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THE MEANING OF THE GLASS TEMPERATURE OF RANDOM COPOLYMERS AND MISCIBLE POLYMER BLENDS

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Abstract

The glass transition temperature of random copolymers and miscible polymer blends exhibits generally a non-additive composition dependence, showing both positive and negative deviations of additivity predicted by 'Gordon-Taylor' like equations, among which the Fox relation represents the simplest additivity rule for the glass temperature of these polymeric systems. It is shown that the real T_g *vs.* composition behaviour of both copolymers and polymer blends can be adapted by a parameterized third order T_g *vs.* composition equation. The fitting parameter, K_1, of the square concentration term of this equation accounts essentially for the effect of binary hetero-sequences in copolymers and for specific contact hetero-interactions in polymer blends. The fitting parameter of the third order concentration term, K_2, is related exclusively to the effects of hetero-triad sequences (copolymers) and conformational entropy changes due to hetero-contact formation (polymer blends), respectively. It is shown that the K_1 parameter correlates roughly with the difference between the solubility parameters of the components.

Keywords: fitting and solubility parameters, glass temperature, miscible polymer blends, random copolymers, T_g *vs.* composition behaviour

Introduction

The glass transition is considered one of the most relevant characteristics to appreciate the practical use of amorphous polymers. Depending on their structure two-component polymeric systems are either two-phase systems, exhibiting more or less accurate the two glass temperatures of the components (block-copolymers and incompatible polymer blends) or one-phase systems, showing a single, composition dependent glass temperature (random copolymers and miscible polymers, i.e. compatible polymer blends).

The morphology of the two-phase systems depends on the composition (either spheres or rods of the minor component dispersed in the matrix of the major component or lamellae for systems of almost equal composition). Interphase binding in two-phase polymeric systems may induce either a more or less pronounced shift of the glass temperatures of the components or show even a third T_g, characteristic of the interphase.

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One-phase polymeric systems exhibit not only a single, composition dependent glass temperature, but show in the same time an enlargement of the glass transition range as it is demonstrated by the respective DSC-curves reproduced in Fig. 1.

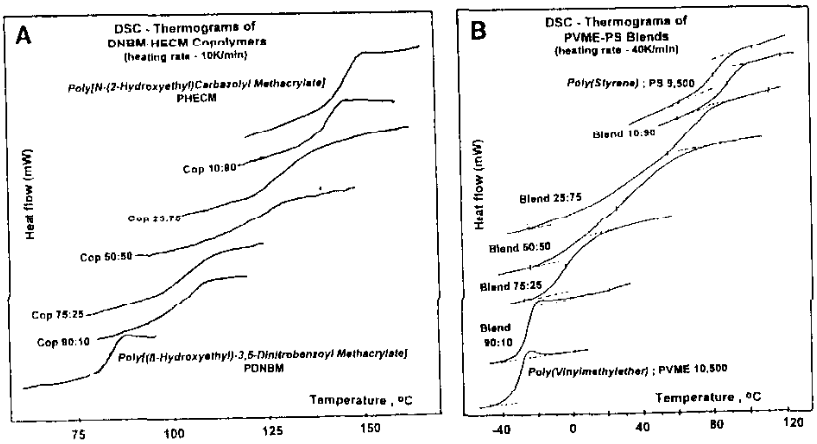

Fig. 1 DSC-curves of random copolymers and miscible polymer blends
A) Poly(acceptor-co-donor) system: poly[β-hydroxyethyl)-3,5-dinitrobenzoyl-methacrylate-co-(2-hydroxyethyl)carbazoyl methacrylate)
B) Poly(styrene), M_w=9500,/poly(vinylmethylether), M_w=10500, blend.
The number indicates the mass fractions of the components

In the following we will restrict ourself to the analysis of the composition dependence of the glass temperature of one-phase polymeric systems.

The glass temperature of random copolymers and compatible polymer blends

In literature, two different theoretical approaches are used to explain the glass temperature of polymers. The 'free volume' model assumes a kinetic control of the glass transition, the glass being considered a metastable 'frozen in' state characterized by a low temperature limit value of the 'free volume'. The thermodynamic based 'conformational entropy' model allows for the influence of conformational changes controlled by 'flexible' bonds, the glass being considered a 'fourth' thermodynamic stable state of matter characterized by a 'second-order phase transition' for 'zero'-conformational entropy.

Both models were used first to explain the composition dependence of the glass transition of random copolymers, the resulted equations being then later adapted for compatible polymer blends too.

