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Relation of glass transition temperature to the hydrogen-bonding degree and energy in poly(*N*-vinyl pyrrolidone) blends with hydroxyl-containing plasticizers. Part 1. Effects of hydroxyl group number in plasticizer molecule

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Abstract

The well-known Fox equation has been modified to express the glass transition temperature, T_g, as an explicit function of the number of polymer–plasticizer hydrogen bonds in miscible poly(*N*-vinyl pyrrolidone) (PVP) blends with ethyl alcohol, water, short-chain poly(ethylene glycol) (PEG), and glycerol. The plasticization effect has been found to be dependent on the fraction of hydroxyl groups in the blend rather than on the plasticizer weight fractions. Negative deviations of the blend T_g from the relationship predicted with the original form of the Fox equation were shown to be in direct proportion to the number of hydroxyl groups in the plasticizer molecule. The following quantities can be evaluated based on the T_g–composition profiles: binding degree, fraction of plasticizer hydroxyl groups forming hydrogen bonds to PVP repeat units, the fraction of plasticizer molecules crosslinking the polymer units by hydrogen bonding through two or more hydroxyl groups in their molecule. The dynamics of PVP–PEG hydrogen bonding over the entire compositional range has been evaluated in terms of hydrogen-bonded network density. The stoichiometric composition of the PVP–PEG hydrogen-bonded complex, determined from the T_g–composition relationship, corresponds to the data obtained with independent methods. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-vinyl pyrrolidone); Glass transition temperature; Hydrogen bonding degree and energy

1. Introduction

The glass transition temperature, T_g, is one of the most fundamental features that relates directly to polymer cohesive energy and packing density. Numerous equations have been offered over last years to describe the plasticization effect of glassy polymers, i.e. the T_g depression as a function of plasticizer concentration. These equations have been derived from the free volume concept or from thermodynamic arguments. The simple rules of mixing have been stated by the Fox [1] and Gordon–Taylor equations [2]. They neglect specific interactions between the polymer and the plasticizer, inferring a complete uniformity of intermolecular forces. In practice, the plasticization effect involves often the specific interactions or excess volume formation upon mixing the polymer and the plasticizer. Negative deviations from the Fox and Gordon–Taylor equations occur when the decrease in T_g is greater than what relevant theory predicts. Adjusting parameters are then introduced into the Gordon–Taylor equation to fit data and estimate empirically the strength of interaction in different arbitrary units [3–5].

Although the number and energy of intermolecular bonds formed between the polymer and the plasticizer are undeniably concealed in specified T_g values of miscible blends, a direct evaluation of these quantities from the T_g–composition relationships has not yet been accomplished. Meantime as far back as 1945 Zhurkov had described phenomenologically the proportionality of the T_g reduction to the mole fraction of the interacting groups in miscible blends of polar plasticizers with hydrophilic complementary polymers [6]. Recently, Di Marzio used the entropy theory of glasses to describe adequately the compositional dependence of T_g in binary blends of interacting polymers by replacing the weight fractions of polymeric components by appropriate bond fractions in a simple rule of mixing represented by the Gordon–Taylor equation [7].

Our research has been performed with two main objectives in mind. First, it is intended to report on a simple

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algorithm for evaluating the polymer–plasticizer binding degree and the range of related quantities as well as the hydrogen-bonding energy based on the compositional dependence of plasticization effect. This is the focus of the first paper of the present series and exemplified by poly(*N*-vinyl pyrrolidone) (PVP) plasticization with ethyl alcohol, water, poly(ethylene glycol) (PEG), and glycerol, bearing, respectively, one, two and three hydrogen-bonding hydroxyl groups in their molecules. The second paper is aimed to refine our understanding of the PVP–PEG complexation mechanism, which is the ultimate goal of our research efforts [8–12] initiated by the unique physical and performance properties of the PVP–PEG composites [13,14] and their increasing pharmaceutical usage [15,16].

