Evaluation of the effect of *N,N′*-bis(1H-benzotriazole) dodecanedioic acid acethydrazide on poly(L-lactic acid)

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Abstract: A serious disadvantage of poly(L-lactic acid) (PLLA) is its poor crystallization properties. In the present work, a novel type of organic nucleating agent – *N,N′*-bis(1H-benzotriazole) dodecanedioic acid acethydrazide (DA) – was synthesized and then applied in PLLA crystallization studies. The thermal performance, including non-isothermal crystallization, melting behavior, and thermal stability of the PLLA/DA blend, was evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In non-isothermal crystallization, DA exhibited excellent nucleating and accelerating effects for the crystallization of PLLA since the relevant characterization parameters, including the onset crystallization temperature, non-isothermal crystallization enthalpy, *etc*., increased. Besides, it was found that an increase in the adjusted final melting temperature in the range from 180 °C to 220 °C led to an enhancement of the PLLA crystallization. DSC measurements under different conditions showed that crystallization temperature, crystallization time, rate, and DA content could affect the melting behavior. According to TGA measurements, all PLLA/DA samples revealed a higher thermal decomposition temperature than neat PLLA. Most probably, the observed behavior results from a strong interaction between PLLA and DA.

Keywords: poly(L-lactic acid), crystallization, melting behavior, thermal stability, 1H-benzotriazole.

Badania wpływu *N,N′*-bis(1H-benzotriazolo)acetohydrazydu kwasu dodekanodiowego na właściwości termiczne poli(kwasu L-mlekowego)

Streszczenie: Poważną wadą poli(kwasu L-mlekowego) (PLLA) w licznych zastosowaniach jest jego mała zdolność do krystalizacji. W niniejszej pracy otrzymano *N,N′*-bis(1H-benzotriazolo)acetohydrazyd kwasu dodekanodiowego (DA), a następnie zastosowano go do modyfikacji PLLA. Metodą różnicowej kalorymetrii skaningowej (DSC) oraz analizy termograwimetrycznej (TGA) badano przebieg nieizotermicznej krystalizacji, temperaturę topnienia i temperaturę krystalizacji oraz stabilność termiczną kompozytów PLLA/DA z udziałem różnej ilości DA (0,5–3,0 % mas.). Na podstawie oznaczanych: temperatury początku krystalizacji oraz entalpii topnienia w procesie nieizotermicznej krystalizacji otrzymywanych kompozytów stwierdzono wyjątkowy nukleujący i przyspieszający krystalizację PLLA wpływ dodatku DA. Zwiększenie końcowej temperatury topnienia do wartości z przedziału 180–220 °C poprawiło zdolność PLLA do krystalizacji. Metodą pomiarów DSC wykonanych w różnych warunkach wykazano, że temperatura krystalizacji, czas krystalizacji, jej szybkość oraz zawartość dodatku DA w kompozycie wpływa na przebieg procesu jego topnienia. Na podstawie badań TGA stwierdzono, że wszystkie otrzymane próbki PLLA/DA wykazują większą odporność termiczną niż czysty PLLA – ulegają rozkładowi termicznemu w wyższej temperaturze, co prawdopodobnie wynika z silniejszych oddziaływań pomiędzy makrocząsteczkami PLLA i DA.

Słowa kluczowe: poli(kwas L-mlekowy), krystalizacja, proces topnienia, stabilność termiczna, 1H-benzotriazol.

Through many years, there exists an increasing demand for the use of biodegradable polymers in industry and daily life to solve the problem of white plastic pollution. Poly(L-lactic acid) (PLLA), produced from renewable resources, exhibits excellent biodegradability, relatively good biocompatibility and processability [1]. These characteristics make PLLA very attractive as an alternative to non-renewable thermoplastic resins [2] and the further developments of PLLA materials has been emphasized in wider applications, such as 3D printing [3], biomaterials [4], automotive interiors [5], *etc*. However, the final PLLA product fabri-

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cated using melting blending technology usually has poor heat resistance and low crystallinity due to its inherent slow crystallization rate in the blending procedure. Thus, enhancing the crystallization rate of PLLA is very essential to achieve its further development and application.

