Direct Measurement of the Enthalpy of Mixing in Miscible Blends of Poly(DL-lactide) with Poly(vinylphenol)

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ABSTRACT: Blends of poly(DL-lactide) (PDLLA) with poly(vinylphenol) (PVPh), obtained by solvent-casting and solution/precipitation, have been studied by DSC and FTIR. DSC results obtained in the first heating scan suggest that as-prepared blends are phase separated in nearly pure components. In addition, the initial FTIR spectra of the as-precipitated blends show no sign of specific interactions, which is also consistent with the phase separation. In solution/precipitation blends, the first calorimetric scan shows an exothermic peak attributed to the enthalpy of mixing. To our knowledge, this is the first polymer blend system for which this thermodynamic parameter has been possible to directly measure. The exothermic peak occurs at temperatures just below the T_g of PVPh. The consecutive DSC scans show a single T_g for the whole composition range, indicating complete miscibility. The interaction energy density (B) has been calculated and shows a strong dependence on composition. The decrease in B (in terms of absolute value) as the content of PVPh decreases is related to the higher energy consumed to break its strong autoassociation. Phase separation into the neat polymers for the as-prepared blends is attributed to accessibility issues between interacting groups, including steric shielding, group spacing, and chain stiffness, aggravated by blending temperatures below the corresponding T_gs. At high temperatures thermal motion increases chain mobility, allowing the development of an intimately mixed single-phase blend. On the other hand, phase separation is observed in solution-cast blends with high PVPh content, certainly due to the $\Delta\chi$ effect, resulting in macroscopic domains that prevent obtaining a homogeneous blend at high temperatures in the absence of a shearing mechanism. Interaction development during heating has been followed by FTIR. Both the hydroxyl and carbonyl stretching regions indicate hydrogen bonding between OH groups of PVPh and C═O groups of PDLLA, suggesting weaker interactions than in other PVPh/polyester systems.

Introduction

Polymers based on lactic acid, termed polylactides, have attracted much attention in recent years because their wide potential range of applications.[1] These polymers are biocompatible and are being used since the 1990s for medical applications.[2,3] Nowadays, they also represent one of the most promising materials to attenuate the environmental impact of plastics because they are biodegradable and the industrial production process is based in renewable resources.[1] Thus, polylactides can be used in the packaging industry. In addition, since the recent beginning of their industrial scale production their applicability field has expanded to include plastic parts such as consumer electronics.

The repetitive unit of the polymer chain presents a chiral atom (see Figure 1), and mechanical properties depend strongly on the stereoregularity of the polymeric chain. Optically pure polylactides, poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), are semicrystalline with a melting point around 180 °C. The atactic polymer, poly(DL-lactide) (PDLLA), is an amorphous material with a glass transition temperature around 60 °C. It is well established that the properties of polylactides vary to a large extent depending on the ratio and the distribution of the two isomers. Nevertheless, polylactides have poor processing properties and are brittle at room temperature.[4] One of the simplest possible modifications to improve polylactide properties is polymer blending, but only a few miscible counterparts have been reported.[5−10]

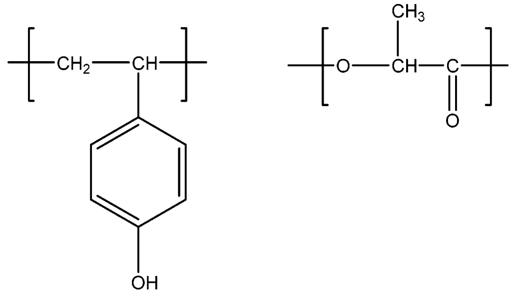

Figure 1. Chemical structures of PVPh and PDLLA.

The miscibility of polylactides, including both PLLA and PDLLA, with hydrogen-bonding counterparts has been studied in several papers,[11−15] but inmiscibility has been found in all cases. This behavior was not expected because hydrogen bonding is a strong interacting force that usually expands the miscibility window between dissimilar polymers to solubility parameter differences of up to 3.0 (cal/cm^3)$^{1/2}$.[16] For example, Zhang et al. studied the miscibility of poly(vinylphenol) (PVPh) with polylactides,[14,15] finding inmiscibility by DSC along with no evidence of hydrogen bonding by FTIR.[15] In contrast to Zhang's results, we have proved in a recent paper the miscibility of PLLA/PVPh blends obtained by solution/precipitation, for which a negative interaction energy density $B = -8.8$ cal/cm^3 was obtained by melting point depression studies.[17] For solvent-cast blends, we obtained phase-separated mixtures, in agreement with Zhang's results,[14] but this behavior was attributed to the $\Delta\chi$ effect.[17]

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However, some intriguing results were also obtained in our study for PLLA/PVPh blends.[17] The first DSC scan for solution/precipitation blends showed phase separation, but after heating above the glass transition temperatures of the feed polymers, miscibility was achieved as revealed in the second DSC scan. Hence, miscibility seems favored at higher temperatures, in contrast to the behavior expected taking into account the typical interassociation loss as temperature increases. Unfortunately, DSC scans of PLLA and its blends showed an intense melting endotherm that obscured any thermal process occurring during the first heating scans. This work deals with blends of poly(vinylphenol) with PDLLA, the amorphous isomer of PLLA, as this system should give additional insight into the blending behavior of polylactides. Similar miscibility behavior can be expected for both PLLA/PVPh and PDLLA/PVPh systems, but the latter is devoid of the complicating factors related to crystallization of PLLA.

