

Poly(vinyl alcohol) and poly(vinyl pyrrolidone) blends: miscibility, microheterogeneity and free volume change

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Blends of crystallizable poly(vinyl alcohol) (PVA) with poly(vinyl pyrrolidone) (PVP) were studied by differential scanning calorimetry (d.s.c.). PVA with different degrees of hydrolysis (88 and 99 wt%) and PVP with different molecular weights (10 000 and 360 000 g mol⁻¹) were used. The blends exhibited a single glass transition, as determined by d.s.c., suggesting the miscibility of the system over the whole composition range studied. The enthalpy of fusion (ΔH_f), as well as the glass transition temperature (T_g), heat capacity (ΔC_p) and glass transition width (Δw), were also determined by d.s.c. These parameters changed with the degree of hydrolysis of PVA, PVP molecular weight and blend composition. The behaviour of ΔC_p vs blend composition was complex for the different pairs of blends, suggesting strong interaction between PVA and PVP. From the analysis of Δw dependence on blend composition we concluded that blends containing PVP of 10 000 g mol⁻¹ exhibit a larger number of relaxations than blends containing high molecular weight PVP, indicating that the density of interactions is larger in the former. © 1997 Elsevier Science Ltd.

(Keywords: miscibility; free volume; microheterogeneity)

INTRODUCTION

There have been many studies of polymer blends in recent years. The interest in novel structures and in the properties of the blends is due to the necessity of materials with different properties than those observed in homopolymers and copolymers.

An important and determinant aspect of the properties of a blend is the miscibility of its components. Miscibility in polymer blends is assigned to specific interactions between polymeric components, which usually give rise to a negative free energy of mixing in spite of the high molecular weight of polymers. The most common interactions present in blends are: hydrogen bonding, ionic and dipole, π -electrons and charge-transfer complexes¹.

The components of the blends studied in the present paper were poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP).

The pyrrolidone rings in PVP contain a proton-accepting carbonyl moiety, while PVA presents hydroxyl groups as side groups. Therefore, a hydrogen-bonding interaction may take place between these two chemical moieties in blends of PVA and PVP^{2–4}. The same interaction is responsible for the solubility of PVA and PVP in water⁵.

Although there have been many studies of PVA/PVP blends in recent years^{4,6–10}, many interesting aspects remain to be elucidated such as the influence of the

degree of hydrolysis of PVA and the molecular weight of the starting polymers on the crystallinity and relaxations in the blends.

In this work the glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH_f), glass transition width (Δw) and the difference in heat capacity between the glassy and the elastomeric state (ΔC_p) associated with the glass transition were determined by d.s.c. These studies were carried out for PVA of different degrees of hydrolysis, and for PVP of different molecular weights.

EXPERIMENTAL

Polymer materials

The polymers used in this work were commercial products whose properties are listed in *Table 1*.

Cast films

The polymer solutions in distilled water were prepared at a concentration of 5 wt% by dissolving dried powder samples of PVA and PVP at 100°C and at room temperature, respectively, under continuous stirring. The two solutions were mixed in the desired proportions and then stirred for 15 min at room temperature. The relative composition of the polymers in the mixed solutions ranged from 10 to 90 (PVA/PVP weight percent ratio). Blend and homopolymer films of PVA and PVP were cast from aqueous solution on a Petri plate by water evaporation at 80°C. The solid films were

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Table 1 Degree of hydrolysis of PVA, and the molecular weight (M_w) of PVA and PVP used to obtain the blends

Code	Degree of hydrolysis (%)	M_w (g mol ⁻¹)	Source
PVA 99	99	124 000	Aldrich
PVA 88	87.7	127 000	Rhodia
PVP 10	—	10 000	Sigma
PVP 360	—	360 000	Sigma

further dried at 110°C for 12 h under vacuum and stored in a desiccator.

Differential scanning calorimetry

Differential scanning calorimetry (d.s.c.) was carried out using an MDSC 2910 TA Instruments equipment.

The experiments were performed according to the following programme:

- initial temperature -20°C;
- heating rate of 20°C min⁻¹ to 200°C;
- cooling to 0°C;
- heating rate of 20°C min⁻¹ to 250°C.