The introduction of a nucleating agent is one of the most important methods to improve the crystallization of semi-crystalline polymers. Reducing the nucleating surface free energy barrier is the main function of nucleating agents for semi-crystalline polymers, resulting in the acceleration of the crystallization rate. Many inorganic nucleating agents, such as layered silicates including talc [6], montmorillonite [7], *etc*., nano-oxides including TiO_2 [8], SiO_2 [9], *etc*., carbon materials such as carbon nanotubes [10], carbon black [11], graphene [12], *etc*., nano-inorganic salts such as $CaCO_3$ [13], $BaSO_4$ [14], *etc*., layered metal phosphonates including calcium phenylphosphonate [15], barium phenylphosphonate [16], zinc phenylphosphonate [17], *etc*., exhibit significant nucleating ability for PLLA. For instance, Naffakh *et al*. [18] reported the effect of tungsten disulphide inorganic nanotubes (INT-WS_2) on the isothermal crystallization of PLLA, showing that PLLA/INT-WS_2 nanocomposites had a shorter overall crystallization time than that of neat PLLA. Moreover, the overall crystallization time further decreased with higher INT-WS_2 concentrations. However, inorganic nucleating agents also have some inherent shortcomings including poor compatibility, poor designability, *etc*., which greatly restricts their use in PLLA matrices.

It was found that organic compounds have a good compatibility with PLLA compared to inorganic nucleating agents. Thus, it is of great interest and important significance for researchers to explore novel organic nucleating agents. In recent years, commercial and synthesized organic nucleating agents were added to PLLA matrices as heterogeneous nucleating agents. In particular, many organic nucleating agents with specific structures and groups were designed to induce the crystallization of PLLA. Multi-amide nucleating agents including tetramethylene-dicarboxylic dibenzoyl-hydrazide [19], aliphatic diacyl adipic dihydrazides with different alkyl moieties [20], tetramethylenedicarboxylic di(2-hydroxybenzohydrazide) [21], *etc*., amino acids such as glycine and L-alanine [22], as well as 1,3:2,4-dibenzylidene sorbitol [23], bisurea derivative [24], *myo*-inositol [25], and other organic compounds [26, 27] can significantly decrease the overall crystallization time of PLLA. Moreover, the report revealed that the nucleation mechanism could be attributed to the intermolecular interaction between the nucleating agent and PLLA [21]. This finding may eventually enhance the development of new, more effective nucleating agents.

The already developed organic nucleating agents still do not meet the requirements expected for commercially available products. Thus, within this work, a novel organic compound – *N,N′*-bis(1H-benzotriazole) dodecanedioic acid acethydrazide (DA) was designed and synthesized. Then, in the next step, we evaluated its nucleation phenomena, as well as the non-isothermal crystallization, melting behavior, and thermal stability of the PLLA/DA system.

EXPERIMENTAL PART

Materials

Poly(L-lactic acid) (PLLA) was purchased from Nature Works LLC, USA. The other chemical reagents were provided by Huanwei Chemical Reagent Company (Chongqing, China).

Synthesis of *N,N′*-bis(1H-benzotriazole) dodecanedioic acid acethydrazide (DA)

The synthetic pathway for *N,N′*-bis(1H-benzotriazole) dodecanedioic acid acethydrazide is shown in Scheme A. A similar synthesis was reported in our previous work [28].

IR (KBr) υ: 3449.1, 3215.2, 2923.9, 2849.7, 1685.7, 1615.6, 1498.3, 1458.5, 1409.4, 1315.7, 1265.8, 1228.8, 1188.2, 1167.9, 804.2, 745.3, 661.8 cm^{-1};

^{1}H NMR (DMSO, 400 MHz) δ, ppm: 10.48 (s, 1H, NH), 9.95 (s, 1H, NH), 7.39~8.07 (m, 4H, Ar), 5.54 (s, 2H, CH_2), 2.09~2.12 (t, 2H, CH_2), 1.48 (s, 2H, CH_2), 1.21 (s, 6H, CH_2).

Preparation of PLLA/DA samples

PLLA samples containing different DA concentrations were obtained through conventional melting blend technology, and the blending procedure was as follows: the blend of dried PLLA and DA was first prepared on a counter-rotating mixer with a rotation speed of 32 rpm for 5 min at 180 °C, then at 64 rpm for 5 min. Finally, the melted PLLA/DA samples were pressed for 10 min at 180 °C, and then pressed again for 10 min under cooling water.

