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Effect of Plasticizer Poly(Ethylene Glycol) on the Crystallization Properties of Stereocomplex-Type Poly (Lactide Acid)

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Abstract: The effects of the plasticizer poly(ethylene glycol) (PEG) on crystallization properties of equimolar poly(L-lactide) (PLLA)/poly(D-lactide) (PDLA) blends were investigated. Formation of the stereocomplex-type poly(lactide acid) (sc-PLA) crystallites was confirmed by Wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) analyses. Sc-PLA crystallites without any homochiral poly(lactide acid) (hc-PLA) formed, as the result of the incorporation of the plasticizer PEG (more than or equal to 10%(wt)) at a processing temperature (240 ℃). Moreover, when the $\overline{M}_{\mathrm{W}}$ of PEG reached 1 000 g · mol^{-1}, the crystallizability of stereocomplex crystallites was the best. Isothermal crystallization kinetics further revealed that PEG could accelerate the crystallization rate of sc-PLA, with the optimum crystallization kinetic parameters being obtained at 10% (wt) PEG . Several crystallization kinetics equations were applied to describe the effect of PEG on the crystallization behavior of sc-PLA. The influence of PEG on the spherocrystal morphologies of sc-PLA was also investigated using polarized optical microscopy.

Key words: plasticizer; stereocomplex-type; poly(lactide acid); crystallization

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0 Introduction

Poly(lactic acid) (PLA) is a kind of environmentally friendly polyester material. Compared with traditional petrochemical polymers, PLA has a bright prospect because it can be produced from starch materials extracted from annually renewable resources such as corn, wheat, and sorghum. It is biodegradable and biocompatible. In addition, resembling frequently-used plastics, high-molecular-weight PLA polymer has excellent mechanical properties and thermoplasticity. Considering many of these excellent properties, PLA can be widely used in the fields of biomedical engineering, agriculture and packaging applications. However, its slow crystallization rate and low crystallinity have limited its application area to some extent [1-3].

PLA exists typically in three isomeric forms, namely poly(L-lactic acid) (PLLA), poly(D-lactic acid) (PDLA), and poly(racemic-lactic acid) (PDLLA), displaying various properties. In 1987, Ikada *et al* [4] first reported that stereocomplexation between enantiomeric PLLA and PDLA was one of the most promising methods for increasing the properties of PLA. The sc-PLA had a melting temperature (T_{m}) of 230 ℃, approximately 50 ℃ higher than that of either PLLA or PDLA. Studies have shown that the stereocrystals showed better thermal stability [5] and mechanical properties [6, 7].

Many recent studies have been carried out on the formation and properties of PLA stereocomplexes, including homopolymer molecular weight [8-10], blending ratio of PLLA to PDLA [8-12], blending temperature [13], and optical purity [8, 12]. It has been documented that the formation of the stereocomplexes is preferential at a blending ratio of 1:1. Bao *et al* [13] reported the stereocomplex of high-molecular-weight polylactide formed more readily at a lower temperature, and exclusive stereocomplex crystallites without any homocrystallites were difficult to form at a processing temperature higher than 220 ℃ in 1:1 PLLA/PDLA blends. The 1:1 PLLA/PDLA blends were in the form of powder at processing temperatures below 200 ℃ and still formed sc-PLA. However, in many industrial applications, processing temperatures must be higher than T_m of sc-PLA (230 ℃). In this regard, obtaining high content stereocomplex crystallites at higher temperature has attracted much attention. During the formation of stereocrystals, PLLA and PDLA chains force a larger diffusion path than that of the conventional folding crystallization mechanisms [14]. Adding a plasticizer is an efficient way to increase the chain mobility. Generally, this is a good way to lower the energy required during the PLA crystallization phase of the chain folding process which will enhance the crystallization rate [15,16]. In previous studies, plasticizers, such as citrate ester [17], triacetine [18], poly (propylene glycol) (PPG) [19], tributyl citrate [15], poly (ethylene glycol) (PEG) [20-22], and triphenyl phosphate (TPP) [23,24] were used to increase the chain mobility and impact resistance of PLA.

In the research described in this paper, PEG was chosen as a plasticizer for 1:1 PLLA/PDLA blends. The effect of plasticizer on the formation and crystallization of sc-PLA were investigated in isothermal and non-isothermal conditions. This study focuses mainly on the formation, crystallization kinetics and morphology of the resulting sc-PLA. The formation and crystallinity were investigated by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The morphology of sc-PLA and its blends with PEG were investigated using polarized optical microscopy (POM).

