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Coherence of thermal transitions in poly(*N*-vinyl pyrrolidone)–poly(ethylene glycol) compatible blends
3. Impact of sorbed water upon phase behaviour

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Abstract

The state of sorbed water in hydrogels based on hydrogen-bonded complexes between poly(*N*-vinyl pyrrolidone) (PVP) and short-chain poly(ethylene glycol) (PEG) has been examined by considering water vaporisation endotherms in d.s.c. heating traces and relating them to characteristics of the amorphous and crystalline phases, i.e. the thermodynamic parameters of glass transition and excess PEG melting. In compatible PVP–PEG blends water behaves as a third component in the PVP–PEG complex and is sorbed mainly by PVP, whereas PEG increases the mobility of sorbed water molecules evaluated in the terms of the entropy of water thermodesorption. Water sorption affects dramatically the state of crystalline (excess) PEG in blends, while the state of the amorphous phase, constituted by the PVP–PEG hydrogen-bonded complex, is practically unaffected by hydration.

Keywords: Poly(*N*-vinyl pyrrolidone)–poly(ethylene glycol) blends; Effect of hydration on phase behaviour; State of water

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1. Introduction

It has been well established that water, with its small molecular size, high mobility and hydrogen bonding capacity, in couple with extremely low glass transition temperature (T_g) affects dramatically the phase behaviour and the physical properties of solid hydrophilic polymer composites that spontaneously absorb water vapour from their surroundings [1]. For many reasons there is considerable concern for the state of water in hydrophilic polymer compatible blends. The three major reasons are: (1) the amount of vapour sorbed is related to its interaction with the blends. By comparing this interaction with the interactions between the water and each of the pure polymers, it is possible to obtain useful information about both water–polymer interaction and interaction between polymer blend components [2–5]. (2) The water vapour has been also reported to be highly informative of the phase state and morphology of polymers [6–9]. (3) The water–polymer interaction is often beneficial or detrimental to the performance of commercial polymers.

A treatment of water state in hydrogels is a greater challenge if the effect of sorbed water is obscured or hidden by a strong specific interaction between the polymer components of the composite. This is just the case for a compatible blend based on a stoichiometric hydrogen-bonded complex formed by mixing high molecular weight poly(*N*-vinyl pyrrolidone) (PVP) with the short chain poly(ethylene glycol) (PEG) [10,11]. The PEG, bearing two hydrogen donor hydroxyl groups at both ends of short chains, has shown to form hydrogen bonds with proton acceptor carbonyl units of significantly longer PVP macromolecules. This way, flexible PEG chains act as comparatively long H-bonded crosslinks, creating free volume between cohesively interacting PVP macromolecules [11] and plasticizing glassy PVP because of the free volume formation and greater molecular mobility of the PEG compared with the PVP chain segments [10].

PVP is an amorphous polymer with a high affinity for water and its interaction with water have became the topic of a large body of research [12–23]. PEG is a comparatively less hygroscopic polymer and its interaction with water has also been extensively studied [24–27]. PVP–PEG hydrogen bonding results in the formation of a hydrogel, containing 2–12 wt.% of water taken up from the environment as vapour and as a residual from composite processing. Tailored viscoelastic [11,28], adhesive [29–31], and

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transport properties [32] of the hydrogel are formulated by mixing PVP and PEG in different ratios. Adhesive PVP–PEG hydrogels have successfully been employed for controlled transdermal delivery of a wide range of drugs [33,34]. Variations in water content affect dramatically the pharmaceutical performance properties of the PVP–PEG hydrogels [35]. As water is capable of being absorbed and desorbed from the hydrogel via the vapour state, it is necessary to know the state of the water and control the phase behaviour of the PVP–PEG compatible blends. In particular, it is important to address the following questions: (1) how much water is associated with PVP–PEG complex under given conditions of relative humidity (RH) and storage time? (2) how the water is distributed between the polymer components of the compatible blend? (3) how does water affect the phase transitions in PVP–PEG blend over the whole composition range?

The resolution of these issues demands a complex approach, involving, among other techniques, isothermal water vapour sorption and differential scanning calorimetry (d.s.c.). While kinetics [36] and thermodynamics [37] of water sorption with PVP–PEG blends have been considered in our recent publications, this paper focuses mainly on the impact of sorbed water upon phase behaviour of the PVP–PEG blends by d.s.c.

Both the PVP and the PEG are easily soluble in water, whereas short-chain liquid PEG is also a good solvent for PVP [32]. Consequently, the PVP–PEG hydrogels may be treated either as ternary compatible blends or PVP solutions in the PEG–water cosolvent. As has been evident from earlier papers in this series [38,39], water is not a compatibilizer in the PVP–PEG systems but rather offers serious competition to the PEG for hydrogen bonding with PVP. This conclusion may be inferred from the finding that the amount of noncrystallizable (bound) PEG in dry PVP–PEG blends is larger than in hydrated blends [39]. The inference is notwithstanding quite suspicious because the dry blends and hydrogels have different thermal prehistory.

For the PVP–PEG compatible systems with well-defined temperature regions of free PEG crystallisation–melting and PVP–PEG blend glass transition, the d.s.c. provides useful information on the PEG state in the complex with amorphous PVP [39]. However, d.s.c. also represents a generally recognised technique to explore the state of water associated with hydrophilic polymers in solutions, hydrogels and in the solid phase. The majority of relevant studies deal with freezing and fusion behaviour of absorbed water [24,25,40–44]. When a wet sample is cooled well below 0°C, the free water freezes but the bound water remains in the non-frozen state. When the frozen sample is heated in a calorimeter, the heat required to melt the frozen water can be measured and, consequently, the amount of free and bound water may be readily determined. As no freezing water was found in the PVP–PEG hydrogels exposed to RH of surrounding atmosphere, such an approach was applied to the analysis of free and bound PEG in the blends with amorphous PVP [39]. The use of the d.s.c. technique to characterise the hydration of polymers through water vaporisation endotherms has received cursory attention in the literature [45]. Meanwhile this procedure is also highly informative on the state of the absorbed water, applicable for the blends containing only bound water and no free water, and invokes directly to the energy of polymer dehydration. This approach is employed in this work for the characterisation of water sorbed with the PVP–PEG hydrogels.

2. Experimental

PVP (Kollidon K-90), $M_w = 1,000,000\ \mathrm{g\ mol^{-1}}$, and PEG-400 (Lutrol E-400), $M_w = 400\ \mathrm{g\ mol^{-1}}$, were obtained from BASF. PEG of the molecular weight of 1000 g $\mathrm{mol^{-1}}$ (PEG-1000) was produced by Fluka. All polymers were used as-received.

The basic experimental procedures employed in this work were introduced in a previous paper in this series [38]. PVP–PEG blends, covering a full range of compositions, were prepared by dissolution of both polymers in common solvents (ethyl alcohol or water) 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 f.t.-i.r.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 fresh blends produced from ethyl alcohol and water was found to demonstrate similar phase behaviour but slightly different hydration.

Samples were analysed with a Mettler TA 4000/DSC 30 thermoanalyser, calibrated with indium and gallium. 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 ml $\mathrm{min^{-1}}$) 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 at a rate of 20°C $\mathrm{min^{-1}}$ to 220°C. The content of absorbed water in the blends was determined by weighing the samples before and after d.s.c. scans using a Mettler Analysis 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 d.s.c. For this comparison only those weight losses were taken into account, which were inherent to the samples demonstrating stable base line behaviour in d.s.c. thermograms for fully dehydrated blends.

