

Thermal and Crystallinity Property Studies of Poly (L-Lactic Acid) Blended with Oligomers of 3-Hydroxybutyrate or Dendrimers of Hydroxyalkanoic Acids

Chengyang Ni, Rongcong Luo, Kaitian Xu, Guo-Qiang Chen

Multidisciplinary Research Center, Shantou University, Shantou, Guangdong 515063, China

Received 12 January 2008; accepted 5 August 2008

DOI 10.1002/app.29182

Published online 30 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly (L-lactic acid) (PLA) is a biodegradable polymer with slow crystallization rate. Oligomers of 3-hydroxybutyrate (OHB) and dendrimers of hydroxyalkanoic acids with different molecular weights were blended with PLA in a hope to improve the crystallization ability and thermal stability of PLA, respectively. Four thermally-degraded PHB products oligomers termed OHB-1, OHB-2, OHB-3, and OHB-4 with various number average molecular weights (M_n) of 4000, 7400, 14,000, and 83,000, respectively, were blended with PLA. The lower cold-crystallization temperature (T_{cc}) and higher heat of cold crystallization (ΔH_{cc}) for blend of PLA/OHB-1 suggested that thermally-degraded OHB-1 formed suitable

crystal size during the cooling process and then acted as nucleation agents for PLA in the subsequent heating process. On the other hand, for the blending systems of PLA/dendrimers of hydroxyalkanoic acids, no obvious change on the thermal properties was observed compared with pure PLA except an improved PLA thermal stability possibly resulted from the crosslinking effects of the dendrimers © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1720–1727, 2009

Key words: PHB; PLA; oligomer; dendrimer; thermal degradation; crystallization; poly (3-hydroxybutyrate); poly (L-lactic acid); blends

INTRODUCTION

Poly-*R*-3-hydroxybutyrate (PHB) is biologically synthesized polyester produced by many types of bacteria as their intracellular reserve of carbon and energy sources.^{1–3} PHB is biodegradable and resembles certain traditional plastics such as polyethylene and polypropylene that are based on petrol-chemicals.⁴ Therefore, PHB has attracted much attention as an environmentally-friendly plastic independent from petroleum.⁵ Studies revealed that naturally occurring PHB is highly isotactic and optically active, demonstrated by its *R*-configuration for the chiral 3-hydroxybutyrate (HB) repeating unit.^{2,6} PHB is thermally unstable above its melting temperature, resulting in difficulty in melt-processing. Mechanism for thermal degradation of PHB was proposed and widely accepted as the *cis*-elimination through a six-

membered ring ester intermediate.⁷ The mechanism suggested that thermal degradation of PHB is a useful way to obtain vinyl oligomers that can be used as component for synthesis of block copolymers.⁶ Furthermore, thermal degradation of PHB is organic solvent free, and thus can be considered as green chemistry.^{6,8–10}

PLA is chemically synthesized biodegradable polyester which can be synthesized from either lactic acid or its cyclic dimer.¹¹ Combined with good biodegradability and reasonable mechanical properties, PLA has been used as environmentally-friendly polymeric material especially in biomedical fields, such as bone fixation,¹¹ surgical sutures,¹² and drug delivery system.¹³ One distinct feature of PLA is that it has a relatively low crystallization rate when compared with other semicrystalline thermoplastics.¹⁴ Many nucleation agents were used to increase the overall crystallization rate of PLA, such as talc, clay, and polylactide sterocomplex.¹⁴

The PLA/PHB blending system was widely investigated without a satisfactory result for improving PLA crystallinity due to the poor miscibility of both polyesters. Blümm and Owen¹⁵ investigated the miscibility and crystallization behaviors for blends of PLA/PHB. Koyyama and Doi¹⁶ studied the miscibility for blends of PHB with different molecular

The first two authors contributed equally to this work.

Correspondence to: G.-Q. Chen (chengq@stu.edu.cn).

Contract grant sponsor: National Science Foundation of China (NSFC); contract grant number: 20474001.

Contract grant sponsor: National High Tech Project 863; contract grant number: 2006AA02Z242.

Contract grant sponsor: Li Ka Shing Foundation.

weights of PLA prepared by methanolysis. PLA was also blended with different molecular weights of amorphous atactic poly [(R, S)-3-hydroxybutyrate].¹⁸ All of these studies did not significantly improve PLA properties.

Dendrimers are regularly tree-like macromolecule compounds. As a major new class of macromolecular architecture, dendrimers show their great potential in many fields, such as application as highly functional matrices for new catalytic systems and molecular electronic devices.^{19,20} They have some unique character, such as high peripheral functionality and spherical structures.¹⁹ Therefore, dendrimers also show their great potential in plastic industry including application as additives in plastic processing. Carr et al.²¹ blended two aryl ester dendrimers with poly(ethylene terephthalate) (PET) and found that lower molecular weight dendrimers acted as plasticizers while those higher molecular weight ones functioned as antiplasticizers.

