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Miscibility and crystallization behaviour of poly(L-lactide)/poly(*p*-vinylphenol) blends

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The miscibility of poly(L-lactide) (PLLA)/poly(*p*-vinylphenol) (PVPh) blends has been studied by differential scanning calorimetry (d.s.c.) and Fourier transform infrared (*FT*i.r.) spectroscopy. PLLA/PVPh blends are partially miscible as characterized by shifts in the glass transition temperatures (T_gs) of the two component polymers. The T_g of the PLLA-rich phase increases with increasing PVPh content, while that of the PVPh-rich phase decreases with increasing PLLA content. The apparent melting temperature of PLLA is significantly depressed with increasing PVPh content. Weak hydrogen-bonding interaction exists between the carbonyl groups of PLLA and the hydroxyl groups of PVPh as evidenced in the *FT*i.r. spectra. In the amorphous state, the hydrogen-bonded hydroxyl band of PVPh shifts to a higher frequency upon blending with PLLA, while the carbonyl stretching band of PLLA shifts to a lower frequency with the addition of PVPh. In addition, a new carbonyl stretching band attributed to the hydrogen-bonded carbonyl groups of PLLA is found at 1700 cm^{-1}. The crystallinity of PLLA in the blends displays a marked decrease with increasing PVPh content. When the PVPh content is above 40 wt%, crystallization of PLLA does not occur under isothermal conditions. Moreover, the cold crystallization process of the PLLA component is also affected significantly by the addition of PVPh. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(L-lactide); poly(*p*-vinylphenol); miscibility)

INTRODUCTION

Polylactides (PLAs) have received much attention in recent years[1,2]. They are synthesized from renewable resources and are biodegradable. They are degraded by hydrolytic cleavage of the ester bonds to give lactic acid and its low-molecular-weight oligomers, which can be metabolized by both soil and marine organisms. PLAs have been used for various biomedical applications, and most of the research in the field was generally aimed at regulating the rate of degradation in drug release systems[3–5].

The most common PLAs are poly(L-lactide) (PLLA) and poly(D,L-lactide) (PDLLA), which are produced from L-lactide and D,L-lactide, respectively. PLLA is a crystalline polyester with a melting temperature of 180°C. It has poor processing properties, and crazes easily due to its high crystallinity. PDLLA is an amorphous, transparent polymer with a glass transition temperature (T_g) of 50°C which is too low for many packaging uses. There are several approaches to produce PLA-based materials with a broad range of properties and improved processability. These approaches include copolymerization, stereocomplexation[2–7] and polymer blending.

A number of studies have focused on the blending of PLLA with poly(D-lactide) (PDLA) or copolymers containing D-lactide units where stereocomplexation occurs between the L-lactide and the D-lactide monomer sequences[8–10]. Blends of PLLA with aliphatic polyesters or copolyesters have been well documented. These polyesters include PDLLA[11–16], poly(ε-caprolactone) (PCL), poly(L-lactide-*co*-ε-caprolactone)[17,18], poly(lactide-*co*-glycolide)[19,20], and bacterial polyesters such as poly(3-hydroxybutyrate) (PHB)[21] and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV)[22]. Blends of PLLA with poly(ethylene oxide) (PEO) have also been investigated by several groups[23–26]. Recently, poly(vinyl acetate) (PVAc) and clay were used to modify the properties of PLLA[27,28]. Blends of PDLLA with low-molecular-weight PDLLA[29], PCL[30,31], PHB[32,33] and ethylene-vinyl acetate copolymer (EVAc)[34,35] have also been studied. However, most of the blends are immiscible. Taking advantage of the interaction between blend components, miscibility or partial miscibility can be achieved. Poly(*p*-vinylphenol) (PVPh) has been found to be miscible or partially miscible with ester-containing polymers such as polyacrylates[36], polymethacrylates[37,38] and polyesters[36,39,40] arising from hydrogen-bonding interaction. The present work focuses on the miscibility and crystallization behaviour of PLLA/PVPh blends.

EXPERIMENTAL

Materials

PLLA was obtained from Sigma. The weight-average molecular weight and molecular weight distribution are 105 kg mol^{-1} and 1.70 as determined by gel permeation chromatography (g.p.c.) using a Waters 600E system controller and Model 410 Differential Refractometer with tetrahydrofuran (THF) as the eluent. PVPh with weight-average molecular weight of 30 kg mol^{-1} was obtained from Polyscience, Inc.

Preparation of blends

All the blends were prepared by casting from 1% (wt/v) THF solution. The solvent was allowed to evaporate at room

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temperature overnight, followed by drying at 40°C *in vacuo* for 48 h, and finally dried at 90°C *in vacuo* for another 48 h.