It is intersting to notice that both models lead to the same 'Gordon-Taylor' type expression

$$T_g=[w_1T_{g1}+Kw_2T_{g2}]/[w_1+Kw_2] \qquad (1)$$

w_i being the weight fractions and T_{gi} the glass temperatures of the components, the index 2 referring to the component with the higher glass temperature, T_{g2}. The parameter K is, however, model specific. The 'free volume' model parameter, $K_{G\text{-}T}=(\rho_1\Delta\alpha_2/\rho_2\Delta\alpha_1)$ [1], considers the different expansivity of the components. $\Delta\alpha=(\alpha_{melt}-\alpha_{glass})_{T_g}$ is the respective increment of the expansion coefficients at T_g, the density, ρ, accounting for the transformation of volume fractions into mass fractions. The 'conformational entropy' model parameter, $K_{DM}=(m_1/r_1)/(m_2/r_2)$ [2], discriminates via the differences between the masses per 'flexible' bonds, m/r, of the monomeric units between the different mobilities of the components.

It has been shown [3] that both K-parameters can be replaced in a very first approximation by the ratio of the T_g's of the components, i.e. $K=T_{g1}/T_{g2}$, the corresponding substitution leading to the well known Fox expression [4]

$$1/T_g=w_1/T_{g1}+w_2/T_{g2} \qquad (2)$$

Thus the Fox relation can be considered to characterize in a very rough approximation the additive behaviour of the glass transition temperature of the one-phasic two-component polymeric systems.

In Fig. 2 are presented typical T_g *vs.* composition curves of random copolymers and compatible polymer blends, respectively. It results that beside apparent additive behaviour, both positive and negative deviations from additivity of the glass temperatures are observed.

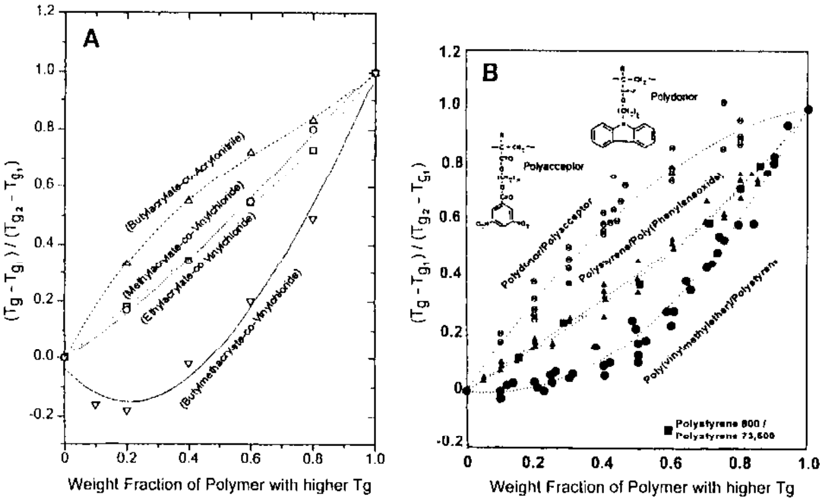

Fig. 2 Composition dependence of the glass temperature of random copolymers and miscible polymer blends
A) Random copolymers, B) miscible polymer blends – Relative representation of the glass temperatures, $(T_g-T_{g1})/(T_{g2}-T_{g1})$ for a better comparison

To explain the experimentally observed deviations from additivity of the glass temperatures of random copolymers the additivity rules were extended to account for contributions of hetero-diad [5, 6] or even of both hetero-diad and triad-sequences of the random copolymer [7]. The drawbacks of these approaches are, however, that the estimation of the diad and triad sequences either supposes the knowledge of the kinetic copolymerization parameters or implies laborious NMR-analysis. Additionally the glass temperatures of the hetero-diads (in the absence of T_g-data of strictly alternating copolymers) and -triads are in fact accessible only via 'fitting' procedures of the T_g *vs.* composition curves.

For compatible polymer blends the contributions to T_g of specific hetero-interactions were considered either by considering an additionally square concentration term in a simple additivity rule, i.e. $T_g=w_1T_{g1}+w_2T_{g2}+b(T_{g2}-T_{g1})w_1w_2$ [8] or by extending the 'Gordon-Taylor' equation by a supplementary concentration square term of the form qw_1w_2 [9]. Both b and q are treated as fitting parameters of the T_g *vs.* composition equation. The main problem of this procedure applied to polymer blends is related with the thermodynamic condition of polymer miscibility. Taking into account that for polymers the contribution to miscibility of combinatorial entropy is negligible, it results that energetic favorable interaction, i.e. specific hetero-interaction is responsible for polymer miscibility [10]. That means for polymer miscibility specific hetero-interactions have to overcome energetically the homo-interactions. Consequently, if only interactions are considered the packing in polymer blends should be denser and thus the glass temperature of the blend should be the higher. But in reality the majority of compatible polymer blends show sooner lower glass temperatures.