Enhanced PVP plasticization with short chain PEG, bearing two proton-donating hydroxyl groups at both chain ends, has been recently shown with FTIR spectroscopy to be the result of hydrogen bonding between the PEG terminal hydroxyls and the carbonyl proton-accepting oxygen atoms in repeat units of high molecular weight PVP [8]. The oxyethylene repeat units of comparatively shorter PEG macromolecules are not involved in complex formation with PVP units. As both PEG terminal hydroxyls are capable of forming the hydrogen bonds with PVP units, the PEG behaves as a crosslinking agent, causing hydrogen-bond network formation in PVP–PEG blends. The supramolecular network structure of the PVP–PEG complex has been established and evaluated in terms of both network density and critical molecular weight between entanglements by rheological methods [8,14]. Due to the considerable length of PEG cross-links creating a space between PVP chains, the PVP–PEG network demonstrates enhanced free volume [8,10,11]. The latter, coupled with the flexibility of PEG chains, governs the high molecular mobility of polymer segments between neighbouring hydrogen-bond entanglements in the PVP–PEG network [8,11]. These features result, eventually, in unique physical properties of PVP blends, such as a rubber-like viscoelasticity [8,14] and pressure-sensitive adhesion toward diverse substrates [13]. A specific feature of the PVP–PEG hydrogen bonding is a stoichiometry of the resulting complex where as much as nearly 15 mol% of PEG-400 macromolecules form strong hydrogen bonds with 30% of PVP repeat units through both terminal hydroxyls, while the other 70 mol% of the units remain either intact or loosely bound within a wide composition range [9]. In essence only the stoichiometric PVP–PEG complex has been shown to exhibit adhesive properties [13,14,17]. Established characteristic peculiarities of PVP–PEG interaction are to be taken into consideration under the analysis of T_g behaviour with composition. The first paper in this series of two works considers the negative T_g deviations from calculated weight-average values in miscible PVP blends with hydroxyl-containing plasticizers as an explicit function of the number of hydrogen-bonding groups in plasticizer molecules. The second and final paper, dealing entirely with PVP plasticization by short-chain PEG ranging in molecular weight from 200 to 1000, reveals the contributions of the length of hydroxyl-terminated PEG chains to the blend T_g.

2. Experimental

PVP (Kollidon K-90), $M_w = 1,000,000\ \mathrm{g\ mol^{-1}}$, and PEG ranging in molecular weight from 200 to $1000\ \mathrm{g\ mol^{-1}}$, were obtained respectively from BASF and Fluka. Ethyl alcohol and glycerol were supplied by Sigma. All polymers and plasticizers were used as received.

The full details of the basic experimental procedures employed in this work were introduced in our previous paper [10]. PVP blends with PEG and glycerol, covering a full range of compositions, were prepared by the dissolution of 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 PVP blends with PEG and glycerol was ascertained by FTIR spectroscopy by 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 blends and unblended PVP were stored at ambient temperature in different environments (surrounding atmosphere at various weather conditions) or equilibrated to controlled pressure of water vapour in desiccators, maintaining RH = 50% at 25°C over different time. The PVP blends with ethanol were obtained by mixing the dry polymer with a required amount of the solvent. The samples of hydrated PVP were produced by equilibrating the PVP in desiccators at 18°C over aqueous H_2SO_4 solutions of controlled density which maintained the required RH ranging from 10 to 90% as described earlier [12].

The T_gs were recorded at half-height of the relevant heat capacity jumps in d.s.c. heating thermograms using 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. In the d.s.c. apparatus the samples were first quench cooled with liquid nitrogen from ambient temperature to −100°C over 2–3 min and then heated up to 220°C at a rate of $20°\mathrm{C\ min^{-1}}$.

The content of absorbed water in the blends was determined by weighing the samples before and after d.s.c. 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

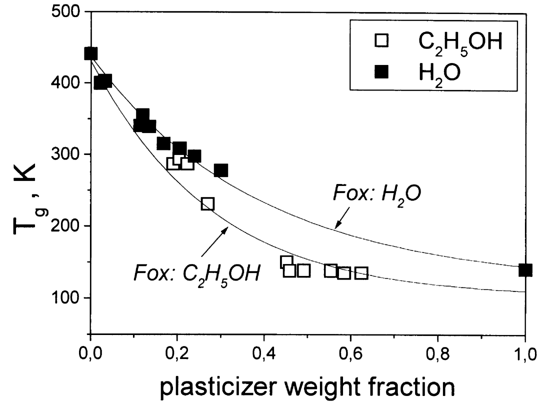

Fig. 1. The T_g plotted against the compositions of binary PVP–water and ternary ethyl alcohol–PVP blends of equilibrium hydration. The solid lines designate the relationships obtained using the Fox equation (1) and the data listed in Table 1. The points denote the T_g values measured on d.s.c. thermograms.

from the sample by d.s.c. With a similar procedure the amount of ethanol in mixtures with PVP was determined.

3. Results and discussion

3.1. Relation of glass transition temperature to the fraction of plasticizer hydrogen-bonding groups in blend

To express the PVP plasticization effect through the number of polymer–plasticizer hydrogen-bonds we have modified the known Fox equation (1). Since PVP is a highly hygroscopic polymer, containing appreciable amount of water sorbed from surrounding atmosphere as vapour or residual from polymer processing, all the PVP–plasticizer blends except the PVP–water system have to be treated as ternary. The plasticizing effects of diluents bearing one hydroxyl group per molecule (ethanol and water) have been shown to follow fairly reasonably the original form of the Fox equation (Fig. 1) that reads for ternary (hydrated) blends as:

$$\frac{1}{T_g} = \frac{w_{PVP}}{T_{g_{PVP}}} + \frac{w_{H_2O}}{T_{g_{H_2O}}} + \frac{w_{pl}}{T_{g_{pl}}}, \qquad (1)$$

