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Li-Sha Zhao, Yan-Hua Cai* and Hui-Li Liu

N, N'-sebacic bis(hydrocinnamic acid) dihydrazide: A crystallization accelerator for poly(L-lactic acid)

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Abstract: Developing more organic nucleating agent with different molecular structure is very instructive to improve the crystallization of poly(L-lactic acid) (PLLA) and explore the crystallization mechanism. In this study, *N, N'*-sebacic bis(hydrocinnamic acid) dihydrazide (HAD) was synthesized to serve as a nucleating agent for PLLA. The effects of HAD on the non-isothermal crystallization, melting behavior, thermal stability and optical performance of PLLA were investigated by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), and light transmittance meter. The melt crystallization behavior showed that HAD was able to promote the crystallization of PLLA *via* heterogenous nucleation in cooling, and it was found that, upon the cooling of 1°C/min, the incorporation of 1 wt% HAD made the crystallization temperature and non-isothermal crystallization enthalpy increase from 94.5°C and 0.1 J/g to 131.6°C and 48.5 J/g comparing with the pure PLLA. Additionally, the melt crystallization significantly depended on the cooling rate and the final melting temperature. For the cold crystallization, when the nucleation density from HAD and PLLA itself was saturated, the influence of the HAD concentration on the cold crystallization process of the PLLA/HAD samples is negligible. The melting behavior after isothermal or non-isothermal crystallization further confirmed the crystallization accelerating effect of HAD for PLLA, and the appearance of the double melting peaks was attributed to the melting-recrystallization. Unfortunately, the addition of HAD decreased the thermal stability and light transmittance of PLLA.

Keywords: poly(L-lactic acid); non-isothermal crystallization; organic nucleating agent; thermal stability; sebacic dihydrazide

1 Introduction

Poly(L-lactic acid) (PLLA), as an alternative to petroleum-based polymers, exhibits many advantages including excellent biodegradability (1), bio-compatibility (2) and renewability (3), which results in that the PLLA has gained increasing attentions and applications in food packaging (4-6), biomedicine (7,8), agricultural machineries (9), etc. For example, PLLA/SiOx layered film, fabricated by plasma-enhanced chemical vapor deposition, exhibited higher Young's modulus and tensile strength comparing to the pure PLLA. And through practical application in equilibrium-modified atmosphere packaging of chilled meat and analysis of gas composition in packaging, the results indicated that the PLLA/SiOx layered film could be potentially applied for equilibrium-modified atmosphere packaging to extend the shelf life of chilled meat (10).

Unfortunately, the crystallization rate of the pure PLLA is very slow and almost no crystallization proceeds under practical processing (11), resulting in lower heat distortion temperature and limited usage of the final products. Thus, improving the crystallization is essential to theoretical research and practical application of PLLA. Usually, four ways, including adding plasticizer or nucleating agent, increasing the amount of L-lactide isomers and playing with the molding conditions, are employed to accelerate the crystallization process of PLLA. Among these methods, adding a nucleating agent, in comparison to other methods, exhibits better nucleation effect, better stability, a more simple operation, etc. Thus, many researchers focus on nucleating agents to improve the crystallization of PLLA. At the primary stage, the typical nucleating agents are clays such as talc (12), montmorillonite (13), mica (14), etc. And these nucleating agents exhibited excellent nucleation effect on PLLA. For

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*** Corresponding author: Yan-Hua Cai,** Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing-402160, P.R. China, e-mail: caiyh651@aliyun.com.
Li-Sha Zhao and Hui-Li Liu, Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing-402160, P.R. China.

instance, only 1 wt% talc could cause the crystallization half-time of PLLA to reduce by more than one order of magnitude to less than one minute (15), furthermore, the higher talc loading had the better nucleation ability for PLLA (16). And then with the continuous in-depth research, the other commercial or nano-sized inorganic compounds, including hydroxyapatite (17), silica (18), multiwall carbon nanotubes (19), carbon black (20), etc., were used to serve as nucleating agents for crystallization of PLLA. Up to now, some novel synthetic inorganic compounds like nanoscaled zinc citrate complex (21), layered metal phosphonate (22,23), metallic salts of phenylmalonic acid (24,25), and WS_2 nanotube (26) were further developed to be applied in improving the crystallization of PLLA. However, for all inorganic nucleating agents, poor compatibility and dispersity are their inhere defects in PLLA matrix, potentially resulting in phase separation and a decrease of nucleation ability. In contrast, organic small mass molecule nucleating agents or stereocomplex based on PDLA and PLLA exhibit better compatibility with PLLA (27,28). Moreover, the molecular structures of the organic small mass molecule nucleating agents can be designed and regulated according to analysis of functional groups for PLLA crystallization, which is very important to continuously develop more efficient organic nucleating agents, as well as reveal the relevant nucleation mechanism. Thus, in recent years, many organic small mass molecules, including myo-inositol (29), orotic acid monohydrate (30), benzoylhydrazine derivatives (31,32), 1H-benzotriazole derivatives (33,34), TMC series (35,36), dimethylbenzylidene sorbitol (37), were selected from commercial nucleating agents for other polymers and synthesized to evaluate their role in improving the crystallization of PLLA. Through unremitting efforts from international scientists, the organic small mass molecule nucleating agent is expected to be a promising alternative to inorganic nucleator due to its better nucleation ability (38) and compatibility. Overall, but the categories and number are still very insufficiency comparing with the inorganic nucleating agents (39). Thus, developing more organic nucleating agents with different structures is very urgent and necessary to further clarify the crucial organic groups for accelerating crystallization of PLLA, and reveal the interaction mechanism between PLLA molecular chain and organic nucleating agents.

Within this study, a new organic compound with multi-amide, benzene, and alkyl chain, *N, N'*-sebacic bis(hydrocinnamic acid) dihydrazide (designated as HAD), was synthesized to use as a crystallization accelerator for PLLA. And then the non-isothermal crystallization and melting behavior of HAD-nucleated PLLA were evaluated *via* differential scanning calorimeter (DSC), the thermal stability and optical performance of PLLA in the presence of HAD were further studied by thermogravimetric analysis (TGA), and light transmittance meter.

