Miscibility and Phase Structure of Binary Blends of Polylactide and Poly(vinylpyrrolidone)

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ABSTRACT: The miscibility, crystallization behavior, and component interactions of two binary blends, poly(L-lactide) (L-PLA)/poly(vinylpyrrolidone) (PVP) and poly(D,L-lactide) (DL-PLA)/PVP, were studied with differential scanning calorimetry and Fourier transform infrared (FTIR) spectroscopy. The composition-dependent changes of the glass-transition temperature (T_g) and degree of crystallinity (X_c) of the L-PLA phase indicated that L-PLA and PVP were immiscible over the composition range investigated. However, the sharp decrease of X_c with increasing PVP content in the second heating run demonstrated that the cold crystallization process of L-PLA was remarkably restricted by PVP. In DL-PLA/PVP blends, the existence of two series of isolated T_g's indicated that DL-PLA and PVP were phase-separated, but evidence showed that there was some degree of interaction at the interface of the two phase, especially for the blends with low DL-PLA contents. FTIR measurements showed that there was no appreciable change in the spectra of L-PLA/PVP with respect to the coaddition of each component spectrum, implying the immiscibility of the two polymers. In contrast to L-PLA, the intermolecular interaction between DL-PLA and PVP was detected by FTIR; this was evidenced by the observation of a high-frequency shift of the C=O stretching vibration band of PVP with increasing DL-PLA content, which suggested some degree of miscibility. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 973–979, 2003

Key words: blends; crystallization; miscibility

INTRODUCTION

Because of their biocompatibility and environmental degradability, polymers derived from lactic acid have become important materials for medical applications, such as surgical sutures,[1] drug delivery systems,[2] and internal bone fixation.[3] The most common polylactides (PLAs) are poly(L-lactide) (L-PLA) and poly(D,L-lactide) (DL-PLA), which are produced from L-lactide and D,L-lactide, respectively. L-PLA is a semicrystalline polyester with a melting temperature (T_m) of 180°C, and it has poor processing and degradation properties because of its high crystallinity. DL-PLA is an amorphous, transparent polymer with a glass-transition temperature (T_g) of about 50°C, which is too low for many packaging uses. To meet various mechanical and degradation requirements, PLA must exhibit a broad spectrum of physical properties while retaining the degradability of the parent polymer.

There are several approaches for improving the properties of PLA, including blending and copolymerization. Extensive efforts have been devoted to the study of the effect of the copolymerization of PLA. For example, the copolymer of PLA with poly(glycolic acid) has been produced to control the degradation rate through compositional modification.[4] The hydrophilicity can be modified by the insertion of poly(ethylene glycol) (PEG) into the PLA backbone.[5] In recent years, there has been a growing interest in blending PLA with other polymers because blending is relatively simple and more cost-effective in comparison with copolymer synthesis. Through the opportune choice and composition of the second polymer, a tailor-made polymer with specific properties can be obtained. Several blending systems of PLA have been investigated previously, such as poly(L-lactide) (PLLA)/poly(ethylene oxide),[6,7] PLLA/poly(vinyl alcohol) (PVA),[8] PLLA/poly(p-vinylphenol) (PVPh),[9] PLLA/poly(ε-caprolactone) (PCL),[10,11] PLA/poly(3-hydroxybutyrate),[12] and PLLA/PEG.[13]

Poly(vinylpyrrolidone) (PVP) is also an environmental friendly synthetic polymer, with good performance and biocompatibility. It has been widely used in biomedical, biochemical, food, textile, and other fields because of its nontoxic and water-soluble properties.[14] Blends of PVP with many other polymers have also been extensively studied.[15–19] Because PVP has good hydrophilicity and high T_g, it is expected, as a result of blending PLA with PVP, that the hydrophilicity and mechanical properties of PLA will be further improved. However, to our knowledge, there are no reports on the studies of blends of PLA with PVP so far.

