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Thermal and infra-red spectroscopic investigations of a miscible blend composed of poly(vinyl phenol) and poly(hydroxybutyrate)

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Thermal properties of poly(vinyl phenol) (PVPh) and poly(hydroxybutyrate) (PHB) blends were investigated by differential scanning calorimetry over the entire range of composition. Mixtures with both bacterial (tactic) PHB and synthetic (amorphous) PHB were considered. In all cases, blends showed a unique glass transition temperature. The presence of 40% PVPh prevents bacterial PHB crystallization. Infra-red spectra showed the presence of hydrogen-bonded carbonyl signals which increased with PVPh fraction, showing the extent of specific interactions.

(Keywords: miscible blends; thermal properties; infra-red spectroscopy)

Introduction

There has been great interest in blends of biodegradable polymers, such as poly(hydroxy alkanoate)s, owing to their potential application in fields such as biomedicine and packaging. The most representative member of the family, poly(hydroxybutyrate) (PHB), is a semicrystalline material with high crystalline content and a fairly high melting temperature, about 450 K, at which the polymer degrades quickly.

Some of the undesirable properties can be modified by copolymerization of hydroxybutyrate (HB) with hydroxyvalerate (HV) units. Increasing HV content reduces the melting temperature and crystallinity, making the polymer more processable. An alternative to PHB modification is blending. The literature contains several reports of blends of PHB with other polymers such as poly(ethylene oxide)[1], poly(vinyl acetate)[2], poly(vinyl chloride)[3], poly(epichlorohydrin)[4] and poly(vinyl alcohol)[5].

Many polyesters have been found to be miscible or partially miscible with other polymers on the basis of specific hydrogen-bonding interactions. Among others, blends of polyesters with poly(vinyl phenol) (PVPh)[6,7] and poly(hydroxy ether of bisphenol A) (phenoxy)[8,9] are well documented.

In the present study we describe thermal and spectroscopic analyses of blends formed by PHB and PVPh. Miscibility is examined by the observation of glass transition temperatures (T_gs). The spectroscopic evidence is also discussed in terms of specific interactions.

Experimental

Materials. Bacterial PHB (i-PHB) was obtained from Aldrich. The average molecular weights, as determined by gel permeation chromatography in chloroform at room temperature, were $M_w = 437\,000$, $M_n = 262\,000$.

PVPh was purchased from Polysciences. The average molecular weight was $M_w = 30\,000$.

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Atactic PHB (a-PHB) was prepared following the method proposed by Agostini *et al.*[10] using DL-β-butyrolactone (Aldrich) as the monomer. The catalyst Et_2Zn/H_2O (1 : 0.6 mol) was used. The polymerization reaction was carried out in toluene at 60°C for 5 days. The reaction yield was about 60%. The resulting polymer was amorphous, with a T_g of 277 K, and the average molecular weights were $M_w = 36\,700$ and $M_n = 31\,000$.

Blend preparation. A systematic study was undertaken in order to identify the most suitable solvent for obtaining homogeneous blends of PVPh and i-PHB. Epichlorohydrin was finally selected. Blends were prepared by dissolving the two polymers in epichlorohydrin (1%). The solution was then cast onto a glass plate and the solvent was evaporated under vacuum at 60°C for 3 weeks. A final treatment (3 h at 150°C) was also given to the sample in order to ensure total elimination of the solvent.

Blends of a-PHB/PVPh were prepared with a similar protocol but using methyl ethyl ketone (MEK) as solvent.

Differential scanning calorimetry. Thermal analysis was performed in a Perkin Elmer DSC-2C, equipped with a TADS (Thermal Analysis Date Station) unit. Samples were first heated from 250 to 473 K at 20°C min^{-1}, maintained at that temperature for 1 min, then cooled quickly (320°C min^{-1}). Glass transition temperatures were measured in a second scan under similar conditions.

Fourier transform infra-red spectroscopy. Infra-red spectra were obtained on a Nicolet 5DXC Fourier transform infra-red (*FT*i.r.) spectrometer. In all cases, a minimum of 64 scans with an accuracy of 2 cm^{-1} were signal averaged and the spectra were stored on a magnetic disk system. Spectra recorded at elevated

temperatures were obtained using a Specac accessory mounted inside the sample chamber. All spectra were within an absorbance range where the Beer–Lambert law is obeyed (< 0.6 absorbance units).

Polymer blends of various compositions were prepared by co-dissolving appropriate amounts of the components in epichlorohydrin or MEK to yield 1% (w/v) solutions. Thin films were obtained by casting the blend solutions onto potassium bromide windows at room temperature. The solvent was removed slowly under ambient conditions for a minimum of 24 h. The samples were then dried in a vacuum oven for 3 days at 100°C to completely remove the residual solvent.

