

Miscibility and Phase Behavior of Poly(D,L-lactide)/Poly(*p*-vinylphenol) Blends

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ABSTRACT: The miscibility of poly(D,L-lactide) (PDLLA) and poly(*p*-vinylphenol) (PVPh) blends has been studied by differential scanning calorimetry and Fourier transform infrared spectroscopy (FTIR). Phase separation was observed in blends over a wide composition range. A PDLLA-rich phase was found to coexist with an almost pure PVPh phase. The quenched blend samples showed two glass transitions (T_g s), except for a blend with a low PVPh content. However, the T_g value of the PDLLA-rich phase showed a gradual increase with increasing PVPh content. No evidence of interassociation (hydrogen bond formation) between PDLLA and PVPh was found by FTIR. The phase behavior of the blends was simulated using an association model. The results suggested that the equilibrium constant of interassociation between PDLLA and PVPh was small. The phase compositions of the two separated phases were calculated using Fox, Gordon-Taylor, and Couchman equations. The amount of PVPh in the PDLLA-rich phase increased with increasing PVPh content in the blend. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 811–816, 1998

Keywords: miscibility; phase behavior; Poly(D,L-lactide); Poly(*p*-vinylphenol)

INTRODUCTION

There has been considerable interest in the study of biodegradable polyesters, such as poly(β -propiolactone) (PPL), poly(ϵ -caprolactone) (PCL), and poly(3-hydroxybutyrate) (PHB). These polyesters are useful in biomedical and packaging applications.^{1,2} In addition, they are also good candidates for forming miscible blends with hydroxyl-, halogen-, or nitrile-containing polymers.^{3–6} Although poly(D,L-lactide) (PDLLA) is well known as a biodegradable polyester, the study of PDLLA as a blend component has received little attention. PDLLA is an amorphous polymer with a glass transition temperature (T_g) of 50°C, which is too

low for many packaging uses. The high price also limits its use as a packaging material.^{7,8} For designing novel biodegradable materials, polymer blends present a faster and economic way. Blending PDLLA with other polymers can improve its undesirable properties, lower cost, and enlarge its applications.

There are some examples of PDLLA blends, including those with low molecular weight PDLLA,⁹ poly(L-lactide),^{10,12} PCL,^{13,14} PHB^{15,16} and ethylene-vinyl acetate copolymer (EVAc).^{17,18} Due to the lack of specific interactions, most of these blends are immiscible. Poly(*p*-vinylphenol) (PVPh) has been found to be miscible or partially miscible with polyacrylates,¹⁹ polymethacrylates,^{20,21} and polyesters^{19,22–24} on the basis of specific hydrogen-bonding interactions. It has also been found that the interassociation between polymers is affected by the structure of ester-containing polymers.^{25,26} In view of the total mis-

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cibility of PVPh with PPL,¹⁹ PCL,¹⁹ and PHB^{22,23} via interassociation, it is of interest to study the miscibility of PDLA/PVPh blends.

EXPERIMENTAL

Materials

PDLA was obtained from Sigma. Its weight-average molecular weight and molecular weight distribution are 5.03×10^4 g/mol and 2.08, respectively, relative to polystyrene standards of narrow dispersity, as determined by gel chromatography (GPC) using a Waters 600E GPC with tetrahydrofuran (THF) as the eluent. PVPh with a weight-average molecular weight of 2.2×10^4 g/mol was obtained from Polyscience Inc.

Preparation of Blends

All the blends were prepared by casting from 1% (wt/v) THF or methyl ethyl ketone (MEK) solutions of the two components. The solvent was allowed to evaporate at room temperature overnight. The blends were then kept at 40°C *in vacuo* for 48 h, followed by drying at 90°C *in vacuo* for another 48 h. All the cast samples were stored in a vacuum oven at 40°C prior to DSC measurements.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed on a TA Instruments 2920 differential scanning calorimeter. The apparatus was calibrated with indium standard and nitrogen atmosphere was used throughout.