Experimental Part

Starting Materials. Poly(DL-lactide) was supplied by PURAC biochem (The Netherlands). According to the supplier, a residual monomer amount of up to a 2% could be expected; hence, the polymer was purified in a Soxhlet with methanol for 24 h before use. The molecular weight of poly(DL-lactide) was measured viscometrically in a Ubbelohde-type viscometer in chloroform at 30 °C, using the relation[18]

$$[\eta] = 2.21 \times 10^{-4} M_v^{0.77}\ (\mathrm{dL/g}) \qquad (1)$$

A value $M_v = 3.8 \times 10^5$ g/mol was obtained.

Poly(vinylphenol) (PVPh) with molecular weight $M_w = 2.0 \times 10^4$ was supplied by Aldrich. The polymer was dried in a oven at 110 °C for an hour before use.

Blend Preparation. Tetrahydrofuran (THF) solutions of the polymers (2 wt %) were mixed in the desired amounts. Blends were prepared by solvent casting at 30 °C or by precipitation in a large excess of *n*-hexane and were dried in a vacuum oven at 50 °C for 2 days.

Differential Scanning Calorimetry. Thermal analysis was carried out on a DSC from TA Instruments, model DSC 2920. Approximately 5−10 mg of each blend was weighed and sealed in an aluminum pan. To remove the moisture picked up by the samples during DSC pan preparation, they were maintained in a vacuum oven at 50 °C for 48 h prior to scanning. Two consecutive scans were performed, with a scan rate of 20 °C/min, up to 200 °C. Glass transition temperatures were obtained in the second scan and were measured as middle point values.

Infrared Spectroscopy. Infrared spectra of blends were recorded on a Nicolet AVATAR 370 Fourier transform infrared spectrophotometer (FTIR). Spectra were taken with a resolution of 2 cm^{-1} and were averaged over 64 scans. THF solutions containing 0.5 wt % blends were cast on KBr pellets, and samples were vacuum-dried at 50 °C for 48 h. In the case of the blends obtained by precipitation, a small quantity of the sample was mixed with KBr, carefully ground in a mill, dried at 110 °C for an hour to remove moisture, and pressed in a hot mold. The absorbance of all the studied samples was within the absorbance range in which the Lambert−Beer law is obeyed. Second-derivative spectra were smoothed with a quartic 15-point Savitzky-Golay smoothing filter.[19,20] Care was taken on the degree of distortion introduced by the smoothing algorithm, which was checked according to the procedure reported elsewhere.[17]

Results and Discussion

DSC Analysis. DSC is a well-known method to study the miscibility of polymer blends, based on the criterion of a single glass transition temperature (T_g) intermediate between those of the pure polymers. Both PDLLA and PVPh are amorphous polymers, showing the T_g at 59 and 179 °C, respectively.

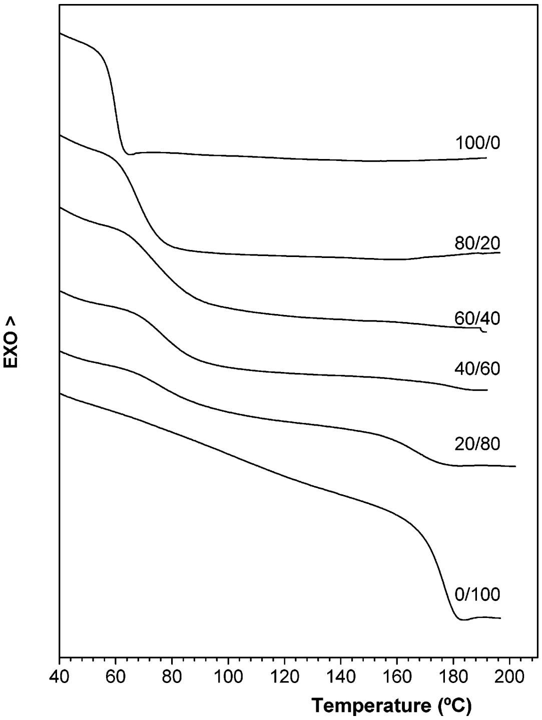

Figure 2. Second scan DSC traces for PDLLA, PVPh, and PDLLA/PVPh blends of different composition obtained by solvent casting.

In the first heating DSC scan (not shown), PDLLA/PVPh blends obtained by solvent casting showed a specific heat jump at a temperature close to the T_g corresponding to pure PDLLA in all the composition range. Hence, phase separation can be concluded, although the specific heat jump corresponding to the PVPh-rich phase was obscured due to hard to remove residual moisture. In the second heating scan (see Figure 2), blends containing less than 50 wt % PVPh show a single T_g, shifted to higher temperatures compared to the value obtained in the first scan. Hence, miscibility is enhanced during the first heating scan to temperatures above the T_gs of the neat components. However, blends exceeding 50 wt % PVPh show two T_gs: the one corresponding to the PDLLA-rich phase is located at about 80 °C, indicating partial miscibility, and the one corresponding to the PVPh-rich phase is located at about 175 °C, indicating mostly pure PVPh. These results are consistent with those reported by Zhang et al.,[15] but they concluded inmiscibility of the system, and we attribute them to $\Delta\chi$ effect.[21] This effect takes into account that phase behavior of a solvent-1−polymer-2−polymer-3 ternary system depends not only on the polymer−polymer interaction parameter χ_{23} but also on the difference in strengths of the polymer−solvent interaction parameters, $\Delta\chi$. Theoretical models of ternary systems predict phase separation, provided that $\Delta\chi$ is sufficiently large, even when the polymers are compatible; these systems usually show closed inmiscibility regions in the ternary phase diagram, leading to phase-separated systems during blend preparation by solvent casting.[21] Taking into account the chemical structures of PLLA, PVPh, and THF, strong hydrogen-bonding interactions can be expected between THF and PVPh; hence, the occurrence of the $\Delta\chi$ effect seems reasonable for PVPh-rich blends.

