

Study of the miscibility and specific interactions between poly(1-vinyl-2-pyrrolidone) and poly(vinyl formal)

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(Received 18 November 1991; revised 15 June 1992)

The phase behaviour of blends of poly(1-vinyl-2-pyrrolidone) and poly(vinyl formal) was studied by means of differential thermal analysis and differential mechanical thermal analysis. Both techniques showed that the blend studied exhibits a single glass transition, which is intermediate between the glass transitions associated with each constituent polymer and depends on polymer concentration. Discussion of this phase behaviour in terms of various common equations is also carried out. The blend preparation method as well as the blend thermal history are found to exert a relevant influence on the phase behaviour associated with the polymer alloy studied here. This behaviour is explained as the consequence of hydrogen-bonding interactions between both polymers as demonstrated by infra-red spectroscopy. An additional study on the mechanism of complex formation associated with poly(1-vinyl-2-pyrrolidone) and poly(vinyl butyral) is also carried out.

(Keywords: blends; miscibility; specific interactions; glass transition; poly(1-vinyl-2-pyrrolidone); poly(vinyl formal))

INTRODUCTION

Owing to the unfavourable configurational entropy of mixing, polymer miscibility in most cases is the result of specific interactions between chains that provide an entropy of mixing negative enough for the Gibbs free energy to be negative also¹. Such specific interactions include donor-acceptor², dipole-dipole^{3,4}, hydrogen-bonding^{5,6}, ion-ion^{7,8}, acid-base⁹ and ion-dipole interactions. Hence, polymer pairs that happen to be miscible usually involve at least one component with polar characteristics. In many cases the introduction of polar groups into the repeat unit of one of the components leads to miscibility in mixtures that previously were not miscible¹⁰. In this connection, the fact that poly(methyl methacrylate) (PMMA), poly(1-vinyl-2-pyrrolidone) (PVP) and poly(vinylpyridine) are incompatible with polystyrene¹⁰, whereas poly(vinylphenol) is miscible with all those polymers¹¹⁻¹³, illustrates the importance of groups amenable to undergoing specific interactions, such as hydroxyl groups, for obtaining miscible polymer blends.

Poly(vinyl acetals) are produced by reacting aldehydes such as formaldehyde and butyraldehyde with partially hydrolysed poly(vinyl acetates). This reaction does not proceed to 100% and consequently the resultant polymer presents acetal groups in conjunction with unreacted hydroxyl groups. These hydroxyl groups are potential electron-acceptor points within the polymer chain and accordingly are amenable to undergoing specific inter-

actions with electron-donating polymers. Furthermore, the low concentration of hydroxyl groups present in these polymers is associated with a low concentration of interacting points, which could allow one to modify certain properties of these polymers by blending with other macromolecules without substantially affecting the intrinsic properties inherent to poly(vinyl acetals).

Studies on polymer blends based on poly(vinyl acetals) and PVP have recently been reported^{14,15}. Thus, Eguiazabal *et al.*¹⁴ have shown that poly(vinyl butyral) and PVP are miscible at high concentrations of the former. Huang and Guo¹⁵ have studied blends of poly(vinyl formal) and PVP, which were shown to be miscible in the entire polymer concentration range. The miscibility encountered was explained in both cases as a result of the presence of unreacted hydroxyl groups, although no structural study was carried out to support this explanation.

This paper is aimed at studying some controversial aspects associated with PVP/poly(vinyl acetals) blends, viz. (i) the influence of the blend preparation procedure on the miscibility behaviour between both polymers, (ii) the variation with polymer concentration of the blend glass transition obtained by means of two different techniques (d.t.a. and d.m.t.a.) and (iii) the clarification of the mechanism associated with the phase behaviour found.

EXPERIMENTAL

Poly(1-vinyl-2-pyrrolidone) (PVP), poly(vinyl formal) (PVFOR) and poly(vinyl butyral) (PVBUT) were com-

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mercial polymers supplied by Aldrich. The molar mass of PVP as determined by Aldrich was $M_w = 40\,000\text{ g mol}^{-1}$. The molar masses and polydispersities of PVFOR and PVBUT were measured by size-exclusion chromatography (s.e.c.) using tetrahydrofuran (THF) as solvent at room temperature. Samples were eluted at a flow rate of 1.0 ml min^{-1} . The columns were first calibrated with standard polystyrene samples of narrow molar-mass distribution. The weight-average molar masses found for PVFOR and PVBUT were $220\,000$ and $36\,000\text{ g mol}^{-1}$, respectively. Their polydispersities were close to 2.3.

