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Description and molecular interpretations of anomalous compositional dependences of the glass transition temperatures in binary organic mixtures

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ABSTRACT

The present study explores the applicability of a three-parameter equation: $T_g = \varphi_1 T_{g,1} + (1-\varphi_1) T_{g,2} + \varphi_1(1-\varphi_1)[a_0 + a_1(2\varphi_1-1) + a_2(2\varphi_1-1)^2]$ (where φ_i and $T_{g,i}$ are, respectively, the weight fraction and the glass transition temperature of the *i*th neat component), recently proposed for describing the T_g vs. composition dependencies in miscible binary polymer blends and copolymers (Brostow et al. Mater. Lett. 62 (2008) 3152 [16]). Its efficacy is postulated here also for mixtures of polymers with low molecular mass organics (solvent, plasticizer or semicrystalline drug molecule phases) and very strongly/weakly associating polymer blends, including interpolymer complexes. Binary systems where entropic factors overcome the enthalpic ones were also considered. For several complicated (asymmetric or sigmoid) dependencies a description with better accuracy was achieved, compared to the common theoretical or semi-empirical functional forms, some of which require parameters that are not always readily available to the experimentalist or contain a superfluous number of fitting parameters. First- (linear) or second-order (parabolic) polynomial dependencies are established among its prime parameter a_0 and "interaction terms" of common $T_g(\varphi)$ functions, which are used as semi-quantitative measures of the strength of intermolecular interactions (e.g., parameter k_{GT} of Gordon–Taylor, b of Jenckel–Heusch, and q of Kwei). Changes in the shape of the $T_g(\varphi)$ plots, and the corresponding a_i fitting parameter estimates, are discussed in relation to important physicochemical phenomena and properties of the mixtures, such as, the strength of the hetero-contact forces and their composition dependence, irregular excess free-volume effects, as well as nanoscale effects arising from variation of components molecular mass, chains' branching or organization in crystalline phases.

1. Introduction

The temperature beyond which the long-range translational motion of the polymer chain segments is active (i.e., the glass transition temperature, T_g), the width of the transition signals recorded by different measuring techniques, and their variation with changes in composition or processing, reflect fundamental properties of systems based on amorphous polymers [1]. Related studies are of paramount importance in the effort to decode the intriguing nature of the glass transition phenomenon through studies of polymer dynamics under confinement (e.g., in cases of fillers' inclusion, polymer intercalation or clay exfoliation) [2–4], in the thermophysical and morphological characterization of polymer-based nanocomposites (blends, copolymers, networks, etc.) [5,6], or when aging, crystallization, polymerization or curing rates need to be monitored or regulated to a desired point [1,7–9].

Polymers' blending at suitable proportions provides materials with full set of desired specific properties (i.e., impact strength, scratch or solvent resistance, thermomechanical stability, and recyclability) at the lowest attainable cost. For that reason, relevant studies cover large part of contemporary research [10]. In routine miscibility studies of binary (1 + 2) blends, the occurrence of a single – although usually broad – glass transition region for all blend compositions is considered "sufficient" for establishing a *homogeneous* state of polymers' dispersion in domain sizes comparable to the macromolecular radius of gyration ($2 \leq d \leq 15$ nm diameter) [10]. A qualitative deduction extracted from free-volume theories is the expectancy of glass transition temperatures and segmental relaxation times intermediate to those of the pure components. Ample experimental evidence exists in favor of this behavior, especially in the presence of strong differences in the respective glass transition temperatures or relaxation functions (i.e., coupling parameters). In such cases of strong dynamic heterogeneity the blends may exhibit an unusually broad relaxation spectrum along with an absence of

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Table 1

Selection of functions proposed for estimating the glass transition temperature of amorphous binary mixtures. φ_i, x_i, $\Delta C_{p,i}$ and $T_{g,i}$ are, respectively, the weight fraction, the molar fraction, the difference in the heat capacity of the liquid and the heat capacity of the glass forms, and the glass transition temperature of the ith blend component.

Function's name	Functional form		Fitting parameters
Gordon–Taylor [12]	$T_g = \dfrac{\phi_1 T_{g,1} + k_{GT}(1-\phi_1)T_{g,2}}{\phi_1 + k_{GT}(1-\phi_1)}$	(1)	k_{GT}
Fox [13]	$\dfrac{1}{T_g} = \dfrac{\phi_1}{T_{g,1}} + \dfrac{1-\phi_1}{T_{g,2}}$	(2)	–
Couchman–Karasz [14]	$\ln T_g = \dfrac{x_1 \Delta C_{p,1} \ln T_{g,1} + \Delta C_{p,2}(1-x_1)\ln T_{g,2}}{x_1 \Delta C_{p,1} + (1-x_1)\Delta C_{p,2}}$	(3)	–
Jenckel–Heusch [15]	$T_g = \phi_1 T_{g,1} + (1-\phi_1)T_{g,2} + b(T_{g,2} - T_{g,1})\phi_1(1-\phi_1)$	(4)	b
Utracki [10]	$T_g = [1 + K^* \phi_1(1-\phi_1)]\left[\phi_1 T_{g,1}^{3/2} + (1-\phi_1)T_{g,2}^{3/2}\right]^{2/3}$	(5)	K^*
Kwei [17]	$T_g = \dfrac{\phi_1 T_{g,1} + k_{Kw}(1-\phi_1)T_{g,2}}{\phi_1 + k_{Kw}(1-\phi_1)} + q\phi_1(1-\phi_1)$	(6)	k_{Kw}, q
Brekner–Schneider–Cantow [20,22]	$T_g = T_{g,1} + (T_{g,2} - T_{g,1})[(1+K_1)\phi_{2c} - (K_1+K_2)\phi_{2c}^2 + K_2\phi_{2c}^3]; \quad \phi_{2c} = \dfrac{k\phi_2}{\phi_1 + k\phi_2}, \quad k \approx \dfrac{T_{g,1}}{T_{g,2}}$	(7)	K_1, K_2
Lu–Weiss [18][a]	$T_g = \dfrac{\phi_1 T_{g,1} + k(1-\phi_1)T_{g,2}}{\phi_1 + k(1-\phi_1)} + \dfrac{A\phi_1(1-\phi_1)}{[\phi_1 + k(1-\phi_1)][\phi_1 + b(1-\phi_1)][\phi_1 + c(1-\phi_1)]^2}; \quad A = \dfrac{-\chi_{12}R(T_{g,1} - T_{g,2})c}{M_1 \Delta C_{p,1}},$ $k = \dfrac{\Delta C_{p,2} - \phi_1 \delta C_p^l}{\Delta C_{p,1} - (1-\phi_1)\delta C_p^g}$	(8)	k, A
Cowie–Harding [19]	$T_g = \dfrac{(\phi_1 + f)T_{g,1} + k(1-\phi_1-f)T_{g,2}}{(\phi_1+f) + k(1-\phi_1-f)} + [q(\phi_1+f)(1-\phi_1-f)]^n$	(9)	n, f, k, q
Brostow et al. [16,23]	$T_g = \phi_1 T_{g,1} + (1-\phi_1)T_{g,2} + \phi_1(1-\phi_1)\left[a_0 + a_1(2\phi_1 - 1) + a_2(2\phi_1 - 1)^2\right]$	(10)	a_0, a_1, a_2

[a] M_i = molar mass per chain segment of the ith component, $b = \rho_1/\rho_2$ densities ratio, $c = M_1/M_2$, and δC_p is the specific heat change due to mixing.

thermorheological simplicity; it is even possible to observe bimodal glass transitions (i.e., two composition-dependent T_gs) using high-resolution techniques [11], when the components have measurably different mobilities and relaxation times within an optically homogeneous mixture.

Insofar, numerous methodologies founded on kinetic or thermodynamic aspects of the glass transition phenomenon have been used to develop *descriptive* or *semi-predictive* equations of the T_g vs. composition dependence encountered in binary polymer mixtures (Table 1) [10,12–25]. Their wide implementation in materials research is promoted by the need to appraise the impact of physicochemical factors and microstructural characteristics that encourage *full* or *partial* miscibility, or the commonly observed *phase separation* behavior of most pairs of macromolecular substances [10].

