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Melt preparation and nucleation efficiency of polylactide stereocomplex crystallites

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Abstract

A melt blending procedure was developed for the preparation of poly(L-lactide) (PLLA)/poly(D-lactide) (PDLA) stereocomplex crystallites dispersed in a PLLA matrix. All PLLA/PDLA blends were prepared in a batch melt mixer with $\geq 95\%$ PLLA. Three PDLA homopolymers with a range of molecular weights were used as the minority ($\leq 5\%$) component. The presence of the stereocomplex in the PLLA matrix was verified by differential scanning calorimetry (DSC) and optical microscopy. The effectiveness of the in situ formed stereocomplex crystallites for nucleating PLLA crystallization was evaluated using self-nucleation and non-isothermal DSC methods. With only 3 wt% of the 14 kg mol^{-1} PDLA, nucleation efficiencies near 100% could be obtained. In addition, fast crystallization kinetics were observed in isothermal crystallization experiments at 140 °C. The stereocomplex crystallites were much more effective at enhancing the crystallization rate of PLLA compared to talc, a common nucleating agent.

Keywords: Polylactide; Nucleation; Stereocomplex

1. Introduction

Polylactide, a polyester derived from renewable resources, can be synthesized using either L-lactide or D-lactide. The polymers that result from the polymerization of these monomers, poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), respectively, are both isotactic and semi-crystalline with identical properties. However, upon blending PLLA and PDLA, they will co-crystallize to form stereocomplex crystals with physical properties distinct from either of the homopolymers; [1,2] the stereocomplex has a melting temperature ($T_m \approx 230$ °C) that is approximately 50 °C higher than the T_m of either PLLA or PDLA. This significant increase in melting temperature is due to strong van der Waals interactions in the stereocomplex crystalline structure [3,4].

Since, Ikada et al. first reported the formation of the polylactide stereocomplex [1], the influence of the homopolymer molecular weight [5–7], blending ratio [4–7] and optical purity [4,8,9] on the formation and properties [10] of the stereocomplex have been well documented [2]. In all of these cases, the stereocomplex was prepared by separately dissolving the PLLA and PDLA samples in a solvent followed by admixing, rapid stirring, and either precipitation or solvent evaporation. The preparation of the stereocomplex through melt blending is a viable option that has not been systematically explored [11]. Direct melt processing of the PLLA/PDLA stereocomplex is not desirable due to the high processing temperatures required (>230 °C), and at these temperatures significant degradation of the polylactide can occur [12]. On the other hand, melt blending the PLLA and PDLA homopolymers below the melting temperature of the stereocomplex allows for in situ formation of stereocomplex crystallites. In this case, melt blends could be prepared at standard processing temperatures for polylactide (190–200 °C). These blends would mimic the melt blends of PLLA and other fillers, such as clay [13–15] and talc [16].

If polylactide stereocomplex crystallites can be formed directly in a PLLA melt, they should effectively nucleate PLLA crystallization [4,17–19]. Since, PLLA is slow to crystallize, added nucleating agents are required in order to make use of industrially relevant processing techniques, such as injection molding [16]. Recently, Schmidt and Hillmyer showed that only a small amount of stereocomplex is necessary to cause a significant change in the crystallization rate of PLLA [17,18]. By solution blending as little as 0.25% of PDLA into PLLA,

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the PLLA crystallization half-time at 140 °C decreased from about 45 min for pure PLLA to about 8 min in the PLLA/PDLA blend containing the stereocomplex [17,18].

We have evaluated the efficacy of a melt blending procedure for the preparation of dispersions of PLLA/PDLA stereocomplex crystallites in a PLLA matrix. The nucleating efficiency of the resulting stereocomplex was assessed using a nucleating efficiency scale that allows for the quantitative evaluation of nucleating agents [17,18,20,21]. In addition, isothermal experiments were performed at 140 °C to determine the ability of the stereocomplex to increase the PLLA crystallization rate.