Results and discussion

Mixtures of both i-PHB and a-PHB with PVPh are miscible in the whole range of compositions, as indicated by the observation of a unique T_g intermediate to those of pure components. *Figure 1* shows the evolution of T_g as a function of blend composition for both systems. The miscibility of these blends can be described by the Gordon Taylor equation, and the values obtained for the average adjustable parameter, k, are 0.57 for a-PHB/PVPh and 0.59 i-PHB/PVPh.

The variation of the melting temperature (T_m) of i-PHB with composition can be observed in *Figure 2*. There is a remarkable change in T_m values when

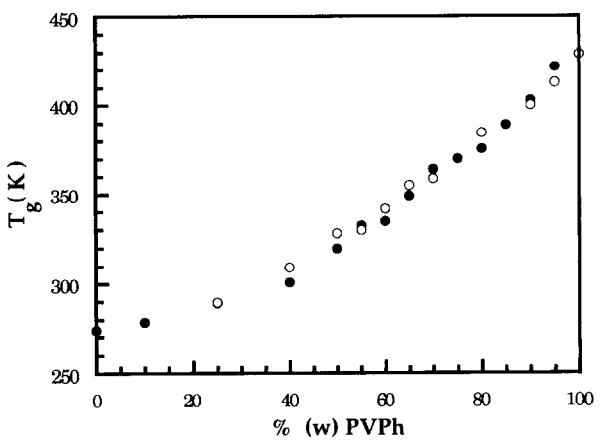

Figure 1 Variation of T_g as a function of composition for i-PHB/PVPh (○) and a-PHB/PVPh (●) blends

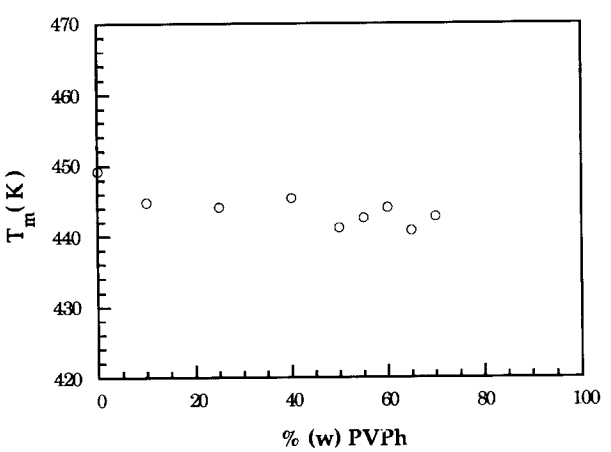

Figure 2 T_m of i-PHB *versus* composition for i-PHB/PVPh blends

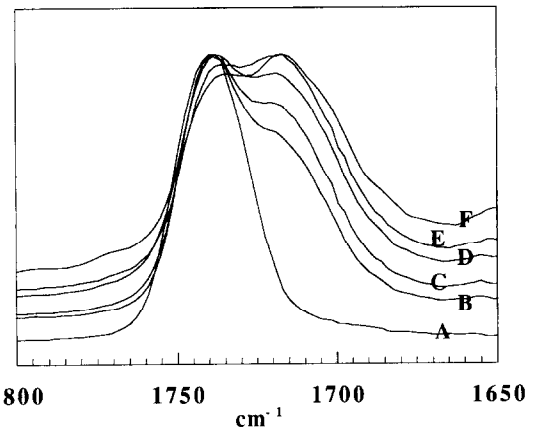

Figure 3 *FT*i.r. spectra recorded at room temperature in the 1800–1650 cm^{-1} region for a-PHB/PVPh blends containing: (A) 100, (B) 50, (C) 40, (D) 30, (E) 20 and (F) 10 wt% a-PHB

Table 1 PHB degree of crystallinity (%) in i-PHB/PVPh blends

Crystallinity (%)	Blend composition
84	100
77	90
51	60
31	50
5	35
2.5	30

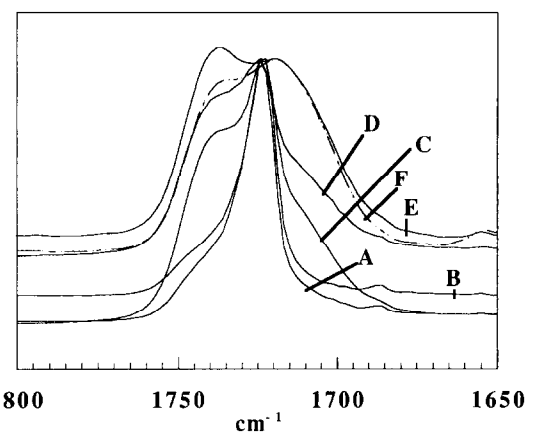

Figure 4 *FT*i.r. spectra recorded at room temperature in the 1800–1650 cm^{-1} region for i-PHB/PVPh blends containing: (A) 100, (B) 75, (C) 50, (D) 40, (E) 20 and (F) 10 wt% i-PHB

