

The Melting Behavior and Thermal Stability of Green Poly(L-lactic acid) with *N, N, N, N'*-Tetra(benzoyl) Ethylene Diamine Tetraacetic Acid Dihydrazide

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Summary: The thermal properties of green poly(L-lactic acid) (PLLA) with *N, N, N, N'*-tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide (NA) at different conditions were investigated. The melting behavior of PLLA/NA sample after isothermal crystallization at 100 °C showed that the low-temperature melting peak shifted to high temperature with increasing of crystallization time. However, the high-temperature melting peak did not show any change. Meantime, the melting enthalpy of cold crystallization was higher than that of hot crystallization, and the difference between cold crystallization and hot crystallization increased from 0.31 J/g to 0.89 J/g with increasing of crystallization time. Heating or cooling rate affected the melting behavior of PLLA, the low-temperature and high-temperature melting peak shifted to low temperature with increasing of rate, and the ratio of melting peak area between low-temperature melting peak and high-temperature melting peak decreased. Thermal stability of PLLA/NA indicated that PLLA/NA only exhibited one decomposition stage as decomposition of PLLA.

Keywords: Poly(L-lactic acid); Multi-amides; Melting behavior; Crystallization; Thermal stability.

Introduction

Multi-amides as very important materials have been widely used in synthetic intermediates [1], material chemistry [2], polymer [3, 4] and so on, due to their excellent antitumour, antibacterial and nucleating properties [5], *etc.* Especially, the importance of the multi-amides in polymer has been highlighted in recent years. For example, Cai et al [6] reported the influence of *N, N'*-bis(benzoyl) alkyl diacid dihydrazides on crystallization of green polymer materials poly(L-lactic acid) (PLLA), the experimental results indicated that five synthesized *N, N'*-bis(benzoyl) alkyl diacid dihydrazides were powerful nucleating agent for PLLA, with introduction of *N, N'*-bis(benzoyl) alkyl diacid dihydrazide, the crystallization peaks became sharper and shifted to higher temperature as the degree of supercooling decreased.

PLLA is the most typical bio-based thermoplastic polymer materials due to its degradable performance [7]. However, PLLA also exhibits some disadvantages such as slow crystallization rate, poor heat resistance, *etc.* Especially, slow crystallization rate seriously restricts the application of PLLA. In our previous work [8], we had synthesized *N, N, N, N'*-tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide (NA), and crystallization performance

indicated that NA as a kind of heterogeneous nucleation agent could improve the crystallization rate of PLLA. Thus, in this paper, to further know the function and role of NA, the melting behavior at different conditions and thermal stability of PLLA/NA were investigated in detail.

Experimental

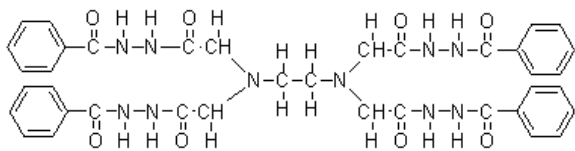
Materials

Poly(L-lactic acid) used in this study was purchased from Nature Works LLC, USA. The materials used to synthesis the nucleating agent NA were of analytical grade (AR). Benzoyl hydrazine and tetraacetic acid were procured from Chengdu Kelong Chemical Reagents Company from Sichuan province in China. Thionyl dichloride, *N, N*-dimethylacetamide and pyridine were procured from Mianyang Rongshen Chemical Reagents Company from Sichuan province in China.

Synthesis procedure of NA

The structure of NA was shown in Scheme-1. And the typical synthesis procedure of NA has been described in our previous paper [8]. And the average size of NA power from SEM is 10 μm (Fig.1).

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Scheme-1: Structure of NA.

