

Thermal performances and optical property of poly(L-lactic acid) under the influence of *N,N'*-dodecanedioic bis(3-phenylpropionic acid) dihydrazide as a crystallization promoter

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Abstract: Poly(L-lactic acid) (PLLA) as an important biodegradable polymer suffers from slow crystallization rate and poor heat resistance. An organic compound *N,N'*-dodecanedioic bis(3-phenylpropionic acid) dihydrazide (BHADD) was synthesized to evaluate its general influences on the physical properties of PLLA. The melt-crystallization process indicated that BHADD could serve as a heterogeneous nucleating agent for improving the crystallization of PLLA, and PLLA/1%BHADD exhibited the sharpest melt-crystallization peak located at the highest temperature, as well as an increase of cooling rate weakened the crystallization ability of BHADD-nucleated PLLA. And the final melting temperature also displayed the significant effect on the crystallization process of PLLA. For the cold-crystallization process, both BHADD concentration and heating rate affected the cold-crystallization behavior of PLLA/BHADD, the increasing of BHADD concentration caused the cold-crystallization peak to shift to the lower temperature; in contrast, a higher heating rate during heating led to the peak's shift toward the higher temperature because of the thermal inertia. The melting behavior of PLLA/BHADD depended on the crystallization temperatures and heating rates, and the double melting peaks were attributed to the melting-recrystallization. Thermal decomposition experiment showed all PLLA/BHADD samples as the pure PLLA only exhibited one thermal decomposition stage, but PLLA/BHADD had a lower thermal stability than the pure PLLA. Additionally, the addition of BHADD seriously decreased the light transmittance of PLLA.

Keywords: poly(L-lactide), dodecanedioic acid dihydrazide, nucleating agent, crystallization.

Wpływ dihydrazidu kwasu bis(3-fenylopropiono) *N,N'*-dodekanodiowego jako promotora krystalizacji na właściwości termiczne i optyczne poli(kwasu L-mlekowego)

Streszczenie: Poli(kwas L-mlekowy) (PLLA) to ważny biodegradowalny polimer charakteryzujący się małą szybkością krystalizacji i słabą odpornością na ciepło. Dihydrazyd kwasu bis(3-fenylopropiono) *N,N'*-dodekanodiowego (BHADD) zsyntetyzowano w celu oceny jego wpływu na właściwości fizyczne PLLA. Przebieg procesu krystalizacji ze stopu świadczy o tym, że BHADD może służyć jako heterogeniczny środek zarodkujący zwiększający szybkość krystalizacji PLLA. Mieszanka PLLA/1% mas. BHADD wykazywała najostrejszy pik krystalizacji ze stopu zlokalizowany w zakresie najwyższej temperatury, a jednocześnie większą szybkość chłodzenia osłabiającą zdolność krystalizacji PLLA zarodkowanej BHADD. Również końcowa temperatura topnienia w istotnym stopniu wpływała na proces krystalizacji PLLA. W procesie krystalizacji na zimno zarówno stężenie BHADD, jak i szybkość ogrzewania oddziaływały na zachowanie PLLA/BHADD podczas krystalizacji, zwiększenie stężenia BHADD powodowało przesunięcie piku krystalizacji na zimno w kierunku niższej temperatury, natomiast większa szybkość ogrzewania prowadziła do, spowodowanego bezwładnością cieplną, prze-

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sunięcia piku krystalizacji na zimno w kierunku wyższej temperatury. Zachowanie PLLA/BHADD podczas topnienia zależało od temperatury krystalizacji i szybkości ogrzewania, a drugi pik topnienia przypisano procesowi rekrytalizacji. Badany przebieg rozkładu termicznego świadczy, że wszystkie próbki PLLA/BHADD, tak jak czysty PLLA, wykazywały tylko jeden etap rozkładu termicznego, mieszanina PLLA/BHADD charakteryzowała się jednak mniejszą stabilnością termiczną niż czysty PLLA. Dodatek BHADD w znacznym stopniu zmniejszył przepuszczalność światła PLLA.

Słowa kluczowe: poli(L-laktyd), dihydrazid kwasu dodekanodiowego, środek zarodkujący, krystalizacja.

In recent years, noxious waste pollution has become increasingly serious with large-scale usage of non-degradable plastics, poly(L-lactic acid) (PLLA) as an environment-friendly polymer can reduce the environmental pollution from the source. Furthermore, the many advantages of PLLA itself including the excellent biodegradability and biocompatibility [1], renewability [2], non-toxicity [3] lead to its wide application in tissue engineering [4, 5], 3D printing [6, 7], packaging [8, 9], *etc.* For instance, Li *et al.* [10] reported that the CZ48 (a 20-O-propionate ester of camptothecin) was incorporated into poly(lactic acid) microbubbles were prepared through a double emulsion technique, and the availability of both CZ48 and its metabolite camptothecin (CPT) were significantly enhanced after the incorporation of CZ48 into PLA microbubbles, which indicated that the CZ48-loaded poly(lactic acid) microbubbles exhibited a much higher anticancer effect. However, the existence of some inherent defects of PLLA itself such as poor heat resistance, low crystallinity and slow crystallization rate seriously restricts its industrial application. Among these aforementioned defects, slow crystallization rate is thought to be the worst, because the crystallization rate of PLLA determines its crystallinity; on the other hand, the high crystallinity must result in the excellent heat resistance. Thus, accelerating the crystallization of PLLA is very necessary to both fundamental research and technical applications.