Volume-additivity (i.e., ideal volume of mixing) and a linear change in volume with temperature derive the commonly used Gordon–Taylor $T_g(\varphi)$ equation [12] (Eq. (1)). By invoking the Simha–Boyer rule and assuming similar specific volume for the two components, the simple Fox equation is further obtained [13] (Eq. (2)). The thermodynamic approach followed by Couchman and Karasz [14], which considered that the entropy of mixing is continuous during the glass transition, offered an equation successful in describing weak monotonic deviations from the linear combination (Eq. (3)). Nonetheless, neglecting the effect of strong interchain interactions, which bring on strong entropy of mixing effects on the glass transition and produce structured mixtures [26], the latter function appears useful only for random mixtures; elaborate modifications are thus required to extent its applicability (e.g., see Refs. [27,28]). Jenckel and Heusch [15] proposed an expression (Eq. (4)) that again accounts for monotonic (all positive or all negative) deviations, with its empirical fitting parameter (b) used to characterize the solvent “quality” of the plasticizer. Likewise, Kim et al. [24] put forward a model based on configurational entropy and the Flory–Huggins theory, introducing a single adjustable parameter (γ) as representative of the strength of specific interaction between two polymers. Incorporating the influence of strong specific interactions, Kwei [17] extended the Gordon–Taylor equation to a concentration second-order power equation (Eq. (6)) by introducing a quadratic term, $q\varphi_1(1-\varphi_1)$. A similar, in form, expression was suggested by Lu and Weiss [18] (Eq. (8)), while a four-parameter modification of the Kwei equation has been proposed by Cowie and co-workers [19] (Eq. (9)). The physical meaning of the frequently reported Kwei parameters, k_{Kw} and q, has been the subject of subsequent interpretations based on the degree of interactions among the components in the mixture. By means of this empirical equation, *s*-shaped curves can be explained, but only with positive deviations from additivity in the low-T_g range and negative deviations in the high-T_g range. To reproduce data showing the reversed behavior, additional correction terms have to be considered (e.g., the virial-like concentration third power Brekner–Schneider–Cantow (BSC) function [20,22]) (Eq. (7)), but again, neither the curve-fitting process is always satisfactory nor the interpretation of its results are straightforward.

Evidently, more complex behaviors and interesting anomalies in the T_g vs. composition dependencies come into sight, when, for example, at least one of the components partly crystallizes in the blend environment, entropic or enthalpic factors prevail at different compositional ranges, or the neat components have almost identical segmental mobilities; in such cases, most approaches fail. In an attempt to overcome these shortcomings, our research group recently proposed a simple empirical equation [16] and provided preliminary evidence of its applicability [23]. In this function, a quadratic polynomial centered around $2\varphi_1 - 1 = 0$ is defined to describe deviations from the simple rule of mixtures, $T_{g,av} = \varphi_1 T_{g,1} + (1-\varphi_1)T_{g,2}$. An important facet of Eq. (10) lays in the fact that the number of the a_i fitting parameters (up to three; a_0, a_1 and a_2) required to describe an experimental $T_g(\varphi)$ dependence, along with their magnitude and sign, can be used as measure of system's complexity [23]. In that way, an attractive and more systems-inclusive classification may be reached. At present, the applicability of the new equation and the physical meaning of its parameters is subjected to intense investigation [23,29–31], in an attempt to correlate their variation with phenomena manipulating the thermal characteristics of miscible binary polymer blends. Besides this, the present work lays emphasis on the analysis of the compositional dependence of the glass transition temperatures of binary systems with components showing low T_g contrast (i.e., $\Delta T_g = T_{g,2} - T_{g,1} \leq 30$ degrees). Such mixtures often demonstrate a series of abnormal perturbations in their dynamics. These include, strong positive [27,30–36] or negative [31,37–44] departures of the glass transition temperature from the mass/volume-additivity mixing rules, with usually asymmetric or sigmoid shapes, and several blend T_gs falling outside the range defined by the glass transition temperatures of the neat components. To account for such dependencies, blending-induced changes in either constrained dynamics or non-zero excess mixing volumes, or a combination of them, are usually considered and discussed below using illustrative examples.

2. Experimental

Published data for a number of miscible binary mixtures, with a broad range of differences in the glass transition temperatures of their components ($T_{g,2} - T_{g,1}$ in the range ≈0 to 200 K), are reexamined (Tables 2a and 2b). Unless otherwise indicated, the single T_g values given in the following figures and used in the calculations, stand for the so-called *blend-average* glass transition temperature, i.e., the single T_g value obtained from the midpoint or the onset temperature of the heat capacity change in second-heating differential scanning calorimetry (DSC) scans. Blends where bimodal glass transition regions have been reported were not considered here; an example of the application of Eq. (10) for analyzing related data (in the frame of the Lodge–McLeish self-concentration model) is given in Ref. [23]. Information on the experimental details and any special procedures used for preparation of the mixtures (temperature of mixing, type of solvent, drying processes, etc.) and their spectroscopic and thermal characterization can be found in the original references. The values reported here for the fitting parameters were obtained by applying a Levenberg–Marquardt least-square minimization routine to the experimental data. The success of each fitting function is judged in terms of the minimization of the coefficient of determination (R^2) values and of the reduced χ-square values (χ^2/DoF, DoF = number of the degrees of freedom).

3. Description and interpretation of characteristic $T_g(\varphi)$ graphs

The shape of the $T_g(\varphi)$ dependence and the number of fitting parameters a_i (Eq. (10)) necessary for describing a particular experimental graph is primarily determined by the interplay between various physicochemical properties and structural factors. These include the strength of the exothermic hetero-contact forces (intermolecular interactions) and their composition dependence, free-volume modifications that may even experience some type of irregular compositional dependency (due to inhomogeneous local interchain orientation), the different types of segregation of the amorphous fractions with respect to the crystalline phase, and the molecular mass as well as the tacticity and branching of the blend constituents.

As a rule of thumb, the sign and absolute magnitude of parameter a_0 represents the strength of the observed positive (for $a_0 > 0$)

Table 2a
Mixture information and curve-fitting results for the parameters incorporated in Eq. (10) for selected binary blends exhibiting positive deviations from the linear mixing rule.

Binary blend (1 + 2)	$\bar{M}_{w,1}$ (g/mol)	$\bar{M}_{w,2}$ (g/mol)	$T_{g,2}-T_{g,1}$ (K)	Fitting parameters				R^2	Ref.
				a_0	a_1	a_2	$a_0/\Delta T_g$		
PECH + PVME			0	24 ± 2	−20.5 ± 3.7	26.7		0.957	[35]
P(S-*co*-MA) (28 mol% MA) + PVP	219,000	94,000	2	238 ± 7	197 ± 13	−157 ± 31		0.990	[32]
PαMS + PCHMA	1500	3400	8	19 ± 1	−14 ± 2	−30 ± 5	2.38	0.995	[34]
SAN (18 wt.% AN) + PMMA	165,000	198,000	10	12	−8	0	1.20	1.000	[54]
SAD17 + SAA18	127,000		17	21.6 ± 0.5	0.1 ± 0.8	17.0 ± 2.4	1.27	1.000	[31]
PVPh + PVPy			17	169.4 ± 6.2	69.6 ± 16.1	77.6	9.96	0.973	[27]
P4VP + PVPh	60,000	21,600	27	95.7 ± 4.3	37.1 ± 11.5	0	3.54	0.987	[45]
PVPhKH + PS-*co*-4VPy	35,200	59,500	30	31.4 ± 4.1	−23.7 ± 8.2	−61.4 ± 18.9	1.05	0.982	[36]
PHEMA + P2VP	20,000[a]	20,000	32	68.2	46.7	−20.1	2.13	1.000	[33]
PS4VP15 + PSMA15	6600	65,500	34	77.5	0.18	−63.3	2.28	1.000	[30]
MK-0591 + PVP K-12	609.10	2,500	29	36.7 ± 1.6	−8.5 ± 3.2	−46.2 ± 8.0	1.26	0.998	[60]
MK-0591 + PVP K-17	609.10	10,000	4	40.3 ± 1.5	−13.1 ± 3.7	−28.4 ± 8.2	9.15	0.991	[60]
MK-0591 + PVP K-30	609.10	50,000	43	12.7 ± 1.5	13.0 ± 3.8	−57.7 ± 8.4	0.29	0.999	[60]
MK-0591 + PVP K-90	609.10	1,000,000	48	23.1 ± 3.4	0	0	0.48	0.989	[60]
MK-0591 + PVP/VA 60:40	609.10	58,000	20	19 ± 2	0	−15.3 ± 8.5	0.87	0.993	[60]
PIMB4VP-20 + PSMA-12			39	13.8 ± 1.7	0	0	0.35	0.997	[47]
PIMB4VP-20 + PSMA-29			76	39.6 ± 8.5	−25 ± 18	−58 ± 43	0.52	0.993	[47]
P2VP + PVPh	41,000	21,600	83	65 ± 2	0	−49 ± 10	0.78	0.999	[45]
PDNBM (2) + PHECM[b]	30,000[a]		49	62 ± 3	−18 ± 7	−23.3 ± 16.5	1.27	0.977	[22,49]
PDNBM (4) + PHECM[b]	23,000[a]		90	89 ± 3	−42 ± 6	−112 ± 16	0.99	0.990	[22,49]
PDNBM (6) + PHECM[b]	51,000[a]		120	131 ± 4	0	−71 ± 1	1.09	0.977	[22,49]