The results reported in this work correspond to the second heating scan.

RESULTS AND DISCUSSION

Thermograms obtained for the different pairs of blends are shown in *Figure 1*. The homopolymer PVA showed T_g at +59°C and at +74°C for the 88 and 99 wt% hydrolysed PVA, respectively. An endothermic peak, due to the melting of the crystalline phase present in this polymer, can be observed at +179°C in PVA 88 and at +228°C in PVA 99. The area related to the melting peak is associated with the enthalpy of fusion (ΔH_f) of the crystalline region, which was larger in PVA 99 than in PVA 88, indicating a high degree of crystallinity of PVA 99. The acetate groups in PVA make chain packaging more difficult, causing the degree of crystallinity and the melting point value to drop. The PVA 99, containing only 1% of acetate groups, showed a degree of crystallinity of 30 wt%, while the PVA 88 presented a degree of crystallinity of 20 wt%.

D.s.c. curves for PVP showed T_g at +124°C and +185°C for the polymer with molecular weights of 10 000 and 360 000 g mol⁻¹, respectively.

Thermograms obtained for the blends showed a single glass transition temperature between the T_g s of the two homopolymers at every composition. The presence of a single glass transition indicates miscibility in the system¹¹. The miscibility of PVA/PVP blends was confirmed by the Flory-Huggins polymer-polymer interaction parameters, χ_{12} , which were negative for all the blends, independently of the PVP molecular weight or of the degree of hydrolysis of PVA¹². This miscibility should be promoted by hydrogen bonding formation between the PVA hydroxyl groups and the PVP carbonyl groups. Blends containing high PVA concentrations also presented a melting peak due to the crystalline phase of PVA. In these cases one can observe crystallization during the d.s.c. experiments, as can be seen from the exothermic process which occurs between the T_g and the T_m . All samples were quickly cooled (cooling rate around 40°C min⁻¹), and for many blends the cooling

time was not enough to allow complete crystallization. Consequently, crystallization took place during the second heating.

The influence of the PVP molecular weight and of the degree of hydrolysis of PVA on the enthalpy of fusion (ΔH_f) for all the blends is shown in *Figure 2*. The enthalpy of fusion in the blends, as well as the melting point, decreased in accordance with the rise of PVP concentration. This effect was more pronounced in the blends containing PVP 360 because it diminished the degree of crystallinity and the crystallization rate of PVA in lower concentrations than PVP 10. This behaviour can be explained by the higher viscosity of PVP 360 blends in the melting state, which makes crystallization more difficult.

The heat capacity (ΔC_p) and the glass transition width (Δw) were determined as illustrated in *Figure 3*. Blends that exhibit crystallization during the second heating in d.s.c. experiments show a poorly defined baseline after the glass transition (as schematized in *Figure 3b*). This crystallization makes the determination of the endset glass transition process, and consequently the determination of the Δw and ΔC_p values, more difficult. In the blends with high PVA content, up to 60 wt%, the Δw and ΔC_p values were determined assuming that the baselines before and after the glass transition were parallel, as observed for blends containing 90 wt% of PVA (*Figure 1*). As crystallization occurs at a higher temperature than T_g over the experimental time scale used, this process should not affect the determination of the glass transition process and, therefore, the determination of the ΔC_p and Δw values. Blends rich in PVP showed nonparallel baselines before and after T_g as a consequence of a broad and intense secondary relaxation of PVP chains, with the temperature ranging from 100°C to T_g ¹³. In these cases, crystallization was not observed, and the baselines are defined enough to allow the determination of the ΔC_p and Δw values.

Figure 4 shows the heat capacity (ΔC_p) in the glass transition region as a function of blend composition. The heat capacity is associated with the change of degrees of freedom in the glass transition resulting from the free volume changes in this region. Additivity of volume is expected for the ideal mixtures, and in this case ΔC_p reflects only the changes of the conformational arrangement and consequently the changes in the entropy of the system. If there were not strong interactions between PVA and PVP, ΔC_p would exhibit a linear dependence on blend composition as a consequence of the additivity of volume. However, the curve profiles shown in *Figure 4* present clearly the non-additivity of volume in these systems, which indicates the presence of strong interactions.