1 Experimental

1.1 Material

The PLLA (trade name Revode 190) was purchased from Zhejiang Hisun Biological Material Co., Ltd. (China). The weight-average molecular weight ($\overline{M}_w$), polydispersity (PDI) and optical purity of the PLLA were 2.1×10^5 g · mol^{-1}, 1.7 and 97%, respectively. PDLA ($\overline{M}_w$)=1.0×10^5 g · mol^{-1}, PDI=1.7, optical purity=99%) was synthesized using the ring-opening polymerization of D-lactic acid, which was obtained from Professor Chen Xuesi's research team at the State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (China). The C.P. grade PEG (PDI=1.2-1.5) was kindly supplied by the Kelong Chemical Reagent Factory (China). The $\overline{M}_W$ of selected PEG were 600 (P_{600}), 1 000(P_{1000}), 1 500(P_{1500}), and 10 000(P_{10000}) g · mol^{-1}.

Before the blend was prepared, PLLA and PDLA were predried in a vacuum oven at 80 ℃ for 48 h. Equimolar PLLA/PDLA were blended with 10% (wt) different $\overline{M}_w$ PEG or 5%, 10%, 15% or 20% (wt) PEG ($\overline{M}_w$ =1 000 g · mol^{-1}) using a SU-70 Plastic-Corder Mixer (Suyuan Science and Technology, China) at 240 ℃ for 15 min at a rotation speed of 40 r/min with N_2 protection. The samples were labeled as LDP$_x$ (x=5, 10, 15, 20), wherein letters L, D, and P refer to PLLA, PDLA, and PEG, respectively, and x refers to the content of PEG ($\overline{M}_w$ =1 000 g · mol^{-1}).The samples for XRD, DSC and POM test were all taken from the products after blending in a SU-70 Plastic-Corder Mixer and crystallized naturally from melt state in air. And the surface smooth blocks were picked out for XRD test, specially.

1.2 Wide-Angle X-ray Diffraction

Wide-angle X-ray diffraction (WAXD) profiles were obtained using a D8 Advance X-ray Diffractometer (BRUKER AXS, Germany) with a Cu K_α radiation source (λ = 0.154 18 nm, 40 kV, 200 mA) in the range of 2θ = 5-50 ° at a scanning rate of 5 °/min. The WAXD results were used to estimate the crystallinity of all samples using Jade software to identify different crystallization peaks and calculate the crystallinity.

1.3 Differential Scanning Calorimetry

Thermal analysis was carried out using an NETZSCH differential scanning calorimeter (DSC) 204 F1 Phoenix (Germany). All samples were heated from 20 to 250 ℃ at a heating rate of 10 ℃/min, and maintained there for 3 min to remove thermal history, then cooled to 20 ℃ at a speed of 5 ℃/min.

For isothermal mode, in order to assure that only sc-PLA, and no hc-PLA, was crystallized selectively, the crystallization temperatures were controlled to be lower than the T_m of sc-PLA and higher than that of the homocrystallites of poly(lactide acid) (hc-PLA). Samples were heated to 250 ℃ at a rapid speed, and maintained there for 3 min to remove thermal history. Then the samples were cooled to the designed crystallization temperature (T_c) at a rate of 80 ℃/min and maintained until the isothermal crystallization was accomplished. The samples were subsequently heated from the designed T_c to 250 ℃ at a rate of 10 ℃/min; the isothermal crystallization and heating curves were recorded.

1.4 Polarized Optical Microscopy

Optical microscopy (Axio Scope A1) equipped with a Linkam LINKSYS 32 hot stage (Zeiss, Germany) was used to observe the morphologies of sc-PLA and its PEG blends following the crystallization. The samples were heated to 250 ℃ for 2 min, and then rapidly cooled to the designated T_c 201 ℃ for 5 min.