[a] M_n value.
[b] The number shown in the parenthesis corresponds to spacer's length.

or negative (for $a_0 < 0$) departures of mixtures' T_gs from the linear mixing rule. The main contribution to the intensity of the deviation and, accordingly, to the magnitude of the "interaction term" a_0, has enthalpic origin, supplemented by entropic factors. Fig. 1 explores the relationships between a_0 and the parameters of the Gordon–Taylor (Fig. 1a) and Jenckel–Heusch (Fig. 1b) functions, both considered semi-quantitative measures of the strength of the intercomponent interactions. This figure combines results from the presently studied binary organic mixtures (Table 2) with previously obtained data [26] for binary polymer blends. All this information is now organized in three categories: a group of systems with low complexity (black-filled circles; only $a_0 \neq 0$), moderately complex systems (gray-filled circles; a_0 and $a_1 \neq 0$, $a_2 = 0$), and highly complex systems (open circles; $a_0, a_1, a_2 \neq 0$). In both cases, second-order polynomial functions (parabolas),

$$a_0 = (-289 \pm 19) + (430 \pm 40)k_{GT} + (-133 \pm 17)k_{GT}^2 \quad (R^2 = 0.849) \tag{11a}$$

and

$$a_0 = (100 \pm 6)b + (-63 \pm 6)b^2 \quad (R^2 = 0.868) \tag{11b}$$

respectively, effectively describe the data. The ascending trend of a_0 with increasing b (or k_{GT}) signifies the strong contribution of system-dependent energetic (enthalpic) components. Conformational and chain-packing (entropic) factors are in part responsible

Table 2b
Mixture information and curve-fitting results for the parameters incorporated in Eq. (10) for selected binary blends exhibiting negative deviations from the linear mixing rule.

Binary blend (1 + 2)	$\bar{M}_{w,1}$ (g/mol)	$\bar{M}_{w,2}$ (g/mol)	$T_{g,2}-T_{g,1}$ (K)	Fitting parameters				R^2	Ref.
				a_0	a_1	a_2	$a_0/\Delta T_g$		
SAD17 + SAA27	127,000	146,000	20	−4.9 ± 1.2	2.6 ± 2.0	−6.2 ± 5.9	−0.25	0.998	[31]
SAD17 + SAA32	127,000	42,700	26	−64.9 ± 1.0	36.0 ± 1.5	−4.5 ± 4.5	−2.49	1.000	[31]
PCB + PVE		27,600	33	−55.2 ± 1.6	7.6 ± 3.5	0	−1.67	0.996	[39]
PIMB4VP-10 + PSMA-12			49	−64.8	74	−12.6	−1.32	1.000	[47]
PS_{low} + P(S-*co*-MA) (4.7 wt.% MA)	1320	207,000	74	−152 ± 4	0	−43 ± 19	−2.05	0.997	[43]
Indomethacin + PVP K-12	357.81		57	−2.3 ± 3.2	29.8 ± 5.4	−30.9 ± 12.5	−0.04	0.998	[62]
Indomethacin + PVP/VA 60:40	357.81		60	−6.4 ± 3.0	0	0	−0.11	0.996	[62]
Indomethacin + PVP K-17	357.81		94	−43.7 ± 5.4	56.8 ± 9.1	−31.4 ± 20.9	−0.47	0.998	[62]
Indomethacin + PVP K-30	357.81		114	−59.1 ± 2.4	46.2 ± 5.5	0	−0.52	0.999	[62]
Indomethacin + PVP K-90	357.81		130	−98.3 ± 3.7	31.9 ± 6.1	−54.4 ± 14.1	−0.76	1.000	[62]
PVME + PS	1000	800	50	−11.1 ± 3.6	27 ± 7	−69 ± 7	−0.22	0.917	[22,50]
	10,500	9500	111	−43 ± 1	−32 ± 2	20 ± 3	−0.39	0.998	[22,50]
	10,500	73,500	135	−69 ± 2	−21 ± 5	0	−0.51	0.988	[22,50]
	73,000	73,500	131	−86 ± 7	−34 ± 1	−28 ± 25	−0.66	0.969	[22,50]
PVAc + PVPh	142,000	21,600	152	−89 ± 4	−32 ± 8	39 ± 19	−0.59	1.000	[45]
PS + PPO	582,000	483,000	107	−30 ± 4	0	0	−0.28	0.997	[52]
	22,400	483,000	113	−50 ± 1	9 ± 3	0	−0.44	0.994	[52]
	5100	483,000	128	−62.5 ± 3.5	0	0	−0.49	0.998	[52]
	859	483,000	205	−152 ± 4	43.3 ± 11.5	0	−0.74	0.999	[52]
PVME + PVPh	164,000	21,600	199	−148 ± 14	0	0	−0.74	0.994	[45]
PCL + PVC (57 wt.% Cl)	40,500	56,800	143	−113	8.45	0	−0.79	1.000	[59]
PCL + PVC (63 wt.% Cl)	40,500	102,000	170	−141	−32.5 ± 1.7	0	−0.70	1.000	[59]
PCL + PVC (67 wt.% Cl)	40,500	106,000	181	−166 ± 3	−68 ± 9	0	−0.92	0.999	[59]

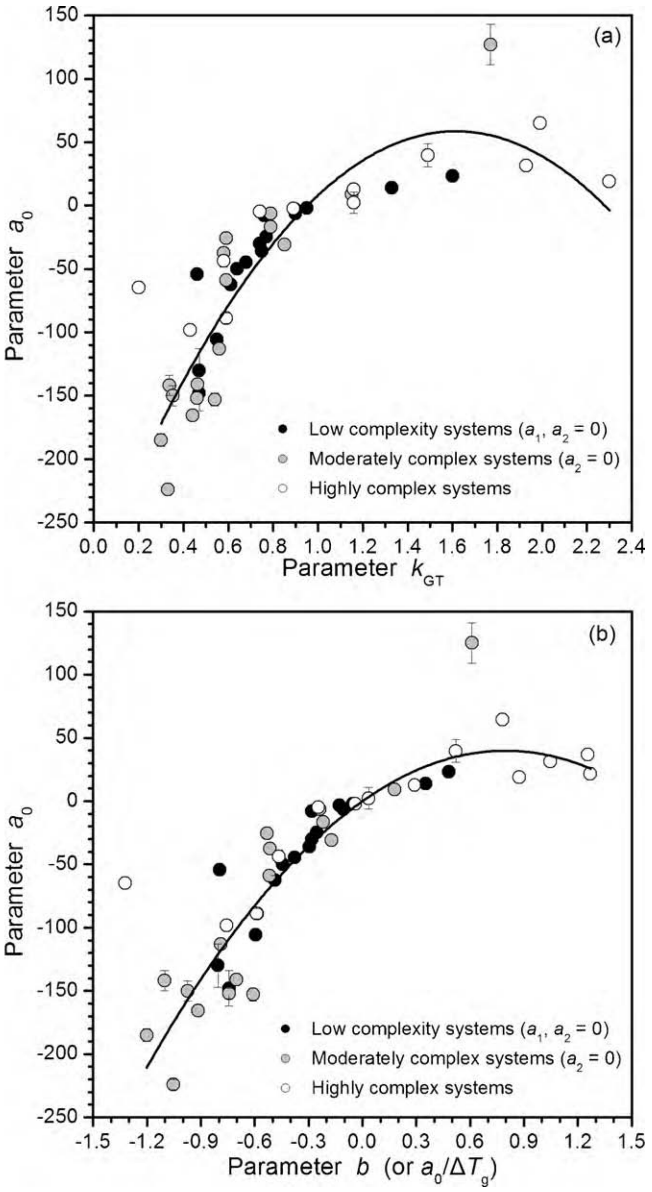

Fig. 1. Parabolic fitting of the dependence between a_0 and the parameters of (a) the Gordon–Taylor, k_{GT}, and (b) the Jenckel–Heusch equation, b ($b \equiv a_0/\Delta T_g$ when $a_1 = a_2 = 0$), for binary miscible organic blends of various complexities. The errors in the data are comparable to the size of the symbols unless otherwise indicated.