Methods of testing

– The FT-IR of DA was recorded on a Thermo Fisher Scientific Nicolet iS50 spectrophotometer from 4000 to 400 cm^{-1} as a KBr pellet.

– The ^{1}H NMR of DA was measured on a Bruker AVANCE 400MHz spectrometer. The deuterated solvent was dimethyl sulfoxide.

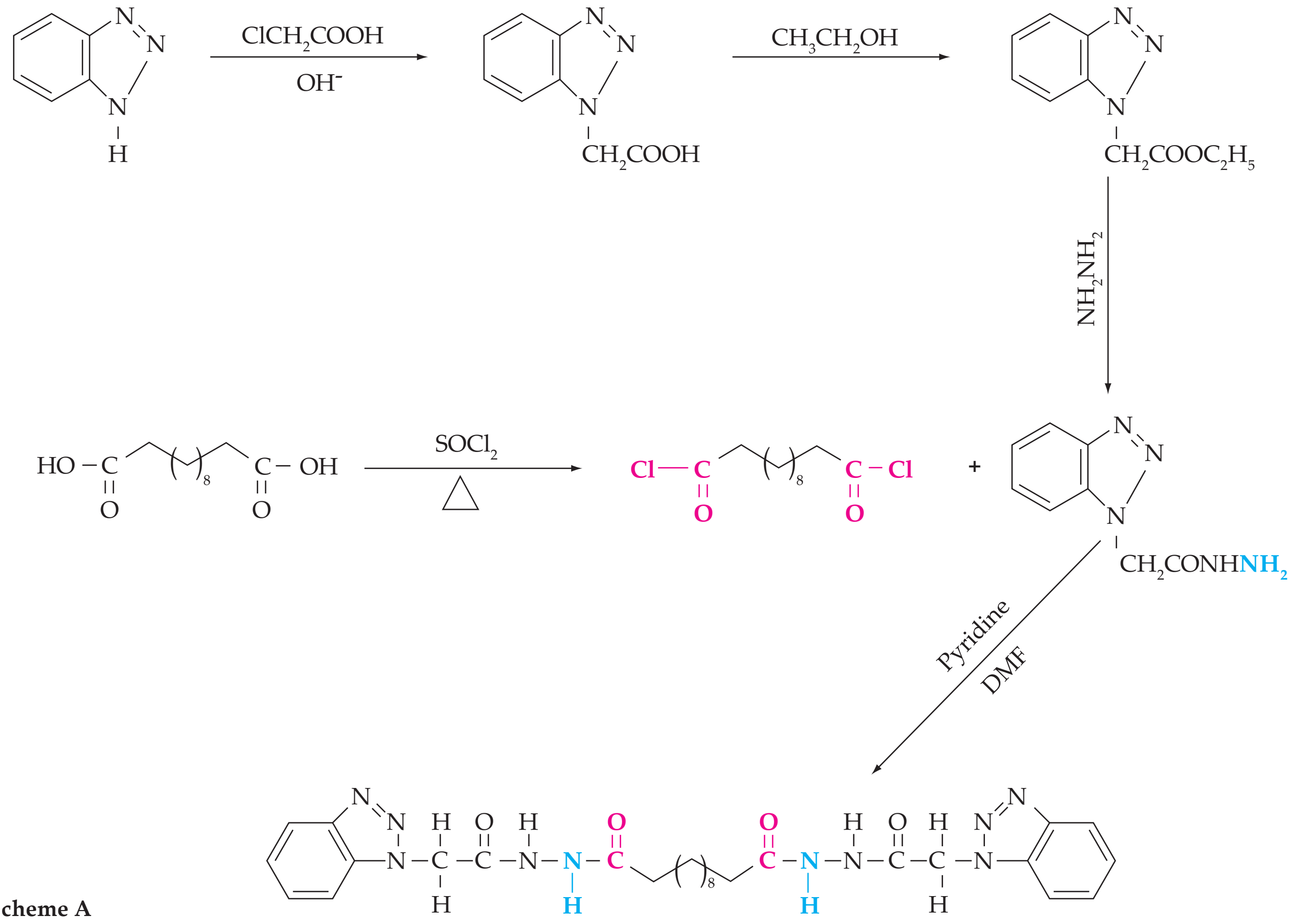
– The TGA measurements of DA, PLLA, and PLLA/DA samples were performed on a TA Instruments Q500 TGA with an air flow of 60 cm^3/min from room temperature to 650 °C and a heating rate of 5 °C/min.

