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Considerations concerning the glass temperature of blends of miscible polymers

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Summary

It is shown that experimental Tg vs. composition data of miscible polymer blends can be adapted by a third order Tg vs. composition equation characterized by two parameters, K_1, and K_2, which result in the supposition that besides the thermodynamically claimed favourable energetic hetero-interaction, contributions of conformational mixing entropy are responsible for miscibility. K_1 comprises mainly energetic interaction effects, whereas K_2 is due to effects of the conformational mixing entropy. It further results surprisingly that K_1 is roughly correlated with the difference of the solubility parameters of the blend components. At the moment no explanation can be offered for this observation.

Introduction

It has been shown that none of the two Tg vs. composition relations based on additivity of either the specific volumes (1) or the “flexible” bonds of the repeating units (2) of the blend components is able to reflect the real glass transition temperature behaviour of compatible polymer blends (3). The same is valid for the expressions based on continuity at Tg of thermodynamic functions and their excess functions (4). All these relations resulted in a Gordon-Taylor like equation

$$Tg_{blend} = (w_1Tg_1+Kw_2Tg_2)/(w_1+Kw_2) \tag{1}$$

where w_i are the weight fractions and Tg_i the glass temperatures of the blend components. K is a parameter specific for the model used, i.e., $K=(\rho_1\Delta\alpha_2)/(\rho_2\Delta 2\alpha_1)$ for additivity of specific volumes or continuity of the thermodynamic volume functions, and $K=(m_1/r_1)/(m_2/r_2)$ for additivity of “flexible” bonds. For continuity of enthalpy, K is equal to $(\Delta c_{p2}/\Delta c_{p1})$. The same expression is valid for continuity of entropy, but the logarithmic form of (1) results in the latter case. ρ_i are the densities, whereas $\Delta\alpha_i$ and Δc_{pi} are the increments at Tg of the expansion coefficients and of the heat capacities at constant pressure, respectively. m_i are the masses and r_i the “flexible” bonds of the monomeric units of the blend components.

Considering the corresponding Simha-Boyer empirical rules (5) and the observed interdependence between m_i/r_i and the glass temperature of polymers (6), it resulted that in a first rough approximation, K may be substituted by $K \sim Tg_1/Tg_2$, independent of the model used for the derivation of Tg vs. composition equation (1). In fact, this confirms more or less provable, the equivalence of the different models.

Substitution of K by Tg_1/Tg_2 results in the well known Fox equation (7)

$$(1/Tg_{blend}) = w_1/Tg_1 + w_2/Tg_2 \qquad (2)$$

which consequently may be considered to be in a first approximation representative for additivity of the blend glass temperature; $Tg_{(additive,Fox)} = Tg_1 Tg_2 /(w_1 Tg_2 + w_2 Tg_1)$

Taking into account that according to the thermodynamic requirements of polymer miscibility the energetic interaction between the blend components has to overcome the interaction within the homopolymers, at the beginning the K parameter of the Gordon-Taylor equation was considered as a pure fitting parameter. Next, the equation was extended by a second order concentration term to account by an additional empirical parameter for the favourable interaction between the blend components (8). But for the stronger interaction between the components required by thermodynamics, a denser packing of the blend should be the result. Thus, these oversimplified approaches are at most able to explain the experimentally observed positive deviations from additivity, i.e., positive values of the fitting parameters, but never the observed negative deviations (negative parameters) of the blend Tg.

It was consequently assumed that, depending on the probability of hetero-contact formation between the blend components, more or less pronounced conformational rearrangements should occur in the neighbourhood of the binary hetero-contacts. This leads to conformational entropy contributions to the mixing free energy of the blend, which were not considered in the initial thermodynamic approach of polymer miscibility. The probability of hetero-contact formation and thus the conformational mixing entropy will depend on both the intensity of the hetero-interaction energy and on structural and energetic symmetry factors of the blend components. The stronger the energy of hetero-interactions and the better the symmetry factors are, the higher is the probability of hetero-contact formation and consequently of the packing of the blend.