2 Results and Discussion

2.1 Stereocomplex Formation

Figure 1 shows WAXD profiles and DSC curves of LD, LDP_5, LDP_{10}, LDP_{15} and LDP_{20}. The corresponding DSC and calculated WAXD data are summarized in Table 1. As shown in Fig. 1(a), WAXD profiles of LD and its blends with 5%, 10%, 15% and 20% (wt) PEG ($\overline{M}_w$ =1 000 g·mol^{-1}) had three characteristic diffraction peaks, at 2θ =12.1°, 20.8°, and 23.9°. These peaks were assigned to the (110), (300) and/or (030), and (220) planes of sc-PLA crystallized in a triclinic unit cell of dimensions $a = b = 1.498$ nm, $c = 0.870$ nm, $\alpha = \beta = 90°$ and $\gamma = 120°$ [25]. For LD and LDP_5, there were three typical diffraction peaks of the sc-PLA crystallites and additional diffraction peaks at 16.4° and 18.8°. These were characteristic peaks of hc-PLA crystallized in the α-phase in a pseudo orthorhombic pattern $a = 1.06$ nm, $b = 0.61$ nm, $c = 2.88$ nm [26]. The first of these two peaks was attributed to the (200) and (110) planes of hc-PLA and the second to the (203) plane. For LD, the crystallinities of hc-PLA (X_c(H)) and sc-PLA (X_c(S)), which were estimated from the WAXD measurements, were 11.7% and 22%, respectively. As shown in Table 1, X_c(S) increased with increase of PEG content first and reached its maximum value, 0.53 at 10%(wt) PEG content; then it decreased to 0.38 and 0.30 as the PEG content was increased further to 15% and 20%(wt). In particular, X_c(S) of all samples plasticized by PEG were higher than that of LD. This demonstrated that the addition of the proper amount of PEG (10% (wt)) was an effective way to prepare sc-PLA crystallites and promoted its crystallization without any additional formation of hc-PLA at a processing temperature of 240 ℃.

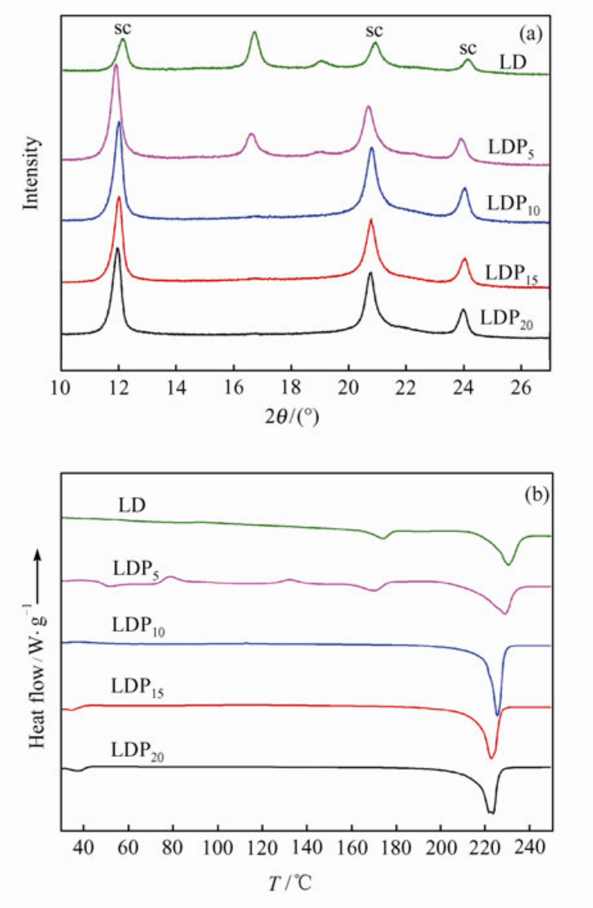

Fig. 1 WAXD profiles (a) and DSC curves (b) of different samples

Table 1 DSC and WAXD data of the various samples

Sample	T_g/℃	$T_m(H)^a$/℃	$T_m(S)^a$/℃	$\Delta H_m(H)^b$/J·g^{-1}	$\Delta H_m(S)^b$/J·g^{-1}	$X_c(H)^c$/%	$X_c(S)^c$/%	$X_c(H+S)^c$/%
LD	58.7	174.0	230.3	10.16	49.86	11.7	22.0	33.7
LDP_5	48.1	170.5	228.9	11.62	60.8	23.8	25.4	49.2
LDP_{10}	40.6	—	225.4	—	78.87	—	52.7	52.7
LDP_{15}	31.4	—	222.6	—	76.73	—	37.6	37.6
LDP_{20}	32.1	—	223.5	—	67.26	—	29.8	29.8

a: T_m(H) and T_m(S) are melting temperatures of homocrystallites and stereocomplex crystallites, respectively; b: ΔH_m(H) and ΔH_m(S) are enthalpy change of homocrystallites and stereocomplex crystallites; c: X_c(H), X_c(S) and X_c(H+S) are crystallinities of homocrystallites, stereocomplex, and both crystallites, respectively, estimated by WAXD measurements; T_g: Glass transition temperature

As shown in Fig. 1(b), the DSC melting curves of LD and LDP_5 exhibited two peaks at 172.0 and 229.6 ℃ corresponding to the melting of hc-PLA and sc-PLA, respectively [27]. For LDP_5, additional two small exothermic peaks (at 80 ℃ and 130 ℃) appeared. These two peaks are corresponding to the cold crystallization of hc-PLA (PLLA or PDLA) and sc-PLA, respectively [28]. Remarkably, the other three blends exhibited only one single melting peak, assigned to sc-PLA, at around 222-226 ℃. The sc-PLA melting enthalpy changed from 49.9 J/g for LD, to 78.9 J/g and 67.3 J/g as the PEG content was increased from 0 to 10% and 20 % (wt); i.e. the sc-PLA enthalpy reached the maximum when PEG content was 10 % (wt).