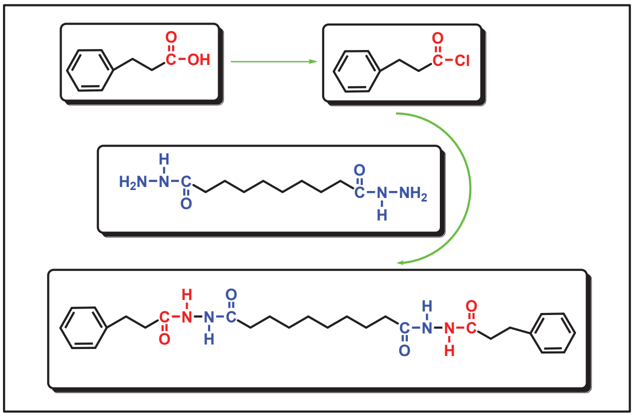
2 Experimental

2.1 Materials and reagents

The PLLA used in this study, PLLA-2002D (M_w: 1.95·10^5, 4.25% D content), was purchased from Nature Works LLC, USA. The nucleating agent HAD was prepared in our lab, and all chemical reagents, used to synthesis HAD, like hydrocinnamic acid, succinic dihydrazide, thionyl chloride, triethylamine and *N, N*-dimethylformamide (DMF) are analytically pure, and these reagents were supplied by Chongqing Huanwei Chemical Co., Ltd. China.

2.2 Synthesis of HAD

The HAD was synthesized through acylation and amination reaction (See Scheme-1). The typical synthesis procedure of HAD was as follows: first, the hydrocinnamoyl chloride was prepared according to our previous similar work (40). Second, 0.01 mol sebacic dihydrazide and 0.015 mol triethylamine was dissolved in DMF of 70 mL using ultrasonic for 30 min and then 0.02 mol hydrocinnamoyl chloride was slowly added onto the mixed solution under nitrogen atmosphere to stir for 60 min under ice bath. Finally, the mixed solution was heated up to 50°C for 240 min with stirring. The resulting solution was poured onto the 300 mL deionized water to be filtered and washed



Scheme 1: Synthetic route of HAD.

for 4 times using the deionized water, and the orange filtrate was dried in vacuum at 45°C. IR (KBr) ν: 3448.0, 3315.8, 3216.3, 3029.2, 2924.0, 2850.4, 1633.4, 1600.7, 1530.3, 1483.5, 1450.9, 1414.5, 1377.3, 1219.4, 1188.7, 1159.4, 1071.1, 1029.9, 933.0, 750.3, 720.9, 698.2 cm^{-1}; ^{1}H NMR (DMSO, 400 MHz) δ: ppm; 9.72 (s, 1H, NH), 9.67 (s, 1H, NH), 7.09~7.33 (m, 5H, Ar), 2.81~2.84 (t, 4H, CH_2), 2.40~2.44 (t, 2H, CH_2), 1.18~1.25 (m, 6H, CH_2).

2.3 Preparation of PLLA/HAD samples

Before blending, PLLA and HAD were dried in a vacuum oven at 35°C for 24 h to further remove water. A counter-rotating mixer (Harbin Hapro Electric Technology Co., Ltd., China) was used to perform the melting blend of PLLA containing different HAD content (0.5 wt%, 1 wt%, 2 wt%, 3 wt%). The processing parameters were: the blending temperature of 180°C, the rotation speed of 32 rpm for 7 min, and 64 rpm for 5 min. Then the blends were hot pressed and cool pressed to form sheets with 0.4 mm thickness.

2.4 Characterization and testing

The molecular structure of HAD was characterized using ^{1}H NMR (Brucker AVANCE III HD 400M nuclear magnetic resonance spectrometer, the deuterium solvent: dimethyl sulphoxide) and FT-IR (IS50 infrared spectrometer, KBr pellet technique). The investigations on the non-isothermal crystallization and melting behavior of the pure PLLA and PLLA/HAD samples were performed on DSC (Q2000, TA instrument, nitrogen atmosphere), the temperature and heat flow were calibrated using an indium standard before testing.

3 Results and discussion

3.1 Non-isothermal crystallization behavior

As mentioned above, HAD was synthesized to act as a nucleating agent for PLLA. To illuminate the role of the HAD in prompting crystallization of PLLA in cooling, the non-isothermal crystallization behavior of the pure PLLA and PLLA/BHSH samples from 190°C at a cooling rate of 1°C/min was investigated with DSC. As shown in Figure 1, upon the cooling of 1°C/min, the pure PLLA does almost not have any non-isothermal crystallization peak in cooling, implying that, although the cooing rate is very slow, the crystallization ability of the pure PLLA is still very poor, which is consistent with the result reported by the literature (41). In contrast, all PLLA/HAD samples exhibit obvious non-isothermal crystallization peaks with different location and height, which indicates that the introduction of HAD is able to facilitate the crystallization of PLLA *via* heterogenous nucleation, and the HAD is regarded as an effective nucleating agent for PLLA. Additionally, it is observed from Figure 1 that HAD concentration can significantly affect the non-isothermal crystallization behavior of PLLA. When the HAD concentration is 0.5 wt% ~ 1 wt%, the non-isothermal crystallization peak shifts toward a higher temperature with an increase of HAD concentration, resulting from the higher nuclei density in PLLA matrix. However, further increasing the HAD concentration from 1 wt% to 2 wt% leads to a drastic shift to low temperature, the probable reason is that an excessive HAD have an inhibition for the melt crystallization process of PLLA, that is, the excessive HAD will weaken the motility of PLLA molecular segment, blocking its attachment on the surface of HAD and the subsequent crystal growth. On the other hand, this result indicates that 1 wt% HAD is its saturated concentration in PLLA matrix. Whereas the non-isothermal crystallization peak slightly shifts to high temperature again, when the loading of HAD increases from 2 wt% to 3 wt%. Compared to the hindrance effect of excessive HAD on the crystallization of PLLA, under the circumstance, the accelerating crystallization effect of oversufficient HAD is predominant. To conclude, the presence of HAD can significantly enhance the crystallization of PLLA, in particular, 1 wt% HAD has the best effect of crystallization for PLLA. Compared to the pure PLLA, with the addition

