

A 1H-Benzotriazole Derivative Nucleated Poly(L-lactic acid): Thermal Behavior and Physical Properties

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Summary: In this study, a 1H-benzotriazole derivative, *N, N'*-bis(1H-benzotriazole) succinic acid acethydrazide (SABHA), was synthesized to nucleate Poly(L-lactic acid) (PLLA). A series of comparative studies on the melt-crystallization, the cold-crystallization, the melting behavior, the thermal stability, as well as the fluidity between the pure PLLA and PLLA/SABHA were performed. The melt-crystallization behavior revealed that the SABHA as a heterogeneous nucleating agent could significantly facilitate the crystallization of PLLA, and a larger amount of SABHA concentration exhibited the better nucleation effect. However, for the cold-crystallization process, the crystallization peak shifted toward the lower temperature with increasing of SABHA concentration. The melting behavior after crystallization at different crystallization temperatures showed that the melting process of PLLA/SABHA samples depended on the crystallization temperature, and the appearance of the double melting peaks was attributed to the melt-recrystallization. The thermal decomposition profile of PLLA was not affected by SABHA, but the addition of SABHA reduced the thermal stability of PLLA. Fortunately, the presence of SABHA improved the fluidity of PLLA, and the effect of SABHA concentration on the fluidity was positive.

Key Words: Poly(L-lactic acid), Organic nucleating agent, Non-isothermal crystallization, Fluidity, Decomposition behavior.

Introduction

Poly(L-lactic acid) (PLLA), derived from renewable resources such as potato, sugarcane and corn [1], has attracted more attentions because of its degradability, biocompatibility, easy processability, etc. In particular, PLLA can eventually get degraded into water and carbon dioxide [2], exhibiting a perfect environment-friendly. These aforementioned characteristics caused PLLA to be the most promising biodegradable polyester material, resulting in that it has been produced industrially since 2002, furthermore it has also been used in food packaging [3], biomaterials [4, 5], disposable tableware [6], biomedicine [7, 8], etc. For instance, Han *et al* [10] reported a hydroxyapatite nanowires modified polylactic acid membrane to achieve barrier/osteinduction dual functions. The immunohistochemical staining showed that the polylactic acid/hydroxyapatite could promote the expression of bone-related markers, and there existed more newly formed bones in polylactic acid/hydroxyapatite group.

Unfortunately, PLLA itself possess some inherent defects including mechanical brittleness, slow crystallization rate, low heat distortion temperature and crystallinity [11], which needs to be overcome to cause PLLA to fully compete with the commercial

thermoplastics. Compared to the other defects, the slow crystallization rate is the one of the most pressing problems of PLLA, because the crystallization rate during manufacturing directly determines the crystallinity and heat distortion temperature of the final PLLA products. Thus, the works to accelerate the crystallization are the focus points of study on PLLA. Usually, adding the nucleating agent in polymer matrix can reduce the surface free energy of the nucleation, and promote the crystallization to occur at a higher temperature and a faster cooling rate. Additionally, the nucleating agent exhibits these advantages such as low dosage, better nucleation effect and the excellent mechanical properties [1]. Therefore, adding the nucleating agent is thought to be the easiest and most feasible way to accelerate the crystallization of PLLA comparing with increasing the amount of L-lactide isomers, playing with the molding conditions, as well as adding the plasticizer [12]. Many commercial or synthesized additives were employed to evaluate their roles in promoting the crystallization of PLLA. Dong *et al* reported that the layered metal phosphonates including zinc phenylphosphonate, calcium phenylphosphonate and barium phenylphosphonate exhibited the excellent crystallization nucleating effect for PLLA. Moreover, 2 wt% zinc phenylphosphonate

