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The Nucleation Effect and Thermal Behavior of Poly(L-lactic acid) in the Presence of a Bisamides Compound

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Summary: The nucleation effect and thermal behavior of bisamides compound(*N*, *N′*-Bis(benzoyl) tridecanedioic acid dihydrazide (NA)) as organic nucleating agent for poly(L-lactic acid) (PLLA) was evaluated by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide angle X-ray diffraction (WAXD). Compared to neat PLLA, NA could increase the overall crystallization rate of PLLA. Upon the addition of 0.8% NA, the crystallization peak temperature increased from 96.28 ℃ to 113.58 ℃, and the crystallization enthalpy increased from 1.379 $J\cdot g^{-1}$ to 30.51 $J\cdot g^{-1}$. POM showed that the spherulite number of PLLA increased and the spherulite size significantly reduced in the presence of NA. The results of melting behavior at different conditions showed that the melting behavior of PLLA/NA samples was affected significantly by crystallization time, crystllization temperature and cooling rate. And there existed double-melting peaks resulting from melting-recrystallization at low crystallization temperature.

Keywords: Poly(L-lactic acid), Nucleation effect, Thermal behavior, Crystallization.

Introduction

Poly(L-lactic acid)(PLLA), as a very important gree plastic, has attracted more and more interest due to decreasing fossil resources and global sustainable development concept in recent years [1-3]. However, there exist still some disadvantages to restrict the practical application of PLLA. Especially, slow crystallization rate, low degree of crystallization and poor heat resistance of PLLA have influence of development of PLLA [4]. Thus, it is necessary to improve the performance of PLLA to make it fully competitive with commercial thermoplastics [5].

There exist many viable methods to improve the crystallization rate and degree of crystallization, mainly including minimizing the amount of D-lactide isomers in the L-lactide, adding nucleating agent, adding plasticizer and playing with the molding conditions [6]. Usually, adding nucleating agent is a good way to improve the degree of crystallization and increase crystallization rate of PLLA [7, 8]. For example, Montmorillonite was widely used to be inorganic nucleating agent of PLLA. Li XX *et al* [9] researched the isothermal crystallization behavior of PLLA/organo- montmorillonite(OMMT) nanocomposites. The temperature and content of OMMT affected the induction periods and the half-time of overall PLLA crystallization. Research results also showed that adding OMMT made the equilibrium melting point of PLLA/OMMT nanocomposites decrease, indicating that the layered structure of clay restricted the full formation of crystalline structure of polymer. Yuya Tachibana *et al* [10] reported biobased myo-inositol as nucleator for PLLA. The isothermal crystallization of PLLA at 100 ℃ finished over 14 min after melting, However, isothermal crystallization of PLLA with 5% myo-inositol finished within 2 min. N. Kawamoto *et al* [11] reported that a series of compounds having hydrazide groups was prepared and evaluated as nucleating agent for PLLA. Benzoylhydrazide type compounds having 10 methylenes decamethylenedicarboxylic dibenzoylhydrazide demonstrated excellent nucleation ability.

In our previous work [5], we reported in detail that *N*,*N′*-bis(benzoyl) suberic acid dihydrazide was a novel nucleating agent for PLLA. Non-isothermal crystallization indicated that the presence of *N*,*N′*-bis(benzoyl) suberic acid dihydrazide accelerated the overall PLLA crystallization. The addition of *N*,*N′*-bis(benzoyl) suberic acid dihydrazide caused shorter crystallization time and faster overall crystallization rate, meaning advanced nucleation ability of *N*,*N′*-bis(benzoyl) suberic acid dihydrazide upon crystallization of PLLA. Upon the addition of 0.8% *N*,*N′*-bis(benzoyl) suberic acid dihydrazide, the crystallization half-time of PLLA decreased from 26.5 min to 1.4 min at 115℃.