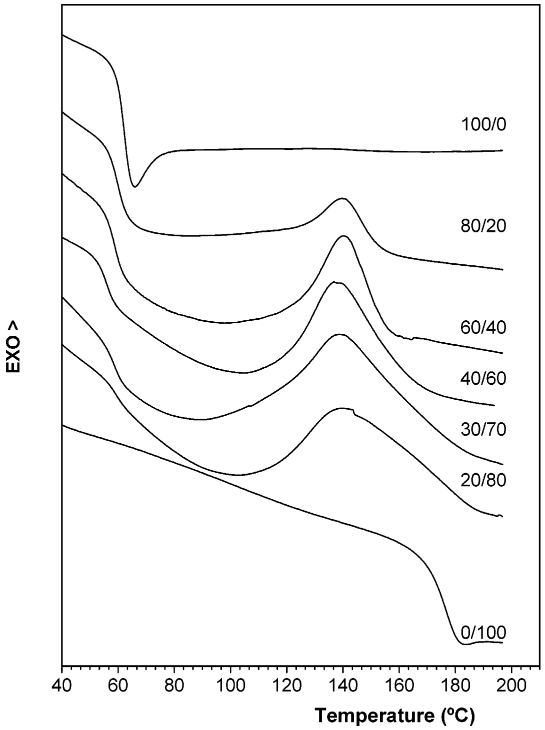

Figure 3. First scan DSC traces for PDLLA, PVPh, and PDLLA/PVPh blends of different composition obtained by solution/precipitation.

Figure 3 shows DSC traces for PDLLA/PVPh blends obtained by solution/precipitation in the first heating scan. In all the composition range, a specific heat jump can be observed at nearly the same location to that corresponding to the T_g of pure PDLLA. In addition, its height indicates that the PDLLA content in this phase amounts closely to the corresponding feed composition (see Table 1), as revealed by the ratio $\Delta C_p/\Delta C_{p,\mathrm{PDLLA}}$. Hence, DSC results suggest nearly complete phase separation for the as-precipitated blends. Additional proof supporting this conclusion is reported in the FTIR results section. At temperatures above the specific heat jump, a wide exothermic peak with a maximum at about 140 °C is observed. This is a completely new feature in polymer blends research, not reported before. This peak is attributed to the enthalpy of mixing (ΔH_m included in Table 1), as will be confirmed with additional proofs given in this paper.

Figure 4 shows DSC traces for PDLLA/PVPh blends obtained by solution/precipitation in the second heating scan. As can be seen, a single intermediate T_g is obtained in all the compositions range, proving the miscibility of the system.

The dependence of T_g on composition of miscible PDLLA/PVPh blends is illustrated in Figure 5 (see Table 1 for numerical values). Several equations have been proposed to describe the T_g–composition dependence of miscible polymer blends. In systems with specific interactions such as hydrogen bonds, the most suitable relation is the Kwei equation,[22] which in systems with symmetric deviations from linearity can be simplified to eq 2:[17]

$$T_g = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2 \tag{2}$$

where w_1 and w_2 are the weight fractions of components 1 and 2, T_{g1} and T_{g2} are the glass transitions of the neat components, and q is a fitting constant related to the strength of the interactions. The fit of experimental data to the simplified Kwei equation is also shown in Figure 5, and the value obtained for the adjustable parameter is $q = -87$. This value is very similar to that reported for PLLA/PVPh blends,[17] suggesting that the specific interactions responsible for miscibility are weaker than expected assuming a proportional rule.

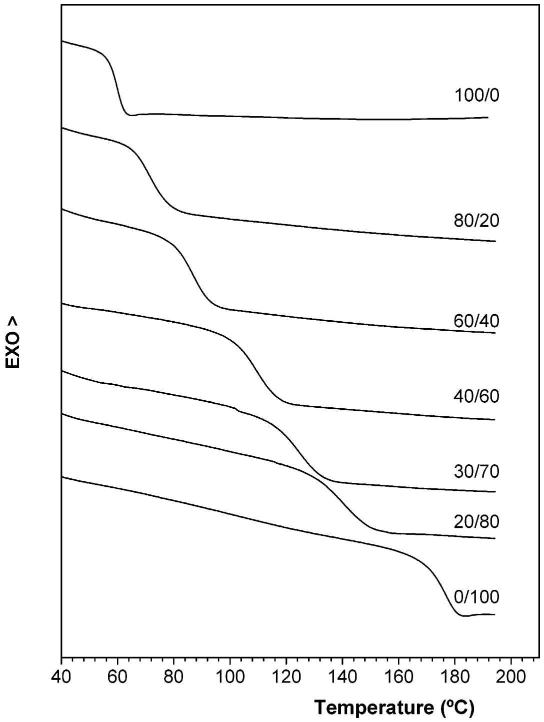

Figure 4. Second scan DSC traces for PDLLA, PVPh, and PDLLA/PVPh blends of different composition obtained by solution/precipitation.