Differential scanning calorimetry (d.s.c.) measurements

D.s.c. measurements were performed on a TA Instruments 2920 Md.s.c. The instrument was calibrated with indium standard and nitrogen atmosphere was used throughout.

Blend samples were first heated from −40 to 200°C at a rate of 20°C min^{-1}. The samples were kept at 200°C for 1 min and were then rapidly quenched to −40°C. The samples were heated again to 200°C at a rate of 20°C min^{-1}. The glass transition temperatures (T_gs), melting temperatures (T_ms), enthalpies of fusion (ΔH_fs), cold crystallization temperatures (T_{cc}s) and enthalpies of cold crystallization (ΔH_{cc}s) were determined from the d.s.c. curves. The T_m and T_{cc} were taken as the peak values of the respective endotherm and exotherm in the d.s.c. curve. In the presence of multiple endothermic peaks, the peak temperature of the high-temperature endotherm was taken as T_m. The T_g was taken as the midpoint of the specific heat increment. All results were based on the second heating run (quenched samples) unless stated otherwise.

Fourier transform infrared (FTi.r.) measurements

*FT*i.r. spectra were obtained with a Bio-Rad 165 *FT*i.r. spectrophotometer. A total of 64 scans were taken with a resolution of 2 cm^{-1} in all cases. Samples were prepared by casting the THF solutions directly onto KBr discs. The discs were dried under the same condition as the cast films mentioned earlier. Spectra recorded at elevated temperature 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.

Polarizing optical microscopy

The crystallization and growth of spherulites of pure PLLA and various blends were observed with an Olympus BH2-UMA polarizing optical microscope, equipped with a Leitz Wetzlar hot stage and an Olympus exposure control unit. Samples sandwiched between two thin glass slides were melted for 1 min on a hot-plate preheated to 200°C, and were then quickly transferred onto the hot stage of the microscope which was maintained at the desired temperature. The sample was allowed to crystallize isothermally under crossed polars. The radial growth rate (G) of PLLA spherulites was measured by photographing the spherulites as a function of time during isothermal crystallization.

RESULTS AND DISCUSSION

Blend miscibility

PLLA is a crystalline polymer with a T_m of 180°C and a T_g of 65°C as shown in *Figure 1*. In addition, an exothermic peak corresponding to the cold crystallization of PLLA is present between the glass transition and melting processes. Blends containing 10 and 20 wt% PVPh show similar features as those of pure PLLA. For most blend compositions, PLLA/PVPh blends show only one T_g close to that of the pure PLLA, which increases with increasing PVPh content. The T_g value of the PLLA-rich phase reaches 78°C for a PLLA/PVPh blend with 80 wt% PVPh. The T_g of PVPh is 159°C, while that of the PVPh-rich phase is 143°C for a blend containing 20 wt% PLLA. The T_gs of PVPh-rich phases in the blends containing 40 wt% or more of PLLA become undetectable because the glass transitions are obscured by the melting and/or cold crystallization processes of PLLA. The phase diagram of PLLA/PVPh

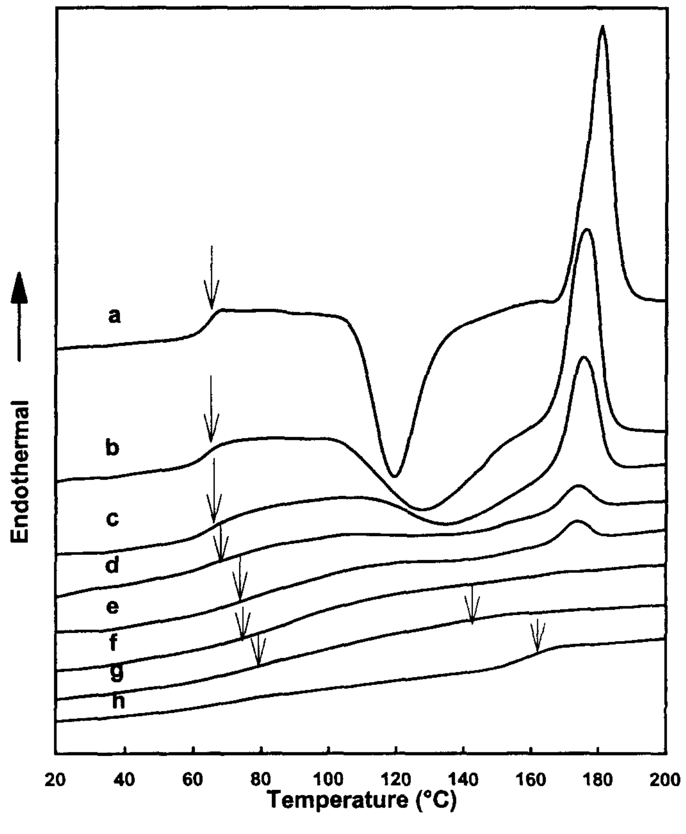

Figure 1 D.s.c. curves of PLLA/PVPh blends after quenching from 200°C: (a) PLLA; (b) 90/10; (c) 80/20; (d) 70/30; (e) 60/40; (f) 40/60; (g) 20/80; (h) PVPh

