Thermal Properties of Poly(L-lactide) Containing Succinic Dihydrazide Derivative

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Abstract: The slow crystallization speed is one of the most important factors restricting the development of Poly(L-lactide) (PLLA). In this paper, a succinic dihydrazide derivative BPASD was prepared to study its influence on the PLLA’s non-isothermal crystallization behavior and thermal decomposition behavior. A comparative study on the melt-crystallization of the PLLA/BPASD and pure PLLA showed that the BPASD could promote the melt-crystallization of PLLA in cooling, and a larger amount of BPASD exhibited the better nucleation effect for PLLA. However, the cold-crystallization peak moved to the lower temperature with increasing of BPASD loading. Additionally, the cooling rate and the heating rate were two improtant factors to the crystallization process of PLLA. Thermal stability measurements showed that the pure PLLA and all PLLA/BPASD samples have only one thermal decomposition profile, but the presence of BPASD reduced the thermal stability of PLLA.

1. Introduction
Among biodegradable polyester, Poly(L-lactide) (PLLA) has played a leading role in research and development or production field. Meantime, its noteworthy advantages such as the excellent compatibility and biodegradability, easy processability lead to a wide application in packaging materials [1], 3D printing [2], etc. Passador et al [3] prepared the PLA composites containing carbon black to be suitable for use as the antistatic packaging for electronic components. The introduction of the carbon black could increase the degradable temperature of PLA, meantime, the addition of the carbon black led to a decrease of the resistance of PLA/carbon composites.

However, PLLA itself suffers from some inherent defects including slow crystallization speed and low heat distortion temperature [4], which seriously restricts its development and application. Aiming at the defect of slow crystallization rate, the blending with a crystallization accelerator is often an important method to promote the crystallization performance of the pure PLLA. Talc [5], zinc phenylphosphonate [6], orotic acid [7], N, N'-bis(1H-benzotriazole) adipic acid acethydrazide [8], and WS₂ [9] could serve as efficient nucleating agents for promoting the PLLA’s crystallization of. For instance, with addition of only 0.8 wt% N, N'-bis(benzoyl) suberic acid dihydrazide and upon the crystallization of 115 °C, the crystallization half-time decreased from 26.5 min to 1.4 min comparing with the pure PLLA [10].

In this work, an organic compound, N, N'-succinic bis(4-phenylbutyric acid) dihydrazide (designated here as BPASD), was synthesized based on the succinic dihydrazide and 4-phenylbutyric acid to be used as a functional additive in PLLA matrix, and the melt-crystallization and cold-crystallization behavior and thermal decomposition behavior of PLLA/BPASD were studied. This work might be helpful to overcome some flaws of PLLA.
2. Experimental section

2.1 PLLA and BPASD
Nature Works LLC supplied the 2002D PLLA. The BPASD (The detailed compound structure is shown in Fig.1) was synthesized in our lab, and the characterization data of the molecular structure are as follows: Infrared spectroscopy (KBr) $\nu$: 3446.5, 3207.8, 3051.0, 2934.9, 2854.9, 1686.4, 1592.4, 1487.7, 1450.9, 1416.3, 1433.2, 1201.4, 1151.9, 1028.1, 911.9, 696.1, 669.3 cm$^{-1}$; 1H nuclear magnetic resonance (DMSO, 400 MHz) $\delta$: ppm; 9.74 (s, 1H, NH), 9.68 (s, 1H, NH), 7.16~7.30 (m, 5H, Ar), 2.56~2.60 (t, 2H, CH$_2$), 2.37 (s, 2H, CH$_2$), 2.11~2.14 (t, 2H, CH$_2$), 1.78~1.82 (t, 2H, CH$_2$).

![Figure 1. The structure of BPASD](image)

2.2 Preparation of PLLA/BPASD
The melting blend of PLLA and BPASD was carried out using a counter-rotating mixer, and the set of the blending parameter and detailed operational process were the same as our previous work [11].

2.3 Characterization and testing
$^1$H nuclear magnetic resonance spectrometer and infrared spectrometer were used to obtain the structure date of BPASD. The melt-crystallization and cold-crystallization behaviors of the pure PLLA and PLLA/BPASD were tested through DSC under nitrogen of 50 mL/min. The thermal decomposition process of the PLLA/BPASD and pure PLLA was observed using TGA from 40 °C to 650 °C under flowing air of 60 mL/min.