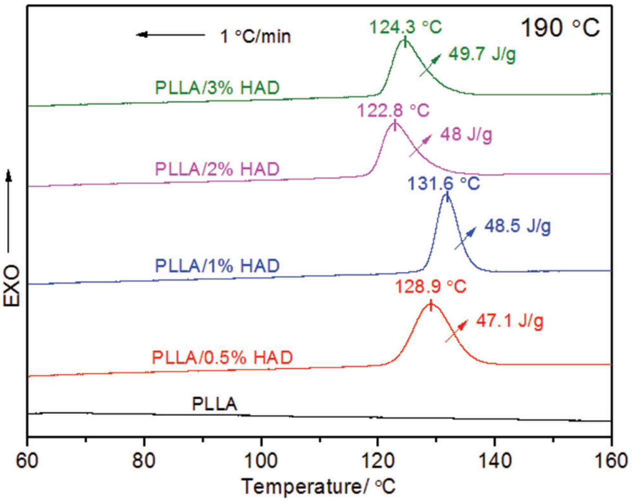


Figure 1: Non-isothermal crystallization DSC curves of the pure PLLA and PLLA/HAD samples from 190°C at a cooling rate of 1°C/min.

of 1 wt% HAD, the crystallization temperature and non-isothermal crystallization enthalpy increase from 94.5°C and 0.1 J/g to 131.6°C and 48.5 J/g, respectively. However, the largest non-isothermal crystallization enthalpy of 49.7 J/g appears at 3 wt% loading of HAD, the corresponding crystallinity runs up to 55.1% on the basis of the relevant equation (42). Moreover, upon cooling at 1°C/min, for a PLLA sample containing different types of nucleating agents with the same concentration, the PLLA/HAD has much higher crystallinity than other blend systems such as PLLA/*N, N'*-bis(1H-benzotriazole) adipic acid acethydrazide (33), PLLA/*N, N'*-bis(1H-benzotriazole) dodecanedioic acid acethydrazide (43), PLLA/*N, N'*-bis(benzoyl) sebacic acid dihydrazide (44), PLLA/talc (16).

The faster cooling is very desirable to an enterprise during practical manufacturing. Thus, it is necessary to further investigate the influence of cooling rates on the non-isothermal crystallization. Considering the very poor crystallization capability of the pure PLLA, here, we focus on the investigation on the effect of cooling rates on the crystallization behavior of PLLA/HAD, and DSC cooling curves of the PLLA/HAD samples are shown in Figure 2. It is very clear that the non-isothermal crystallization peak of a given PLLA/HAD sample, with increasing of cooling rate from 2°C/min to 30°C/min, becomes wider and shifts to the lower temperature. Even when the cooling rate is 30°C/min, apart from PLLA/3%HAD, all PLLA/HAD samples only cause a tiny non-isothermal crystallization peaks in the DSC cooling curves, reflecting the important of an appropriate cooling rate to the crystallization of PLLA (30) and the the competition between the cooling rate and the crystallization rate (33). However, it is surprising that the PLLA/3%HAD sample still exhibits obvious non-isothermal crystallization peak upon the cooling of 30°C/min, meaning that the crystallization accelerating effect of 3 wt% HAD for PLLA is predominant over the negative effect of high cooling rate, which is beneficial the fast production of PLLA products. Overall, in non-isothermal conditions, the non-isothermal crystallization peaks are still observed even at a cooling rate of 30°C/min implying that the nucleation role of HAD in PLLA crystallization is quite effective. In addition, when the cooling rate is higher 10°C/min, the non-isothermal crystallization peak shifts to the higher temperature with increasing of HAD concentration, which is different from the result obtained when the cooling rate is from 1°C/min to 10°C/min. The reason may be that a higher cooling rate (≥15°C/min) can seriously weaken the crystallization promoting effect of HAD, under this circumstance, a higher HAD concentration is beneficial to maintain crystallization of PLLA.

For an organic nucleating agent, the final melting temperature is another influential factor to crystallization behavior, because the final melting temperature directly affects the solubility of an organic nucleating agent in polymer matrix. Figure 3 is non-isothermal crystallization behavior of PLLA/HAD samples from the different melting temperatures at a cooling rate of 1°C/min. When the final melting temperature is 180°C, the effect of HAD concentration on crystallization behavior of PLLA is similar with that from 190°C (see Figure 1), but quite different from that from 200°C. That is to say, as seen in Figure 3, the non-isothermal crystallization peak continuously shifts to the higher temperature with increasing of HAD concentration, when the final melting temperature is 200°C. The higher final melting temperature often causes the more HAD to be dissolved in PLLA matrix, spontaneously resulting in a drop of the undissolved HAD after exceeding its saturated solubility, and these undissolved HAD as nuclei determine the nucleation density of PLLA matrix. Therefore, a higher HAD concentration is required to supply the nuclei for PLLA crystallization. Additionally, the non-isothermal crystallization enthalpy obtained *via* cooling from 200°C is the largest, the reason is that the motility of PLLA molecular segment is better in higher temperature zone, leading to a faster crystal growth and the formation of the more crystals. It is important to note that the non-isothermal crystallization enthalpy of PLLA/3%HAD is 58.0 J/g, meaning that the crystallinity is 64.3%. In all, the crystallization process can be obviously influenced by the final melting temperature as the cooling rate.

For cold crystallization process, the nuclear rate is faster comparing with the melt crystallization process because of the homogeneous nucleation ability of PLLA itself in low temperature zone, the crystal growth rate is the rate-determining step under this circumstance, which possibly results in the different crystallization behavior. Figure 4 displays the non-isothermal crystallization process of PLLA/HAD samples from 60°C at a heating rate of 1°C/min. It is easily found from Figure 4 that the DSC curve profiles of PLLA/HAD samples do almost not depend on HAD concentration, and the cold crystallization peak temperature increases with increasing of HAD concentration from 0.5 wt% to 1 wt%. However, when the HAD concentration is more than 2 wt%, the HAD concentration has no discernible effect on the cold crystallization peak temperature. The reason may be that a same heating rate gives rise to the subequal motility of PLLA molecular segment, as a result, the cold crystallization process of the PLLA/HAD samples