2. Results and discussion

2.1. Stereocomplex formation

The molecular characteristics of the PLLA and the PDLA homopolymers used to prepare the melt blends are given in Table 1. Blends of PLLA and PDLA were prepared by first dry mixing the two homopolymers at RT followed by melt blending in a Haake Rheomix batch mixer at 190 °C.

Formation of the stereocomplex in the melt blends was confirmed by differential scanning calorimetry (DSC). DSC traces obtained on heating the as-prepared melt blended samples from RT to 260 °C at 10 °C min^{-1} are given in Fig. 1 for the PLLA homopolymer and three PLLA/PDLA melt blends prepared using PDLA5.8. The glass transition temperature of PLLA is around 55 °C in all samples. In addition, a PLLA crystallization exotherm is noted in all of the samples around 100 °C. The 99/1 PLLA/PDLA5.8 blend showed the smallest crystallization exotherm. In a more controlled experiment (i.e. in which all samples experience the exact same thermal history), the crystallization exotherms for the three PDLA5.8 blends are nearly identical (Table 2). In all the samples, the melting peak from the PLLA homopolymer is present around 173 °C, while the stereocomplex melting peak, around 215 °C, is only seen in the DSC scans of the blends containing PDLA5.8. The area of the melting endotherm for the stereocomplex decreased as the amount of PDLA in the blend decreased showing that the initial composition of the blend can be used to control the amount of stereocomplex in the final material. Assuming a $\Delta H_{\mathrm{m}}^{\infty}$ of 142 J g^{-1} for the stereocomplex [22,23] and accounting for the weight fraction of stereocomplex in the sample, the level of crystallintity for the stereocomplex was calculated (Section 4). For all of the PLLA/PDLA blends, the stereocomplex crystallinity ranges from 61 to 66% [24].

Table 1
Characterization of polylactide samples

Sample	T_{g}[a] (°C)	T_{m}[a] (°C)	M_{n}[b] (kg mol^{-1})	PDI[b]
PLLA[c]	59	175	56	2.11
PDLA5.8	[d]	154	5.8	1.15
PDLA14	[d]	165	14	1.05
PDLA48	59	176	48	1.26

[a] Determined from DSC (Section 4).

[b] Determined by SEC versus polystyrene standards (Section 4).

[c] PLLA supplied by Toyota Motor Corporation.

[d] We did not observe a strong enough DSC signal to accurately measure a T_{g} in these samples due to their high crystallinities.

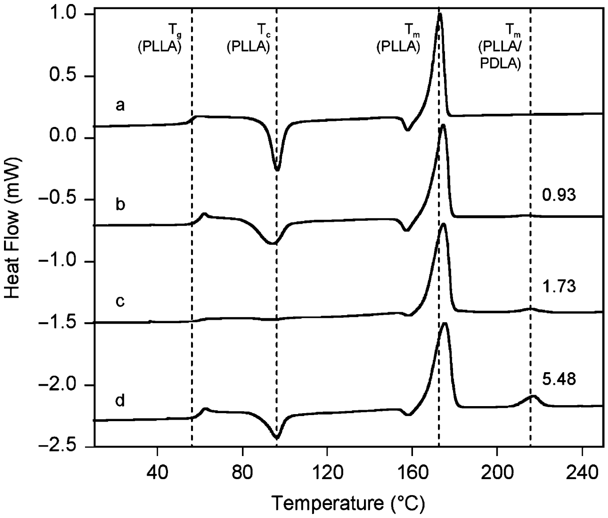

Fig. 1. DSC heating scans of (a) melt processed PLLA (b) 99.5/0.5 PLLA/PDLA5.8 melt blend (c) 99/1 PLLA/PDLA5.8 melt blend (d) 97/3 PLLA/PDLA5.8 melt blend. The ΔH_{m} (J g^{-1}) values are given next to the stereocomplex endotherms.