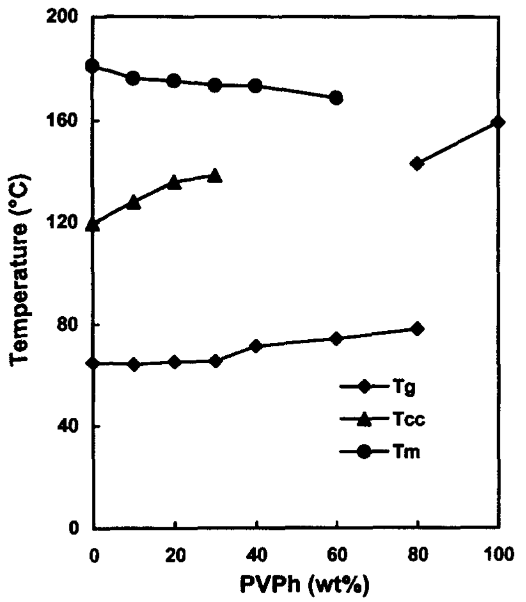

Figure 2 Phase diagram of PLLA/PVPh blends

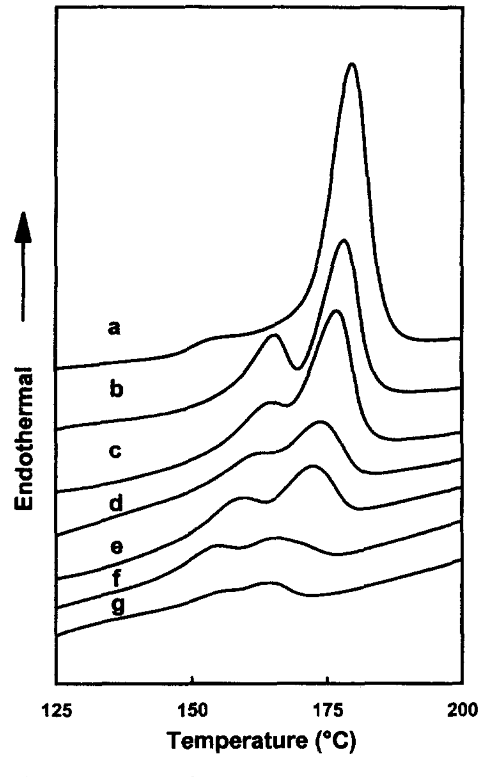

Figure 3 D.s.c. curves of PLLA/PVPh cast blends: (a) PLLA; (b) 90/10; (c) 80/20; (d) 70/30; (e) 60/40; (f) 40/60; (g) 20/80

blends is summarized in *Figure 2*. It is concluded that the PLLA/PVPh blends are partially miscible.

The T_m of the crystalline component in a polymer blend depends on both morphological and thermodynamic factors[41]. The former is related to crystallization conditions (temperature, time, etc.), blend composition and scanning rate. These factors can cause an increase or a decrease of T_m. In the cases of miscible blends, the thermodynamic factor must be considered whose contribution induces a decrease of T_m. Thus, when a crystalline component is miscible with an amorphous polymer, a depression of T_m is observed. As for the present blends, the melting process of PLLA is significantly affected by the PVPh component even though PLLA is only partially miscible with PVPh. *Figure 2* shows the T_m data of quenched samples during d.s.c. heating runs. PLLA and blend samples show T_ms at about 168–181°C. The T_ms of PLLA in the blends decrease with increasing PVPh content. For the PLLA/PVPh 20/80 blend, T_m cannot be detected from the d.s.c. curve. Although equilibrium melting temperatures were not determined in this work, the depression of T_m is substantial (12°C for PLLA/PVPh 40/60 blend). In fact, cast blend samples also show significant depression of apparent T_m as shown in *Figure 3*. It is noted that the cast blends show two separate endothermic peaks as a result of lamellar rearrangement of PLLA[26]. This indicates that the crystallization of PLLA in the blends is also affected by the addition of PVPh.

