Association Equilibria and Miscibility Prediction in Blends of Poly(vinylphenol) with Poly(hydroxybutyrate) and Related Homo- and Copolymers: An FTIR Study

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ABSTRACT: Blends composed of poly(vinylphenol) (PVPh) and bacterial (tactic) poly(hydroxybutyrate) (PHB) and synthetic (atactic) poly(hydroxybutyrate) (PHBa) have been investigated by FTIR. From quantitative analyses of hydrogen bonded PHB carbonyl groups as a function of temperature and composition, the interassociation constant, K_A, describing the formation of hydroxyl−carbonyl interaction as well as the related enthalpy of hydrogen bond formation have been determined. Using the association model of Painter and Coleman, phase diagrams have been predicted for blends of PVPh with the poly(hydroxyalkanoate) family.

Introduction

Poly(hydroxybutyrate), PHB, is an optically active, naturally occurring polymer produced by a wide variety of bacteria. It serves as an intracellular storage material for carbon and energy source, and it is susceptible to biodegradation by the action of a wide variety of microorganisms. Discovered by Lemoigne[1] in 1925, PHB is the most representative member of the poly(hydroxyalkanoate) family. There has been a great interest on the part of biomedical and packaging applications for finding polymers that can replace synthetic materials and can degrade into harmless, naturally occurring small molecules. The development of the poly(hydroxyalkanoate) family and their blends can help us in partially resolving the concerns caused by the use of nondegradable plastics. The good gas barrier properties of PHB, comparable to PVC and PET, associated to its biodegradability properties, open the possibility of using it as a potential commodity material in the packaging industry.

Some of the undesirable properties of PHB that prevents its use as a commodity material are the brittleness of the melt-processed material and/or the thermal degradability of the polymer at the processing temperatures. They can be overcome by copolymerization of PHB with other comonomers. Hydroxybutyrate/hydroxyvalerate copolymers are the most important copolymers of this family. Although they are also highly crystalline polymers, increasing the HV content in the copolymer reduces the melting temperature and crystallinity, making the polymer more processable.

An alternative to PHB modification is blending. Polymer blends usually represent a faster and less expensive way of designing novel materials, having extended and improved ranges of physical characteristics, such as processing, toughness, barrier, or crystalline properties. Literature contains several reports of blends of PHB with other polymers such as poly(ethylene oxide),[2] poly(vinyl acetate),[3] poly(vinyl chloride),[4] poly(vinylidene fluoride),[5] poly(epichlorhydrin),[6] poly(vinyl alcohol),[7] cellulose esters,[8] and poly(lactic acid).[9]

The miscibility of a pair of macromolecules is the exception rather than the general rule in polymer blending. To obtain a miscibile polymer system we first need to understand the factors that govern the miscibility of a pair of high molecular weight structures in terms of the free energy of mixing. Describing it in terms of the Flory−Huggins lattice theory and accepting that the entropic contribution to the total free energy of mixing has only a small effect on enhancing miscibility, we can consider that the enthalpic contributions usually govern the miscibility of polymer blends. In general, miscibility is observed when there is a significant interaction between the constituent polymers in the blend and, therefore, when the enthalpic contribution is negative. Then, we can enhance the miscibility of a couple of polymer materials, designing a favorable enthalpic contribution to mixing by the incorporation of attractive interacting units in the polymers. In this way, polymers that have specific interacting functional groups can be selected to enhance miscibility of polymer systems. In this way, hydrogen bonding is one of the most desirable specific interactions, owing to its diversity and strong interacting characteristics.

There exists a wealth of literature with respect to enhancing miscibility through hydrogen bonding interactions.[10] Blending hydroxyl groups containing polymers such as poly(vinyl phenol)[11] (PVPh) or poly(hydroxy ether of bisphenol A)[12] (phenoxy) with polymers containing hydrogen bonding acceptor units, we can obtain potentially miscible systems. So, many polyesters have been found to be miscibile or partially miscible with other polymers on the basis of specific hydrogen-bonding interactions. Among others, miscibility of blends of polyesters[13,14] with PVPh or phenoxy are well documented.