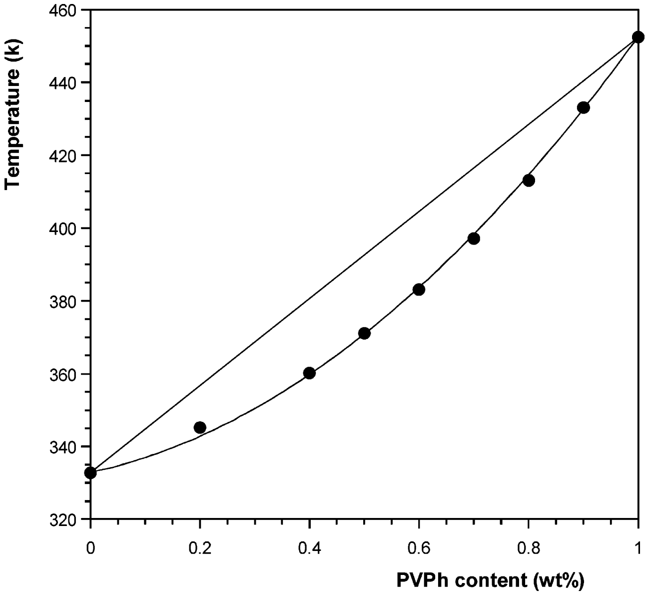

Figure 5. T_g vs composition for PDLLA/PVPh blends. The straight line represents linear behavior, and the curve is the fit to the simplified Kwei equation ($q = -87$).

Finally, from the enthalpies of mixing the interaction energy density B can be obtained, according to

$$\frac{\Delta H_m}{V} = B\phi_1\phi_2 \tag{3}$$

Table 1. DSC Results for PDLLA/PVPh Blends of Different Composition Obtained by Solution/Precipitation, Listed According to the Corresponding Scan

	first scan					second scan
PDLLA/PVPh (wt %)	T_g (°C)	ΔC_p (J/(g °C))	$\Delta C_p/\Delta C_{p,\text{PDLLA}}$	ΔH_m (J/g)	B^a (cal/cm^3)	T_g (°C)
0/100	179	0.437	0			
10/90				−10.8	−38.5	160
20/80	59	0.135	0.26	−18.7	−37.1	140
30/70	59	0.214	0.42	−23.2	−34.6	124
40/60	58	0.243	0.47	−15.6	−20.1	110
50/50	58	0.284	0.55	−12.3	−15.1	98
60/40	59	0.344	0.67	−9.8	−12.4	87
80/20	60	0.376	0.73	−6.4	−11.8	72
100/0	59	0.515	1.0			

[a] Values for the interaction energy density *B* were calculated from eq 4.

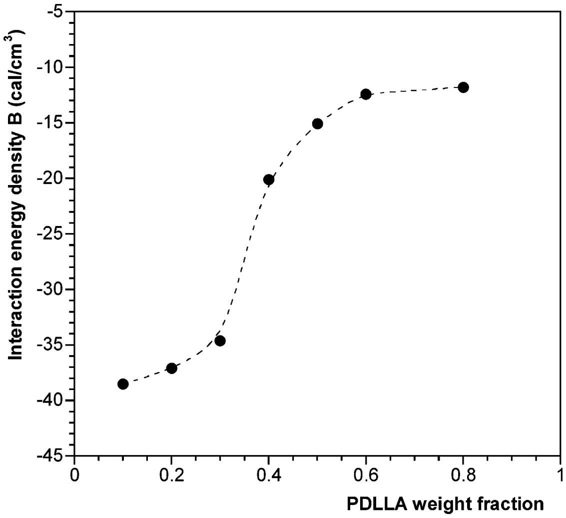

Figure 6. Interaction energy density vs composition for PDLLA/PVPh blends.

where V is the total volume of mixture and ϕ_1 and ϕ_2 are the volume fractions. Molar volumes of the repetitive units of PDLLA and PVPh are 53.3 and 100 cm^3/mol, respectively, obtained by group contribution methods.[16] Calculated values of B are listed in Table 1 and are displayed in Figure 6. It must be noted that these values can be affected by certain error due to incomplete purity of the separated phases in the as-precipitated blends. Nevertheless, FTIR results (see the following section) are much more conclusive than DSC ones, supporting nearly pure phases. Hence, errors due to incomplete purity of the separated phases should be small. As can be seen, the strength of the interactions shows a marked dependence on composition. In systems with high PVPh content, B shows a higher value of about −40 cal/cm^3. As the PVPh content decreases, the magnitude of B decreases, showing a maximum dependence in the vicinity of the stoichiometric composition (62.5 wt % PDLLA). Finally, in systems with high PDLLA content, B tends asymptotically to a value of about −11 cal/cm^3. This value is close to $B = -8.8$ cal/cm^3, reported for PLLA/PVPh blends from melting point depression studies.[17] The observed difference can be attributed to several reasons. First, PLLA and PDLLA show different conformational statistics, PLLA being stiffer;[23] hence, a lower energy density value could be expected for blends based on this polymer. Second, the value of B in the above-mentioned PLLA/PVPh system corresponds to a temperature of about 210 °C, and although in the original form of the Flory−Huggins theory B does not depend on temperature, a lower absolute value at higher temperatures seems reasonable because interassociation is expected to decrease with temperature. Finally, the value obtained for the PLLA/PVPh system is affected by uncertainities in experimental parameters used for the calculation, such as the melting enthalpy of PLLA.[24]

In summary, PDLLA shows an unusual miscibility behavior. Perhaps the most intringuing features are the enhanced miscibility observed for solution/precipitation blends over solvent-cast blends and the direct detection of the enthalpy of mixing. Promoted miscibility over the solvent-cast systems has also been found in solution/precipitation blends of poly(L-lactide)/poly(methyl methacrylate)[9] and poly(L-lactide)/poly(vinylphenol)[17] and can be attributed to the $\Delta\chi$ effect.[21] Regarding the direct determination of the mixing exotherm, it has been claimed that measuring the enthalpy of mixing in polymer systems is impossible because diffusion between solid components in solid state is so slow that the value of ΔH_{mix} cannot be measured by any sensitive calorimetry.[25,26] However, polylactide blends obtained by solution/precipitation show a microstate that has not been considered until now but can be reasonably explained.