In this article, the blends of both L-PLA and DL-PLA with different compositions of PVP were prepared. The miscibility, crystallization behavior, and component interactions of these blends were studied with differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy.

EXPERIMENTAL

Materials

The L-PLA samples used in this study were synthesized in our laboratory according to the literature.[20] The viscosity-average molecular weight was 55 kg/mol, as determined by the measurement of the intrinsic viscosity in a chloroform solution at 30°C. DL-PLA was purchased from Sigma-Aldrich Chima Inc. (Shanghai, China) and used as received. Its weight-average molecular weight was 150 kg/mol, relative to polystyrene standards of narrow dispersity, as determined by gel permeation chromatography (GPC) with a Waters PL-210 GPC (U.S.A.) instrument using tetrahydrofuran (THF) as an eluent. PVP with a molecular weight of 30 kg/mol was obtained from the Beijing Chemical Agent Co. (Beijing, China) and used without further purification.

Film preparation

Three polymer solutions in chloroform were prepared separately at a concentration of 5% (w/v). Two solutions were mixed in the desired composition and then cast onto glass plates. The solvent was allowed to evaporate at room temperature for 24 h; the films were further dried at about 50°C for another 48 h *in vacuo* and then stored in a desiccator until they were used.

Measurements

FTIR spectra were recorded over the $4000–400\text{-cm}^{-1}$ range at room temperature on a Bruker IFS 55/FTIR spectrometer (Germany); 32 time scans were coadded at a 4-cm^{-1} resolution. All sample films used for FTIR measurements were prepared by direct solution casting onto KBr crystals.

A Mettler–Toledo 822e differential scanning calorimeter (Switzerland), calibrated with indium, was used to analyze the thermal properties of the blends. The samples were first heated from room temperature to a high temperature (200°C) at a heating rate of 10°C/min; they were annealed for 1 min at this temperature and then quickly cooled to 0°C at about 80°C/min. The samples were subsequently heated again to 200°C at a heating rate of 10°C/min. The thermograms of the first and second DSC heating runs were both recorded. In the first heating scans, the thermograms were distorted in the range of 50–100°C
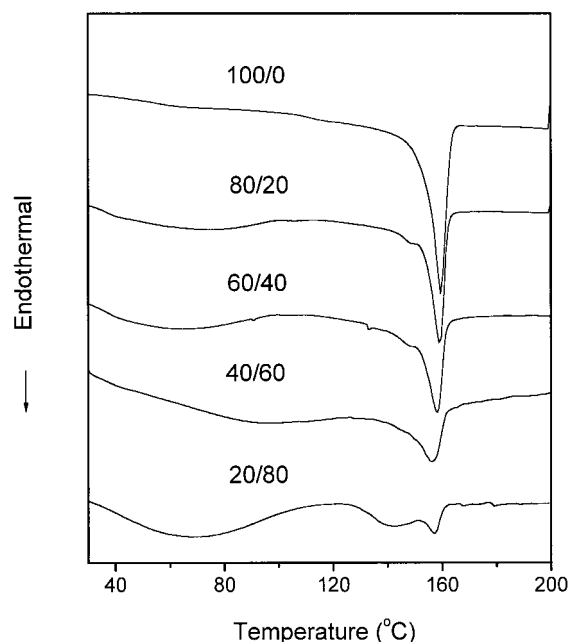

Figure 1 First-heating-scan DSC melting thermograms of L-PLA/PVP blend samples with compositions of 100/0 to 20/80.

because of the presence of a trace amount of water, so only T_m is reported for this scan. T_m and the apparent enthalpy of fusion (ΔH_f) of each sample were determined from the maximum and the area of the melting endothermic peaks, respectively. T_g, estimated in the second heating scan, was taken as the temperature at the midpoint of the discontinuity in the heat flows. All the DSC measurements proceeded under N_2 of 10 mL/min.