The result of these reflections was a third order Tg vs. composition equation (9)

$$(Tg_{blend}-Tg_1)/(Tg_2-Tg_1) = (1+K_1)w_{2c} - (K_1+K_2)w_{2c}^2 + K_2 w_{2c}^3 \qquad (3)$$

Tg_2 being the glass temperature of the component with the higher Tg and w_{2c} the weight fraction of that component corrected for additivity, w2c= $w_2 Tg_1/(w_1 Tg_2 + w_2 Tg_1)$

Results and Discussions

Introducing the corrected weight fraction of the component with the higher Tg_2 and the parameter $K=Tg_1/Tg_2$ approximated for additive behaviour, the Gordon-Taylor equation (1) may be reformulated as follows, $(Tg_{add,Fox}-Tg_1)/(Tg_2-Tg_1) = w_{2c}$.

Consequently, the deviation from additivity of the glass temperature of the blend may be expressed as

$$\Delta Tg = Tg_{blend}-Tg_{add,Fox} = (Tg_2-Tg_1)[K_1 w_{2c} - (K_1+K_2)w_{2c}^2 + K_{2c}^3 \qquad (4)$$

respectively $\Delta Tg/(Tg_2-Tg_1) = K_1 w_{2c} - (K_1+K_2)w_{2c}^2 + K_2 w_{2c}^3$

It results that the deviation from additivity depends exclusively on the values of the two additional parameters K1 and K2 of the third order Tg vs. composition relation (3).

Besides the difference between the interaction energies of the *hetero-* and *homo-*contacts $\Delta E=[(E_{12\text{-}\underline{1}}-E_{11\text{-}\underline{1}})+(E_{12\text{-}\underline{2}}-E_{22\text{-}\underline{2}})]$ in the vicinity of the blend components 1 and $\underline{2}$, respectively, K_1 comprises additionally energetic contributions of the conformational mixing entropy ($e_{ij\text{-}k}$) caused by conformational rearrangements induced by the substitution of the homo-contacts *11* with hetero-contacts *12* in the vicinity of the pure components (values in bracket).

$$K_1/(Tg_2-Tg_1)= \Delta E - [(e_{12\text{-}2}-e_{11\text{-}2})-(e_{12\text{-}1}-e_{11\text{-}1})]$$

$K_2/(Tg_2-Tg_1) = [(2e_{12\text{-}1}-(e_{11\text{-}1}+e_{22\text{-}1}) - (2e_{12\text{-}2}-(e_{22\text{-}2}+e_{11\text{-}2})]$ accounts exclusively for the additional energetic effects of the conformational mixing entropy.

Because the corrected weight fraction w_{2c} of the blend component with the higher Tg has been chosen as the independent variabel of the third order Tg vs. composition equation (3), K_1 reflects by the share of the energetic effects of the conformational mixing entropy a certain asymmetry. This is evidenced if the difference of the two parameters K_1-K_2 is considered. Besides ΔE it includes the entropy effects of the substitution of the homo-contacts *22* by hetero-contacts *12*:

$$(K_1-K_2)/(Tg_2-Tg_1) = \Delta E - [(e_{12\text{-}1}-e_{22\text{-}1})-(e_{12\text{-}2}-e_{22\text{-}2})]$$

Consequently, asymmetric Tg vs. composition curves of polymer blends are characterized by very different values of these parameters K_1 and (K_1-K_2), that means by similar values of the parameters K_1 and K_2. Absolute values of K_2 larger than of K_1 are characteristic of S-shaped Tg vs. composition curves.

Typical Tg behaviours of miscible binary polymer blends are shown in Fig 1. Using both own and literature data, ΔTg vs. composition curves for blends of poly(phenylether phenylsulfone) with various poly(phenylether phenylketone)s and for different blends of polystyrene are presented comparatively in Fig 1A. Shown in Fig. 1B are the respective curves for polydonor/polyacceptor blends and for blends of polyhydroxyether of bisphenol A. It results, with the exception of PS/PPO blends, that the glass temperatures of real miscible polymer blends show either positive or negative deviations of additivity predicted by the Fox eq. (2).