Interassociation

PVPh is a self-associated polymer. However, it can form interassociations with various carbonyl-containing polymers such as polyacrylates, polymethacrylates[36,37] and aliphatic polyesters[38–40]. The equilibrium constants (K_{ab}) describing the interassociation of PVPh with PCL and PHB are 66.2 and 38.4, respectively[36,40]. As an aliphatic polyester, PLLA shows some different behaviour compared with PCL and PHB. As shown in *Figure 4*, the stretching hydrogen-bonded hydroxyl band (self-association) of PVPh is broad and centred at 3323 cm^{-1}, and that of the free hydroxyl band is evident as a shoulder at 3510 cm^{-1} at room temperature. The frequencies of hydrogen-bonded hydroxyl bands of PVPh in the blends remain almost the same as that of pure PVPh. On heating to 185°C, the intensity of the free hydroxyl absorption band at 3510 cm^{-1} increases, and that of the hydrogen-bonded hydroxyl band decreases and shifts to 3390 cm^{-1} due to the de-association of PVPh at elevated temperatures. For the PLLA/PVPh blends, the

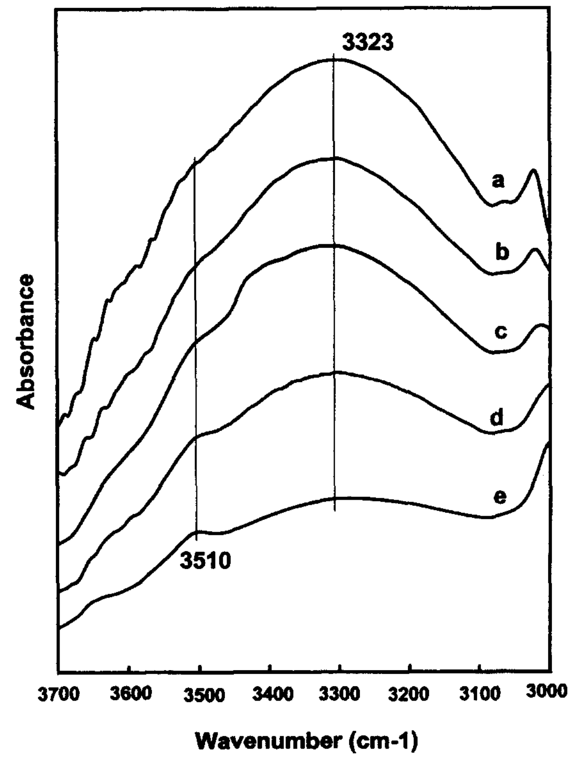

Figure 4 *FT*i.r. spectra in the hydroxyl stretching region for PLLA/PVPh blends recorded at room temperature: (a) PVPh; (b) 20/80; (c) 40/60; (d) 60/40; (e) 80/20

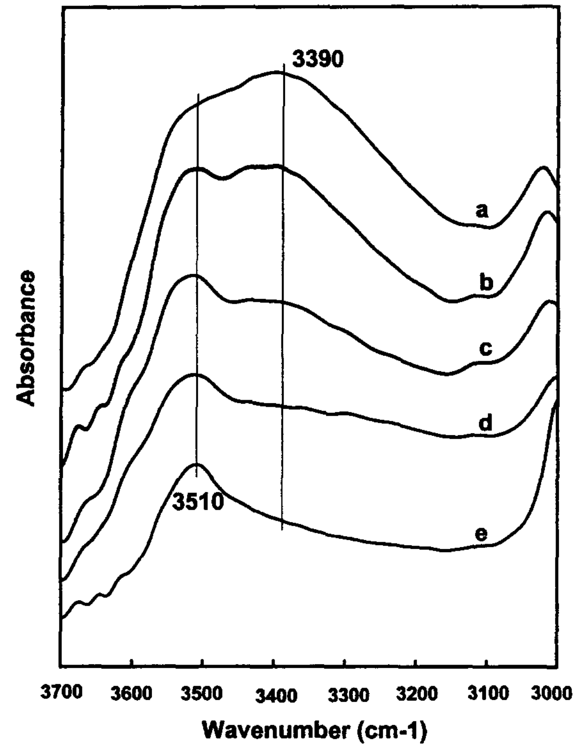

Figure 5 *FT*i.r. spectra in the hydroxyl stretching region for PLLA/PVPh blends recorded at 185°C: (a) PVPh; (b) 20/80; (c) 40/60; (d) 60/40; (e) 80/20