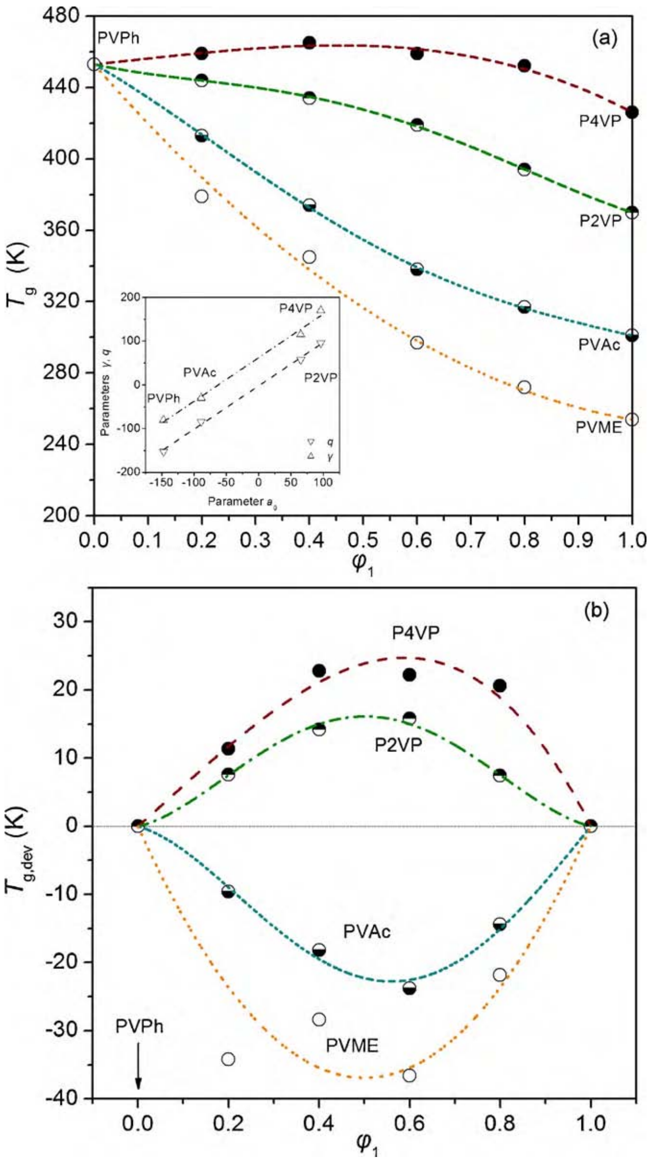

Fig. 2. Compositional variation of the glass transition temperatures (a), and the deviation from the rule of mixtures (b), recorded for mixtures of PVPh with P4VP, P2VP, PVAc and PVME.

Table 3
Comparison of parameters representative of the strength of specific interactions between the components in selected blends of PVPh.

Binary blend	Interaction-related parameters				
	$\Delta\nu_H$ (cm^{-1})[a]	χ_{12}	γ	a_0	q[b]
P4VP + PVPh	410	18.2	170	96	95.7
P2VP + PVPh	395	2.9	115	65	57.7
PVAc + PVPh	72	−2.67	−30	−89	−83.7
PVME + PVPh	210	−0.45	−80	−148	−152.2

[a] One should compare these estimates with the value of $\Delta\nu_S$ = 150 cm^{-1}, obtained when self-association between PVPh units is involved.

[b] Estimates obtained by fixing k_{kw} = 1.

for the curvature observed. With increasing system complexity the data demonstrate a progressively increasing scattering around the fitting curves. This is particularly strong in the complex systems with outermost a_0 estimates, cases where single-parameter equations provide poor fits to the experimental data and significant error in their estimates exists. In view of that, several of the extreme responses treated in Sections 4.1 and 4.2 were excluded from the above analysis.

Additional paradigms of phenomenological relationships between a_0 and other model parameters can be extracted from recent comparative Fourier-Transform infrared spectroscopy (FTIR) and DSC studies on binary polymer blends of poly(vinyl phenol) (PVPh) [45]. Fig. 2 compares the compositional dependence of the glass transition temperatures (Fig. 2a) and of their deviation from linearity (Fig. 2b) for mixtures of PVPh with poly(4-vinyl pyridine) (P4VP), poly(2-vinyl pyridine) (P2VP), poly(vinyl acetate) (PVAc) and poly(vinyl methyl ether) (PVME). For these systems, Yang and Han [45] have supplied estimates of parameters representative of the strength of attractive interactions between the components (Table 3): i.e., the difference in wavenumber, $\Delta\nu_H$, between the FTIR absorption bands of hydrogen-bonded and free hydroxyl groups, which illustrates the relative strength of hydrogen-bonding; the Flory–Huggins [46] interaction parameter χ_{12}, obtained by the Lu–Weiss theory [18]; and the interaction parameter γ of Kim group's theory [24] proposed for miscible blends. The estimates obtained of the prime parameter of Eq. (10), a_0, and of the Kwei parameter q, are also included in this table for comparison purposes. Linear dependencies emerge between the interaction terms a_0 and γ

$$a_0 = (0.99 \pm 0.06)\gamma - (62 \pm 7) \quad (R^2 = 0.992) \qquad (12a)$$

and among a_0 and q (with $k_{Kw} = 1$, insert of Fig. 2a)

$$a_0 = (0.99 \pm 0.03)q - (2.0 \pm 3.5) \quad (R^2 = 0.998) \qquad (12b)$$

The trends evidenced in Table 3 and the dependences described by Eqs. (12a) and (12b) suggest an increasing excess stabilization energy and show clearly that the extent of the intermolecular interaction steadily increases when the acidic vinyl phenol ($-C_6H_4OH$) group of PVPh independently associates with –O– (ether group), $-OCOCH_3$ (acetate), or the stronger $-C_5H_4N$ (pyridine) proton accepting units. These trends substantiate further the notion of parameter a_0 being strongly determined by the strength of intermolecular interactions.

Apart from changes in the nature of the interacting units, varying the density of specific interacting units within a pair of polymers drastically affects the "affinity" of their chains and several thermal properties of their blends, such as, thermal stability (decomposition temperature) and segmental mobilities (magnitude of T_g and shape of the $T_g(\varphi)$ plot). The compositional variation of the glass transition temperatures recorded for miscible copolymer blends of poly(styrene-*co*-methacrylic acid) (PSMA) with poly(isobutyl methacrylate-*co*-4-vinylpyridine) (PIBM4VP) offers an illustrative example (Fig. 3a) [47]. By increasing the content of the proton-acceptor monomer (4-vinylpyridine) in PIBM4VP from 10 to 20 mol% or the proton-donor monomer (methacrylic acid) in PSMA from 12 to 29 mol%, miscibility is induced [48] and extensive hydrogen-bonding interactions develop [47,48]. Following this change, the estimates of both, the prime parameter of Eq. (10), a_0, and Kwei's parameter q, progressively increase. Notice the close proximity of the estimates for parameters a_0 and q; in fact $a_0 \equiv q$, when both $a_{1,2} = 0$ and $k_{Kw} = 1$. Eq. (10) describes better the curvature exhibited in the $T_g(\varphi)$ dependence of the PIBM4VP-10 + PSMA-12 copolymer blend; the value of $k_{Kw} = 0.09$ that could improve Kwei's fitting seems irrational. The development of strong steric hindrances may limit or even reverse the abovementioned trend. For an illustrative paradigm – and another example of advantageous application of Eq. (10) – the reader is directed to the recent studies of Hamou et al. [31] on poly(styrene-*co*-N,N-dimethylacrylamide) (containing 17 mol% of N,N-dimethylacrylamide; SAD17) + poly(styrene-*co*-acrylic acid) (SAA) copolymer blends (Fig. 3b). In this series of systems, by increasing the acrylic acid content from 18 to 27 and finally to 32 mol%, $T_{g,dev}$ and a_0 gradually shift from positive to negative values. This is in agreement with the growth of steric crowding and accessibility limitations that progressively shift the balance between inter- and intramolecular interactions to the side of the latter ones.

The dependence of the $T_g(\varphi)$ function on the architecture and conformations of components chains or their molecular masses is another interesting issue. An example provide the strongly interacting mixtures of poly(ω-hydroxyethyl-3,5-dinitrobenzoyl methacrylate) (PDNBM) with poly[N-(2-hydroxyethyl)carbazolyl methacrylate] (PHECM), for which the shape of the $T_{g,dev}$ or T_g vs. composition plots depends on the spacer length between the electron-acceptor group and methacrylic backbone of PDNBM (Fig. 4). By increasing spacer's length (i.e., by increasing the number of methylenic units in the spacer of PDNBM from 2 to 4 and finally to 6 [22,49]), the probability of neighboring hetero-contact formation by charge transfer complexation of the polyacceptor PDNBM with the polydonor PHECM is strengthened; accordingly, the level of deviation – and its measure, a_0 – increases.