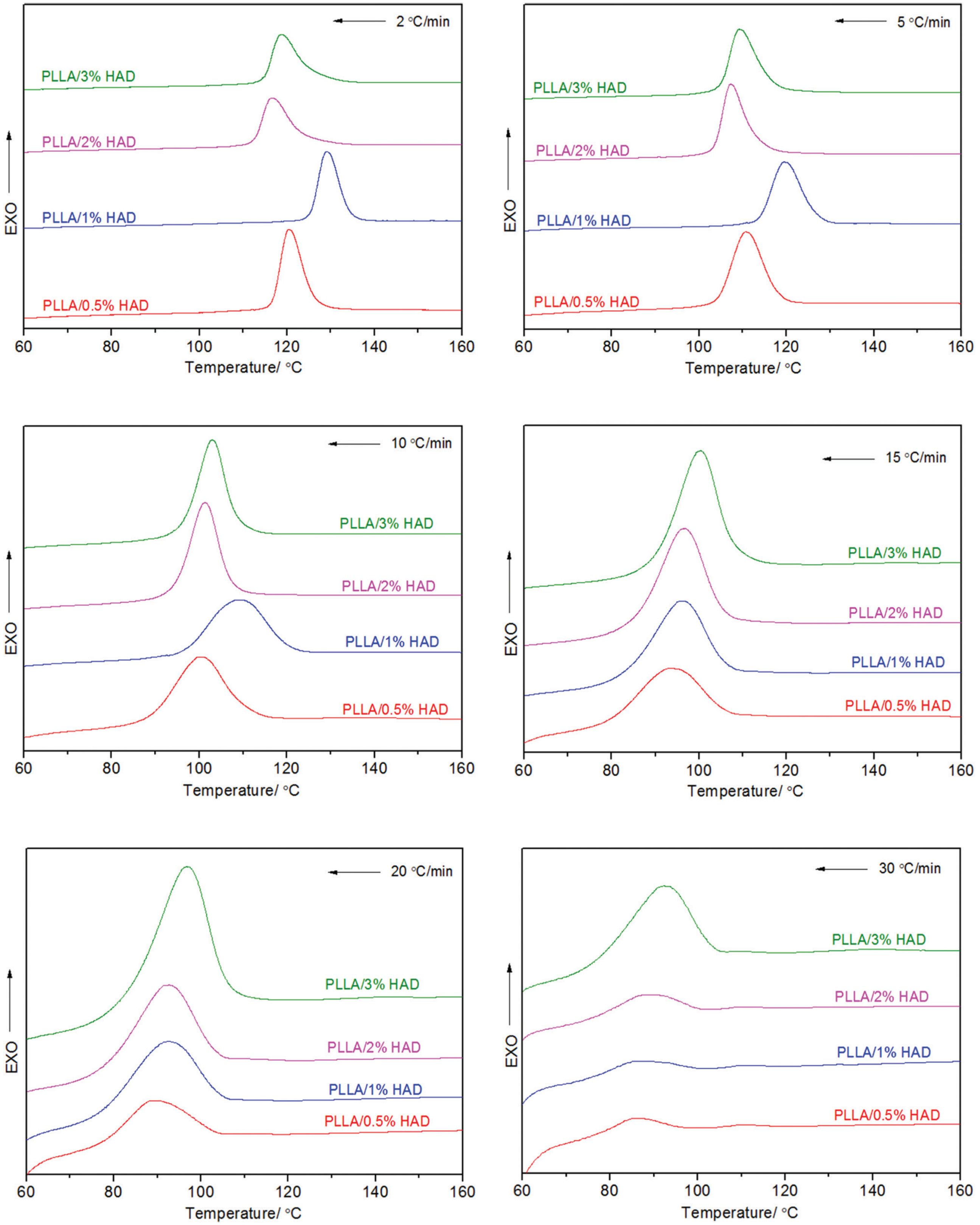


Figure 2: DSC curves of PLLA/HAD samples at different cooling rates.

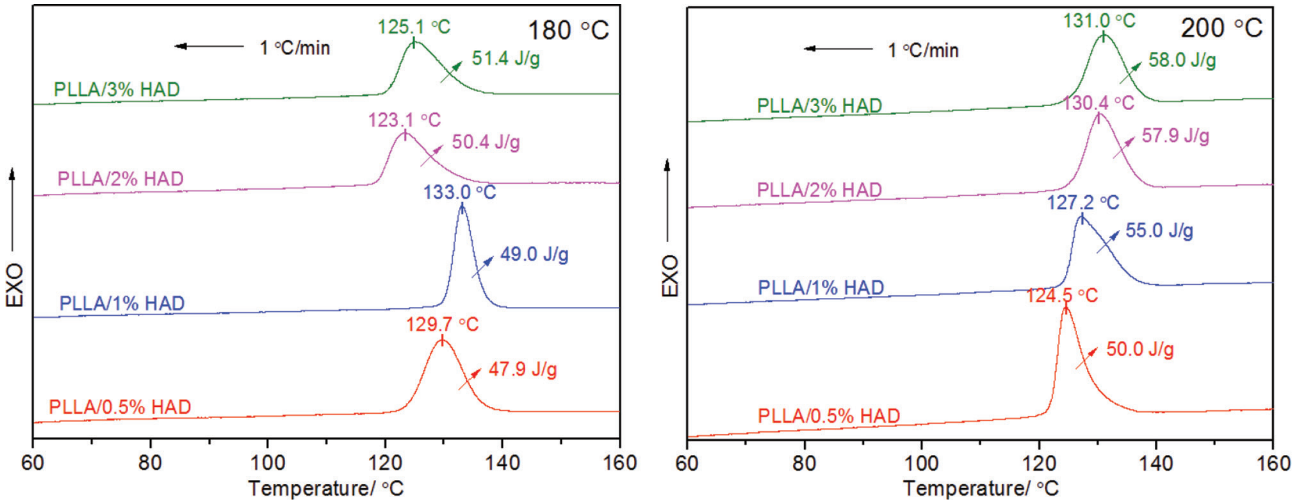


Figure 3: Non-isothermal crystallization of PLLA/HAD samples from the different melting temperatures at a cooling rate of 1°C/min.

