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Peculiarities of glass transition temperature relation to the composition of poly(*N*-vinyl pyrrolidone) blends with short chain poly(ethylene glycol)

Mikhail M. Feldstein*

A.V. Topchiev Institute for Petrochemical Synthesis, Russian Academy of Sciences, 29, Leninsky Prospekt, 117912 Moscow, Russia

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Abstract

Analysis of compositional T_g behaviour in poly(*N*-vinyl pyrrolidone) (PVP)–poly(ethylene glycol) (PEG) blends, performed in the terms of the equations offered by Gordon and Taylor, Couchman and Karasz, Kovacs and Braun–Kovacs provides an insight into the PVP–PEG complexation mechanism. Blending PVP with short chain PEG has been shown to be a two-stage process. At the first stage, the enhanced PVP–PEG interaction and excess free volume formation proceeds (the stage of formation of stoichiometric PVP–PEG hydrogen bonded complex) followed by nearly ideal mixing of the formed PVP–PEG stoichiometric complex with an excess amount of liquid PEG (the stage of weak favourable interaction in which no excess volume formation occurs). The first stage may be defined as PVP plasticization, whereas the second stage consists in gradual dissolving the plasticized PVP in excess PEG. The blend containing 36% of PEG-400 may be taken as an edge between the stages. This work complements the results of T_g analysis by including into consideration the effects of polymer chains mutual orientation, free volume and interaction within the PVP–PEG blends. To accomplish this aim, the Brekner–Schneider–Cantow (BSC) approach has been employed. In the ladder-like interpolymeric complexes, formed due to the interaction of complementary groups in repeating polymer chain units, the complexation is accompanied usually by the mutual orientation of polymer backbones and the decrease of blend free volume. In contrast, in PVP–PEG systems, the location of reactive hydroxyl groups at the PEG chain ends results in the increase of free volume and in formation of a carcass-like, flexible network. These particular features of PVP–PEG interaction have been demonstrated to be embedded in a specific compositional behaviour of the blend glass transition temperature.

Keywords: Poly(*N*-vinyl pyrrolidone)–poly(ethylene glycol) blends; Glass transition temperature; Composition dependence and interaction mechanism

1. Introduction

The miscibility of polymer blends is often ascertained by the measurement of a single glass transition temperature (T_g) as a function of composition [1]. Over the years, numerous equations have been proposed to express the T_g–composition dependence in miscible polymer blends and plasticized systems [2–7]. In general, it is observed that T_g varies monotonically as a function of composition demonstrating a rapid initial reduction followed by a gradual levelling off the response as a plasticizer is added. The difference between measured T_g values and those predicted with relevant equation is usually considered as a measure of the strength of interactions between molecules of involved components [8–14]. The T_g in miscible polymer blends has been also reported to relate directly to other important molecular parameters of polymers such as chain stiffness [15], conformation [16] and excess volume [17].

The miscibility of high molecular weight poly(*N*-vinyl pyrrolidone) (PVP) with short chain poly(ethylene glycol) (PEG) has been shown to be the result of hydrogen bonding of the PEG terminal hydroxyls to the carbonyls in the repeating units of comparatively longer PVP macromolecules [18,19]. Since both H-donor hydroxyls at the ends of PEG chains are involved into H-bonding with complementary PVP units, the PEG chains behave as relatively long and flexible cross-links, assembling the longer PVP macromolecules into an ordered specific supramolecular 'carcass' structure which demonstrates enhanced free volume and molecular mobility [20,21], rubber-like elasticity [18] and unique physical properties such as pressure-sensitive adhesion [22], featured only for PVP–PEG complex of stoichiometric composition but not for parent polymers [23]. The molecular structure and stoichiometry of the PVP–PEG network complex have been established using

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* Fax: +7-95-230-2224.
E-mail address: mfeld@ips.ac.ru (M.M. Feldstein).

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FTIR spectroscopy [18], DSC [24–29], WAXS [19,28] and rheological methods [18,30].

Using the modified Fox equation, we have recently estimated the T_g relation in PVP–PEG blends to the quantity of PEG molecules and PVP units involved in the complexation [27–28]. This work displays how the comprehension of PVP–PEG interaction mechanism can be expanded by the analysis of the PVP plasticization effect with PEG-400 as a function of composition in terms of the equations offered by Gordon and Taylor (G–T [3]), Couchman and Karasz (C–K, [5–7]), Kovacs (K) and Braun–Kovacs (B–K, [31]). The effects of polymer chains mutual orientation, free volume and interaction on the T_g of PVP–PEG blends are also included into consideration employing the Brekner–Schneider–Cantow (BSC) approach [32–35].