After first testing the freshly prepared blends were either stored at ambient temperature within the period of 12 months in different environments (surrounding atmosphere

Table 1
Climatic conditions at the day of DSC examination of PVP–PEG hydrogels

Date	Indoor		Outdoor	
	T (°C)	RH (%)	*T* (°C)	RH (%)
7 February	20	42	−16.6	70
17 April	21	50	7.0	62
27 May	22	65	14.4	75

at various weather conditions) or equilibrated in desiccators, maintaining RH = 50% at 25°C. The blends were then re-evaluated at random intervals within early February, mid April and late May, that is 9, 11 and 12 months after the first d.s.c. measurement. The weather conditions at the date of d.s.c. testing of the aged PVP–PEG blends exposed to atmosphere humidities and temperatures are presented in Table 1.

Isotherms of water vapour sorption with PVP and PVP–PEG blends were measured gravimetrically. The PET-supported films of 0.25–0.30 mm in thickness were prepared by casting and drying the PVP–PEG solutions in ethyl alcohol. As constant weight was attained, the films were dried in a vacuum of 1×10^{-5} Torr at 80°C and then subjected to fixed RHs in desiccators over aqueous H_2SO_4 solutions of controlled density which maintained the required RH ranged from 10 to 90%.

Multiple regression analysis of the relationships examined in this work was performed with an Intel Celeron PC (366 MHz) using a MICROCAL ORIGIN 4.1 software.

3. Results and discussion

3.1. The state of water in PVP–PEG hydrogels

As has been earlier reported [38], after having been set aside for a period of up to one year after first d.s.c. measurement, freshly prepared PVP–PEG compatible blends demonstrate evidences of long-term evolution or "ageing", manifested by significant changes in phase behaviour. For instance, the blend containing 53 wt.% of PEG-400 that initially shows crystalline phase, loses its crystallinity after nine months of storage at ambient temperature and RH (Fig. 14 in Ref. [38]). This fact is explicable in view of an observed T_g increase that has been shown to enhance dramatically a kinetic restriction imposed upon the PEG cold crystallisation process in the blends dilute with amorphous PVP [39]. The samples conditioned in different environments for different times reveal coherent but distinct relationships between T_g, a maximum cold crystallisation rate temperature, T_c, and the temperature of PEG melting, T_m. Those are affected by the sample prehistory, as has been exemplified by the data in Figs. 6 and 7 in Ref. [38].

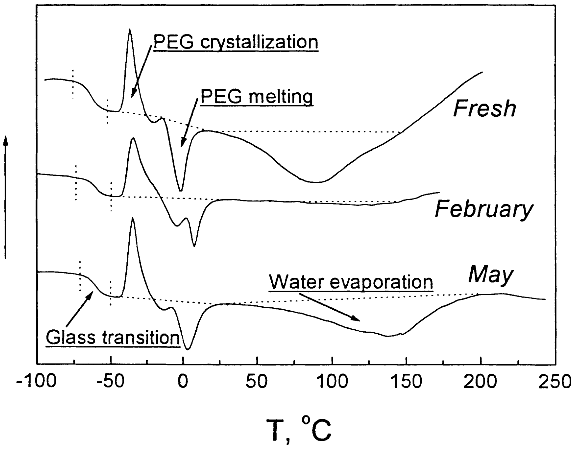

Fig. 1. D.s.c. heating thermograms of freshly prepared PVP blends with 69 wt% of PEG-400 and those conditioned in atmosphere environments for 9 (February) and 12 (May) months.

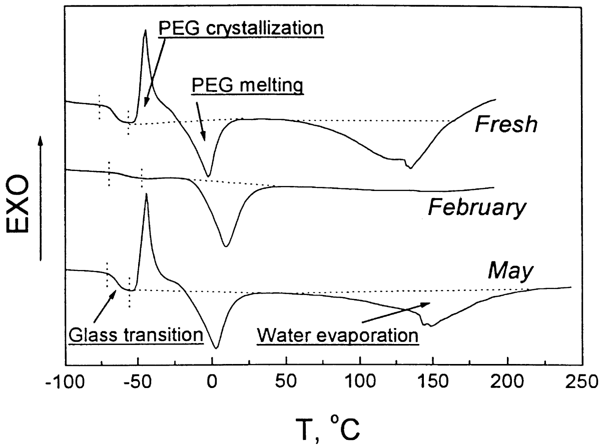

Fig. 2. D.s.c. traces of heating freshly prepared PVP blends containing 85 wt% of PEG-400 and those exposed to surrounding atmosphere conditions for 9 (February) and 12 (May) months.

Other examples of storage conditions effect on the phase behaviour of PVP–PEG blends are presented in Figs. 1 and 2. Long-term exposure of freshly prepared blends (hydrogels) to surrounding atmosphere humidity leads to drying of the samples as is indicated by the area under broad endotherm of water desorption at high temperatures. In accordance with seasonal variations in RH (Table 1), the so-called February blends have found to be much drier than the same samples re-evaluated within May. The blend T_g is not markedly affected by hydration, but the change in heat capacity between the glassy and viscoelastic states, ΔC_p, is increased as the enthalpy of water vaporisation endotherm increases. A major characteristic feature of PVP blends containing 69 wt.% of PEG-400 (Fig. 1) is multiple melting peaks whose sizes and temperatures are dependent on hydration. The drier the blend the larger the area of the lowest temperature endotherm of PEG fusion and the higher relevant melting point. In general, there are two plausible explanations for this phenomenon. One is that the multiple peaks reflect the presence of different crystal structures related to different states of PEG-400 in hydrogen bonded

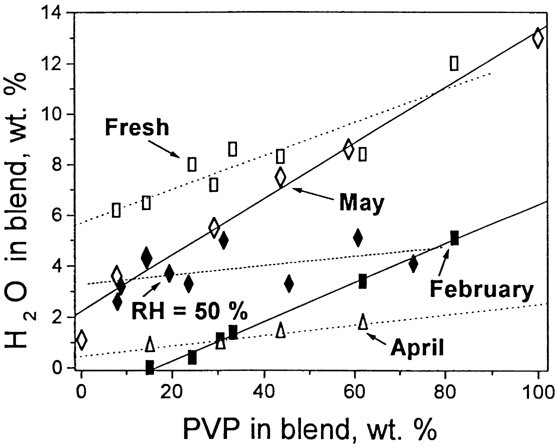

Fig. 3. Sorbed water content relation to PVP concentration in freshly prepared and aged PVP–PEG hydrogels conditioned in different environments.

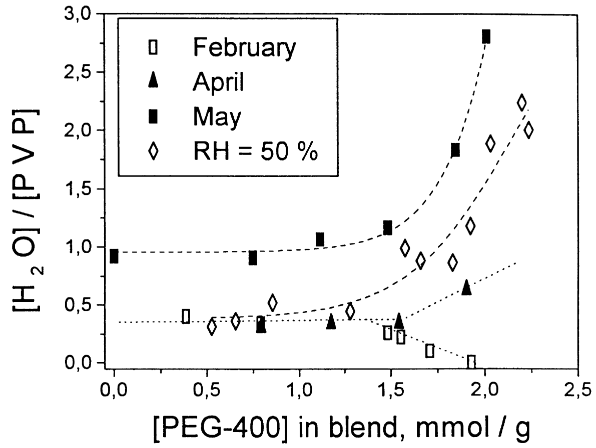

Fig. 4. The number of water molecules sorbed in PVP–PEG blends per every PVP unit as a function of 10-unit PEG chains concentration in the systems exposed to different environments.

complex with PVP [10,11,46]. The other explanation is that the peaks are a consequence of reorganisation occurring during the heating process, perhaps involving the superposition of PEG melting and cold crystallisation or merely processes such as PEG lamellar thickening. The mechanism of this phenomenon is not yet well understood and goes beyond the frameworks of the present study. The most interesting feature of the PVP–PEG blend phase behaviour in Fig. 2 is that PEG cold crystallisation occurs solely in hydrated systems and does not appear in quench-cooled dry (February) blends, while the presence of the crystalline phase in these kinetically non-restricted systems is verified by the PEG fusion endotherm. In common with amorphous PVP, absorbed water causes a diluent effect on PEG cold crystallisation [39]. As has been expected, the drier the blends the higher the PEG melting temperature.