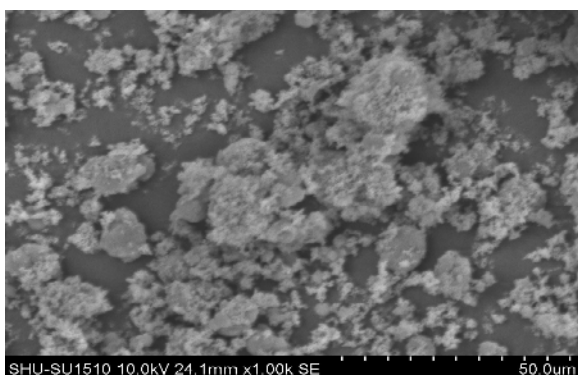
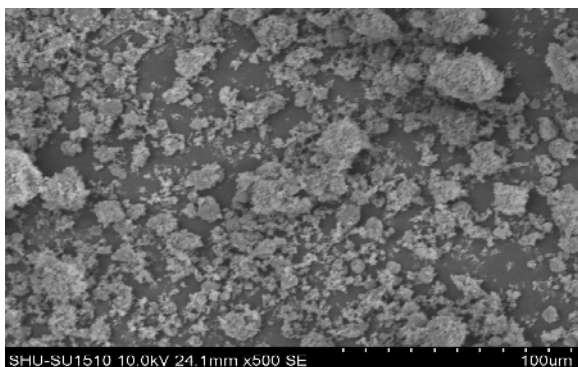


Fig.1: SEM of NA.

Preparation of PLLA/NA sample

Firstly, PLLA and NA were dried, then blending of PLLA and NA was performed on a counter-rotating mixer, and the preparation process of PLLA/NA sample is similar to that of our previous papers [9, 10].

Characterization

The thermal stability of PLLA/NA sample was measured by Q500 TGA (TA Instruments-Waters LLC, USA). The thermal decomposition process at different heating rate under air flow (60 ml/min) from room temperature to 550 °C was recorded.

The melting behavior of PLLA/NA sample was measured by DSC Q2000 (TA

Instruments-Waters LLC, USA). The temperature and heat flow at different condition were calibrated using an indium standard.

Result and discussion

Melting behavior of PLLA/NA sample after isothermal crystallization

Usually, the melting behavior of PLLA would be significantly affected by the additive, and there existed quite some literatures about melting behavior of PLLA composites [11, 12]. Thus, we investigate the melting behavior of PLLA with NA at different conditions. Fig. 2 shows the melting behavior of PLLA/NA sample at the heating rate of 10 °C/min after isothermal crystallization at 100 °C. Fig. 2 A represents the melting behavior of PLLA/0.5%NA after isothermal crystallization at 100 °C from melt (hot crystallization), and Fig. 2 B represents the melting behavior of PLLA/0.5%NA after isothermal crystallization at 100 °C from 20 °C (cold crystallization). As shown in Fig. 2, it is clear that there exist double-melting peaks during melting process after isothermal crystallization at 100 °C. Double-melting peaks of PLLA have been investigated by many authors [13], and up to now, there exists two different melting mechanisms, including melting of crystals of different stability and the melting re-crystallization and re-melting process [14, 15]. It is also observed from Fig. 2 that the low-temperature melting peak shifts to high temperature with increasing of crystallization time both hot crystallization and cold crystallization. With increasing of crystallization time at 100 °C, NA can further promote the crystallization of PLLA because of nucleating effect of NA, resulting in the formation of more PLLA crystals. On the other hand, the crystals of PLLA also further grow and exhibit more perfect crystal structure. However, the high-temperature melting peak do not move, the possible reason is the second crystallization of PLLA at same heating rate. Meantime, the melting enthalpy of isothermal hot crystallization and cold crystallization is different. As seen in Fig. 3, the melting enthalpy of cold crystallization is higher than that of hot crystallization, and the difference between cold crystallization and hot crystallization gets large with increasing of crystallization time. Cold crystallization process makes the form of crystal nucleus become easier, and the more crystal nucleus is, the more crystal of PLLA is, resulting in the increasing of melting enthalpy.