RESULTS AND DISCUSSION

Thermal properties of the PLA/PVP blends

The results of the DSC measurements carried out for PLA/PVP blends are shown in Figures 1–5. Figure 1 displays the melting thermograms obtained in the first heating run for samples of L-PLA/PVP with a composition range of 100/0 to 20/80. As shown in Figure 1, the thermograms of the blends reveal a broad endotherm of water thermodesorption over 40–100°C because of the presence of a trace amount of water, but this does not affect the record T_m values of L-PLA. L-PLA is a semicrystalline polymer, and pure L-PLA gives a relatively sharp melting endotherm with a peak maximum at 160°C. With an increase in the PVP content of up to 80 wt %, the endothermic peak of L-PLA tends to lose its prominence with a small depression in the T_m values. This proportional reduction in the magnitude of the endothermic peak area corresponds to the decrease in the L-PLA content in the blends of L-PLA with PVP.
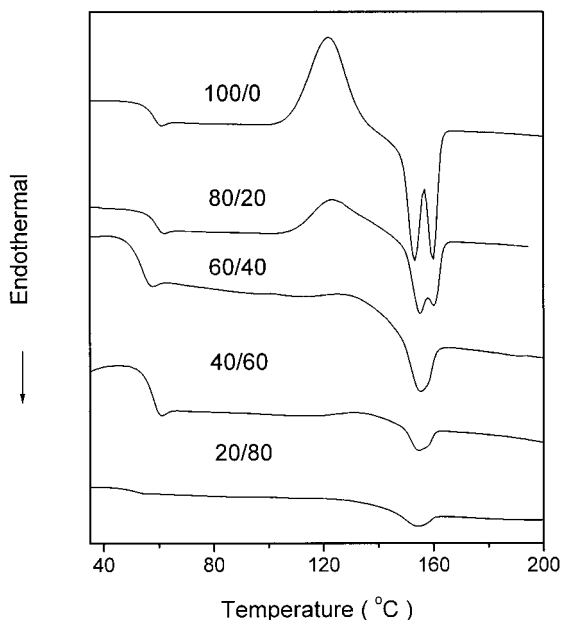
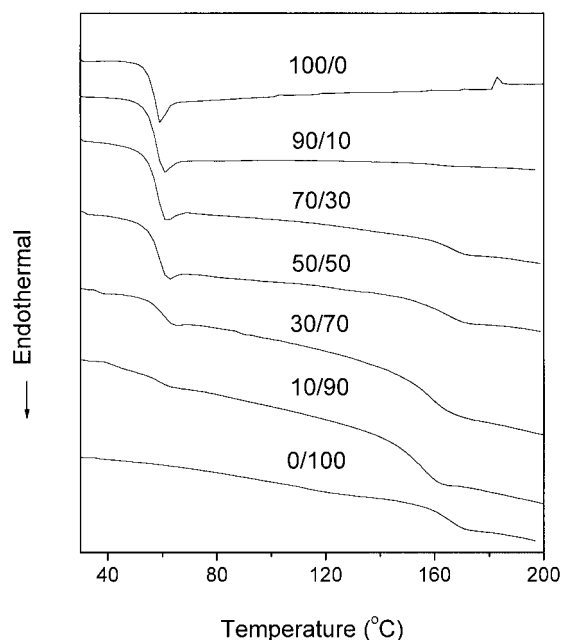**Figure 2** Second-heating-scan DSC thermograms of L-PLA/PVP blend samples with compositions of 100/0 to 20/80.

Table I shows the DSC measurement results of blends of L-PLA/PVP in the first heating run. The degree of crystallinity (X_c) of L-PLA is calculated by the following equation:

$$X_c = \Delta H_f / (\Delta H_f^0 W)$$

where ΔH_f is the apparent enthalpy of fusion (indicated in DSC thermograms as the melting enthalpy per

gram of blends) corresponding to the component, W is the weight fraction of the component, and ΔH_f^0 is the enthalpy of fusion per gram of the component in its completely crystalline state (93 J/g for L-PLA[21]).