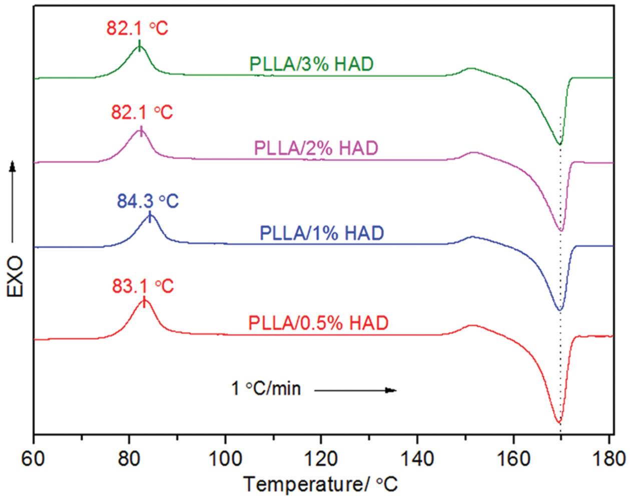


Figure 4: Cold crystallization process of PLLA/HAD samples at a heating rate of 1°C/min.

is irrelevant with the HAD concentration, when the nucleation density from HAD and PLLA itself is saturated.

3.2 Proposed nucleation mechanism

In non-isothermal crystallization behavior section, HAD exhibited a powerful accelerating effect on the crystallization process of PLLA. Here, a probable chemical nucleation mechanism is proposed according to the molecular structure analysis of the PLLA and HAD, because an interaction between the C=O of PLLA and the N-H of HAD can occur easily during heating blend. A theoretical calculation about molecular structure was performed using DMol3 to confirm the probable chemical interaction. The optimal geometry structures, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of PLLA with ten repeating unit and HAD were obtained (see Figure 5), and the HOMO and LUMO are -11.082 eV and 0.251 eV for PLLA, -0.203 eV and -0.052 eV for HAD. Frontier molecular orbital theory thinks that the reactivity model is based upon the LUMO-HOMO energy gap ΔE, the smaller the ΔE is, the more the intermolecular interaction occurs easily. the ΔE of 11.03 eV between PLLA and HAD is smaller than that of 11.333 eV of PLLA itself, indicating that the interaction between PLLA and HAD can form more easily during melting blend.

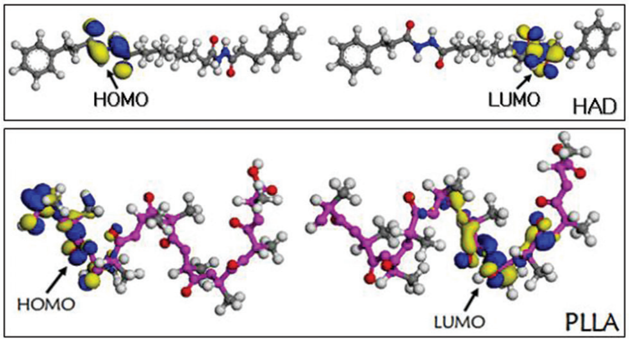


Figure 5: The optimal geometry structures and frontier orbital energy of PLLA and BADH.

3.3 Melting behavior

The melting behavior is an important part of thermal performances, on the other hand, the melting behavior can also effective reflect the accelerating effect of a nucleator for semi-crystalline polymers (45). Figure 6 is the melting behavior of PLLA/HAD samples

