

Thermoanalytical and spectroscopic study of poly(vinyl pyrrolidone)/poly(styrene-co-vinyl phenol) blends

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In the present study a series of poly(vinyl pyrrolidone) (PVP) blends with a series of styrene-vinyl phenol copolymers (SVP) have been prepared and studied. Copolymers with a vinyl phenol content greater than 4 mol% show complete miscibility with PVP over the whole blend composition range. Copolymers containing more than 25 mol% vinyl phenol form complexes with PVP, which precipitate in solution with a common solvent. The miscibility was verified both by visual inspection of the blends and by differential scanning calorimetry measurements, which showed a single glass transition temperature (T_g) throughout the whole composition range. Unusually large positive deviations from linearity were observed in the T_g versus composition diagrams of some blends. The extensive hydrogen bonding interactions between the mixed polymers were studied by FTi.r. spectroscopy. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In the last few decades the development and study of new polymer blends has drawn considerable attention in both academia and industry^{1–4}. Mixing of two already available polymers can be attractive from both an economical (lower cost compared to developing a totally new polymer) and technical (easy adjustment of the product's final properties by adjusting the component amounts) point of view. The rule, however, is the immiscibility rather than the miscibility of high polymers. This is most easily understood by taking into account the thermodynamic description of mixing: $\Delta G = \Delta H - T\Delta S$. For two polymers to be miscible we should have $\Delta G < 0$. Unfortunately, in polymer blends the contribution of the entropic term is very low because of the large size of the mixed molecules and combinatorial considerations. This leaves the enthalpic term as the main factor determining polymer miscibility. Generally, in the absence of any specific interactions, it is $\Delta H > 0$ and, as a result, most polymer pairs are immiscible.

Therefore, for two polymers to be miscible, a specific interaction must usually develop between them. In this case, the specific interaction can have a significant negative contribution upon the enthalpy change possibly making ΔH (and thus ΔG) negative and effecting miscibility. Some of the most common specific interactions are hydrogen bonding, donor–acceptor, ion–dipole or cation–anion (electrostatic) interactions. Hydrogen bonding especially has been shown to be the main driving force behind the miscibility of a large number of miscible polymer blends^{2,4}.

Poly(vinyl pyrrolidone) (PVP) is a water soluble tertiary amide and a strong lewis base. As a result, it is susceptible to hydrogen bonding with substances containing hydrogen donor groups. It has been shown to form miscible blends

with a large number of polymers such as poly(acrylonitrile-co-methyl acrylate)⁵, poly(vinyl chloride) and poly(epichlorhydrin)⁶, poly(vinylidene fluoride)^{7–9}, poly(chloromethyl methacrylate) and poly(2-chloroethyl methacrylate)¹⁰, poly(2-hydroxyethyl methacrylate) and poly(2-hydroxypropyl methacrylate)¹¹, copolymers of 2-hydroxyethyl methacrylate with methyl methacrylate and n-propyl methacrylate¹², poly(hydroxy ether of biphenol A) (phenoxy)¹³, partially hydrolysed poly vinyl acetate¹⁴, poly(monobenzyl itaconate)¹⁵, copolyamide¹⁶, modified poly(*a*-methyl styrene)¹⁷ and polyvinyl alcohol^{18,20}.

Poly(vinyl phenol) is another polymer which is known to form miscible blends with PVP^{21,22}. This miscibility was attributed to hydrogen bond formation between the phenolic hydroxyl and the amidic carbonyl as shown by FTi.r. study²¹. The hydroxyl–carbonyl hydrogen bond, however, is already strong enough and a complete miscibility of PVP is expected with copolymers of vinyl phenol with moderate contents in vinyl phenol.

The present study deals with blends of PVP and styrene/vinyl phenol copolymers with varying vinyl phenol contents. It aims at determining the effect that the composition of the copolymer has on its miscibility with PVP.

EXPERIMENTAL

Materials

Styrene/vinyl phenol copolymers were synthesized by hydrolysis of the corresponding styrene/acetoxystyrene copolymers according to the procedure described in the literature²³. A total of seven copolymers were prepared containing 1.4, 4, 10, 25, 60, 70, and 100% mole vinyl phenol, respectively. The vinyl phenol content was determined by n.m.r. spectroscopy. Hereafter, the copolymers will be referred to as SVP#, where # is the vinyl phenol content

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(i.e. the copolymer with 10% vinyl phenol will be referred to as SVP10, etc.).