3. Results and discussion

3.1 Non-isothermal crystallization behavior
The melt-crystallization is very important to practical manufacturing, thus, this study firstly focuses on the melt-crystallization process. Figure 2 displays the melt-isothermal crystallization behavior of the pure PLLA and PLLA/BPASD samples in cooling of 1 °C/min. For the pure PLLA, there is almost not the melt-crystallization in cooling DSC curve, indicating that the pure PLLA has very poor crystallization ability. However, all PLLA/BPASD samples exhibit the obvious melt-crystallization peaks in DSC curves, meaning that the

![Figure 2. Melt-crystallization behavior of the pure PLLA and PLLA/BPASD in cooling of 1 °C/min](image)

BPASD promotes the crystallization of PLLA during process. Furthermore, with increasing of BPASD content, the melt-crystallization peak shifts toward the higher temperature, implying that a larger amount of BPASD possesses the better promoting role for the PLLA’s crystallization, because a larger amount of BPASD often has the higher nucleation density. 3 wt% BPASD can make the melt-crystallization
peak temperature and the melt-crystallization enthalpy increase to the maximum values of 128.2 °C and 48.4 J/g comparing with the neat PLLA, respectively.

However, the negative role of an increase of the cooling rate on the melt-crystallization process is obvious (See Fig.3), that is, the melt-crystallization peak becomes wider and shifts to the lower temperature with increasing of cooling rate to 3 °C/min, which indicates that a higher cooling rate weakens the PLLA/BPASD’s crystallization. This effect may depend on the competitive relationship between the cooling rate and BPASD. An increase of cooling rate causes the PLLA molecular chain to have no sufficient time to form a regular structure, although the presence of BPASD can promote the crystallization of PLLA.

![Figure 3. Melt-crystallization process of PLLA/BPASD in cooling of 3 °C/min](image)

For the cold-crystallization process, PLLA itself has fast nucleus rate via homogeneous nucleation of PLLA itself in the low temperature region, possibly exhibiting the different crystallization behaviors. Figure.4 is the cold-crystallization of PLLA/BPASD sample in heating of 1 °C/min. As shown in Fig.4, except PLLA/1%BPASD sample, an increase of BPASD content makes the cold-crystallization peak move to the lower temperature, and the cold-crystallization enthalpy of other PLLA/BPASD samples increases, which differs from the result of the melt-crystallization. Additionally, it is found from Fig.4 that the PLLA containing the larger amount of BPASD content has the higher melting temperature, showing a better perfection of crystals formed in heating.

![Figure 4. Cold-crystallization process of PLLA/BPASD in heating of 1 °C/min](image)

Similarly, the heating rate also significantly affects the cold-crystallization of BPASD-nucleated PLLA. As shown in Fig.5, for a given PLLA/BPASD sample, the shift to the higher temperature occurs with increasing of heating rate owing to the thermal inertia. But the effect of BPASD content on the cold-crystallization process of PLLA at a given heating rate is consistent with the aforementioned result of Fig.4.
3.2 Thermal decomposition behavior
The heating decomposition behaviors of the pure PLLA and all PLLA/BPASD were further studied using TGA (See Fig.6). All PLLA/BPASD samples like the neat PLLA have only one thermal decomposition stage, and the thermal weightlessness occurs in the temperature range from 275 °C to 375 °C, showing that the BPASD cannot change the PLLA’s thermal decomposition profile. However, the BPASD reduces the PLLA’s onset thermal decomposition temperature ($T_d$), and the corresponding onset thermal decomposition temperature of the PLLA, PLLA/0.5%BPASD, PLLA/1%BPASD, PLLA/2%BPASD, PLLA/3%BPASD are 341.3 °C, 333.2 °C, 327.0 °C, 334.7 °C and 334.3 °C, respectively. Although the onset thermal decomposition temperature of any PLLA/BPASD slightly decreases, the onset thermal decomposition temperatures of all PLLA/BPASD samples are above 300 °C, which still satisfies the daily use requirement.

4. Conclusions
In this work, BPASD as an organic nucleating agent could obviously accelerate the PLLA’s crystallization in cooling, and the melt-crystallization peak, with increasing of BPASD content, shifted to the higher temperature, as well as the 3 wt% BPASD had the best crystallization promoting role. For the cold-crystallization process, an increase of BPASD content caused the cold-crystallization peak to move to the lower temperature, exhibiting the opposite result with the melt-crystallization. The increasing of cooling rate could weaken the crystallization ability of PLLA/BPASD, but a higher heating rate caused the cold-crystallization peak to shift to the higher temperature. The BPASD could not change the PLLA’s thermal decomposition profile, however, and reduced the PLLA’s thermal stability.

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