Adding the nucleating agent is very effective way to facilitate the crystallization of semi-crystalline polymer, the reason is that a nucleating agent can reduce surface free energy barrier of nucleation. Additionally, the nucleating agent also exhibits other advantages such as low dosage, excellent nucleation effect, *etc.* [11]. Upon to now, many compounds with inorganic structures, organic structures, or inorganic/organic hybrid structures had been employed to investigate their nucleation effect on the crystallization process of PLLA. And the current typical nucleating agents include talc [12, 13], montmorillonite [14, 15], silicon dioxide [16], calcium carbonate [17, 18], phenylphosphonate metals [19, 20], metallic phenylmalonate salts [21], 1H-benzotriazole derivatives [22, 23], benzoyl hydrazine derivatives [24, 25], *etc.* For examples, upon the addition of 0.5 wt % commercial graphene oxide nanoplatelets, the half-time of crystallization of the PLA stereocomplex lower to around 5.5 min at 165°C [26]. Even

then, the current nucleating agents for PLLA are still not able to meet the commercial requirements. Thus, developing more efficient nucleating agents becomes very urgent, only in this way, the nucleation mechanism can be thoroughly revealed through a significant amount of research on the effect of nucleating agents on the crystallization process of PLLA, and then more commercial nucleating agents for PLLA will appear. Especially for organic nucleating agents, it is urgent to establish the structure-activity relationship between molecular structures and nucleation ability of PLLA.

Given this, in the current study, a new organic nucleating agent, *N,N'*-dodecanedioic bis(3-phenylpropionic acid) dihydrazide (designated as BHADD), was synthesized to evaluate its potential influences on the properties of PLLA. In particular, the melt-crystallization, cold-crystallization, melting behavior, thermal stability, as well as optical property of BHADD-nucleated PLLA were investigated in detailed using various testing techniques including differential scanning calorimeter (DSC), thermal gravimetric analyzer (TGA) and light transmittance.

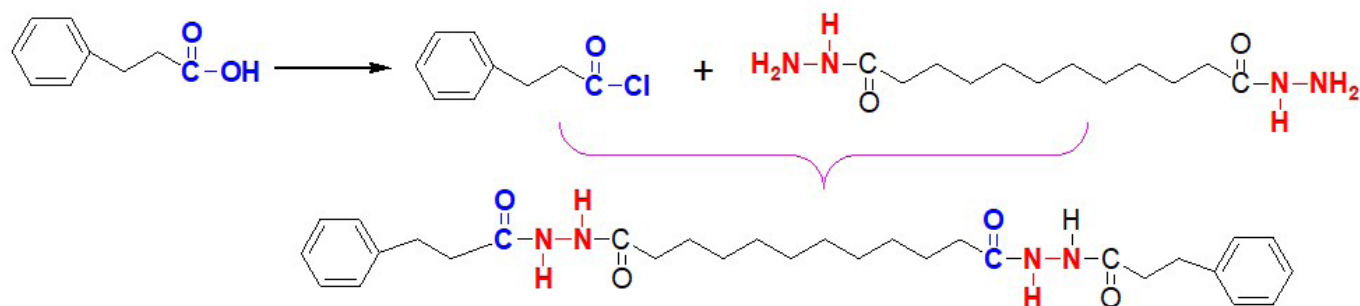
EXPERIMENTAL PART

Materials

The 4032D PLLA with 1.20% of D content was purchased from Nature Works LLC, USA, and the M_w of 4032D was $1.70 \cdot 10^5$ g/mol. The BHADD was synthesized in our lab, and during the synthesis process, all used chemical reagents including 3-phenylpropionic acid, dodecanedioic dihydrazide, trimethylamine, thionyl chloride and *N,N*-dimethylformamide (DMF) were obtained from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of BHADD

The synthesis of BHADD was completed via two step reaction of acylation and amination (Scheme A). Firstly, the 3-phenylpropionic acid was added into the excessive thionyl chloride solvent in the presence of DMF as catalyst to synthesize the 3-phenylpropionyl chloride. And then the 3-phenylpropionyl chloride of 0.008 mol was added into the dodecanedioic dihydrazide of 0.004 mol mixed solution including 70 cm³ DMF and 0.008 mol trimethylamine, and the mixture was stirred under ice bath



Scheme A

for 1 h, heated up to 60°C for 4 h with stirring. Finally, the mixed solution was poured into the distilled water to obtain the precipitate, followed by filtrating, and the crude filter was further washed by the distilled water to obtain the resulting yellow product BHADD. Fourier transform infrared spectroscopy (FT-IR) ν [cm^{-1}]: 3316.7, 3217.4, 2921.7, 2849.7, 1633.0, 1600.5, 1535.7, 1483.2, 1413.3, 1379.9, 1338.8, 1270.9, 1213.6, 1162.3, 1011.9, 973.7, 932.8, 697.7; ^1H nuclear magnetic resonance (^1H NMR) δ [ppm]: 9.72 (s, 1H, NH), 9.67 (s, 1H, NH), 7.17–7.30 (m, 5H, Ar), 2.80–2.84 (t, 4H, CH_2), 2.40–2.50 (t, 2H, CH_2), 1.98–2.11 (m, 4H, CH_2), 1.22–1.24 (m, 4H, CH_2).

Preparation of PLLA/BHADD samples

Before blending, the PLLA and BHADD were thoroughly dried in a vacuum oven for 36 h to remove probable water. And a counter-rotating mixer was used to perform the blend of PLLA with various BHADD concentrations from 0.5 to 3 wt %. The similar operation process was reported in our works [27, 28], and the blending temperature was set at 190°C, the blending time was 10 min at a rotation speed of 32 rpm and 7 min at a rotation speed of 64 rpm. The resulting mixture was further hot pressed at 190°C and cool pressed at room temperature in a sheet mold with 0.4 mm thickness, respectively.

Methods of testing

BHADD structure characterization

The FT-IR (IS50, Thermo Fisher Scientific) and ^1H NMR (AVANCE 400MHz, Bruker) were employed to characterize the molecular structure of BHADD. Before FT-IR measurement, KBr pellet was used to prepare the testing sample, and the testing wave number was from 4000 to 400 cm^{-1} . For ^1H NMR characterization, the dimethyl sulfide was selected to dissolve the BHADD.