Table 1
The glass transition temperatures of PVP and plasticizers

Component	T_g (K)	References
PVP dry	445	[10]
Ethyl alcohol	97	[18]
Water	140	[19]
PEG-200	197	
PEG-300	200	
PEG-400	206	[10]
PEG-600	202	
Glycerol	200	

where T_g refers to the glass transition temperatures and w to the weight fractions of PVP, water and plasticizer, respectively. The T_gs of PVP and plasticizers employed for the calculations are listed in Table 1. The applicability of the simple rule of mixing embedded by the Fox and Gordon–Taylor equations for successful description of the plasticizing effect of water has been also demonstrated earlier by many authors for PVPs of various molecular weights [20–23].

In contrast to the ideal behaviour of ethanol and water, displayed in Fig. 1, the plasticizers bearing two and three hydroxyl groups per molecule, PEG and glycerol, respectively, have been found to decrease the blends' T_g significantly lower than is predicted from a simple weighted average, displaying large negative deviations from the relationship outlined by the Fox equation (1) (Fig. 2). The more number of hydroxyl groups in the plasticizer molecule the larger the negative deviation. It is logical therefore to suppose that the negative deviations observed are due to the contribution of the second and third hydroxyl groups in the plasticizer molecule. In other words, in agreement with Di Marzio's results relating to the Gordon–Taylor equation, the T_g reduction caused by diol and triol plasticizers is supposed to be proportional to the fractions of hydroxyl groups rather than to the weight fractions of the plasticizers [7].

By introducing an adjusting parameter, w^*_{pl}, into the original form of the Fox equation (1), we are able to fit the negative deviations from the T_g's ideal behaviour:

$$\frac{1}{T_g} = \frac{w_{PVP}}{T_{g_{PVP}}} + \frac{w_{H_2O}}{T_{g_{H_2O}}} + \frac{w_{pl} + w^*_{pl}}{T_{g_{pl}}}. \qquad (2)$$

The fitting parameter, w^*_{pl}, in the Eq. (2) is defined as a measure of the negative T_g deviations from the values predicted by the Fox equation (1), $-\Delta T_g = T_{gFOX} - T_g$. It is therefore no wonder that a linear relationship has been found between the w^*_{pl} and $-\Delta T_g$ quantities both for PEG and glycerol ($R = 0.96$–0.99, data not shown). Figs. 3 and 4 display the w^*_{pl} and $-\Delta T_g$ quantities as the functions of blend composition and T_g. The more hydroxyl groups bear plasticizer molecule the greater the w^*_{pl} parameter and the T_g deviations are negative. In agreement with the data shown in Fig. 2, the plots of both the T_g deviations from the Fox rule and w^*_{pl} exhibit maximum at comparatively small plasticizer concentrations (Fig. 3). While for PVP blends with glycerol the maximum is observed in the mid-T_g region (Fig. 4), PEG shifts its position toward lower T_g values. To the right of the maximum in Fig. 3 and to the left in Fig. 4 the w^*_{pl} fitting parameter and the negative T_g deviations are nearly linear functions of blends composition and T_g. This linearity reflects a dual character of the w^*_{pl} quantity, which relates both to blend T_g and composition. The data in Figs. 3 and 4 are of fundamental importance in the present approach as will be shown in subsequent sections of this series of papers.

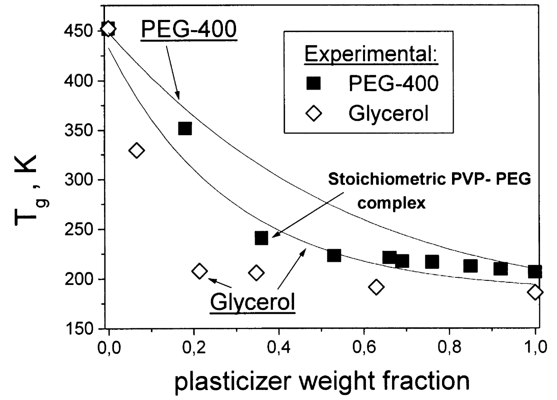

Fig. 2. Plasticizing effects of PEG-400 and glycerol on PVP. Solid lines denote the curves predicted with the Fox equation (1), points are the data of experimental measurements.

3.2. The composition dependence of hydrogen-bonding characteristics evaluated with the negative T_g deviations from the Fox rule of mixing

Within the context of the modified Eq. (2) the parameter w_{pl}^* has a clear physical meaning. Assuming that the negative deviations displayed only by diol and triol plasticizers (short-chain PEG and glycerol) are due to the formation of more than one hydrogen bond per plasticizer molecule, w_{pl}^* defines the weight fraction of the plasticizer molecules forming with the polymer units additional hydrogen-bonds through the second and third OH groups in the plasticizer molecule. By this way, the negative deviations in T_g–composition dependence from the weight-average magnitudes relate (by the modified Eq. (2)) T_g to the fractions of the plasticizer reactive groups in the blend rather than to the weight fractions of the plasticizer with the original form of the Fox equation (1). This conjecture is in full agreement with Di Marzio's conclusions drawn from the analysis of the Gordon–Taylor equation [7] and with the Zhurkov rule [6].