– The non-isothermal crystallization and melting behavior of the neat PLLA and PLLA/DA samples under different conditions were measured on a TA Instruments Q2000 DSC under nitrogen with 50 cm^3/min.

RESULTS AND DISCUSSION

Non-isothermal crystallization behavior

In industry, non-isothermal crystallization is very necessary to explore the production and application of semi-crystalline polymers. Figure 1 shows the non-isother-



Scheme A

mal crystallization curves of neat PLLA and PLLA with different DA contents from the melt at a cooling rate of 1 °C/min. It is found from Fig. 1 that the non-isothermal crystallization peak of pristine PLLA is almost absent due to its poor crystallization ability. In contrast, all PLLA samples containing DA give clear, sharp non-isothermal crystallization peaks, indicating that DA has an excellent acceleration effect on the crystallization of PLLA under the same cooling process. For neat PLLA, homogeneous nucleation is predominant during the cooling crystallization process. In contrast, the addition of DA plays a more important role in cooling crystallization of PLLA, and heterogeneous nucleation is predominant for PLLA/DA samples. Compared to neat PLLA, the appearance and shift to higher temperature of the non-isothermal crystallization peak of PLLA/DA samples also confirm the heterogeneous nucleation effect of DA [29]. Meantime, the effect of DA concentration on the non-isothermal crystallization behavior of PLLA shows that the non-isothermal crystallization peak shifts to higher temperature along with an increase of DA concentration in the range from 0.5 wt % to 1 wt %. However, with a further increase of DA concentration, the increase in the non-isothermal crystallization peak temperature is very small, the non-isothermal crystallization temperature of PLLA/2%DA is even slightly lower than that of PLLA/1%DA. The relevant DSC data of the neat PLLA and PLLA/DA samples, including the onset crystallization temperature (T_o), the crystallization peak temperature (T_{cp}), and the non-isothermal crystallization enthalpy (ΔH_c), are listed in Table 1. Compared to neat PLLA, 3 wt % DA gives rise to an increase from 101.4 °C to 107.1 °C in T_o, while the T_{cp} increases from 94.5 °C to 99.5 °C, the ΔH_c also increases from 0.1 J/g to 30.4 J/g. However, the PLLA/1%DA sample exhibits the largest ΔH_c value of 31.5 J/g.

A small amount of organic nucleating agent may dissolve in the PLLA matrix during the melting blend stage, which can affect the non-isothermal crystalliza-

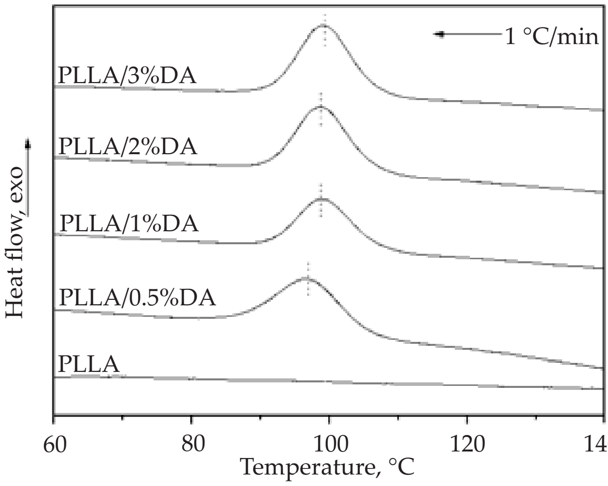


Fig. 1. Non-isothermal crystallization of PLLA and PLLA/DA samples from melt at a cooling rate of 1 °C/min

Table 1. DSC data of PLLA and PLLA/DA from melt at a cooling rate of 1 °C/min

Sample	Rate, °C/min	T_o, °C	T_{cp}, °C	ΔH_c, J/g
PLLA	1	101.4	94.5	0.1
PLLA/0.5%DA	1	105.8	96.9	26.3
PLLA/1%DA	1	107.0	99.1	31.5
PLLA/2%DA	1	106.7	98.9	30.9
PLLA/3%DA	1	107.1	99.5	30.4