Whether or not the PVP–PEG–water ternary compatible blend has reached its thermodynamic equilibrium state depends upon storage time and conditions, which affect the blend composition through sorption of water vapour from the surrounding atmosphere. It is readily possible that this compatible system may not be molecularly homogeneous under a particular set of conditions and that individual molecules of each component may cluster in very small domains. Clustering of PEG-400 in the amorphous phase constituted by PVP has been established with a w.a.x.s. technique [10]. An average cluster size of sorbed water in PVP–PEG hydrogels has been found to range between 1 and 2 molecules [37], which is indicative of homogeneous distribution of water molecules associated with PVP–PEG blends. The implication of the data in Fig. 2 is that the PEG clustering in dry (February) blend is much advanced compared with that following three months of further relaxation in May systems; and that only water sorption but not ageing time is primarily responsible for the partial dilution of PEG clusters and the appearance of PEG cold crystallisation phenomena within the period from February to May. Indeed, the phase behaviour of the blends equilibrated to controlled RH = 50% has shown to be practically invariable with the storage duration.

Based on the results of the water desorption comparative study from PVP–PEG hydrogels with d.s.c. and thermogravimetric analysis (t.g.a.) presented in Table 2 of Ref. [38], we have assessed blend hydration as a ratio of the area under water thermodesorption endotherm in d.s.c. thermograms (in Joules per gram sample) to the reference value of water cluster vaporisation enthalpy (2255 J g^{-1}). As is evident from the data in Fig. 3, PVP is much more hygroscopic than PEG. The blend hydration is therefore linearly proportional to the PVP content indicating that water vapour is mainly associated with PVP. Observed seasonal fluctuations in the water sorption are the results of variations in the RH of surrounding atmosphere (Table 1). The slopes of the linear relationships in Fig. 3 represent the amount of water sorbed within the blend per unit weight of PVP and the plots' linearity is therefore indicative of predominant water association with PVP. Replotting these data in the terms of the number of water molecules absorbed in the blends per every PVP repeat unit versus the molar concentration of 10-unit PEG-400 macromolecules (Fig. 4) demonstrates that over a wide range of PVP–PEG compositions the water vapour sorption is in essence invariant with PEG content and equal to one water molecule associated with two PVP units in aged blends and to equimolar water sorption in freshly prepared (hydrated) systems. Bending of the curves in Fig. 4 for PEG-overloaded blends relates most likely to low PVP content at which the PEG contribution to vapour uptake becomes important.

In order to confirm and refine more strictly the inference derived from the data in Figs. 3 and 4, the isotherms of water vapour sorption with PVP–PEG blends have been measured accurately with an isopiestic method [37]. The amount of sorbed water vapour, expressed as the number of water molecules sorbed in blends per one PVP unit, is plotted in

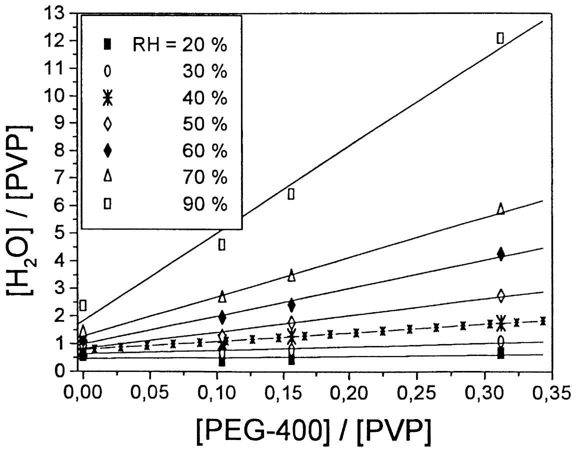

Fig. 5. The number of water molecules, sorbed in PVP–PEG blends per one PVP unit, as a function of the blend composition for different relative humidities (RH) of surrounding atmosphere at 20°C.

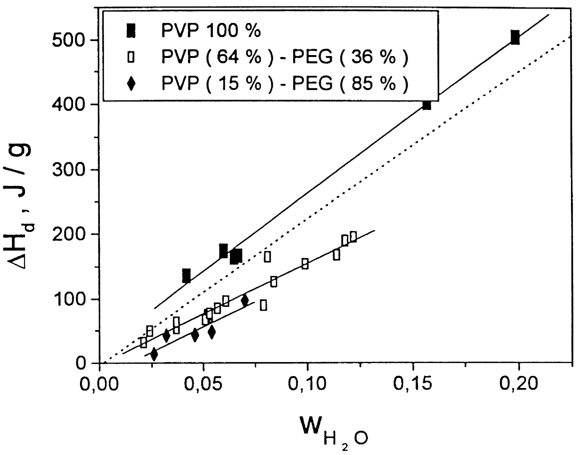

Fig. 6. The heat of water vaporisation, normalised by unit sample weight, as a function of sorbed water in PVP and PVP–PEG blends (in grams of water per gram of the sample).

Fig. 5 against the blend composition, expressed in the terms of the number of PEG-400 macromolecules available in the blends per PVP unit. All the plots in Fig. 5 are unequivocally linear, with the intercepts relating to the number of water molecules associated with PVP unit at zero PEG concentration, and with the slopes determining the average number of water molecules arranged per 10-unit PEG-400 macromolecule, $[H_2O]/[PEG\text{-}400]$. Water binding degree with PVP units, $[H_2O]/[PVP]$, is found by subtracting the quantity of water associated with PEG (the slope) from the total amount of sorbed water, and shown to coincide exactly with relevant intercepts. Only at RH = 20% all the absorbed water is solely associated with PVP units, as the slope of this plot (Fig. 5) is zero. The higher RH the more water molecules are associated with PEG. The plot linearity provides an evidence that hydrogen bonding of PEG hydroxyls to the carbonyls in PVP units proceeds directly through water molecules arranged at PVP units causing no appreciable desorption of the water. In this respect the mechanism of PVP–PEG interaction in hydrogels may be treated as the binding of PEG terminal groups with equilibrium hydrated PVP units. In other words, the ternary blend PVP–PEG–water may be regarded as a binary blend formed by PEG and equilibrium hydrated PVP.

In this way both d.s.c. and isothermal water sorption furnish similar information concerning which component of the PVP–PEG compatible blend is the water associated. Water sorption isotherms confirm qualitatively the d.s.c. applicability to characterise the state of water in the blends, but at the same time they reveal serious quantitative discrepancies in the amount of sorbed water evaluated with both methods. The water sorption measured with the isopiestic method has been established to give values that are nearly twice as large as those estimated on the size of water desorption endotherms in d.s.c. heating thermograms. A range of reasons can be responsible for the lower level of sorbed water assessed with d.s.c. First, water sorption isotherms have been obtained in thin films, whereas rather thick samples tested with d.s.c. require longer time to reach equilibrium sorption and, being exposed to ever-changing RH of surrounding atmosphere, cannot be really equilibrated. Second, the isotherms have been measured in the course of isopiestic water absorption at fixed temperature, while the d.s.c. data relate to water desorption under heating and, consequently, hysteresis phenomena can contribute to the observed deficiency of equivalence between d.s.c. and isothermal sorption. Third, a Mettler instrument represents a thermoanalyser, measuring a sample pan temperature against the temperature of reference pan. In the process of water vaporisation the sample temperature can be non-uniform. Also, vapour exchange with the surroundings may be impeded as the amount of sample increases. Although d.s.c. measurements of sample hydration revealed also good agreement with t.g.a. results [38], firm conclusions necessitate the examination of a larger data set.