From the date in Table I, we note that X_c of L-PLA is quite constant over the entire composition range of the blends. The crystallization of L-PLA in these blends can be seen as a process independent of the presence or absence of PVP. It is well known that, for polymer

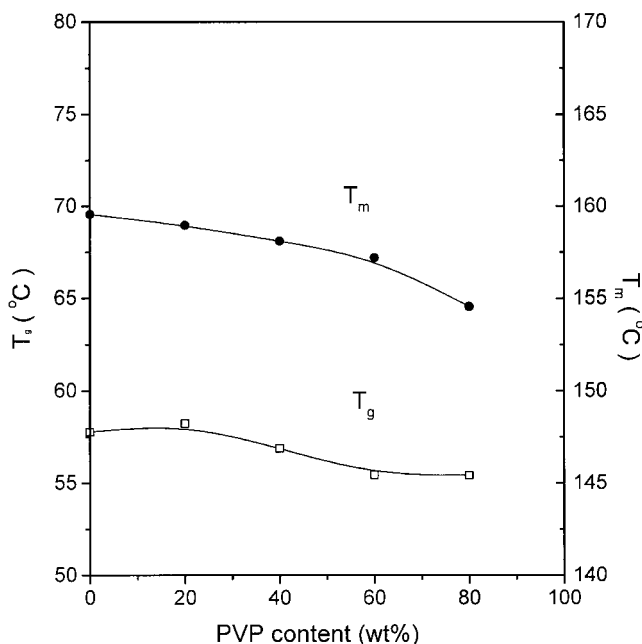**Figure 4** Second-heating-scan DSC thermograms of DL-PLA/PVP samples with compositions of 100/0 to 0/100.

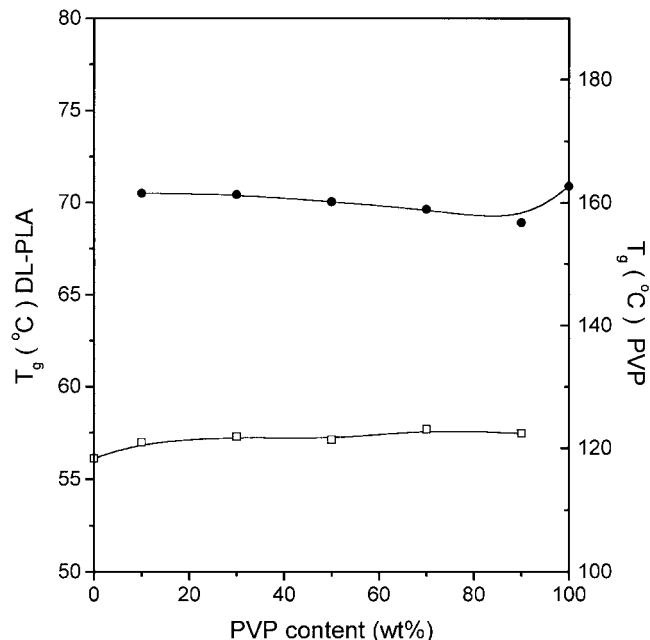**Figure 3** Composition dependence of T_g and T_m of L-PLA in blends of L-PLA/PVP.

Figure 5 Composition dependence of T_g for DL-PLA/PVP.

TABLE I
DSC Measurement Results of Blends of PLLA and PVP in the First Heating Run

Composition (w/w) of PLLA/PVP	T_m (°C)	ΔH_f (J/g of PLLA)	X_c (%)
100/0	160	40	43
80/20	159	33	44
60/40	157	25	45
40/60	156	16	43
20/80	154	—	—
0/100	—	—	—

blends containing a semicrystalline component, the variations in the values of X_c are usually due to the interactions between components and the morphological changes in the blends.[22,23] The fact that there is no obvious difference in the X_c values corresponding to those of the L-PLA phase when the PVP content varies from 0 to 80% implies that there are no morphological changes in the L-PLA phase. This result indicates clearly that L-PLA/PVP blends are immiscible over the entire composition range investigated.