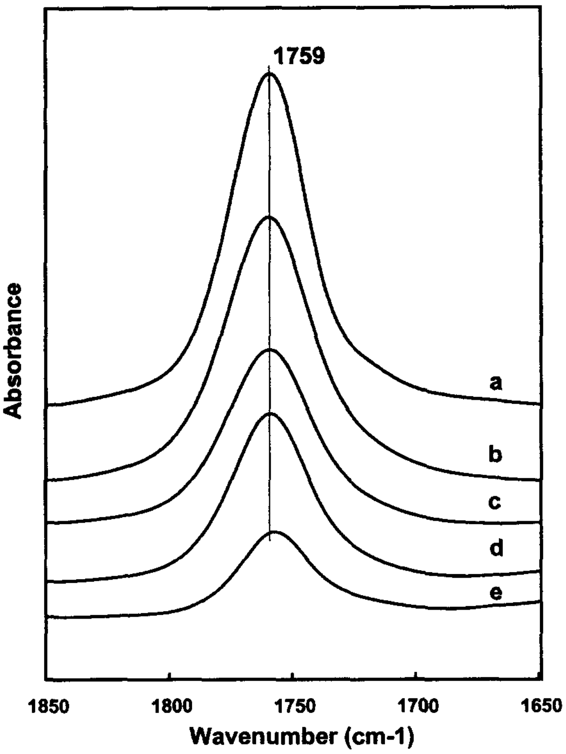

Figure 7 *FT*i.r. spectra in the carbonyl stretching region for PLLA/PVPh blends recorded at room temperature: (a) PLLA; (b) 80/20; (c) 60/40; (d) 40/60; (e) 20/80

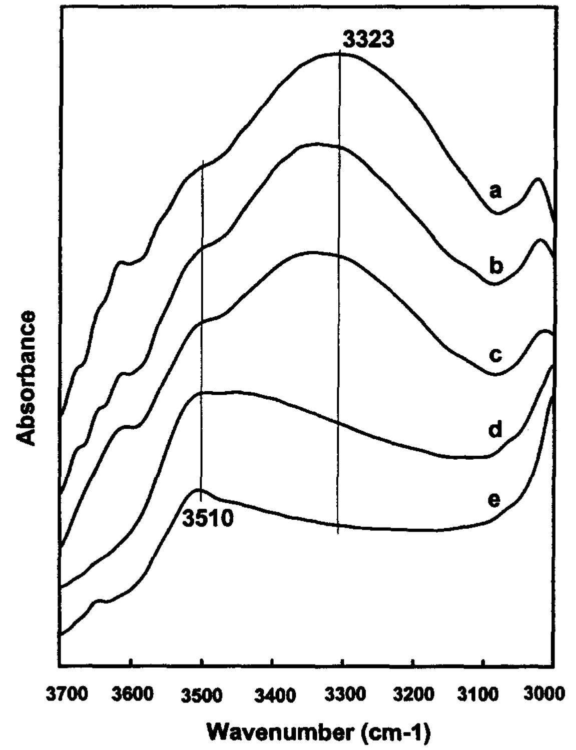

Figure 6 *FT*i.r. spectra in the hydroxyl stretching region for PLLA/PVPh blends recorded at room temperature after cooling from 185°C: (a) PVPh; (b) 20/80; (c) 40/60; (d) 60/40; (e) 80/20

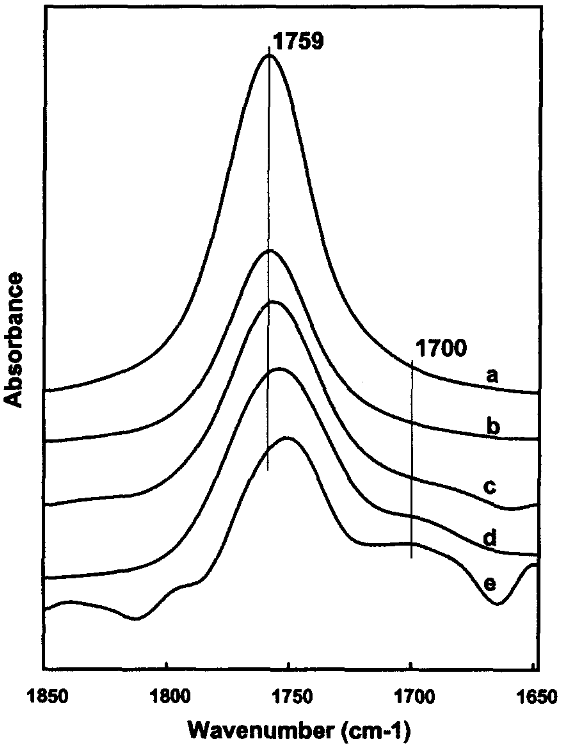

Figure 8 *FT*i.r. spectra in the carbonyl stretching region for PLLA/PVPh blends recorded at 185°C: (a) PLLA; (b) 80/20; (c) 60/40; (d) 40/60; (e) 20/80

hydrogen-bonded hydroxyl bands of PVPh are lower in intensity compared with that of pure PVPh (*Figure 5*). As the PLLA content increases, the free hydroxyl band of PVPh in the blends becomes more obvious. After cooling to room temperature from 185°C, the frequency of the stretching band of hydrogen-bonded hydroxyls is found at 3323 cm^{-1} for pure PVPh again, while those for PLLA/PVPh 20/80 and 40/60 blends remain at higher values at about 3385 cm^{-1} due to the formation of intermolecular hydrogen bonds between PLLA and PVPh components (*Figure 6*).