For this purpose the enthalpy of water thermodesorption upon heating the blends by d.s.c. has been studied as a function of blend hydration determined by weight loss after scanning. Fig. 6 shows a plot of water thermodesorption enthalpy, ΔH_d, against the weight fraction of water, evaporated from PVP and its blends with 36 and 85 wt.% of PEG-400. The data sets involve both freshly prepared and aged blends as well as the samples exposed to RH = 50%. The linear relationships indicate that ΔH_d depends solely on the water content and is unaffected by the time of blend storage. Consequently, the state of water in PVP–PEG blends is not subjected to any long-term evolution as has been found for the state of PEG. The slopes, equal to $2415 \pm 102\ \mathrm{J\,g^{-1}}$ for PVP ($R = 0.997$, $p < 0.0001$), $1569 \pm 122\ \mathrm{J\,g^{-1}}$ for PVP blend with 36 wt.% of PEG ($R = 0.960$, $p < 0.0001$), and $1577 \pm 386\ \mathrm{J\,g^{-1}}$ for 15% PVP solution in PEG-400 ($R = 0.921, p = 0.027$), represent the heats required to remove a unit mass of water from the listed systems. The dotted line designates

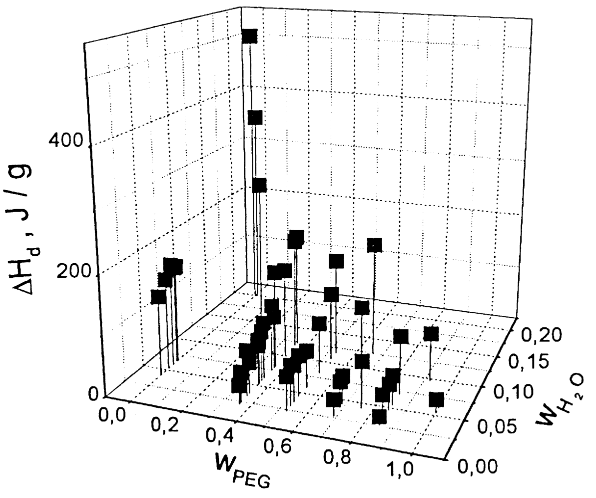

Fig. 7. Effects of hydration and PEG content in blends, expressed in weight fractions, on the enthalpy of water thermodesorption, normalised by unit sample weight.

the heat of pure (cluster) water evaporation, determined upon heating bulk water in the same Mettler apparatus and found to match the reference value of 2255 J g^{-1} under normal conditions. The found values are thus somewhat increased for PVP and significantly decreased for the hydrogels spanning a wide range of PVP–PEG compositions.

Multiple linear regression analysis of the relationship between the heat of water desorption, ΔH_d, and the weight fractions of desorbed water and PEG in blends, shown in Fig. 7, yields the following equation:

$$\Delta H_d(\mathrm{J\,g^{-1}}) = \underset{p<0.0001}{(1670 \pm 114)w_{H_2O}} - \underset{p<0.0001}{(115 \pm 17)w_{PEG}} + \underset{p=0.0005}{(51 \pm 14)} \quad (1)$$

$$R^2 = 0.895$$

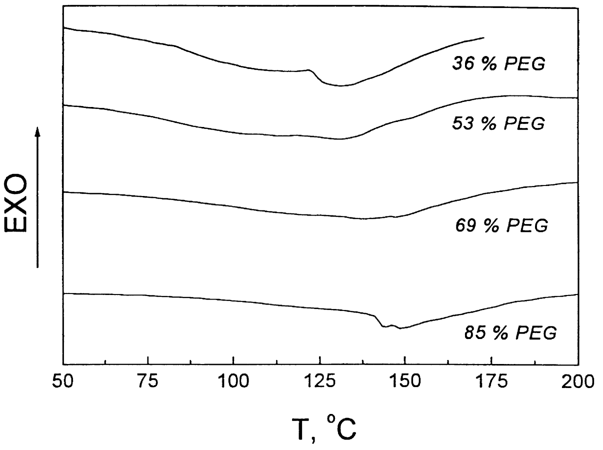

Fig. 8. Effect of composition on the endotherm of water desorption from the PVP–PEG blends evaluated within the month of May.

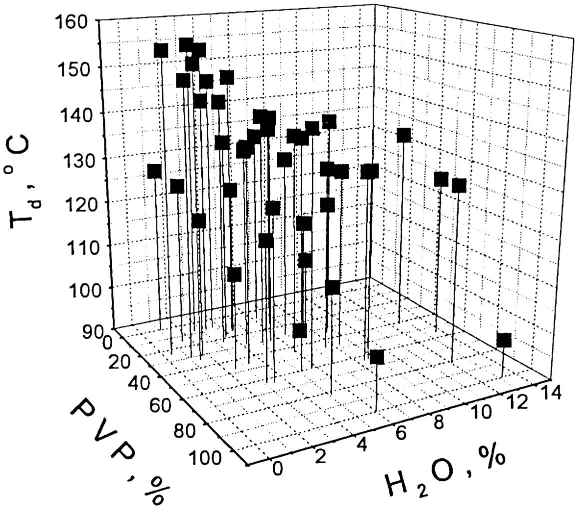

Fig. 9. Temperature of water thermodesorption from PVP–PEG blends, T_d (°C), plotted against the concentrations of PVP and water (in weight percent).

Blend hydration, measured through the enthalpy of water desorption, increases with the content of most hygroscopic polymer, PVP. In full accordance with the data presented in Figs. 3 and 6, the ΔH_d dependence on hydration and PEG content follows a linear law, that is evident from fairly reasonable fit. The intercept is acceptably close to zero, whereas the slope for the ΔH_d dependence on water content matches closely the value determined earlier from the data in Fig. 6.

As is seen from Figs. 1, 2 and 8, the temperature of water desorption, T_d, is affected both by blend hydration and polymer composition. The peak temperature of water vaporisation endotherm tends to increase with decrease in hydration and the rise in PEG content. Multiple thermodesorption behaviour of sorbed water reveals the occurrence of distinct states of the water associated with PVP–PEG blends, and complicates significantly T_d establishment for highly broad endotherms as well as for split peaks. While similar difficulties have been bypassed in the ΔH_d analysis by taking into account the integrated heats of water desorption, such an approach provides very rough estimate of T_d and all the quantities related to this temperature. On this basis, it is not surprising that the T_d relation to PVP–PEG composition and water content, presented in Fig. 9, gives a fairly bad fit ($R^2 = 0.262$):

$$T_d(°\mathrm{C}) = \underset{p<0.0001}{(145.2 \pm 4.4)} - \underset{p=0.0211}{(0.21 \pm 0.09)\%\mathrm{PVP}} - \underset{p=0.111}{(1.10 \pm 0.68)\%\mathrm{H_2O}} \quad (2)$$

The intercept is reasonably close to the water desorption peak temperature for PEG-400, obtained from d.s.c. traces. An elevation of T_d upon adding PEG-400 to PVP is also quite reliably established by regression analysis, while the

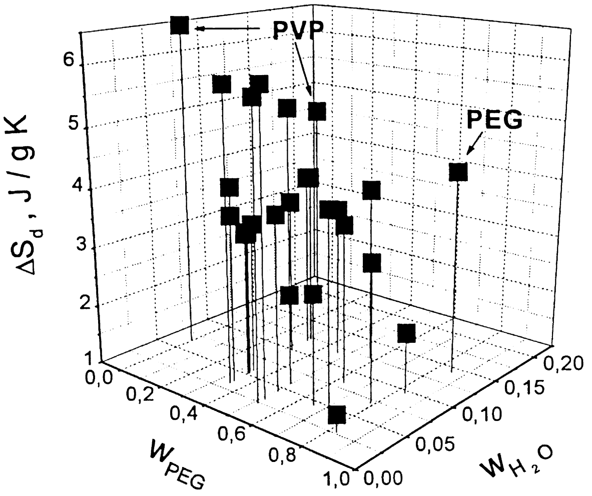

Fig. 10. The plot of the change in entropy, associated with water vaporisation from PVP–PEG hydrogels, ΔS_d, versus PEG content and blend hydration. The ΔS_d values are normalised to unit weight of desorbed water.