Samples as cast were first heated from -40 to 180°C at a heating rate of 20°C/min. After 1 min, the samples were rapidly quenched to -40°C to obtain quenched samples. The samples were then heated at a rate of 20°C/min to 180°C. The glass transition temperatures (T_g s) and specific heat increments of T_g transitions (ΔC_p) were determined from the DSC curves. The T_g was taken as the midpoint of the specific heat increment.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained with a Bio-Rad 165 FTIR spectrophotometer; 64 scans were taken with a resolution of 2 cm⁻¹ in all cases. Samples were prepared by casting the 1% (wt/v) THF solutions directly onto KBr discs. After the evapo-

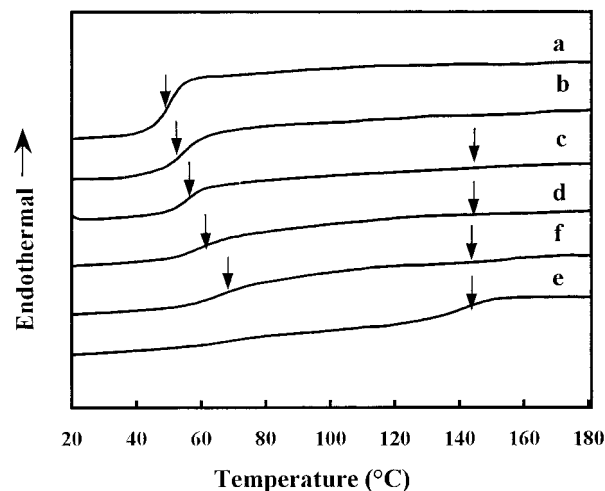


Figure 1 DSC curves of PDLA/PVPh blends after quenched from 180°C: (a) PDLA, (b) 80/20, (c) 60/40, (d) 40/60, (e) PVPh, and (f) 20/80.

ration of the solvent at room temperature, the discs were vacuum dried at 40°C for 48 h, and then at 90°C for 48 h. Spectra recorded at elevated temperatures were obtained using a SPECAC high-temperature cell mounted inside the sample chamber. All the films used in this study were sufficiently thin to be within an absorbance range where the Beer-Lambert law is obeyed.

RESULTS AND DISCUSSION

Blend Miscibility

The DSC curves of THF-cast PDLA/PVPh blends after being quenched from 180°C are shown in Figure 1. Two separate glass transitions were found over a wide range of PVPh content. The higher T_g value is almost the same as that of pure PVPh, while the lower T_g value increases with increasing PVPh content in the blend, suggesting the presence of PVPh in the PDLA-rich phase (Fig. 2). Moreover, the C_p s of the two separate phases given in Table I decrease with increasing amount of the second component.

To assess a possible solvent effect on the miscibility of PDLA/PVPh blends, blends were also cast from MEK. The blends were also immiscible, as indicated by the presence of two T_g s. The miscibility and phase behavior of THF-cast blends were further examined and discussed in the following sections.

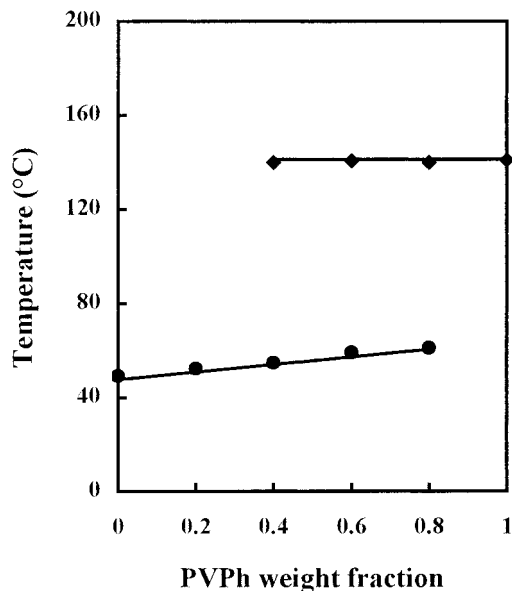


Figure 2 T_g -composition plot for PDLLA/PVPh blends.

Interassociation has been found in the blends of PVPh with various ester-containing polymers through specific hydrogen-bonding interactions between hydroxyl and carbonyl groups.²⁷ In those systems, both hydrogen-bonded hydroxyls and hydrogen-bonded carbonyls show noticeable change in their stretching bands compared with those nonassociated bands. FTIR was used to examine the possible segmental interaction in PDLLA/PVPh blends at different conditions (Figs. 3 and 4).