Based on established physical meaning of the w_{pl}^* parameter, a number of important hydrogen-bonding characteristics may be easily evaluated from the T_g values measured using Eq. (2). To understand the mechanism of PVP interaction with hydroxyl-containing plasticizers, the entire composition range may be useful to analyse. Effects of blend composition are however embedded in the w_{pl}^* parameter because the latter is obtained from the compositional dependence of blend T_g. This complicates the treatment of the analysis results. In order to justify the definition of the w_{pl}^* quantity as the weight fraction of plasticizer molecules forming two and more hydrogen bonds with PVP units, the evaluated factors related to the w_{pl}^* parameter are compared, whenever possible, with the data of independent measurements. This issue is mainly discussed in the second paper of this series.

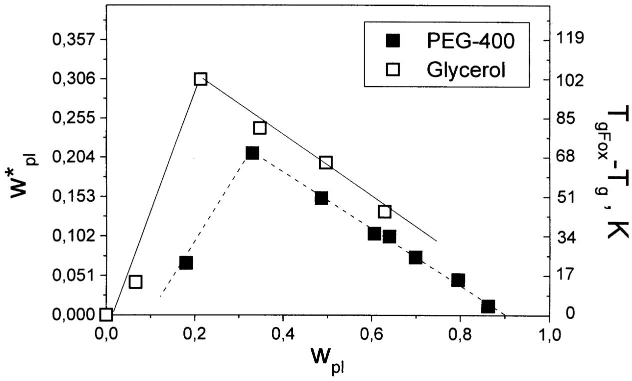

Fig. 3. The plot of adjusting parameter, w_{pl}^*, in Eq. (2) and the negative T_g deviations from the weight-average magnitude found with Eq. (1) against the weight fraction of PEG-400 and glycerol in the blends with PVP, w_{pl}.

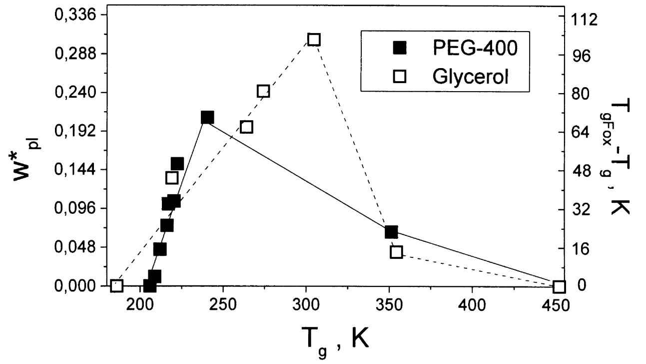

Fig. 4. Dependence of the fitting parameter w_{pl}^* in Eq. (2) and the negative T_g deviations from the values predicted with the Fox equation (1) on the glass transition temperature in PVP blends with glycerol and PEG-400.

If the blend is completely miscible as blends of PVP with hydroxyl-containing plasticizers [8–12], then any functional group of the plasticizer is able to interact with a complementary group of the polymer. As has been defined by Eq. (2), w_{pl} is the weight fraction of the plasticizer molecules capable of forming one hydrogen bond with PVP carbonyls, whereas w_{pl}^* is the weight fraction of the plasticizer molecules forming extra hydrogen bonds with polymer units through the second and third hydroxyl groups in

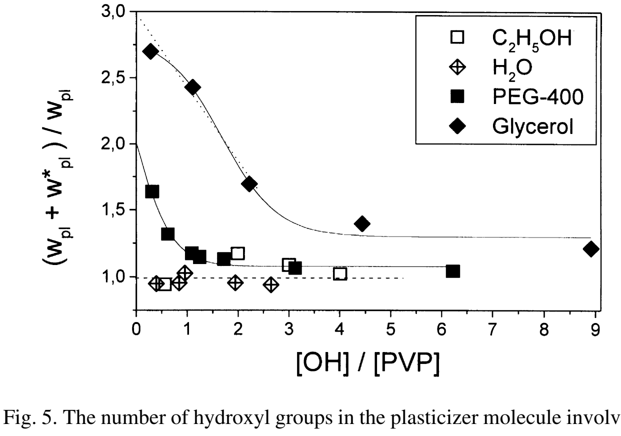

Fig. 5. The number of hydroxyl groups in the plasticizer molecule involved in hydrogen bonding with PVP units over the composition range, evaluated with expression (3). The blends composition is presented as the number of plasticizer hydroxyl groups available in the blend per one PVP repeat unit.