Poly(vinyl pyrrolidone) (Aldrich) had a MW of 10900. Before use, it was dried under vacuum at 90°C for 48 h to remove the adsorbed water. It is well known that PVP is a very hygroscopic polymer and can retain up to 0.5 mol of water per monomer unit²⁴. PVP was kept afterwards in a desiccator to prevent any water absorption. Tetrahydrofuran (Lab-Scan) was of analytical purity.

Blends preparation

The blends were prepared by mixing appropriate amounts of 2 wt% solutions of each polymer in tetrahydrofuran in order to obtain the desired blend composition. In the case of blends with SVP1.4, SVP4 and SVP10 the resulting solutions were clear. These solutions were cast onto aluminium dishes and the solvent was left to slowly evaporate under ambient conditions.

On the contrary, for SVP25, SVP60, SVP70, and SVP100 blends with PVP a white precipitate was formed immediately after mixing, which is an indication of complexation between the component polymers. The solutions were filtered and the isolated precipitates were rinsed with tetrahydrofuran and dried under ambient conditions.

After initial drying, all blends were heated under vacuum at 90°C for at least 72 h to remove all traces of residual solvent. All blends were kept afterwards in a desiccator to prevent any moisture absorption (the blends, primarily due to PVP, are hygroscopic and readily absorb moisture when exposed to ambient conditions).

Cloud point measurements

Cloud point measurements were performed with a Mettler FP82HT Hot Stage, controlled by a FP90 controlling unit. Initially, pieces of the studied sample were placed into the hot stage onto a glass microscope slide and heated at a high temperature (i.e. 150°C) until the polymer exhibited fluidity. The polymer was kept at this temperature for 1–2 min in order to remove any traces of solvent. Then, a thin cover glass was placed upon the polymer melt and pressed to obtain a thin polymer film. The sample was subsequently cooled to room temperature and placed back into the hot stage. The stage was put under a microscope and the sample was heated at a rate of 2°C min⁻¹ up to 300°C. During measurements the amount of transmitted light was monitored with a photodiode mounted on a microscope's eyepiece. In the case of phase separation a sudden drop in the transmitted light would be observed.

Thermal analysis

The glass transition temperatures were determined by using a Shimadzu fast quencing differential scanning calorimeter, model d.s.c.-50Q. Approximately 10 mg of each blend were weighed and sealed in aluminium pans. Each sample was initially heated at a temperature 40° above its T_g and held at that temperature for 10 min. It was subsequently quenched with liquid nitrogen and rescanned again at a rate of 10°C min⁻¹ up to a final temperature approximately 40° above the T_g of the blend. The above procedure was repeated until two consecutive scans gave the same T_g within experimental error ($\pm 1^\circ\text{C}$). The T_g was defined as the midpoint of the transition peak.

The thermal degradation of PVP was followed by a Shimadzu thermogravimetric analyser, model TGA50.

Table 1 Appearance of PVP/SVP blends

% vinyl phenol in copolymer	Solution appearance	Dried blend appearance
1.4	Clear	Opaque film
4	Clear	Transparent film
10	Clear	Transparent film
25	Precipitate formed	White powder
60	Precipitate formed	White powder
70	Precipitate formed	White powder
100	Precipitate formed	White powder

I.r. spectroscopy

In the case of clear solutions, samples for FTi.r. measurements were prepared by directly casting 2 wt% polymer solutions on KBr plates. The cast solutions were left to evaporate under ambient conditions and the last traces of solvent were removed by heating under vacuum at 90°C for 48 h. FTi.r. spectra of powdered complexes were taken in KBr pellets. The spectra were collected in a Biorad FTS 45-A FTi.r. spectrometer at a 2 cm⁻¹ resolution. To obtain each spectrum, 64 consecutive scans were collected and averaged.