The scatter of the data reported by the different authors is relatively large and depends not only on the molecular weights of the blend components - see Fig 9. in (10) - but mainly on the modes of preparation and operation (cooling/heating rates, mode of Tg evaluation). In Fig. 1A are compared for illustration Tg data of PS/PαMS blends obtained either by precipitation - PaMS(p)/PS - or by press moulding - PaMS(g)/PS - (11). (For significance of used polymer abbreviations see footnote Tab.I.). It results that press moulding increases the probability of hetero-contact formation expressed by a reduction of the free volume available for conformational mobility, which is reflected in an approach to additivtiy of the negative deviation of the blend glass temperatures. It is interesting to notice that literature data of Lin and Roe (12) are comparable with Tg data of mould-pressed blends, whereas data of Cowie et al. (13) are similar to the data of blends obtained by precipitation.

The influence of structural-mismatch results by comparison of Tg data of the blends PEK/PES and PEEK/PES (Fig. 1A). The monomeric unit of PEK contains an even number of phenyl-units like PES, whereas PEEK an od number. On the other hand, the probability of charge-transfer interaction (CT-interaction), and thus of hetero-contact formation in structural symmetric polyacceptor/polydonor blends is increased due to an increased mobility of the interacting groups by the spacer length between the acceptor group and the polymeric backbone (Fig. 1B). In both cases stronger positive deviations of additivity of the blend glass temperatures are observed. Finally, compared in Fig. 1C are the glass temperatures of blends of PVC. It is interesting to notice, that the Tg of blends with the structural symmetric polymethacrylates show positive, whereas those with the asymmetric polyesters exhibit negative deviations from additivity.