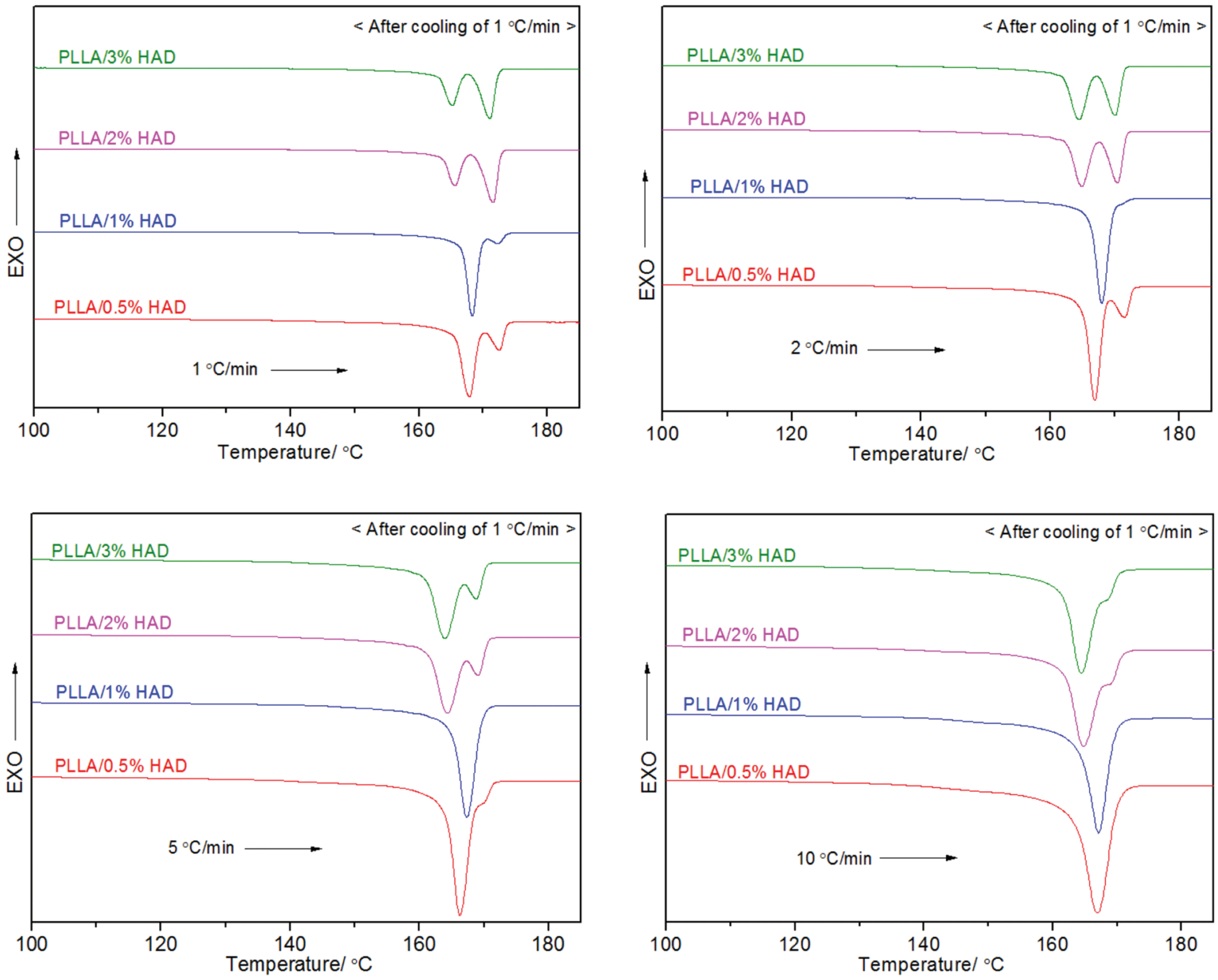


Figure 6: Melting behavior of PLLA/HAD samples after non-isothermal crystallization at different heating rates.

after non-isothermal crystallization (Cooling of 1°C/min) at different heating rates. Upon the heating of 1°C/min, for all PLLA/HAD samples, the double melting peaks appear in all DSC curves, the low-temperature melting peak is attributed to the primary crystallites formed in cooling, and high-temperature melting peak stemmed from the crystallites reformed after reorganization and possible new crystals formed during the heating scan (46). What is more, for a given PLLA/HAD sample, the low-temperature melting peak almost does not move because the low-temperature melting peak resulted from the crystals formed in cooling, which further confirms the melting-recrystallization mechanism of double melting peaks in PLLA/HAD systems. However, with increasing of the heating rate, the high-temperature melting peak shifts to low-temperature melting peak, and gradually merge into a single melting peak, resulting from that there is no enough time to crystallize at a higher heating rate. Meantime, it is noteworthy that the high-temperature melting peak of PLLA/1%HAD sample, in comparison to PLLA/HAD samples, is tinier, and even disappear at the same condition, indicating that there is only few crystal regenerated in heating, the reason may be that the crystallization of PLLA/1%HAD sample has been completed in previous cooling, which is also consistent with aforementioned DSC results.

Figure 7 presents the melting behavior of PLLA/HAD samples at different heating rates that corresponded to the rates of non-isothermal crystallization at different cooling rates. The double melting peaks still exist, and the increase in the rate leads to a shift to the lower temperature for the double melting peaks of PLLA/HAD samples, but the area ratio of the high-temperature melting peak and the low-temperature melting peak increases, even when the rate is 10°C/min, apart from PLLA/1%HAD sample, other PLLA/HAD samples only

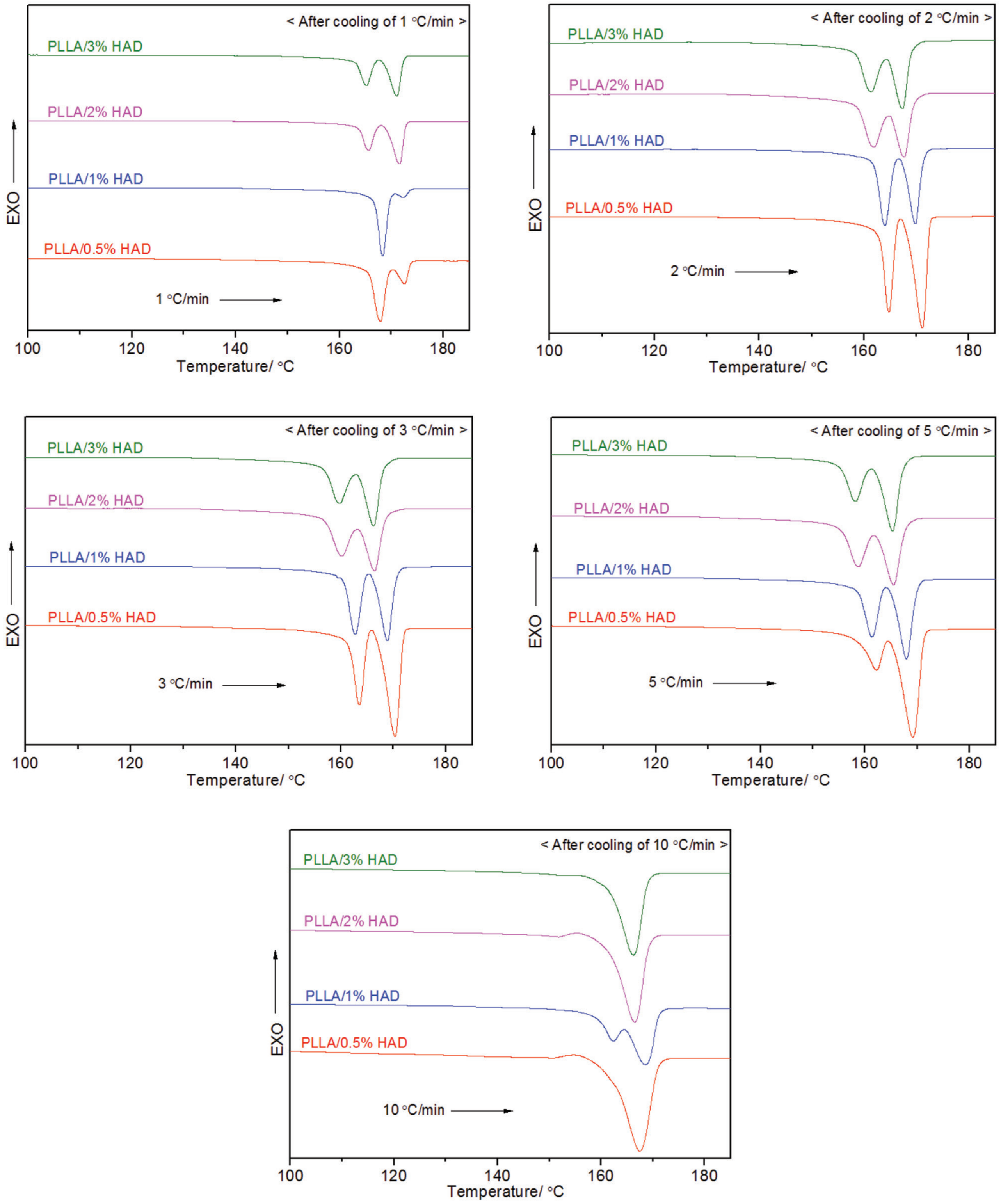


Figure 7: Melting behavior of PLLA/HAD samples at different heating rates corresponding to the rate of non-isothermal crystallization at different cooling rates.

exhibit a very wide single melting peak. A faster rate often makes the PLLA macromolecule segment not form a regular structure in cooling or heating process, resulting in a drop in the number and perfection of the crystal, and the shift toward lower temperature of melting peaks.