In this study, for the first time, 3-hydroxybutyrate oligomers (OHB) of different molecular weights obtained from thermally-degraded PHB were blended with PLA to increase miscibility of both molecules. These OHB were chosen with two considerations: one was to investigate the molecular weights depended miscibility of OHB with PLA; the other was to improve the PLA thermal properties using OHB as a nucleating agent with biodegradability, biocompatibility, and sustainability. With the same goal, a hydroxyalkanoic acid containing dendrimer named F3312 containing a three dendron polyester core consisting of 12 peripheral C18 hydrocarbon chains and 12 peripheral hydroxyl end groups was blended with PLA. The effect of the dendrimer addition on PLA matrix was investigated by evaluating their thermal properties and thermal stability.

EXPERIMENT

Materials

The PLA sample ($M_n = 110,000$, $M_w = 253,000$) was kindly donated by Natureworks, USA. The PLA was used as received without further purification. The bacterial PHB sample ($M_n = 330,000$, $M_w = 680,000$) was purchased from Jiangsu LanTian Group of China. The PHB sample was purified by dissolving it in hot chloroform, filtration, and precipitation in 10 volume methanol. The procedure of PHB thermal degradation can be referred to the previous literature.⁶ By controlling the reaction time and heating temperature, four different molecular weights of OHBs were prepared. According to the molecular weights based on gel permeation chromatogram (GPC), they were termed as the followings: OHB-1

($M_n = 4000$); OHB-2 ($M_n = 7400$); OHB-3 ($M_n = 14,000$); and OHB-4 ($M_n = 83,000$). The dendrimer F3312 was supplied by Shantou Polymer Additives Co. (China), the M_w of F3312 is 5800 according to GPC. The sketch of the hydroxyalkanoic acid dendrimer is illustrated as following.

Preparation of blend films

All the blend films were prepared using the conventional solvent-casting method. Blends of PLA/OHB-1, PLA/OHB-2, PLA/OHB-3, and PLA/OHB-4 in following compositions (PLA/OHB) of 100/0, 80/20, 60/40, 50/50, 40/60, and 0/100, respectively, were dissolved in hot chloroform (5% w/v) and then cast on glass Petri dishes. The solvent was evaporated at room temperature, and the films were vacuum dried at 40°C for 48 h to completely eliminate the residual chloroform. All the films were stored at room temperature for over 3 weeks prior to further analysis. Similar treatment was applied for the PLA/dendrimer blending system.

Analytical procedures

All molecular weights data were obtained by gel permeation chromatography (GPC) using a Waters 1525 pump connected to four styragel columns series (Styragel HR, 5 μ m). A 2414 differential refractive index detector and a 2487 UV detector were employed. Chloroform was used as an eluent at a flow rate of 1 mL/min and a sample concentration of 1 mg/mL was applied. Five polystyrene standards (Showa Denko, Japan) with a narrow polydispersity were used for establishing the calibration curves.

The ¹H-NMR spectra of OHBs were recorded with a Bruker AV 400 NMR spectrometer. The samples were dissolved in CDCl₃ and the internal standard was tetramethylsilane.

Optical rotation measurement of the OHBs was made at 589 nm (Na lamp) on a WZ2SS digital polarimeter (Shanghai ShenGuang Instrument Factory, China) at 25°C using spectroscopic grade chloroform as a solvent. Sample concentration was 10 g/L, and a 200-mm length cell was used for this analysis.

Thermal properties of all samples were recorded on a TA DSC-Q100 instrument. The equipment was run under nitrogen atmosphere. For the miscibility study, 3 mg samples were encapsulated in aluminum pans and heated from -60 to 200°C at a heating rate of 10°C/min (1st scan). The samples were maintained at 200°C for 1 min and then rapidly quenched to -60°C at a cooling rate of ~ 50°C/min. Subsequently, the samples were reheated from -60 to 200°C at a heating rate of 10°C/min (2nd scan) again. The T_g value was taken as the midpoint of the heat capacity change. For the study of