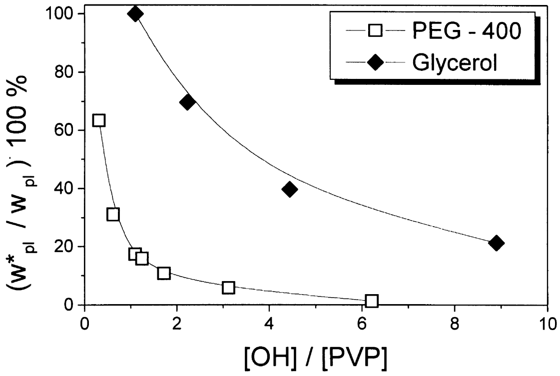

Fig. 6. Effect of blend composition on the fraction of plasticizer molecules (%) forming with PVP units two and more hydrogen bonds through the second and third hydroxyl groups.

the molecule. Consequently, the sum ($w_{\mathrm{pl}} + w^*_{\mathrm{pl}}$) divided by the plasticizer weight fraction characterizes the average number of interacting hydroxyl groups per plasticizer molecule in the blend:

$$\frac{w_{\mathrm{pl}} + w^*_{\mathrm{pl}}}{w_{\mathrm{pl}}}. \tag{3}$$

As the data in Fig. 5 demonstrate, the number of hydroxyl groups involved in hydrogen bonding with polymer units per molecule of plasticizer decreases with an increase of the plasticizer concentration for PEG and glycerol (bearing two and three hydroxyl groups available for interaction). As the plasticizer concentration tends to zero, the number of interacting OH groups in the plasticizer molecule approaches unity for ethanol and water, two for PEG and three for glycerol. This observation confirms unequivocally that the plasticizing effect is an explicit function of the number of hydrogen bonds formed between plasticizer molecules and polymer units.

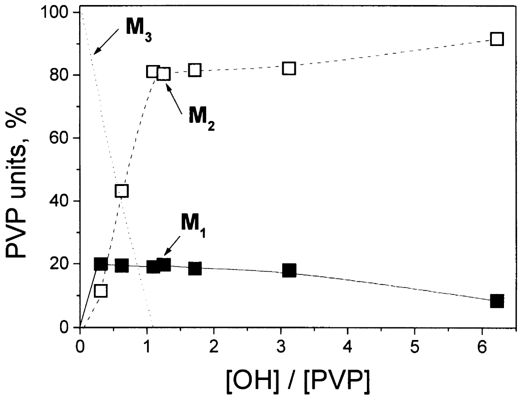

Fig. 7. Dynamics of PVP monomer units involved in crosslinking and hydrogen bonding with PEG-400 as the function of blend composition, estimated using Eqs. (4) and (5). M_1 is the mole percent of crosslinked PVP units; M_2 is the mole percent of PVP units bound with PEG chains, whose opposite terminal hydroxyl groups remain free of hydrogen bonding with polymer; M_3 is the mole percent of PVP units free of hydrogen bonding with PEG hydroxyls.

The question arises why does water plasticizing effect obeys the original form of the Fox equation ($w^*_{\mathrm{pl}} \approx 0$) (Fig. 1), despite the water molecules bearing two protons available for hydrogen bonding with PVP carbonyls? The explanation invokes the steric inability of water molecule to cover simultaneously two PVP units in the glassy state where the conformational rearrangements of polymer backbone are frozen. The distance between protons in water molecule is reported to be 0.150 nm whereas that between the oxygen atoms of neighbouring PVP carbonyls in the glassy state is 0.417 nm. Only within hydrated PVP in solid state above T_g or in solution the pyrrolidone rings in PVP macromolecule have been shown to be able to come closer to each other, allowing the water molecule to use both its proton-donating vacancies in order to form simultaneously two hydrogen bonds with neighbouring PVP repeat units [24]. However, it becomes only possible at relatively large degrees of hydration ($w_{\mathrm{PVP}} > 0.25$) as follows from the T_g dependence on PVP hydration presented in Fig. 1. Measurement of the T_g values within this region of water content is however difficult.

3.3. Dynamics of PVP units cross-linking through hydrogen bonding with PEG and glycerol

As is evident from a linear w^*_{pl}–w_{pl} relationship in Fig. 3, the slope, $w^*_{\mathrm{pl}}/w_{\mathrm{pl}}$, is nearly invariable with PVP and plasticizer weight fractions over a wide concentration range where no lack of plasticizer occurs. By w^*_{pl} definition, $w^*_{\mathrm{pl}}/w_{\mathrm{pl}}$ is a fraction of plasticizer molecules forming with PVP units more than single hydrogen bond. The compositional plot of $w^*_{\mathrm{pl}}/w_{\mathrm{pl}}$ demonstrates a monotonous reduction with the rise of plasticizer concentration, which is especially pronounced within the region where the total numbers of plasticizer hydroxyls available in the blend per one PVP repeat unit is below the number of this group in the plasticizer molecule (Fig. 6). Since the formation of two and more hydrogen bonds per plasticizer molecule leads to crosslinking of PVP units, $w^*_{\mathrm{pl}}/w_{\mathrm{pl}}$ defines the fraction of crosslinker. As is evident from Fig. 6, the crosslinking capability of glycerol is invariably higher than that for PEG within the entire composition range.