In a previous publication[15] we have described the thermal and spectroscopic analyses of blends formed by PVPh/PHB and PVPh/PHBa. Miscibility was examined by the observation of a unique glass transition temperature, and the spectroscopic evidence was also discussed in terms of specific interactions. In this paper we provide results of more extensive research conducted on these systems by FTIR. From the analysis of the infrared spectral data and using the association model of Painter and Coleman,[16] we have calculated the interassociation equilibrium constants and the corresponding enthalpies for both miscible blends. From the

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knowledge of these parameters we can predict the phase behavior of PVPh blends with the poly(hydroxyalkanoate) family.

Summary of the Painter and Coleman Association Model for Binary Blends

In this model, the free energy of mixing two polymers with specific interactions between them can be rewritten using the following expression:

$$\frac{\Delta G_m}{RT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi\phi_A\phi_B + \frac{\Delta G_H}{RT} \quad (1)$$

where ϕ_A, ϕ_B, N_A, and N_B are the volume fractions and degrees of polymerization of polymers A and B, respectively, and χ is a conventional Flory–Huggins interaction parameter that embodies the unfavorable physical interactions to mixing. If we disregard free volume effects and the small contribution from the combinatorial entropy contained in the first two terms of the equation, we could consider the miscibility as a balance between the number and strength of favorable interactions, embodied in the last term of the equation, and the unfavorable physical interactions. The unfavorable physical interactions are always against the mixing of the polymers, and they can be evaluated by using the non-hydrogen-bonded solubility parameters, according to the Scatchard–Hildebrand relation. On the other side, the contribution from the $\Delta G_H/RT$ term may be readily calculated knowing the polymer structure describing parameters and the association characteristics in the form of equilibrium constants and interaction enthalpies. For PVPh systems, self-association is correctly described using the two self-association models,[17] K_2 for dimer, and K_B for multimer formation. The interassociation is described by K_A.

Experimental Section

Materials. Bacterial PHB was obtained from Aldrich. The average molecular weights, as determined by GPC in chloroform at room temperature, were $M_w = 437000$, $M_n = 262000$. PVPh was purchased from Polysciences. The average molecular weight was $M_w = 30000$.

Atactic PHB was prepared following the method proposed by Agostini et al.,[18] using DL-β-butyrolactone (Aldrich) as the monomer. The catalyst Et_2Zn/H_2O system (1:0.6 mol) was used. The polymerization reaction was carried out in toluene at 60 °C during five days. The reaction yield was about 60%. The resulting polymer was amorphous with a T_g of 277 K, and the molecular weight averages were $M_w = 36700$ and $M_n = 31000$.

Blend Preparation for FTIR Analysis. Due to the intrinsic difficulties in having common solvents for PVPh and bacterial PHB giving homogeneous blends, a systematic study was undertaken in order to select the most adequate solvent. Among the investigated solvents, epichlorohydrin was finally selected. So, PVPh/PHB/epichlorohydrin (1%) solutions were cast 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 three days at 100 °C to completely remove the residual solvent. The samples were maintained under vacuum conditions until their use.

Blends of PVPh/PHBa were prepared with a similar protocol, but using MEK as solvent.

Infrared spectra were obtained on a Nicolet 5DXC Fourier Transform infrared 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).

In order to avoid the influence of solvents and the crystallinity of some of the samples, the spectra were taken after a thermal treatment from room temperature to 160 °C (for PHBa) and up to a temperature where PHB was completely melted. The spectra were recorded in the cooling process.

The required polymeric parameters as the molar volume and the solubility parameter of the studied systems were obtained by group contribution methods. Quantitative analysis of the hydrogen bonded carbonyl groups present in the studied blends were calculated from a least-squares fit of two Gaussian bands to the overall carbonyl absorption band. The interassociation equilibrium constant, K_A, was evaluated by a least-squares fitting procedure. Finally, the theoretical spinodal phase diagrams were predicted from the second derivatives of free energy. The required programs are included in a software package developed by Painter and Coleman.[16]

Results and Discussion

FTIR Analysis Results. There is a wealth of literature about the miscibility involving strong specific interactions as well as the qualitative and quantitative characterization of these interactions by infrared spectroscopic analysis.[13,17] In these studies it is shown that the precise distribution of the different association species is dependent upon the composition of the mixture, the temperature, and the equilibrium constants describing both self- and interassociation.