T_m of the crystalline component in a polymer blend depends on both morphological and thermodynamic factors. Because all the blends are prepared under the same conditions in this study, the T_m changes of the components depending on the composition could be due to specific interactions between the components. As shown in Table I and Figure 3, the T_m values of L-PLA are almost constant when the PVP content increases from 0 to 60%. No significant compositional dependence is found, and this shows that the blends are immiscible. A slight decrease in T_m is detected only when the content of L-PLA is less than 40%. This small T_m depression is due to the reduction of the crystallite size of L-PLA in the blends.

Figure 2 shows the results of the second heating scan for a series of L-PLA/PVP samples with exactly the same thermal history. Here stable DSC traces could be obtained over the whole temperature range of the measurements; therefore, it is now possible to estimate precisely the composition dependence of the glass transition, cold crystallization, and melting be-

havior. The DSC measurement results for L-PLA/PVP blends in the second heating run are shown in Table II.

It is well known that T_g of a polymer is one of the most important criteria for the miscibility of components. The definition for miscible and partially miscible blends has been well established. If the two components of a binary blend are miscible in the amorphous phase, only one T_g intermediate between those of the two component polymers will be detected. For ideal systems, over the entire composition ranges, the relationship between T_g and the composition of the blend can be described by a simple equation, such as the Fox equation.[24] The immiscibility of two polymers is demonstrated by the retention of the T_g values of both individual components. If two components are only partially miscible, the T_g values of each component phase are shifted toward each other because of some degree of molecular mixing at the interface between the two polymeric phases; it is usually composition-dependent. In the DSC traces of blends of L-PLA/PVP recorded during the second scan (Fig. 2), the heat capacity jump in the heat flow at about 57°C corresponds to the glass transition of the L-PLA phase. Because of the overlap of the L-PLA melting peak and the PVP glass transition, it is difficulty to determine an accurate PVP T_g for the blends.

Figure 3 shows the composition dependence of T_g and T_m of the L-PLA phase in the blends of L-PLA/PVP. As shown in Figure 3, the difference in the T_g values found for the blends is smaller than the error in the measurements. Therefore, there are no systemic composition changes of T_g. The presence of a glass transition at 57°C for all the blends is strong evidence of total immiscibility.

In the DSC thermograms of pure L-PLA in Figure 2, an exothermic peak at about 122°C, which is assigned to the cold crystallization of L-PLA, appears. As shown in Figure 2, the exothermic area decrease sharply with increasing PVP concentration, and the temperature of cold crystallization (T_{cc}) increases slightly with increasing PVP concentration. For a composition rich in PVP (20/80), it is impossible to discern a crystallization exotherm in the DSC curves. The composition dependence of T_{cc} is listed in Table II.

TABLE II.
DSC Measurement Results of Blends of L-PLA and PVP in the Second Heating Run

Composition (w/w) of L-PLA/PVP	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	T_{cc} (°C)	ΔH_f (J/g)	X_c (%)
100/0	58	153	160	122	39	42
80/20	58	155	160	124	13	18
60/40	57	155	159	127	4	7
40/60	55	154	—	128	3	7
20/80	54	154	—	—	—	—
0/100	—	—	—	—	—	—

T_{m1} and T_{m2} are first and second melting points, respectively.

Theoretically, the increase or decrease in T_{cc} changes of a component may indicate that the crystallization of this component becomes more difficult or easier, respectively, upon blending with another component. As for these L-PLA/PVP blends, after the blending with PVP, L-PLA cold crystallization peaks in the DSC curves become flat, and this makes it difficult to determine the onset and offset of the transition. The shift of T_{cc} to a higher temperature with increasing PVP concentration cannot be used as evidence of miscibility.