Melt-crystallization behavior

The melt-crystallization processes of the pure PLLA and PLLA/BHADD samples were recorded by DSC (Q2000, TA instrument) with 50 cm^3/min nitrogen. The samples were heated to a set melting temperature

(180–200°C) and maintained at that temperature for 3 min to eliminate thermal history, and then the samples were cooled from the melt to 40°C at different cooling rates (1, 5, 10°C/min), and the relevant DSC curves were recorded for further analyzing.

Cold-crystallization behavior

The cold-crystallization behaviors of PLLA/BHADD samples were still tested by DSC. The PLLA/BHADD sample was firstly heated to 190°C for 3 min to eliminate thermal history, and then was rapidly cooled to 40°C for 3 min. Finally, the sample was heated to 190°C at different heating rates (1, 5, 10°C/min) under nitrogen.

Melting behavior

The melting processes after melt-crystallization and isothermal crystallization were also recorded by DSC. After completing the melt-crystallization at cooling of 1°C/min, the subsequent melting processes were performed at different heating rates including 1, 3, 5, 10°C/min. For the melting behavior after isothermal crystallization at 100°C and 130°C for different time (60, 30 min), the heating rate was 10°C/min.

Thermal decomposition behavior

The thermal decomposition under flowing air were tested by TGA (Q500, TA instrument), and the testing temperature range was from 50 to 650°C, and the heating rate was 5°C/min.

Optical property

A light transmittance meter (DR82, Donru Electronic Technology) was used to test the light transmittance, and the light transmittance of a given sample was obtained by averaging over five measurements.

RESULTS AND DISCUSSION

Non-isothermal crystallization behavior

The difference in non-isothermal crystallization behavior can effectively reflect the role of the additive

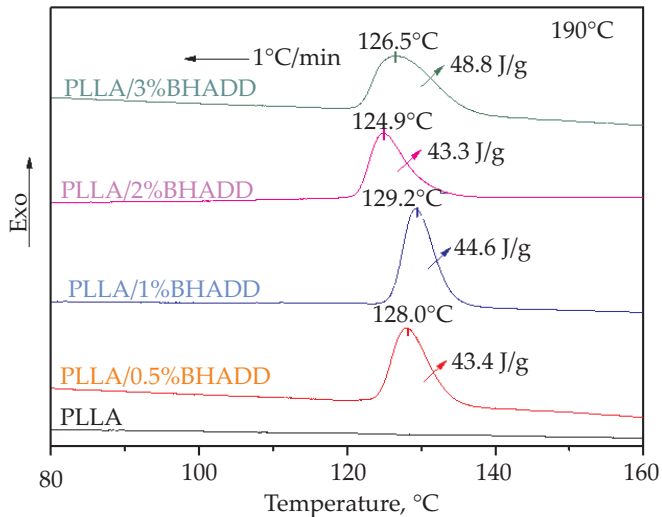


Fig. 1. Melt-crystallization of the pure PLLA and PLLA/BHADD samples at a cooling rate of 1°C/min

for PLLA. Hence a comparative study on the non-isothermal crystallization of the pure PLLA and PLLA/BHADD was firstly performed by DSC. Figure 1 shows the DSC curves of the melt-crystallization of the pure PLLA and

PLLA/BHADD samples from 190°C at a cooling rate of 1°C/min. For the pure PLLA, the melt-crystallization peak can almost not be observed in DSC curve, meaning the appearance of no crystal in cooling, which results from the very poor crystallization ability of PLLA itself.

However, for any PLLA/BHADD sample, an obvious melt-crystallization peak appears in DSC curve, indicating that the addition of BHADD promotes the crystallization of PLLA in cooling, because the BHADD as a heterogeneous nucleating agent can provide a great deal of nucleus in PLLA matrix, resulting in that the PLLA/BHADD sample has very fast nuclear rate. Under this circumstance, a slow cooling rate (1°C/min) in high-temperature region can also make the PLLA molecular chain possess the excellent mobility. As a result, the crystals can be rapidly formed in cooling. Additionally, as seen in Fig. 1, the BHADD concentration also exhibits its distinct influence on the crystallization process of PLLA. With increasing of BHADD concentration from 0.5 to 3 wt %, the melt-crystallization peak firstly shifts toward the high-temperature, and then moves to the low-temperature, finally, the melt-crystallization peak shifts to the high-temperature again. On one hand, a larger

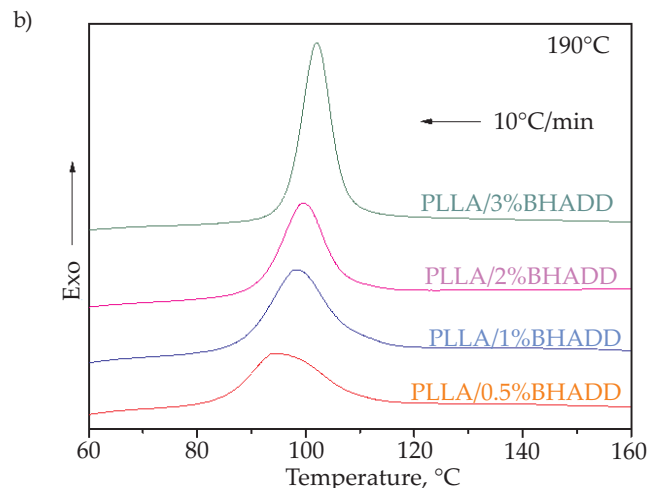
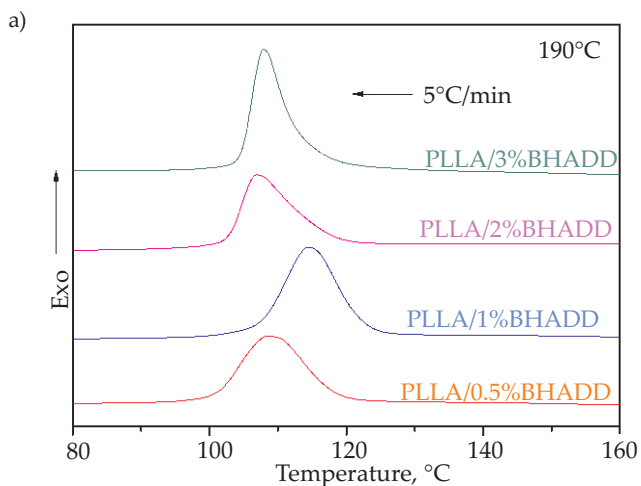