RESULTS AND DISCUSSION

Poly(vinyl pyrrolidone), because of its structure consisting of a polar imide group and non-polar methylene and methine groups, has an amphiphilic character. Because of its unique structure, PVP forms macromolecular complexes with a variety of compounds. These complexes are formed usually through hydrogen bonding to which PVP is highly susceptible. In certain cases, however, other forces such as polar forces and hydrophobic interactions may also be responsible for the strong complexing ability of PVP.

With phenols, PVP has the ability to form strong complexes²⁵. These complexes are sometimes insoluble in water such as those with pyrogallol and resorcinol. The stability of the formed complexes depends on the acid strength of the phenolic hydrogen, which participates in complex formation in its neutral (non-ionized) form. Thus, it is expected for PVP to be also able to form complexes with polymeric phenols such as poly(vinyl phenol) and some of its copolymers with styrene. In a previous study it was found that, in the case of poly(vinyl phenol), insoluble complexes are formed when methanolic solutions of the two polymers are mixed²². On the contrary, no complex formation was observed when mixing solutions of the two polymers in DMSO, which is known to be a strong hydrogen bonding acceptor.

Table 1 reports the appearance of solutions and blends prepared with various styrene/vinyl phenol copolymers.

It can be observed that above a certain vinyl phenol content (25 mol%) a precipitate is formed upon mixing, which is an indication of strong complex formation. Blends of PVP with SVP copolymers containing low amounts of vinyl phenol (1.4 mol%) give opaque films upon drying, which is an indication of immiscibility. In the intermediate range, clear transparent films are formed which usually suggests complete miscibility between the two polymers. However, blend appearance is not definite proof of miscibility, as two polymers with similar refractive indices can also give transparent films even if they are immiscible.

d.c.s.

A single T_g (glass transition temperature), which is concentration dependent and is lying between those of the

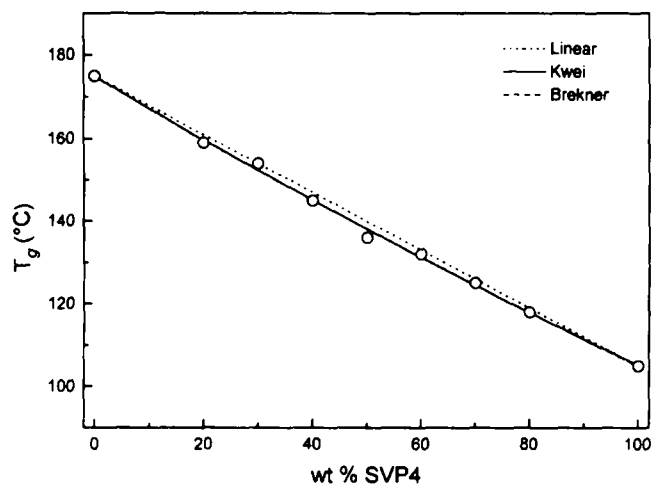


Figure 1 T_g temperature versus blend composition diagram for PVP/SVP4 blends

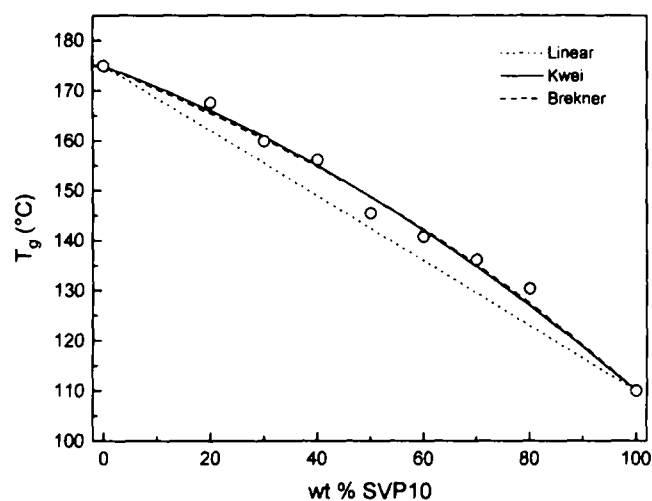


Figure 2 T_g temperature versus blend composition diagram for PVP/SVP10 blends

pure polymers, is a much more valid criterion to establish miscibility, provided that the T_g values of the two polymers differ significantly (i.e. more than 10–20°C). Two T_g values, in contrast, appearing close to those of the two pure polymers, are an indication of a heterogeneous system and suggest immiscibility.