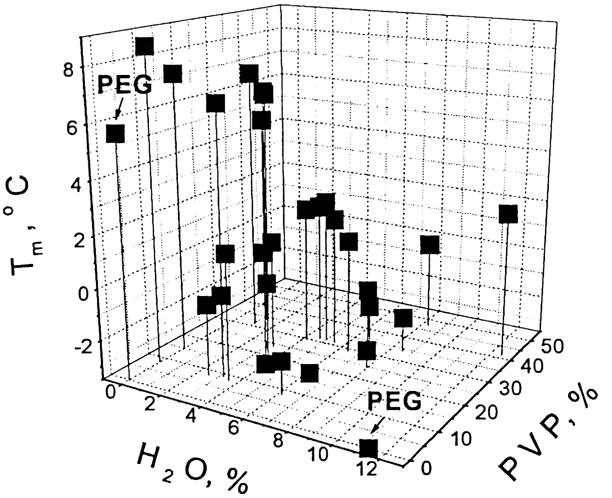

Fig. 11. Relation of PEG melting temperature, T_m, to the composition and hydration of PVP–PEG compatible blends.

hydration effect on T_d is insufficiently plausible, apparently due to the mentioned problems with T_d measurements.

The enthalpy of thermal water desorption from PVP–PEG hydrogels relates to the T_d through the change in entropy associated with water desorption, $\Delta S_d = \Delta H_d/T_d$. The latter is shown in Fig. 10 as a function of PEG and water weight fractions in the blends:

$$\Delta S_d(\mathrm{J\ g^{-1}\ K^{-1}}) = \underset{p<0.0001}{(5.35 \pm 0.66)} - \underset{p=0.009}{(2.65 \pm 0.94)}w_{\mathrm{PEG}} - \underset{p=0.607}{(2.53 \pm 4.85)}w_{\mathrm{H_2O}} \qquad (3)$$

$$R^2 = 0.260$$

Similar to the T_d behaviour, the multiple regression shows quite reliable ΔS_d reduction with an increase in the PEG content, while the effect of hydration, determined by the weight loss of the samples after scanning, is found to be unreliable. This is however the result of the overall regression of complete data set, spanning a whole range of PVP–PEG compositions and a wide range of blend hydration. Closer inspection of the data in Fig. 10 allows us to refine our insight into the state of water in PVP–PEG hydrogels. Water sorption in PVP and PVP–overloaded systems is accompanied by an appreciable reduction in ΔS_d. In contrast, in PEG and PEG-overloaded blends the increase in water sorption reveals growth of ΔS_d. Within an intermediate region of PEG concentrations, ΔS_d is invariable with hydration.

Considering that in the vapour phase a water molecule possesses a maximum number of degrees of freedom, defined as the number of independent variables that must be specified to fix the position of the molecule and its velocity, higher ΔS_d values correspond to a maximum order of water accommodation in solid (or liquid) blend, i.e. maximum strength of sorption. The increase in ΔS_d with the rise of PVP concentration (Fig. 10) is therefore indicative of water immobilisation and structural organisation in the course of sorption with PVP units. At the same time, adding PEG to PVP increases the number of degrees of freedom of water molecules in polymer blends. In dry PVP and PVP-rich blends all the water is tightly bound, and hydration leads to the appearance of loosely bound water. In contrast, in dry PEG and PEG-overloaded blends the strength of hydrogen bonds formed between water molecule and PEG is much looser than those formed between water molecules in clusters, and hydration, accompanied by the clustering of sorbed water, results in an appreciable ΔS_d increase. The intercept in Eq. (3) relates to the entropy of water evaporation from dry PVP. The experimental magnitude obtained for PVP containing 6.5% of sorbed water, $\Delta S_d = 6.50\ \mathrm{J\ g^{-1}\ K^{-1}}$, is higher than the reference value for bulk water vaporisation, $\Delta S_d = 6.05\ \mathrm{J\ g^{-1}\ K^{-1}}$. It follows that, unlike for pure PEG, the hydrogen bonds between water molecules and PVP units are stronger than those in water clusters.

3.2. Effects of sorbed water on phase behaviour of PVP–PEG blends

To gain further insight into the interactions within triple blend PVP–PEG–sorbed water, the melting behaviour of the crystalline phase, constituted by PEG-400, and glass transition behaviour of amorphous PVP–PEG complex should be taken into consideration.

As expected, the melting temperature (T_m) behaviour of short-chain PEG is complicated due to the interactions of all the components in PVP–PEG–water compatible blends, both separately and in a concerted manner (Fig. 11). At

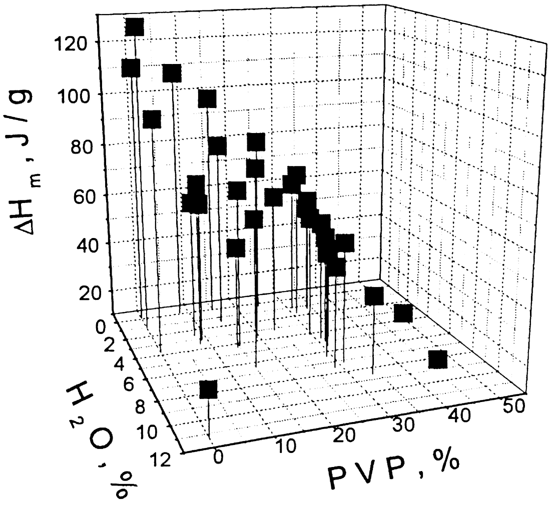

Fig. 12. Enthalpy of PEG fusion, normalised by 1 g of added PEG-400, as a function of PVP and water content within fresh and aged PVP–PEG blends.

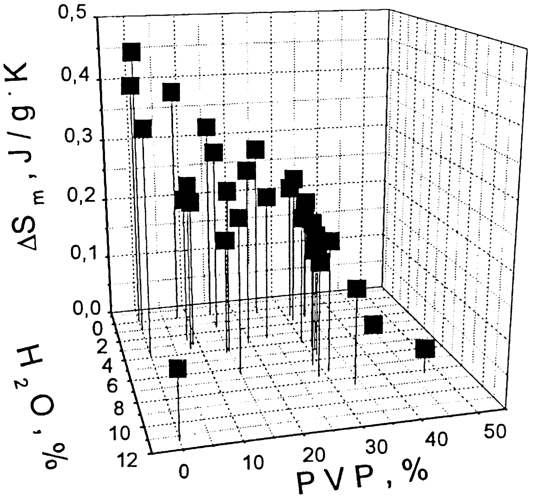

Fig. 13. Entropy of PEG melting, normalised to unit weight of PEG-400, plotted against PVP content and blend hydration.

low blend hydration level (<2% H_2O), PVP causes some composition-dependent T_m depression that is indicative of blend compatibility. In contrast, for hydrated blends (>6% H_2O) the T_m tends to increase as PVP concentration increases. Taking water associated with PVP–PEG blends away from the PEG, hygroscopic PVP improves the perfection of PEG crystals. Within the intermediate range of blend hydration the PVP does not affect appreciably the melting point of blended PEG. The PEG macromolecules interact with PVP units through terminal hydroxyl groups, which have been reported to be exposed outward crystalline grains [47]. The postulated structure of the PVP–PEG complex may be therefore treated as the PVP chains sorbed on the end faces of the PEG crystals. Decreasing the surface energy of PEG crystals, the PVP–PEG interaction should cause an increase in the PEG melting point. Indeed, as is seen from Fig. 11, at low water content the PEG blends with a small amount of PVP demonstrate significantly higher melting temperatures than found for dry PEG-400, while further PEG mixing with amorphous PVP shows a distinct T_m depression.