These results were consistent with the WAXD analysis, supporting the conclusion that, after addition of equal to or more than 5% (wt) PEG, even at such high processing temperatures, here 240 ℃, sc-PLA crystallites with relatively high crystallinity can be produced from 1:1 PLLA/PDLA blends without any homocrystallites so long as equal to or more than 5% (wt) PEG is added. Presumably sc-PLA is generated and maintained by the hydrogen bonding of $CH_3 \cdots O{=}C$ [29] between the two neighboring isomer chains. Incorporation of plasticizer PEG at a relative low content improves chains mobilities of both PLLA and PDLA, and accelerates the combination of the chains of PLLA and PDLA to form sc-PLA. However, excess plasticizer enlarges the distance between PLLA and PDLA molecule chains and retards the formation of the $CH_3 \cdots O{=}C$ hydrogen bonding between the two isomers, eventually leading to the decrease of sc-PLA crystallinity.

DSC heating curves of PLLA/PDLA plasticized with 10% (wt) PEG of different molecular weight are shown in Fig. 2. The obtained thermal parameters are summarized in Table 2. Compared with PLLA/PDLA sample, the T_g of PEG plasticized PLLA/PDLA samples were lower. As a plasticizer, the molecular weight of PEG is significantly smaller than PLA. It can move easily and enlarge the distance between PLLA and PDLA molecular chains. So the presence of PEG decreases the T_g of PLLA/PDLA blends. As shown in Fig. 2, at the presence of plasticizer, exclusive sc-PLA crystallites formed and melting enthalpy significantly enhanced. However, PEG with different M_w shows different effects on melting enthalpy. For example, with an increase in $\overline{M}_w$ of PEG from 600 to 1 000 $g \cdot mol^{-1}$, melting enthalpy of sc-PLA increased from 64.69 to 78.87 J/g, which was 49.86 J/g for LD sample. Melting enthalpy of sc-PLA decreased from 78.87 to 68.95 J/g when $\overline{M}_w$ of PEG increased from 1 000 to 1 500 $g \cdot mol^{-1}$. These results show that addition of PEG with proper $\overline{M}_w$ (1 000 $g \cdot mol^{-1}$) can enhance the formation of sc crystallites from the melt.

In the following research, we only discuss the properties of PLLA/PDLA plasticized with PEG having $\overline{M}_w$ values of 1 000 $g \cdot mol^{-1}$.

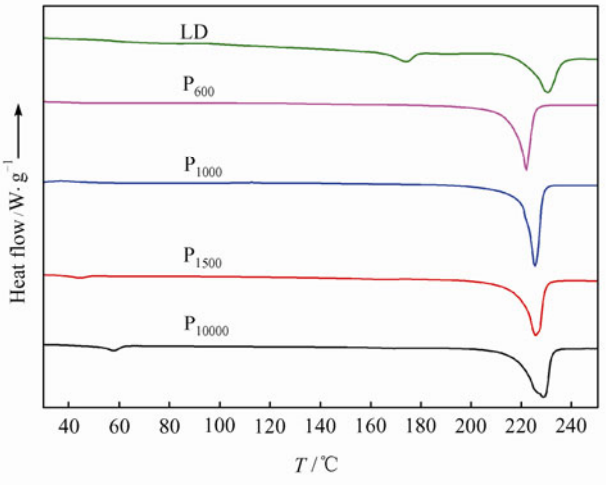

Fig. 2 DSC curves of LD and its blends containing 10% different molecular weight of PEG

Table 2 DSC data of LD and its blends containing 10% different molecular weight of PEG

Sample	T_g/℃	T_m(H)/ ℃	T_m(S)/ ℃	ΔH_m(H)/J · g^{-1}	ΔH_m(S)/J · g^{-1}
LD	58.7	174	230.3	10.16	49.86
P_{600}	41.1	—	221.9	—	64.69
P_{1000}	40.6	—	225.4	—	78.87
P_{1500}	40.9	—	225.7	—	68.95
P_{10000}	55.2	—	228.9	—	71.85