At room temperature, the stretching absorption of hydrogen-bonded hydroxyls of PVPh (self-association) is broad and centered at 3323 cm^{-1}

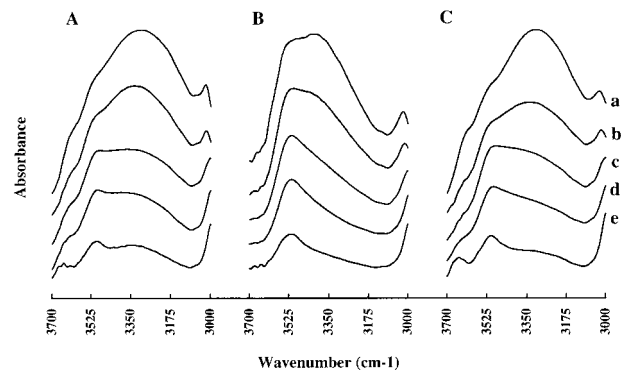


Figure 3 FTIR spectra in the hydroxyl stretching region for PDLLA/PVPh blends: (A) at room temperature; (B) at 185°C ; (C) at room temperature after being cooled from 185°C . (a) PVPh, (b) 20/80, (c) 40/60, (d) 60/40, and (e) 80/20.

and that of free hydroxyls is evident as a shoulder at 3510 cm^{-1} . The stretching bands of hydrogen-bonded hydroxyls of PVPh in the blends remain at almost the same position as pure PVPh [Fig. 3(A)]. Upon heating to 185°C , the stretching band of hydrogen-bonded hydroxyls shifts to a higher frequency at about 3400 cm^{-1} . The intensity of the absorption becomes lower compared with that at room temperature due to the breakdown of the self-association of PVPh at elevated temperatures [Fig. 3(B)]. After being cooled to room temperature from 185°C [Fig. 3(C)], the hydrogen-bonded hydroxyl bands are found at almost the same position as those in Figure 3(A). In all cases, the intensity of the hydrogen-bonded hydroxyls in the blends is lower than that in pure PVPh. With increasing PDLLA content, the free hydroxyl bands of PVPh in the blends become more obvi-

Table I Glass Transition Temperatures and Specific Heat Increments of PDLLA/PVPh Blends

Composition PDLLA/PVPh	PDLLA-Rich Phase		PVPh Phase	
	T_g , $^\circ\text{C}$	ΔC_p , $\text{J/g} \cdot ^\circ\text{C}$	T_g , $^\circ\text{C}$	ΔC_p , $\text{J/g} \cdot ^\circ\text{C}$
100/0	49.3	0.97	—	—
80/20	52.5	0.66	—	—
60/40	54.8	0.45	140	0.12
40/60	59.2	0.34	141	0.22
20/80	61.1	0.30	140	0.36
0/100	—	—	141	0.71

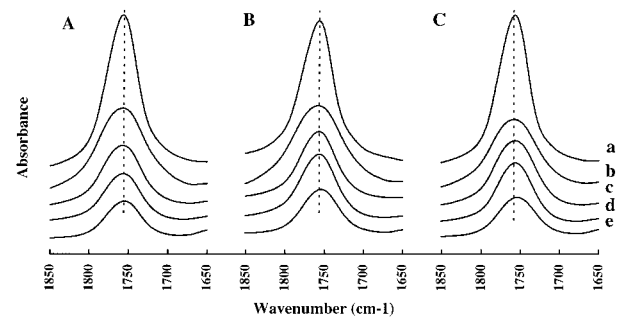


Figure 4 FTIR spectra in the carbonyl stretching region for PDLLA/PVPh blends: (A) at room temperature; (B) at 185°C ; (C) at room temperature after being cooled from 185°C . (a) PDLLA, (b) 80/20, (c) 60/40, (d) 40/60, and (e) 20/80.

ous. However, no new hydroxyl absorption corresponding to hydrogen-bonding interaction between hydroxyls of PVPh and carbonyls of PDLA is revealed by FTIR, as shown in Figure 3.

Furthermore, the carbonyl stretching regions of the spectra in Figure 4 show that the absorption bands of PDLA at 1755 cm^{-1} are independent of PVPh content at both room temperature (before or after being cooled from 185°C) and 185°C . In conclusion, the FTIR results show that only the self-association of PVPh exists in the blends, and specific interaction between the two components is not detected.