tion. Thus, the influence of the set final melting temperature on non-isothermal crystallization was investigated (Fig. 2). For PLLA/3%DA, the solubility of DA in the PLLA matrix will increase with a higher set final melting temperature, leading to the enhancement of compatibility between undissolved DA and PLLA matrix. Meantime, the improvement of compatibility can further enhance the interaction between PLLA and DA, and this interaction can promote the PLLA molecular chain to form a regular arrangement. On the other hand, the thermal decomposition of PLLA starts to occur above 200 °C [30], resulting in the formation of more small molecular chain segment with stronger dynamics. According to the above two factors, along with an increase of the set final melting temperature, the non-isothermal crystallization peak shifts to higher temperature, indicating the enhancement of crystallization ability. The higher set final melting temperature makes the T_{cp} of PLLA/3%DA give a rise to an increase from 100.1 °C to 100.9 °C. These results can help us to reveal the nucleation mechanism to some extent.

Melting behavior

Melting behavior is an important research parameter to understand the thermal performance of polymer materials, the difference of melting behavior can also effectively reflect the function of the additive. In this section, the melting behavior of the PLLA/3%DA sample under different conditions was conducted using DSC. Figure 3 gives the melting behavior curves of PLLA/3%DA at different heating rates corresponding to the rate of non-isothermal crystallization at different cooling rates. The common double melting peaks reported in the literature [31, 32] are also clearly observed in the PLLA/DA system. Besides, from 1 °C/min, the low-temperature melting peak, attributed to the primary crystals formed in the melt crystallization, shifts to a higher temperature with an increase of rate because of thermal inertia. This result also indicates the competitive relationship between rate and nucleation because the nucleation is predominant at low rates. However, the high-temperature melting peak shifts to higher temperature at lower rates, the reason is that the low heating rate makes the crystals of PLLA become more prefect in the presence of DA during the seconding heating step.

Figure 4 shows the melting curves of PLLA/3%DA at a heating rate of 10 °C/min after isothermal crystallization at 100 °C for different times. It is clear that the low-temperature melting peak significantly moves to higher temperatures along with a longer isothermal crystallization time at 100 °C, this result depends on the fact that the longer crystallization time is in favor of crystal growth of PLLA. However, the high-temperature melting peak shifts slightly to higher temperature, the reason is that the high-temperature melting peak reflects the crystals formed in the second heating stage, the same heating

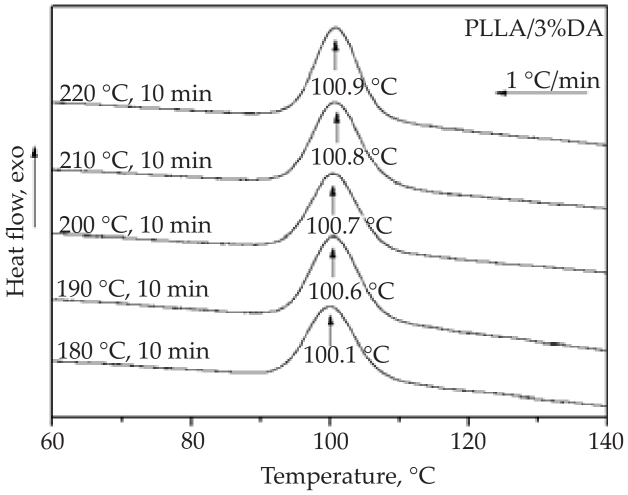


Fig. 2. Non-isothermal crystallization of PLLA/3%DA at a cooling rate of 1 °C/min from final different melting temperatures for 10 min

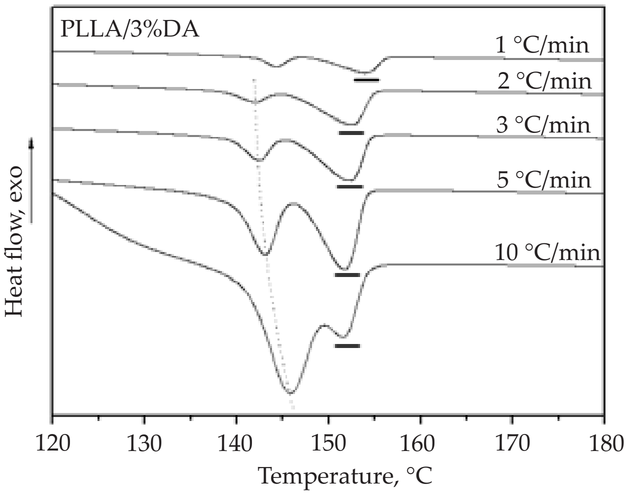


Fig. 3. Melting behavior of PLLA/3%DA at different heating rates corresponding to the rate of non-isothermal crystallization at different cooling rates