PVA 88 presented a ΔC_p smaller than PVA 99, as a consequence of the smaller free volume change in the former. The presence of 12 wt% bulky acetate groups in PVA 88 makes chain packaging in the glassy state more difficult, generating a higher free volume and consequently more flexible chains, in comparison with PVA 99, which contains only 1 wt% of acetate groups. These results agree with the thermal expansion coefficient ($\Delta\alpha$) in the glass transition region obtained by thermomechanical analysis (t.m.a.): $3.9 \times 10^{-4} \text{ K}^{-1}$ for PVA 88 and $5.3 \times 10^{-4} \text{ K}^{-1}$ for PVA 99¹². The influence of the PVP molecular weight on the ΔC_p of PVP may also be observed. The ΔC_p of PVP 10 is smaller than the value

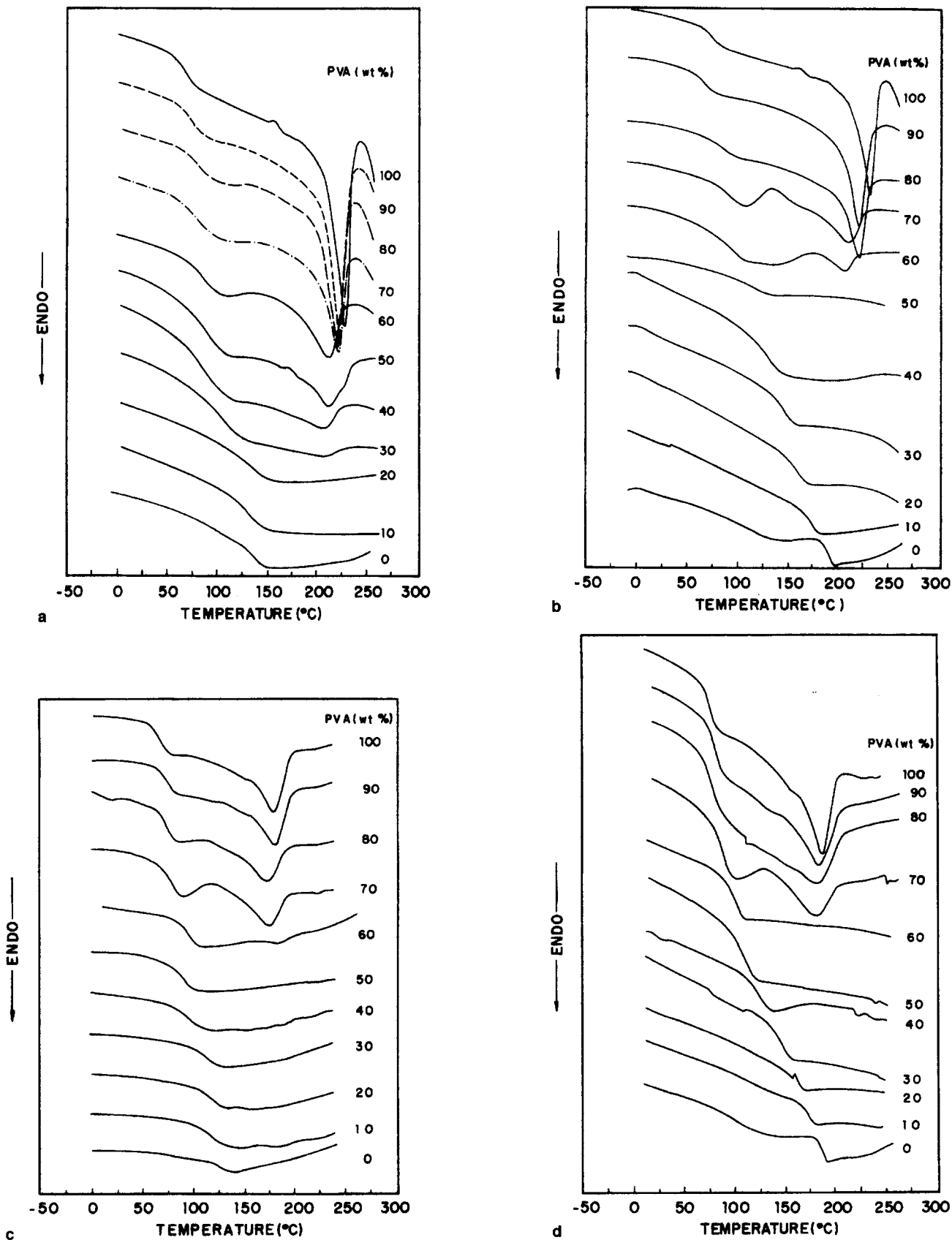


Figure 1 Thermograms obtained by d.s.c. for blends: (a) PVA 99/PVP 10; (b) PVA 99/PVP 360; (c) PVA 88/PVP 10; (d) PVA 88/PVP 360