Optical microscopy images of a 99.5/0.5 wt% PLLA/PDLA5.8 melt blend are shown in Fig. 2. The samples were prepared by melting the blended sample on a hot plate at 190 °C (above the melting point of PLLA but below the melting point of the stereocomplex), pressing it between two cover slips, and quenching to RT. The images were acquired at 200 °C using a heat stage. At this temperature the stereocomplex crystallites are preserved in a PLLA melt. In the image of the 99.5/0.5 wt% PLLA/PDLA5.8 blend, the crystallites of the stereocomplex are dispersed throughout the PLLA

Table 2
Non-isothermal and isothermal DSC data for PLLA/PDLA melt blends

Additive	Additive weight %	T_{c}[a] (°C)	ΔH_{c}[a] (J g^{-1})	PLLA crystallinity[b] (%)	NE (%)	$t_{1/2}$[c] (min)
None	0.0	105	39	41	0	17
PDLA5.8	0.5	130	53	57	67	2.3
PDLA5.8	1.0	135	51	56	74	1.8
PDLA5.8	3.0	137	52	58	84	1.2
PDLA14	0.5	136	56	60	83	1.3
PDLA14	1.0	138	53	58	87	1.1
PDLA14	3.0	141	51	58	94	<1.0
PDLA48	0.5	130	51	55	66	2.4
PDLA48	1.0	133	52	56	73	1.9
PDLA48	3.0	135	54	61	81	1.3
Talc	6.0	123	47	54	50	6.5

[a] DSC program: heat at 200 °C min^{-1} to 183 °C, hold for 5 min, cool at 5 °C min^{-1} to 80 °C. The T_{c} and heat of crystallization (ΔH_{c}) were determined from the final cooling ramp.

[b] Calculated using Eq. (2) (see Section 4 for details).

[c] DSC program: heat at 200 °C min^{-1} to 183 °C, hold for 5 min, cool at 200 °C min^{-1} to 140 °C, hold for 30 min.

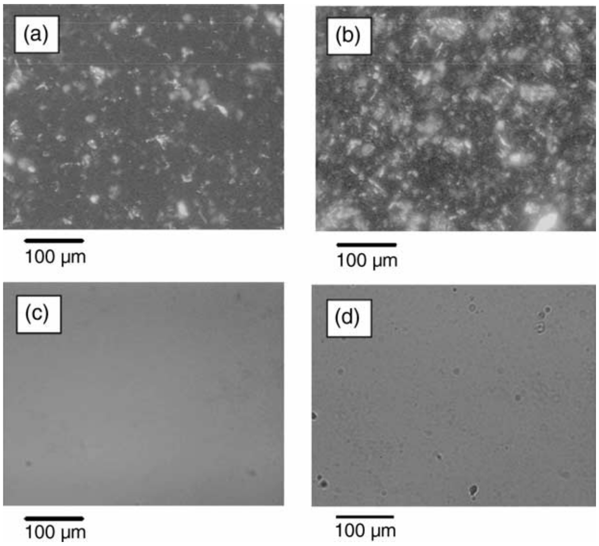

Fig. 2. Optical microscope images of PLLA/PDLA blends. (a) 99.5/0.5 wt% PLLA/PDLA5.8 blend (image acquired at 200 °C) (b) 97/3 wt% PLLA/PDLA5.8 blend (image acquired at 200 °C) (c) PLLA homopolymer (virgin material/image acquired at 200 °C) (d) PLLA homopolymer (melt processed/image acquired at room temperature).

matrix material. The stereocomplex crystallites range in size from approximately 1–20 μm. In the image of the 97/3 wt% PLLA/PDLA5.8 blend, (Fig. 2(b)), a higher density of the stereocomplex crystallites is noted, consistent with the increased level of the PDLA in the blend. In contrast, the image of the PLLA homopolymer (unprocessed) is featureless at 200 °C; an image of melt processed PLLA homopolymer (without PDLA) acquired at room temperature does have a small amount of foreign material dispersed throughout the matrix. There are no spherulites in this image because the PLLA was quenched to below the glass transition temperature fast enough to prevent appreciable crystallization. This melt processed PLLA was used as the control material in all subsequent crystallization experiments.