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reduced the crystallization time of PLLA from 29.45 min to 0.57 min at 130 °C of crystallization temperature [13]. Yin *et al* synthesized an organic compound *N, N'*-bis(benzoyl)sebacic acid dihydrazide (BASD) to investigate its effect on the crystallization behavior of PLLA, it was found that the incorporation of BASD could significantly enhance the crystallization rate of PLLA, and the crystallization time of PLLA/2%BASD was only 2.36 min at 110 °C comparing with the 33.76 min of the pure PLLA, as well as that the phase separation temperatures were used to control the crystal morphology of PLLA [14]. Overall, the organic nucleating agents have gained considerable momentum in recent years, because the organic nucleating agent, in comparison to the inorganic nucleating agent, has more advantages, such as better compatibility, better nucleation effect, and greater adjustability in molecular design. Therefore developing the efficient organic nucleating agents becomes the focus point of research on nucleating agents for PLLA.

In our previous works, a series of amide compounds were prepared to be used as organic nucleating agents for PLLA [15, 16], the relevant results as reported by other literatures [1] adequately confirmed that the amide compounds could accelerate the crystallization process of PLLA. However, investigating on the nucleation mechanism should be based on the more organic nucleating agents with different molecular structures. Additionally, the most of the current works only focused on the influence of the organic nucleating agents on the crystallization behavior of PLLA. Thus, in this study, a new organic nucleating agent, *N, N'*-bis(1H-benzotriazole) succinic acid acetylhydrazide (designated as SABHA in this study), was synthesized through acylation reaction and amination reaction to nucleate PLLA. Besides the melt-crystallization and cold-crystallization, the melting

behavior, thermal stability, fluidity of SABHA-nucleated PLLA were investigated using differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), melt index instrument, etc.

Experimental

Materials and reagents

PLLA of 2002D was obtained from Nature Works LLC, USA, and the M_w was $1.95 \cdot 10^5$ and the D content was 4.25 %. All reagents in this study, including succinic acid, 1H-benzotriazole, *N, N*-dimethylformamide (DMF), thionyl chloride, chloroacetic acid, ethanol, hydrazine hydrate and pyridine, were purchased from Chongqing Huanwei Chemical Co., Ltd. China.

Synthesis of SABHA

The synthetic route of SABHA was described as Figure.1. Firstly, the detailed synthetic operations of the succinyl chloride and the 1H-benzotriazole aceto-hydrazide are similar to our previous work [17]. And then the 1H-benzotriazole aceto-hydrazide was dissolved in DMF with stirring, followed by slowly adding the succinyl chloride and pyridine. And the mixture was maintained at room temperature for 2 h and heated up to 70 °C for 4 h with stirring. Finally, the reaction mixed solution were poured into 300 mL of water to precipitate, and the filtration of the turbid solution was performed, as well as the crude product was washed by water for 3 times, the resulting SABHA was dried overnight 45 °C under vacuum. Infrared spectra (IR) ν : 3448.9, 3246.4, 1730.5, 1668.2, 1618.6, 1580.2, 1524.6, 1490.7, 1474.4, 1457.3, 1400.3, 1272.0, 1231.1, 1165.8, 1136.9, 1100.1, 953.4, 769.6, 749.2, 671.2, 570.1 cm^{-1}

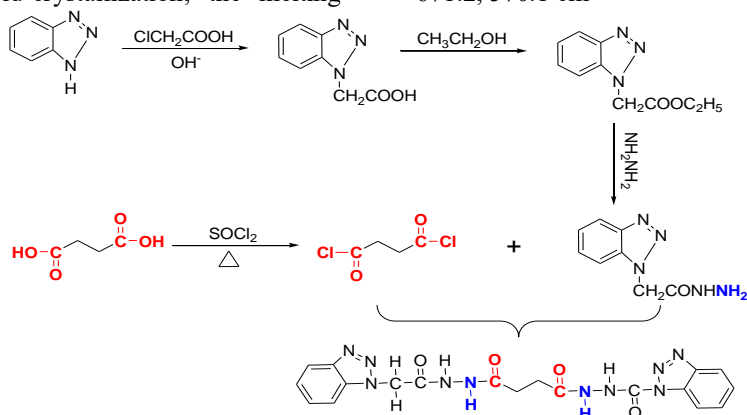


Fig. 1: Synthetic route of SABHA.