found for PVP 360, reflecting an effect of the terminal group of the chains. In this case, the experimental determination of $\Delta\alpha$ was not possible because PVP 10 is brittle and consequently its films are difficult to obtain by casting. The $\Delta\alpha$ obtained for PVP 360 was

$3.2 \times 10^{-4} \text{ K}^{-1}$. The $\Delta\alpha$ values found for PVA and PVP agree with the data found in literature for many vinyl polymers, $4.0 \times 10^{-4} < \Delta\alpha < 9.5 \times 10^{-4} \text{ K}^{-1}$, and for amorphous polymers, $1.5 \times 10^{-4} < \Delta\alpha < 6.0 \times 10^{-4} \text{ K}^{-1}$.

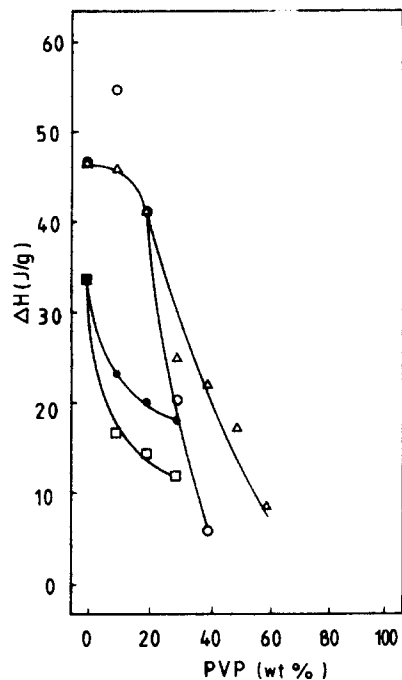


Figure 2 Influence of PVP molecular weight and degree of hydrolysis of PVA on the enthalpy of fusion: PVA 99/PVP 10 (Δ); PVA 99/PVP 360 (\circ); PVA 88/PVP 10 (\bullet); PVA 88/PVP 360 (\square)