The d.s.c. scans of the blends revealed that blends with SVP1.4 have two glass transition temperatures throughout the whole composition range, whereas the rest of the blends have a single T_g . These findings confirm the miscibility of PVP with styrene/vinyl phenol copolymers containing more than 4% mol vinyl phenol.

Figures 1–4 present the T_g versus blend composition diagrams for some of the miscible blends. Blends with SVP4 show an almost linear dependence of T_g on composition. The rest of the blends, however, show positive deviations from linearity which increase with the vinyl phenol content of the SVP copolymer. In particular, for the complexes of PVP with SVP60, SVP70 and SVP100, the T_g values of the blends lie above those of the pure component polymers. This behaviour is in accordance with a previous study of PVP/SVP100 blends prepared from methanolic solutions²² in which the T_g of the blends exceeded those of the pure components. In the same study, however, it is also mentioned that for blends

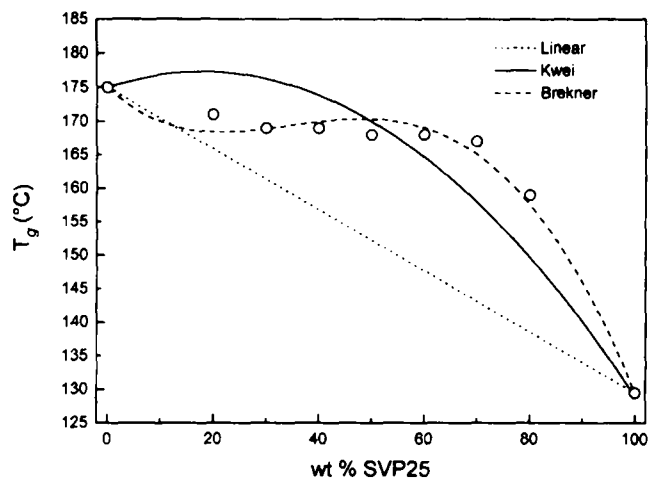


Figure 3 T_g temperature versus blend composition diagram for PVP/SVP25 blends

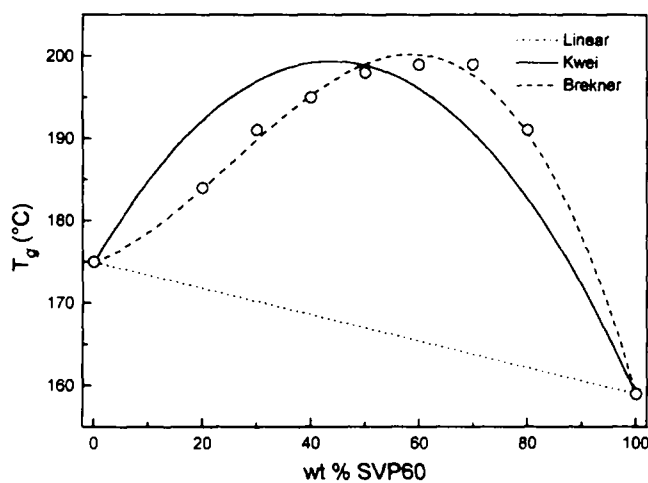


Figure 4 T_g temperature versus blend composition diagram for PVP/SVP60 blends

cast from DMSO, negative deviations from linearity were observed.

Positive deviations from linear behaviour in polymer blends is a usual phenomenon in the case where hydrogen bonding and other strong specific interactions are developed between the two polymers. Hydrogen bonds in this case act as virtual crosslinks, decreasing macromolecular mobility and thus increasing the T_g . The large deviations, however, observed for some of our blends, which are referred to as complexes, are rather unusual. This may be the result of multiple hydrogen bonding across the two complexed macromolecular chains. As a result, the macromolecular chains are stiffened considerably and a large increase in T_g is observed. The complex between PVP and acrylic acid, for example, was reported to soften in temperatures in excess of 260°C without melting²⁶. This assumption is enhanced by the fact that, as has already been mentioned, PVP/SVP100 blends cast from DMSO (in which no complex formation is observed) show negative deviations from linearity²². Negative deviations from linearity appear also in some other cases of hydrogen bonded PVP blends such as the blends with 2-hydroxyethyl methacrylate/methyl methacrylate and 2-hydroxyethyl methacrylate/n-propyl methacrylate copolymers¹², poly(vinyl alcohol)²⁰ and copolyamide¹⁶.