Fig. 2. Melt-crystallization of PLLA/BHADD samples at different cooling rates: a) 5°C/min, b) 10°C/min

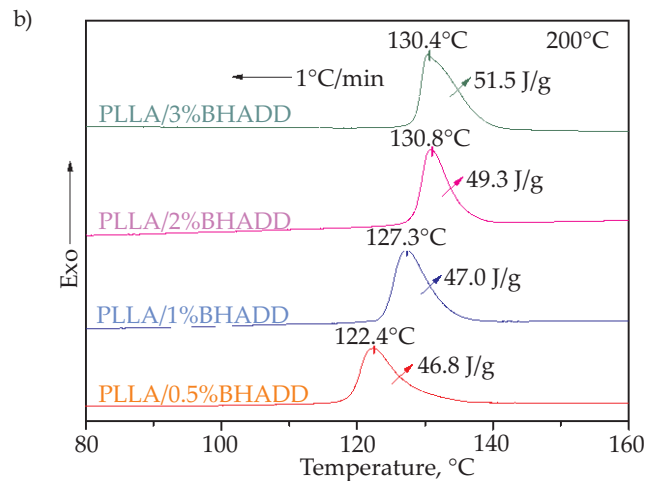
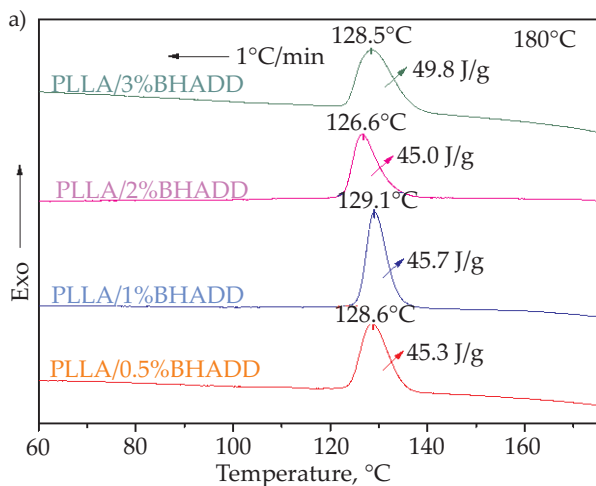


Fig. 3. Melt-crystallization of PLLA/BHADD samples from different T_f at a cooling rate of 1°C/min: a) $T_f = 180^\circ\text{C}$, b) $T_f = 200^\circ\text{C}$

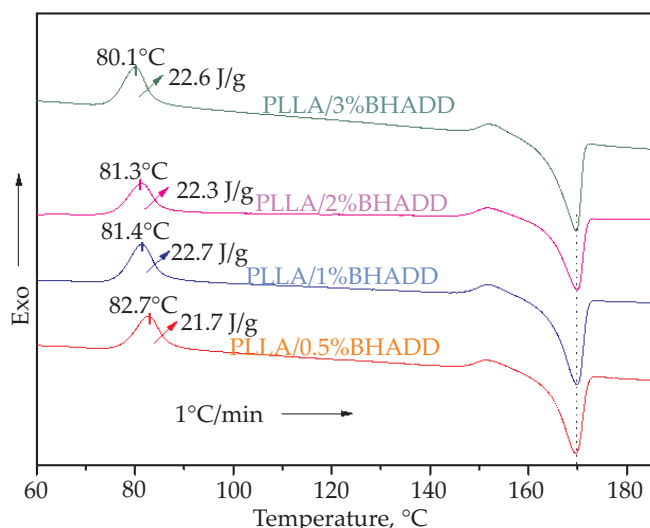


Fig. 4. Cold-crystallization behavior of PLLA/BHADD

number of BHADD must lead to the higher nuclear density in PLLA matrix, which promotes the PLLA to crystallize at a higher temperature; on the other hand, the excessive BHADD has an inhibition for the mobility of PLLA molecular chain. This competitive relationship determines the location of melt-crystallization peak in DSC curve. Compared to the other PLLA/BHADD samples, PLLA/1%BHADD exhibits the sharpest melt-crystallization peak and the highest melt-crystallization peak temperature of 129.2°C, but the PLLA/3%BHADD has the largest melt-crystallization enthalpy of 48.8 J/g.

Usually, a higher cooling rate is required during industrial production, meanwhile, the crystallization behavior at a higher cooling rate can more fully characterize the nucleation effect of BHADD for PLLA.

Figure 2 is the melt-crystallization process of PLLA/BHADD samples from 190°C at different cooling rates. It is clear that the melt-crystallization peak of a given PLLA/BHADD sample shifts toward the low-temperature with increasing of cooling rate from 5 to 10°C/min, indicating that an increase of cooling rate weakens the nucleation ability of BHADD for PLLA.