The multiple regression analysis of PVP and hydration effects on the PEG melting temperature reveals the reliable dependence on all the variables ($R^2 = 0.762$):

$$T_m(°\mathrm{C}) = \underset{p=0.0018}{(2.9 \pm 0.9)} - \underset{p<0.0001}{(1.07 \pm 0.12)\%\mathrm{H_2O}} + \underset{p<0.0001}{(0.14 \pm 0.03)\%\mathrm{PVP}} \quad (4)$$

The water contribution to T_m depression dominates the PVP effect, which is by, and large opposite in direction. The intercept, defined as the melting point of dry PEG-400, is acceptably close to measured value (5.8°C).

A change in the entropy of PEG melting, normalised to unit PEG weight, ΔH_m, is a measure of PEG crystallinity degree in blend. For the complete data set, including both freshly prepared and aged blends, the crystallinity decreases as PVP and hydration grow in the blend (Fig. 12), but the water diluent effect on PEG crystallinity is much more pronounced than the effect of the amorphous PVP:

$$\Delta H_m(\mathrm{J\ g^{-1}}) = \underset{p<0.0001}{(108.4 \pm 5.0)} - \underset{p<0.0001}{(4.91 \pm 0.78)\%\mathrm{H_2O}} - \underset{p<0.0001}{(1.18 \pm 0.18)\%\mathrm{PVP}} \quad (5)$$

$R^2 = 0.805$

An intercept specifies the heat of fusion of pure PEG-400. It is in a close agreement with the reference value ranged between 112 and 121 J g^{-1}. The obtained fit indicates that no PEG structural rearrangement occurs in PVP–PEG blends and that the earlier mentioned long-term evolution processes in phase behaviour are solely due to the fluctuations in water vapour sorption. Small and mobile water molecules penetrate deeper into the crystalline phase than PVP chain segments, leading to crystal deterioration.

A change in PEG fusion entropy, $\Delta S_m = \Delta H_m / T_m$, is informative of the change in PEG order at transition from crystalline phase to melt. It should be emphasized that PEG oligomers have been reported to retain in the melt a crystal-like parallel chain orientation, although interchain distances are rather typical of amorphous polymers [48]. For this reason the change in entropy of PEG-400 melting is not so large as has been reported [47] for high molecular weight poly(ethylene oxide) (0.58 J g^{-1} K^{-1}) and found to be $\Delta S_m = 0.44$ J g^{-1} K^{-1} for dry polymer, decreasing rapidly with hydration. As the PEG-400 is bound with PVP in molten state and their complex is characterised with PEG parallel chain arrangement [11], the entropy of PEG fusion in blends is expected to be reduced compared with pure polymer.

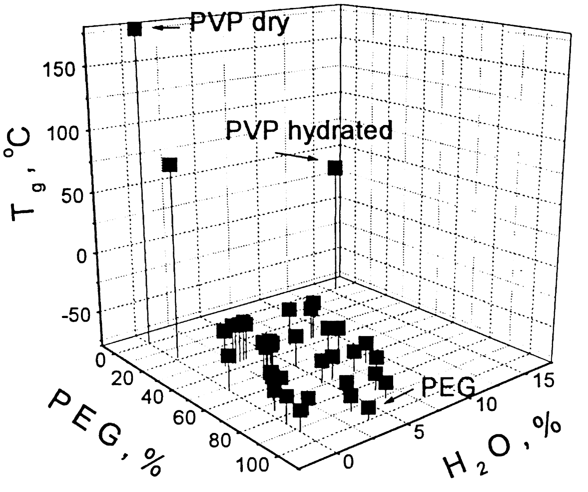

Fig. 14. The glass transition temperature of PVP–PEG compatible blends as a function of PEG and water content.

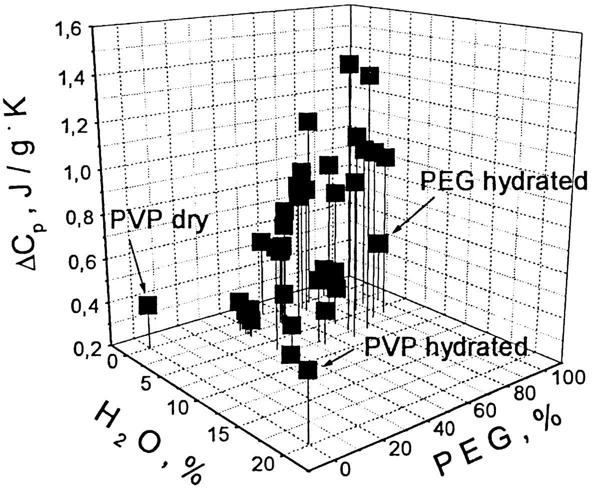

Fig. 15. Effects of PEG and hydration on ΔC_p of PVP–PEG compatible blends.

Indeed, as Fig. 13 demonstrates, for the complete data set, combining both fresh and aged blends conditioned in different environments, at low PVP content the ΔS_m reveals a rapid decline as sorption of water vapour proceeds, indicating unequivocal disordering of the PEG crystalline phase. To the contrary, as PVP content exceeds 30 wt.% the ΔS_m becomes lower and essentially invariant with blend hydration. Highly hygroscopic PVP protects the PEG from water uptake. At the same time, similar to water, mixing PEG with PVP causes a pronounced ΔS_m reduction. Low ΔS_m values reveal a similarity between PEG degrees of freedom in the crystalline phase and in the melt. Either PVP serves to bind PEG chains in the melt, or it causes disordering of PEG crystals, or both. Order of the bound PEG chains arrangement within the complex has been shown to match closely that of crystalline phase [11]. The multiple regression of the ΔS_m dependence on PVP and water content gives a reasonable fit ($R^2 = 0.786$):

$$\Delta S_m(\mathrm{J\,g^{-1}\,K^{-1}}) = \underset{p<0.0001}{(0.39 \pm 0.02)} - \underset{p<0.0001}{(0.017 \pm 0.003)}\%\mathrm{H_2O} - \underset{p<0.0001}{(0.004 \pm 0.001)}\%\mathrm{PVP} \qquad (6)$$

The intercept obtained by multiple regression analysis is in close agreement with the ΔS_m value determined for pure PEG-400. The contribution of water to the ΔS_m depression is nearly four-times greater than that of PVP.

The reported results on the PEG melting behaviour relate to the PEG-overloaded blends and to the state of PEG at the stage of PVP–PEG complex dissolution in excess PEG-400. The complex formation occurs at the stage of glassy PVP plasticization with relatively small amount of liquid PEG where no crystalline phase has been observed. It is of great importance therefore to include into consideration the PEG-underloaded amorphous blends. This is made possible by the analysis of the PEG and hydration effects on the characteristics of blend glass transition, T_g and ΔC_p. The implication of PEG effect on T_g and ΔC_p has been discussed in an earlier paper [38] and here the impact of blend hydration is examined along with the PEG effect (Figs. 14 and 15).