It is reasonable to assume that every hydrogen bond links one hydroxyl group in the plasticizer molecule only to a single PVP carbonyl, and vice versa, every PVP carbonyl can be bonded only with a single hydroxyl group of the plasticizer. Consequently, the amount of hydrogen bonds formed by the plasticizer hydroxyls is equal to the number of bonded PVP units. Since every plasticizer molecule, which forms with PVP units two and more hydrogen bonds, acts as a crosslinker, the mole percent of crosslinked

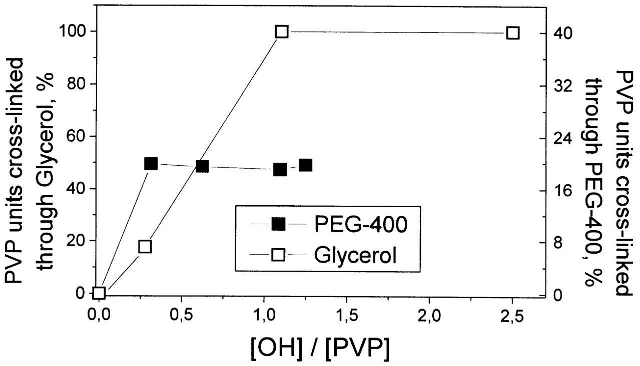

Fig. 8. The content of PVP units (in mole percent) crosslinked by hydrogen bonding with glycerol (left axis) and PEG-400 (right axis) as the function of polymer–plasticizer composition.

PVP units, M_1, may be calculated as:

$$M_1 = \frac{w^*_{\mathrm{pl}}}{w_{\mathrm{pl}}}\frac{[\mathrm{OH}]}{[\mathrm{PVP}]} \times 100\%. \tag{4}$$

The mole percent of PVP units bound with the plasticizer molecule whose other hydroxyl groups remain free of hydrogen bonding with the polymer, M_2, is:

$$M_2 = \left[1 - \frac{w^*_{\mathrm{pl}}}{w_{\mathrm{pl}}}\right]\frac{[\mathrm{OH}]}{[\mathrm{PVP}]} \times 100\%, \tag{5}$$

where [OH] and [PVP] are the mole concentrations of the plasticizer hydroxyl groups and the PVP monomer units in the blend. The mole percent of PVP units free of hydrogen bonding with the plasticizer molecules, M_3, can be obtained as the remainder: $M_3 = 100 - M_1 - M_2$.

Fig. 7 illustrates the dynamics of the variation in the state of PVP units over the composition of PVP blends with PEG-400. No PVP carbonyls, free of hydrogen bonding with PEG terminal hydroxyls, occur in the blends containing an excess of hydroxyl groups ($M_3 = 0$ at [OH]/[PVP] > 1). This finding is expected because in the modified Fox equation (2) the weight fraction of the plasticizer, w_{pl}, has been defined as the fraction of molecules capable of forming at least a single hydrogen bond with the PVP unit and by this definition both the M_2 and M_3 quantities have been determined as remainders (Eq. (5)). For this reason the concentration profiles of M_2 and M_3 quantities have to be ascertained with independent methods such as FTIR spectroscopy in order to make firm conclusions. At the same time, the prediction of the content of crosslinked PVP units, M_1, is unequivocal.

The compositional profile of the M_1 quantity (Fig. 7) achieves a limiting value, nearly 20 mol%, as the number of hydroxyl groups in the blend approaches [OH]/[PVP] = 0.3 (or [PEG-400]/[PVP] = 0.15). The invariability of crosslinked PVP units content in blends over a wide composition range at [OH]/[PVP] $>$ 0.3 is a sign of the stoichiometry of the PVP–PEG network complex.

A similar behaviour also demonstrates the concentration profile of the mole percent of PVP units crosslinked through glycerol molecules (Fig. 8), however the PVP–glycerol network complex has a stoichiometry close to equimolar (more than 80% of crosslinked PVP units for glycerol-overloaded compositions). This complex is completely formed at [OH]/[PVP] = 1. In contrast, the PVP hydrogen-bonded network stoichiometric complex with PEG-400, containing around 20 mol% of crosslinked polymer units, is formed at [OH]/[PVP] = 0.3.