The carbonyl stretching region of the spectra recorded at room temperature shows that the stretching band of PLLA at

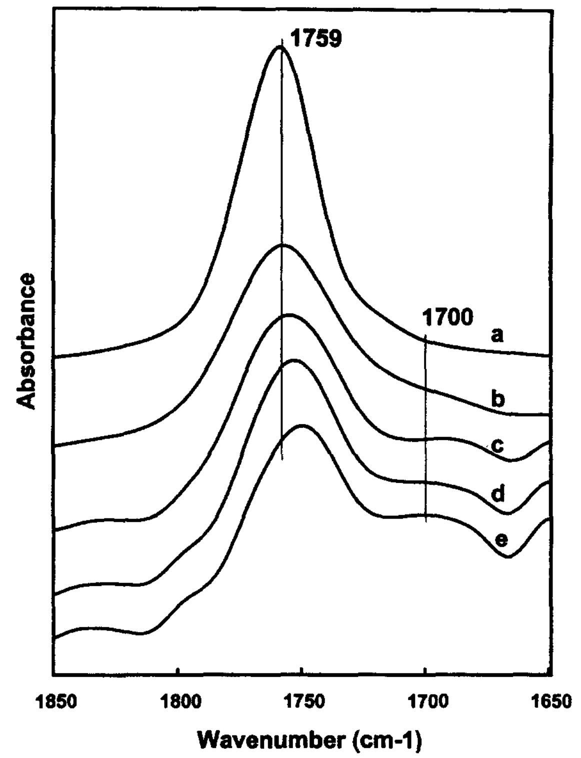

Figure 9 *FTi.r.* spectra in the carbonyl stretching region for PLLA/PVPh blends recorded at room temperature after cooling from 185°C: (a) PLLA; (b) 80/20; (c) 60/40; (d) 40/60; (e) 20/80

1759 cm^{-1} is independent of PVPh content, except for a slight decrease in the frequency for PLLA/PVPh 20/80 blend (*Figure 7*). The frequency of the carbonyl stretching absorption of PLLA decreases from 1759 cm^{-1} for pure PLLA to 1751 cm^{-1} for PLLA/PVPh 20/80 blend at both 185°C (*Figure 8*) and room temperature after being cooled from 185°C (*Figure 9*). Furthermore, a new absorption band at 1700 cm^{-1} attributed to the hydrogen-bonded carbonyls in PLLA is found for PLLA/PVPh 60/40, 40/60 and 20/80 blends. These results indicate that interassociation between PLLA and PVPh is present in these blends. Because of the strong self-association of the PVPh component, the interassociation can only be found at high temperatures where the self-association of PVPh is significantly reduced, allowing some possibility to form interassociations with PLLA. After being cooled to room temperature from 185°C, the interassociation is maintained. However, the interassociation is weaker than the self-association of PVPh as shown by the position of the stretching band of the hydrogen-bonded hydroxyls. The K_{ab} values for PLLA/PVPh blends should be much lower than those for PCL/PVPh and PHB/PVPh blends.

Crystallization behaviour

The cold crystallization of pure PLLA is found at 119°C, intermediate between the T_g and T_m during the heating run. For PLLA/PVPh 90/10, 80/20 and 70/30 blends, cold crystallization peaks were also found as shown in *Figure 1*. For blends with PVPh content more than 30 wt%, crystallization was not observed in the d.s.c. curves. The cold crystallization temperatures and enthalpies of cold crystallization of the blends are significantly dependent on the blend composition as shown in *Table 1*. Compared with that of pure PLLA, the T_{cc}s of the blends shift to higher temperatures, indicating the difficulty in crystallization of PLLA in the blends. This result confirms the effect of PVPh content on the crystallization of PLLA. Analogous to the supercooling temperature ($T_m - T_c$) in non-isothermal crystallization from the melt, a characteristic temperature, $\Delta T = T_{cc} - T_g$, is introduced to describe the kinetic crystallizability during the non-isothermal crystallization process from the glass state. A higher ΔT value indicates a lower kinetic crystallizability in the range of T_g to T_m. ΔT is calculated from the T_g in *Figure 2*, and T_{cc} in *Table 1*. As shown in *Table 1*, ΔT values of the blends are much higher than that of the pure PLLA, indicating the lower kinetic crystallizability of the blends. Moreover, the enthalpies of cold crystallization of the PLLA phase in the blends, ΔH_{cc}^{PLLA}, calculated from those of the blends (ΔH_{cc}), $\Delta H_{cc}^{PLLA} = \Delta H_{cc}/W^{PLLA}$ (W^{PLLA} is the weight fraction of PLLA in the blends), are much lower than that of pure PLLA due to the influence of the PVPh component.