2. Materials and methods

PVP (Kollidon K-90), $M_w = 1{,}000{,}000\ \mathrm{g\ mol^{-1}}$, and PEG of molecular weight $400\ \mathrm{g\ mol^{-1}}$ (Lutrol E-400) were obtained from BASF. The polymers were used as received.

The full details of basic experimental procedures employed in this work were introduced in our recent paper [24]. The PVP blends with PEG, covering a full range of compositions, were prepared by dissolving both polymers in common solvent (ethyl alcohol) followed by removing the solvent by drying at ambient temperature and relative humidity (RH) until weight loss was terminated. Removal of ethyl alcohol from freshly prepared blends was ascertained by FTIR spectroscopy on the absence of methylene group stretching vibrations at 2974 and $1378\ \mathrm{cm^{-1}}$ using a Bruker IFS-113v spectrometer with a resolution of $1\ \mathrm{cm^{-1}}$ after averaging from 128 scans. The freshly prepared dry blends and unblended PVP were equilibrated to controlled pressure of water vapour in desiccators, maintaining RH = 50% at 25°C over different times.

In the DSC apparatus, the samples were first quench cooled with liquid nitrogen from ambient temperature to −100°C over 2–3 min and then heated up at a rate of $20°\mathrm{C\ min^{-1}}$ to 220°C. Upon heating, a heat capacity jump followed by single exotherm coupled with symmetric endotherm, and high temperature endotherm were normally observed for PVP–PEG blends. These four transitions were, respectively, attributed to the glass transition, PEG cold crystallization, melting and water thermodesorption [24–26]. The T_gs were recorded at half-height of the relevant heat capacity jumps (ΔC_p) in DSC heating thermograms with a Mettler TA 4000/DSC 30 thermoanalyser, calibrated with indium and gallium. All reported values are the average of replicate experiments varying less than 1–2%. Samples of 5–15 mg in weight were sealed in standard aluminium pans supplied with pierced lids so that absorbed moisture could evaporate upon heating. An argon purge ($50\ \mathrm{ml\ min^{-1}}$) was used to avoid moisture condensation at the sensor.

The content of absorbed water in the blends was determined by weighing the samples before and after DSC scans using a Mettler Analytical Balance, AE 240, with an accuracy of ±0.01 mg. Weight loss of the sample after scanning was compared to the amount of desorbed water evaluated from the enthalpy change associated with water evaporation from the sample by DSC. Depending on the RH of the surrounding atmosphere, PVP hydration ranged from 6 to 8 wt%, while the PEG contained less sorbed water (0–1 wt%). The so-called 'hydrated' blends contained 6–12% of sorbed water.

3. Results and discussion

3.1. A two-stage mechanism of PVP–PEG interaction and mixing in view of the Couchman–Karasz, Fox, Gordon–Taylor, Kovacs and Braun–Kovacs equations

As liquid PEG is added to glassy PVP, the T_g falls dramatically over 220°C, tending to a limit found for PEG-400 (Fig. 1). The change in heat capacity at glass transition, ΔC_p, increases as PEG concentration increases.

Among the equations describing the T_g–composition dependence of miscible polymer blends the more general is the C–K equation and it reads, for a binary PVP–PEG mixture, assuming that ΔC_p of polymer does not depend on temperature:

$$\ln T_g = \frac{(w\Delta C_p \ln T_g)_{\mathrm{PEG}} + (w\Delta C_p \ln T_g)_{\mathrm{PVP}}}{(w\Delta C_p)_{\mathrm{PEG}} + (w\Delta C_p)_{\mathrm{PVP}}} \tag{1}$$

where w is the weight fraction of the polymers in blend. Eq. (1) describes the T_g–composition relationship better for PVP–PEG blends compared to the Fox and G–T equations as is evident from the data presented in Fig. 2.

Eq. (1) can be reduced to several other equations which have been proposed for the same purpose, following a

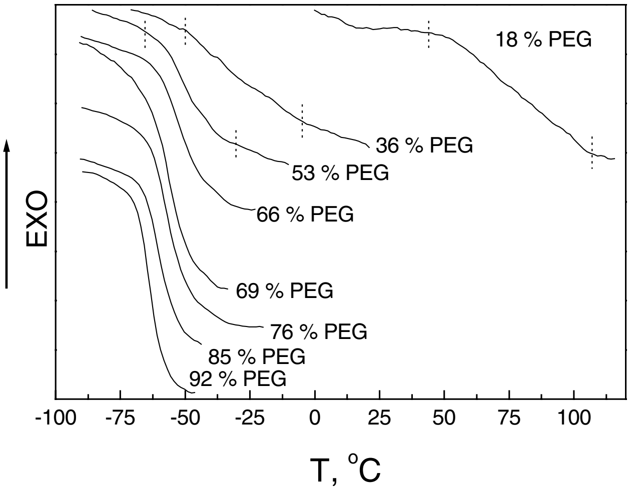

Fig. 1. DSC heating thermograms of glass transition for dry PVP–PEG blends over the range of PEG/PVP compositions (in wt%).