The blends were prepared using three methods: coprecipitation, freeze-drying and solvent casting. With regard to the first method, chloroform solutions of the blends, having different compositions of each constituent polymer, are precipitated with ethyl ether. The precipitate is subsequently filtered and dried under vacuum. In the second method, blends with different compositions of each constituent were prepared by dissolving corresponding masses of both polymers in *p*-dioxane and freeze-drying for 10 h. In the last method, chloroform solutions of both polymers at a total polymer concentration of 3 g dl^{-1} were placed into Petri dishes and allowed to evaporate slowly in air at room temperature to form polymer films. The films were subsequently dried in vacuum for one week to complete removal of solvents. In all cases, the blends prepared were stored in a desiccator in order to prevent the adsorption of water by the poly(1-vinyl-2-pyrrolidone).

Differential thermal analysis (d.t.a.) measurements were carried out using a Mettler TA2000 differential calorimeter. The temperature and energy calibration was made with indium as standard. The blends were first heated to 393 K for 5 min to remove the water adsorbed by PVP. They were then cooled very quickly to 323 K and heated to 463 K using a heating rate of $10^\circ\text{C min}^{-1}$. Sample weight varied between 10 and 12 mg. Glass transition temperatures were calculated as the half-height of the corresponding heat-capacity jump.

Dynamic mechanical thermal analysis (d.m.t.a.) was carried out using a Polymer Laboratories Mark II analyser. The samples were prepared by pressing the blends obtained from the precipitation method between hot plates for 3 min. The mean dimensions for the samples between the clamps were $10 \times 40 \times 0.65\text{ mm}^3$. The samples were analysed using the single cantilever mode with a heating rate of 2 K min^{-1} , at a frequency of 1 Hz and constant elongation of $45\text{ }\mu\text{m}$.

The infra-red spectra associated with the constituent polymers and blends were obtained with a Nicolet Fourier-transform infra-red (FTi.r.) spectrophotometer, model 520. Thin films of PVP/polyacetal blends were prepared by casting chloroform solutions (2 g dl^{-1}) onto potassium bromide pellets at room temperature. All the films used in this study were sufficiently thin to be within an absorbance range where the Beer-Lambert law is obeyed (less than 0.4). In all cases the spectra were obtained with 2 cm^{-1} resolution and after 200 scans.

RESULTS AND DISCUSSION

The simplest criterion to confirm miscibility between two polymers is the observation of a single glass transition temperature. This criterion is valid for mixtures whose pure components have a noticeable difference in T_g values, as happens for the polymers used in this work: 381 K for PVFOR and 432 K for PVP. The following