Preparation of PLLA/SABHA sample

The preparations of all PLLA samples containing various SABHA concentrations (99.5/0.5, 99/1, 98/2, 97/3) were carried out in a torque rheometer. The detailed blending parameters were as follows: the melt-blending temperature of 190 °C, the rotation speed of 32 rpm for 10 min, as well as the rotation speed of 64 rpm for 10 min. And then the mixture were further processed into sheets with 0.4 mm thickness through moulding (the pressure of 20 MPa, the hot press at 190 °C for 7 min, the cool press at room temperature for 10 min).

Characterization and testing

The molecular structure of SABHA was determined using FT-IR (KBr pellet). The melt-crystallization, cold-crystallization, and melting behavior of the pure PLLA and PLLA/SABHA samples were tested by DSC (Q2000, TA Instruments) under nitrogen with 50 mL/min, and an indium standard was employed to calibrate the temperature and heat flow before testing. TGA (Q500, TA Instruments) was used to characterize the thermal decomposition process of the pure PLLA and PLLA/SABHA samples, the testing temperature covered the range of 40-650 °C, and the atmosphere was the flowing air of 60 mL/min. The effect of SABHA on the processing fluidity of PLLA was measured by the melt index instrument, and the temperature was set at 180 °C, the load was 10 Kg.

Results and discussion

Non-isothermal crystallization

The primary goal of this work was to synthesis a new organic nucleating agent for PLLA. Thus, the effect of SABHA on the melt-crystallization behavior of PLLA was firstly evaluated using DSC. Figure.2 displays the melt-crystallization DSC curves of the pure PLLA and PLLA/SABHA samples from 190 °C at a cooling rate of 1 °C/min. It is clearly observed from Fig.2 that the pure PLLA have no discernible melt-crystallization peak in DSC curve, indicating that the melt-crystallization can not occur in cooling, the reason is that the crystallization ability of the pure PLLA itself is very poor, although the cooling rate is very slow. And the similar result can be also found from other studies on the melt-crystallization behavior of PLLA itself [11, 18]. Differing from the pure PLLA, all PLLA incorporating SABHA samples exhibit the obvious

melt-crystallization peaks, showing that the introduction of SABHA promotes the crystallization of PLLA in cooling, and the SABHA could be used as a heterogeneous nucleation site to increase the nucleation density of PLLA matrix. Additionally, Figure.2 shows the influence of SABHA concentration on the melt-crystallization process of PLLA, with increasing of SABHA concentration, the melt-crystallization peak shifts toward the higher temperature, and has the larger melt-crystallization enthalpy, which further reflects the nucleation effect of SABHA and the best crystallization promoting effect of 3 wt% SABHA for PLLA, because a larger amount of SABHA often result in the higher nucleation density in PLLA matrix. However, on the other hand, this result also indicates that 3 wt% SABHA can not still reach the saturated concentration in PLLA matrix. Compared to the pure PLLA, with the addition of 3 wt% SABHA, the crystallization peak temperature and the melt-crystallization enthalpy exhibit the maximum value of 131.3 °C and 45.2 J/g, respectively. According to the relevant equation [19], the crystallinity of PLLA/3%SABHA is 50.1%.

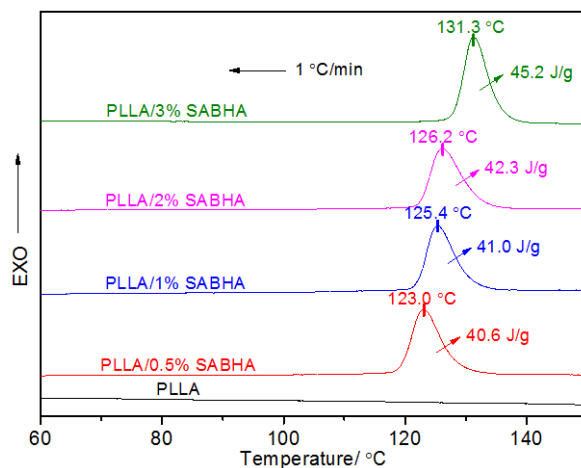


Fig. 2: Melt-crystallization process of the pure PLLA and PLLA/SABHA samples from the melt at a cooling rate of 1 °C/min.