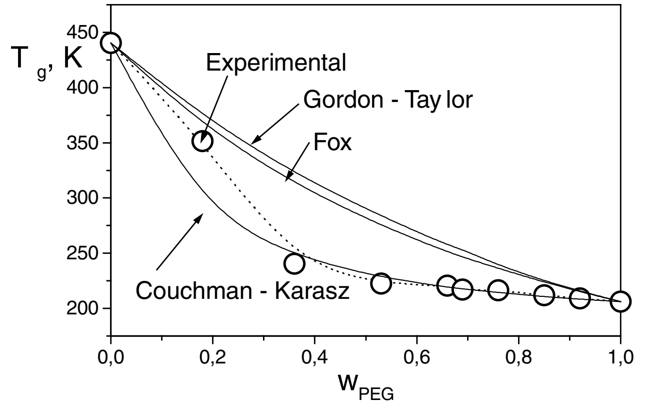

Fig. 2. The T_g of PVP–PEG blends plotted against PEG weight fraction.

certain number of simplifying assumptions. Assuming that the ΔC_p of two polymers are close in their values, rearrangement and expansion of the logarithm terms gives the Fox equation, written here for hydrated PVP–PEG mixture in a ternary form:

$$\frac{1}{T_g} = \frac{w_{\mathrm{PVP}}}{T_{g_{\mathrm{PVP}}}} + \frac{w_{\mathrm{PEG}}}{T_{g_{\mathrm{PEG}}}} + \frac{w_{\mathrm{H_2O}}}{T_{g_{\mathrm{H_2O}}}} \tag{2}$$

With the first term of expansion of the logarithm in Eq. (1) and if $T_{g_1} \approx T_{g_2}$, the known G–T equation (3a) can be derived from the C–K equation:

$$T_g = \frac{(wT_g)_{\mathrm{PEG}} + k(wT_g)_{\mathrm{PVP}}}{w_{\mathrm{PEG}} + kw_{\mathrm{PVP}}} = T_{g_{\mathrm{PEG}}} + k\frac{w_{\mathrm{PVP}}}{w_{\mathrm{PEG}}}(T_{g_{\mathrm{PVP}}} - T_g) \tag{3a}$$

where

$$k = \frac{\Delta C_{p_{\mathrm{PVP}}}}{\Delta C_{p_{\mathrm{PEG}}}} \approx \frac{\Delta\alpha_{\mathrm{PVP}}}{\Delta\alpha_{\mathrm{PEG}}} \tag{3b}$$

and $\Delta\alpha$ is the cubic expansion coefficient of polymer. Strictly speaking, the assumptions accepted under reducing the C–K equation to the Fox and G–T equations are invalid for PVP–PEG blend because $T_{g_{\mathrm{PVP}}} = 167.5°\mathrm{C}$, $T_{g_{\mathrm{PEG}}} = -67°\mathrm{C}$, $\Delta C_{p_{\mathrm{PVP}}} = 0.26\ \mathrm{J\ g^{-1}\ K^{-1}}$. For amorphous PEG-400, the $\Delta C_{p_{\mathrm{PEG}}} = 1.49\ \mathrm{J\ g^{-1}\ K^{-1}}$ [18]. The Fox and G–T equations are generally recognized to hold for miscible blends where only weak intermolecular interactions occur. It is highly cognitively to employ them for the analysis of the composition behaviour of PVP–PEG blends taking into account that the observed deviations from predicted relationships are to be related to the interpolymer interaction strength.

Experimental points in Fig. 2 outline the large negative T_g deviations from the weight-average values calculated with both the Fox (Eq. (2)) and G–T (Eq. (3a)) equations. The G–T plot in Fig. 3 reveals an enhanced PVP–PEG interaction that occurs when a small amount of PEG is blended with PVP. As PEG content in the blends achieves a value corresponding to the stoichiometric PVP–PEG H-bonded complex composition (about 36 wt% [19,28]), a further mixing gives a linearity (Fig. 3), that indicates rather the gradual swelling and dissolution in an excess PEG of the stoichiometric network PVP–PEG complex formed within earlier mixing stage, than the following increase in PVP–PEG binding degree. This finding is confirmed with the results of independent FTIR, rheological and WAXS measurements [18,19,28].