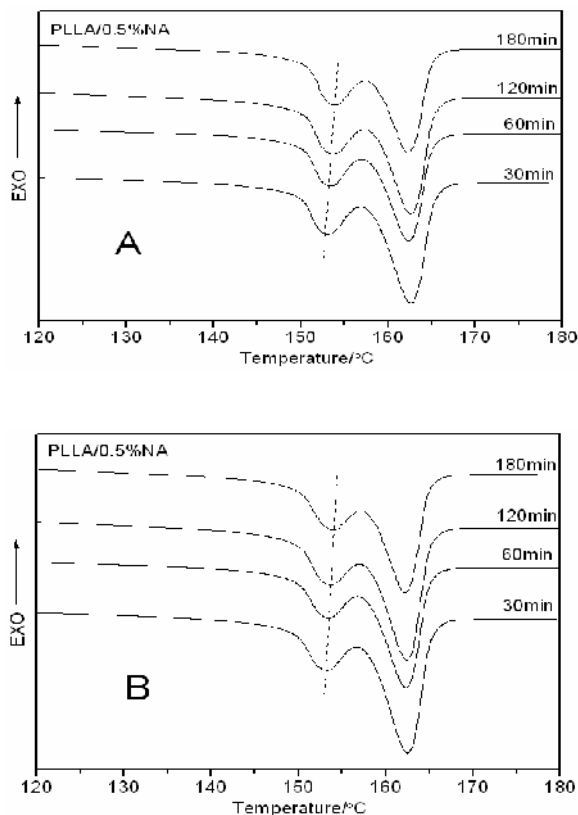


Fig. 2: Melting behavior of PLLA/NA at heating rate of 10 °C /min after isothermal crystallization at 100 °C.

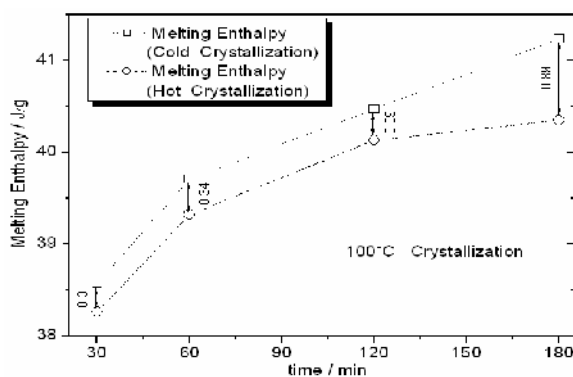


Fig. 3: Melting enthalpy of PLLA/0.5%NA after isothermal cold crystallization and isothermal hot crystallization.

Melting behavior of PLLA/NA sample at different rate

Heating or cooling rate is very important to define melting behavior of polymer. Thus, the

melting behavior of PLLA/NA sample at the respective same rate after non-isothermal crystallization at different cooling rate was investigated (Fig. 4). With increasing of the cooling rate, the low-temperature and high-temperature melting peaks shift to low temperature, the reason for this is that the crystal of PLLA formed during cooling crystallization and second heating is more perfect with decreasing of cooling or heating rate, the result results in melting peaks shifting to high temperature with decreasing rate. It is observed from Fig. 4 that the ratio of melting peak area between low-temperature melting peak and high-temperature melting peak decreases with increasing rate. Especially, the primary crystallites is less at cooling rate of 5 °C/min, which obtains from smaller melting peak represents primary crystallites of PLLA during non-isothermal crystallization process. This result further indicates that high cooling rate would hinder the forming of more crystal of PLLA during non-isothermal crystallization process. On the other hand, the nucleation effect of NA on crystallization of PLLA also weakens resulting from the high cooling rate.