The aforementioned result of the melt-crystallization behavior has evidenced the crystallization accelerating effect of SABHA for PLLA. To further reveal the role of SABHA in PLLA matrix, the cold-crystallization behaviors of PLLA/SABHA samples were further investigated. Figure.3 is the cold-crystallization curves of PLLA/SABHA sample at a heating rate of 1 °C/min. As shown in Fig.3, the effect of SABHA content

on the cold-crystallization behavior of PLLA is contrary to the result from the melt-crystallization. That is, the cold-crystallization peak shifts toward the lower temperature with increasing of SABHA content. Differing from the melt-crystallization process, all PLLA/SABHA samples have very high nucleation density during the cold-crystallization process, resulting from the heterogeneous nucleation of SABHA and homogeneous nucleation of PLLA itself in the low-temperature region. Under this circumstance, the crystal growth rate must be the rate-determining step during crystallization. Unfortunately, the larger amount of SABHA often has a greater inhibition for the mobility of PLLA molecular chain, resulting in that the shift to low temperature with an increase of SABHA content. Additionally, the influence of SABHA concentration on the cold-crystallization enthalpy is insignificant, the reason may be that the same heating rate and the high nuclear rate in the low-temperature region lead to nearly the same crystallization. And the PLLA/2%SABHA sample, in comparison to other PLLA/SABHA samples, has the largest cold-crystallization enthalpy of 26.5 J/g.

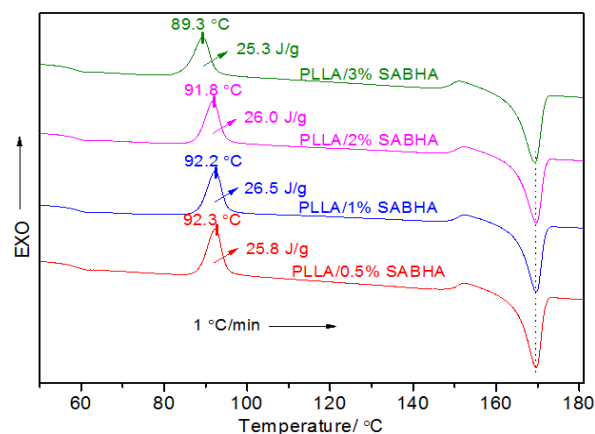


Fig. 3: Cold-crystallization process of the PLLA/SABHA samples at a heating rate of 1 °C/min

Melting behavior

The melting behavior of PLLA/SABHA samples after sufficient crystallization at different crystallization temperature (cooling from the melt) was further studied by DSC (See Fig.4). It is clear that there exist the double melting peaks after isothermal crystallization at 100 °C, whereas only the single melting peak appears after crystallization at 130 °C, indicating that the melting behavior of PLLA/SABHA sample depends on the

crystallization temperature. In the low temperature region, although the nuclear rate is very fast, the mobility of PLLA molecular chain is very poor, resulting in that the crystallization can not be completed. Upon heating, the primary crystals formed during isothermal crystallization are firstly melted, and then the melted crystals attach to the surface of SABHA to form the new crystals. Because these new crystals are rapidly formed in the same temperature region in heating, resulting in that the melting temperatures of the high-temperature melting peak are near. This phenomenon can be found in the multiple melting transformation behavior of PLLA [20]. However, in the high temperature region, the PLLA/SABHA has the fast nuclear rate and excellent mobility of molecular segment, which causes the PLLA to efficiently complete the crystallization in a short period of time, leading to the appearance of the single melting peak in heating.