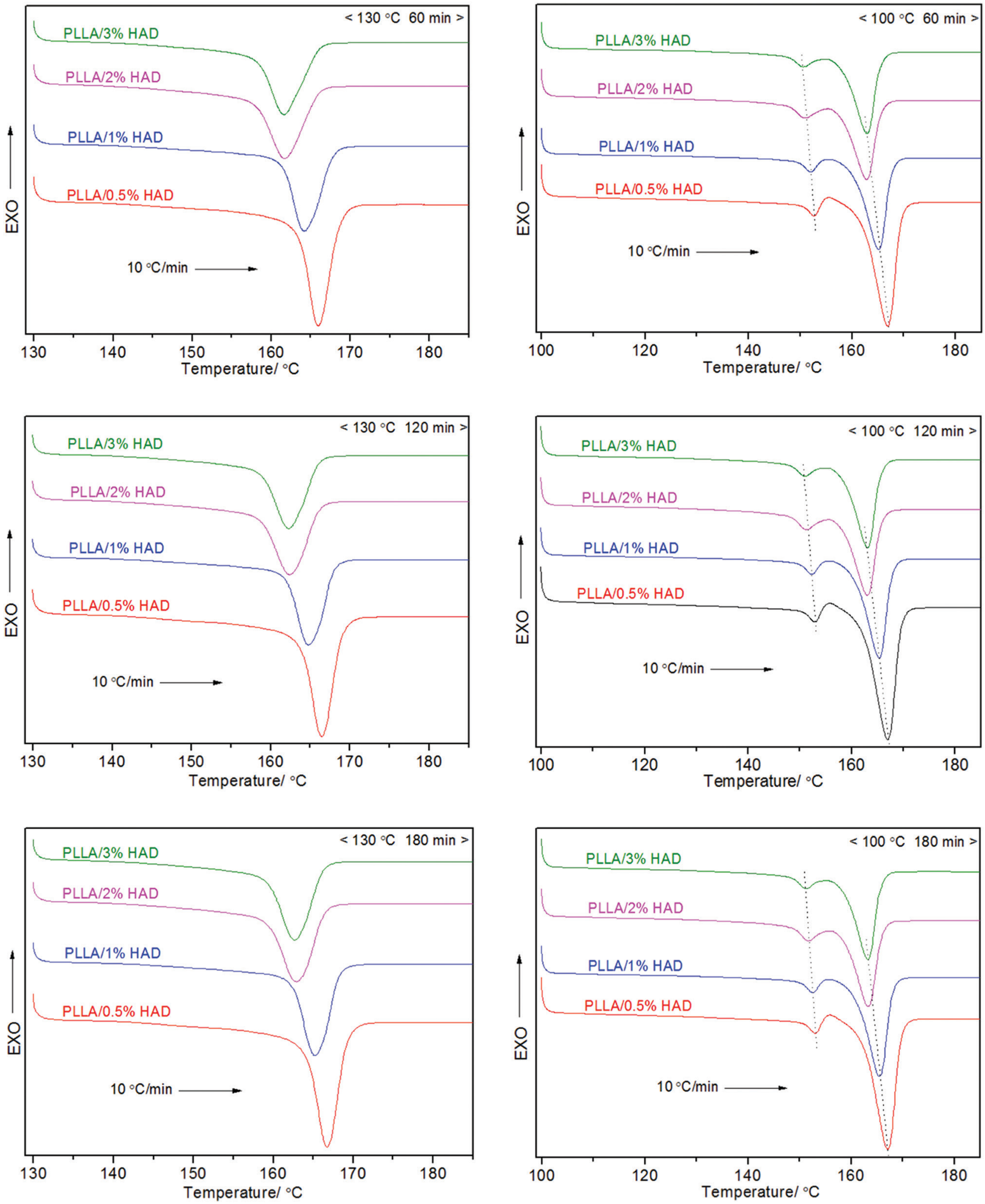


Figure 8: Melting behavior of PLLA/HAD samples after isothermal crystallization at different temperature for different time.

Additionally, the effects of crystallization temperature and crystallization time on the melting behavior of PLLA/HAD samples were compared by DSC measurement (see Figure 8). It is clear that, after isothermal crystallization at 130°C for different times, all PLLA/HAD samples only have a single melting peak comparing with the double melting peaks after isothermal crystallization at 100°C. Furthermore, an increase of crystallization time can almost not affect the melting peak profile and location, indicating that the crystallization process of PLLA/HAD samples has completed after isothermal crystallization at 130°C for 60 min. This result strongly demonstrates the powerful nucleation effect of HAD for PLLA, because it is very difficult for PLLA itself to nucleate and grow crystal at crystallization temperature of 130°C. However, the double melting peak still exist after isothermal crystallization at 100°C for different times, the key reason is that, although all PLLA/HAD samples have the high nucleation density, the motility of PLLA macromolecule segment is very poor in low crystallization temperature zone, which leads to a slow crystal growth rate and insufficiency crystallization. And then the recrystallization behavior will occur with increasing of temperature in heating. The results from the melting behavior after isothermal crystallization indicate that the melting behavior of PLLA/HAD systems depends on the crystallization temperature, and the double melting peaks phenomenon becomes more obvious in the lower crystallization region. Besides, it is also observed from Figure 8 that the melting peak shifts toward a lower temperature with increasing of HAD concentration, this effect depends on the perfection of PLLA crystals. A small amount of HAD in PLLA matrix correspondingly possess a low nucleation density , and the low nucleation density can make the crystal grow better to avoid to impinge on crystal's neighbors to form imperfect crystals because of the high nucleation density resulting from the existence of a larger number of HAD in PLLA matrix. And the melting process of these more perfect crystals must occur at a higher temperature.