Dissolved polymer pairs can establish attractive or repulsive interactions. When attractive interactions are very strong (for example, in polymer blends with strong hydrogen bonding), dissolved polymers can spontaneously precipitate even at dilute concentrations, leading to interpolymer complexes.[27,28] When omnipresent dispersive (repulsive) interactions are strong, the polymer solution is turbid, indicating phase separation. When both attractive and repulsive intermolecular interactions are weak, polymer coils can be considered randomly dispersed in the solution. In blends prepared by solution/precipitation, chains are “frozen” during the precipitation step, although certain phase development can occur during this step depending on the relative strength of attractive and repulsive interactions. In our experimental system, PDLLA and PVPh show similar solubility parameters, 10.1 and 10.6 (cal/cm^3)$^{1/2}$, respectively;[17] hence, repulsive forces that could drive phase separation during the precipitation step can be considered weak. In addition, DSC results obtained in the first heating scan indicate the absence of mixing at the molecular level; thus, weak attractive interactions have to be assumed in the dissolved polymer. Note that weak attractive interactions can be due to specific interactions between weak interacting groups but also to esteric hindrances or accessibility issues between strong interacting groups.[29−31] The first DSC scan shows an important exothermic peak, indicating the occurrence of strong interactions when miscibility is achieved. Hence, the weak interactions observed in solution for PDLLA/

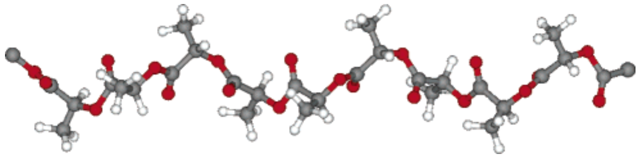

Figure 7. Molecular model for a polylactide chain in its most stable conformation at room temperature. Carbonyl groups point to the helical chain and are shielded from the environment by the "molecular hole" in which they locate.

PVPh blends must be attributed to functional group accessibility issues.[29−31]

The influence of the chemical structure of PDLLA on group accessibility can be discussed by comparison with polyesters of similar structure, such as poly(hydroxy butyrate) (PHB), which shows the typical miscibility behavior of polyester/PVPh blends.[32,33] The repetitive unit of PHB resembles that of PDLLA, presenting an additional CH_2 group located between the two consecutive carbon atoms of the polylactide. Functional group accessibility includes several steric effects, such as intramolecular screening,[34,35] steric hindrances,[36,37] steric shielding effects,[38] group spacing,[39−42] and chain stiffness.[42] Intramolecular screening is due to chain bending back on itself, so that there are a greater number of like−like contacts in polymer blends than in mixtures of low molecular weight analogues. According to recent modifications of the Painter−Coleman association model,[35] the contribution of this effect to the free energy of Gibbs is accounted by the factor γ, which for blends of linear polymers is $\gamma \sim 0.3$. Hence, this effect is nearly similar for any blend of linear polymers and cannot explain the differences between PHB and PDLLA. Steric hindrances occur when the functional group is close to another vicinal group hindering molecular interassociation. The methyl group of PDLLA is in the carbon atom vicinal to the hydrogen bond accepting carbonyl group, and some steric hindrance can be expected compared to PHB. Nevertheless, the real 3D structure must be considered to evaluate this effect. The spatial structure of the most stable helical conformation of a polylactide chain is shown in Figure 7,[52] where the dihedral angle measured between the C═O bond and the C_α−CH_3 bond is 100°. Thus, the methyl group alone does not seem to represent a strong obstacle for the interaction. Steric shielding effects appear when a portion of the molecule shields the functional group and sometimes can be difficult to discern from steric hindrances. Turning back to Figure 7, carbonyl groups in the most stable helical conformation of polylactides point to the helical axis, being the oxygen atom of the carbonyl group shielded from the surrounding environment by the helical backbone. This structure seems more restrictive than those found in similar polyesters because in PDLLA the acceptor group is located into some sort of "molecular cavity". For example, in the case of PHB, carbonyl groups in the preferred helical conformation point to the outside of the helical backbone,[44] and interassociation seems easier to occur. Regarding group spacing, it has been proved that a higher distance between functional groups favors interassociation; hence, the shorter group spacing in PDLLA can negatively affect miscibility compared to PHB. Finally, chain stiffness can also play an unfavorable role as it impairs the conformational changes needed for a intimate contact between interacting groups. PDLLA shows a higher characteristic ratio ($C_\infty = 9.5$)[23] than PHB ($C_\infty = 7.5$),[45] indicating that miscibility can be harder to achieve with the polylactide. In summary, steric shielding seems the most important factor affecting the particular behavior of polylactides, although group spacing and chain stiffness should also play an unfavorable role.

Finally, the hypothesis of group accessibility to explain the miscibility behavior of PDLLA finds support in the overall miscibility behavior shown by this family of polymers. Polylactides show a wide range of miscible counterparts when miscibility is driven by dipole−dipole interactions. Miscibility has been found with poly(3-hydroxy butyrate) (PHB),[7] poly(methyl methacrylate) (PMMA),[8,9] poly(methyl acrylate) (PMA),[8] and poly(vinyl acetate) (PVAc).[46] Because dipole−dipole interactions are long-range adirectional forces, shielding of the carbonyl group by the chain backbone does not prevent the interaction. However, when short-range directional interactions such as hydrogen bonds are involved, miscibility is harder to achieve. In fact, PVPh is the first miscible hydrogen-bonding counterpart for which miscibility is found with polylactides.