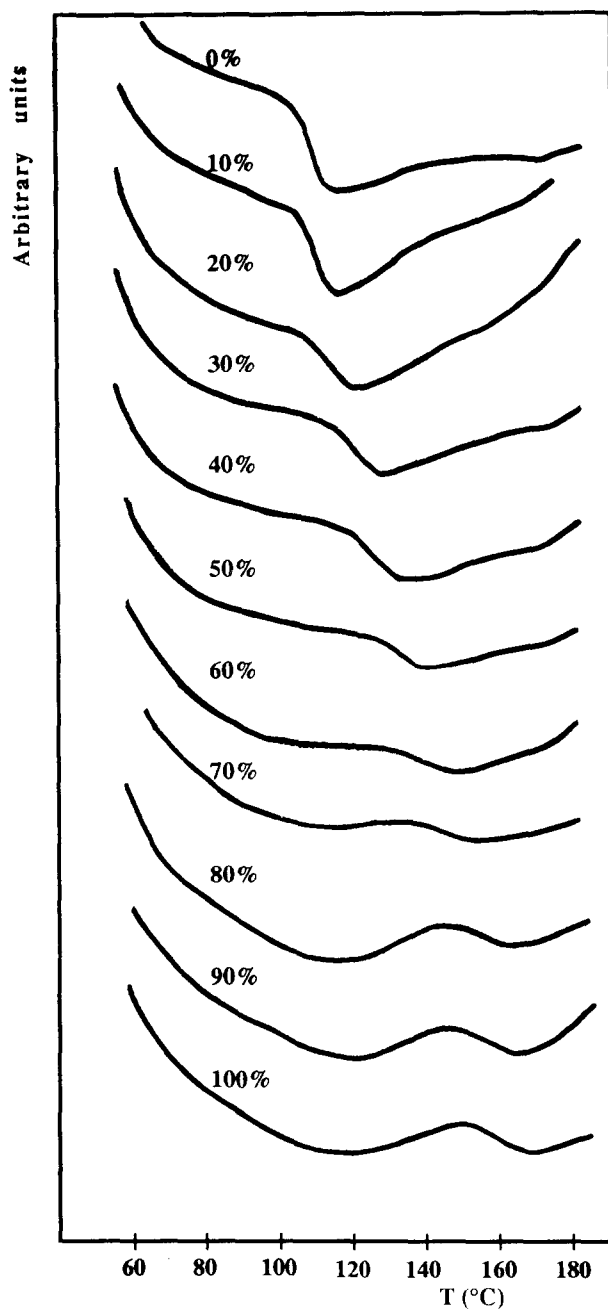


Figure 1 Differential thermal analyses of PVP/PVFOR blends as a function of PVP content

analysis will distinguish between different methods of preparation, since this factor, as will be shown later, has an appreciable influence on the phase behaviour of the mixture.

The d.t.a. thermograms obtained for blends of PVP and PVFOR showing different polymer concentrations are given in Figure 1. As can be seen, these blends show a single glass transition temperature, which can be qualitatively interpreted as the existence of miscibility between these two polymers in the entire composition range. Although, in principle, the d.t.a. thermograms are self-substantiating, d.m.t.a. measurements have also been carried out in this work in order to corroborate the findings given above. Figure 2 shows the variation with temperature of the loss tangent of various PVP/PVFOR blends having different content of each constituent polymer. It is apparent from this figure that a single peak characterizes each specific blend, that is, a single T_g is

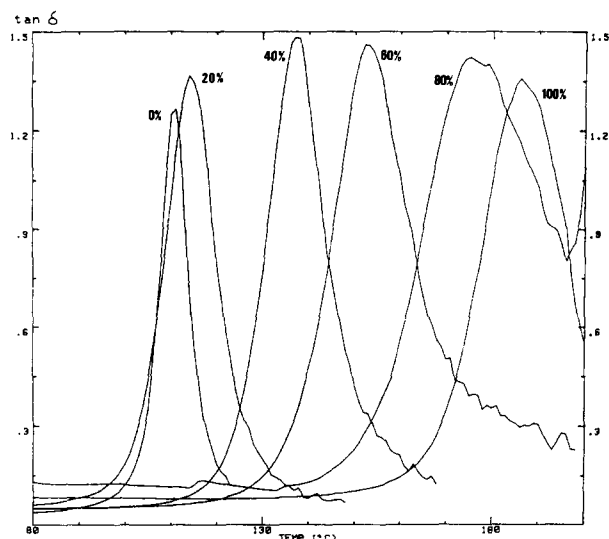


Figure 2 Variation of loss tangent ($\tan \delta$) with temperature for PVP/PVFOR blends as a function of PVP content

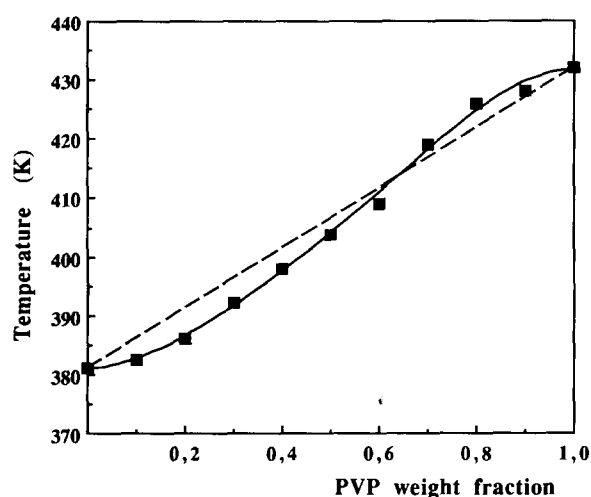


Figure 3 Variation of glass transition temperature T_g of PVP/PVFOR blends as a function of PVP content

detected in all cases, which is indicative of polymer/polymer miscibility.

The variation of the blend glass transition as a function of PVP content is given in Figure 3. This figure shows that at low PVP concentrations the blends show T_g values that are below the theoretical line (broken line) calculated as the mean value of the constituent polymer glass transitions. On the other hand, however, at high PVP contents, the blend T_g values are above the theoretical line. It should be noted that the deviation of the experimental T_g values from the theoretical ones is very small. Thus, for a PVP concentration of 0.2, the difference between experimental and theoretical values is ≈ 5 K, whereas for 0.9 is ≈ 3 K. It is also relevant to note that the T_g values obtained by means of d.m.t.a. confirm the S shape found from d.t.a. measurements.