The melting curves of L-PLA in the second heating run are different from those of the first heating run. As shown in Figure 2, a double melting peak appears around 155 and 160°C for pure and high-content (80/20) L-PLA samples. These double peaks indicate that two populations of crystals with different lamellar thicknesses exist. The lower temperature peak is due to the melting of less thick crystals rather than that of crystals corresponding to the high temperature. Because, according to high-temperature X-ray diffraction measurements performed up to 180°C, the diffraction pattern of the sample did not change up to T_m, the phase transition did not occur.[25]

One noteworthy phenomenon is that the melting enthalpy of L-PLA in the second heating run decreases drastically with increasing PVP concentration; this apparent disproportional reduction in the magnitude of the endothermic peak area corresponds to a rapid decrease in X_c of L-PLA. As shown in Table II, X_c of pure L-PLA in the second heating run equals that in the first heating run (42%), but it decrease to 18 and 7% when the blend compositions are 60/40 and 40/60, respectively. Meanwhile, the following question is pertinent: is the decrease in X_c due to specific interactions with the amorphous component or is it a result of kinetic effects imposed by the amorphous polymer upon the crystallization process? From the previous discussion, we know that the blends are immiscible, so the decrease in the melting enthalpy is only a kinetic effect. At lower L-PLA concentrations, the L-PLA domains are dispersed in the continuous PVP phase. When the amorphous PVP concentration is very high, the domains of the L-PLA phase may become very small. In this case, the mobility and rearrangement of L-PLA segments will be confined by PVP, especially at the interface. Although the crystallization takes place only in the L-PLA phase, the crystalline rate will be affected to some degree by amorphous PVP. Therefore, the cold crystalline peak can not be detected on the timescale of the heating process when the L-PLA content is very low.

Figure 4 shows the DSC thermograms of DL-PLA/PVP blends in the second heating run. From the DSC curves, T_g's of pure DL-PLA and PVP samples were estimated to be 56 and 162°C, respectively. There obviously exist two isolated T_g series corresponding to
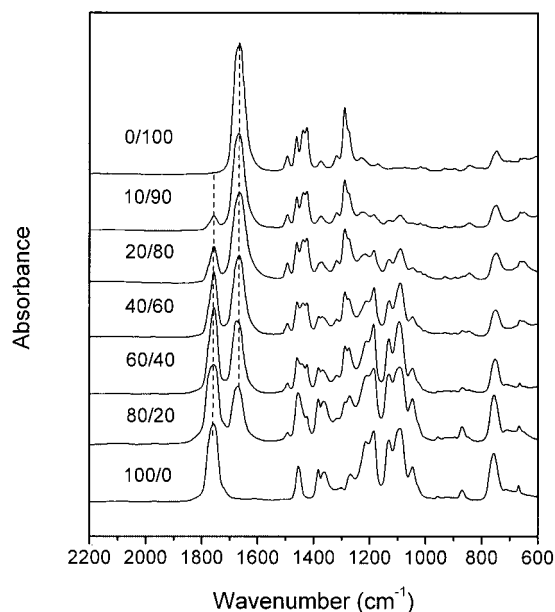

Figure 6 FTIR spectra of L-PLA/PVP blends with different compositions.

the DL-PLA phase and PVP phase over the whole range of PLA contents, respectively, and this suggests that DL-PLA and PVP are phase-separated. Figure 5 shows the composition dependence of the glass transition for DL-PLA/PVP. As shown in Figure 5, the value of the DL-PLA phase increases slowly with increasing PVP content in the blends, suggesting the presence of PVP in the DL-PLA phase. However, because the increase is very small, it indicates that DL-PLA/PVP is very poorly miscible. The T_g changes in the PVP phase with the blend compositions are very particular. The higher DL-PLA content blends do not show a large depression in the T_g value of PVP in comparison with those of lower DL-PLA contents. It seems to have its lowest value when the DL-PLA content is 10% in the blends; that is, the interactions between DL-PLA and PVP become stronger when the content of DL-PLA decreases. From the previous discussion, we conclude that, if some interaction exists between DL-PLA and PVP, it only takes place at the interface of the two phases.