The nature of observed nonequimolar stoichiometry of the PVP–PEG network complex is a subject of our discussion in the second paper in this series. However, it is worth while to note, that the estimated stoichiometry of the PVP–PEG complex, as well as the total degree of hydrogen bonding have been found to match closely the results of our independent measurements [9] provided by FTIR spectroscopy and the analysis of the compositional behaviour of PEG-400 melting enthalpy in miscible blends with PVP [11]. Taking into account both kinetic and thermodynamic contributions to the relationship between the temperatures of glass transition, excess PEG cold crystallization and melting, the non-crystallizing PEG has been earlier identified as that bound with PVP [11]. In the FTIR spectra of the PVP–PEG blends, the bands of 1716, 1680, and 1650 cm^{-1} have been assigned, respectively, to the free of bonding,

Table 2
Comparative evaluation of the hydrogen bonded PVP carbonyl groups mole percent in the blends containing 30, 56, and 280 hydroxyl groups of PEG-400 per 100 PVP units

Method of analysis	Interacting PVP units (mol%)		
	[OH]:[PVP] = 0.3	[OH]:[PVP] = 0.56	[OH]:[PVP] = 2.8
Glass transition temperature	In all: 30 Crosslinked: 20 Loosely bonded: 10	In all: 62 Crosslinked: 20 Loosely bonded: 42	In all: no data Crosslinked: 20
PEG melting enthalpy	No data	In all: 61.6 Strongly H-bonded: no data	In all: 61.6 Strongly H-bonded: no data
FTIR spectroscopy	In all: 23.7 Crosslinked: 15.3 Loosely bonded: 8.4	Not measured	In all: 56.0 Crosslinked: 26.2 Loosely bonded: 29.8

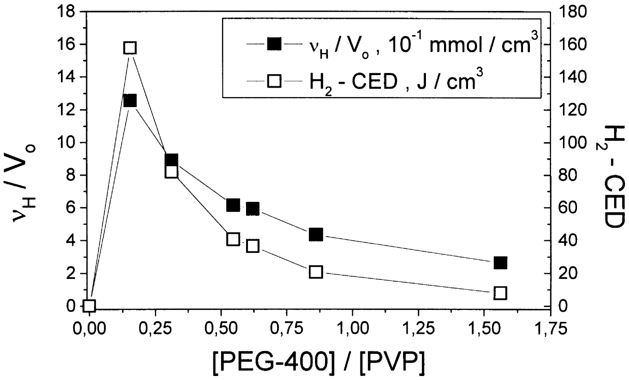

Fig. 9. The composition profiles of the hydrogen bonded network density, ν_H/V_0, and cohesive energy density, H$_2$-CED, evaluated using Eqs. (6) and (7), for PVP blends with PEG-400.

relatively loosely and strongly hydrogen-bonded PVP carbonyls [9]. Involvement of PEG hydroxyls into hydrogen bonding with the carbonyls in the PVP repeat units has been also evaluated on FTIR spectra. The respective bond fractions and energies have been assessed. The obtained data are presented in Table 2 along with the results of the PVP–PEG complex stoichiometry prediction described in this paper.

Three major conclusions may be drawn from the comparative data in Table 2. First, all three independent methods employed to determine the stoichiometry of the PVP–PEG complex yield reasonably close values for the involvement of PVP units into both hydrogen bonding and crosslinking with PEG terminal hydroxyl groups, verifying the validity of the algorithm based on the w^*_{pl} quantity and that presented in this work to describe the dynamics of polymer bonding and crosslinking with multivalent plasticizers. Second, the so-called strong bonding observed with FTIR spectroscopy may be identified as crosslinking the PVP units by hydrogen bonding through both terminal hydroxyls of the PEG chain, while loose bonding most likely results in hydrogen bonding through the single terminal hydroxyl of the PEG macromolecule, whose opposite chain end remains free of hydrogen bonding with the polymer. Third, Eq. (5) allows adequate evaluation of the M_2 quantity in plasticizer-underloaded blends, whereas for plasticizer-overloaded mixtures (at [OH]/[PVP] > 1) the assumption that all PVP units form hydrogen bonds with the plasticizer hydroxyl groups is only adequate for the plasticizers producing equimolar stoichiometric complexes with PVP (exemplified in our study by glycerol and monovalent plasticizers).

3.4. Parameters of hydrogen-bonded network in PVP stoichiometric complex with multivalent plasticizers

Both PEG-400 and glycerol are good solvents for PVP. However, as the data in Figs. 7 and 8 indicate, the stoichiometric PVP–plasticizer crosslinked complexes are stable even in comparatively dilute PVP solutions in respective plasticizers. This follows immediately from the fact that $w^*_{pl} > 0$ even at the excess of plasticizer content (Fig. 3). The dissolution of the network complex in the excess of plasticizer must be naturally preceded by gradual swelling of the hydrogen-bonded network. The T_g-based approach allows evaluating this process.