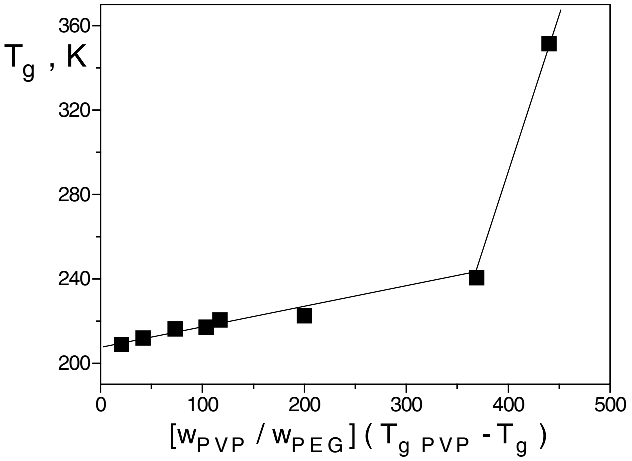

Fig. 3. The Gordon–Taylor plot for dry PVP–PEG blend (Eq. (3a)).

To fit obtained T_g values with those predicted with the Fox equation, Eq. (2) may be presented in the form [27,28]:

$$\frac{1}{T_g} = \frac{w_{\mathrm{PVP}}}{T_{g_{\mathrm{PVP}}}} + \frac{w_{\mathrm{PEG}}}{T_{g_{\mathrm{PEG}}}} + \frac{w^*_{\mathrm{PEG}}}{T_{g_{\mathrm{PEG}}}} + \frac{w_{\mathrm{H_2O}}}{T_{g_{\mathrm{H_2O}}}} \tag{4}$$

where w^*_{PEG} is an adjusting parameter related to the negative T_g deviations from the weight-average magnitudes found with the Fox equation (2) and defined as a weight fraction of PEG molecules forming with PVP two H-bonds through both terminal hydroxyls, and w_{PEG} is the total weight fraction of the PEG in the blend (assuming that all the PEG molecules in miscible blend are available to form, at least, one H-bond with PVP units). The approach based on Eq. (4) allows evaluating the numerous quantities related to PVP–PEG H-bonding degree [27,28], e.g. H-bonded network density, stoichiometry and free energy of PVP units cross-linking through hydrogen bonding with hydroxyl-terminated PEG short chains.

If the difference in T_g between two polymers involved in miscible blend is larger than about 50°C, as is the case for PVP–PEG blends, the Kovacs equation (5) holds (Fig. 4):

$$T_g = T_{g_{\mathrm{PEG}}} + \frac{f_{g_{\mathrm{PVP}}}}{\Delta\alpha_{\mathrm{PEG}}}\frac{\phi_{\mathrm{PVP}}}{\phi_{\mathrm{PEG}}}$$

$$= (203 \pm 2) + (36.6 \pm 1.3)\frac{\phi_{\mathrm{PVP}}}{\phi_{\mathrm{PEG}}} \tag{5}$$

where f_g is the fractional free volume of PVP at T_g and ϕ the polymer volume fraction in a blend. The Kovacs equation

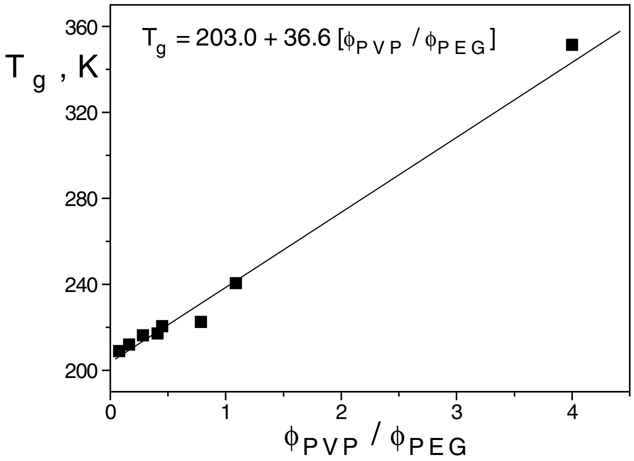

Fig. 4. The Kovacs plot for miscible PVP–PEG blends (Eq. (5)).

(5) is valid at temperatures below a some critical T_c value:

$$T_c = T_{g_{PVP}} - \left(\frac{f_{g_{PVP}}}{\Delta\alpha_{PVP}}\right)$$

Assuming for PVP the 'universal' values $f_{g_{PVP}} = 0.025$ and $\Delta\alpha_{PVP} = 4.8 \times 10^{-4}\ K^{-1}$, the T_c is found to be 114.5°C for PVP–PEG mixtures.

The Kovacs equation (5) has been derived assuming negligible excess volume between two polymers upon mixing. The validity of the Kovacs equation (5) for PVP–PEG mixture ($r^2 = 0.992$) (Fig. 4) reveals therefore that there is no appreciable excess volume upon PVP–PEG blending. The regression coefficients of the linear relationship shown in Fig. 4 allows evaluating $T_{g_{PEG}}$ and $\Delta\alpha_{PEG}$ if $f_{g_{PVP}} = 0.025$ (universal value found for variety of polymers). The calculated $T_{g_{PEG}}$ is in a good agreement with known value (206 K). The obtained $\Delta\alpha_{PEG} = 6.83 \times 10^{-4}\ K^{-1}$ value is also fairly reasonable [36].