The most striking feature of the infrared spectra (carbonyl stretching vibration region) in blends involving specific interactions like hydrogen bonding in PVPh/polyester systems, is the appearance of a new band at lower frequencies with respect to the corresponding polyester carbonyl band, attributable to the hydrogen bonded carbonyl group fraction in the blend. Quantitative determinations of the fraction of hydrogen bonded carbonyl groups present at a given temperature and composition can be obtained from a least-squares fit of two Gaussian bands to the carbonyl stretching absorptions. Then, the fraction of hydrogen bonded carbonyl groups can be calculated by:

$$f_B = \frac{1}{1 + a_r(A_F/A_B)} \quad (2)$$

where A_F and A_B are the areas corresponding to the free and hydrogen bonded carbonyl groups, respectively, and a_r is the absorption ratio which takes into account the difference between the absorptivities of the hydrogen bonded and free carbonyl groups. In the case of PVPh/polyesters systems, a_r is accepted to be 1.5.[17]

Although quantitative analysis of these carbonyl bands provides a direct measure of the degree of mixing in a particular blend sample, it does not necessarily imply the existence of a thermodynamically stable single phase mixture. Information concerning the phase behavior of these samples can be obtained from the stoichiometry of the system and by monitoring trends in the carbonyl region as a function of temperature.

PVPh/PHBa. The infrared bands attributed to the hydrogen bonding interaction were readily identified in the hydroxyl and carbonyl regions of the spectra. A change in the relative contribution of these bands may be observed when the blend composition is modified.

In the hydroxyl stretching region, the relative contribution of the hydrogen bonded hydroxyl group increases as the concentration of the polyester in the blends is increased. The interaction may be characterized as the frequency shift between the free hydroxyl

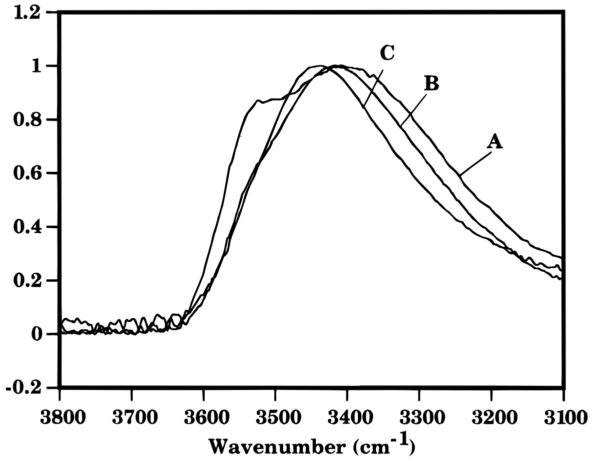

Figure 1. Normalized FTIR spectra recorded at 100 °C in the 3800−3100 cm^{-1} region for (A) PVPh, (B) PVPh/PHBa (80/20), and (C) PVPh/PHBa (60/40).

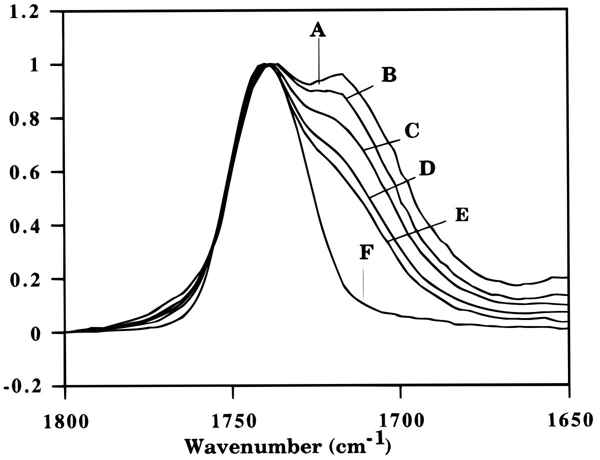

Figure 2. Normalized FTIR spectra recorded at 160 °C in the 1800−1650 cm^{-1} region for PVPh/PHBa blends containing (A) 90, (B) 80, (C) 70, (D) 60, (E) 50, and (F) 0 wt % PVPh.