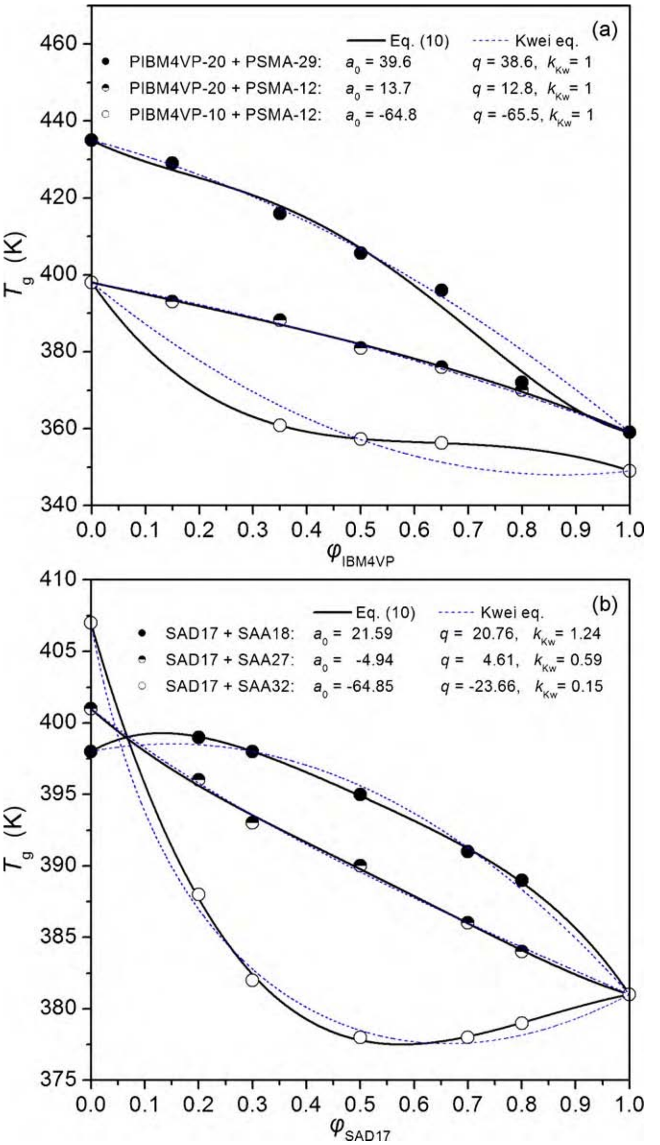

Fig. 3. Compositional variation of the glass transition temperatures recorded for miscible (a) PIBM4VP + PSMA [47] and (b) SAD17 + SAA [31] copolymer blends (see text for information on neat components' chemical composition).

The molecular mass of the polymeric components has also been reported to proffer a decisive contribution in the creation of contacts between unlike neighboring chains, especially in cases of weakly interacting polymers. For such blends, local ordering due to hetero-contact formation is minimal and conformational mobility in enhanced. A sound example provides the behavior of the weakly interacting mixtures of polystyrene (PS) with PVME (Fig. 4 [22,50,51]). According to Schneider [22], the higher the molecular mass of the components is, the more probable the coiling of the polymer chains and the more highly screened the interacting groups become. Hence, mixtures' T_g lowers and, following the increasing departure from linearity with increasing molecular masses for the blend components, parameter a_0 attains more negative values. The above "trend" is not without exceptions. The relationship between the extend of hetero-contact formation and components' molecular mass is not explicit; differences in the tacticity and branching of the chains, differences in the chemical nature and their location in the chain of the species liable to interaction, or even special procedures followed during blends' preparation that can affect chain conformations and crystallinity,

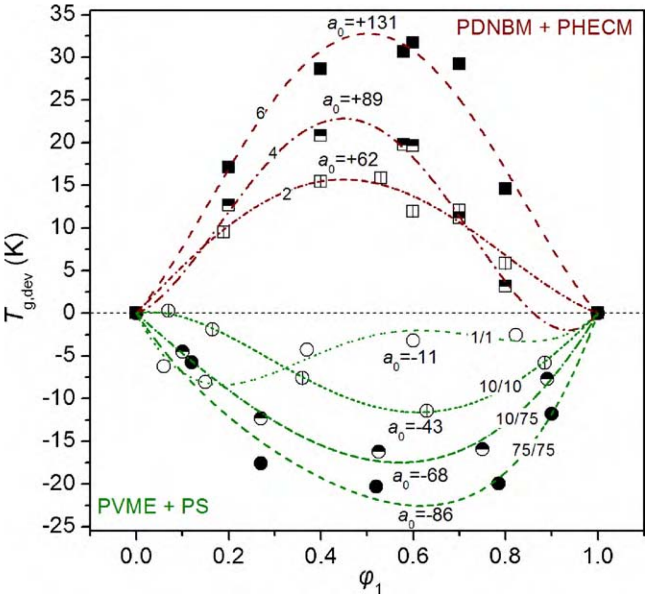

Fig. 4. Variation of the $T_{g,dev}$ vs. φ_1 graphs of PDNBM+ PHECM blends with changes in the spacer length between the acceptor group and methacrylic backbone of PDNBM, and of PVME + PS blends with changes in the molecular mass of the blend components (1/1, 10/10, 10/75 and 75/75 denote the molecular masses – in thousands – of PVME and PS). Adapted data from Refs. [22,49–51]. For each system, estimates of the a_0 parameter are included.

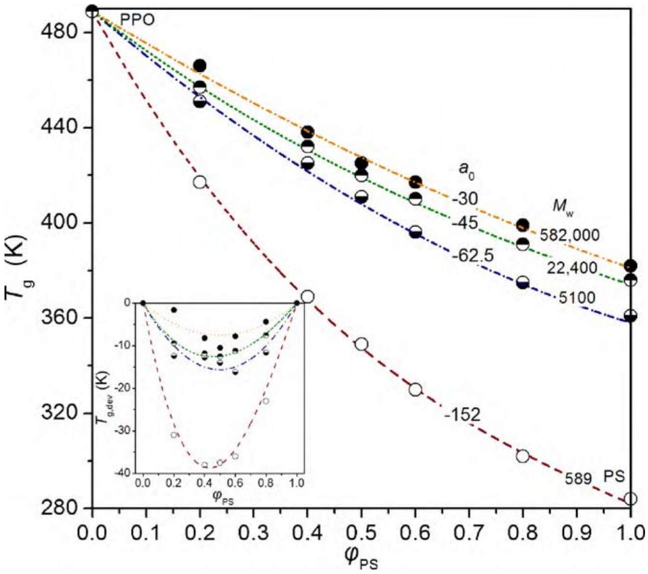

Fig. 5. Compositional variation of the glass transition temperatures and the deviation from additivity (insert) recorded for mixtures of poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) with polystyrene (PS) of different molecular masses: M_w = 859, 5100, 22,400 and 582,000 g/mol. Adapted data from Ref. [52]. For each system, estimates of the prime a_0 parameter are presented.

are likely to produce different dependencies. As an example, the compositional variation reported for the T_gs of the miscible binary blends formed by the weakly interacting PS and poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) ($\chi_{12} = -0.06$; [52]) shows a decreasing departure from linearity with increasing molecular mass of PS (Fig. 5) [52,53]. Note that the dissimilarity in the behaviors exhibited by PVME + PS and PS + PPO is reflected to the trends of a_0, k_{GT} and of their normalized (dimensionless) $a_0/\Delta T_g$ estimates (see Table 2b).

The other parameters (a_1, a_2) being null, the departure from the linear mixing rule is maximal for the intermediate blend composition ($\varphi_1 = \varphi_2 = 0.5$). For strongly inter-associating polymers ($a_0 > 0$), when this maximum is observed for a mixture with the high-T_g component in excess (i.e., for $\varphi_1 < 0.5$), parameter a_1 demonstrates negative values and *vice versa*. This situation is observed in the PDNBM + PHECM blends with 2 or 4 methylenic units in the spacer, and signifies an enhancement of the deviation from the predictions of the linear mixing rule for mixtures with PDNBM as minority component. On the molecular level, this behavior can be interpreted considering higher density and/or strength for the hetero-contacts formed at low loadings of the flexible PDNBM chains. Anomalous curvatures – i.e., strongly asymmetric or sigmoid shapes – especially at regions near the pure component compositions ($\varphi_1 \geq 0.8$ or $\varphi_1 \leq 0.2$), bring about strong values for parameter a_2 (e.g., PDNBM+ PHECM blends with 4 methylenic units in the spacer, or the 1/1 PVME + PS mixtures included in Fig. 4). The above variations point to a complex binary mixture, in the sense that at least one important blend property (e.g., the degree of polymers' mixing, the relative balancing between hetero- and homo-contacts, the counterbalancing between enthalpic and entropic contributions, or the crystallization rate) has a distinctive compositional dependence.