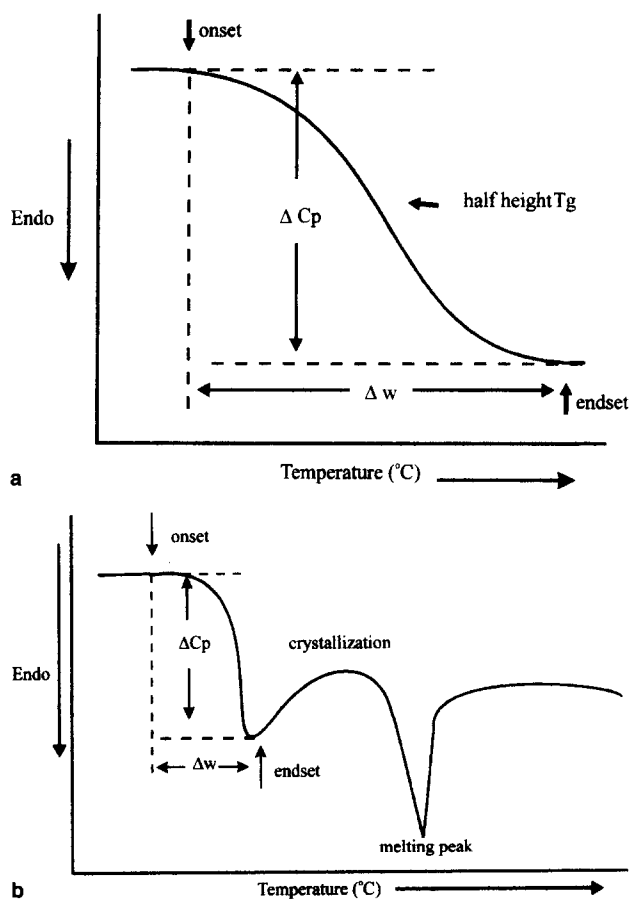


Figure 3 Determination of glass transition width (Δw) and heat capacity (ΔC_p): (a) ideal d.s.c. curve; (b) d.s.c. curve for sample which exhibits crystallization

Most of the blends showed a ΔC_p larger than that of the homopolymers, indicating a higher change of degrees of freedom in the glass transition for the blends. The hydrogen bonding between the PVA and PVP chains

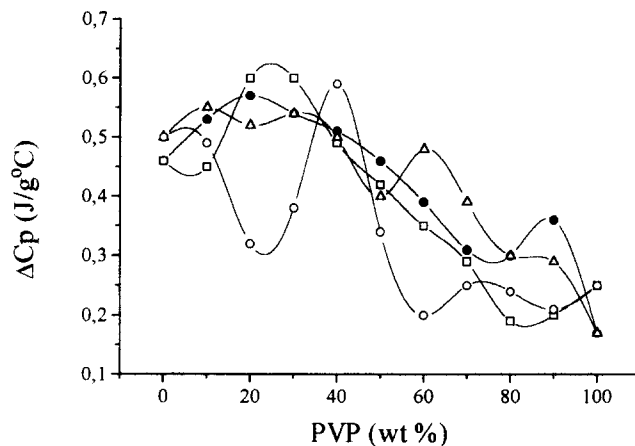


Figure 4 Heat capacity (ΔC_p) in the glass transition region as a function of the blend composition: PVA 99/PVP 10 (Δ); PVA 99/PVP 360 (\circ); PVA 88/PVP 10 (\bullet); PVA 88/PVP 360 (\square)

should restrict the number of possible conformational arrangements in the glassy state. The density of interactions, defined as the number of interactions between PVA and PVP chains for unit volume of samples, depends on the PVP molecular weight, the degree of hydrolysis of PVA and the blend composition. It is also influenced by the presence of the crystalline phase and is characteristic of each composition¹². The larger ΔC_p values were found in blends exhibiting a crystalline phase (high PVA concentration), which restricts chain mobility in the amorphous phase and consequently diminishes the probability of the formation of hydrogen bonding and the number of degrees of freedom in the glassy state. Above the T_g , hydrogen bonding interactions are weak, as the strength of these interactions decreases as the temperature rises, which does not cause significant interference in chain mobility. Consequently, there is a larger change in the number of degrees of freedom in the glass transition region for semicrystalline samples than for amorphous ones.

Glass transition width (Δw) d.s.c. curves are defined as the difference between onset and endset glass transition processes expressed in $^{\circ}\text{C}$, as illustrated in *Figure 3a*. The glass transition width reflects the number of relaxations responsible for the transition. If the mixture exhibits microenvironments caused, for example, by steric hindering, dipole-dipole interactions, hydrogen bonding, etc., then this mixture should undergo many relaxation processes with different relaxation times, resulting in a broadening of the glass transition. In PVA/PVP blends the glass transition width showed a strong dependence on the blend composition (*Figure 5*).