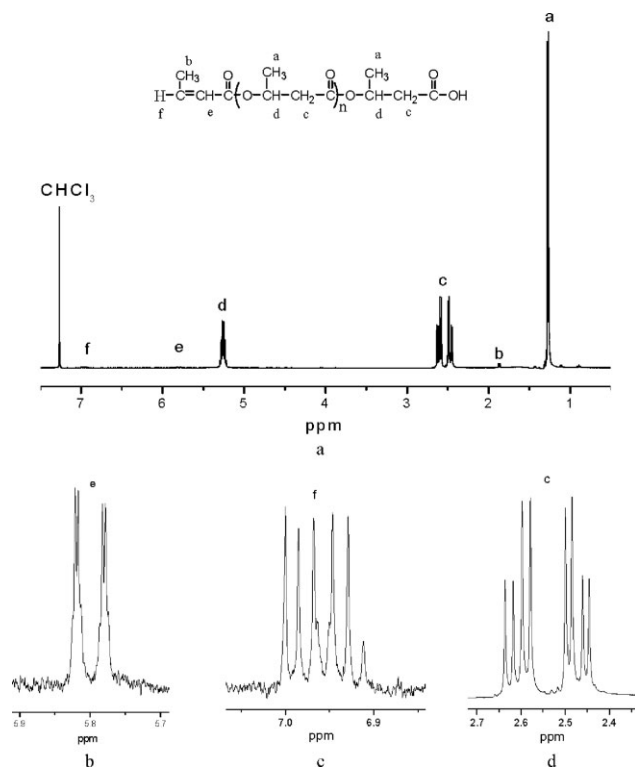


Figure 1 400-MHz ¹H-NMR spectrum of OHB-2 obtained via thermal degradation of PHB. (a) 400-MHz ¹H-NMR spectrum of OHB-2. (b) Expanded spectrum of 5.70–5.90 ppm. The resonance at 5.75–5.85 ppm was assigned to that of proton e of the double bonding in the chain end of OHB-2. (c) Expanded spectrum of 6.85–7.50 ppm. The resonance at 6.90–7.00 ppm was assigned to that of proton f of the double bonding in the chain end of OHB-2. (d) Expanded spectrum of 2.40–2.70 ppm. The doublet (2.57 ppm) of quadruplet was assigned to the resonance of proton c in the methylene group. The doublet of quadruplet of the methylene group indicated the isotactic nature of OHB-2.

crystallization behaviors, a constant heating and cooling rate of 10°C/min was adopted and maintained throughout the studies. The cold crystallization peak temperature (T_{cc}) and the heat of cold crystallization (ΔH_{cc}) were determined from the DSC exothermal peaks.

RESULTS AND DISCUSSION

Characterization of thermally-degraded PHB Products OHBs

Thermal degradation of PHB occurred through the *cis*-elimination reaction mechanism, which produced a carboxylic acid end group and a propenyl end group for PHB.⁷ Formation of 3-hydroxybutyrate oligomers was clearly observed in the overall ¹H-NMR spectrum for OHB-2 [Fig. 1(a,b)]. The resonance at 5.75–5.85 ppm was assigned to that of proton e of the double bonding in the chain end of OHB-2. The resonance at 6.90–7.00 ppm was

assigned to that of proton f of the double bonding in the chain end of OHB-2 [Fig. 1(c)]. According to Kunioka and Doi,⁷ the strong proton resonances a, c, and d were assigned to the methyl, methylene, and methane proton resonances in 3-hydroxybutyrate units, respectively. The weak resonances e and f were assigned to that of olefinic protons in the chain end of the OHB. The weak resonance b was assigned to that of the methyl proton in the chain end. Figure 1(d) was the expanded spectrum at 2.40–2.70 ppm. According to Ramachander et al.,²² the signal multiplicity by a proton as a quadruplet or octlet in case of protons of CH₂ group was obtained because of protons coupling in isotactic form unlike in syndiotactic form where duplet signal was obtained due to coupling. For OHB-1, OHB-3, and OHB-4, they had the same ¹H-NMR spectra with that of OHB-2 (spectra not shown). These results indicated that OHBs prepared by thermal degradation were in isotactic form and bore a carboxylic acid group and a propenyl group in each end of the chain. When comparing the intensity ratios of signals b, e, and f of the protons in the chain end units to those a, c, and d of protons in the 3-hydroxybutyrate, one can estimate that the absolute M_n of OHB-2 was 6860, which was in good agreement with the relative M_n of OHB-2 (7400) calculated from GPC.

Glass transition temperature (T_g), melting temperature (T_m), and cold crystallization temperature (T_{cc}) of PHB thermally degraded products OHBs were determined by DSC measurements (Fig. 2). DSC results indicated that these OHB products were crystal components because T_m and T_{cc} can not be detected in amorphous polymers, such as atactic PHB.¹⁷

The specific optical rotation values for various molecular weights of OHBs were summarized in Table I. All OHBs showed the same sign of optical rotation with that of naturally occurring PHB containing only (R)-hydroxybutyrate repeating units. The results

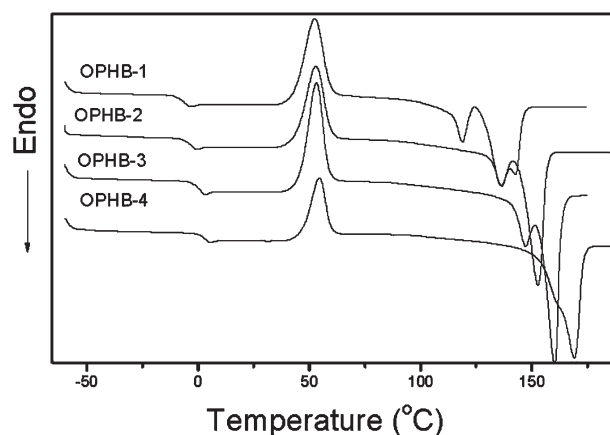


Figure 2 DSC curves (2nd scan) of OHBs with different molecular weights.