The isothermal crystallization of PLLA from the melt was observed using polarizing optical microscopy at both 130 and 140°C. Well-defined spherulites were found for pure PLLA. For PLLA/PVPh 90/10, 80/20, 70/30 and 60/40 blends, PLLA can also crystallize according to a spherulitic morphology as shown in *Figure 10*. However, no spherulite of PLLA was observed for the blends with PVPh content above 40 wt%. The results are related to the depression of the spherulite growth rate (G) of PLLA as shown in *Table 1*.

This finding can be explained by considering that the presence of the PVPh component causes a dilution of the PLLA nuclei. In addition, there may be some degree of chain interference of PLLA and PVPh chains due to the partially miscible nature of PLLA and PVPh components. Both effects would result in a decrease in the overall crystallization rate G, and an increase in the cold crystallization temperature T_{cc}. On the contrary, in the case of immiscible PHB/atactic PMMA (a-PMMA) blends (cooled and annealed samples), where the PHB component crystallized from its own phase, the crystallization of PHB was not affected by the presence of the a-PMMA phase and the cold crystallization peak was present more or less at the same temperature for blend compositions up to 50/50[41]. For PHB/a-PMMA quenched samples, which were miscible, the T_{cc}

Table 1 Crystallization characteristics of PLLA/PVPh blends

Sample code	T_{cc} (°C)	ΔT^a (°C)	ΔH_{cc} (J g^{-1})	$\Delta H_{cc}^{PLLA\ b}$ (J g^{-1})	G^c (μm min^{-1})
PLLA	119.5	54.8	48.4	48.4	2.4
PLLA/PVPh 90/10	127.9	63.9	38.6	42.9	1.7
PLLA/PVPh 80/20	135.7	70.6	15.4	19.2	1.7
PLLA/PVPh 70/30	138.2	72.9	4.85	6.93	0.34

[a] $\Delta T = T_{cc} - T_g$, see text for detail
[b] $\Delta H_{cc}^{PLLA} = \Delta H_{cc}/W^{PLLA}$, see text for detail
[c] T_c = 140°C