4. Handling of extreme $T_g(\varphi)$ dependences

4.1. Strongly associating polymer mixtures

An intriguing result in thermal characterization studies of miscible binary polymer blends, involves the observation of glass transition temperatures for some blend compositions exceeding the highest neat component value ($T_{g,2}$) [27,30–36,45,54–57]. In an attempt to explain such anomalous behaviors several scenarios have been invoked. Typically, one considers either blending-induced changes in the intermolecular constraints (e.g., strongly favored hetero-contacts due to relatively strong intercomponent interactions between specific functional groups [27]), changes in volume due to blending (i.e., a negative excess mixing volume [34]), significant contributions from the strongly negative entropy of mixing [28], and non-random mixing. In view of that, the assumptions used to develop most of the conventional $T_g(\varphi)$ equations (Eqs. (1)–(9), Table 1) render their application problematic (see below), supporting the need for alternative approaches.

In general, strong positive deviations from the rule of mixtures stem from well-described interconnection-favorable exothermic enthalpic factors, verified by molecular spectroscopy studies [27,30–33,45,55]. The presence of specific interactions – i.e., charge transfer (electrostatic interactions), hydrogen-bonding, dipolar and van del Waals forces, in order of decreasing strength – is commonly considered a prerequisite for achieving miscibility and at the same time for the production of blends with adaptable rheological properties and increased thermal stability (i.e., of higher glass transition and decomposition temperatures). For example, FTIR studies of mixtures of poly(styrene-*co*-maleic anhydride) [P(S-*co*-MA)] copolymer containing 28 mol% of maleic anhydride with poly(vinyl pyrrolidone) (PVP) [32] (Table 2a and Fig. 6a) suggest that the intermolecular *hydrogen-bonding* interactions between the proton-acceptor pyrrolidyl units and carboxylic acid (donor/acceptor) are stronger than the dimeric self-associated acid ones. The positive deviation from linearity recorded in these blends is intensified also by *ionic interactions*, namely protons transfer from the carboxylic groups of P(S-*co*-MA) to the nitrogen atoms of PVP.

The strong proton-acceptor character of the pyridine groups, introduced in several polymers to promote miscibility, produces strong hydrogen-bonding effects in their blends with polymers incorporating suitable proton-donor sites. Representative examples provide the strongly associating blends of polyvinylpyridine (PVPy) with PVPh [27], of poly(styrene-*co*-4-vinylpyridine) containing 15 mol% of 4-vinylpyridine (PS4VP-15)

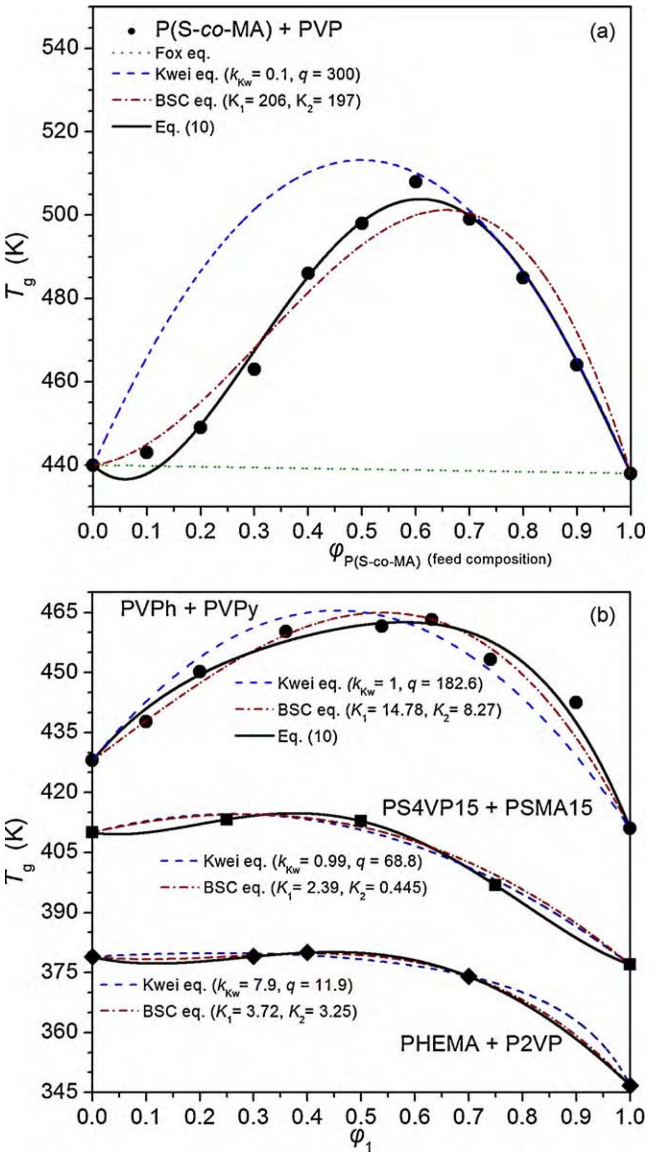

Fig. 6. Compositional variation of the glass transition temperature T_g (DSC data) for selected miscible blends of strongly inter-associating polymers: P(S-*co*-MA) (28 mol% MA) + PVP complexes [32], PVPh + PVPy [27], PS4VP15 + PSMA15 [30] and PHEMA + P2VP blends [33].

with poly(styrene-*co*-methacrylic acid) containing 15 mol% of methacrylic acid (PSMA-15) [30], and of P2VP with poly(2-hydroxyethyl methacrylate) (PHEMA) [33] (Table 2a and Fig. 6b). In these blends, strong polymer inter-association occurs through the interaction of the basic pyridine groups with phenolic hydroxyls [27], carboxylic acid [30] or lateral hydroxyls [33], producing remarkably intense deviations from the rule of mixtures. In the latter system, e.g., one anticipates self-association through carbonyl–hydroxyl hydrogen-bonding interactions (>CO. . .HO–), while in the blend environment infrared data verify that the pyridine nitrogen in P2VP strongly interact with PHEMA's hydroxyls. One should observe the decreasing trend of parameter a_1 for the three systems of Fig. 6b, which changes from $a_1 = 69.1$ in PVPh + PVPy, to $a_1 = 46.7$ in PS4V15 + PSMA15, and finally to nearly zero ($a_1 = 0.18$) for PHEMA + P2VP (Table 2a). The highest value is obtained for the first system (i.e., maximum blend T_g attained at $\varphi_1 > 0.5$) advocating for maximal density – and probably strength – of the interpolymer interactions at blends with very high PVPh loadings.

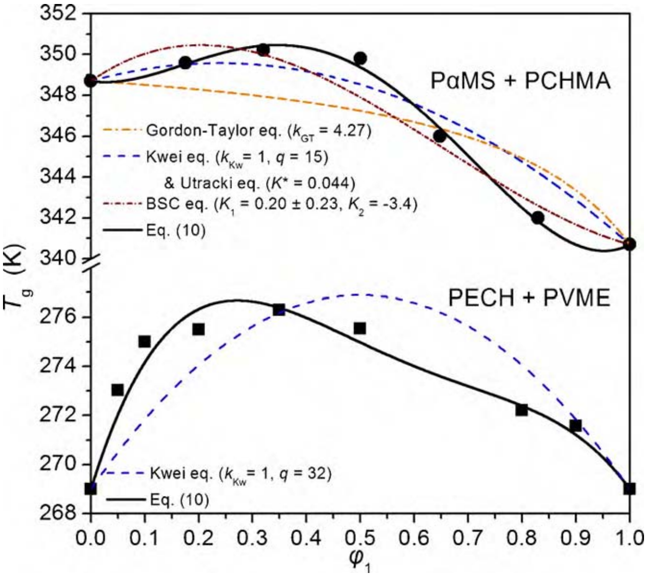

Fig. 7. $T_g(\varphi)$ plots of miscible blends of polymers with low-T_g contrast: PECH + PVME (DRS data, $\Delta T_g \approx 0$ K) [35], PαMS + PCHMA (DSC data, $\Delta T_g = 8$ K) [34]. The glass transition temperatures shown for the first system correspond to the temperature at which the frequency at the maximum of the dielectric loss (ε'') peak is 1 kHz.