3.4 Thermal stability and optical performance

The thermal stability and optical performance of the pure PLLA and PLLA/HAD samples were further investigated by TGA and light transmittance meter. Figure 9 is the TGA curves of the pure PLLA and PLLA/HAD samples at a heating rate of 5°C/min from 50°C to 650°C under air. It is clearly observed that the addition of HAD can not change the thermal decomposition profile of PLLA, that is to say, the thermal decomposition profile of all samples only exhibits one decomposition stage, which is attributed to thermal decomposition of PLLA ester groups in the region of 300°C to 400°C (47). This result indicates the excellent compatibility between PLLA and HAD to a certain extent. However, it is also a fact that the onset decomposition temperature (T_o) (defined by TGA software) remarkably depends on the HAD concentration, and the T_o of the pure PLLA, PLLA/0.5%HAD, PLLA/1%HAD, PLLA/2%HAD, PLLA/3%HAD are 341.3°C, 334.0°C, 327.5°C, 320.0°C, 310.8°C, respectively. Through the analysis of T_o, the T_o significantly decreases with increasing of HAD concentration, probably resulting from the low thermal decomposition temperature of HAD itself. When the HAD concentration is 3 wt%, the T_o even decreases by 30.5°C comparing with the pure PLLA, which implies that the presence of HAD leads to a worse thermal stability. But the T_o of all PLLA/HAD samples is over 300°C, indicating that PLLA/HAD samples can meet the daily usage.

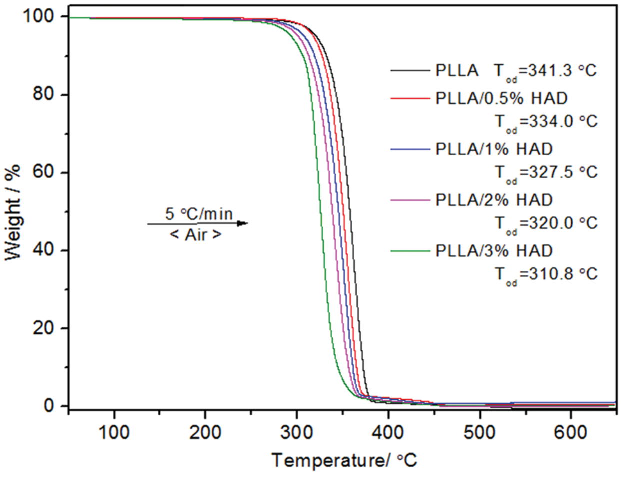


Figure 9: TGA curves of the pure PLLA and PLLA/HAD samples.

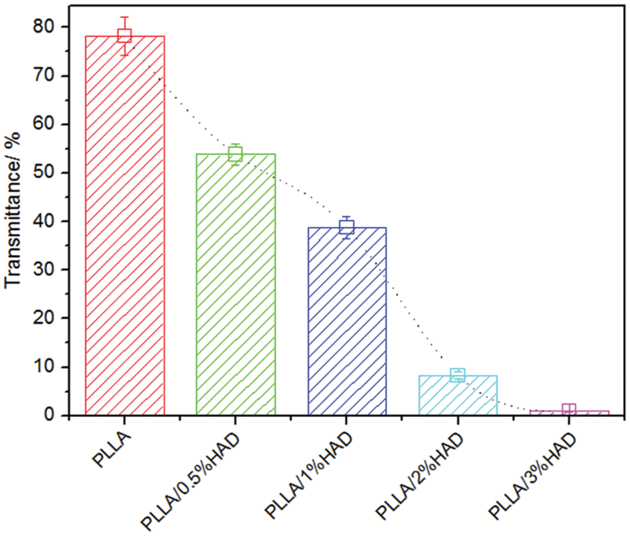


Figure 10: Light transmittance of the pure PLLA and PLLA/HAD samples.

As seen in Figure 10, the effect of HAD on the light transmittance of PLLA can be concluded into two stages. For the first stage, the HAD concentration is 0.5 wt% to 1 wt%, the light transmittance of PLLA moderately decreases with an increase of HAD concentration. However, for the second stage, when the HAD concentration is over 1 wt%, the addition of HAD leads to a serious drop in light transmittance, even when the HAD concentration is 3 wt%, the light transmittance of PLLA/BHSH samples is almost zero. This effect is due to the synergistic effect of the crystallization and orange HAD itself. The introduction of HAD makes the amorphous PLLA to be crystal, leading to a decrease of the light transmittance. The continuous increase of the orange HAD further decreases the light transmittance.

4 Conclusions

HAD was synthesized using sebacic dihydrazide and hydrocinnamic acid through acylation and amination to evaluate its influence on non-isothermal crystallization, melting behavior, thermal stability and optical performance of PLLA. The non-isothermal crystallization results revealed that HAD as a heterogenous nucleating agent exhibited an excellent nucleating effect for the crystallization of PLLA, and 1 wt% HAD has the best effect of crystallization for PLLA. Upon the cooling of 1°C/min, with the addition of 1 wt% HAD, the crystallization temperature and non-isothermal crystallization enthalpy increase from 94.5°C and 0.1 J/g to 131.6°C and 48.5 J/g comparing with the pure PLLA. However, the PLLA/3%HAD sample had the largest non-isothermal crystallization enthalpy value of 49.7 J/g. Meantime, in melt crystallization section, the melt crystallization behavior was also affected by the cooling rate and the final melting temperature besides HAD concentration. For the cold crystallization process, PLLA/HAD system had the faster nuclear rate because of HAD and PLLA itself, which resulted in that the cold crystallization behavior of PLLA/HAD sample did almost not depend on the HAD concentration, when the HAD concentration was over 2 wt%. After isothermal and non-isothermal crystallization, the difference in melting behavior of PLLA/HAD in the second heating further demonstrated the accelerating effect of HAD in promoting crystallization of PLLA, and the double melting peak was thought to be due to the melting-recrystallization. Finally, the effects of HAD on the thermal stability and optical property of PLLA showed that both the onset thermal decomposition temperature and light transmittance of PLLA decreased with increasing of HAD concentration.

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