Although PLLA/BHADD sample has the high nucleation rate, it still takes time to form crystals at the crystal growth stage, whereas there is no enough time to cause the nucleus to grow into crystals at a high cooling rate. Thus, the crystallization can only be completed in a lower temperature region. Meantime, it is noted that, when the cooling rate is 10°C/min, the melt-crystallization peak moves toward the high-temperature with increasing of BHADD concentration. This result may depend on the competitive relationship between the cooling rate and BHADD concentration, that is, a higher BHADD concentration can offset the negative effect of a higher cooling rate on the crystallization ability of PLLA/BHADD samples. Moreover, PLLA/3%BHADD exhibits very sharp melt-crystallization peak at 102.1°C, further showing the powerful nucleation ability of BHADD for PLLA. However, the effect of BHADD on

the melt-crystallization of PLLA at cooling of 10°C/min is different from that at cooling of 1 and 5°C/min, indicating a complicated crystallization process, and more in-depth experiments will be conducted to explain this result in a future study.

For the melt-crystallization, the final melting temperature (T_f) is another important influencing factor for the crystallization behavior [29]. Figure 3 displays the melt-crystallization behavior of PLLA incorporating different BHADD concentration from the different T_f at a cooling rate of 1°C/min.

It is observed that the differences in melt-crystallization peak temperature and enthalpy of a given PLLA/BHADD sample are greatly obvious, because the solubility of BHADD in PLLA matrix depends on the T_f and it is solubility that determines the compatibility between PLLA and BHADD and the undissolved BHADD concentration, which further determines the nucleation density in PLLA matrix. For a given PLLA/BHADD sample, the melt-crystallization enthalpy firstly decreases, and then increases with increasing of the T_f from 180°C to 200°C. That is to say, when the T_f is 190°C, PLLA/BHADD sample exhibits the minimum melt-crystallization enthalpy. In contrast, the melt-crystallization enthalpy from 200°C possesses the maximum value. Even the melt-crystallization enthalpy of PLLA/3%BHADD runs up to 51.5 J/g, meaning that the crystallinity is 57.1% according to the equation (1) [30].

$$X_c = \frac{\Delta H_c}{93(1-y\%)} \cdot 100\% \quad (1)$$

X_c – crystallinity, ΔH_c – the melt-crystallization enthalpy, $y\%$ – the percentage content of additive.

Figure 4 shows the cold-crystallization process of PLLA containing different BHADD concentration at a heating rate of 1°C/min. Differing from the complicated melt-crystallization process, the influence of BHADD concentration on the cold-crystallization of PLLA is relatively simple. That is, the cold-crystallization peak shifts toward the lower temperature with increasing of BHADD concentration, indicating that a larger loading of BHADD can cause the crystallization of PLLA to occur at a lower temperature. This effect may depend on the weakening role of intermolecular interactions of PLLA molecular chains, because any PLLA/BHADD sample has very fast nucleation rate in low temperature region due to the heterogeneous nucleation of BHADD and homogeneous nucleation of PLLA itself. Under this circumstance, the crystal growth rate is rate-determining step for the overall crystallization process. On the other hand, a larger loading of BHADD exhibits a stronger weakening role in intermolecular interactions of PLLA molecular chains (This result will be further proved in the subsequent fluidity study section), resulting in the better mobility of PLLA molecular chain. According to the above-mentioned two reasons, the PLLA incorporating a larger loading of BHADD can crystallize at a lower temperature.

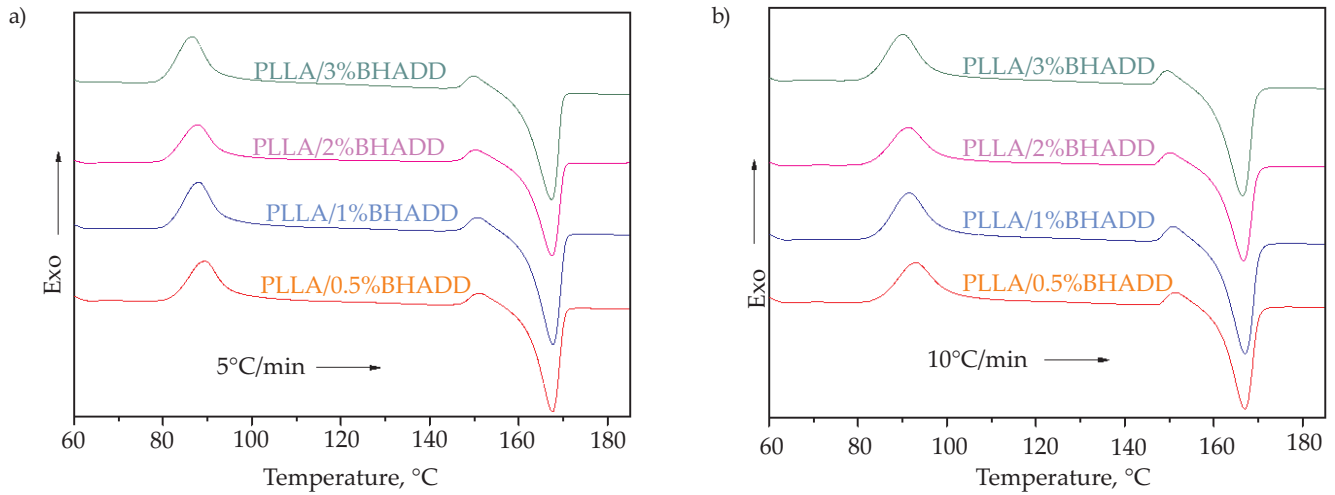


Fig. 5. Cold-crystallization process of PLLA/BHADD at different heating rates: a) 5°C/min, b) 10°C/min