FTIR Analysis. Infrared spectroscopy has been widely used to investigate specific interactions in polymer blends in which the driving force for miscibility is hydrogen bonding. The chemical structures of the studied polymers (Figure 1) support the possibility of hydrogen bonding between hydroxyl groups of PVPh and carbonyl groups of PDLLA. Miscibility between PVPh and polyesters of similar nature of PDLLA, such as poly(L-lactide)[17] and poly(hydroxy butyrate),[32,33] has also been reported, and hydrogen bonding has been confirmed by FTIR in these systems. However, Zhang et al. studied PDLLA/PVPh blends, concluding inmiscibility according to DSC and FTIR results.[15]

According to DSC results on solvent-cast blends, a good dispersion of the polymer components is only achieved for blends with up to a 60% of PVPh. Hence, solvent casting on KBr pellets is an appropriate technique for these compositions. Infrared samples of blends with higher PVPh content must be obtained by grinding the solution/precipitation blend with KBr. This was the case for the 20/80 and 10/90 compositions. Unfortunately, the 30/70 composition lead to unacceptably wide bands and was not measured. Spectra were recorded during heating to 200 °C at 5 °C/min and in the cooling step from 200 °C.

Figure 8 shows the hydroxyl spectral region of pure PVPh and PDLLA/PVPh blends at room temperature, after heating the samples to 200 °C. Neat PVPh shows two main contributions attributable to the free and associated hydroxyl groups, respectively. The broad band governing this region at about 3380 cm^{-1} corresponds to autoassociated hydroxyl multimers. The free hydroxyl band appears as a relatively narrow shoulder at about 3530 cm^{-1}, as confirmed by second-derivative analysis.[47] As can be observed in the PDLLA/PVPh spectra, the hydrogen-bonded hydroxyl band shifts to higher frequencies, due to the replacement of the hydroxyl stretching band of hydroxyl−hydroxyl hydrogen-bonded multimers by a new band corresponding to hydroxyl groups of PVPh bonded to carbonyl groups of PDLLA. The wavenumber corresponding to this spectral contribution is about 3500 cm^{-1}, as reflected by a PDLLA/PVPh 70/30 system (Figure 8). The spectral shift, with respect to the location of the free hydroxyl band, is related to the strength of the interactions, and

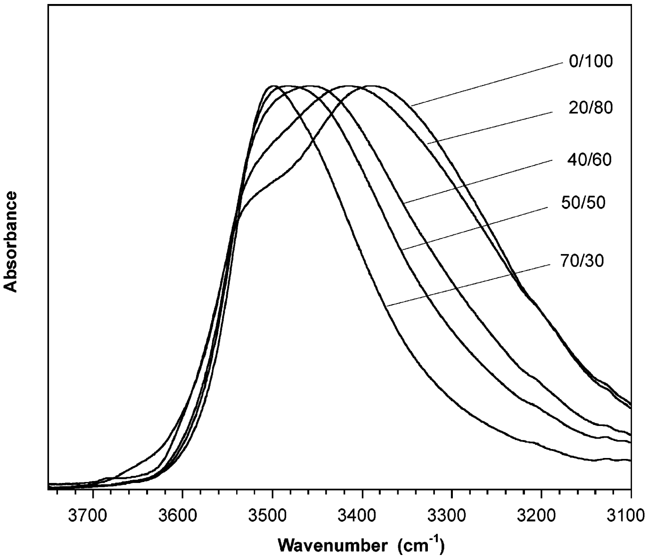

Figure 8. Hydroxyl stretching region for PDLLA/PVPh blends of different composition at room temperature.

these results indicate that hydroxyl−hydroxyl hydrogen bonds (shift ∼150 cm^{-1}) are replaced by much weaker hydroxyl−carbonyl interactions (shift ∼30 cm^{-1}). Although this change may seem counterintuitive, the association of a strongly self-associating polymer A with an unassociated polymer B is possible as long as there is a reasonable interassociation because the free energy “losses” of polymer A in mixing with polymer B can be offset by the “gains” made by the polymer B in associating with polymer A.[48] In addition, the location of the interassociated hydroxyl band in typical PVPh/polyester blends is about 3440 cm^{-1} (shift ∼90 cm^{-1});[47,49] hence, the strength of O−H⋯O═C hydrogen bonds in PDLLA/PVPh blends is much weaker than expected. Recently, Rozenbeg et al.[50] have proposed a linear relation between the enthalpy of hydrogen bonding and the square root of the spectral shift, from which the strength of O−H⋯O═C hydrogen bonds in PDLLA/PVPh blends with respect to typical PVPh/polyester systems can be calculated giving a relative value of about $(30/90)^{1/2} \times 100 = 60\%$.

The difference in strength between hydroxyl−hydroxyl and hydroxyl−carbonyl bonds can be related to the marked dependence of interaction energy density with composition observed in Figure 6. In systems with low PDLLA content, high values of B of about −40 cal/cm^3 were obtained, probably because there is only a limited autoassociation break of PVPh, as the low relative quantity of carbonyl groups should interact first with nonautoassociated hydroxyl groups. However, in blends with low PVPh content, the high dilution of this polymer makes impossible a strong autoassociation, as confirmed by the spectral changes in the hydroxyl stretching region. The energy needed to disrupt PVPh autoassociation is reflected in low B values of about −11 cal/cm^3. In other words, the interaction energy density B varies with composition because the number of self- and interassociation H-bonds vary in a nonlinear manner with composition.