If the excess volume is not negligible, as is expected at free volume formation under PVP–PEG mixing, Braun and Kovacs [31] have modified the initial theory to read:

$$T_g = T_{g_{PEG}} + \frac{\phi_{PVP}(f_{g_{PVP}} + g\phi_{PEG})}{\phi_{PEG}\Delta\alpha_{PEG}} \tag{6}$$

Table 1
Dependence of the PVP–PEG interaction parameter (g) and fractional excess volume (V_e/V) upon PVP–PEG mixing as a function of the composition of the dry PVP–PEG miscible blends

ϕ_{PEG}	g	V_e/V
0.20	0.017	0.00272
0.39	0.003	0.00071
0.56	−0.005	−0.00123
0.69	0.005	0.00107
0.71	0.000	0.00000
0.78	0.005	0.00086
0.86	0.005	0.00060
0.93	0.007	0.00046

where g is an interaction term defined by Eq. (7):

$$g = \frac{V_e}{V\phi_{PVP}\phi_{PEG}} \tag{7}$$

where V is the volume of sample blend and V_e the excess volume. The V_e (and g) are positive if the interactions within the blend are stronger than the average interactions between molecules of the same species, and are negative otherwise. Typical values for g found in literature range from −0.020 to +0.020 [4,37]. The calculated interaction parameters for dry PVP–PEG blend are displayed next to corresponding the fractional excess volume V_e/V values in Table 1.

As follows from the data in Table 1, a relatively strong PVP–PEG interaction is only observed at small PEG content in the blends ($\phi_{PEG} = 0.20$), i.e. in the course of PVP–PEG complexation. As further mixing of the stoichiometric PVP–PEG complex with PEG proceeds, both the Braun–Kovacs interaction term and fractional excess volume become negligible.

Summing up the above-presented results of the T_g–composition relationship analysis in PVP–PEG blends employing the C–K, Fox, G–T, K and B–K equations (1)–(7), it can be concluded that a strong PVP–PEG interaction and a formation of some excess volume is only observable at the first stage of PVP–PEG mixing. As the PEG content in the blends achieves the stoichiometric composition of 36 wt%, the interaction becomes weaker and no excess volume formation occurs. The validity of the Kovacs equation (5) to describe the T_g–composition behaviour in PVP–PEG blends implies that the particular features of this behaviour are defined rather by the properties of plasticizer (PEG) than the high-T_g long chain polymer (PVP). Actually, if we follow the concept that the fractional free volume for majority of polymers at their own T_gs is $f_g \approx 0.025$, the value assumed in our analysis for PVP, it means that in view of Eq. (5) the blend T_g relates to the properties (T_g and $\Delta\alpha$) of plasticizer only. Consequently, if we will take the PEG blends with different higher-T_g polymers, containing the complimentary proton-accepting functional groups in their repeat units, we would most likely obtain the similar mechanism of blend T_g–composition behaviour. This prediction needs an experimental confirmation.

3.2. Effects of PVP–PEG interaction, free volume formation and interchain orientation in view of the BSC approach

According to the BSC approach, the PVP–PEG blend T_g relates to the composition by second-power equation (8) [32,33]:

$$\frac{T_g - T_{g_{PEG}}}{w_{PVP_c}(T_{g_{PVP}} - T_{g_{PEG}})} = (1 + k_1) - (k_1 + k_2)w_{PVP_c} + k_2 w_{PVP_c}^2 \tag{8}$$

where w_{PVP_c} is the so-called corrected PVP weight fraction

Table 2
The parameters of glass transition and Gordon–Taylor constants, *k*, for dry and hydrated polymers

	Dry PVP	Dry PEG	Hydrated PVP
T_g (K)	440.5	206	343.3
ΔC_p (J g^{-1} K^{-1})	0.26	1.49	0.49
$\Delta\alpha$ ($\times 10^{-4}$ K^{-1})	4.8	6.83	–
$k = T_{g_1}/T_{g_2}$	0.468		0.600
$k = \Delta C_{p_2}/\Delta C_{p_1}$	0.174		0.329
$k = \Delta\alpha_2/\Delta\alpha_1$	0.703		–
k (experimental)	0.085		0.043

in blend defined as

$$w_{\mathrm{PVP_c}} = \frac{k w_{\mathrm{PVP}}}{w_{\mathrm{PEG}} + k w_{\mathrm{PVP}}}$$