In this paper, in order to investigate in detail

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the nucleation effect and thermal behavior of bisamides compound with different methylene chain and develop more bisamides type nucleation agent for PLLA, *N*, *N'*-Bis(benzoyl) tridecanedioic acid dihydrazide(NA) was synthesized, and the nucleation effect and thermal behavior of bisamides compound NA as nucleating agent for PLLA was evaluated by using DSC, POM and WAXD.

Results and Discussion

Crystallization Behavior

Nucleation effect of NA on crystallization of PLLA was evaluated by non-isothermal crystallization. Fig. 1 shows the DSC curves of non-isothermal crystallization of PLLA and PLLA/NA samples from melt at a cooling rate of 1℃/min. As seen in Fig. 1, up the same cooling rate, the crystallization peak of PLLA can almost not be detected. However, there exists obvious crystallization peak in the DSC cooling curves of PLLA/NA samples. Compared to the neat PLLA, adding NA leads to the shift of crystallization peak to higher temperature indicating the increase of crystallization temperature. And crystallization peak for PLLA containing NA becomes much sharper in the cooling process, this result indicates that NA can increase the overall crystallization rate of PLLA [12, 13]. Upon cooling at 1℃/min, as seen in Table-1, with increasing content of NA, the initial crystallization temperature (T_o) and the crystallization peak temperature (T_{mo}) increase, upon the addition of 0.8% NA, Compared to neat PLLA, the T_{mo} increases from 96.28 ℃ to 113.58 ℃, which is the highest T_{mo} value, and the highest T_o value appears in PLLA with the content of 1% NA. However, the crystallization enthalpy (ΔH_c) of PLLA/0.8%NA appears the biggest value, which indicates the best nucleating effect of crysallization at 0.8% NA.

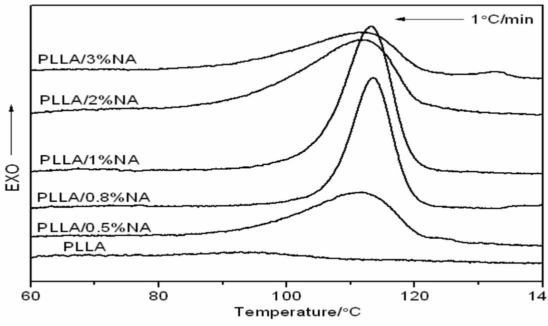


Fig. 1: DSC curves of PLLA and PLLA/NA crystallized from melt at a cooling rate of 1 ℃/min.

Table-1: DSC date of PLLA and PLLA/NA crystallized from melt at a cooling rate of 1℃/min.

Sample	T_o/℃	T_{mo}/℃	ΔH_c/J·g^{-1}
PLLA	105.88	96.28	1.379
PLLA/0.5%NA	120.70	111.93	22.33
PLLA/0.8%NA	119.21	113.58	30.51
PLLA/1%NA	119.36	113.25	29.55
PLLA/2%NA	121.04	112.43	24.62
PLLA/3%NA	121.11	112.19	22.42

The effect of NA on the crystallization of PLLA was further investigated by WAXD. Fig. 2 shows the WAXD of NA and PLLA/NA samples fabricated by melt blending and hot-press forming process. As seen in Fig. 2, the WAXD peaks of the PLLA/NA samples are wide, which results from inadequate crystallization of PLLA/NA samples. However, it is clear that the characteristic peak at 2θ= 16.6° of PLLA with addition of 0.8%NA is the strongest, this result is consistent with the aforementioned non-isothermal crsytallization results, and further confirms the best nucleation effect of 0.8% NA.

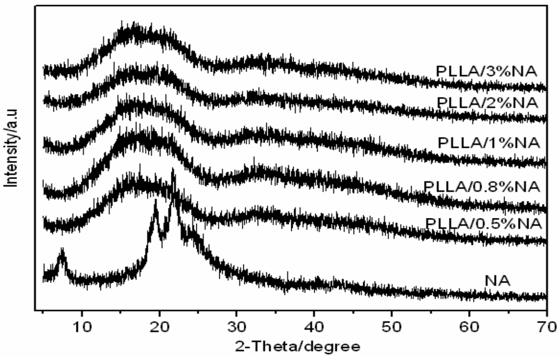


Fig. 2: WAXD patterns of NA and PLLA/NA samples.

