Fourier transform infra-red and thermal analysis studies of poly(vinyl alcohol)–poly(vinyl pyrrolidone) blends

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The Fourier transform infra-red and differential scanning calorimetry studies of blends of poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) of various compositions were made by casting films of the blends on a mercury surface. The prominent infra-red bands of PVA undergo both frequency and intensity changes in the blends indicating the effect of intermolecular interactions as well as reduction in crystallinity. The composition with 70 wt% PVA shows drastic changes in the spectra, and 30 wt% PVA shows changes in the glass transition temperature.

(Keywords: *FT*i.r.; d.s.c.; blends; crystallinity; intermolecular intractions)

INTRODUCTION

It has been increasingly recognized that intermolecular interactions strongly influence the mechanical properties of polymer blends, and Fourier transform infra-red (*FT*i.r.) studies offer a useful means of studying the intermolecular interactions and hence the compatibility of blends. However, such studies of poly(vinyl alcohol) (PVA) blends with other polymers are very few. The *FT*i.r. study of PVA with chitosan has been reported earlier by Miya[1] who analysed the bands due to chitosan. According to Miya, PVA is compatible with chitosan and the intermolecular interaction is at a maximum for the 80:20 PVA–chitosan blend composition. This was also supported by the finding that the tensile strength is at a maximum for this composition. The compatibility was attributed to the strong interaction between the OH group of PVA and the OH or NH_2 of chitosan. Further, it was reported that the crystallinity of PVA was not destroyed in the blends as indicated by the persistence of a crystalline sensitive band in the blends.

Another technique for studying the miscibility of the blends is the determination of the glass transition temperature (T_g) of the blends by differential scanning calorimetry (d.s.c.). Blends of cellulose with PVA have recently been studied by Nishio and Manley[2] using this technique. As the cellulose content was increased from 0 to 60 wt%, the T_g of PVA was found to shift to higher values and the transition was characterized by a broadening of the width. For higher concentrations of cellulose, the T_g of PVA was undiscernible. They concluded that the blends were strongly miscible at higher concentrations of cellulose.

In the present study, PVA is blended with poly(vinyl pyrrolidone) (PVPLN) in different ratios, and both *FT*i.r. and d.s.c. studies were carried out. From a study of the shift and intensity of the i.r. bands and the changes in T_g, it appears that the inter-molecular interactions are quite significant in the blend with a PVA:PVPLN composition of 70:30. Also, contrary to the findings in the case of chitosan blends[1] with PVA, the crystallinity of PVA is destroyed in the blends with higher composition of PVPLN as indicated by the disappearance of the corresponding i.r. bands.

EXPERIMENTAL

The PVA and PVPLN samples were purchased from Aldrich Chemical Company. The PVA was 98.5% hydrolyzed and no details are known about its molecular weight. The average molecular weight of PVPLN is 24 000.

Thin films of PVA:PVPLN blends were cast from 2.5 wt% water solution, on to a mercury surface at room temperature in a desiccator. After evaporation of the solvent, the film was removed from mercury and dried in a vacuum desiccator above room temperature for 2 days.

I.r. spectra were obtained on a Nicolet 5DXB *FT*i.r. instrument. Sixty-four scans at a resolution of $2\,cm^{-1}$ were signal averaged. The frequency scale was internally calibrated with a reference He–Ne laser to an accuracy of $0.2\,cm^{-1}$.

The d.s.c. studies were carried out using DuPont 9900 instrument. The T_g of PVA is around 80°C while that of PVPLN is 94°C. The heating rate was $10°C\,min^{-1}$, and the samples were kept in a nitrogen atmosphere.

RESULTS AND DISCUSSION

FT*i.r. spectra*

The prominent i.r. bands of PVA which occur at 852, 1094, 1143 and $1333\,cm^{-1}$ in the region $800–1400\,cm^{-1}$ are considered.

Figure 1 shows the *FT*i.r. scale expanded spectra of pure PVA (curve A) and the spectra of PVA-PVPLN blends with PVA composition of 90–40 wt% (B-G) taken in the $700–950\,cm^{-1}$ region. Krimm[3] has assigned the band at $852\,cm^{-1}$ to CH_2 (amorphous) deformation. As the concentration of PVA in the blend decreases, this band shifts to lower frequency up to $841\,cm^{-1}$ in the