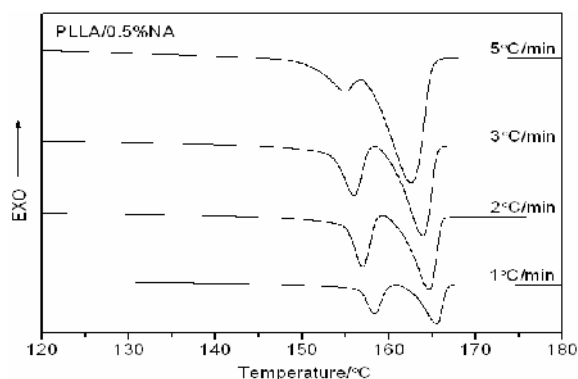


Fig. 4: Melting behavior of PLLA/NA at the respective same heating rate after non-isothermal crystallization at different cooling rate

However, the melting behavior is different at heating rate of 10 °C/min after non-isothermal crystallization at different cooling rate. Fig. 5 shows the melting behavior of PLLA/NA sample at heating rate of 10 °C/min after non-isothermal crystallization at different cooling rate. As seen in Fig. 5, besides from 5 °C/min, the high-temperature melting peak hardly move at other cooling rate. What is more, the high-temperature melting peak area decreases significantly with decreasing of non-isothermal crystallization cooling rate.

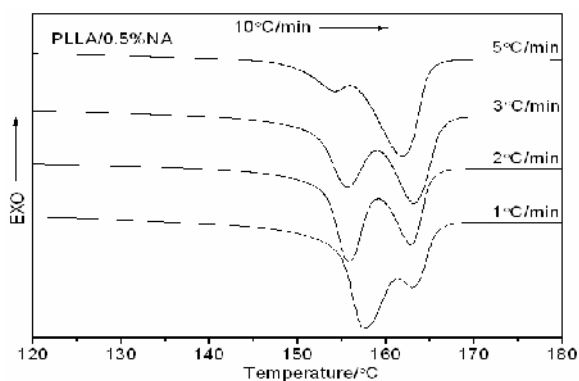


Fig. 5: Melting behavior of PLLA/NA after non-isothermal crystallization at different cooling rate

Thermal stability of PLLA/NA

Thermal stability of polymer will decide the field of application of PLLA. Thus, thermogravimetric (TGA) curves of thermal decomposition for PLLA/NA sample at different heating rate are presented in Fig.6. PLLA/NA sample decomposes fast and completes in one stage above 300 °C, and there exists only one decomposition stage, which refers to decomposition of PLLA. This result indicates that addition of NA do not affect the decomposition of PLLA, which depends on the fact that a little amount of NA has been introduced. Moreover, the onset decomposition temperature of PLLA/NA sample increases with increasing of heating rate, as it is observed from decomposition of other compound reported in literatures [6, 16]. In addition, the increasing rate of decomposition temperature also slows down.

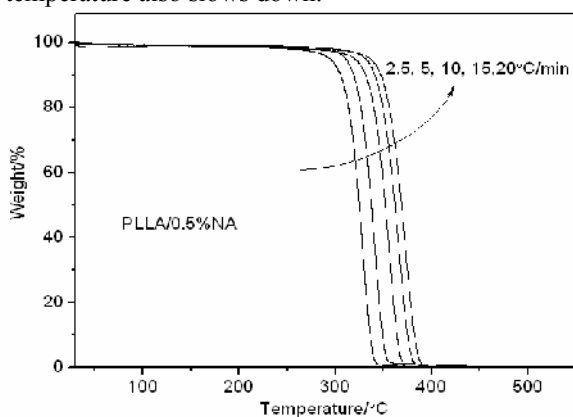


Fig. 6: TGA curves of PLLA/NA at different heating rate

Conclusion

The melting behavior and thermal stability of PLLA/NA was investigated in this paper. The melting behavior of PLLA/NA after isothermal crystallization showed the increasing of crystallization time made the low-temperature melting peak shift to high temperature, and the melting enthalpy of cold crystallization was higher than that of hot crystallization. In addition, heating or cooling rate affected the melting behavior of PLLA, Thermal stability indicated that PLLA/NA sample decomposed fast and completed in one stage above 300 °C, exhibiting a promising application in daily life.

Acknowledgements

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