compared with the usual melting-point depressions reported in the literature for other amorphous–semicrystalline polymer mixtures. However, it is worthwhile mentioning that these data have not been obtained under strict equilibrium conditions. The degree of crystallinity decreases considerably when the PVPh content is increased, as can be observed in *Table 1*. Furthermore, during a second scan blends with a PVPh content close to 40% and above do not crystallize, probably owing to a decrease in the PHB crystallization rate because of the presence of PVPh.

Figure 3 shows infra-red spectra in the carbonyl stretching region (1800–1650 cm^{-1}) of pure a-PHB (curve A) and a-PHB/PVPh blends containing 50, 60, 70, 80 and 90 wt% PVPh (curves B–F, respectively), all

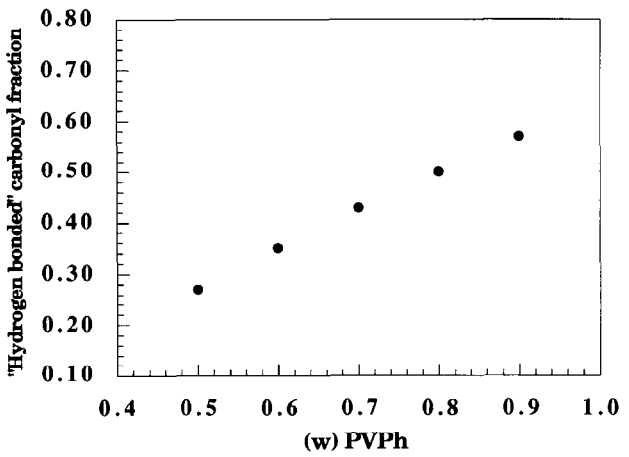

Figure 5 Variation of the 'hydrogen-bonded' carbonyl fraction with composition for a-PHB/PVPh blends

recorded at room temperature. The most striking feature of these spectra is the appearance and increasing intensity of a shoulder centred at approximately 1712 cm^{-1} with increasing concentration of PVPh. This band can be reasonably assigned to a hydrogen-bonded carbonyl group. This band is indicative of an intermolecular interaction involving the PHB carbonyl group and the hydroxyl group of the PVPh.

*FT*i.r. spectra of pure i-PHB and i-PHB/PVPh blends recorded at room temperature exhibit additional features attributed to crystalline PHB. *Figure 4* shows the carbonyl stretching region of these blends at different compositions. The spectrum of pure i-PHB exhibits two bands: a relatively sharp one centred at 1724 cm^{-1} is attributed to PHB in its preferred conformation ('crystalline') and another, seen as a small shoulder at 1742 cm^{-1}, is associated with amorphous conformations. Spectra B, C and D in *Figure 4* exhibit three distinct components. The components at 1742 and 1724 cm^{-1} are attributed to PHB in amorphous and preferred conformations, respectively. A minor contribution at approximately 1709 cm^{-1} is also observed, attributable to the PHB carbonyl group hydrogen-bonded to the hydroxyl group of PVPh. At PVPh concentrations of 70 wt% and above, the PHB component of the blend appears completely amorphous. The contribution of the 1709 cm^{-1} band increases as a function of PVPh concentration.

In an attempt to quantify the fraction of hydrogen-bonded carbonyl groups present in a-PHB/PVPh blends at room temperature, a least-squares fit of two Gaussian bands to the carbonyl stretching absorptions was applied[11]. The results are shown in *Figure 5* for all blend compositions studied. In calculating the fraction of hydrogen-bonded carbonyl groups, band areas were corrected for absorption coefficient differences by applying the ratio, $a_{hb}/a_f = 1.5$, where a_{hb} and a_f represent the absorption coefficient of the hydrogen-bonded and 'free' carbonyl bands, respectively. This value was taken from literature[12], where values for some aliphatic polyesters were reported.

The presence of a significant fraction of hydrogen-bonded groups together with the results obtained by d.s.c., allow us to confirm that these systems are miscible in the entire range of compositions.

Acknowledgements

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