Figure 9 shows the carbonyl stretching region of PDLLA/PVPh blends recorded at room temperature after heating to 200 °C, along with its second derivatives. The spectrum of neat PDLLA shows two bands located at 1777 and 1757 cm^{-1} according to second-derivative analysis. Splitting in the C═O spectral region of polylactides has been attributed to intermolecular transition dipole coupling,[51] although we are considering the possibility of intramolecular coupling among C═O groups along the chain.[43] In any case, a correct explanation for this complex spectral region is still lacking.[43]

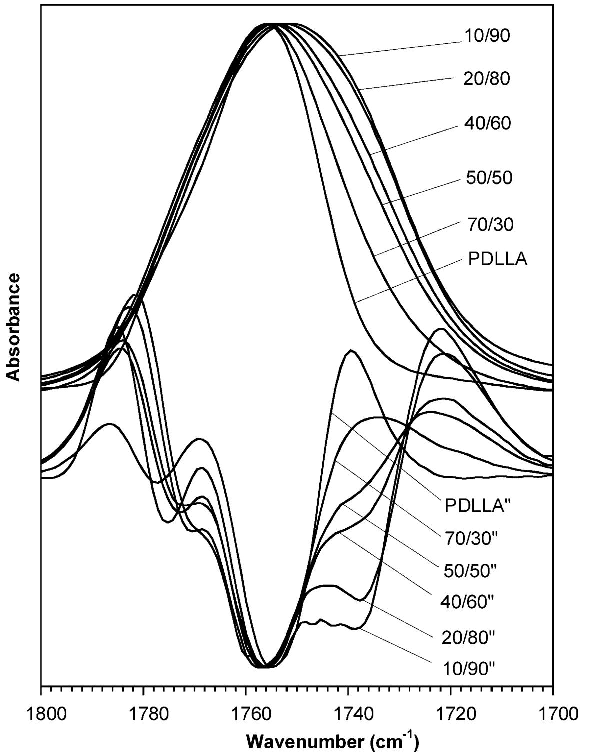

Figure 9. Autoscaled spectra of the carbonyl stretching region for PDLLA/PVPh blends of different composition at room temperature. Second-derivative spectra are displayed in the bottom side.

For PDLLA/PVPh blends, the carbonyl band becomes wider as the PVPh content in the blend increases (Figure 9). This behavior is attributed the presence of a new band at lower wavenumbers, attributed to hydrogen-bonded C═O groups. As can be seen, the relative intensity of the new band increases steadily with the content of PVPh. Second-derivative spectra increase spectral resolution, and the location for the new band can be resolved at about 1738 cm^{-1}. Hence, a spectral shift of about 20 cm^{-1} is observed in the C═O spectral region, lower than its typical value in polymers with similar interacting groups.[32] We want to note that this spectral shift value should be taken with caution due the particular behavior observed for the C═O stretching band of polylactides.[43,51] In most polymers, the carbonyl stretching band shows a localized nature, and a single component can be distinguished for the amorphous unassociated polymer. However, as briefly discussed earlier, the C═O band in polylactides shows important splitting, complicating the interpretation of the obtained spectral shift.

The development of interassociation with temperature has also been studied, and Figure 10 shows the spectrum of the PDLLA/PVPh 40/60 solvent-cast blend. As can be seen, the spectrum of the blend at room temperature prior to the heating process is very similar to that of pure PDLLA; hence, interassociation can be considered negligible. This result agrees with the phase separation obtained in the first heating scans by DSC. As the sample is heated, the C═O band widens to lower wavenumbers, with a maximum variation at tempera-

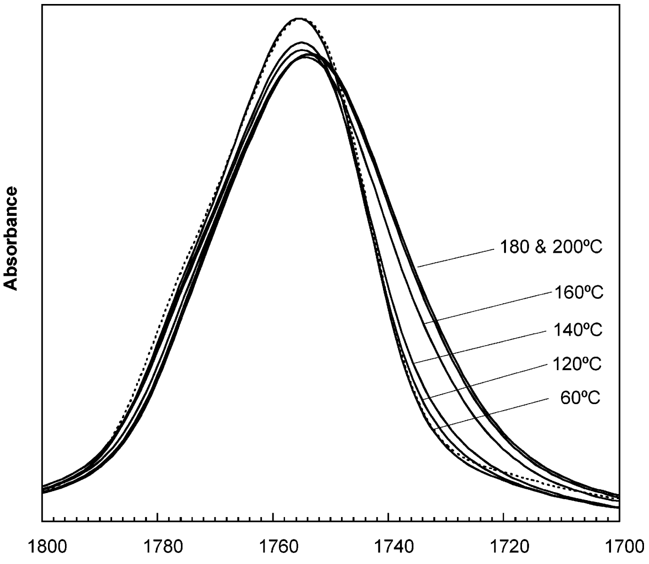

Figure 10. Changes in carbonyl spectral region during the first heating scan for a PDLLA/PVPh 40/60 blend. The spectrum of pure PDLLA at 60 °C (highlighted with a dotted line) is also shown for reference.