FTIR spectroscopy

FTIR spectroscopy is a powerful tool for investigating the structures of polymer blends. It is known that, if two polymers form completely immiscible blends, there should be no appreciable changes in the IR spectrum of the blends with respect to the coaddition of each component spectrum. However, if the polymers are miscible, interactions in the blends will result in differences (peak positions and shapes) in the spectra. Figure 6 shows the spectra of L-PLA/PVP blend sam-
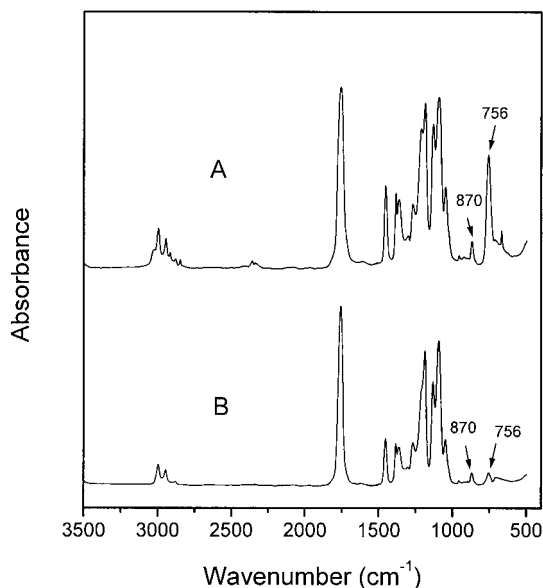
Figure 7 FTIR spectra of L-PLA: (A) a casting film from chloroform and (B) a sample quenched from the melt.

ples in cast films prepared from chloroform; the strong absorption band at 1754 cm^{-1} is assigned to the carbonyl stretching vibration of L-PLA, and the band centered at 1671 cm^{-1} is a mixing band of the C=O and C—N stretching vibration of PVP. These two absorption peaks can conventionally be used to study the interactions of the two components of the blends. As shown in Figure 6, with the addition of PVP, there are no obvious changes in these two peaks when the PVP content increases from 0 to 80%. This result suggests that the specific interaction between the two components can be negligible. Therefore, L-PLA and PVP are not miscible.

Figure 7 shows the FTIR spectra of two L-PLA samples that underwent different thermal treatments; therefore, the crystallinity values of the two samples were different. The peaks at 756 and 870 cm^{-1}, which are assigned to the crystalline phase and amorphous phase, are different.[26] These two peaks are designated C (crystalline) and A (amorphous), respectively, so the absorbance ratio could be used to present the crystallinity of L-PLA quantitatively. It is apparent that the solution-casting sample exhibits a larger X_c value than the quenched one. From the spectra of all the L-PLA/PVP blend samples, we note that the C/A ratio is approximately constant, indicating that X_c of L-PLA has no obvious change. This finding is fully consistent with the DSC measurements.

Figure 8 shows the FTIR spectra of DL-PLA/PVP blends. With the addition of DL-PLA, the peak of PVP at 1672 cm^{-1} is observed to shift to a higher frequency by 12 cm^{-1} when the DL-PLA content increases from 0 to 40%; this suggests some changes in the intermolecular interactions due to blending. Unlike blends of