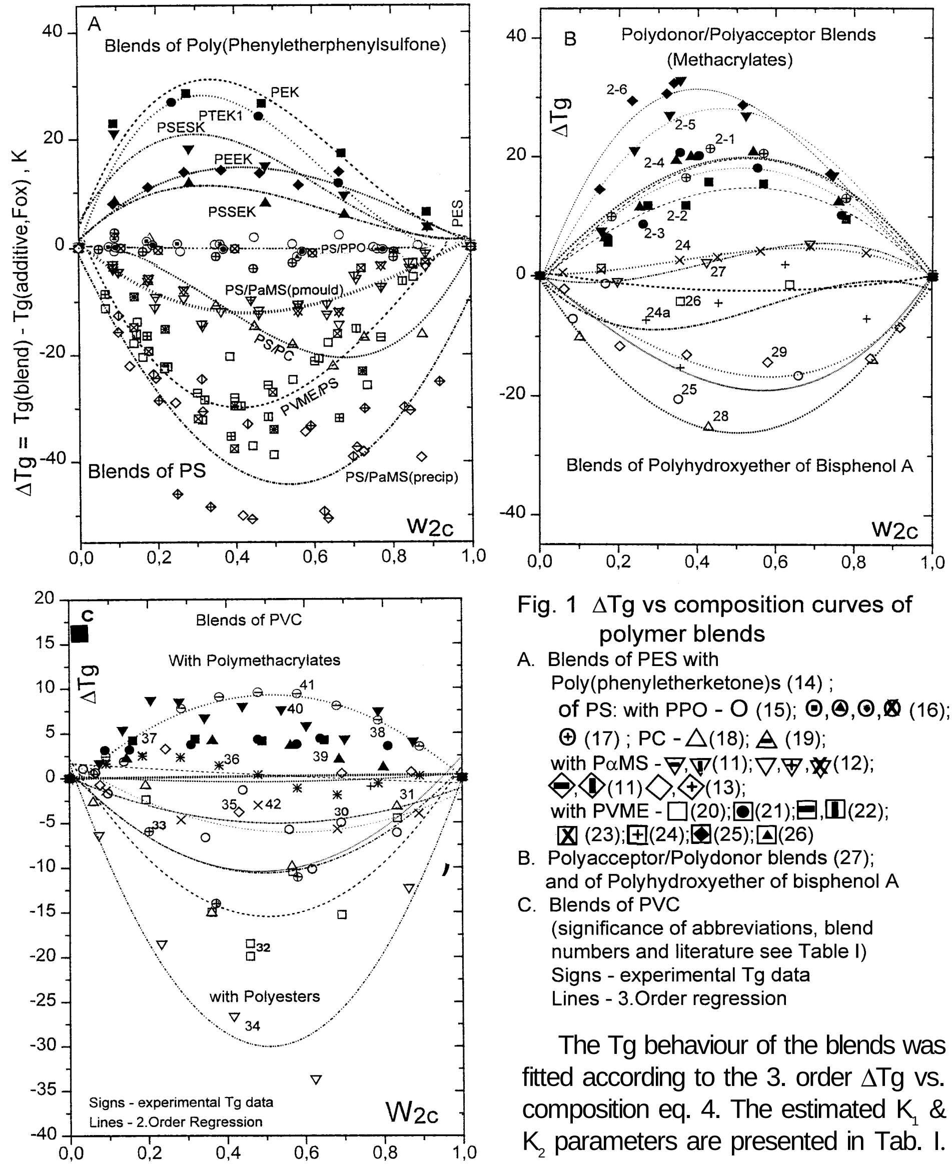

Fig. 1 ΔTg vs composition curves of polymer blends

A. Blends of PES with Poly(phenyletherketone)s (14) ; of PS: with PPO - ○ (15); ⊡,◬,⊙,⊗ (16); ⊕ (17) ; PC - △(18); △ (19); with PαMS - ▽,▽(11); ▽,▽,▽(12); ◈,◈(11)◇,◈(13); with PVME - □(20); ▣(21); ⊟,◫(22); ⊠ (23); ⊞(24); ▣(25); ▣(26)

B. Polyacceptor/Polydonor blends (27); and of Polyhydroxyether of bisphenol A

C. Blends of PVC (significance of abbreviations, blend numbers and literature see Table I) Signs - experimental Tg data Lines - 3.Order regression

The Tg behaviour of the blends was fitted according to the 3. order ΔTg vs. composition eq. 4. The estimated K_1 & K_2 parameters are presented in Tab. I.

Table I. Characteristic Parameters of compatible Polymer Blends

Blend[a)]	**Tg_2-Tg_1**	**K_1**	**K_2**	$(\delta_2-\delta_1)$	**Lit.**
Polyacceptor-/Polydonor-methacrylate (-acrylate) Blends[b)]					
Poly(ω–hydroxyalkyl–3,5-dinitrobenzoyl-) / Poly[N-(2-hydroxyethyl)carbazoyl-methacrylate)					
1. PDNBM-2/PHECM-2	53	1.026	-0.298	1.056	27
2. PDNBM-3/PHECM-2	74	1.035	-0.048	0.929	"
3. PDNBM-4/PHECM-2	89	0.868	-0.155	0.812	"
4. PDNBM-5/PHECM-2	113	1.278	0.415	0.704	"
5. PDNBM-6/PHECM-2	123	1.494	0.973	0.605	"
6. PDNBM-2/PHECM-1[c)]	50	1.498	-0.21	1.155	"
7. PDNBA-2/PHECA-2	54	1.156	0.603	1.132	28
Poly(phenylether(thioether/sulfones)phenylketone) / Poly(phenyletherphenylsulfone) -PES-					
8. PEK[c)]/PES	56	3.326	3.215	1.68	14
9. PT1EK/PES	71	2.745	2.994	1.812	"
10. PSEK/PES	40	1.727	1.814	0.749	"
11. PSSEK/PES	42	2.828	3.013	0.222	"
12. PEEK/PES	67.8	1.062	0.547	2.045	"
Blends of Polystyrene - PS					
13. PS/PPO	112	0.052	0.108	0.118	15-17
14. PS/PαMS					
a. all hM data	71.9	-1.722	-0.596	-0.477	
b. hM precipitated	74.5	-2.093	0.22	"	11, 13
c. hM press moulded	69.2	-0.976	-0.432	"	11, 12
15. PVME/PS	130.6	-1.394	-0.764	-1.898	20-26
16. PEMA/PS	32.5	-1.536	-0.79	-1.257	29
17. PPMA/PS	56.47	-0.68	-0.312	-0.915	29
18. PS/PC (Barlow)	90.5	-0.107	1.231	-0.642	18
19. PS/PC (Higgins)	96.6	0.309	1.986	"	19
Blends of Tetramethyl bisphenol-A polycarbonate - PC					
20. PαMS (IM)/ PC	125.5	-0.85	-0.011	-0.165	18
21. P(εCL)/PC	261.5	-0.69	-1.504	-0.546	30
22. P(ButSeb)/PC	255.5	-1.061	-1.775	-0.758	"
23. P(HexmethSeb)/PC	253.5	-0.666	-0.566	-0.926	"
Blends of Polyhydroxyether of bisphenol-A - PHyE					
24. P(εCL)/PHyE (Brode)	174.1	-0.030	0.053	-0.49	31
a. (Barlow)	164.7	-0.394	-0.517	-0.49	32
25. P(EthAdip)/PHyE	143.7	-0.385	0.294	0.14	"
26. P(PropAdip)/PHyE	149.7	-0.289	0.256	-0.053	"
27. P(ButAdip)/PHyE	164.7	-0.071	0	-0.22	"
28. P(PropSucc)/PHyE	113.7	-0.892	0.038	-0.367	"
29. P(CyhxSucc)/PHyE	97.7	-0.172	-0.634	-0.054	"
Blends of PVC with Polyesters (Barlow)					
30. P(εCL)/PVC	153.5	0.01	0.335	-1.395	33
31. P(ButAdip)/PVC	153.5	-0.326	-0.07	-1.124	"
32. P(ButSeb)/PVC	155.5	-0.415	0.063	-1.607	34
33. P(HexmethSeb)/PVC	145.5	-0.568	-0.445	-1.777	33
34. P(PropSucc)/PVC	102.5	-0.896	0.615	-0.537	"
35. P(CyhxSucc/PVC	86.5	0.035	0.073	-0.959	"