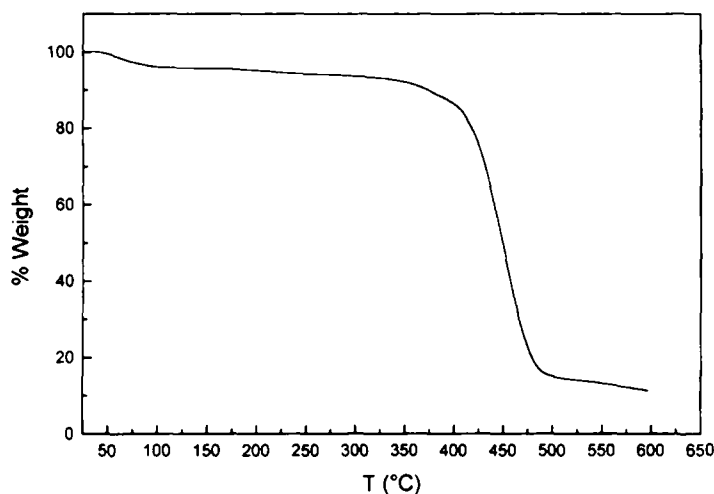


Figure 5 TGA thermogram of PVP

T_g data correlation

Several empirical or semi-empirical equations were proposed in the past in order to correlate or predict the dependence of glass transition temperature on the composition of the polymer blend. A recent development, based on the LFHB (Lattice-Fluid Hydrogen Bonding) theory is also available²⁷. Application of this model, however, requires the Lattice-Fluid scaling constants for the pure components. These constants for the polymers of our interest are not yet available. Some classic and frequently employed equations include those proposed by Gordon-Taylor²⁸, Henckel-Heusch²⁹, Fox³⁰, Couchman^{31,32}, Kwei³³ and Brekner *et al.*³⁴. In our study, the equations of Kwei and Brekner were used to fit the T_g data as they are able to describe positive deviations from linearity.

The Kwei equation has the form:

$$f_g^{\text{blend}} = \frac{w_{g1} + kw_{g2}}{w + kw} + qw$$

where w_i and T_{gi} are the weight fractions and the glass transition temperatures of the pure components, respectively, whereas k and q are adjustable empirical parameters. Although both parameters (k and q) can be adjusted during the fit, this is usually done for blends presenting an S-shaped curve (both negative and positive deviations from linearity) as suggested by Kwei. In the case of blends showing positive deviations, the k is usually kept constant to a value of 1 and the above equation reduces to:

$$f_g^{\text{blend}} = w_{g1} + w_{g2} + qw$$

In this case, the q value derived from the fit is considered to be a measure of the interaction strength between the two polymers, but no direct connection with the Flory-Huggins χ interaction parameter exists.

The Brekner equation is based on polymer solution thermodynamics and has the form:

$$\frac{f_g^{\text{blend}} - f_{g1}}{f_{g2} - f_{g1}} = (1 + |K_1|)\phi - (|K_1| + |K_2|)\phi^2 + |K_2|\phi^3$$

where ϕ is the corrected weight fraction of the polymer with the higher T_g and is defined as: $\phi = Kw_2/(w_1 + Kw_2)$. K_1 , K_2 and K are constants and are generally treated as adjustable parameters. K_1 and K_2 are considered to be related to the intensity of the polymer-polymer interaction and configurational redistribution in the neighbourhood of the binary