band at 3525 cm^{-1} and the hydrogen bonded hydroxyl band, which is a measure of the average relative strength of the interaction. The frequency shift in pure PVPh is about 165 cm^{-1} and varies from about 105 cm^{-1} in the PVPh/PHBa system at 25 °C. This value is lower than that in pure PVPh hydroxyl−hydroxyl interaction, indicating that the hydroxyl−ester interaction is weaker.

Figure 1 shows the hydroxyl region spectra of PVPh and two PVPh/PHBa blends at 100 °C, in the cooling process. As we can see, PVPh shows two contributions to the overall OH stretching band attributable to the free and associated hydroxyl groups, respectively. However, the contribution of the free hydroxyl groups to the hydroxyl band in the blends is clearly reduced, and the band corresponding to the associated hydroxyl groups is shifted to a higher wavenumber, owing to the existence of new hydroxyl−ester associations. This shift is highly dependent on the composition of the blend.

In addition, in the carbonyl stretching region, the contribution of the hydrogen bonded carbonyl groups increases when PVPh concentration in the blends is increased. Figure 2 shows the scale expanded FTIR (1800−1650 cm^{-1}) of pure PHBa and PVPh/PHBa blends containing 50, 60, 70, 80, and 90 weight % of PVPh, all recorded at 160 °C. PHBa spectrum shows a single band centered at 1740 cm^{-1}, attributable to the nonassociated carbonyl group. The main feature of the spectra of the blends is the appearance of a shoulder, centered at approximately 1712 cm^{-1}, of increasing intensity as PVPh concentration in the blend increases. This band can be reasonably assigned to the hydrogen bonded carbonyl groups, indicative of the intermolecular interaction involving the PHB carbonyl group and the PVPh hydroxyl group.

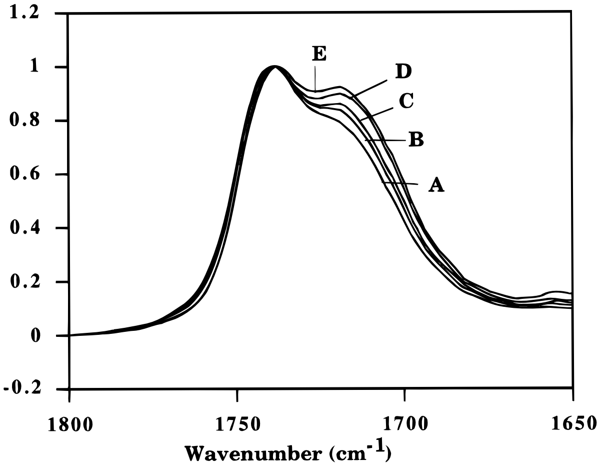

Figure 3. Normalized FTIR spectra in the 1800−1650 cm^{-1} region for a 70/30 PVPh/PHBa blend at (A) 160 °C, (B) 130 °C, (C) 110 °C, (D) 50 °C, and (E) 25 °C.

Table 1. FTIR Data for the Determination of K_A and h_A from PVPh:PHBa Blends

blend composition vol ratio	fraction of free carbonyl groups					
	110 °C	120 °C	130 °C	140 °C	150 °C	160 °C
88:12	0.384	0.403	0.416	0.435	0.450	0.451
76:24	0.456	0.469	0.483	0.492	0.505	0.517
66:34	0.516	0.527	0.537	0.561	0.574	0.629
56:44	0.619	0.621	0.625	0.634	0.649	0.664
46:54	0.686	0.694	0.703	0.708	0.717	0.720
K_A	7.91	6.64	5.65	4.77	4.07	3.43

As an illustration of the observed trends, the scale-expanded FTIR of a 70/30 PVPh/PHBa blend recorded as a function of increasing temperature (25−160 °C) is presented in Figure 3. As the temperature is raised the intensity of the free band increases at the expense of the hydrogen bonded band.