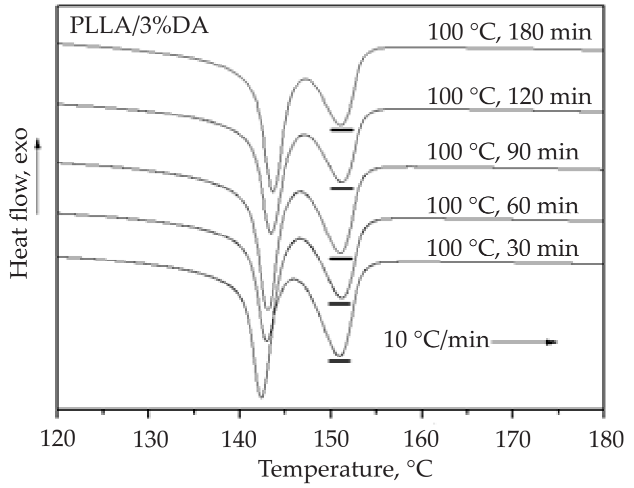


Fig. 4. Melting curves of PLLA/3%DA after isothermal crystallization at 100 °C for various times

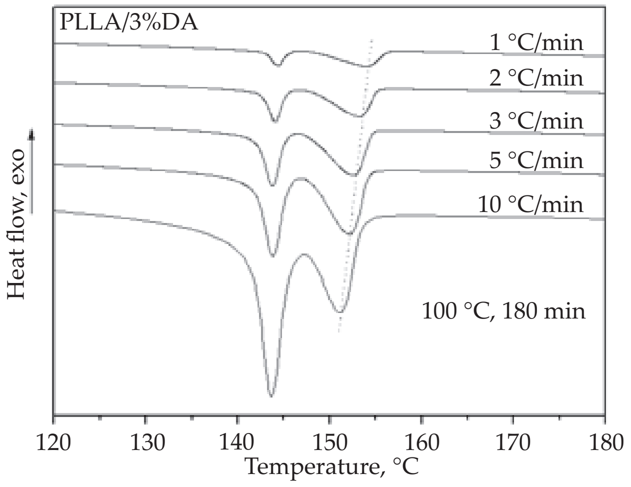


Fig. 5. Melting curves of PLLA/3%DA at various heating rates after isothermal crystallization at 100 °C for 3 h

rate and DA concentration make the number and perfection of crystals little different. Similar results can also be observed in the literature [33, 34]. Besides, this melting behavior also indicates that the double melting peak mechanism of PLLA/3%DA should be assigned to melting recrystallization.

After isothermal crystallization at 100 °C for 3 h, the decrease of the second heating rate makes the melting peak for the high-temperature melting peak of PLLA/3%DA significantly shift to higher temperature and the melting peak temperature exhibits a linear increase (Fig. 5), which shows that the melting behavior of PLLA/3%DA was affected by the heating rate. Due to the aforementioned melting behavior, the low heating rate is in favor of formation of prefect crystals.

The melting behavior of PLLA/3%DA at the heating rate of 1 °C/min after isothermal crystallization at different temperatures for 3 h (Fig. 6) shows that the increase of crystallization temperature makes the double melting peaks shift to higher temperatures. Usually, the higher the crystallization temperature, the stronger the mobility of the molecular chains, which makes PLLA easily form perfect structures. In addition, it is observed that the temperature difference between the low-temperature and high-temperature peaks decreases along with an increase in the crystallization temperature, indicating that the crystals formed in isothermal crystallization and in the second heating procedure become more uniform at the low heating rate of 1 °C/min.