Continuation Table I

		Blends of PVC with Methacrylates			
36. PVC/PMMA	29.9	0.654	1.332	-0.196	35
37. PEMA/PVC	11.34	2.292	1.463	-0.234	36
38. PPMA/PVC	30.55	0.535	0.051	-0.576	"
39. PBMA/PVC	50.08	0.459	0.296	-0.847	"
40.PAMA/PVC	76.18	0.581	0.356	-1.071	"
41. PVC/PCHMA	31.53	1.057	-0.362	1.268	35
42. P(thFurMA)/PVC	26.9	-0.234	0.925	0.061	37
43. PVF2/PMMA	141.15	1.38	1.885	1.49	38
44. PS800/PS73,500	121.0	-0.237	-0.073	0	39
		Blends of Poly(epichlorohydrine) - PepiCH			
45. P(EthAdip)/PepiCH	25.5	-0.247	0.138	-0.564	40
46. P(ButAdip)/PepiCH	46.5	0.313	1.407	-0.924	"
47. PepiCH/P(PropSucc)	4.5	-0.458	-0.078	0.048	"
48. P(PropAdip))/PepiCH	26.0	-0.088	0.804	0.238	"
49. PepiCH/P(CyhexSucc)	20.5	-0.484	0.583	0.349	"

[a] The second listed component of the blend has the higher Tg; [b] figures indicate the number of methylene groups between electron interacting and methacrylic/acrylic groups

[c] Significane of used polymer abbreviations: PHEM-1 poly[(N-methyl)-1-hydroxyethyl-carbozolyl methacrylate]; PEK – poly[(bis-phenylketone)-(bis-phenylether)]; PT1EK – poly[(phenylketonephenyl-thioether-phenylketone-(bis-phenylether)]; PSEK – poly[(bis-phenylketone)-phenylether-phenylsulfone-phenylether)]; PSSEK – poly(phenylketone-phenylsulfone-phenylether-phenylsulfone-phenylether); PEEK – poly[phenylketone-(bis-phenylether)]; PPO – poly(2,6-dimethyl-1,4-phenylene oxide); PaMS – poly(α-methylstyrene); PVME – poly(vinylmethylether); PEMA – poly(ethyl methacrylate); PPMA – poly(propyl methacrylate); P(εCL) – poly (ε-caprolactone); P(ButSeb) – poly(1,4-butylene sebacate); P(HexmethSeb) – poly(hexamethylene sebacate); P(EthAdip) – poly(ethylene adipate); P(PropAdip) – poly(2,2-dimethyl-1,3-propylene adipate); P(ButAdip) – poly(1,4-butylene adipate); P(PropSucc) – poly(2,2-dimethyl-1,3-propylene succinate); P(CyhexSucc) – poly(1,4-cyclohexane dimethylene succinate); PBMA – poly(butyl methacrylate); PAMA – poly(amyl methacrylate); PCHMA – poly(cyclohexyl methacrylate); p(thFurMA) – poly(tetrahydrofurfuryl methacrylate); PVF2 – poly(vinylidene flouride)

Besides the parameters of the 3. order Tg vs composition equation, presented in Table I are the differences between the glass temperatures (Tg_2-Tg_1) and between the solubility parameters (δ_2-δ_1) of the blend components, the index 2 refering to the component with the higher Tg.