2.2 Isothermal Crystallization Kinetics

To understand the effect of PEG on the crystallization of sc-PLA, the isothermal crystallization kinetics of LD and its blends with different amounts of PEG were studied further at various temperatures by using DSC. As examples, DSC traces of all samples recorded during isothermal crystallization at 199 ℃ and DSC traces of LDP_{10} recorded during isothermal crystallization at various temperatures from 199 ℃ to 207 ℃ are shown in Fig. 3 and Fig. 4. Compared with neat sc-PLA (Fig. 3(a)), the crystallization peaks and crystallization times of all specimens incorporating PEG are relatively sharper and shorter, respectively. Dramatically, the sample with 10%(wt) PEG shows the shortest crystallization time and sharpest crystallization peak of any of the specimens. In addition, the crystallization peak becomes much sharper and the crystallization time becomes much shorter as the crystallization temperature decreases (Fig. 4(a)).

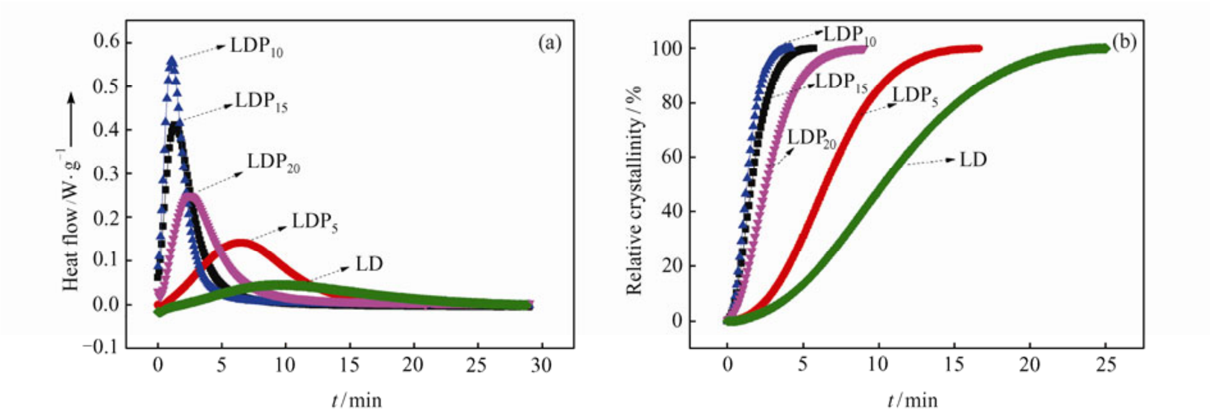

Fig. 3 DSC traces recorded during isothermal crystallization at 199 °C (a) and corresponding relative degree of stereocomplexation (b) for different samples

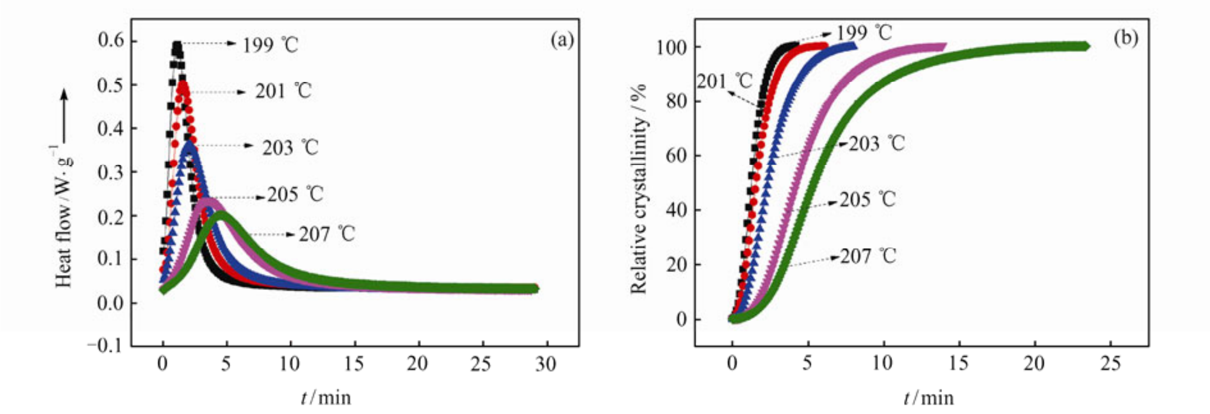

Fig. 4 DSC traces recorded during isothermal crystallization at different temperatures (a) and corresponding relative degree of stereocomplexation (b) for LDP_{10}

The relative degrees of crystallinity (X_t) of all blends, as a function of crystallization time are shown in Figs. 3(b) and 4(b), respectively. X_t is a relative parameter at time t and it is calculated as follows [30]:

$$X_t = X_t(t)/X_t(t_\infty) = \int_0^t \left(\mathrm{d}H(t)/\mathrm{d}t\right)\mathrm{d}t \Big/ \int_0^\infty \left(\mathrm{d}H(t)/\mathrm{d}t\right)\mathrm{d}t = \Delta H_t/\Delta H_\infty \qquad (1)$$

Here, t=0 and t_∞ are the starting and finishing time, respectively, d$H(t)$/dt is the rate of heat evolution, ΔH_t is the enthalpy generated by time t, and ΔH_∞ is the total enthalpy.