Further analysis of the results obtained was carried out by comparing the blend T_g values with those calculated from various relevant equations. The Fox¹⁶ and Gordon-Taylor¹⁷ equations are usually employed to model the thermal behaviour of miscible polymer

blends. The former is usually written as:

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \quad (1)$$

where w_A , w_B , T_{gA} and T_{gB} are the weight fractions and the glass transitions corresponding to polymer A and B, respectively, and T_g is the glass transition associated with a blend having a content w_A of the polymer A. As can be observed from Figure 4, this equation predicts a slight negative deviation of the theoretical T_g from the mean-value assumption. With regard to the Gordon-Taylor equation, the blend T_g values are predicted through the application of the following equation:

$$T_g = \frac{w_A T_{gA} + k w_B T_{gB}}{w_A + k w_B} \quad (2)$$

In equation (2) T_g , T_{gA} , T_{gB} , w_A and w_B denote the same variables as in equation (1) whereas k is a factor given by:

$$k = (a_r - a_g)_B / (a_r - a_g)_A$$

where a is the thermal expansion coefficient of each constituent polymer and r and g refer to the rubbery and glassy state respectively. The value of k was found to be 0.5 from d.t.a. measurements. Figure 4 shows that the Gordon-Taylor equation also predicts a negative deviation from the mean-value assumption. Consequently, the behaviour encountered for the PVP/PVFOR blend differs from the three theoretical predictions used in this paper, e.g. the ideal behaviour represented by the mean-value assumption, Fox equation and Gordon-Taylor equation.

Similar results to those described in this paper for the PVP/PVFOR blend have been reported previously²⁰. Curiously enough, the polymer alloys that exhibit an S-shaped behaviour were found to present specific interactions of the hydrogen-bonding type. This is the case for the blend PMMA/Novolac resins. Accordingly, the unreacted hydroxyl groups present in poly(vinyl acetals) would appear to play an important role in the phase behaviour of this type of polymer when blended with electron-donating polymers such as PVP. For the sake of clarification, the experimental T_g values obtained for blends of PVP and PVFOR studied in this paper have also been compared with those calculated from the Kwei

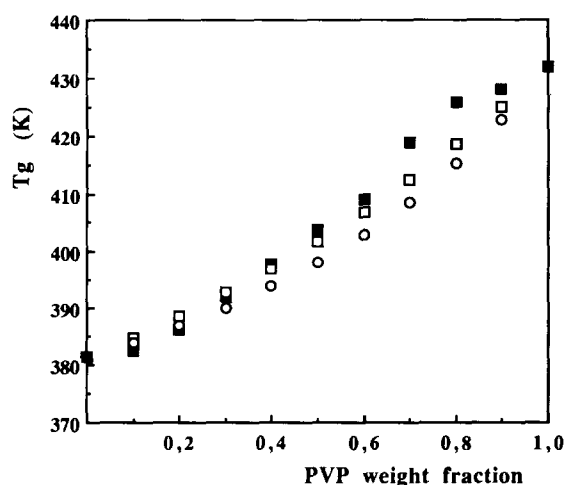


Figure 4 The T_g -composition dependence of PVP/PVFOR blends: (■) experimental; (□) Fox equation; (○) Gordon-Taylor equation

equation^{20,21}. Kwei proposed that polymer blends in which hydrogen bonding is giving rise to miscibility between both macromolecules should be modelled with the following equation:

$$T_g = \frac{w_A T_{gA} + k w_B T_{gB}}{w_A + k w_B} + q w_A w_B \quad (3)$$

where k and q are adjustable parameters. However, experimental data reported here do not fit this equation for the case of the PVP/PVFOR mixture. At this point it is necessary to take into account that the Kwei equation is proposed for systems with a greater extent of hydrogen bonding than is expected to be present for the PVP/PVFOR pair.

These results must also be compared to those found by Huang and Guo¹⁵. Those authors reported a negative deviation of T_g values in the whole composition range. In principle, this different behaviour found by these authors could be ascribed to the nature of the PVFOR used in this work, viz. to a different hydroxyl content than the sample employed here. However, no experimental evidence can be provided.