TABLE I
Optical Rotation Values for OHBs with Different Molecular Weights

Samples	M_n^a	M_w^b	$[\alpha]_{589}^{25}$ ^c
OHB-1	4000	8400	-2.1
OHB-2	7400	15,000	-2.5
OHB-3	14,000	26,000	-2.3
OHB-4	83,000	166,000	-2.9
Natural PHB	330,000	680,000	-2.5

^a M_n is the number-average molecular weight measured by GPC.

^b M_w is the weight-average molecular weight measured by GPC.

^c Optical rotation values measured in chloroform at a concentration of 10 g/L.

indicated that OHBs generated from thermally-degraded PHB were rich in (R)-configuration repeating units and the enantiomeric purity of natural PHB was retained during the process of thermal degradation.

Miscibility study for the PLA/OHB blend films

Miscibility of binary blending system is mainly determined by its T_g . A miscible blend normally shows a single T_g . A partially miscible blend should show two T_g between the respective T_g of the individual components. An immiscible blend shows two distinct T_g which have the same values with that of the respective T_g of the components. T_g of the binary blends PLA/OHB were determined by DSC (2nd scan). All data were summarized in Table II.

For blend of PLA/OHB-1, a single T_g was detected when OHB-1 was lower than 40% in the blend. T_g decreased from 40 to 30°C with increasing amount of OHB-1 component in the blends. How-

ever, two T_g were observed when OHB-1 contents were above 40%; this suggested a biphasic separation occurring in the melt. While T_g corresponding to PLA decreased from 61 to 45°C and appeared as a long and smooth shoulder, indicating a partial dispersion of OHB-1 component in PLA phase.

PLA/OHB-2 and PLA/OHB-3 showed similar thermal properties. Both blending systems exhibited two T_g when the OHB components were above 20% in the blends, demonstrating immiscibility between PLA and OHB-2 and OHB-4. The lower T_g related to OHB components increased slightly with increasing PLA component, also indicating partial dispersion of the OHBs in the PLA phase.

Two distinct T_g independent of composition ratios were observed in PLA/OHB-4. T_g related to PLA was only observed in the PLA/OHB-4 (80/20) blend. Two distinct T_g independent of composition ratio revealed that the two components were totally immiscible.

From the above analysis of T_g , one can conclude that the miscibility of PLA/OHB blending systems depended on both the molecular weights and blending ratio of the components. It was worth recalling that in the research of Koyama and Doi,¹⁶ the PLA with a M_n of 12,000 was miscible with PHB with a M_n of 300,000. In Ohkoshi's article,¹⁷ the atactic OHB with a M_n of 6000 was miscible with PLA with a M_n of 300,000. In this article, PLA with a M_n of 110,000 showed immiscibility with isotactic OHB even when the OHB had a relatively low molecular weight ($M_n = 4000$). These differences indicated that in the blending system of PLA with isotactic OHB, the miscibility is mainly determined by the molecular weights of isotactic OHB component. This may come from the specific crystallization behaviors of isotactic OHB and further investigation is in process.

TABLE II
 T_g Values of PLA/DPHB Blend Films

Samples	Composition (W/W)	T_g (°C) ^a	Samples	Composition (W/W)	T_g (°C) ^a
PLA/OHB-1	100/0	61	PLA/OHB-3	100/0	61
	80/20	40		80/20	48
	60/40	30		60/40	3, 45
	50/50	-3, 42		50/50	2, nd
	40/60	-4, 45		40/60	2, nd
	0/100	-8		0/100	1
PLA/OHB-2	100/0	61	PLA/OHB-4	100/0	61
	80/20	45		80/20	0, 60
	60/40	2, 43		60/40	2, nd
	50/50	1, nd ^b		50/50	2, nd
	40/60	0, nd		40/60	2, nd
	0/100	-4		0/100	2

^a Glass transition temperature measured by DSC (2nd scan) from -60 to 200°C at 10°C/min.

^b nd: The T_g values of PLA could not be detected because of the crystallization of DPHB.

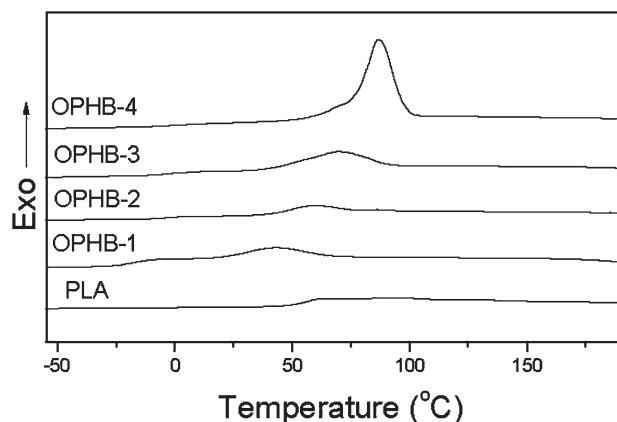


Figure 3 Cooling process for PLA and OPHBs from 200°C to -60°C at a constant cooling rate of 10°C/min.