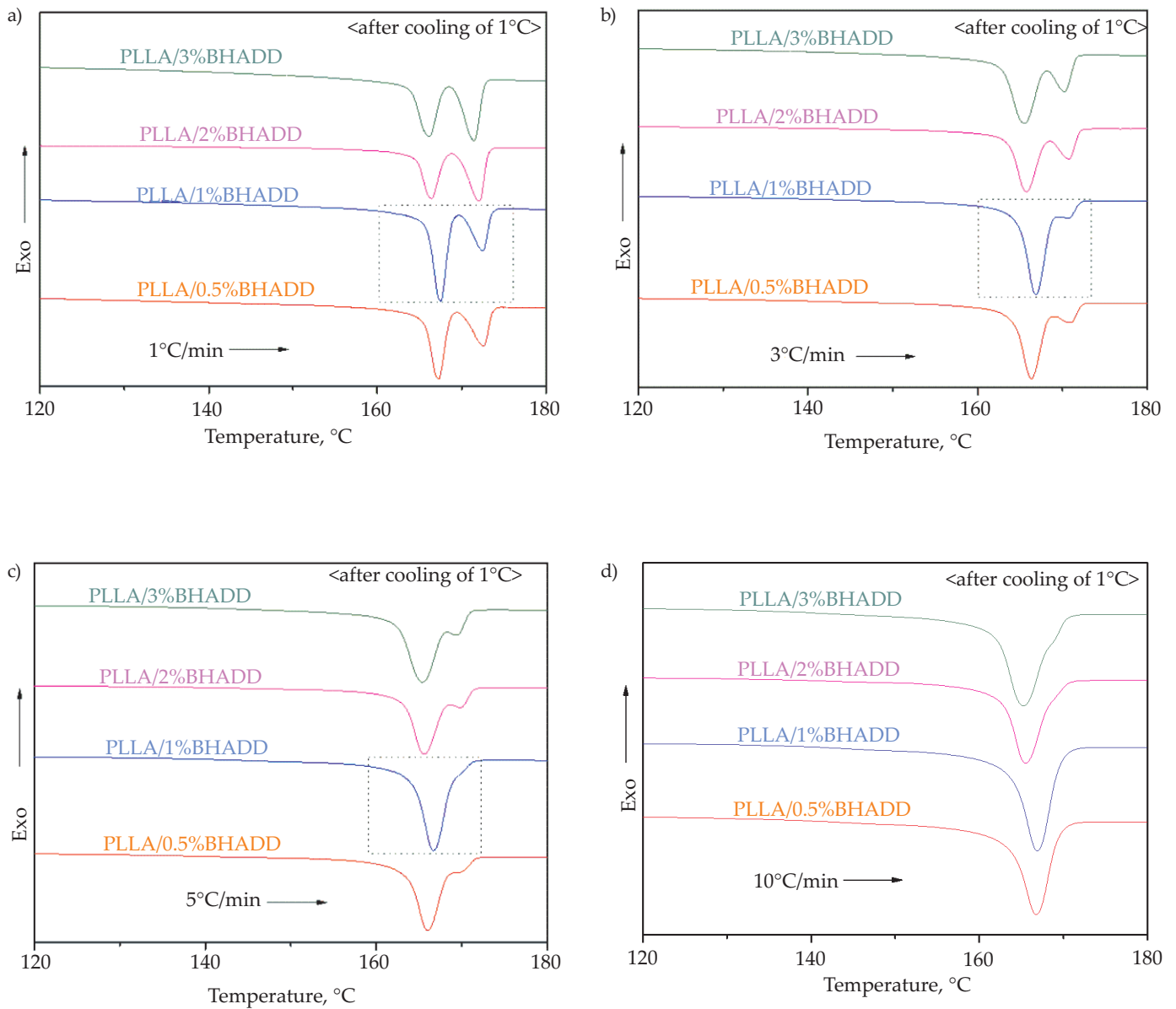


Fig. 6. Melting behavior of PLLA/BHADD samples at a different heating rate after melt-crystallization: a) 1°C/min, b) 3°C/min, c) 5°C/min, d) 10°C/min

Additionally, for a given PLLA/BHADD sample, the increase of heating rate leads to the shift to the higher temperature (Fig. 5), which be thought to be because of the thermal inertia.

Melting behavior

The melting behavior not only can represent the role of the BHADD in PLLA matrix but also is the important part of thermal property. Figure 6 shows the melting behavior of PLLA containing different BHADD concentration at a different heating rate after cooling of 1°C/min from the melt. With increasing of heating rate, the high-temperature melting peak gradually degenerates and form the single peak together with the low-temperature melting peak, the reason is that a higher heating rate exhibits a greater inhibition for the formation of the second crystal in heating. This result also

reveals that the double-melting peak behavior in this study ascribes to the melting-recrystallization mechanism. And the melting-recrystallization mechanism thinks that the low-temperature melting peak results from the primary crystallites formed in cooling, and high-temperature melting peak reflects the crystallites reformed in heating [31].

Meantime, it is noted that PLLA/1%BHADD has the sharper low-temperature melting peak comparing with other PLLA/BHADD samples, as well as this low-temperature melting peak locates at the higher temperature, which shows that the crystallites formed in cooling are more perfect. In addition, the high-temperature melting peak area of PLLA/1%BHADD is also the minimum under the same circumstance, indicating that the PLLA/1%BHADD only forms the least crystallites in heating, because the most crystallization have been completed in cooling, further confirming the best accelerat-