Unlike blends of PVPh with various polyesters where specific intermolecular hydrogen-bonding interactions are effective,^{19,22–24} there is no such interaction in the PDLA/PVPh blends. Polymers such as poly(vinyl chloride),⁴ poly(hydroxyether of bisphenol-A),³ polyepichlorohydrin²⁹ are miscible with aliphatic polyesters having suitable CH_x/COO ratios. These polymers are immiscible with a polyester that has a large or a small CH_x/COO ratio. PVPh is miscible with several polyesters such as PPL,¹⁹ PCL,¹⁹ PHB,^{22,23} poly(ethylene succinate)²⁴ (PES), poly(ethylene adipate),²⁴ and poly(butylene adipate).²⁴ It is of interest to note that PVPh is miscible with PES but not with PDLA, even though both polyesters have the same CH_x/COO ratio of 2. However, the chemical structures of PES and PDLA are slightly different. PES contains $-\text{CH}_2-$ groups in its polymer chain, but PDLA contains methyl groups attached to its main chain. For polymers near the verge of the immiscibility/miscibility boundary, a slight change in the chemical structure could lead to a significant change in their miscibility behavior. In this case, the methyl groups appear to have interfered the interaction between the carbonyl groups of PDLA and the hydroxyl groups of PVPh.

Simulated Spinodal Phase Diagrams

Coleman and Painter^{27,28} have developed an association model to predict the thermodynamics of polymer blends involving specific interactions. The model has been used to predict the phase diagrams, miscibility windows, and some thermal properties of polymer blends. The application of this model requires a knowledge of equilibrium constants and enthalpies of hydrogen bond formation relevant to a particular blend system. For polymer blends involving a self-association poly-

mer such as PVPh, equilibrium constants describing the formation of dimers (k_2) and higher multimers (k_B) can be obtained from infrared studies of a lower molecular weight model compound. The interassociation constant (k_A) can be determined directly from experimental infrared studies of miscible polymer blends. The enthalpies of various hydrogen bond formation (h_2 , h_B , h_A) can be calculated from the temperature dependence of the appropriate equilibrium constants.

We have used the association model to simulate the phase diagram of the PDLA/PVPh blend using a miscibility guide and phase calculation software (MG & PC).³⁰ The k_2 , k_B , h_2 , and h_B values for PVPh are 21.0, 66.8, -5.6 , and -5.2 kcal/mol, respectively.¹⁹ Other polymer properties such as molar volumes and solubility parameters can be calculated using the MG & PC software. For PVPh/PCL blend, k_A is 66.2 and h_A is -4.3 kcal/mol.¹⁹ However, when these k_A and h_A values are used to simulate the phase diagram, a completely miscible PDLA/PVPh blend system is predicted. Because the present study has shown the absence of or at best a very weak interassociation between PVPh and PDLA, it seems inappropriate to use the k_A and h_A values for the strongly interacting PVPh/PCL blend in our calculation. Instead, we have assumed a series of k_A values to simulate the phase diagram while considering h_A to be -4.3 kcal/mol. Some of the resulting phase diagrams are shown in Figure 5.

In the case of $k_A > 5$, the simulated phase diagram shows that the two polymers are miscible in the whole temperature range for all blend compositions. As indicated in Figure 5, blends of PDLA with PVPh are predicted to be thermodynamically stable throughout the entire temperature range except for a small region of immiscibility at high PVPh contents and high temperatures by assuming $k_A = 4$. The area of immiscibility loop increases when the k_A value is further reduced to 2 or 1. In the case of $k_A = 1$, the simulated phase diagram shows that the two polymers are miscible at low temperatures but not at high temperatures over a wide range of blend compositions, showing a lower critical solution temperature behavior. It is noted that the simulated phase diagram predicts the existence of a nearly pure PVPh phase and a PDLA-rich phase, and the prediction agrees well with our experimental results. The small k_A value indicates a very weak interassociation between PVPh and PDLA.