Crystallization behaviors of OPHB and the PLA/OPHB blend films

Crystallization of polymers can take place after the cooling process from the melt to the temperature below its T_g , followed by heating to the polymer melting temperature. In this article, crystallization study for the blend films was carried out using DSC by introducing a constant heating and cooling rate at 10°C/min.

Figure 3 shows the cooling processes for PLA, OPHB-1, OPHB-2, OPHB-3, and OPHB-4. The crystallization peaks for PLA could not be detected, whereas those for OPHB were observed clearly. The results indicated that OPHB had a higher degree of crystallinity than that of PLA. OPHB can crystallize much easier than PLA does under the same processing condition. The heat of crystallization and crystallization temperature characterized by the DSC peaks in the curves of cooling process could be plotted as a function of OPHB molecular weights (Fig. 4). With the increasing molecular weights of OPHB, the heat of crystallization and crystallization temperature

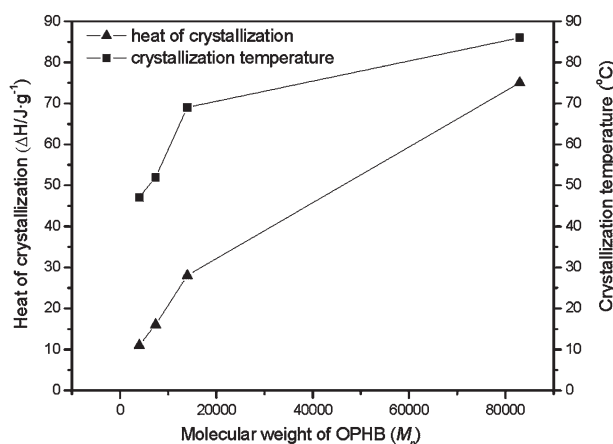


Figure 4 Heat of crystallization and crystallization temperature determined from the cooling process as a function of OPHBs with different molecular weights.

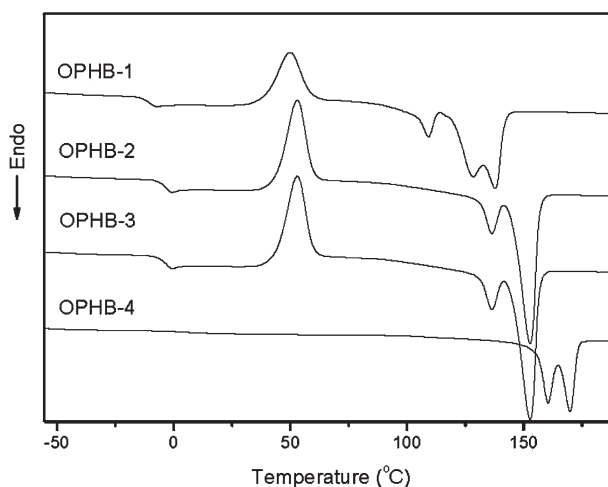


Figure 5 Subsequent heating process for OPHBs after they were cooled from 200°C to -60°C at a constant cooling rate of 10°C/min.

increased accordingly. This suggested that higher molecular weights of OPHB such as OPHB-4 had a higher degree of crystallinity and a faster crystallization rate. This suggestion was further supported by the following heating process: T_g and cold crystallization peak of OPHB-4 could not be detected due to a full crystallization in the cooling process while those for OPHB-1, OPHB-2, and OPHB-3 were observed clearly (Fig. 5).

As observed in the DSC exothermal peaks in the curves of the heating process, ΔH_{cc} could be plotted as a function of OPHB content in the blends (Fig. 6). T_{cc} of PLA decreased to a lower value from 117 to 82°C while ΔH_{cc} increased from 25 to 75 J/g with increasing ratio of OPHB-1 in the blend [Figs. 6 and 7(a)]. This may suggest that crystallization rate of PLA was increased in the presence of OPHB-1. This may be reasonable when considering that OPHB-1 formed

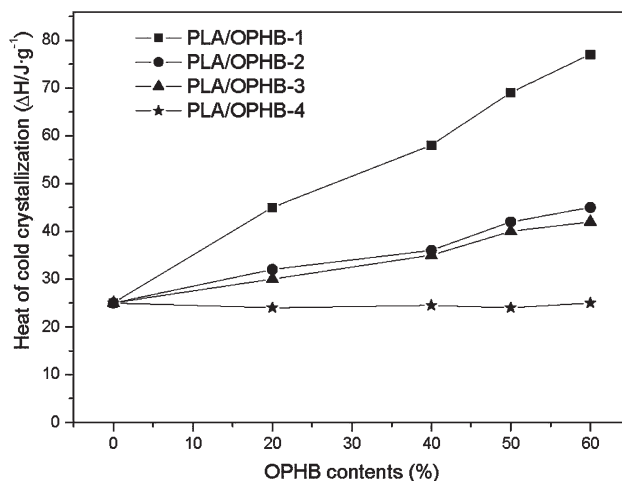


Figure 6 Heats of cold crystallization of PLA as a function of various molecular weights of OPHBs in the PLA/OPHB blends.