The totally amorphous binary systems included in Fig. 6b exhibit non-zero a_2 parameter values, which indicate the presence of additional sources of non-random mixing, such as, composition-dependent excess mixing volume effects. To validate this attribution, the behavior of blends of poly(epichlorohydrine) (PECH) with poly(vinyl methyl ether) (PVME) [35] and of poly(α-methyl styrene) (PαMS) with poly(cyclohexyl methacrylate) (PCHMA) [34] is illustrated in Fig. 7. The observed patterns can be explained only by bearing in mind the combined effect of hetero-contact formation on interchain orientation and the corresponding conformational entropy changes. A negative excess volume, which signifies less space for molecular and macromolecular chain relaxation, is highly probable in the case of the PECH + PVME mixture. Here, according to the IR and ^{13}C nuclear magnetic resonance (^{13}C NMR) data of Alegría et al. [35], the hetero-contacts between PECH (with –Cl as electron-acceptor moieties) and PVME (with $-OCH_3$ as electron-donating moieties) are only slightly favored. Specific volume determinations corroborate an analogous interpretation in the case of the PαMS + PCHMA mixtures; in the intermediate composition ($\varphi_1 = 0.5$), the specific volume calculated for the blend assuming volume-additivity is $V_g = 0.966$ mL/g, while the experiment value is only 0.958 mL/g. Note that the $T_g(\varphi)$ pattern of PECH + PVME is a distinctive case owing to the complete matching of pure components' glass transition temperatures, which renders inappropriate the application of the conventional equations for its description.

Summing up, for the systems considered in this section, Eq. (10) provides better fit to the experimental data, and in a wider compositional range, in comparison to the typically used single-parameter Gordon–Taylor equation and the two-parameter Kwei or Brekner–Schneider–Cantow equation. Eq. (10) serves remarkably well in the special case of the P(S-*co*-MA) (28 mol% MA) + PVP mixtures [32], which are in fact interpolymer complexes; their T_g values are higher than those of miscible blends of the same system with similar compositions. The strongly positive values of the prime parameters of the most successful fitting functions, a_0 (Eq. (10)), q (Eq. (6)) and K_1 (Eq. (7)), are indicative of the anomalous deviation from the ideal rule of mixtures; the positive deviation is further highlighted in the normalized $a_0/\Delta T_g$ estimates based on Eq. (10). No matter the source, the anomalous dependences presented in Figs. 6 and 7, reflect to significant non-zero values of a least one of the higher-order fitting parameters a_1 and a_2, consonant with the higher *complexity* of these systems [23].

4.2. *Weakly associating binary organic mixtures*

A number of dielectric relaxation, dynamic mechanical relaxation and proton correlation spectroscopy studies of the component dynamics in several small-molecule glass former + polymer mixtures or binary polymer blends {e.g., polychlorinated biphenyl (Aroclor 1248, PCB) + poly(vinylethylene) (PVE) [39,40,42], 1,1-bis(*p*-methoxyphenyl)cyclohexane (BMC) + poly(methylphenylsiloxane) (PMPS) [37], polychloroprene (PC) + epoxidized polyisoprene (EPI) [41], polystyrene (PS) + PαMS [57], polychlorinated biphenyl (Aroclor 1254) + oligostyrene (PS_{low}) [38], and PS_{low} + P(S-*co*-MA) with 4.7 wt.% maleic anhydride [43]}, have offered solid experimental evidence of another interesting anomaly, namely, an acceleration of the small-molecule [37–40,42] or low-T_g polymer [31,41,43,58] relaxation dynamics in the presence of a stiffer polymeric component. As a result, several blend compositions exhibit single glass transition-related calorimetric signals at highly reduced temperatures [i.e., at T ($\equiv T_g$) $\leq T_{g,1}$]. The analytical description of their $T_g(\varphi)$ patterns in terms of Eq. (10), is possible only by using strongly negative a_0 (or normalized $a_0/\Delta T_g$) values.

Considering the effect of interactions only, one may explain negative deviations from simple additivity mixing rules as result of the weakening of the interactions between chain segments of the stiffer component due to the effect of the relatively more flexible chains of the low-T_g component. A decrease in the absolute number and/or strength of hetero-contact formations is also likely to induce weaker interchain orientation. Accordingly, the larger the mobility in the neighborhood of the interchain bonds, the more probable the occurrence of conformational entropy changes. A marked decrease in mass density (i.e., increase in unoccupied volume, *positive* excess mixing volume) is considered to mitigate intermolecular constraints on the segmental dynamics and increase the relaxation rate in the blend environment. A decrease in intermolecular cooperativity in the blends relative to the neat components has been invoked by Roland et al. [41] to explain the anomalous behavior observed in PC + EPI blends.

As an example of the abovementioned behavior Fig. 8 shows the dependencies recorded for two solvent + polymer systems, which show a drastic enhancement in segmental mobility in solvent-rich mixtures. For the PS_{low} + P(S-*co*-MA) (with 4.7 wt.% maleic anhydride) system, in which the solvent is *sec*-butyl-terminated oligostyrene, the enhancement is intense and comprises a wider compositional window (for $\varphi_{PS} \geq 0.60$; Fig. 8a) compared to that observed in PCB + PVE (for $\varphi_{PCB} \geq 0.75$; Fig. 8b). The low-T_g component in the latter system is a special mixture of individual chlorinated biphenyl compounds with different degree of chlorination; the commercial mixture considered here (Aroclor 1248) contains 48 wt.% Cl. The smooth curvature of the $T_g(\varphi)$ dependence in these systems can be explained using two-parameter fitting functions (e.g., those of Kwei or Brekner–Schneider–Cantow), with somewhat better description obtained when Eq. (10) is applied (Table 2b). The strongly negative estimates for the prime parameters of the two most successful fitting functions (i.e., $a_0 = -152$, $q = -120$ and $a_0 = -55$, $q = -34$, respectively) point to the presence of weak intersegmental interactions and/or free-volume enhancement in the blends' environment. According to Abetz et al. [43], the *sec*-butyl end groups of oligostyrene do not only participate to the decrease of the glass transition by the additional free space induced by the end group, but also by their incompatibility with the repeating units of the PS chain. In that way, the oligomers become very efficient plasticizers, in a relatively broad composition range ($\varphi_{PS} \geq 0.60$).

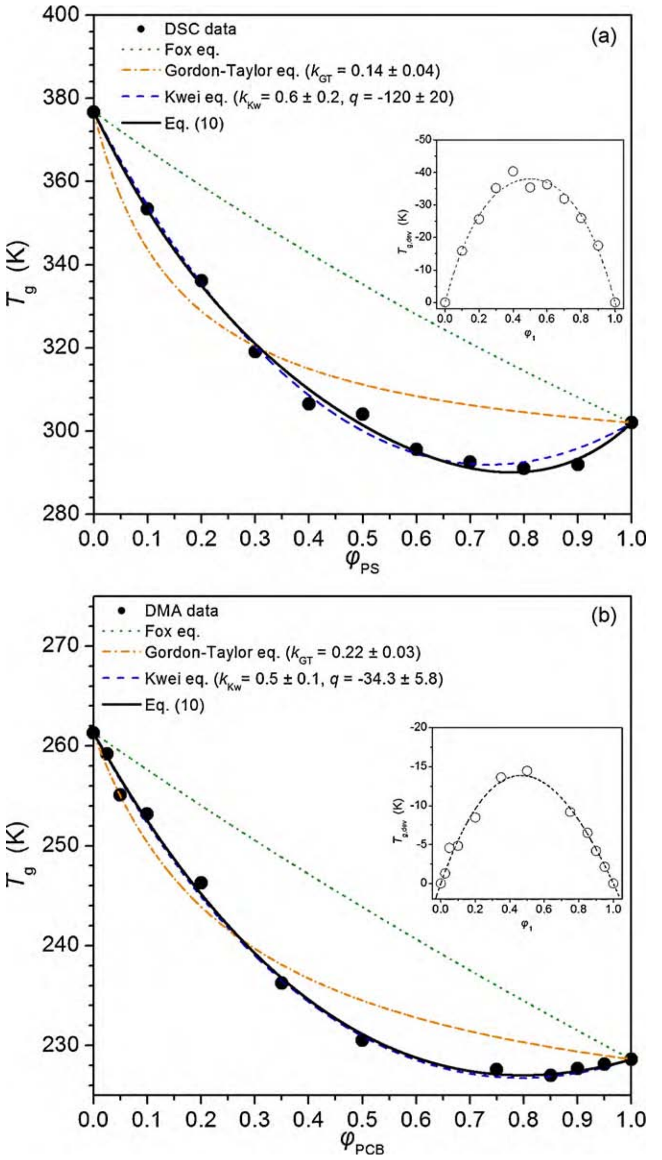

Fig. 8. $T_g(\varphi)$ plots of amorphous binary mixtures of a low-molecular mass organic (solvent) with a polymer: (a) PS_{low} + P(S-*co*-MA4.7) [43], (b) PCB + PVE [39]. The glass transition temperatures shown in (b) are defined as the temperatures at which the mechanical relaxation time equals 100 s. The deviation from linearity plots ($T_{g,dev}$ vs. φ_1) are shown in the inserts.