Based on this observation, Brekner *et al.* [11] supposed that strong specific hetero-contact formation may imply conformational redistributions in the contact neighbourhood and depending on structural and energetic asymmetries of the blend components local conformational entropy changes may increase the mobility in the neighborhood of the contacts, causing an equivalent increase of the 'free volume', i.e. a corresponding decrease of the blend T_g [12].

The result of these reflections resulted in a third order T_g *vs.* composition equation

$$T_g = \underset{\substack{\text{Gordon-Taylor}\\ \text{equation}}}{w_{1c}T_{g1} + w_{2c}T_{g2}} + \underset{\substack{\downarrow\\ \text{hetero-}\\ \text{interaction}}}{k_1w_{1c}w_{2c}} + \underset{\substack{\downarrow\\ \text{conformational-}\\ \text{redistribution}}}{k_2w_{1c}^2w_{2c} + k_3w_{1c}w_{2c}^2} \tag{3}$$

w_{1c} and w_{2c} are 'corrected mass fractions' to account via K for the different expansivity respective mobility of components: $w_{2c}=Kw_2/(w_1+Kw_2)$; $w_{1c}+w_{2c}=1$. For miscible polymer blends k_1 characterizes the specific interactions, whereas k_2 and k_3 consider the conformational entropy effects induced by hetero-contact formation. It has been later shown that the third order T_g *vs.* composition equation can be extended to random copolymers too, if the sequence distribution is unknown [13]. k_1 accounts then for the effect of hetero-diads, whereas k_2 and k_3 characterize the effect of hetero-triads on the glass transition of random copolymers.

Using 'corrected mass fractions' i.e. $w_{2c}=Kw_2/(w_1+Kw_2)$ and $w_{1c}+w_{2c}=1$, the Gordon-Taylor Eq. (1) becomes:

$$T_{g_{add}}=w_{1c}T_{g1}+w_{2c}T_{g2} \text{ i.e. } (T_{g_{add}}-T_{g1})/(T_{g2}-T_{g1})=w_{2c}$$

For K–T_{g2}/T_{g1} it is identical with the Fox expression Eq. (2). After substitution in Eq. (3) of w_{1c} by $(1-w_{2c})$ the deviation of the T_g from additivity, respective the non-additivity effects can be expressed as

$$\Delta T_g=[(T_{g2}-T_{g1})][K_1w_{2c}-(K_1+K_2)w_{2c}^2+K_2w_{2c}^3] \qquad (4)$$

with $K_1=(k_1+k_2)$; $K_2=(k_2-k_3)$ and respective $K_1-K_2=(k_1+k_3)$. K_1 and K_2 are the fitting parameters of the third order T_g *vs.* concentration Eqs (3) and (4). Unfortunately they are not accessible by independent on physics based procedures. However, K_2 is related exclusively to the effects of conformational redistributions in the neighborhood of the hetero-contacts respective of the hetero-triads, positive values indicating a stronger effect exerted on component 1. K_1 includes not only the effect of specific hetero-interaction (respective of hetero-diads) but also shares of the conformational redistribution effects (respective of the hetero-triads). Unfortunately, there is no way to separate this two effects.

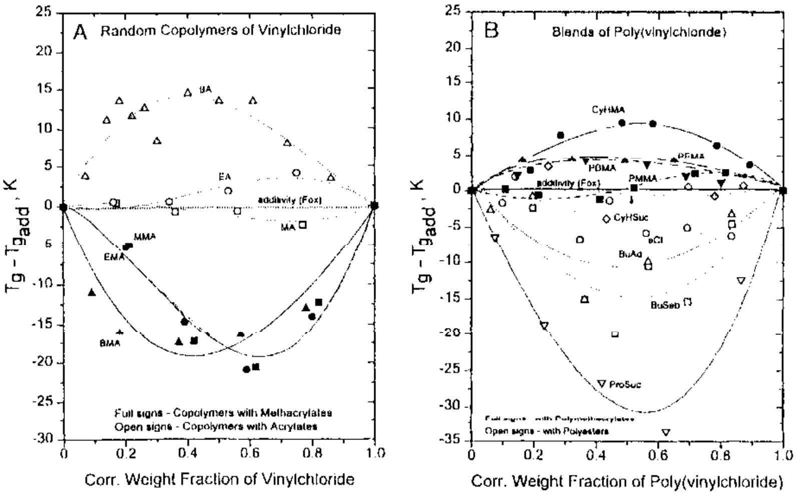

Fig. 3 Deviation from additivity of the glass temperature of random copolymers and miscible polymer blends
A) Copolymers of vinylchloride with acrylates (methyl-, MA, ethyl-, EA, *n*-butyl-, BA) and methacrylates (MMA, EMA and BMA)
B) Blends of poly(vinylchloride) with poly(methacrylate)s and polyesters – for significance of abbreviations see text