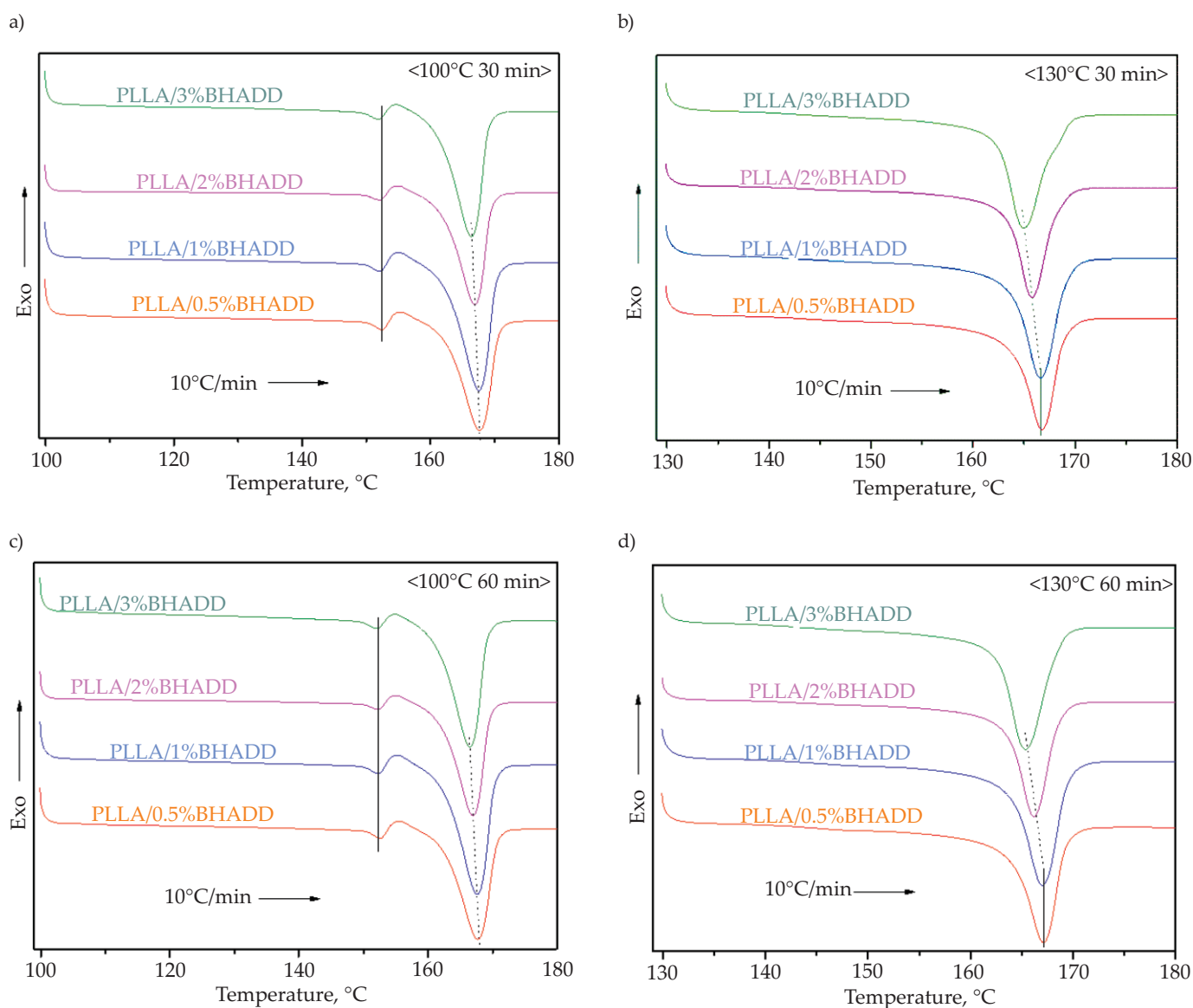


Fig. 7. Melting behavior of PLLA/BHADD samples at a heating rate of 10 °C/min after isothermal crystallization: a) 100°C 30 min, b) 130°C 30 min, c) 100°C 60 min, d) 130°C 60 min

ing effect of 1 wt % BHADD for PLLA crystallization, which is consistent with the aforementioned melt-crystallization DSC results.

For the semi-crystalline polymers, the crystallization temperature is range from glass-transition temperature to melting temperature, thus, the crystallization temperature is very important factor for the crystallization behavior as reported by literatures [32, 33]. With it, the melting behavior of PLLA/BHADD must be affected by the crystallization temperature. Figure 7 shows the melting behavior of PLLA/BHADD samples at a heating rate of 10°C/min after isothermal crystallization at different temperatures for different time. After isothermal crystallization at 100°C, all PLLA/BHADD sample exhibit the double-melting peaks, whereas the PLLA/BHADD sample has only the single melting peak after crystallization at 130°C.

In low temperature region, the mobility of PLLA molecular chain is very poor, resulting in very slow crystal growth. As a result, it is hard to form a large number of crystallites at 100°C. In contrast, when the crystallization temperature is 130°C, PLLA molecular chain possesses the excellent mobility, at the same time, the existence of BHADD can promote the crystallization process to be rapidly completed, ultimately representing as a single melting peak at melting stage. It is also observed from Fig. 7 that the difference in melting behavior after crystallization at a given temperature for 30 min or 60 min is negligible, confirming the importance of crystallization temperature again.

Thermal stability and optical property

For any materials, thermal decomposition temperature is the critical temperature of usage. Here, the thermal decomposition process of the pure PLLA and PLLA/BHADD samples was studied by TGA. Figure 8 shows the TGA curves of the pure PLLA and

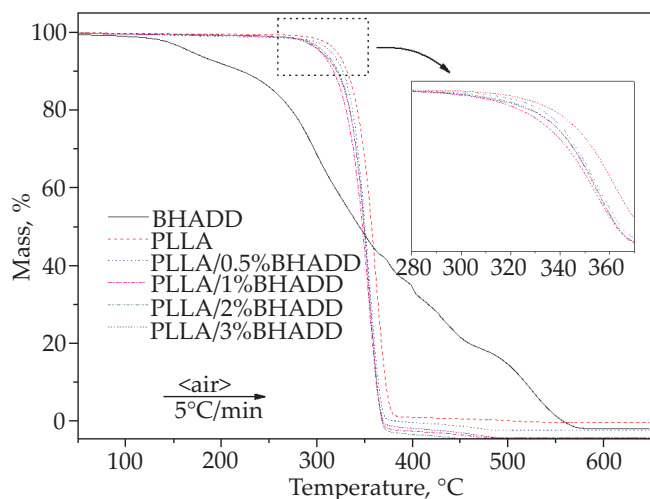


Fig. 8. TGA curves of the BHADD, pure PLLA and PLLA/BHADD samples

PLLA/BHADD at a heating rate of 5°C/min from the room temperature to 650°C under air. It is clear that the BHADD exhibits different thermal decomposition process comparing with the pure PLLA and PLLA/BHADD samples.