All these spectra were employed to determine the fraction of free carbonyl groups in miscible PVPH/PHBa blends of different compositions and temperatures. These data are summarized in Table 1, together with the equilibrium constants (K_A) describing the interassociation of PVPh with PHB that were calculated by a least-squares fitting procedure to the equations describing the stoichiometry of the hydrogen bonding in the system. From the slope of a plot of ln K_A vs $1/T$ the enthalpy of hydrogen bond ($h_A = -5.47$ kcal/mol) can be obtained. Extrapolating at 25 °C a value of $K_A = 62.1$ was obtained. The value obtained for K_A is similar to that obtained for PVPh/poly(ϵ-caprolactone) and PVPh/poly(vinyl acetate)[17] systems.

A complete summary of the parameters used in the calculations presented in this paper is given in Table 2. The values for the molar volumes and solubility parameters were calculated from group contribution methods.[19]

PVPh/PHB. FTIR spectra of pure PHB and PVPh/PHB blends recorded at different temperatures exhibit additional features attributed to crystalline PHB. Figure 4 shows the carbonyl stretching region of PHB at different temperatures. The spectra of pure PHB at temperatures below the melting point exhibit two

Table 2[a]

segment	molar volume ($cm^3\ mol^{-1}$)	solubility parameter ($(cal\ cm^{-3})^{0.5}$)	equilibrium constants at 25 °C K_2	K_B
VPh	82.3	10.6	21.0	66.8
HB	69.8	9.61	–	–

[a] Enthalpy of hydrogen bond formation: $h_2 = -5.6$ and $h_B = -5.2$ kcal/mol.

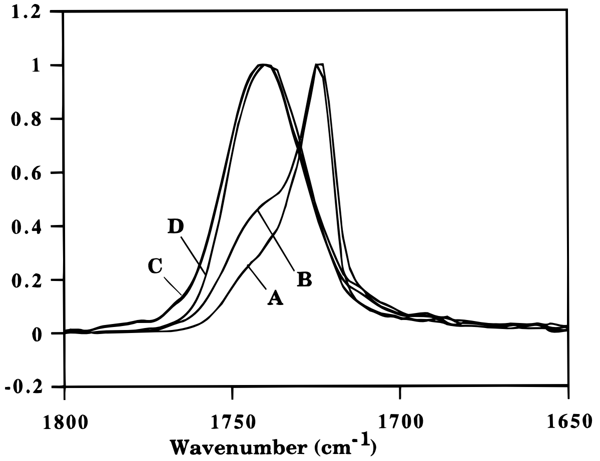

Figure 4. Normalized FTIR spectra recorded in the 1800–1650 cm^{-1} region for (A) PHB (25 °C), (B) PHB (175 °C), (C): PHB (175 °C, cooling process), and (D) PHBa (160 °C).

bands: A relatively sharp one centered at 1724 cm^{-1}, attributed to PHB in its preferred conformation ("crystalline"), and a small shoulder at 1742 cm^{-1} associated with amorphous conformations. The spectrum at 175 °C, registered during the heating process, evidences the crystallinity of the material. However, the spectrum taken at this temperature during the cooling process, after the melting of the polymer, is very similar to that of PHBa.

The PVPh/PHB spectra, in the carbonyl region, exhibit three distinct components.[15] The components at 1742 cm^{-1} and 1724 cm^{-1} are attributed to PHB in amorphous and preferred conformations, respectively. The contribution at approximately 1709 cm^{-1} is also observed and can be attributed to the PHB carbonyl groups hydrogen bonded to the hydroxyl group of PVPh. This contribution increases as a function of PVPh concentration. At concentrations of 70 weight % of PVPh and higher, the PHB component of the blend appears completely amorphous. In order to assure no influence of the crystalline carbonyl band in the analysis of the system, the study is restricted to rich PVPh blend compositions and at elevated temperatures. The blends were heated up to 200 °C, and after melting the material, the spectra were recorded at different cooling temperatures. During the acquisition process no crystallization was observed.