Taking into account that the enthalpy of mixing of polymers is connected in a very first aproximation to the reciprocal solubility of the components, it was attempted (10) to correlate the fitting parameter of the 3. order concentration power equation with the difference between the respective solubility parameters, (δ_2-δ_1). Surprisingly the better interdependence resulted for K_1 than for the difference (K_1-K_2), although both comprise the same contribution of interaction energies ΔE, but different shares of energetical contribution of the conformational mixing entropy. The scatter of the difference of the two parameters (K_1-K_2) was excesively large mainly for S-shaped Tg curves characterized by absolute values of K_2 larger than of K_1, which results in an inversion of the sign of (K_1-K_2) compared to the sign of K_1.

The solubility parameters were estimated for the repeating units of the polymers according to the group contribution method by using sets of group constants (molar attraction constants) of Small, based on measurements of the heat of vaporization. Missing values of group constants were estimated by comparison of solubility parametrs of solvents of identical chemical structure but containing either the missing group or groups listed in the table of Small (41).

Finally, Fig. 2 illustrates the correlation between the K1 parameter of the 3. order concentration power eq. (3) and the difference of the solubility parameters (δ_2-δ_1) for the polymer blends listed in Table I. Although the scatter of the data is large, it results surprisingy that positive differences of the solubility parameters are sooner accompanied by positive deviations from additivity, whereas negative differences point more likely at negative deviations of the blend Tg. At the moment no explanation can be offered for this observation. It is, however, reliable that energetic stronger hetero-interactions and favourable structural/steric symmetry factors of the components increases the probability of hetero-contact formation by a “zipp”-like arrangement of the interacting sites, the result being a denser packing of the blend accompanied by positive deviations of the blend Tg. Less stronger interactions and lack of symmetry effects decrease the probability of hetero-contact formation. The corresponding looser packing of the blend enhances the possibility of conformational mobility withing the blend, decreasing the blend Tg below additivity inspite of the favourable hetero-intercation claimed for polymer mixing by thermodynamics.

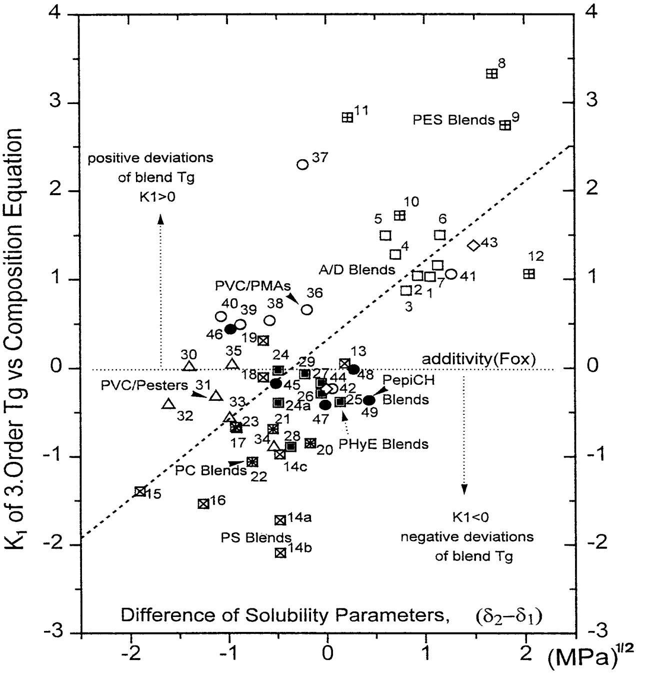

Fig. 2 K_1 parameter of 3.Order Tg - Composition Eq. vs. Difference of Solubility Parameters

For blend numbers see Tab. I

Acknowledgments

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