The *k* is the constant of G–T equation which is given by a ratio (9a):

$$k = \frac{\rho_{\mathrm{PEG}}\Delta\alpha_{\mathrm{PVP}}}{\rho_{\mathrm{PVP}}\Delta\alpha_{\mathrm{PEG}}} \tag{9a}$$

where $\Delta\alpha$ is the change in polymer thermal expansion coefficient at T_g. Neglecting the differences of the appropriate densities, ρ, as a first approximation, the ratio (9a) can be replaced by the corresponding ratios of $\Delta\alpha$, T_g and ΔC_p if one assumes the validity of both the Simha–Boyer rule ($\Delta\alpha T_g = 0.113$) and the Boyer criterion ($\Delta C_p T_g = 115$ J g^{-1}) [38]:

$$k = \frac{\Delta\alpha_{\mathrm{PVP}}}{\Delta\alpha_{\mathrm{PEG}}} = \frac{T_{g_{\mathrm{PEG}}}}{T_{g_{\mathrm{PVP}}}} = \frac{\Delta C_{p_{\mathrm{PVP}}}}{\Delta C_{p_{\mathrm{PEG}}}} \tag{9b}$$

The *k* values for dry and equilibrium hydrated PVP–PEG blends, calculated as the ratios defined by relation (9b), are presented in Table 2 along with relevant T_g, ΔC_p, $\Delta\alpha$ magnitudes and with *k* constants obtained by fitting the experimental G–T plot shown in Fig. 3.

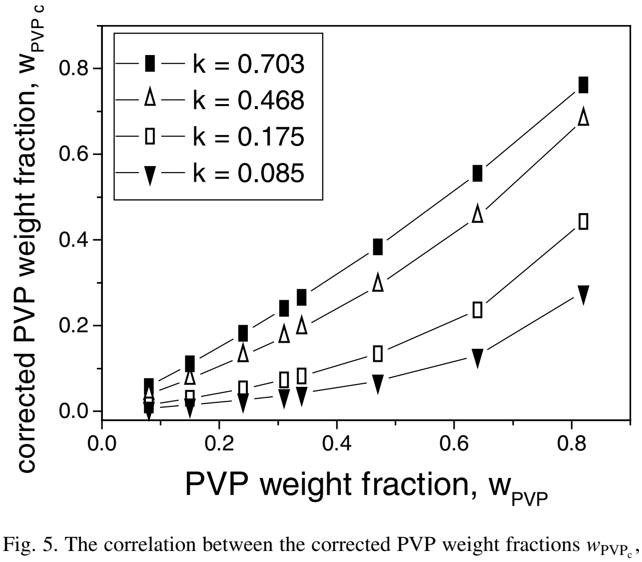

Fig. 5. The correlation between the corrected PVP weight fractions $w_{\mathrm{PVP_c}}$, and PVP weight fractions in blends with PEG at different values of the Gordon–Taylor constants.

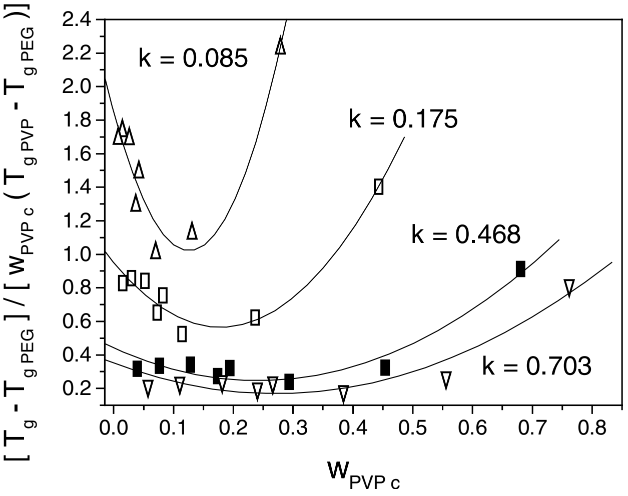

Fig. 6. Impact of the Gordon–Taylor constant magnitudes upon the BSC plots (Eq. (8)).

The correlation between the PVP weight fraction in blends and the corrected weight fraction, $w_{\mathrm{PVP_c}}$, is shown in Fig. 5. The *k* values affect appreciably the corrected PVP weight fractions and the BSC plots for PVP–PEG blends (Fig. 6). Fortunately, the polynomial regression of the BSC curves allows us a separate determination of k_1 and k_2 constants from the first and third terms of Eq. (8), whereas the second term, defined as $k_1 + k_2$ [33], provides an additional criterion to assess the validity of obtained k_1 and k_2 values. By this way, only those G–T constants were included into further consideration which provided a closer agreement with $k_1 + k_2$ value found by polynomial fitting procedure of BSC plots.