In order to verify the existence of lower critical solution temperature (*LCST*) behaviour in these blends, thermal stabilities of the pure components were studied by d.t.a. and thermogravimetry. Analysis of pure components showed that both polymers undergo thermal degradation with appreciable mass loss at temperatures above 503 K. Accordingly, thermal stability analysis of PVP/PVFOR mixtures were performed at different temperatures below 503 K by annealing for up to an hour. D.t.a. showed no indication of phase separation phenomena. However, by annealing at temperatures above 500 K, broadening of the glass transition temperature range was found by d.t.a., which could be attributed to phase separation, but could also be the result of polymer degradation.

The method of preparation of polymer blends is known to have a decisive importance on miscibility²². PVP/PVFOR blends were prepared by three different methods, coprecipitation, solvent casting and freeze-drying, as we have indicated above. Compatibility and thermal stability analyses were performed in all cases.

As mentioned before, PVP/PVFOR mixtures prepared by coprecipitation were found to be compatible in the whole composition range. However, it is important to note that the first d.t.a. scan indicates that the sample obtained by coprecipitation is not totally homogeneous. Thus, samples presenting high PVFOR or high PVP contents exhibit a single, although not well defined, T_g located near the T_g of the component present in higher proportion. Samples of intermediate compositions show two glass transition temperatures, each one placed very near to the T_g of the corresponding pure component. However, subsequent scans always show a single T_g (see Figure 2). Hence, coprecipitation leads to homogeneous mixtures if the sample is heated up above T_g of PVP (around 463 K). The blends exhibit permanent homogeneity after the first scan as determined by d.t.a. of dried samples weeks after.

Similar results were observed for those samples prepared by solvent casting. Nevertheless, samples of intermediate compositions exhibit a higher initial degree of homogeneity than those prepared by coprecipitation, as indicated by the presence of less well defined double T_g during the first scan.

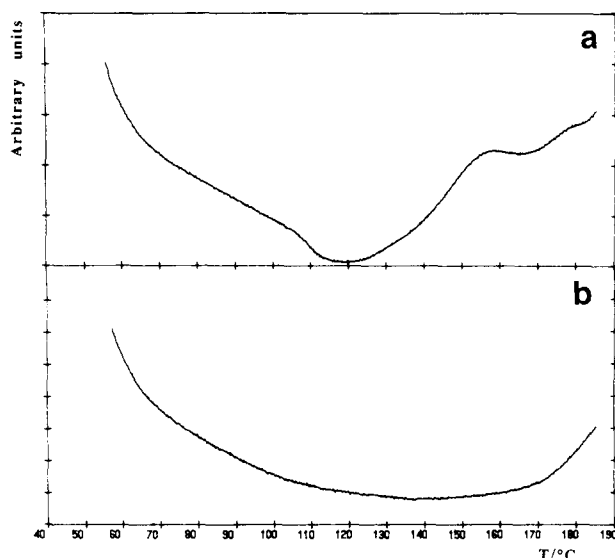


Figure 5 D.t.a. curves for PVP/PVFOR blend prepared by freeze-drying (60% PVP composition): (a) first scan and (b) second scan

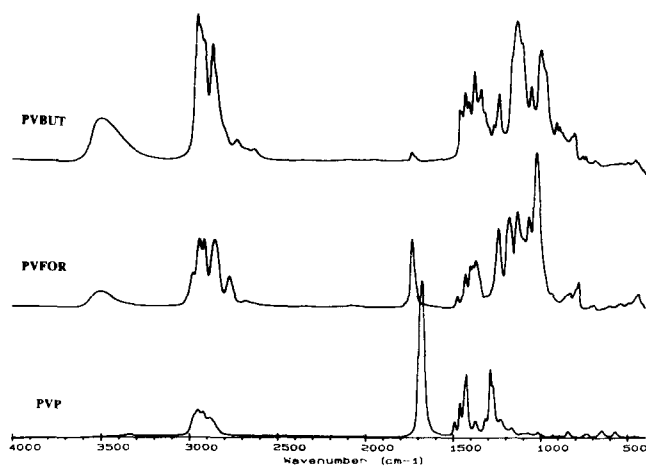


Figure 6 FTi.r. spectra of pure polymers: PVP, PVFOR and PVBLT

Different results were found in the analysis of samples prepared by freeze-drying of solutions in *p*-dioxane. Thus, Figure 5a shows that blends having PVP contents ranging from 20 to 60 wt% present two different T_g located near the two corresponding T_g of the pure components. Subsequent scans give rise to a thermogram in which a well defined glass transition cannot be located (Figure 5b). This thermogram could be interpreted as a broad continuous glass transition temperature that could be indicative of the presence of a number of domains of different compositions. This result suggests a selective precipitation of the polymers during the freezing step previous to freeze-drying. The subsequent thermal treatment is not enough to reach complete homogeneity owing to the limited chain mobility of the highly viscous medium. In the case of mixtures prepared by coprecipitation and by solvent casting, the initial degree of homogeneity appears to be higher and the thermal treatment used produces homogeneous blends.