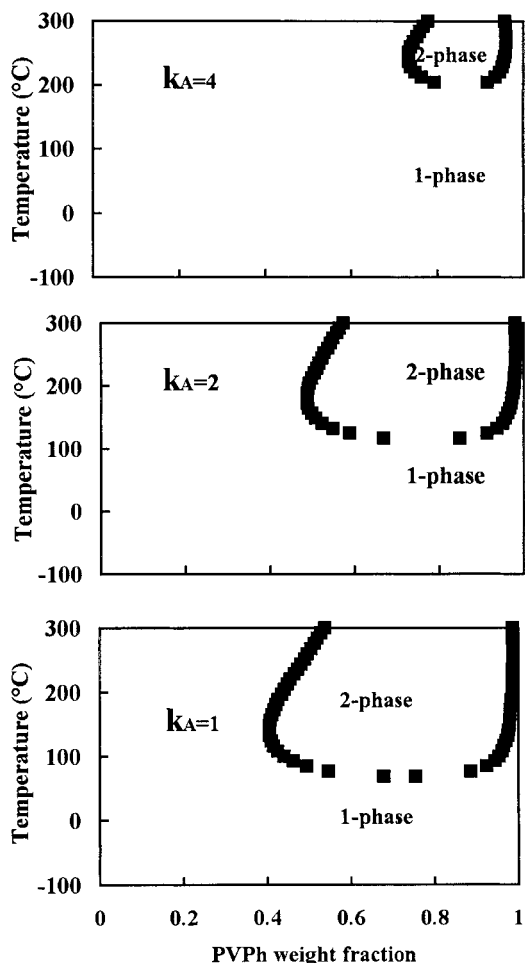


Figure 5 Simulated spinodal phase diagrams for PDLA/PVPh blends using different k_A values.

Calculation of Phase Compositions

As shown by DSC measurements, the PDLA/PVPh blends are phase separated. However, the T_g values suggest the presence of PVPh in the PDLA-rich phase. The composition of the PDLA-rich phase can be estimated from its T_g value.

The T_g behavior of miscible polymer blends is usually described by several equations, such as those of Fox,³¹ Gordon-Taylor,³² and Couchman.³³

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (\text{Fox}) \quad (1)$$

$$T_g = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2) \quad (\text{Gordon - Taylor}) \quad (2)$$

$$\ln T_g = (w_1 \ln T_{g1} + k w_2 \ln T_{g2}) / (w_1 + k w_2) \quad (\text{Couchman}) \quad (3)$$

where w is the weight fraction, and subscripts 1 and 2 denote the pure polymers. k is the ratio of the specific heat increments from the glassy to the liquid state:

$$k = \Delta C_{p2} / \Delta C_{p1} \quad (4)$$

Assuming that the T_g of the PDLA-rich phase can also be described by these equations, the weight fraction of PVPh in the PDLA-rich phase (w_{2A}) can be calculated from the following equations:³⁴

$$w_{1A} = (T_{g2}/T_{gA} - 1) / (T_{g2}/T_{g1} - 1) \quad (5)$$

$$w_{1A} = k(T_{gA} - T_{g2}) / \{k(T_{gA} - T_{g2}) - (T_{gA} - T_{g1})\} \quad (6)$$

$$w_{1A} = k \ln(T_{gA}/T_{g2}) / \{k \ln(T_{gA}/T_{g2}) - \ln(T_{gA}/T_{g1})\} \quad (7)$$

$$w_{2A} = 1 - w_{1A} \quad (8)$$

where subscript A represents PDLA-rich phase. Equations (5)–(7) are derived from eqs. (1)–(3), respectively. According to the data in Table I, k is 0.735. The phase composition of the PDLA-rich phase is shown in Table II, and the results obtained from eqs. (5)–(7) are quite close to each other.

Again, the phase compositions shown in Table II confirm that a PDLA-rich phase exists in the blend. The amount of PVPh in the PDLA-rich phase, w_{2A} , increases with increasing PVPh content in the blend. In the blend containing 0.8 weight fraction of PVPh, w_{2A} reaches a value of about 0.17.

Table II Phase Composition of PDLA-Rich Phase in PDLA/PVPh Blends

Weight Fraction of PVPh in Blend	Weight Fraction of PVPh in PDLA-Rich Phase		
	Fox equ.	Gordon-Taylor Equ.	Couchman Equ.
0.2	0.044	0.047	0.053
0.4	0.076	0.081	0.091
0.6	0.134	0.141	0.157
0.8	0.160	0.167	0.186

CONCLUSIONS

Although PVPh is miscible with a large number of aliphatic polyesters, the PDLLA/PVPh blends are immiscible. The blends were phase separated over a wide range of composition. The T_g s of the PDLLA-rich phase increased with increasing PVPh content in the blends. No evidence of hydrogen-bonding interaction between PDLLA and PVPh was revealed by FTIR. The phase diagram of PDLLA/PVPh blends can be simulated using an association model by assuming a small k_A value. The phase compositions of the PDLLA-rich phase calculated by Fox, Gordon-Taylor, and Couchman equations agreed well with each other.

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