The isothermal crystallization kinetics of LD and its blends with PEG were analyzed by using the Avrami equation [31]:

$$1 - X_t = \exp\left(-kt^n\right) \qquad (2)$$

or

$$\ln\left[-\ln\left(1 - X_t\right)\right] = \ln k + n \ln t \qquad (3)$$

Here, n is the Avrami exponent which depends on the mechanism of nucleation and crystal growth pattern, and k is the overall crystallization rate constant. k and n can be determined from the intercept and slope of $\ln[-\ln(1-X_t)]$ *vs*. $\ln t$, respectively. The obtained values of k and n of neat LD and its blends with PEG in the isothermal crystallization temperature range of 199-207 ℃ are given in Table 3. The average value of the Avrami exponent (n) was about 2.0 for LD, which is similar to that reported in the literatures (for PLA consisting of 98% L-lactic acid and 2% D-lactic acid content, n=2.1-2.4 [32] while for Nature Works PLA 4032D, n=2.0 [23]). Because in the actual experiment, the density of the polymer increased with the crystallization processing and it led to sample volume shrinkage [33]. The value of Avrami exponent n decreased because of the volume shrinkage and sample thickness reduce [34]. After plasticizing LD with PEG, the average value of n was also about 2.2, it means, for the plasticized PLA, the nucleation type should mostly be heterogeneous nucleating and its growth dimension should mostly be two-dimensional space extension. These results suggested that the crystallization mechanisms of sc-PLA and its blends were not affected significantly by the incorporation of the plasticizer PEG [23].

The crystallization rate constant k decreased with increase of crystallization temperature among all samples. On the other hand, at a fixed temperature, the value of k increased when the PEG contents were increased and reached its maximum value at 10 %(wt) PEG (see Table 3), and then decreased when the PEG contents were increased further. This is attributed to two factors: firstly, the incorporation of PEG increases the chain mobility of sc-PLA, which greatly accelerated the crystallization rate. Secondly, the added PEG is a diluent for sc-PLA, which retarded its crystallization [23]. When the addition of PEG was below 10% (wt) the former factor played a dominant role, but once the PEG content was above 10% (wt) the latter factor was the decisive factor.

The crystallization half-time ($t_{1/2}$), which can be obtained from n and k, is another important parameter to discuss the crystallization kinetics of sc-PLA. The value of $t_{1/2}$ can be calculated as follows:

$$t_{1/2} = \left(\ln 2/k\right)^{1/n} \qquad (4)$$

Here, k and n are the same as in Eq.(3). The calculated values of $t_{1/2}$ are also given in Table 3. As expected, the values of $t_{1/2}$ increased as the crystallization temperature increased for all samples. When the crystallization temperature was 201 ℃, the $t_{1/2}$ of the LD sample was 12.7 min, and it decreased to 7.2, 1.6, 2.4 and 4.7 min when the PEG content increased to 5%, 10%, 15% and 20% (wt), respectively. A similar trend was observed at the other crystallization temperatures, wherein the lowest $t_{1/2}$ was also found at 10% (wt) PEG.

Table 3 Isothermal crystallization kinetic parameters for different samples

Sample	T_c /℃	n	k /10^{-3} min^{-n}	$t_{1/2}$ /min
LD	199	2.2	4.64	9.7
	201	2.0	4.29	12.7
	203	2.1	2.83	13.7
	205	2.0	2.20	17.7
	207	2.3	1.30	23.1
LDP_5	199	2.4	7.58	6.6
	201	2.3	7.32	7.2
	203	2.2	6.14	8.6
	205	2.1	4.51	10.9
	207	2.1	3.07	13.2
LDP_{10}	199	2.1	427.41	1.3
	201	2.0	280.83	1.6
	203	2.1	118.84	2.3
	205	2.3	24.72	4.3
	207	2.3	13.98	5.5
LDP_{15}	199	2.0	278.88	1.6
	201	2.0	119.47	2.4
	203	2.4	42.44	3.2
	205	2.5	11.75	5.1
	207	2.3	8.14	6.9
LDP_{20}	199	1.8	124.93	2.6
	201	2.1	27.38	4.7
	203	2.3	12.58	5.7
	205	2.0	10.38	8.2

The crystallization activation energy (ΔE_a) can be approximately calculated as follows:

$$(1/n)\ln k = \ln k_0 - \Delta E_a / RT_c \qquad (5)$$

Here k_0 is the temperature independent pre-exponential factor, R is the gas constant and T is the absolute crystallization temperature.