Intermolecular specific interactions in the PVP/PVFOR system were studied by Fourier-transform infra-red spectroscopy. Figure 6 shows the spectra of pure components. The PVFOR spectrum presents the following

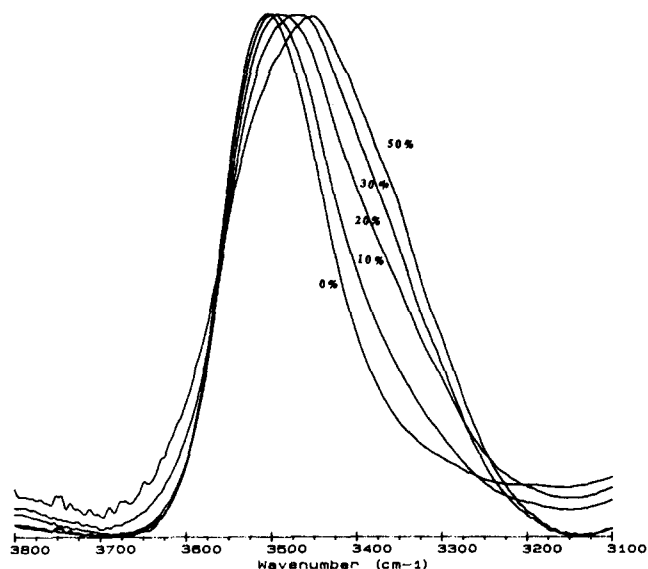


Figure 7 FTIR spectra of different PVP/PVFOR blend compositions (0 to 50 wt% of PVP) in the hydroxyl stretching region (3100–3800 cm^{-1})

characteristics: (i) a broad and weak absorption band at 3505 cm^{-1} corresponding to the stretching vibration of hydroxyl groups; (ii) a strong intensity band at 1024 cm^{-1} due to the asymmetric vibration of the ether group; and (iii) a medium intensity absorption band at 1736 cm^{-1} due to the vibration of carbonyl groups. This latter band could be attributed to residual acetate groups, since this polymer is obtained from partially hydrolysed poly(vinyl acetate) as pointed out above. On the other hand, PVP also presents a strong absorption band at 1680 cm^{-1} due to the vibration of carbonyl groups and a medium intensity band at 1280 cm^{-1} ascribed to the vibration of the C–N group. As mentioned before, PVP is a very hygroscopic polymer and, accordingly, caution must be taken to dry the sample before infra-red analysis. Otherwise, a broad band located between 3640 and 3450 cm^{-1} corresponding to the vibration of hydroxyl groups of adsorbed water could appear. Adsorbed water also produces a small displacement of the carbonyl band towards lower frequencies (1677 cm^{-1}) due to hydrogen bonding between the carbonyl group and water. Consequently, the presence of adsorbed water makes the interpretation of the spectra more difficult and can also mask the spectral features of the polymer blend. For this reason all samples were dried for 5 min under vacuum, at 393 K . The PVP spectrum of Figure 6 shows no trace of the OH band located at 3500 cm^{-1} after this thermal treatment.

The spectra of polymer mixtures present some changes with respect to those of the pure components. Figure 7 shows the spectra of PVFOR/PVP mixtures with high PVFOR content in the region from 3100 to 3800 cm^{-1} . It is apparent that the broad absorption band observed for PVFOR at 3505 cm^{-1} is broader in the blend and is shifted towards higher wavenumbers as PVP content increases. The band located at 3505 cm^{-1} is usually associated with hydroxyl groups. The possible self-association present in PVFOR could take place between unreacted hydroxyl and acetate groups or other groups. The displacement observed in the blends seems to indicate that the intermolecular interactions in PVP/PVFOR

are stronger than intramolecular interactions in PVFOR. Similar characteristics have been reported in the case of PVP/poly(vinylphenol) mixtures¹². It must be noted that PVP produces a weak band at 3340 cm^{-1} (probably a harmonic or combination band). In Figure 7 this weak band was subtracted. This arithmetic spectral treatment has no effect on the absorption band of the hydroxyl group. It is also interesting to highlight that the PVP carbonyl band does not undergo any significant change in either position or intensity at high PVP content. This behaviour contrasts with that reported for blends of PVP with other polymers such as poly(vinyl alcohol)²³ or poly(vinylphenol)¹². For low PVP contents a slight broadening of the absorption band and a small shoulder at 1660 cm^{-1} were observed. The position of the small shoulder coincides with the position assigned to vibration of associated carbonyl of PVP in other blends¹².