4.3. *Polymer-based drug delivery systems*

Studies of the compositional dependence of the glass transition temperature of *drug + polymer* systems are particularly important for their potential application in controlled drug delivery, since by adjusting the composition and the polymer–drug interactions the release profile (molecular mobility) of a drug formulation can be regulated [39,44,60–64]. In view of that, the relative influence of microstructural and thermophysical characteristics (e.g., local density variations, strength of intercomponent interactions, and polymer's functional groups and molecular mass) in determining components miscibility is currently a matter of intense discussion [65]. Even in *simply behaving* binary pharmaceutical systems, the application of the Fox, Gordon–Taylor and Couchman–Karasz equations offers *theoretical* predictions of the $T_g(\varphi)$ dependence

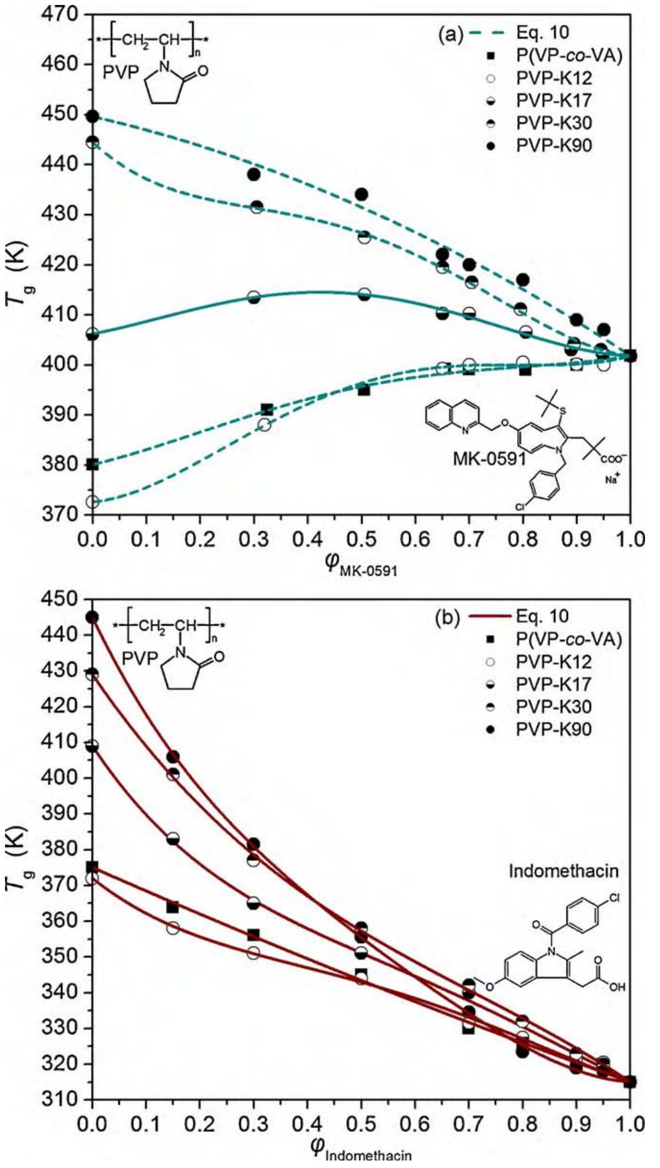

Fig. 9. Compositional variation of the T_g of solid dispersions of (a) MK-0591 [60] and (b) Indomethacin [62] drugs with different pharmaceutical grades of PVP or P(VP-*co*-VA). Lines are fits to equation 10. Blends' information is given in Table 2.

that either underestimate [60] or overestimate [62–64] the experimental pattern. Complete failure of these functions has been observed is several systems [44]. The compositional variation of the glass transition temperatures recorded in miscible solid dispersions of MK-0591 (Fig. 9a) and Indomethacin (Fig. 9b) drugs in different grades of PVP and in poly(vinyl pyrrolidone-*co*-vinyl acetate) (PVP/VA 60:40) provide representative examples of successful application of Eq. (10) in drug + polymer mixtures, and stress further the interplay among entropic and enthalpic factors in determining blends' behavior.

The model hydrophobic drug MK-0591 forms solid solutions with glass transition temperatures above the ideal rule of mixtures [60]. Maximal deviation is observed for the MK-0591 + PVP K-30 system, for which components asymmetry is negligible ($\Delta T_g \cong 5$ K). For the particular drug molecule no apparent tendencies can be isolated regarding the dependence of the extent of intercomponent interactions from variations in the molecular mass of the polymer host. It has been pointed out that a_0 mainly reflects the differences between the interaction energies of the binary hetero- (intercomponent) and homo- (intracomponent) interactions; thus, an increase in a_0 signifies the increasing energetic contribution of hetero-contacts. In view of that, it appears that implementation of a lower molecular mass polymer promotes drug–polymer interactions (higher a_0 and $a_0/\Delta T_g$ estimates, Table 2a). The latter conclusion can also be securely inferred from the analysis of the miscible Indomethacin + PVP mixtures [62]. These blends show a steady increase of the negative deviation from the ideal linear mixing rule ($a_0 < 0$) with increasing length of the macromolecular chain (Table 2b). Each of the above systems demonstrates different *critical* drug loadings above which drug molecules begin to organize in crystalline phases; crystallization inhibition becomes more efficient as polymer's M_w increases. The resulting complexity is consonant with the observation of non-zero estimates for the higher-order fitting parameters (a_1 and a_2).

The different behavior of the solid dispersions of MK-0591 ($a_0 > 0$) and Indomethacin ($a_0 < 0$) in various molecular mass grades of PVP can be explained considering differences in the chemical structure and molecular volume of the drug molecules and the synergetic effects of free-volume modifications and variations in the degree of steric hindrances. Based on FT-IR data, the hydrogen-bonding interaction in the Indomethacin containing systems is stronger than that of the ion–dipole interaction observed in MK-0591 + PVP mixtures, and thus one would expect higher values for the *interaction* parameter (a_0) in blends containing Indomethacin; this is clearly not the case. Apparently, the behavior of each system is also affected by differences in drug molecule's size and the degree of shielding or the type of the interacting specific groups. Moreover, dissimilar degrees of conformational changes in the macromolecular chains and filling of the intra-chain spaces may contribute to the observed variations. The negative deviation may be related in part to a stronger interaction between like components, such as the dimerization of Indomethacin, compared with the interactions between the unlike components.

5. Concluding remarks

The present study provides evidence of the advantageous applicability of a recent equation proposed for the explanation of several, complex (asymmetric or sigmoid), compositional dependences of the glass transition temperatures of miscible blends. Experimental results for a wide range of organic systems can be described with better accuracy, compared to other common functional forms, some of which require parameters that are not always readily available to the researcher [e.g., the quantities of $\Delta C_{p,i}$ and δC_p in Eqs. (3) and (8)], contain a seemingly superfluous number of fitting parameters [e.g., the four-parameter Eq. (9)], or their application leads to unrealistic results (e.g., k_{GT} or k_{Kw} fitting estimates much different from the expected value of $\rho_1 T_{g,1}/\rho_2 T_{g,2} \approx T_{g,1}/T_{g,2}$). In addition to the usual polymer + polymer blends, the behavior of mixtures of polymers with low molecular mass organics (solvent, plasticizer or drug molecules) can be described with success. The new equation allows for an accurate description of deviations from the linear mixing rules even in blends with neat components of comparable segmental mobilities ($\Delta T_g = T_{g,2} - T_{g,1} \approx 0$, e.g., see Figs. 6a and 7), where earlier approaches fall short. In effect, the usability and reliability of the latter equation is critically determined by the accuracy and the density of the experimental data; this condition becomes particularly important in systems of high complexity.

Parameters a_i are not yet accessible by other means but only by fitting of Eq. (10) to experimental T_g vs. concentration data. Thus, it is not possible to separate the compositional dependent enthalpic from the conformational induced entropic contributions to the glass transition deviations from the linear mixing rule. Nonetheless, their sign and absolute magnitude provide indirect information about important physicochemical and structural properties of binary blends. For instance, parameter a_0 offers a semi-quantitative measure for the strength of hetero-contact forces (e.g., see Eqs. (11) and (12)) and of their dependence from components' chemical composition and molecular mass. It is not surprising the fact that parameter a_0 correlates well – showing parabolic or linear dependencies – with those in single-parameter fitting functions (k_{GT}, b; Fig. 1) and the principal parameters of the other common functions (e.g., q, and probably also k, A, K_1 or the difference K_1–K_2; study in progress). Significant contributions of entropic factors have also been observed in several systems. In conjunction with the estimates for the other two fitting parameters, a_1 and a_2, it is possible to quantify – among other – effects arising from free-volume modifications that may experience some type of irregular compositional dependency (due to inhomogeneous local interchain orientation) and the influence of a crystalline phase.

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