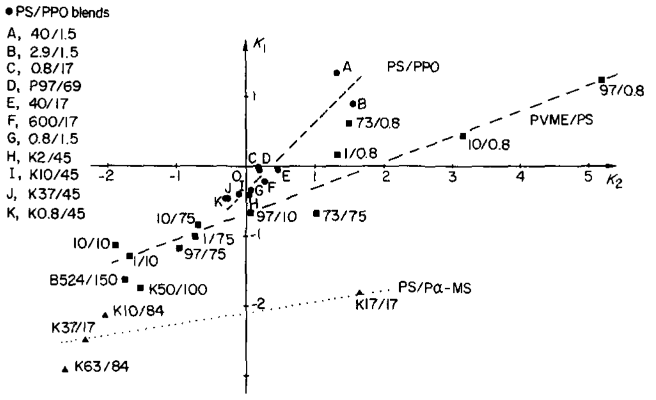

Figure 8 K_1 vs. K_2 representation of the fitting parameters of equation (22) for $K' = 1$. Molecular weights of the blend components are indicated in thousandths. The letters P indicate data of Prest and Porter[22] and K of Kwei and Frisch[23]. The latter are also analysed by Couchman[24]. (Pα-MS stands for poly(α-methylstyrene)

characterized by their ability to form hydrogen bonds[3].

Concerning the K_2 parameters it is interesting to note that for the PVME/PS blends the values are generally higher the lower the molecular weight of the more rigid polymer component PS. This tendency is confirmed also by data for the PS/PPO blends, where PPO is the more rigid component, as shown in *Figure 8*.

The specific influence of the molecular weight of the more rigid polymer component is also observed if the T_g vs. composition data of the PVME/PS blends are analysed with respect to the molecular weights of the components. From *Figure 9* it is evident that the shapes of the T_g vs. composition curves are essentially influenced by the molecular weight of the more rigid PS component.

The observed variation of the K_2 parameters in the PHECM/PDNBM-*n* blends with the length of the hydroxyalkyl spacer suggests that K_2 may reflect some orientation effects. Better interaction results with the longer spacer length because of increased decoupling from the chain backbone.

A more detailed discussion of the significance of these two fitting parameters K_1 and K_2 will be presented in a second paper.

CONCLUSIONS

The model presented in this paper concerning the composition dependence of T_g of compatible polymer blends makes use of the concepts of polymer solution thermodynamics. As applied to T_g, the approach is in fact a static one, which is surely acceptable because of the relative molecular immobility of the glassy state.

The energy parameters E (for the binary contact interaction) and e (for the influence of the molecular neighbourhood on the binary contacts) characterize the glassy state, i.e. its ability to transform from the glassy to the rubbery state. The result is a third-power equation with respect to the concentration of the more rigid polymer component. This equation describes satisfactorily the composition dependence of T_g of several miscible polymer blends. The fitting parameters introduced have well defined physical meanings and offer interesting possibilities for the interpretation of intermolecular interactions.

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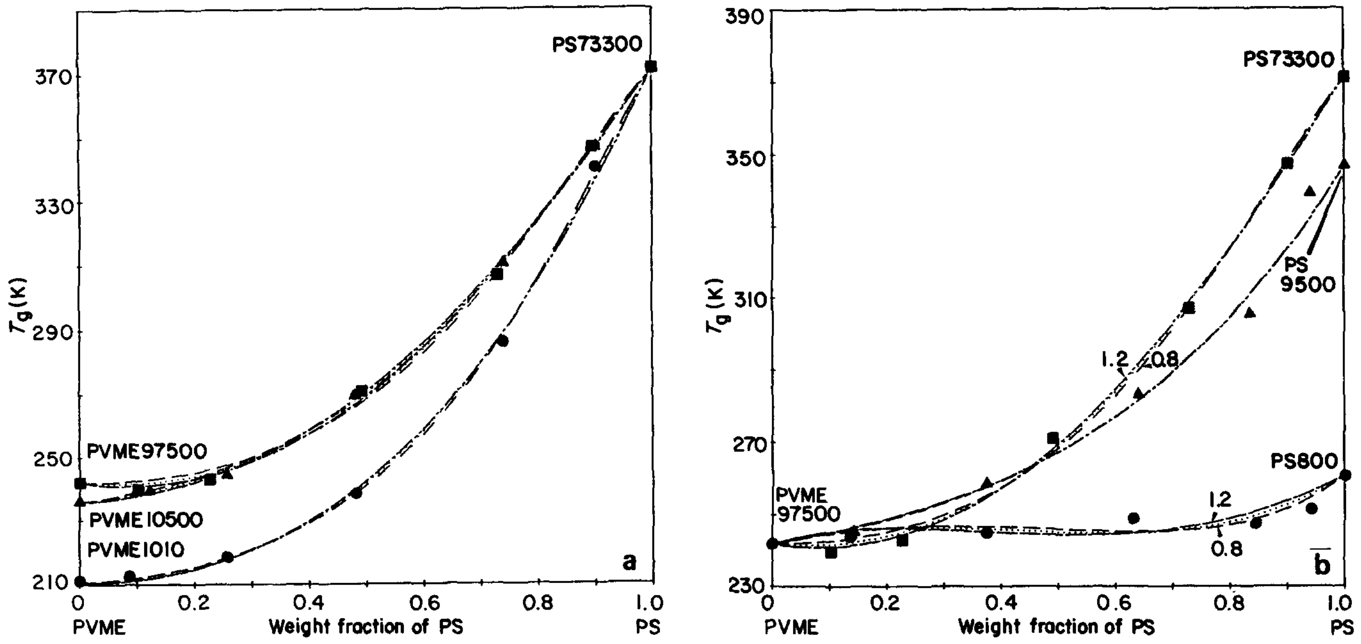

Figure 9 Influence of molecular weight of the blend components on the shape of the T_g vs. composition curves of PVME/PS blends. (Data of Schneider and Leikauf[8].) (a) Variable molecular weight of PVME. (b) Variable molecular weight of the stiffer PS

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