2.2. Nucleation efficiency

The melt blend procedure results in a dispersion of PLLA/PDLA stereocomplex crystallites within the PLLA matrix. To assess the ability of the crystallites to act as nucleating agents, a nucleation efficiency scale was developed following the procedure originally outlined by Wittmann et al. [20,21]. A nucleation efficiency scale for a given polymer is determined by cooling a polymer sample from the melt. Upon cooling, the sample will crystallize at a given temperature, and an effective nucleating agent will cause the crystallization temperature (T_c) of the homopolymer to increase, with a higher temperature corresponding to an increased level of nucleation [20,21]. The nucleation efficiency (NE) can be calculated from this T_c using the following equation [20,21]

$$\mathrm{NE} = \frac{T_c - T_c^{\min}}{T_c^{\max} - T_c^{\min}} \times 100 \tag{1}$$

where $T_c^{\min}$ and $T_c^{\max}$ for the homopolymer are determined from a self-nucleation experiment as described in detail by, for example, Schmidt and Hillmyer [17,18]. $T_c^{\min}$ is the crystallization temperature of the control sample and $T_c^{\max}$ is the crystallization temperature from a 'self-nucleated' melt. Self-nucleation is considered to be the ideal case for homopolymer crystallization due to an optimum dispersion of crystallites and the favorable interactions between the polymer melt and the polymer crystal fragments [21]. Therefore, Eq. (1) affords a way to directly compare the nucleating agent to the ideal self-nucleation case. For the melt processed PLLA, $T_c^{\min}$ was determined to be 104.3 °C, while $T_c^{\max}$ was determined to be 142.9 °C. This is the highest T_c that would be expected for this PLLA using a 5 °C min^{-1} cooling rate.

To determine the nucleation efficiency of the PLLA/PDLA stereocomplex as formed in the melts, the T_c's for the PLLA/PDLA blends were determined by quickly heating the samples to 183 °C (5 °C above the predetermined PLLA 'melt-out' temperature from the self-nucleation experiment). At 183 °C the homopolymer PLLA is completely melted, but the stereocomplex crystallites are left intact (Fig. 2). After 5 min at 183 °C, the samples were cooled at 5 °C min^{-1} and the T_c and area of the crystallization exotherm (ΔH_c) were recorded. The NE values were then calculated using Eq. (1).

Using the three different PDLA homopolymers, asymmetric blends with PDLA amounts ranging from 0.5 to 3.0 wt% were prepared and evaluated. The results from the DSC analysis of these blends are given in Table 2. The minimum nucleation efficiency was 66%, which was obtained when using 0.5 wt% of the 48 kg mol^{-1} PDLA. A significant increase in the T_c was noted for the 97/3 wt% PLLA/PDLA14 blend. For this sample the nucleation efficiency was close to 100%, suggesting that the stereocomplex behaved as a nearly ideal nucleating agent. As we [18] and others [4] have pointed out previously, epitaxial crystallization of PLLA from the PLLA/PDLA stereocomplex crystallites may be responsible for the enhanced nucleation efficiencies observed. Interestingly, at all compositions the PDLA14 blends stand out as having the best nucleation efficiency. The PDLA5.8 and PDLA48 blends had almost identical and lower nucleation efficiencies indicating that there may be an optimum PDLA molecular weight that may in turn be related to the size, shape, morphology and chemical nature of the stereocomplex crystallites [25]. Schmidt and Hillmyer also saw an improvement in the NE value when using 15 kg mol^{-1} PDLA compared to 4.7 and 49 kg mol^{-1} PDLAs in the solution blends with PLLA [17]. The 97/3 wt% PLLA/PDLA14 melt blend had the highest T_c of 141 °C, a temperature 12 °C higher than an analogous sample prepared by Schmidt and Hillmyer [17,18]. Interestingly, using the same DSC methods (i.e. heating to 240 °C), the melt blended samples had similar T_c values to those reported by Schmidt and Hillmyer [17,18] for the PLLA/PDLA solution blends [26].