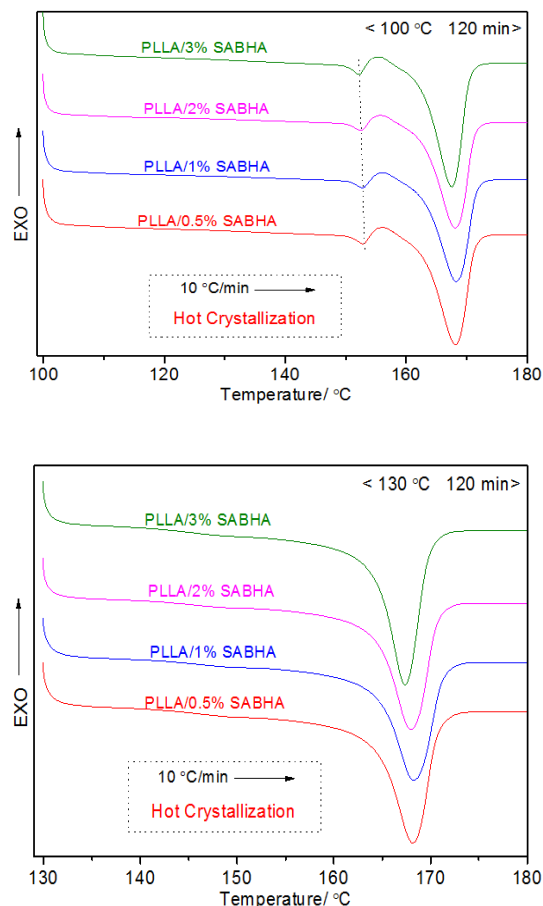


Fig. 4: Melting behavior of PLLA/SABHA after isothermal crystallization at a heating rate of 10 °C/min.

Thermal stability

For any polymer, the thermal decomposition temperature must be evaluated before usage. Figure.5 is the TGA curves of the pure PLLA and PLLA/SABHA samples from 40 °C to 650 °C at a heating rate of 5 °C/min under air. It is observed that the addition of SABHA can not change the thermal decomposition profile of PLLA. That is to say, both the pure PLLA and all PLLA/SABHA samples exhibit only one decomposition step, and the thermal weightlessness occurs at the temperature range from 300 °C to 375 °C, stemming from the chain scissions and loss of ester groups [21]. However, the SABHA significantly affects the onset decomposition temperature (T_{od}) of PLLA. The T_{od} of the pure PLLA, PLLA/0.5%SABHA, PLLA/1%SABHA, PLLA/2%SABHA, PLLA/3%SABHA are 341.3 °C, 317.6 °C, 302.0 °C, 328.1 °C and 335.3 °C, respectively. Through analysis of T_{od} data, it is easily found that the addition of SABHA decreases the thermal stability of PLLA, and the effect of SABHA concentration on the T_{od} of PLLA is irregular. With increasing of SABHA concentration from 0.5 wt% to 3 wt%, the T_{od} firstly decreases, and then increases. Compared to the other PLLA/SABHA samples, the PLLA/3%SABHA sample has the highest T_{od} value of 335.3 °C. On the one hand, the addition of SABHA must give rise to some defects in PLLA matrix, which reduces the T_{od} of PLLA in heating. On the other hand, the presence of SABHA has an inhibition for the mobility of PLLA molecular chain, resulting in an increase of T_{od} . As well as the probable interaction between C=O of PLLA and N-H of SABHA also leads to an increase of T_{od} , this influence of the intermolecular interaction on the T_{od} can also be found in PLLA/TBOD system [18] and PLLA/BAAD system [22]. As a result, the T_{od} depends on the aforementioned competitive relationship.

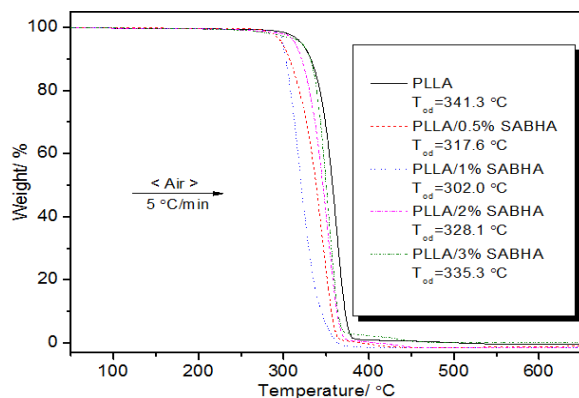


Fig. 5: Thermal decomposition process of the pure PLLA and PLLA/SABHA samples.