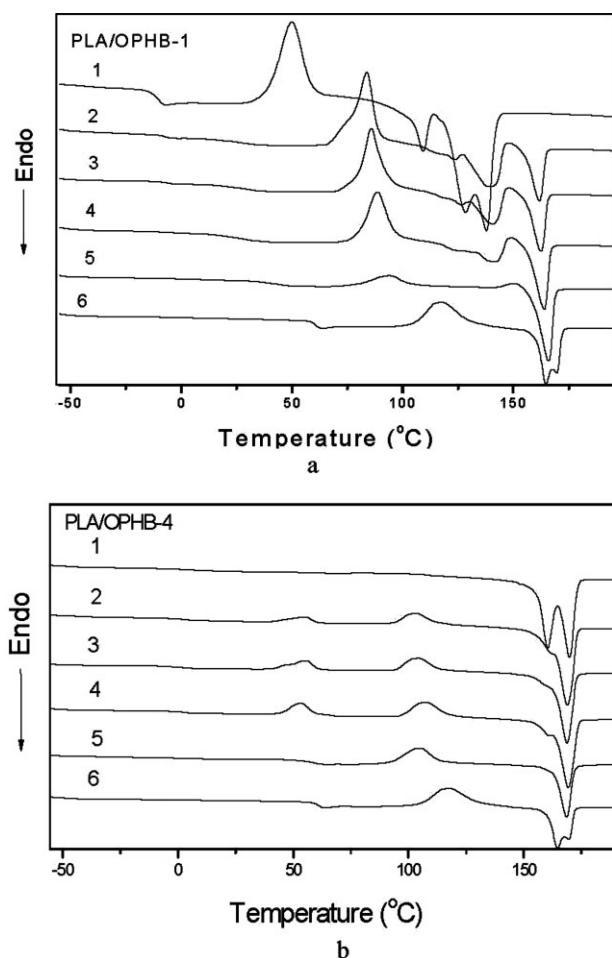


Figure 7 DSC curves of heating processes for PLA/OHB blends (a) DSC curves of heating processes for PLA/OHB-1 with the following composition ratios: (1) 0/100, (2) 40/60, (3) 50/50, (4) 60/40, (5) 80/20, and (6) 100/0. (b) DSC curves of heating processes for PLA/OHB-4 with the following composition ratios: (1) 0/100, (2) 40/60, (3) 50/50, (4) 60/40, (5) 80/20, and (6) 100/0.

fine and suitable size of spherulitic crystals during the cooling process, the spherulitic crystals then acted as efficient nucleation agents for PLA, and thus, leading to increasing crystallization rate. However, for PLA/OHB-4, ΔH_{cc} and T_{cc} of PLA were

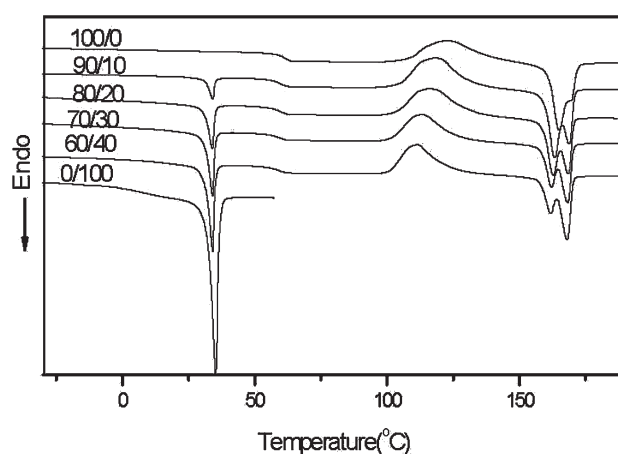


Figure 8 DSC curves (2nd scan) of PLA/F3312 blend with the latter number referring to the percentage of F3312 in the blends.

maintained almost unchanged with increasing contents of OHB-4 [Figs. 6 and 7(b)]. This may also be explained as the effect of OHB-4 nucleation agent. As OHB-4 had a higher molecular weight than that of OHB-1, it should form bigger spherulitic crystals during the cooling process, and the bigger spherulitic crystals were not effective nucleation agent for PLA, therefore, OHB-4 contributed less to the crystallization rate of PLA.^{23,24}