The PLLA ΔH_c values for all of the PLLA/PDLA melt blends were higher than the homopolymer PLLA. The ΔH_c of the melt processed PLLA was 39 J g^{-1}. This corresponds to a PLLA crystallinity of 41% assuming a ΔH_m^{∞} of 94 J g^{-1} for the PLLA (Section 4) [27]. For the 99.5/0.5 wt% PLLA/PDLA14 blend, the ΔH_c was determined to be 56 J g^{-1} resulting in a

PLLA crystallinity of 60% after accounting for a loss of 0.66% of the sample due to stereocomplex formation (taking into account that based on the stereocomplex crystallinity, 66% of the available 1 wt% of PDLA/PLLA crystallized). Therefore, the crystallinity obtained using this experimental protocol increased by approximately 20% upon addition of the stereocomplex nucleating agent. This is contrary to the solution blend data of Schmidt and Hillmyer, who found that the ΔH_c values decreased upon addition of the PDLA [17,18]. Yamane et al. also investigated the nucleating ability of the stereocomplex in asymmetric solution blends of PLLA and PDLA [19]. Similar to our results, Yamane et al. found that the ΔH_c values increased in the PLLA/PDLA blends compared to the PLLA homopolymer [19].

In order to directly compare our data to that of Yamane et al. [19], the nucleating efficiency of the melt blends was also evaluated using a cooling rate of 2 °C min^{-1}. First, the self-nucleation experiment was performed on the melt processed PLLA using the new cooling rate, and the new $T_c^{\min}$ and $T_c^{\max}$ were found to be 111 and 146 °C, respectively. The T_c, ΔH_c, and NE values for the PLLA/PDLA melt blends were then determined and are given in Table 3. Using the slower cooling rate, higher T_c values and higher NE values were obtained for all blends. The highest NE value was 107% thus indicating the provocative result that the stereocomplex crystallites in the 97/3 wt% PLLA/PDLA14 blend were actually more effective at nucleating the crystallization of PLLA than even the PLLA crystallites coming from the self-nucleation experiment. This may be a result of more favorable interactions between preformed PLLA/PDLA stereocomplex crystallites and an 'incoming' PLLA chain. Once again the PDLA14 samples exhibited the highest nucleation efficiencies at all compositions. Comparing our data to the samples of Yamane et al., who used a DSC program where the solution blended samples were heated to 200 °C, we see that using a 2 °C min^{-1} cooling rate our highest T_c value of 149 °C was significantly higher than their highest reported T_c value of 128 °C, which was obtained in a blend containing 5 wt% PDLA [19].

Table 3
Non-isothermal DSC data for PLLA/PDLA melt blends at a 2 °C min^{-1} cooling rate

Additive	Additive weight %	T_c[a] (°C)	ΔH_c[a] (J g^{-1})	NE (%)
None	0.0	112	53	0
PDLA5.8	0.5	140	59	82
PDLA5.8	1.0	142	57	88
PDLA5.8	3.0	145	53	97
PDLA14	0.5	145	60	97
PDLA14	1.0	146	67	100
PDLA14	3.0	149	57	107
PDLA48	0.5	140	59	81
PDLA48	1.0	142	61	88
PDLA48	3.0	144	52	94
Talc	6.0	130	57	57

[a] DSC program: heat at 200 °C min^{-1} to 183 °C, hold for 5 min, cool at 2 °C min^{-1} to 80 °C. The T_c and heat of crystallization (ΔH_c) were determined from the final cooling ramp.