In Figure 5 we present the evolution of different PVPh/PHB blend compositions at 110 °C, in the cooling process. The hydrogen bonded carbonyl band contribution is greater at higher PVPh concentrations and the crystallinity band is not observed.

From the analysis of the evolution of the free carbonyl group fractions at several blend compositions and temperatures, and using the parameters previously described in Table 2, K_A at different temperatures were obtained and the results are summarized in Table 3. From these values K_A at 25 °C and h_A were obtained (38.4 and −4.97 kcal/mol). The value of K_A, although smaller than that obtained for amorphous PHB, is similar to those obtained for PVPh/poly(*n*-alkyl methacrylates).[13]

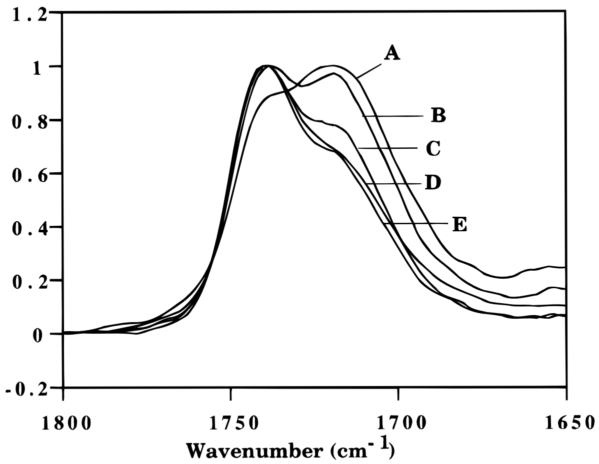

Figure 5. Normalized FTIR spectra recorded at 110 °C in the 1800–1650 cm^{-1} region for PVPh/PHB blends at different compositions, (A) 90/10, (B) 80/20, (C) 70/30, (D) 60/40, and (E) 50/50.

Table 3. FTIR Data for the Determination of K_A and h_A from PVPh:PHB Blends

blend composition vol ratio	fraction of free carbonyl groups 120 °C	130 °C	140 °C	150 °C	160 °C
88:12	0.460	0.469	0.484	0.489	0.498
76:24	0.519	0.527	0.535	0.543	0.569
66:34	0.611	0.620	0.630	0.640	0.662
61:39	0.637	0.645	0.654	0.665	0.675
56:44	0.694	0.704	0.712	0.720	0.727
K_A	4.98	4.27	3.68	3.22	2.74

The obtained h_A values are higher than those commonly reported in the literature for PVPh/polyester systems. The reasons for this discrepancy can be due to associated errors to the method employed in the calculations as well as the narrow ranges of temperature used to assure the equilibrium conditions and to prevent the degradation of poly(hydroxybutyrate).

Different factors can be responsible for the differences on the calculated K_A values. On one side, we can consider those factors associated to the experimental procedure, as the selected solvents and the influence of the crystallinity of PHB. In our case, the effect of the different solvents can be neglected due to the thermal treatment submitted to all the samples. Furthermore, the possible influence of the crystallinity as an error source in the calculation of K_A has also been minimized by the fact of recording the spectra in the cooling process. Figure 6 shows the spectra of PVPh/PHB (60/40) at different temperatures. As can be seen, the spectrum registered at 100 °C during the heating process clearly shows the crystalline character of PHB. However, the spectra obtained at 175 °C, 100 °C, and 25 °C during the cooling process do not show any evidence of the existence of crystallinity. On the other hand and besides the pure interactions between different functional groups of the components, other structural characteristics such as chain flexibility, steric factors, or chain connectivity[10] can be included in the experimental K_A.