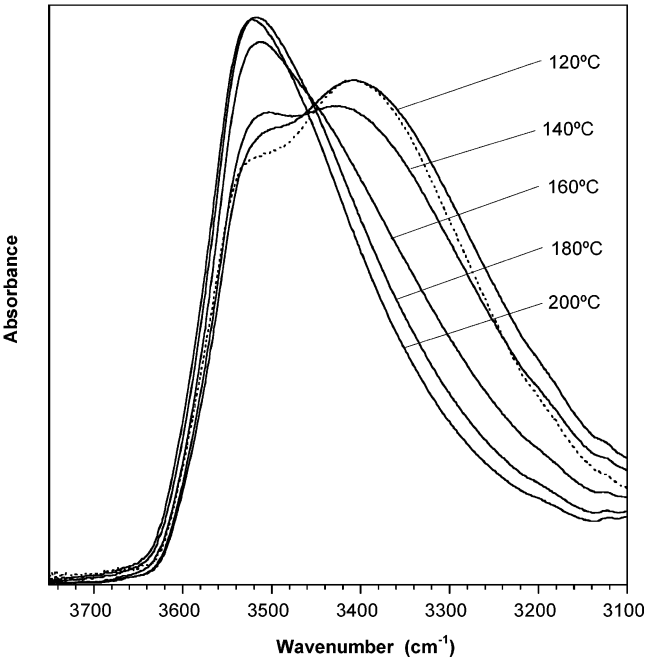

Figure 11. Changes in the hydroxyl spectral region during the first heating scan for a PDLLA/PVPh 40/60 blend. The spectrum of pure PVPh at 120 °C (highlighted with a dotted line) is also shown for reference.

tures between 140 and 160 °C. These results support the assignment for the exotherm observed by DSC, showing also a good correlation in the temperature range of the transition.

Interassociation changes during the first heating step are also evident if observed in the OH stretching region (Figure 11). As can be seen, the spectrum of the PDLLA/PVPh 40/60 blend at 120 °C is very similar to that of PVPh at the same temperature, indicating a high degree of autoassociation and negligible interassociation. However, during heating to temperatures above the glass transition of PVPh, autoassociation clearly decreases. Moreover, an additional heating above the T_g of PVPh (from 180 to 200 °C) barely changes the interassociation degree. These results are in full agreement with DSC scans and with FTIR results discussed for the carbonyl spectral region.

Conclusions

Miscibility has been found in the PDLLA/PVPh system in all the compositions range. Blends have been prepared by solution/precipitation and solvent casting. As-obtained blends are phase separated in the neat components, but heating above the T_gs of the polymers promotes miscibility. For solution/precipitation blends, miscible single phase blends are obtained after thermal treatment, but for solvent-cast blends phase separation is obtained for PVPh-rich systems due to the $\Delta\chi$ effect.

In solution/precipitation blends, an exotherm corresponding to the enthalpy of mixing is obtained, from which interaction energy densities (B) have been calculated. Parameter B shows a strong dependence with composition, related to the energy needed to disrupt the strong autoassociation of PVPh. At high polylactide contents, the value for $B = -11$ cal/cm^3 agrees quite well with that obtained for PLLA/PVPh blends by melt depression studies ($B = -8.8$ cal/cm^3). To our knowledge, this is the first system for which the direct determination of the heat of mixing is reported, being a feature of extraordinary interest for researchers working in the development of miscibility models. In polymer blends, the entropy of mixing is usually very small, and the enthalpy of mixing is nearly equal to the Gibbs free energy of the process. Hence, this can be considered a model system for testing developed free energy equations. Until now, enthalpies of mixing have been obtained by indirect methods, based on experimental assumptions that introduced unavoidable errors.[26]

This thermal feature has been explained in terms of the particular microscopic phase domains obtained in solution/precipitation blends. Solubility parameters of both PDLLA and PVPh are similar, (10.1 and 10.6 (cal/cm^3)$^{1/2}$), and weak dispersive interactions can be assumed. In addition, DSC and FTIR results confirm the absence of mixing at the molecular level for as-cast blends, probably due to accessibility constraints between interacting groups. Hence, the solution/precipitation blends can be considered a mostly random mixture of polymer chains because both attractive and repulsive interactions are very weak. During heating, thermal motion increases both chain mobility and the probability of dissimilar contacts, resulting in miscible systems at temperatures above the T_g of PVPh.

FTIR results indicate that specific interactions develop in the first heating step at temperatures below the T_g of PVPh, confirming DSC results. In the hydroxyl stretching region, the observed spectral shift is 30 cm^{-1}, lower than the typical value of about 90 cm^{-1} found in hydrogen-bonded hydroxyl−ester groups. According to these results, the estimated strength of the interactions relative to its typical value is about 60%. Weaker interactions must be attributed to impaired group accessibility, which forces the system to adopt constrained hydrogen-bonding distances and angles. The weaker strength of the interactions is also reflected by lower values of B than expected relative to typical polyester/PVPh blends. For example, a value $B = -12.5$ cal/cm^3 has been reported for PHB/PVPh blends[33] by melting point depression studies, valid for blends of high PHB content. Considering that the solubility parameters for PHB, PDLLA, and PVPh are $\delta = 9.6$ (cal/cm^3)$^{1/2}$, $\delta = 10.1$ (cal/cm^3)$^{1/2}$, and $\delta = 10.6$ (cal/cm^3)$^{1/2}$, respectively, weaker repulsive interactions occur in the PDLLA/PVPh system relative to PHB/PVPh blends; hence, weaker attractive interactions must be assumed to account for the lower magnitude of B found in this work for blends of high PDLLA content ($B = -11$ cal/cm^3).

The hypothesis of group accessibility to explain the miscibility behavior of PDLLA finds support in the overall miscibility behavior shown by this family of polymers. Polylactides show a wide range of miscible counterparts when miscibility is driven by dipole−dipole interactions. Miscibility has been found with poly(3-hydroxy butyrate) (PHB), poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), and poly(vinyl acetate) (PVAc). Because dipole−dipole interactions are long-range adirectional forces, shielding of the carbonyl group by the chain backbone does not prevent the interaction. However, when short-range directional interactions such as hydrogen bonds are involved, miscibility is harder to achieve. In fact, PVPh is the first miscible hydrogen-bonding counterpart for which miscibility is found with polylactides.

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