Talc, a common nucleating agent used for PLLA, was also melt blended with the PLLA as a comparison to the nucleating ability of the stereocomplex. With 6% talc, a nucleation efficiency of 32% was obtained by Schmidt and Hillmyer [17,18]. When 6 wt% of talc was melt blended with the PLLA in this study using the same protocol as the PLLA/PDLA blends, the nucleation efficiency was 50% (Table 2). Better dispersion of the talc in the melt blends may account for this slight improvement in the nucleation efficiency. Overall, the nucleation ability of the talc was lower than the stereocomplex crystallites even at higher weight fractions.

2.3. Isothermal crystallization

Another measure of the effectiveness of a nucleating agent is the crystallization half-time in an isothermal crystallization experiment. Here, the polylactide samples were directly heated to 183 °C, quenched to 140 °C and the crystallization at 140 °C was monitored by DSC. By integrating the resultant crystallization exotherms, a relative percent crystallinity based on the total area of the crystallization exotherm can be calculated at any given time, with 100% crystallinity being the total area of the peak (at long times). A representative example is given in Fig. 3. From this curve, the time it takes to reach 50% of the maximum crystallinity, $t_{1/2}$, can then be determined. The $t_{1/2}$ values are given in Table 2 for all of the blends.

We observed a significant decrease in the $t_{1/2}$ values when the PDLA was present in the melt blends. Similar to the NE data, the $t_{1/2}$ values for the PDLA14 blends were noticeably smaller than either the PDLA5.8 or the PDLA48 blends at the same compositions. Using this DSC method, an extremely short $t_{1/2}$, <1.0 min, was obtained in the 97/3 wt% PLLA/PDLA14 blend. The smallest $t_{1/2}$ at 140 °C seen by Schmidt and Hillmyer in the solution blends was 75 s and that was with 10% PDLA incorporation [17,18,28]. When compared to talc, a standard nucleating agent, the $t_{1/2}$ values of the blends containing the stereocomplex were considerably smaller than the talc blends in every case (Table 2). Kolstad et al. also investigated talc as a nucleating agent for isothermal crystallization of PLLA [16]. With 6 wt% talc, the $t_{1/2}$ at 120 °C was

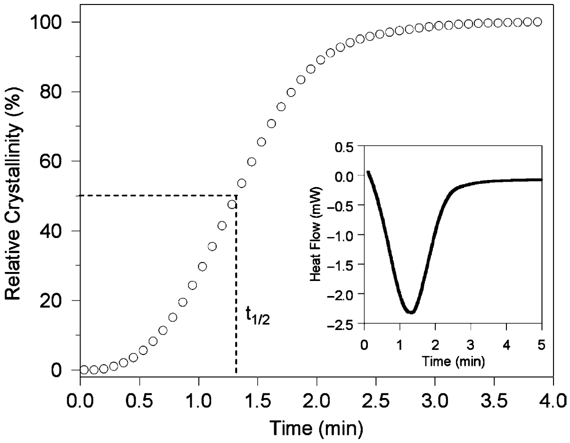

Fig. 3. Representative curve for determining the crystallization half-time ($t_{1/2}$) from the isothermal DSC trace taken at 140 °C (inset).

also less than 1 min [16]. The lower isothermal crystallization temperature accounts for the reduced $t_{1/2}$ value in their study.