Mixing PVP with liquid PEG results in a rapid drop of T_g over 220°C within the PEG concentration region from 0 to 36 wt.% followed by the levelling off the response at higher PEG content (Fig. 14). The impact of water on T_g behaviour is evidently negligible compared to the PEG effect. Regression of T_g dependence on the PEG and sorbed water contents yields:

$$T_g(°\mathrm{C}) = \underset{p=0.015}{(41.02 \pm 16.00)} - \underset{p<0.0001}{(1.34 \pm 0.22)}\%\mathrm{PEG} - \underset{p=0.104}{(2.70 \pm 1.62)}\%\mathrm{H_2O} \qquad (7)$$

Linear regression does not explain the trends ($R^2 = 0.499$) because the PVP plasticization is a pronounced two-stage process that does not obey any linear relationship. The intercept is also unacceptably distinct from the T_g of dry PVP (178°C). The interesting feature of the analysed relationship (7) is that the sorbed water plasticizing action, though insufficiently reliable, dominates that of PEG-400. To describe the relationship in Fig. 14 more accurately, we have performed its multiple regression analyses separately at the stage of PVP plasticization (complexation) with PEG, i.e. within the PEG concentration region <40 wt.%, and at the stage of PVP–PEG stoichiometric complex dissolution in liquid PEG-400 (>40% PEG). At the first stage of PVP–PEG complexation the glass transition temperature follows the relationship (8):

$$T_g(^\circ\mathrm{C}) = \underset{p<0.0001}{(160.78 \pm 15.42)} - \underset{p<0.0001}{(5.02 \pm 0.42)}\%\mathrm{PEG} - \underset{p=0.0004}{(6.58 \pm 1.32)}\%\mathrm{H_2O} \quad (8)$$

$$R^2 = 0.944$$

This regression is highly significant, yielding the intercept reasonably close to the obtained T_g magnitude of pure PVP. At the second stage of PVP–PEG complex dissolution in excess PEG-400 (>40 wt.% PEG):

$$T_g(^\circ\mathrm{C}) = -\underset{p<0.0001}{(34.62 \pm 1.28)} - \underset{p<0.0001}{(0.34 \pm 0.02)}\%\mathrm{PEG} - \underset{p=0.0004}{(0.51 \pm 0.13)}\%\mathrm{H_2O} \quad (9)$$

$$R^2 = 0.919$$

A physical meaning of the intercept is a characteristic value of PVP–PEG stoichiometric complex glass transition temperature at zero hydration. The plasticizing action of sorbed water is comparable with PEG-400 effect.

A specific form of ΔC_p dependence on PEG concentration, shown in Fig. 5 of a recent paper [38], cannot be fitted adequately by any linear regression. It is therefore explicable that the fit of the data in Fig. 15 is rather poor ($R^2 = 0.296$):

$$\Delta C_p(\mathrm{J\,g^{-1}\,K^{-1}}) = \underset{p=0.516}{(0.10 \pm 0.15)} + \underset{p=0.051}{(0.026 \pm 0.013)}\%\mathrm{H_2O} + \underset{p=0.0009}{(0.007 \pm 0.002)}\%\mathrm{PEG} \quad (10)$$

Nevertheless, the PEG and hydration effects on ΔC_p are quite plausible as is indicated by regression parameters. The conflicting contributions of free volume and interaction energy are embedded in the plot shown in Fig. 15 as has been earlier reported [38].

Although both PEG and sorbed water contribute significantly in the amorphous phase characteristics within PVP–PEG–water ternary blends confirming the compatibility of all the components, it is evident from Figs. 14 and 15 that only PVP interaction with PEG is responsible for the peculiarities in T_g and ΔC_p behaviour. At the same time, water in PVP–PEG hydrogels behaves not as an impurity but rather as essential third component of hydrogen-bonded complex formed in these systems. The hydrogen bonding of PEG hydroxyls to the carbonyls in PVP units is thought to occur directly through water molecules associated with the PVP carbonyls, increasing water mobility but causing no desorption of bound water.

4. Conclusions

Since in compatible polymer blends a homogeneous phase is obtained due to the existence of specific favourable interactions between all the components, allowing mixing on a molecular scale, the change in any component concentration affects simultaneously the phase behaviour of other components. As a result, evident coherence can be readily observed in the compositional behaviour of phase transitions in compatible blends. If one of the blend components is an amorphous polymer, while another polymer is capable of forming a crystalline phase, and the third component is a low molecular weight volatile liquid, the d.s.c. technique enables the characterisation of the states of every blend components and their interactions by observing the compositional behaviour of the amorphous and crystalline phases in couple with the examination of the vaporisation endotherms of the liquid component. In the present work such an approach is realised by the example of PVP–PEG–water compatible blends.

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References

[1] Rowland SP, editor. Water in polymers ACS Symposium Series, 127. Washington, DC: American Chemical Society, 1980.

[2] Hopfenberg HB, Paul DR. Transport phenomena in polymer blends. In: Paul DR, Newman S, editors. Polymer blends, 1. New York: Academic Press, 1978. p. 445–87.

[3] Vrentas JS, Vrentas CM. Differential sorption in glassy polymers. J Appl Polym Sci 1999;71:1431–40.

[4] Vrentas JS, Vrentas CM. Integral sorption in rubbery polymers. J Polym Sci, Polym Phys 1998;36:171–80.

[5] Dayantis J. The effect of pressure on the determination of the Flory–Huggins χ parameter by vapour pressure measurements. Polymer 1992;33(1):219–21.

[6] Hodge RM, Simon GP, Whittaker MR, Hill DJT, Whittaker AK. Free volume and water uptake in a copolymer hydrogel series. J Polym Sci, Polym Phys 1998;36:463–71.

[7] Soles CL, Chang FT, Bolan BA, Hristov HA, Gidley DW, Yee AF. Contributions of the nanovoid structure to the moisture absorption properies of epoxy resin. J Polym Sci, Polym Phys 1998;36:3035–48.

[8] Vrentas JS, Vrentas CM. Hysteresis effects for sorption in glassy polymers. Macromolecules 1996;29:4391–6.

[9] Young TH, Chang LP, Hsieh CC, Chen LW. Phase behaviour of EVAL polymers in water–2-propanol cosolvent. Macromolecules 1998;31:1229–35.

[10] Feldstein MM, Lebedeva TL, Shandryuk GA, Igonin VE, Avdeev NN, Kulichikhin VG. Stoichiometry of poly(*N*-vinyl pyrrolidone) complex with poly(ethylene glycol). Polym Sci 1999;41(8):867–75.

[11] Feldstein MM, Lebedeva TL, Shandryuk GA, Kotomin SV, Kuptsov SA, Igonin VE, Grokhovskaya TE, Kulichikhin VG. Complex formation in poly(*N*-vinyl pyrrolidone) blends with poly(ethylene glycol). Polym Sci 1999;41(8):854–66.

[12] Kirsh YE. Water soluble poly(*N*-vinylamides), New York: Wiley, 1998, chap. 3.

[13] Tan YY, Challa G. The glass transition temperature of poly(*N*-vinyl pyrrolidone) and the effects of water. Polymer 1976;17(8):739–40.

[14] Shult KA, Paul DR. Water sorption and transport in blends of poly(vinyl pyrrolidone) and polysulfone. J Polym Sci Polym Phys 1997;35(4):655–74.