DSC study for PLA/dendrimers blend films

Figure 8 was the 2nd heating run of DSC curves for PLA/F3312. The T_g , T_{cc} , ΔH_{cc} , T_m , and ΔH_f were summarized in Table III. T_g of the binary blends remained constant at the same temperature independent of the PLA/F3312 component ratios. The same trend was also observed for T_{cc} , ΔH_{cc} , T_m , and ΔH_f , suggesting that the addition of dendrimer F3312 in PLA did not affect the thermal properties of PLA in the blending system. The calculated X_c of PLA based on eq. (1).²⁵

$$X_c \% = 100 \times \Delta H_f / [W_{PLA}(\Delta H_{f0})] \quad (1)$$

TABLE III
Thermal Properties of PLA/F3312

Samples	Composition (w/w)	T_g (°C) ^a	T_{cc} (°C) ^b	ΔH_{cc} (J/g) ^c	T_m (°C) ^d	ΔH_f (J/g) ^e
PLA/F3312	100/0	60.0	115.5	25.8	165.1	26.8
	90/10	60.0	113.4	26.7	164.3	27.4
	80/20	59.3	115.2	26.5	163.5	27.5
	70/30	59.5	114.3	25.5	163.1	26.5
	60/40	59.2	112.6	24.7	164.2	25.7
	0/100	-nd	-nd	-nd	35.2	36.4

^{a,b,c} T_g , T_{cc} , and ΔH_{cc} were determined by the 2nd scan of DSC.

^{d,e} T_m and ΔH_f were determined by the 1st scan of DSC.

nd: not detected.

showed that the X_c of PLA remained almost unchanged with the increase of F3312 content (Fig. 9). The above results demonstrated that F3312 had poor compatibility with PLA. The suggestion was further supported by heating the PLA/F3312 blend films at 60°C for 24 h in an oven. The surface of PLA/F3312 blend films turned viscous quickly. It was therefore concluded that instead of wrapping by molecular chains of PLA, F3312 was excluded and separated from PLA domain.

Thermal stability study of PLA/dendrimer blends

TGA was used to investigate the thermal stability of PLA/dendrimer blends by measuring their thermal decomposition temperature at the onset of weight loss. Higher decomposition temperature means better thermal stability for the blends.

The thermal decomposition temperature at the onset of weight loss (T_{onset}) for PLA/F3312 was shown in Figure 10. With the addition of F3312, the thermal stability of PLA component was increased. For example, T_{onset} of PLA increased from 219.6°C to 239.2°C when the weight component of F3312 increased from 0 to 10%. Combined with the DSC results mentioned above, it was further suggested that the increase of thermal stability of PLA came from the crosslinking effect of F3312. With the addition of F3312, the molecular chain of PLA was restricted and twisted, which would reduce heat sensitivity of PLA, and thus increase its thermal stability.²⁶

CONCLUSIONS

Miscibility of PLA and isotactic oligomers of 3-hydroxybutyrate (OHB) prepared by thermal-degradation of naturally PHB was found to be mainly determined by the molecular weights of OHBs.

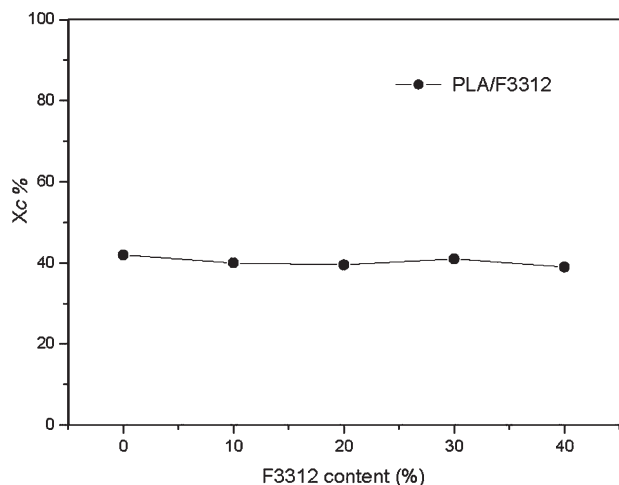


Figure 9 Degree of crystallinity for OHB and PLA versus the component weight of F3312.

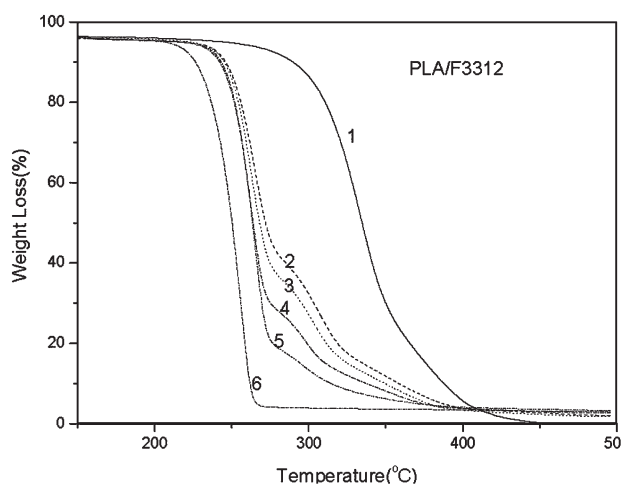


Figure 10 TGA curves of PLA/F3312 with different composition ratios: (1) 0/100, (2) 60/40, (3) 70/30, (4) 80/20, (5) 90/10, (6)100/0.