Infra-red analysis was also performed on PVP/PVBUT mixtures previously studied by Eguiazabal *et al.*¹⁴ in order to find a possible mechanism for polymer/polymer miscibility data given by these authors. Results were similar to those corresponding to PVP/PVFOR blends. Figure 6 presents a spectrum in which the vibration of hydroxyl groups can be observed to appear at 3504 cm^{-1} . The sample contains free acetate groups. Figure 8 shows the region of hydroxyl groups stretching vibration for the pure components and for two mixtures having different PVP content. As was found for PVFOR, PVBUT also presents associated hydroxyl groups. Again, a clear displacement of the maximum towards lower frequencies is observed as PVP content increases. The shoulder assigned to associated carbonyl groups of PVP appears more clearly for high PVBUT contents, as can be seen in Figure 9, probably due to hydrogen-bonding

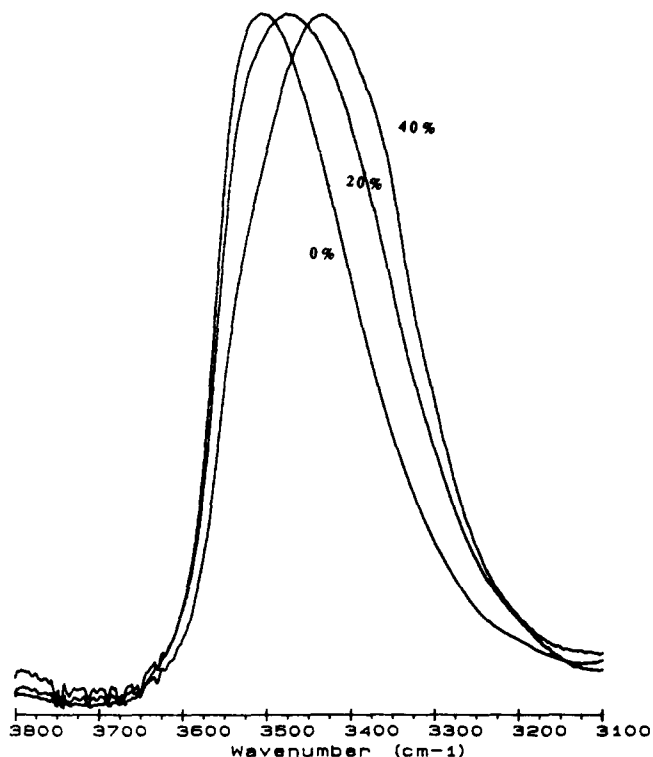


Figure 8 FTIR spectra of different PVP/PVBUT blend compositions (0, 20 and 40 wt% of PVP) in the hydroxyl stretching region (3100 – 3800 cm^{-1})

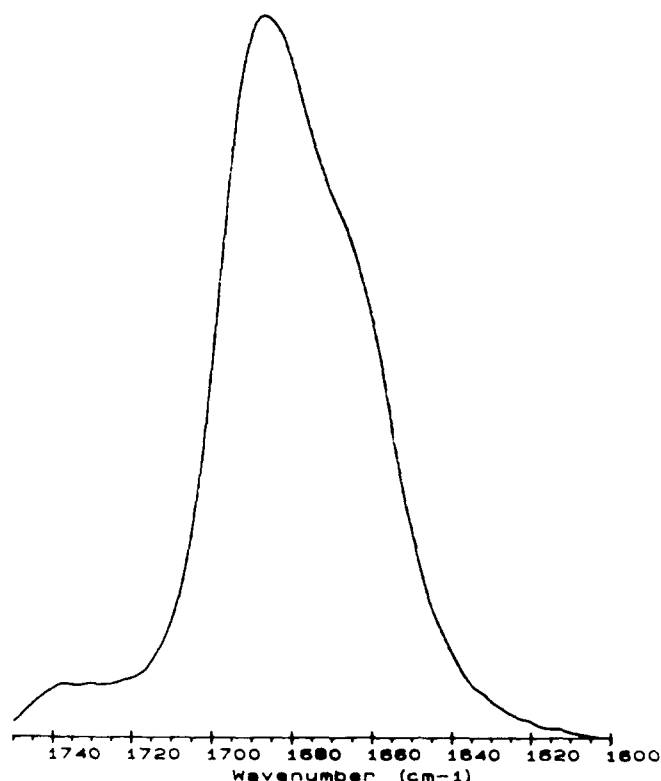


Figure 9 Carbonyl group stretching region of a 20:80wt% PVP/PVBUT blend

interactions between the carbonyl groups of PVP and hydroxyl groups of PVBUT.