[15] Davis TP, Hugglin MB. Effect of composition on properties of copolymeric *N*-vinyl-2 pyrrolidone/methyl methacrylate hydrogels and organogels. Polymer 1990;31(3):513–9.

[16] Al-Isso M, Davis TP, Huglin MB, Rego JM, Rehab MA-M, Yip DCF, Zakaria MB. Observation on the swelling behaviour of copolymeric hydrogels containing *N*-vinyl-2-pyrrolidone. Makromol Chem 1990;191(2):321–30.

[17] Tsang CJ, Clark JC, Wellinghoff ST, Miller WC. Structure-property relationships in poly(*n*-vinyl pyrrolidone)–phenoxy–water gels. J Polym Sci Polym Phys 1991;29(2):247–59.

[18] Sakellariou P. Theta temperature of poly(*N*-vinyl pyrrolidone) in water. Polymer 1992;33(6):1339–42.

[19] Guven O, Sen M. Preparation and characterization of poly(*n*-vinyl pyrrolidone) hydrogels. Polymer 1991;32(13):2491–5.

[20] Sen M, Guven O. Determination of solubility parameters of poly(*N*-vinyl-2-pyrrolidone)/ethylene glycol dimethacrylate gels by swelling measurements. J Polym Sci Polym Phys 1998;36(1):213–9.

[21] Oksanen CA, Zografi G. The relationship between the glass transition temperature and water vapor absorption by poly(vinyl pyrrolidone). Pharm Res 1990;7(6):654–7.

[22] Hancock BC, Zografi G. The relationship between the glass transition temperature and the water content of amorphous pharmaceutical solids. Pharm Res 1994;11(4):471–7.

[23] Hancock BC, Zografi G. The use of solution theories for predicting water vapour absorption by amorphous pharmaceutical solids: a test of the Flory–Huggins and Vrentas models. Pharm Res 1991;10(9): 1262–7.

[24] Graham NB, Zulfigar M, Nwachku NE, Rashid A. Interaction of poly(ethylene oxide) with solvents: 4 Interaction of water with poly(-ethylene oxide) crosslinked hydrogels. Polymer 1990;31(5):909–16.

[25] Hager SL, Macrury TB. Investigation of phase behaviour and water binding in poly(ethylene oxide) solutions. J Appl Polym Sci 1980; 25:1559–71.

[26] Daoust H, Darveau R, Laberge F. Microcalorimetric investigation on interaction between poly(acrylic acid) and oxyethylene oligomers in water. Polymer 1990;31(10):1946–9.

[27] Abdel Azim A-AA, Boutros WY, Abdel-Bary EM. Estimation of the compatibility of poly(ethylene glycol)/poly(ethylene oxide) blends from solution viscosity measurements. Polymer 1998;39(12):2543–9.

[28] Kotomin SV, Igonin VE, Feldstein MM, Kulichikhin VG, Platé NA. Rheological, relaxation and adhesive properties of hydrogels explored with squeezing-flow technique. Proc Int Symp Control Release Bioactive Mater 1998;25:906–7.

[29] Chalykh AA, Chalykh AE, Feldstein MM. Effects of composition and hydration on adhesive properties of poly(*N*-vinyl pyrrolidone)–poly(ethylene glycol) hydrogels. Polym Mater Sci Engng 1999;81:456–7.

[30] Chalykh AE, Chalykh AA, Feldstein MM. Fracture mechanics of poly(*N*-vinyl pyrrolidone)–poly(ethylene glycol) hydrogel adhesive joints. Polym Mater Sci Engng 1999;81:427–8.

[31] Feldstein MM, Chalykh AE, Chalykh AA, Platé NA. Quantitative relationship between molecular structure and adhesion of PVP–PEG hydrogels. Polym Mater Sci Engng 1999;81:465–6.

[32] Igonin VE, Makarova VV, Avdeev NN, Feldstein MM, Kulichikhin VG. Optical microinterference measurements of polymer miscibility, dissolution and interdiffusion. Proc Int Symp Control Release Bioactive Mater 1999;26:391–2.

[33] Feldstein MM, Tohmakhchi VN, Malkhazov LB, Vasiliev AE, Platé NA. Hydrophilic polymeric matrices for enhanced transdermal drug delivery. Int J Pharm 1996;131(2):229–42.

[34] Bairamov DF, Markin VS, Iordanskii AL, Feldstein MM. Drug diffusion in adhesive hydrogels. Proc Int Symp Control Release Bioactive Mater 1999;26:389–90.

[35] Feldstein MM, Igonin VE, Grokhovskaya TE, Lebedeva TL, Kotomin SV, Kulichikhin VG, Platé NA. Performance of hydrophilic transdermals as an explicit function of the molecular structure of polymer matrix. In: Brain KR, James VJ, Walters KA, editors. Perspectives of percutaneous penetration, 5b. Cardiff: STS Publishing, 1997. p. 228–32.

[36] Chalykh AE, Razgovorova VM, Feldstein MM. Syneresis of water sorbed with glassy and plasticized poly(*N*-vinyl pyrrolidone). Proc Int Symp Control Release Bioactive Mater 1999;26:721–2.

[37] Chalykh AE, Chalykh AA, Feldstein MM, Siegel RA. Isotherms of water sorption with the blends of poly(*N*-vinyl pyrrolidone)–poly(ethylene glycol). Proc Int Symp Control Release Bioactive Mater 1999;26:393–4.

[38] Feldstein MM, Shandryuk GA, Kuptsov SA, Platé NA. Coherence of thermal transitions in poly(*N*-vinyl pyrrolidone)–poly(ethylene glycol) compatible blends: 1 Interrelations among temperatures of melting, maximum cold crystallization rate and glass transition polymer. Polymer 2000;41:5327–38.

[39] Feldstein MM, Kuptsov SA, Shandryuk GA. Coherence of thermal transitions in poly(*N*-vinyl pyrrolidone)–poly(ethylene glycol) compatible blends: 2. The temperature of maximum cold crystallization rate versus glass transition polymer. Polymer 2000;41:5339–48.

[40] Burghoff HG, Pusch W. Characterization of water structure in cellulose acetate membranes by calorimetric measurements. J Appl Polym Sci 1979;23:473–84.

[41] Yoshida H, Hatekayama T, Hatekayama H. Phase transitions of the water–xanthan systems. Polymer 1990;31(4):692–8.

[42] Ishikiriyama K, Todoki M. Heat capacity of water in poly(methyl methacryale) hydrogel membrane for an artificial kidney. J Polym Sci, Polym Phys 1995;33:791–800.

[43] Hofmann K, Hatekayama H. The influence of thermal history on water associated with polyelectrolytes and cellulose. Macromol Chem Phys 1995;196:99–113.

[44] Fushimi H, Ando I, Iijima T. States of water in cationically charged poly(vinyl alcohol) membranes. Polymer 1991;32(2):241–7.

[45] Zang YH, Sapieha S. A differential scanning calorimetric characterization of the sorption and desorption of water in cellulose/linear low-density polyethylene composites. Polymer 1991;32(3):489–92.

[46] Feldstein MM, Lebedeva TL, Igonin VE, Platé NA. The varieties of poly(ethylene glycol) state in H-complex with poly(*N*-vinyl pyrrolidone). Proc Int Symp Control Release Bioactive Mater 1998;25: 850–1.

[47] Wunderlich B. Macromolecular physics, vol. 2. Crystal nucleation, growing, annealing, vol. 3. Crystal melting. New York/London: Academic Press, 1978.

[48] Lipatov YS, Shilov VV, Kruglyak NE. X-ray examination of polymer systems, Kiev: Naukova Dumka, 1982, p. 92–105.