3. Conclusions

Melt blending proved to be an effective route to prepare and disperse the PLLA/PDLA stereocomplex in asymmetric blends of PLLA and PDLA. The nucleation efficiency of the stereocomplex prepared in this manner was evaluated and remarkable increases in the nucleation efficiency were observed. In addition, in isothermal experiments the $t_{1/2}$ values were extremely small indicating significant enhancement of the PLLA crystallization rate. The blends with the intermediate molecular weight, PDLA14, stood out as having the highest nucleation efficiencies and smallest $t_{1/2}$ values, indicating that there may be an optimum molecular weight of the PDLA for stereocomplex nucleating agents. All of the blends containing the stereocomplex showed more significant improvements in the crystallization rate of PLLA compared to talc. This study demonstrates the feasibility of using PDLA at very low levels as a nucleating agent for the commercially relevant PLLA in a simple melt blending process. For example, as little as 0.5 wt% of 14 kg mol^{-1} PDLA melt blended into high molecular weight, commercially relevant PLLA exhibited a crystallization temperature of 145 °C (a nucleation efficiency of nearly 100%) upon cooling from the melt as compared to 130 °C using 6.0 wt% talc.

4. Experimental section

4.1. Materials

A commercial grade poly(L-lactide) PLLA was supplied by Toyota Motor Corporation. Ultratalc 609 was provided by Cargill-Dow Polymer, LLC. Poly(D-lactide) (PDLA) was synthesized by the ring opening polymerization of D-lactide with diethylaluminum-ethoxide (Et_2AlOEt) in toluene. The following is a general procedure for the synthesis of PDLA with a targeted molecular weight of 12 kg mol^{-1} (assuming 80% conversion of lactide). In a glovebox, a Teflon-coated stir bar, 10.0 g of D-lactide (0.06939 mol) (purified by recrystallization from ethyl acetate), 69 mL of purified toluene, and 12.5 μL of Et_2AlOEt (1.6 M in toluene, 0.667 mmol) were placed into a 150 mL Chemglass high-pressure vessel. The mixture was stirred in an oil bath at 90 °C for 30 h. The polymerization was then terminated with approximately 3 mL of 1.0 M HCl (5 times molar excess with respect to living chains). The polylactide was then precipitated into methanol and dried in a vacuum oven for 24 h at 60 °C (6.7 g, 67% conversion of lactide). Three PDLA homopolymers with a range of molecular weights were synthesized using this method.

4.2. Blend preparation

Melt blending was performed at 190 °C in a Haake Rheomix 600 batch mixer at 50 rpm blade rotation speed. Prior to blending, the PLLA pellets and the PDLA homopolymer, in the form of a powder or small flakes, were manually pre-mixed in the desired compositions. The pre-mixed material was added to the chamber of the mixer, which was heated to 190 °C and had the blades rotating at 30 rpm. Once all of the material was in the chamber, the plunger was lowered to enclose the chamber and the rotation was increased to 50 rpm. After 15 min at 50 rpm, the blades were stopped and the blends were removed from the chamber using a spatula. The hot blend was cut into small pieces using scissors and allowed to cool to room temperature on the bench top.

4.3. Molecular weight determination

The molecular weights of the PLLA and PDLA homopolymers were determined on a Hewlett–Packard 1100 series liquid chromatograph equipped with a Hewlett–Packard 1047A refractive index detector and three Jordi polydivinylbenzene columns with 10^4, 10^3, and 500 Å pore sizes. The mobile phase was tetrahydrofuran (40 °C, 1 mL min^{-1}). The columns were calibrated using polystyrene standards from Polymer Laboratories.

4.4. Microscopy

Optical microscopy images of the melt blended samples were obtained using an Olympus BX51 polarizing microscope equipped with a video camera and heat stage. Samples were prepared by melting a sample between two cover slips on a hot plate and gently pressing them together with tweezers.

4.5. Differential scanning calorimetry (DSC)

DSC was performed on a TA Instruments Q1000 instrument. The T_m's and glass transition temperatures (T_g) of the homopolymers reported in Table 1 were determined using a 5–10 mg sample that was heated at 5 °C min^{-1}. To remove the thermal history of the samples prior to testing, the samples were annealed for 5 min at 200 °C highest test temperature and then cooled to 5 °C at 2 °C min^{-1} and held for 5 min before heating again for the thermal analysis. The percent crystallinity was calculated using the following equation

$$\%\ \text{Crystallinity} = 100 \times \frac{\Delta H_m}{f \Delta H_m^\infty} \qquad (2)$$

where ΔH_m is the measured heat of fusion, f is the weight fraction of the component in question and ΔH_m^∞ is the enthalpy of fusion for a crystal having infinite crystal thickness (94 J g^{-1} for PLLA [27]).