Since w^*_{pl} has been defined as the weight fraction of crosslinker, and every PEG molecule bears two hydroxyl groups, the weight fraction of the PVP–PEG hydrogen-bonded network junctions is $2w^*_{pl}$. By this way, the PVP–PEG hydrogen-bonded network density, i.e. the number of PEG terminal groups crosslinking the comparatively longer PVP chains by hydrogen bonding per unit volume of a system (ν_H/V_0, mol cm^{-3}), may be evaluated from the T_g–composition relationship using Eq. (6):

$$\frac{\nu_H}{V_0} = \frac{2w^*_{pl}}{MW_{pl}}\rho. \tag{6}$$

The blend densities, ρ, have been calculated from the weight-average values of specific volumes, using $\rho = 1.25$ and 1.125 g cm^{-3} for unblended PVP and PEG, respectively. The data are presented in Fig. 9.

The density of the PVP–PEG hydrogen-bonded network passes through a maximum in the vicinity of stoichiometric complex composition: [OH]/[PVP] = 0.3. For glycerol the network density has been found to be significantly higher. Subsequent increase in plasticizer concentration causes gradual network swelling that results in the decrease of density. Nevertheless, the polymer units remain appreciably crosslinked even at large plasticizer excess, indicating a high resistance of hydrogen-bonded network with respect to the swelling in liquid PEG.

Based on the crosslinks density, other important network characteristics can be readily obtained, e.g. the cohesive energy density of the PVP–PEG hydrogen bonded network, defined as the total average energy of hydrogen bonds crosslinking PVP chains per one PVP macromolecule in the unit volume of blend, H$_2$-CED, J cm^{-3}:

$$\text{H}_2\text{-CED} = \epsilon\left(\frac{\nu_H}{V_0}\right)w_{PVP}. \tag{7}$$

The PVP mixing with PEG-400 has been shown by FTIR spectroscopy to result in the shift of hydrated carbonyls stretching vibration from 1679 to 1655 cm^{-1} and to the corresponding displacement of PEG hydroxyl band from 3455 to 3322 cm^{-1}. This is indicative of a strong hydrogen bonding between these groups ($\Delta H = 21.42$ kJ mol^{-1}) [25]. Taking this value as the energy of the PVP–PEG hydrogen bond, ϵ, using Eq. (7) we can estimate the H$_2$-CED, displayed in Fig. 9.

The composition dependence of H$_2$-CED follows the pattern presented by network density. This finding has been employed to explain the molecular origin of PVP–PEG hydrogel adhesive properties which appear within a narrow range of blend compositions, just in the vicinity of the composition of stoichiometric network complex [13]. The PVP–PEG blend providing the maximum strength of adhesive joints with standard substrate has been found to demonstrate the peak in H_2-CED quantity at [OH]/[PVP] = 0.3, arguing in favour of hydrogen-bonded network contribution to the adhesive behaviour of the PVP–PEG blends.

The existence and features of the hydrogen-bonded network in PVP blends with PEG, evaluated here on the T_g–composition relationship, correlate also to the rubber-like elasticity of the stoichiometric PVP–PEG network complex, established earlier with a variety of rheological methods [8,17]. In particular, specific two-step flow curves inherent in the PVP–PEG adhesive hydrogels reveal the occurrence of yield stress which is an integral characteristic of polymer cohesive strength. Abrupt reduction in the yield stress value with the growth of PEG concentration above the composition corresponding to the formation of stoichiometric complex, coupled with the yield stress vanishing above 135°C, reflect the contributions of the hydrogen-bonded network and confirm the applicability of the w^*_{pl}-based approach for the evaluation of hydrogen-bonded network characteristics.

4. Conclusions

The large negative deviations of the T_g from the weight-average values in the PVP blends have been found typical only for the plasticizers, whose molecules bear two or more reactive hydroxyl groups. Applying the simple rule of mixing presented by the well-known Fox equation and replacing the weight fractions of blend components by the appropriate bond fractions allow us to describe adequately the compositional behaviour of T_g in binary and ternary blends containing such plasticizers. The simple algorithm offered in this work introduces an adjusting parameter, w^*_{pl}, in the Fox equation. The w^*_{pl} is assigned to be the weight fraction of the plasticizer capable of forming two or three hydrogen bonds with PVP repeat units through the second and the third hydroxyl groups in a plasticizer molecule. A range of important characteristics of polymer–plasticizer hydrogen bonding may be easily evaluated using this parameter. These include: the hydrogen-bonding degree and stoichiometry, the composition dependence of reactive groups involvement in hydrogen bonding, the fraction of polymer repeat units crosslinked by hydrogen bonding with hydroxyl groups of multivalent plasticizers. In addition, this approach proved to be capable of estimating the density of a hydrogen-bonded polymer–plasticizer network in terms of average length and molecular weight of polymer chain segments between neighbouring hydrogen-bonded junctions.

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