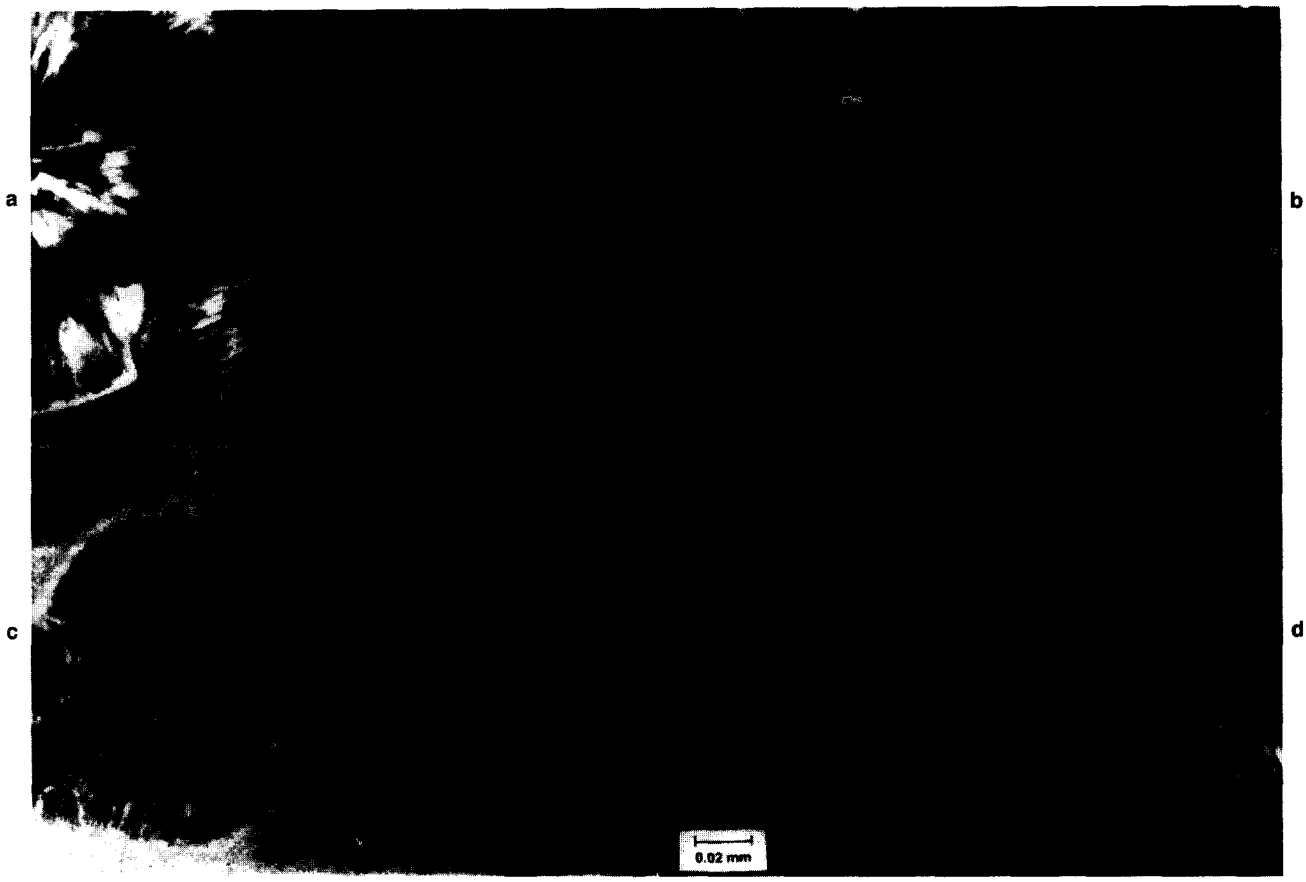

Figure 10 Polarizing optical micrographs of PLLA and PLLA/PVPh blends under crossed polars (same magnification, scale bar = 0.02 mm): (a) PLLA, T_c = 130°C, t_c = 20 min; (b) 90/10, T_c = 130°C, t_c = 20 min; (c) 70/30, T_c = 140°C, t_c = 30 min; (d) 60/40, T_c = 140°C, t_c = 30 min

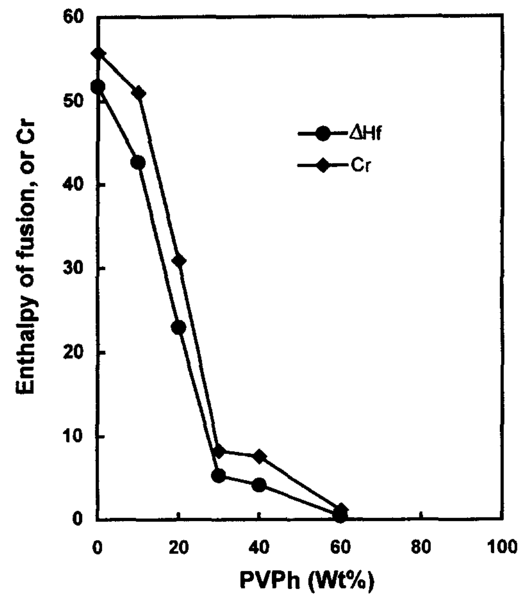

Figure 11 Apparent enthalpy of fusion (ΔH_f, J g^{-1}) and phase crystallinity (C_r, %) of PLLA as functions of blend composition

moved towards higher temperatures with the *a*-PMMA component[41].

The apparent enthalpy of fusion of the blends (ΔH_f), which is related to the crystallinity of the blends, decreases significantly with increasing PLLA content. The crystallinity of the PLLA phase in the blends, C_r, is calculated by the following equation

$$C_r = \left[\Delta H_f/\left(W^{\mathrm{PLLA}} \times \Delta H_f^0\right)\right] \times 100\%$$

where ΔH_f^0 is the thermodynamic enthalpy of fusion per gram of a completely crystalline PLLA (ΔH_f^0 = 93 J g^{-1})[42]. As shown in *Figure 11*, C_r shows a marked decrease when the PVPh content is 30 wt% or above.

CONCLUSIONS

PLLA/PVPh blends are partially miscible in the amorphous state. The T_g of the PLLA-rich phase increases with increasing PVPh content. The interassociation of PLLA/PVPh is relatively weak compared with that of PVPh/PCL and PVPh/PHB blends. The cold crystallization peaks of PLLA are dependent on the blend composition. The T_{cc}s of PLLA in the blends are higher than that of pure PLLA. The growth of PLLA spherulites from the melt under isothermal conditions is slowed down by PVPh. The significant depression in the apparent T_m and the decrease in crystallinity of PLLA are related to the partially miscible nature of the PLLA/PVPh blends.

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