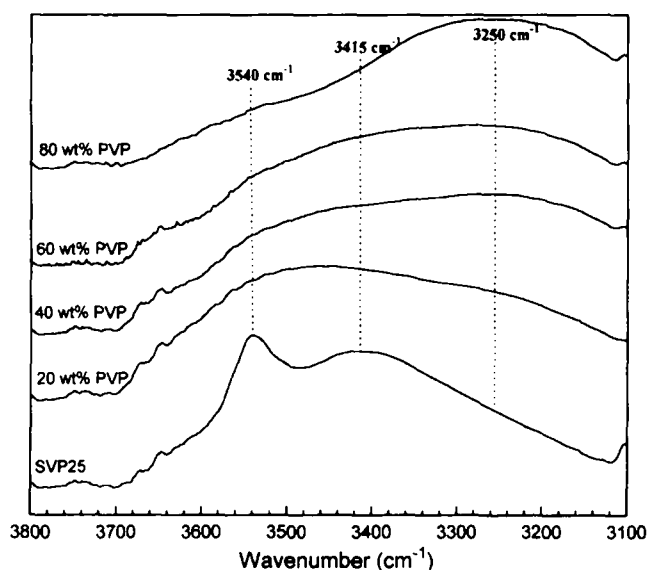


Figure 6 Hydroxyl stretching region of PVP/SVP25 blends

Table 2 Fit parameter values for PVP/SVP blends

Polymer	q	K_1	K_2
SVP4	-8	0.075	0.03
SVP10	25	0.68	0.82
SVP25	71	3.65	4.11
SVP60	127	13.53	11.16
SVP70	136	66	-139
SVP100	171	35	21

contacts, respectively. The K parameter is characteristic of the nature of the two polymers and in its simplest case is equal to the ratio of the T_g values of the two polymers, or $K = T_{g1}/T_{g2}$. This assumption was made in our case as well, and only K_1 and K_2 were used as fitting parameters.

The calculated T_g values with the Kwei and Brekner equation are represented as solid and dashed lines, respectively, in Figures 1-4. The values of the adjustable parameters (q for the Kwei equation and K_1 and K_2 for the Brekner equation), which give the best fit for the various blends, are shown in Table 2.

Generally, Brekner's formula gives a much better fit, especially for SVP blends with high vinyl phenol content. In

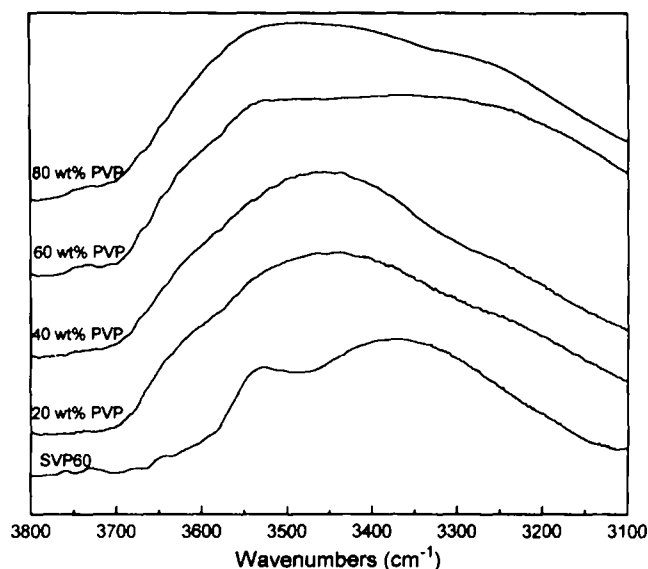


Figure 7 Hydroxyl stretching region of PVP/SVP60 blends

this case, the T_g curves are asymmetric, a form for which the simplified Kwei formula cannot account. Brekner's formula, on the other hand, seems to give good results for asymmetrically shaped curves as well.

As can be seen in Table 2, both q and K_1 values are increasing monotonically with increasing vinyl phenol content of the SVP copolymers. This is an indication of increasing interaction between the components since both of these parameters are related to interaction strength. The abnormal values of the K_1 and K_2 parameters for the SVP70 blends must be attributed to the small T_g difference between PVP (175°C) and SVP70 (176°C). Since this difference appears in the denominator of the first term in the Brekner equation, it makes it very sensitive to experimental errors. This is verified by the large standard errors of the K_1 and K_2 parameters (16 and 30, respectively). Nevertheless this small disturbance does not change the general trend.

The parameter values for the blends with SVP4 are especially low and, as a result, these blends follow a linear (ideal) behaviour. The fact that there are no positive deviations in these blends may be attributed to the low number of hydrogen bonds formed, since the concentration of -OH groups in SVP4 is very low (only 4% mol). As a result the hydrogen bonds formed are not adequate to stiffen the macromolecular chains.