That is, the BHADD has three thermal decomposition stages, whereas both PLLA/BHADD sample and the pure PLLA only exhibit one thermal decomposition stage, and the predominant thermal weightlessness occurs at 300°C to 375°C, attributing to the chain scissions and loss of ester groups [11, 34]. This result shows that the influence of the dosage of BHADD in this study on the thermal decomposition profile of PLLA is negligible. On the other hand, this result also directly indicates the agglomeration of BHADD does almost not appears to a certain extent, because the serious agglomeration can leads to a fact that the thermal decomposition feature of BHADD must appears in TGA curves. However, as seen in Fig. 8, the addition of BHADD can significantly affect the onset thermal decomposition temperature of PLLA (T_{od}). And the T_{od} of the pure PLLA, PLLA/0.5%BHADD, PLLA/1%BHADD, PLLA/2%BHADD and PLLA/3%BHADD appears at 341.3°C, 335.0°C, 331.1°C, 334.4°C and 334.6°C, respectively. Through the analysis of T_{od} data, it is a fact that the all PLLA/BHADD samples have a lower thermal stability than the pure PLLA. Additionally, it is noted that the T_{od} firstly decreases with increasing of BHADD concentration, and then increases. An increase of the T_{od} may result from the hydrogen-bonding interaction between the C=O of PLLA molecular chain and the N-H of BHADD, and the thermal decomposition process of PLLA/BHADD firstly needs to destroy this hydrogen-bonding interaction, and then the thermal decomposition of PLLA occurs.

The light transmittance of the pure PLLA and PLLA/BHADD samples was compared using the light

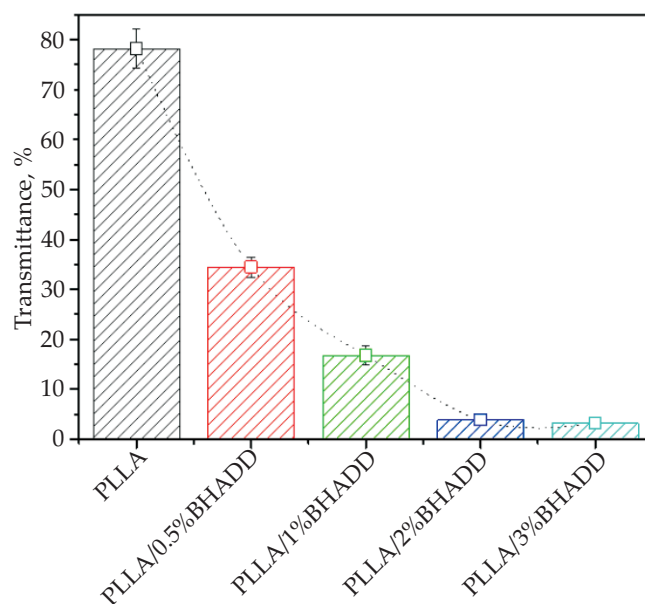


Fig. 9. Light transmittance of the pure PLLA and PLLA/BHADD samples

transmittance meter, and the corresponding measurement result was demonstrated in Fig. 9.

Contrary to the result of MFR, the introduction of BHADD seriously decreases the light transmittance of PLLA. Two probable reasons are used to explain the drop in the light transmittance, one is yellow BHADD itself which is main reason for decreasing of light transmittance; another may be a slight increase of crystallinity of PLLA/BHADD samples after melting blend.

CONCLUSIONS

In this work, BHADD as a crystallization promoter was designed and synthesized to accelerate the crystallization of PLLA. Non-isothermal crystallization confirmed the crystallization promoting effect of BHADD for PLLA. Upon cooling of 1°C/min, PLLA/1%BHADD exhibited the sharpest melt-crystallization peak and the highest melt-crystallization peak temperature of 129.2°C, but the PLLA/3%BHADD had the largest melt-crystallization enthalpy of 48.8 J/g. An increase of cooling rate weakened the crystallization ability of BHADD-nucleated PLLA, but the existence of the obvious crystallization peak, which formed in cooling at a higher cooling rate, evidenced the powerful crystallization ability of PLLA/BHADD again. The effect of T_f on the crystallization process of PLLA/BHADD was distinct, when the T_f was 200°C, PLLA/BHADD had the largest melt-crystallization enthalpy. For the cold-crystallization behavior, the BHADD concentration and heating rate were two important factors for the cold-crystallization process, but the influence of BHADD concentration and heating rate on the cold-crystallization peak was opposite. The melting behavior of PLLA/BHADD after different crystallization process further confirmed the crystallization accelerating effect of BHADD for PLLA, additionally, the crystallization temperature and heating rate significantly affected the melting behavior of PLLA/BHADD. The appearance of double melting peaks in heating was thought to result from the melting-recrystallization. The addition of BHADD could not change the thermal decomposition profile of PLLA, however, decreased the T_{od} of PLLA, indicating the drop in thermal stability. It is noted that the T_{od} increased with increasing of BHADD concentration from 1 to 3 wt %, possibly resulting from the hydrogen-bonding interaction between PLLA and BHADD. Compared to the pure PLLA, the light transmittance of the PLLA/BHADD samples seriously decreased.

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