FTIR results indicate the presence of hydrogen-bonding interactions between poly(vinyl acetals) and PVP. Nevertheless, the low contents of hydroxyl groups in these poly(vinyl acetals) make it difficult to evaluate this interaction in comparison with other types of blends. In this connection, identification of associated carbonyl groups is only possible for high contents in poly(vinyl acetals). In fact, in these cases, the ratio of carbonyl to hydroxyl groups is close to unity and the associated carbonyl population is enough to allow its detection. Anyway, the observation of noticeable changes in hydroxyl group bands is always possible because these groups have a lot of carbonyl groups that can interact with them. We can consider these interactions as responsible for miscibility of the blends studied in this paper.

ACKNOWLEDGEMENTS

This work has been possible thanks to financial support of Vicerrectorado de Investigación de la Universidad del País Vasco and Departamento de Educación, Universidades e Investigación del Gobierno Vasco. J. R. Isasi Allica acknowledges the award of a fellowship by the Departamento de Universidades, Educación e Investigación del Gobierno Vasco. We also thank Dr Alvaro Ramirez Garcia of Universidad Industrial de Santander (Colombia) and Dr José Manuel Rego López for their help during the translation of this paper.

REFERENCES

- 1 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer-Polymer Miscibility', Academic Press, New York, 1979
- 2 Rodriguez-Parada, J. M. and Percec, V. *J. Polym. Sci. (A) Polym. Chem.* 1986, **24**, 579
- 3 Belorgey, G. and Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 191
- 4 Woo, E. M., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1983, **28**, 1347
- 5 Coleman, M. M., Skrovanek, D. J., Hu, J. and Painter, P. C. *Macromolecules* 1968, **21**, 59
- 6 Lee, J. Y., Painter, P. C. and Coleman, M. M. *Macromolecules* 1988, **21**, 954
- 7 Tsuchida, E., Osada, Y. and Ohno, H. *J. Macromol. Sci., Phys. (B)* 1980, **17**, 683
- 8 Domard, A. and Rinaudo, M. *Macromolecules* 1980, **14**, 620
- 9 Zhou, Z. L. and Eisenberg, A. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 595
- 10 Krause, S. in 'Polymer Blends' (Eds. D. R. Paul and S. Newman), Academic Press, New York, 1978
- 11 Serman, C. J., Xu, Y., Painter, P. C. and Coleman, M. M. *Macromolecules* 1989, **22**, 2015
- 12 Moskala, E. J., Varnell, D. F. and Coleman, M. M. *Polymer* 1985, **26**, 228
- 13 Lee, J. Y., Moskala, E. J., Painter, P. C. and Coleman, M. M. *Appl. Spectrosc.* 1986, **40**, 991
- 14 Eguiazabal, J. Y., Iruin, J. J., Cortazar, M. and Guzmán, G. M. *Makromol. Chem.* 1984, **185**, 1761
- 15 Huang, J. and Guo, Q. *Makromol. Chem., Rapid Commun.* 1990, **11**, 613
- 16 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1**, 123
- 17 Gordon, M. and Taylor, J. S. *J. Appl. Chem.* 1952, **2**, 493
- 18 Tremblay, C. and Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 1857
- 19 Schneider, H. A. and Brekner, M. J. *Polym. Bull.* 1985, **14**, 173
- 20 Kwei, T. K. *J. Polym. Sci., Polym. Lett. Edn.* 1984, **22**, 307
- 21 Kwei, T. K., Pearce, E. M., Pennacchia, J. R. and Charton, M. *Macromolecules* 1987, **20**, 1174
- 22 Saeki, S., Cowie, J. M. G. and McEwen, I. J. *Polymer* 1983, **24**, 60
- 23 Ping, Z. H., Nguyen, Q. T. and Néel, J. *Makromol. Chem.* 1988, **189**, 437