In blends containing PVP 10 the Δw values passed maxima at PVP concentrations of 30 and 70 wt% in PVA 99/PVP 10 blends, and at PVP concentrations of 10, 60 and 90 wt% in PVA 88/PVP 10 blends. In blends containing PVP 360, the maxima of Δw were found in PVP concentrations of 50 wt% for PVA 99/PVP 360 and 60 wt% for PVA 88/PVP 360. The blends showed broader glass transitions than the homopolymers as a result of the higher microheterogeneity in the system. This microheterogeneity is caused by an infinite number of environments of different compositions and different densities of interactions in each blend¹⁴. Interactions by hydrogen bonding observed between the hydroxyl-hydroxyl groups and the hydroxyl-carbonyl

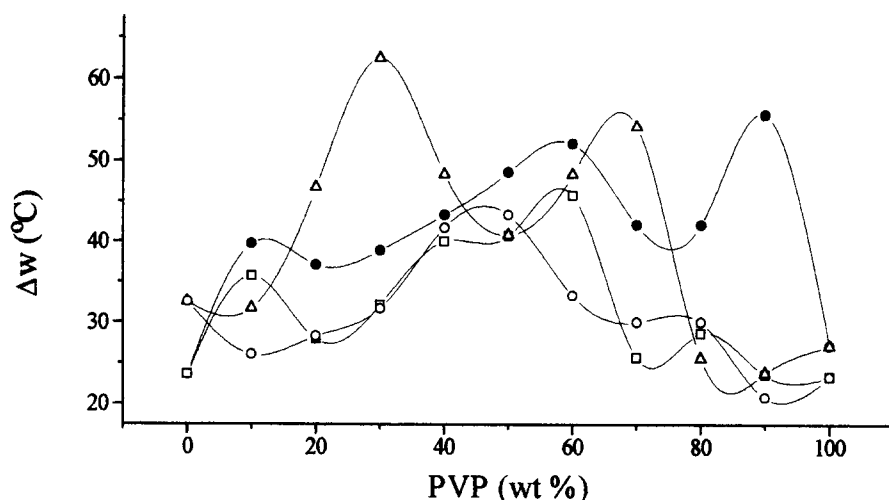


Figure 5 Dependence of glass transition width (Δw) on blend composition: PVA 99/PVP 10 (Δ); PVP 99/PVP 360 (\circ); PVA 88/PVP 10 (\bullet); PVA 88/PVP 360 (\square)

groups can occur as: intra-chain and inter-chain multiple hydrogen bonding in organized (and crystalline) PVA regions; cross-interaction of a PVP carbonyl group with a PVA hydroxyl group whose oxygen atom is involved as a proton-acceptor of another PVA hydroxyl group in the crystalline interface; cross-interaction between a PVP carbonyl group and a PVA hydroxyl group in the amorphous region; or simple hydrogen bonding between two hydroxyl groups in non-organized PVA regions⁴.

Blends containing PVP 10 showed larger Δw values than the respective PVP 360 blends, as can be observed in Figure 5. This indicates that the density of interactions in PVP 10 blends should be larger than in PVP 360 blends. This fact can be associated with the larger mobility of PVP 10 chains due to their lower molecular weight and higher free volume, which allow better accommodation of PVP 10 chains among the PVA chains. Consequently, a large number of interactions can occur between PVP and the different chains.

The same mobility effect can be considered in PVA containing different degrees of hydrolysis. The acetate groups present in PVA 88 (12 wt%), which are bulkier than the hydroxyl groups, should cause a larger free volume in this polymer than in PVA 99 in the glassy state. The PVA 88 should also present intra-chain interactions between the acetate and hydroxyl groups.

CONCLUSIONS

The PVA/PVP blends were miscible at every composition, as observed by d.s.c. The lower molecular weight of PVP and the higher degree of hydrolysis of PVA promoted higher crystallinity in the blends.

ΔC_p at the glass transition showed a similar behaviour for the blends obtained from PVP with different molecular weights as well as the different degrees of hydrolysis of PVA. The behaviour of ΔC_p as a function of the blend composition was complex for all the pairs of blends as a consequence of the non-additivity of volume, which suggests strong interaction between PVA and PVP. The analysis of glass transition width (Δw)

dependence on blend composition showed that the blends containing PVP with lower M_w exhibit a larger number of relaxations, indicating that the density of interactions is larger in this case as a consequence of the higher free volume associated with lower molecular weights of PVP. This effect was also observed for blends of PVA with lower degrees of hydrolysis, in which there is a higher free volume.

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