ΔE_a can be obtained from the slope of a line of $(1/n)\ln k$ *vs*. $1/T_c$ (see Fig. 5). The values of ΔE_a obtained from Fig. 5 are given in Table 4. The value of ΔE_a is negative because sc-PLA releases energy in the isothermal crystallization process. As shown in Table 4, the absolute value of ΔE_a was 209.2 kJ/mol for LD; after the addition of PEG with 5%, 10%, 15% and 20% (wt) the values first decreased to 186.3 and then increased to 335.4, 341.1 and 348.1 kJ/mol, respectively. The decrease was attributed to improvement in the chain mobilities of PLLA and PDLA and acceleration of the combination of the chains of PLLA and PDLA in the formation of sc-PLA caused by the incorporation of plasticizer PEG.

The incorporation of PEG at a relative low content (5% (wt)) improved the chain mobility of PLLA and PDLA and accelerated the combination of the chains of PLLA and PDLA to form sc-PLA. However, once excess PEG (above 10% (wt)) was added, the distance between the PLLA and PDLA molecular chains were enlarged, so the absolute value of ΔE_a increased with increase of PEG content.

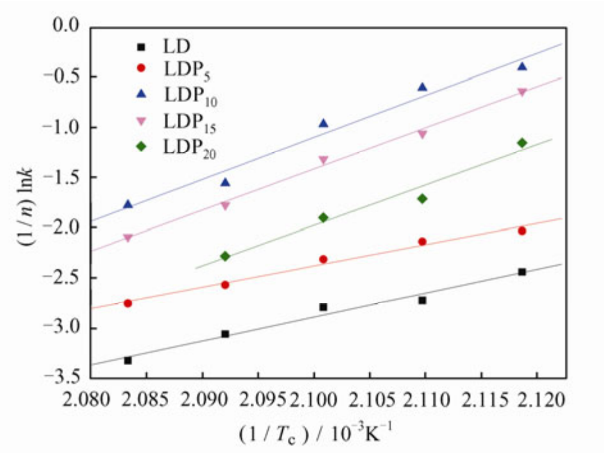

Fig. 5 Plots of (1/*n*)ln*k vs.* 1/T_c for LD and its blends containing PEG

Table 4 Values of crystallization activation energy (ΔE_a) for LD and its blends containing PEG

kJ/mol

Sample	LD	LDP_5	LDP_{10}	LDP_{15}	LDP_{20}
ΔE_a	−209.2	−186.3	−335.4	−341.1	−348.1

According to Hoffman-Weeks theory, the equilibrium melting point T_m^0 can be obtained from the intersection of the resulting straight line with the T_m=T_c equation. The Hoffman-Weeks equation is as follows [32]:

$$T_m = \eta T_c + (1-\eta)T_m^0 \qquad (6)$$

The value of η, which ranges from 0 to 1, can be determined from the slope of the Hoffman-Weeks plot. It can be used to measure the stability of crystals during this type of melting process [32]. The value 0 of slope η indicates that the crystals are perfectly stable, and the value of 1 indicates inherently unstable crystals.

Figure 6 presents the Hoffman-Weeks plots for LD, LDP_5, LDP_{10}, LDP_{15} and LDP_{20} and the results are shown in Table 5. The T_m^0 for LD was about 243.5 ℃ and increased in the presence of PEG, wherein the highest T_m^0 was determined at 260 ℃ for LDP_5 sample. Furthermore, the η increased slightly with the presence of PEG, which indicates that the crystalline phase of sc-PLA remains relatively stable after the addition of PEG.