Crystallization study of OHB showed that OHB had a higher degree of crystallinity and a faster crystallization rate with increasing OHB molecular weights. The crystallization rate of PLA was increased when blended with a low-molecular weight OHB-1. When blended with a high-molecular weight OHB-4, the crystallization rate of PLA remained unchanged. This indicated that OHB-1 formed suitable size of spherulitic crystals in the cooling process and then acted as effective nucleation agents for PLA.

Thermal properties of PLA changed little in the presence of a hydroxyalkanoic acid dendrimer; this was resulted from the poor miscibility of the dendrimer with PLA. However, the dendrimer can enhance the thermal stability of PLA.

References

- Hu Y.; Zhang, J. M.; Sato, H.; Noda, I.; Ozaki, Y. *Polymer* 2007, 48, 4777.
- Krzan, A.; Hemjinda, S.; Miertus, S.; Corti, A.; Chiellini, E. *Polym Degrad Stab* 2006, 91, 2819.
- Furukawa, T.; Sato, H.; Murakami, R.; Zhang, J. M.; Noda, I.; Ochiai, S.; Ozaki, Y. *Polymer* 2007, 48, 1749.
- Tian, G.; Wu, Q.; Sun, S. Q.; Noda, I.; Chen, G. Q. *Appl Spectrosc* 2001, 55, 888.
- Deng, Y.; Zhao, K.; Zhang, X.; Hu, P.; Chen, G. Q. *Biomaterials* 2002, 23, 4049.
- Nguyen, S.; Gaer, Y.; Marchessault, R. H. *Biomacromolecules* 2002, 3, 219.
- Pietrini, M.; Rose, L.; Patel, M. K.; Chiellini, E. *Biomacromolecules* 2007, 8, 2210.
- Lehrle, R. S.; Williams, R. J. *Macromolecules* 1994, 27, 3782.
- Grassie, N.; Murray, E. *Polym Degrad Stab* 1984, 6, 47, 95, 127.
- Morikawa, H.; Marchessault, R. H. *Can J Chem* 1981, 59, 2306.
- Wanamaker, C. L.; O'Leary, L. E.; Lynd, N. A.; Hillmyer, M. A.; Tolman, W. B. *Biomacromolecules* 2007, 8, 3634.
- Iriondo, P.; Iruin, J. J.; Fernandez-Berride, M. *Polymer* 2000, 36, 3435.
- Baiardo, M.; Frisoni, G.; Scandola, M.; Rimelen, M.; Lips, D.; Ruffieux, K.; Wintermantel, E. *J Appl Polym Sci* 2003, 90, 1731.
- Hongbo, L.; Michel, A. H. *Polymer* 2007, 48, 6855.

15. Blümm, E.; Owen, A. J. *Polymer* 1995, 36, 4077.
16. Koyama, N.; Doi, Y. *Polymer* 1997, 38, 1589.
17. Ohkoshi, I.; Abe, H.; Doi, Y. *Polymer* 2000, 41, 5985.
18. Focarete, M. L.; Ceccorulli, G.; Scandola, M. *Macromolecules* 1998, 31, 8485.
19. Tomalia, D. A. *Prog Polym Sci* 2005, 30, 294.
20. Balogh, L.; Valluzzi, R. K.; Laverdure, S. P.; Gido, G. L.; Hagnauer, D. A.; Tomalia, J. *Nanoparticle Res* 1999, 1, 353.
21. Carr, P. L.; Davies, G. R.; Feast, W. J.; Stainton, N. M.; Ward, I. M. *Polymer* 1996, 37, 2395.
22. Ramachander, T. V. N.; Rohini, D.; Belhekar, A.; Rawal, S. K. *Int J Biol Macromol* 2002, 31, 63.
23. Withey, H. *Polymer* 1999, 40, 5147.
24. Furukawa, T.; Sato, H.; Murakami, R.; Zhang, J. M.; Duan, Y. X.; Noda, I.; Ochiai, S.; Ozaki, Y. *Macromolecules* 2005, 38, 6445.
25. Barham, P.; Keller, A. J.; Otun, E. L.; Holmes, P. A. *J Mater Sci* 1984, 19, 2781.
26. Lee, S. N.; Lee, M. Y.; Park, W. H. *J Appl Polym Sci* 2002, 83, 2945.