PLA with polymers containing active hydrogen, such as PLA/PVA and PLA/PEG, in which specific intermolecular hydrogen-bonding interactions are effective, there is no such interaction in the DL-PLA/PVP blends. This high-frequency shift could not be interpreted as the formation of intermolecular hydrogen bonding. One reason was that the formation of hydrogen bonding would decrease the stretching vibration frequency of the carbonyl bound, giving rise to a shift to a lower frequency, as extensively studied in other blend systems.[27] Another reason was that there was no proton donor in the system investigated. Blueshifts of the C=O stretching mode have been observed in a few blends of carbonyl group-containing polymers with halogenated polymers. For example, in PVC/PVP blends, the C=O stretching vibration shows a 18-cm^{-1} blueshift when the PVC content increases from 0 to 80%.[28] In PCL/PVC blends, the C=O band at 1724 cm^{-1} gradually increases to 1737 cm^{-1} with increasing PVC content from 20 to 80%.[29] Allard and Prudhomme[30] pointed out that the interaction between PCL and PVC could not be due to the hydrogen bonding between α-H of the chlorinated polymer and C=O of PCL. They suggested that a dipole–dipole C=O···Cl—C interaction was the major reason for the observed phenomena because in another polymer blend such as poly(vinylidene chloride) with PCL, there was no α-H of the chlorinated polymer; a redshift of the C=O stretching absorption could also be observed.[31] However, in this system, we cannot attribute the blueshift of the C=O vibration of PVP to C=O···O=C dipole–dipole interactions because the C=O stretching vibration of DL-PLA is independent
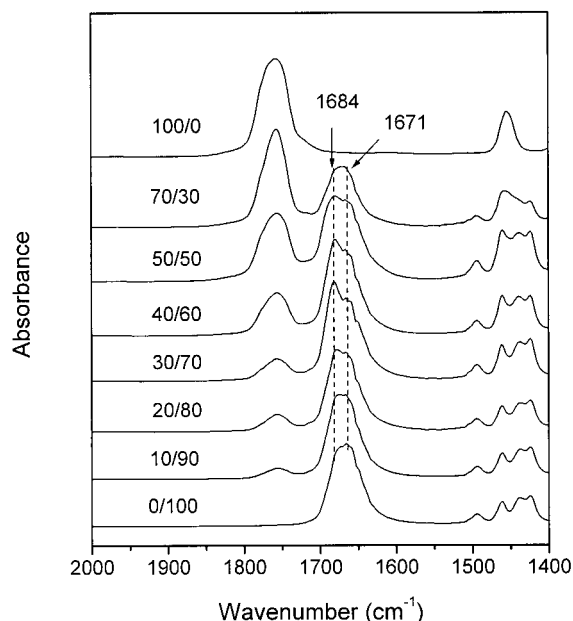

Figure 8 FTIR spectra in the carbonyl stretching region for DL-PLA/PVP blends with different compositions.

of the PVP content. The changes in P–π conjugation associated with amide functional groups of PVP may cause the C=O stretching vibration to shift to a higher frequency. The inclusion of miscible DL-PLA possibly gives rise to the disassociation of PVP chains. As a result, the carbonyl stretching vibration of PVP will shift to a higher frequency. Further studies should be performed.

CONCLUSIONS

Two binary blends, L-PLA/PVP and DL-PLA/PVP, were prepared by the casting of a film from mixed polymer solutions of chloroform. The crystallization behavior, component interaction, and miscibility of these blends were studied by DSC and FTIR. DSC measurements reveal that in L-PLA/PVP blends, T_g and X_c of L-PLA are almost constant over the entire composition range investigated. These observations enable us to conclude that the polymer pairs are immiscible. The small T_m depression of L-PLA with an increasing PVP content is caused by the reduction of the crystallite size of L-PLA in the blends. The cold crystallization process of L-PLA is affected significantly by the addition of PVP. In blends of DL-PLA/PVP, two series of isolated T_g's are observed. These results indicate that DL-PLA and PVP are phase-separated. However, evidence has shown that there are some interactions at the interface of the two phases. In FTIR measurements, a blueshift of the C=O stretching vibration with increasing DL-PLA contents in the blends indicates that intermolecular interactions between the two polymers exist. In contrast, the absorption peaks of the L-PLA/PVP blends in this region are independent of the PVP content, and this suggests that L-PLA and PVP are immiscible. These results are in good agreement with the DSC results.

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