4.6. Self nucleation experiment (DSC)

Melt processed PLLA was initially heated at 200 °C min^{-1} to 200 °C and held for 5 min. The sample was then cooled at 5 °C min^{-1} to 80 °C and immediately heated at 200 °C min^{-1}

to a temperature in the partial melting zone for PLLA. The sample was held at this temperature for 5 min and then cooled at 5 °C min^{-1} to 80 °C and the crystallization temperature (T_c) was determined. Using this protocol, we determined that the 'melt out' temperature (i.e. the temperature at which all of the PLLA crystallites have completely melted) for this PLLA sample was 178 °C.

4.7. Nucleation efficiency experiment (DSC)

A melt blended sample was heated at 200 °C min^{-1} to 183 °C (5 °C above the determined melt out temperature for PLLA) and held for five minutes and then cooled at either 5 or 2 °C min^{-1} to 80 °C. The T_c and heat of crystallization (ΔH_c) were determined from the final cooling ramp. The T_c was taken as the peak temperature.

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[24] These values for the stereocomplex crystallinity may be lower than the actual levels of crystallinity. Loomis et al. indicate that the heat of fusion for the stereocomplex is the same as that of the homopolymer and report this value as 142 J g^{-1} [22]. The value for the homopolymer heat fusion, however, is reported to range from 93 up to 148 J g^{-1} (see: Sodergard A, Stolt M. Prog Polym Sci 2002;27:1123–1163). When analyzing the homopolymer crystallinity we have chosen to use 94 J g^{-1} based on our previous convention.
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[26] Using the same DSC program as Schmidt and Hillmyer [17,18]: heat at 200 °C min^{-1} to 240 °C, hold for 5 min, cool from 240 to 200 °C at 5 °C min^{-1}, cool at 2 °C min^{-1} to 80 °C, heat at 200 °C min^{-1} to 183 °C, hold for 5 min, cool at 5 °C min^{-1} to 80 °C, similar NE and T_c values were obtained. For example, a 99.5/0.5 wt% PLLA/PDLA14 melt blend evaluated using this method had a T_c of 120.1 °C and an NE value of 41%, while Schmidt and Hillmyer report a T_c of 125.3 °C and an NE value of 37% for a solution blend containing 0.5% of a 15 kg mol^{-1} PDLA [17,18]. The lower T_c and NE values for the PLLA/PDLA melt blends using the high temperature DSC program of Schmidt and Hillmyer is likely a result of intermolecular transesterification reactions occurring at 240 °C between the PLLA and PDLA. This would alter not only the distribution but also the size and number of stereocomplex crystallites that could reform during the cooling step and as a result lower the nucleation efficiency.
[27] Witzke DR, Narayan R, Kolstad JJ. Macromolecules 1997;30:7075.
[28] Using the same DSC program as Schmidt and Hillmyer: [17,18] heat at 200 °C min^{-1} to 240 °C, hold for 5 min, cool from 240 to 200 °C at 5 °C min^{-1}, cool at 2 °C min^{-1} to 80 °C, heat at 200 °C min^{-1} to 183 °C, hold for 5 min, cool at 200 °C min^{-1} to 140 °C, hold for 30 min, similar $t_{1/2}$ values were obtained. For example, the 99.5/0.5 wt% PLLA/PDLA14 blend evaluated using this method had a $t_{1/2}$ of 4.1 min, while Schmidt and Hillmyer report a $t_{1/2}$ of 4.4 min for a solution blended sample containing 0.5% of a 15 kg mol^{-1} PDLA [17,18].