Cloud point measurements

The miscible blends were examined for their behaviour in terms of phase separation when heated at elevated temperatures. Homogeneous polymer mixtures and, in particular, mixtures where specific interactions develop exhibit lower critical solution temperature (LCST) behaviour, i.e. phases separate when heated above a certain temperature. All miscible PVP/SVP blends, however, showed no phase separation when heated to temperatures up to 300°C. Above this temperature a brown colour developed, an indication of extensive degradation of PVP. This is verified by a TGA scan of PVP shown in Figure 5, which shows significant weight losses above 300°C. This means that the cloud points of the blends lie above the degradation temperature of one of the polymers (in this case PVP). The fact that no cloud point can be detected means that the degree of hydrogen bonding, even in the case of

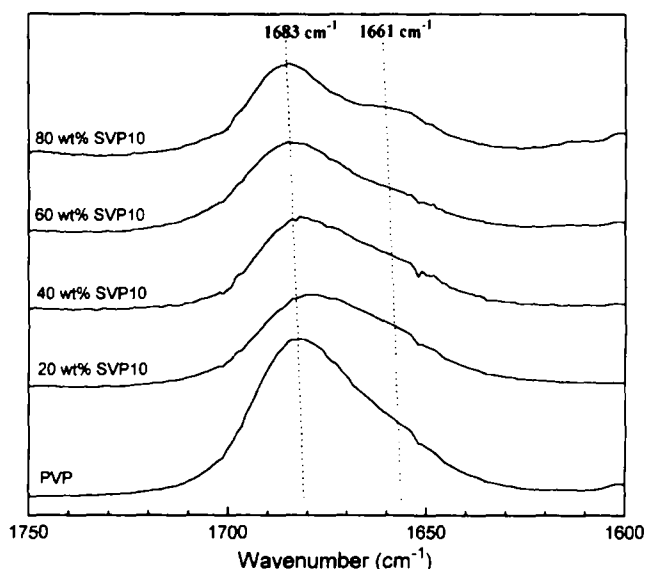


Figure 8 Carbonyl stretching region of PVP/SVP10 blends

SVP4 blends where the number of intermolecular hydrogen bonds is relatively limited, is sufficient to induce miscibility even at high temperatures.

FTi.r. measurements

In a previous study²¹ it has been shown by FTi.r. measurements that the driving force for PVP/SVP100 miscibility is the intermolecular hydrogen bonding between the amide carbonyl of PVP and the phenolic hydroxyl of SVP100. From the spectroscopic point of view the main areas of interest are the hydroxyl and carbonyl regions of the FTi.r. spectra in the blends.

Figure 6 presents the FTi.r. hydroxyl region spectra for various PVP/SVP25 blends. In the SVP25 spectrum the sharp peak at 3540 cm^{-1} is attributed to free (unassociated) hydroxyls, whereas the second broad peak at 3415 cm^{-1} is due to the self-associated hydroxyls. Upon blending with PVP, as the amount of PVP increases, there is a disappearance of the peak at 3540 cm^{-1} . Concurrently, there is a gradual shift of the broad peak attributed to associated hydroxyls to 3250 cm^{-1} . The same pattern appears in blends with SVP60 blends, as shown in Figure 7.

The spectral changes occurring during blending indicate that there is an increased hydrogen bonding in blends with PVP. New hydrogen bonds are formed between the amide carbonyl of PVP and the phenolic hydroxyls of SVP copolymers. The fact that the new hydrogen bonded hydroxyls formed absorb at a lower frequency (3250 cm^{-1}) compared to those of self-associated hydroxyls suggests that the PVP-SVP hydrogen bonds are stronger than those of the self-associated SVP molecules. This is a factor favouring miscibility since the energy gains when hydrogen bonds are formed between PVP and vinyl phenol are higher.