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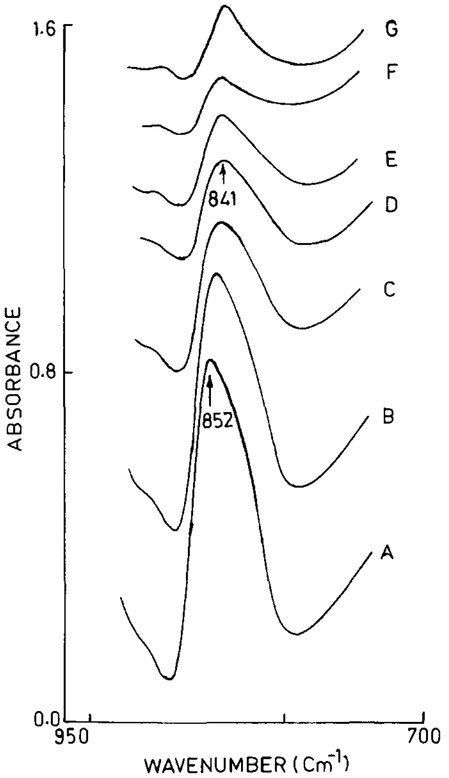

Figure 1 *FT*i.r. spectra in the region 700–950 cm^{-1} of pure PVA (A) and 90–40 wt% PVA (B–G) in the PVA–PVPLN blend. Absorbance indicated is for spectrum A only. Spectra B–G are drawn for comparison

70:30 blend (curve D) and slightly increases to 843 cm^{-1} in the lower concentrations of PVA. This shows that the band is sensitive to intermolecular interactions and the blend with 70:30 composition of PVA–PVPLN indicates the maximum change.

The spectral changes occurring in the band at 1333 cm^{-1} are shown in *Figure 2*. This has been assigned to the deformation of the OH group by Krimm[3]. It may be noticed that the band shifts by a larger extent, from 1333 cm^{-1} in pure PVA (curve A) to 1316 cm^{-1} in the 70:30 blend (curve D), and does not show any significant change for lower concentrations of PVA. The larger shifts to lower frequencies can be attributed to hydrogen bonding in the presence of large concentrations of PVPLN.

The spectra recorded in the range 900–1250 cm^{-1} are shown in *Figure 3*. Krimm assigned the strong band at 1094 cm^{-1} and the medium intensity band at 1141 cm^{-1} to CO stretching strongly coupled to the COH group based on the fact that these two bands shift on deuteration. Further these two bands have been shown to be crystalline sensitive. Iwamoto *et al.*[4] have reported that the crystallinity of PVA increases upon heating based on the fact that the crystalline sensitive bands in the Raman spectra increased in intensity. Miya[1] found that the crystallinity of PVA is not destroyed in the blends of PVA with chitosan. It may be noted from *Figure 3* that the band at 1143 cm^{-1} gradually disappears when the PVA concentration in the blend is reduced up to 60 wt% and is absent for lower concentrations of PVA. The band at 1094 cm^{-1} shows a drastic reduction in intensity as the concentration of PVA is decreased suggesting both weakening of hydrogen bonding and reduction in crystallinity. A weak band at 1123 cm^{-1}, attributed to the amorphous phase, persists in all the concentrations and develops more distinctly in lower concentrations of PVA. This shows that the crystallinity of PVA is destroyed in the blends when the PVA composition is lower than 60 wt%, contrary to the findings in the chitosan blends.

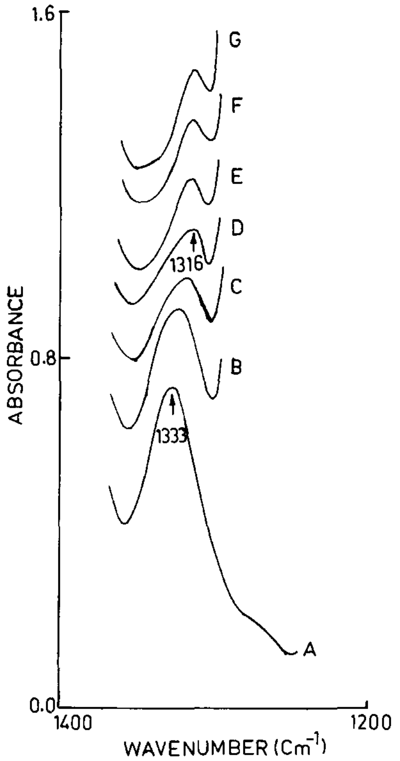

Figure 2 *FT*i.r. spectra in the region 1200–1400 cm^{-1} of pure PVA (A) and 90–40 wt% PVA (B–G) in the PVA–PVPLN blend. Absorbance indicated is for spectrum A only. Spectra B–G are drawn for comparison