Considering that tacticity can have a pronounced effect on the mentioned characteristics, the different tacticity of PHB and PHBa can relate to the observed differences in the calculated interassociation constants.

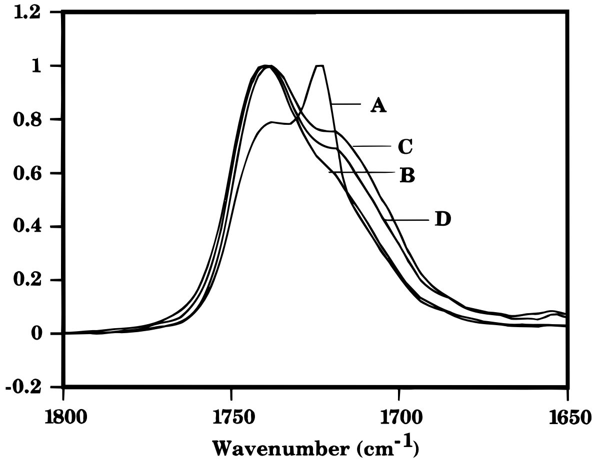

Figure 6. Normalized FTIR spectra in the 1800−1650 cm^{-1} region for a PVPh/PHB (60/40) blend at different temperatures: (A) 100 °C (heating process), (B) 175 °C, (C) 100 °C and (D) 25 °C.

Although there is a great number of reported studies about the influence of the tacticity on the miscibility of polymer blends, we do not know of any work relating the influence of the tacticity on the interassociation equilibrium constant values.

Miscibility Predictions. PVPh/PHB and PVPh/PHBa. On the basis of the obtained K_A and h_A values for the PVPh/PHB and PVPh/PHBa amorphous blends, assuming equilibrium can be attained, it is possible to predict the theoretical spinodal phase diagrams for both blends from the locus of points whose numerically determined second derivatives of free energy with respect to blend composition are equal to zero.

The results of such calculations for temperatures between −100 °C and 300 °C are indicative of the miscibility of PVPh with PHB and PHBa, obtaining a single phase system prediction in the whole range of compositions in the selected temperature range.

PVPh/Poly(hydroxyalkanoates). The poly(hydroxyalkanoates) are a wide family of polymers whose principal component is the 3-hydroxybutyrate unit. As we have stated in the introduction, an alternative way to overcome the undesirable properties of PHB is copolymerization. Unfortunately, few systems are commercially available and they are restricted to copolymers of 3-hydroxybutyrate and 3-hydroxyvalerate, P(3HB-co-3HV), rich in hydroxybutyrate content. However, in the last years, hydroxyvalerate rich copolymers and polyhydroxyvalerate homopolymer, PHV, have been isolated and some of their blends studied.[20]

Upon the basis of the observed miscibility of PHB with PVPh, and taking into consideration the association behavior presented in this work, it is possible to predict the miscibility behavior for PVPh/poly(hydroxyalkanoate) blend systems. In other words, taking into account that the different members of the hydroxyalkanoates family can be obtained from the structure of PHB by the addition of different units of methylene group in the structure of the polymer, the final aim is to get to know the effect of the methylene units incorporation on the miscibility prediction for these systems.

Table 4

segment	molar volume (cm^3 mol^{-1})	solubility parameter (cal cm^{-3})$^{0.5}$
PHV	86.3	9.30
PHH	102.8	9.10
PHO	135.8	8.83
methylene	16.50	8.0

Due to the isotacticity and the high molecular weight of the naturally occurring polyhydroxyalkanoates, we have taken as an adequate interassociation constant value that corresponding to the PVPh/PHB system. The parameters employed for the study are described in Table 4.

As can be seen, as methylene groups are incorporated to the PHB structure, the solubility parameter of the corresponding poly(hydroxyalkanoate) is reduced continuously, and for polyhydroxyoctanoate, PHO, a δ = 8.83 (cal cm^{-3})$^{0.5}$ is obtained.