Discussions

Using literature data in Fig. 3 are presented some typical ΔT_g *vs.* composition curves of both copolymers of vinylchloride with acrylates respective methacrylates and blends of poly(vinylchloride) with poly(methacrylates)s respective polyesters.

For random copolymers are shown the ΔT_g *vs.* composition dependences of vinylchloride with methyl-(MA), ethyl-(EA) and *n*-butyl-(BA) acrylates and methacrylates (MMA, EMA, BMA), respectively [13]. To exhibit the corresponding behaviour of miscible blends of poly(vinylchloride) with poly(methacrylate)s were used data of Parmer *et al.* [14] – PMMA, PCyHMA i. e. poly(cyclohexyl methacrylate) – and of Perrin and Prud'homme [15] – PEMA and PBMA. For the blends with polyesters – i.e. poly(1,4-cyclo-hexane dimethylene succinate), –CyHSuc–, poly(ε-caprolactone), – eCL-, poly(1,4-butylene adipate), -BuAd-, poly(1,4-butylene sebacate), -BuSeb- and poly(2,2-dimethyl-1,3-propylene succinate), ProSuc, were used data of Barlow and Paul [16].

Taking into account of the significance of $K_1=(k_1+k_2)$, it may be supposed that this fitting parameter of the third order T_g *vs.* composition curves (3) is essentially influenced by specific effects within hetero-diads in copolymers respective specific interactions between binary hetero-contacts in polymer blends, although it includes via k_2 additionally nonseparable shares of hetero-triad or conformational entropy contributions, respectively. Consequently it was attempted to correlate K_1 with the respective difference between the solubility parameters of the components, $(\delta_2-\delta_1)$, taking into account that the Flory-Huggins interaction parameter, χ, is related to the

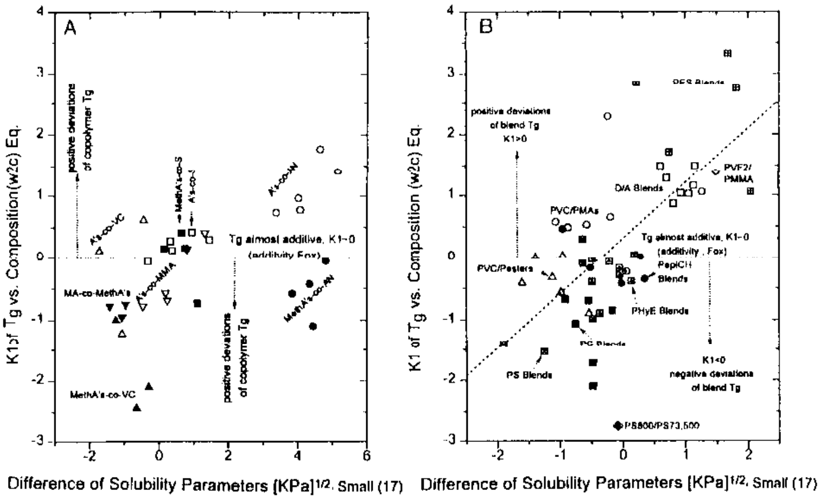

Fig. 4 Correlation of the K_1 parameter of the third order T_g *vs.* composition equation with the difference between the solubility parameters
A) Random copolymers, B) miscible polymer blends

difference of the squares of solubility parameters. For evaluation of the solubility parameters of the monomeric units was used the group contribution method recommended by Small [17].

The results of this attempt are shown in Fig. 4 for a series of random copolymers [13] and miscible polymer blends [18].

Although increasing K_1 with increasing difference of the solubility parameters seems to be the general tendency, there remain still a series of open questions, which can not be explained yet. Thus for instance, accordingly to Fig. 3, the deviations from additivity of the glass temperatures of random copolymers of vinylchloride with methacrylates are characterized by negative K_1 values, whereas the blends of poly(vinylchloride) with poly(methacrylates)s by positive K_1 values, although the difference between the solubility parameters is the same.

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