Fluidity

The fluidity is very important index to the manufacturing process, thus, investigating on the effect of SABHA on the fluidity is very necessary. Usually, the fluidity is characterized using the melt flow rate (MFR), the larger the MFR value is, the better the fluidity is. Figure.6 shows the MFR of the pure PLLA and all PLLA/SABHA samples. As seen in Fig.6, the introduction of SABHA improves the fluidity of PLLA, because all PLLA/SABHA samples have the larger MFR value than the pure PLLA. In particular, with the addition of only 0.5 wt% SABHA, the MFR increases from 1.67 g/10min to 6.51 g/10min comparing with the pure PLLA. With further increasing of SABHA concentration, the MFR of PLLA also further increases. This result is very instructive to the actual manufacturing, because the SABHA not only facilitate the crystallization, but also improve the fluidity of PLLA.

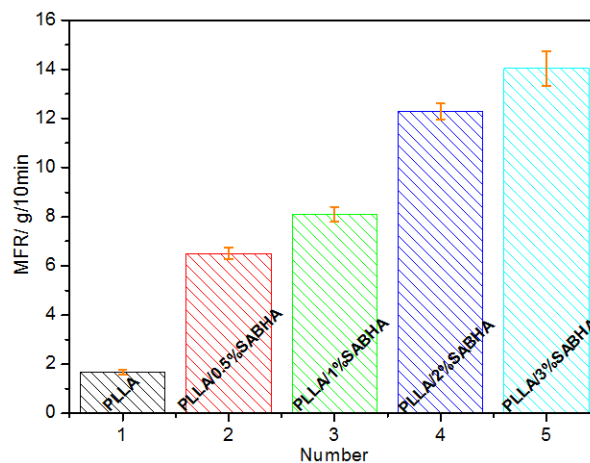


Fig. 6: MFR of the pure PLLA and PLLA/SABHA samples.

Conclusion

SABHA was synthesized to investigate its influence on the melt-crystallization, cold-crystallization, melting behavior, thermal stability, and fluidity of PLLA. The comparative study on the melt-crystallization behavior of the pure PLLA and PLLA/SABHA samples showed that the SABHA could significantly facilitate the crystallization of PLLA in cooling, and the melt-crystallization peak shifted toward the higher temperature with increasing of SABHA concentration, meaning that 3 wt% SABHA had the best crystallization promoting effect on PLLA.

in this study, and the 3 wt% SABHA could cause the crystallization peak temperature and the melt-crystallization enthalpy to rise to 131.3 °C and 45.2 J/g, respectively. However, for the cold-crystallization process, the effect of SABHA concentration on the cold-crystallization enthalpy was not effective, even, with an increase of SABHA concentration, the cold-crystallization peak shifted toward the lower temperature. After sufficient crystallization at different crystallization temperature, the difference in the melting behavior indicated that the melting behavior of PLLA/SABHA samples depended on the crystallization temperature, and the melt-recrystallization mechanism had been proposed to explain the double melting peaks in DSC curves. The presence of SABHA in PLLA matrix reduced the thermal stability of PLLA, but the decrease of the T_{od} was irregular with an increase of SABHA concentration. Among the PLLA/SABHA samples, PLLA/3%SABHA sample had the highest T_{od} value of 335.3 °C. The effect of SABHA on the fluidity of PLLA was positive, and PLLA containing a larger amount of SABHA concentration had the better fluidity. Overall, the SABHA-nucleated PLLA exhibited the excellent crystallization performance and fluidity, which may be used as a promising modified plastic to make plastics product.

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