Theoretical spinodal phase diagrams for the PVPh/Poly(hydroxyalkanoates) blends were calculated for temperatures between −100 °C to 300 °C and are shown in Figure 7. As indicated in the figure, blends of PVPh with PHV are predicted to be thermodynamically stable throughout this entire temperature range except for a small region of immiscibility at high PVPh concentrations and high temperatures. Results obtained for the PVPh/PHH and PVPh/PHO systems predict the emergence of an immiscibility loop at high temperatures and high PVPh compositions, as well as a reduction in temperature of the higher phase boundary compared to that of PHV blends.

As an alternative to showing conventional phase diagrams of volume fraction of PVPh in the blend as a function of temperature, it is possible to display a type of miscibility window where the volume fraction of PVPh in the blend is plotted against a hypothetical "copolymer" of varying composition at a particular temperature. Figure 8 shows the miscibility window for PVPh blends with hypothetical methylene-*co*-hydroxybutyrate copolymers containing different methylene units varying from 0 (PHB) to 10 at 25 °C, 100 °C, and 200 °C. As can be

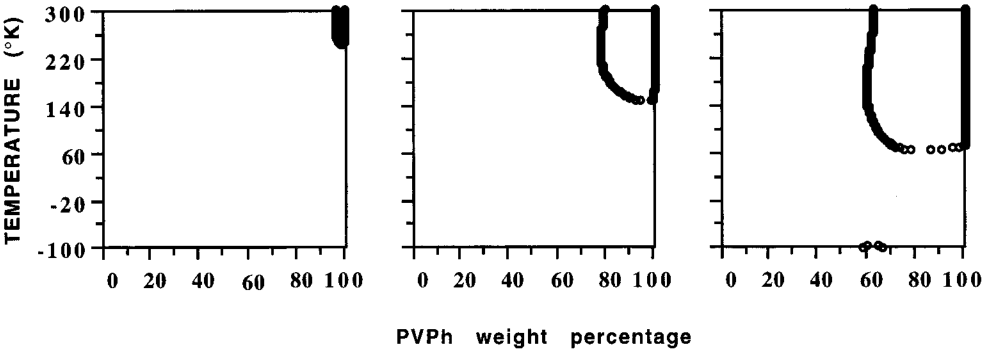

Figure 7. Theoretical spinodal phase diagrams for PVPH/poly(hydroxyalkanoate) blends. (A): poly(hydroxyvalerate), (B): poly(hydroxyhexanoate) and (C): poly(hydroxyoctanoate).

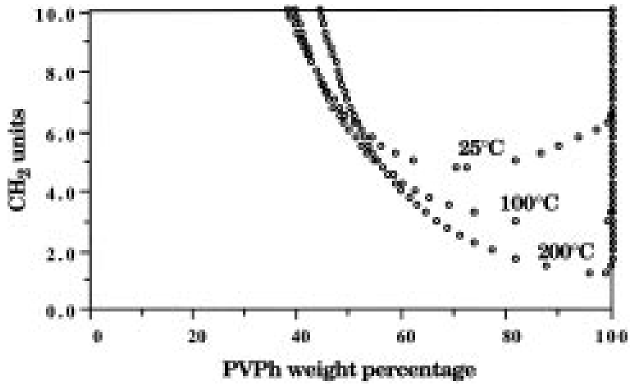

Figure 8. Theoretical spinodal phase diagrams for PVPh blends with hypothetical methylene-*co*-hydroxybutyrate at 25 °C, 100 °C, and 200 °C.

seen, the miscibility window decreases as temperature increases.

Conclusions

FTIR results indicate high interassociation constant values for PHB/PVPh systems, similar to other PVPh/polyester systems. However, the equilibrium constant values obtained for PVPh/PHB and PVPh/PHBa are quite different, and the explanation of this difference could be expressed in terms of the crystallinity and/or tacticity effects on the specific interaction strength. The characterization of the PVPh/PHB blend system allows us to predict miscibility behavior of PVPh with the wide family of poly(hydroxyalkanoates) and in a similar way to extend the miscibility of PVPh copolymers to PHB and its copolymers.

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