Interesting results can also be obtained by examining the carbonyl region spectra of the blends. Figures 8 and 9 present the carbonyl region spectra of PVP blends with SVP10 and SVP60, respectively. As seen in Figure 8, pure PVP shows a single asymmetric broad peak at 1683 cm^{-1} . Upon mixing with SVP10, a second peak appears at around 1661 cm^{-1} . This peak is assigned to hydrogen bonded PVP carbonyls. This peak becomes more prominent with increasing SVP10 content in the blend. This is expected

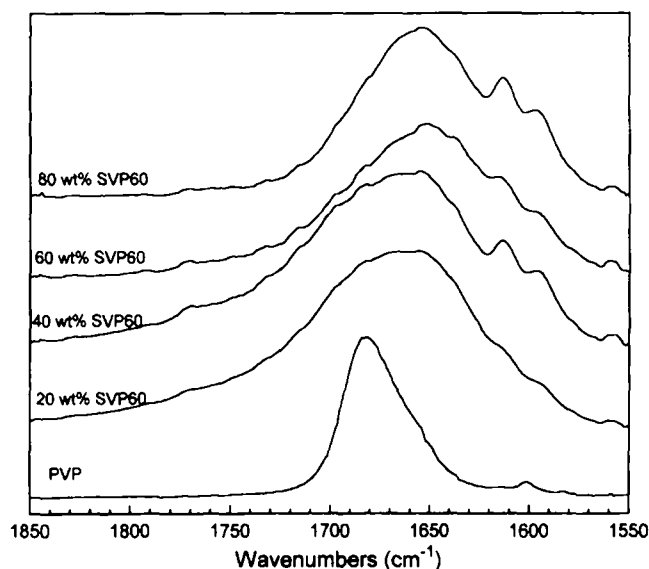


Figure 9 Carbonyl stretching region of PVP/SVP60 blends

since as the concentration of SVP10 (and therefore of hydroxyls) increases in the blend, so does the number of hydrogen bonds formed with PVP. Blends with SVP60 show a similar behaviour. The only difference is that the bonded carbonyl peak is more prominent, since the concentration of hydroxyls in this polymer is greater, and more hydrogen bonds are formed with PVP.

At this point it would be interesting to examine whether we can quantitatively determine the fraction of hydrogen bonded carbonyls. The peak areas usually are a direct measure of carbonyl concentration and permit the direct calculation of the fraction of bonded carbonyls. This approach has already been taken in the case of PVP blends with poly(monobenzyl itaconate)¹⁵ and with epoxy resin³⁵. However, some difficulties are encountered in trying to extract any quantitative information from the FTIR spectra. The main reason is that the carbonyl peak of PVP is actually a mixed mode containing contributions from the carbonyl stretching and the N–C stretching vibrations²¹. This fact complicates the interpretation of the results and makes them somewhat ambiguous. Curve fitting, for example, which is a routine method used to determine peak areas, uses mathematically derived peaks, usually Lorentzian or Gaussian, which are by definition symmetric around the peak centre. PVP carbonyl peak, however, is asymmetric and this will result in poor fitting. Thus, the areas calculated by this procedure will be subject to considerable error.

CONCLUSIONS

In the present study, the behaviour of a series of PVP blends with styrene–vinyl phenol copolymers has been studied. It has been found that for vinyl phenol content above somewhere between 1.4 and 4 mol%, complete miscibility is obtained over the whole composition range. Above a certain vinyl phenol content, complexation between the macromolecules occurs even in the common hydrogen bonding solvent tetrahydrofuran. The FTIR study of the blends showed that, upon mixing, extensive hydrogen bonding occurs between the amide carbonyl of PVP and the phenolic hydroxyl of vinyl phenol units of the copolymer. As a result of these interactions there are

positive deviations from linearity in the T_g versus composition curves. These deviations could be satisfactorily described by using the Brekner equation. In blends, where macromolecular complexes are formed, the deviations are especially high and the T_g sometimes exceeds those of the pure component polymers. This may be the result of drastic chain stiffening due to extensive hydrogen bonding between the two types of polymeric chains that form the precipitating complex.

The average percentage of the hydrogen bonding sites actually involved in intermolecular hydrogen bonds decreases as the vinyl phenol content of the copolymers increases. Stereochemical or kinetic factors are apparently responsible for this behaviour. Long annealing times could probably somewhat increase this percentage of the actually interacting hydrogen bonding sites in the macromolecular complexes.

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