Thermal stability

For applications, the evaluation of the thermal stability can directly affect the use of polymers. Figure 7 presents the TGA curves of DA, PLLA, and PLLA/DA samples at a heating rate of 5 °C/min from room temperature to 650 °C under air. It is clear that DA has three thermal decomposition stages, but there is only one thermal decomposition stage for PLLA and PLLA/DA samples. For DA, the thermal decomposition occurs in a broad temperature range, up to 600 °C, until thermal decomposition is complete. In addition, the initial thermal decomposition of DA should

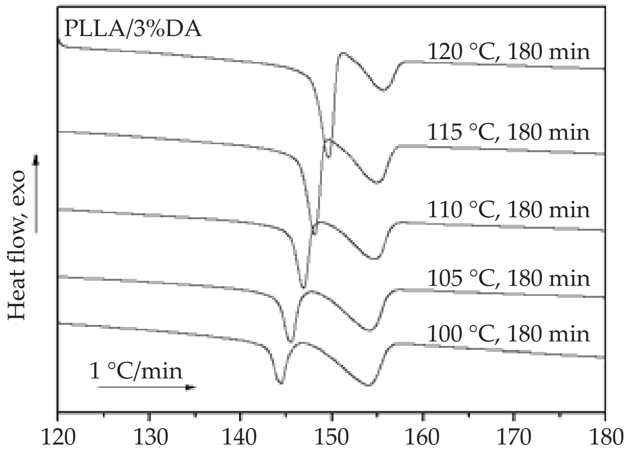


Fig. 6. Melting behavior of PLLA/3%DA at a heating rate of 1 °C/min after isothermal crystallization at various temperatures

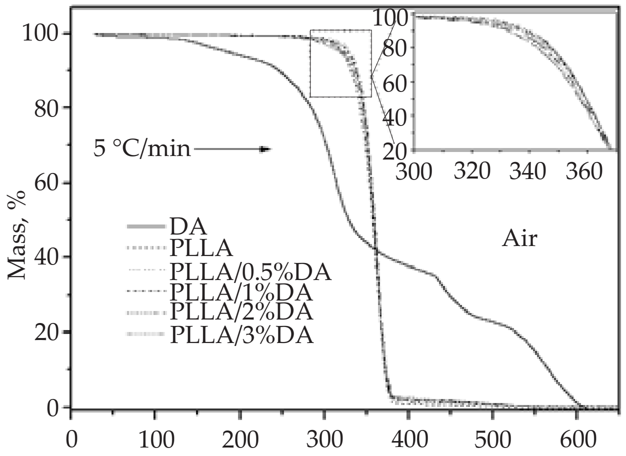


Fig. 7. TGA curves of DA, PLLA, and PLLA/DA samples

include absorbed water formed in the synthesis procedure. For PLLA and PLLA/DA samples, the thermal decomposition occurs in a very narrow temperature range, showing the rapid decomposition of PLLA and PLLA/DA samples. The onset thermal decomposition temperatures of DA, PLLA, PLLA/0.5%DA, PLLA/1%DA, PLLA/2%DA, and PLLA/3%DA are 280.8 °C, 341.2 °C, 345.3 °C, 344.9 °C, 344.6 °C, 343.1 °C, respectively. The data for the thermal decomposition temperatures show that PLLA containing DA has a higher thermal decomposition temperature than neat PLLA, the probable reason is that there exists a strong interaction between PLLA and DA, resulting in their decomposition only at higher temperatures, which also indicates that the major nucleation mechanism of DA is chemical nucleation [35]. On the other hand, the thermal decomposition temperature of DA is higher than the processing temperature of PLLA, this result confirms that DA can meet the basic requirement as an excellent stabilizer as a heterogeneous nucleating agent for PLLA.

CONCLUSIONS

A new and quite effective nucleating agent based on a 1H-benzotriazole derivative for PLLA was synthesized and a series of measurements on the thermal performance was conducted. The non-isothermal crystallization behavior of PLLA/DA samples showed that DA could significantly improve the crystallization of PLLA. Compared to neat PLLA, 3 wt % DA made the T_o, T_{cp} and ΔH_c increase from 101.4 °C, 94.5 °C and 0.1 J/g, and to 107.1 °C, 99.5 °C and 30.4 J/g. Meantime, a higher set final melting temperature in the range 180 °C to 220 °C for PLLA/3%DA gives rise to an increase from 100.1 °C to 100.9 °C in T_{cp}. The crystallization temperature, crystallization time, rate, and the existence of DA depended on the melting behavior of PLLA/3%DA, in addition, the competition between rate and nucleation also resulted in the difference of melting behavior. DA, PLLA, and PLLA/DA samples exhibited excellent thermal stability, and PLLA/DA samples had higher thermal decomposition temperature than that of the neat PLLA.

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