Table 3 lists the values of G–T constants, *k*, and the k_1, k_2 coefficients of the BSC concentration power equation (8). They have been obtained by the least-squares fit method to the data displayed in Figs. 6–9. The quality of data fitting by the second power equation (8) has been characterized in terms of the square regression coefficient (r^2) and the probability (p) of experimental point deviation from the law outlined by the BSC equation (8). The closer the r^2 value to unity, and the lower the p magnitude, the better the fitting. The experimental curves analysis has been performed taking into account all the G–T constants, *k*, presented in Table 2. However, only the $k = 0.703$ for the dry blends and $k = 0.600$ for hydrated ones provided the best fit, giving also the $(k_1 + k_2)$ values which corresponded fairly reasonably to the constants found at the second term of obtained second power polynomial relationship.

The third-power polynomial fitting of the BSC curves improves the regression compared to the second-power equation (8), Fig. 7. This is a characteristic feature of PVP–PEG blends only and not observed for reference blends reported in literature [33,39] and shown in Fig. 8. This fact may be considered as an indication that the

Table 3
The BSC equation regression parameters

Blend	k	k_1	k_2	r^2	p
PVP–PEG dry	0.703	−0.649	2.483	0.917	0.002
PVP–PEG hydrated	0.600	−0.837	1.523	0.935	0.004
PHMCM–PDNBM[a] [33]	n/a	4.324	6.074	0.988	<0.0001
PS–PαMS[a] [39]	n/a	−3.169	−3.235	0.881	0.041

[a] PHMCM, poly(*N*-ethylcarbazol-3-yl-methyl methacrylate); PDNBM, poly(β-hydroxyethyl-3,5-dinitrobenzoyl methacrylate); PS, polysterene; PαMS, poly(α-methylstyrene).

second-power BSC equation (8) can be, in principle, extended to the third-power equation for the specific case of strong intermolecular association, accompanied by mutual chain orientation and free volume formation. Although the third-power polynomial regression provides better fitting of experimental points, the physical meaning of relevant relationship constants remains to be obscured, and therefore the second-power equation (8) has been employed in present work for the evaluation of k_1 and k_2 constants.

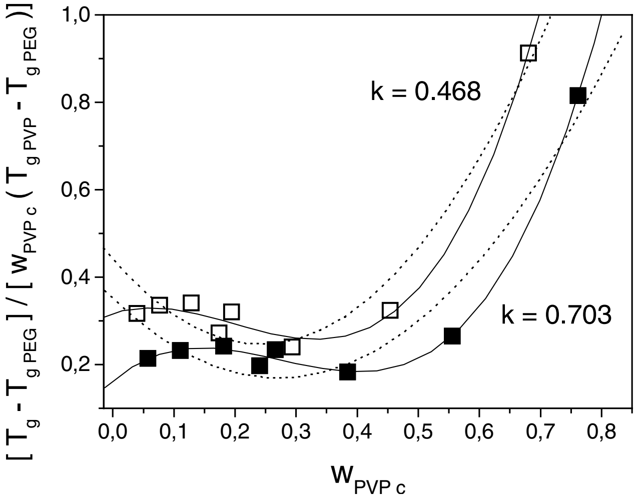

Fig. 7. BSC plot for dry PVP–PEG-400 blends: comparison of three-power (solid lines) and two-power (dotted lines) polynomial fitting.

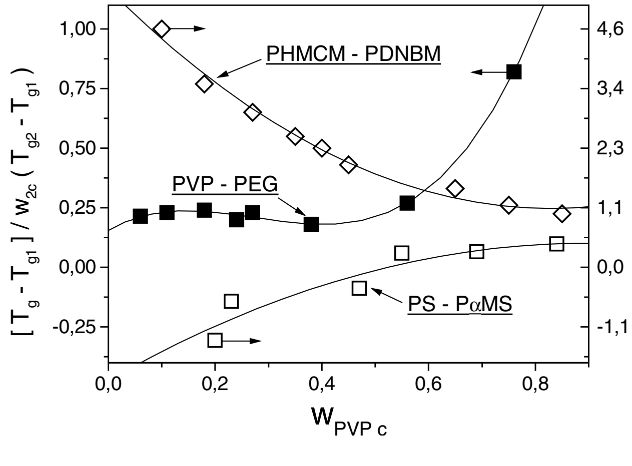

Fig. 8. The BSC plots in terms of Eq. (8) for PVP–PEG blends ($k = 0.703$) in comparison with the reference data related to different types of energetic and chain orientation contributions to glass transition temperature. The indexes 1 and 2 refer to the lower and higher T_g polymers, respectively.