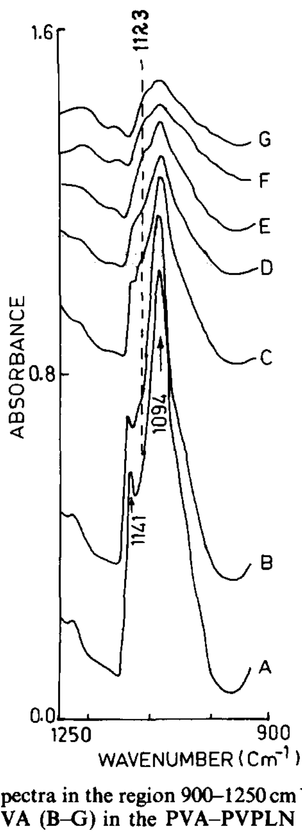

Figure 3 *FT*i.r. spectra in the region 900–1250 cm^{-1} of pure PVA (A) and 90–40 wt% PVA (B–G) in the PVA–PVPLN blend. Absorbance indicated is for spectrum A only. Spectra B–G are drawn for comparison

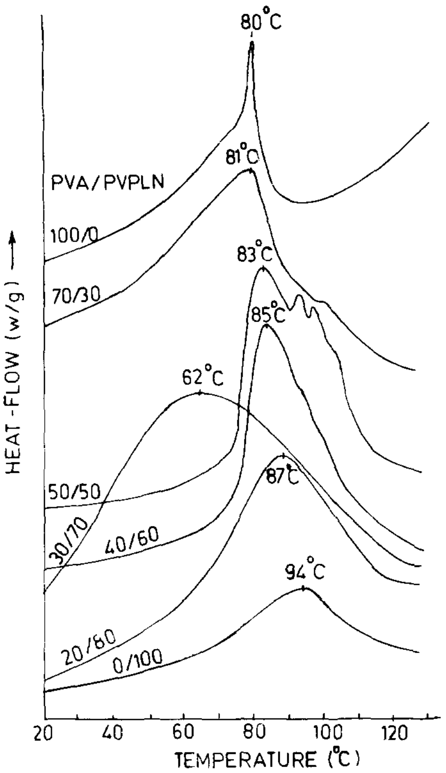

Figure 4 D.s.c. curves for PVA–PVPLN blends

D.s.c. measurements

Figure 4 shows the curves obtained in the d.s.c. studies. It may be observed that the T_g of PVA occurs around 80°C whereas that of PVPLN occurs at 94°C. The T_g values for the blends occur approximately as expected on a proportional basis, as indicated by the straight line obtained in *Figure 5* where T_g values are plotted as a function of the blend composition. *Figure 5* also includes the plot obtained using the Fox equation[5]. What is striking, however, is the unexpected lowering of T_g to about 60°C in the blend composition of 30 wt% PVA and 70 wt% PVPLN. This was checked for samples of this composition prepared at different times. There is a gradual broadening of the endotherm curves from 90 wt% which reaches a maximum at 70 wt% PVPLN. The effects of PVA start showing as the concentration of PVPLN is reduced below this. In fact, the curves have one or two inflections showing the presence of both phases which might arise from improper miscibility.

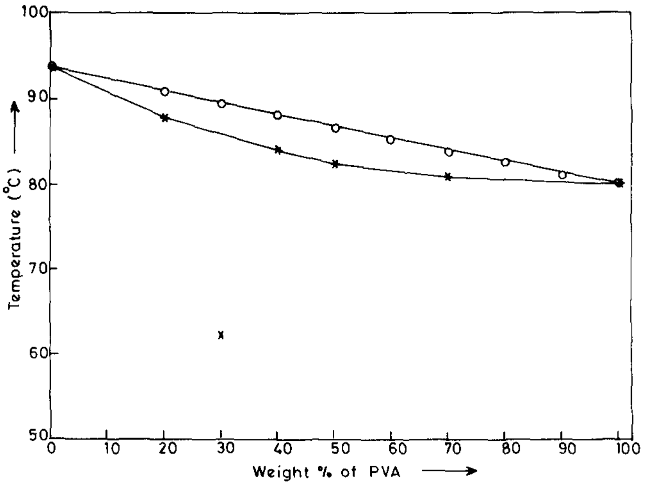

Figure 5 Plot of glass transition temperature *versus* blend composition of PVA in the PVA–PVPLN blends. X, Measured value; O, calculated by Fox equation

In conclusion, the present *FT*i.r. studies on the PVA/PVPLN blends indicate two main features: (1) the blends show strong compatibility, the maximum compatibility occurring for a composition of 70:30 (PVA:PVPLN) wt%. This arises from hydrogen bonding interactions as indicated by the shifts in the i.r. bands sensitive to hydrogen bonding; (2) the disappearance of the crystalline sensitive band for blend compositions below 60:40 wt% PVA–PVPLN indicates that the crystallinity of PVA is destroyed in these blend compositions, as opposed to the findings in chitosan–PVA blends. The d.s.c. studies also support the findings on the compatibility of the blends, in general. The existence or otherwise of the crystalline phase could not be detected in d.s.c. as conclusively as in the *FT*i.r. studies.

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