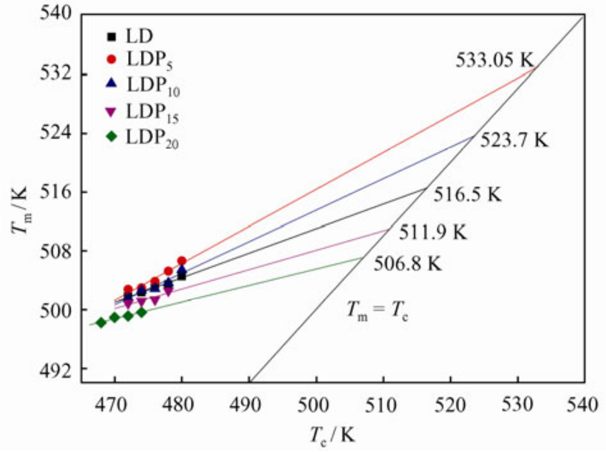

Fig. 6 Hoffman-Weeks plots for LD and its blends containing PEG

Table 5 Results of Hoffman-Weeks analysis of the melting behavior of LD and its blends containing PEG

Sample	T_m^0/℃	η
LD	243.5	0.335
LDP_5	260.0	0.505
LDP_{10}	250.7	0.430
LDP_{15}	237.9	0.275
LDP_{20}	233.8	0.220

2.3 Optical Microscopy Observations

The spherulitic morphology of neat LD and its blends containing various PEG contents after 5 min crystallization at 201 ℃ are shown in Fig. 7. It was obvious that the sc-PLA exhibited typical spherulites. The density and size of the sc-PLA spherulite in LDP samples increased up to 10% PEG content then decreased with further increase of PEG content. This was because incorporation of PEG facilitated chain movement thus accelerating the spherulitic growth rate of sc-PLA, but the promoting effect was limited by the dilution effect of the plasticizer on the PLLA and PDLA molecule chains, which retarded its crystallization [35].

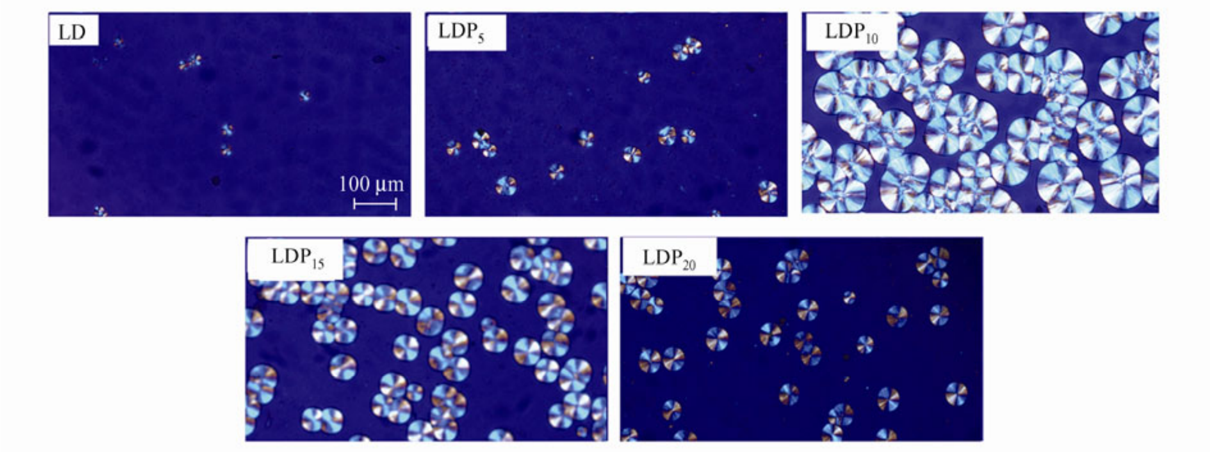

Fig. 7 Polarizing optical micrographs of the various samples crystallized isothermally at 201 ℃ for 5 min

3 Conclusion

The effects of the plasticizer PEG on the formation and crystallization behaviors of sc-PLA were investigated. When PLLA and PDLA were blended at 240 ℃, which is higher than the melting temperature of sc-PLA, both hc-PLA and sc-PLA formed in the blend. However, the WAXD and DSC analysis showed that exclusive sc-PLA crystallites, without any hc-PLA crystallites, formed after the incorporation of PEG. The crystallinity of the sc-PLA crystallites increased with increase of PEG content and reached the maximum value 52.66% at 10% (wt) PEG content. Isothermal crystallization observations also indicated that PEG could accelerate the crystallization rate of sc-PLA. During the crystallization, the half crystallization time of sc-PLA decreased significantly at 10% (wt) PEG content, while the crystallization activation energy of sc-PLA decreased with 5%(wt) PEG, both factors then increasing with further increase in PEG. The density and size of the sc-PLA spherulite in LDP samples increased up to 10% PEG content then decreased with further increase of PEG content. These results showed that the addition of the proper amount of PEG (10 %(wt)) is an effective way to prepare sc-PLA crystallites and promote its formation without any additional formation of hc-PLA at a processing temperature of 240 ℃.

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