Although the BSC equation (8) as well as the Gordon–Taylor (Eq. (3a)), Couchman–Karasz (Eq. (1)) and Kovacs (Eq. (5)) expressions have been only derived for binary blends, they can be also applied to ternary PVP–PEG blends containing the equilibrium amount of water sorbed as a vapour from surrounding atmosphere or residual from blend preparation. Indeed, in hydrated PVP–PEG blends, the sorbed water has been shown to be mainly associated with PVP, whereas the PVP–PEG H-bonding proceeds directly through water molecules sorbed at PVP units, causing no water desorption [26]. It means that the ternary (hydrated) blend can be easily reduced to the binary one at a fixed hydration degree by substituting the T_g magnitude for hydrated PVP in corresponding equations instead of that for dry PVP. By this way, the blend hydration has been found to exhibit no principal effect on k_1 and k_2 parameters of BSC relationship (Table 3, Fig. 9).

The BSC equation (8) assumes that free volume distribution and the conformational mobility in polymer mixtures depend on the specific interaction between the blend components [33] and the mutual orientation of their chains [32]. The parameter k_1 depends mainly on the differences between the interaction energies of the binary hetero

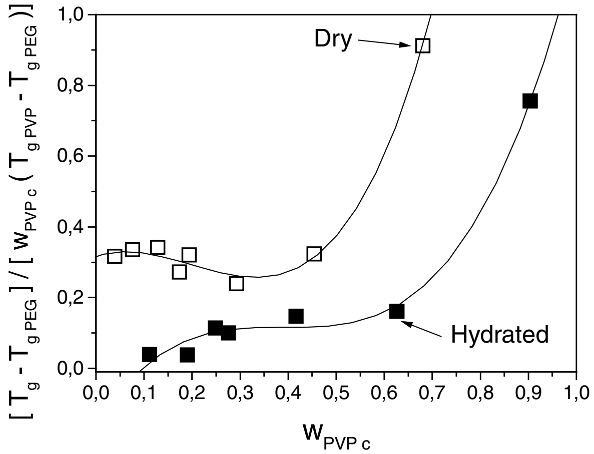

Fig. 9. Effect of PVP–PEG blends hydration on the BSC plot. $k = 0.468$ for dry and 0.600 for hydrated blend (6–10 wt% of water).

and homo contacts. Conformational redistributions in the neighbourhood of the binary contacts accompanied by entropy changes are considered supplementary. Positive k_1 values suggest a predominant contribution of the energetic effects of the hetero interactions, whereas negative values are indicative of prevailing effect of the conformational rearrangement accompanied by the increase in free volume. The k_2 value is a measure of chains orientation. If no specific chain orientation occurs $k_2 \rightarrow 0$. The higher the positive k_2 value, the greater the chain orientation. The disorientation of the chains upon polymer mixing is reported to relate to negative k_2 values.

Two typical cases of energetic, free volume and orientation effects are described in literature [33,39]. They are exemplified in Fig. 8 along with PVP–PEG compatible blend behaviour. In Case I, blending of a polydonor, poly(*N*-ethylcarbazol-3-yl-methyl methacrylate) (PHMCM), and polyacceptor, poly(β-hydroxyethyl-3,5-dinitrobenzoyl methacrylate) (PDNBM), leads to positive T_g deviations, the decrease in mixture volume and pronounced chain orientation [33]. In Case II [39], mixing polysterene (PS) with poly(α-methylstyrene) (PαMS) is accompanied by an excess volume formation and chain disorientation (Table 3). Note, that in both cases, both k_1 and k_2 are identical in their signs. In contrast to known behaviour, the PVP–PEG blends demonstrate an excess volume formation ($k_1 = -0.87$), accompanied by highly pronounced interchain orientation effect ($k_2 = 1.26$).

4. Conclusions

Analysis of the compositional behaviour of T_g provides an extra insight into polymer complexation mechanism in miscible PVP–PEG blends. Blending PVP with short chain PEG induces first enhanced PVP–PEG interaction and excess volume formation (the complexation stage) followed by an ideal mixing of formed PVP–PEG complex with liquid PEG (the stage of weak favourable interaction in which no excess volume occurs). Within the frameworks of classical polymer plasticization–dissolution concept, the first stage may be identified as PVP plasticization, whereas the second stage consists in gradual dissolving the plasticized PVP in excess PEG. The blend containing 36% of PEG-400 may be taken as an edge between two stages.

For favourably interacting polymers, containing complementary groups in their repeating units, specific bonding has been shown to result often in positive T_g deviations from the rules of mixing that is an evidence of free volume decrease through hetero chain association. This case is embedded by positive k_1 and k_2 values in the BSC equation (8). If no specific interaction of topologically distinct polymers occurs, the driving force of compatibility is an excess in free volume upon mixing and both k_1 and k_2 parameters are negative. In contrast to this known behaviour described in literature, the PVP compatible blends with PEG-400 represent a unique example of interpolymer complex formation accompanied by specific chain orientation and essential increase in free volume that is due to the location of bonding groups at the ends of short PEG chain.

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