Cooling rate is very important factor to investigate the non-isothermal crystallization of PLLA. Fig. 3 shows that the non-isothermal crystallization exotherms of PLLA and PLLA/0.8%NA sample from the melt at different cooling rate. With increasing of the cooling rate, the crystallization peak gradually becomes wider and shifts to a lower temperature. As to PLLA, the crystallization peak of PLLA can not be detected at the cooling rate of 2℃/min. However, there exist obvious crystallization peak of PLLA/0.8%NA samples at the cooling rate of 2℃/min. What is more, the crystallization onset temperature and crystallization exotherms of PLLA/0.8%NA sample is higher than those of PLLA at the same cooling rate. These results further confirm that NA can accelerate the crystallization of PLLA.

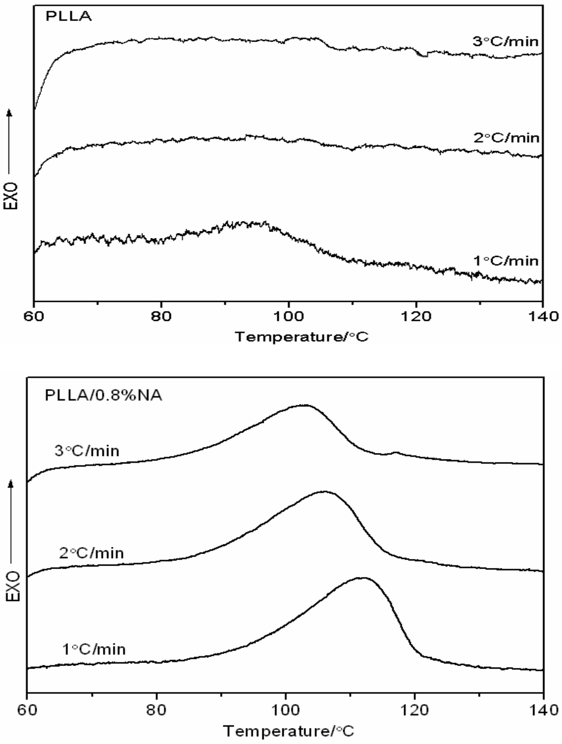


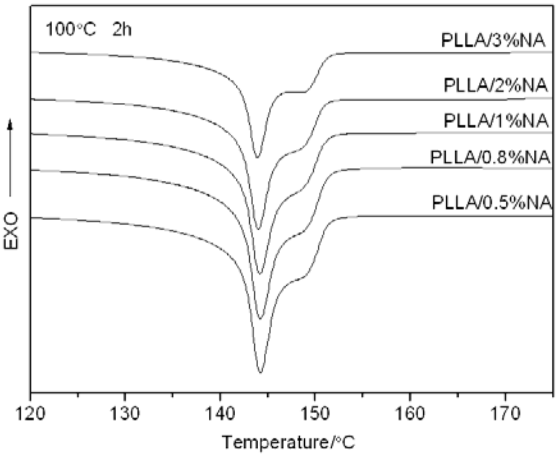
Fig. 3: The non-isothermal crystallization exotherms of PLLA and PLLA/0.8%NA sample at different cooling rates.

The spherulite morphology of PLLA/0.8%NA was compared with that of the neat PLLA by POM analysis. Fig. 4 presents the POM images of the neat PLLA and PLLA/0.8%NA sample after isothermal melt-crystallizing at 115℃. As for neat PLLA, the spherulite size is large and the spherulite number is small. 0.8% NA makes the spherulite size of PLLA decrease dramatically and the spherulite number become large.

Fig. 4: POM images of PLLA and PLLA/0.8%NA at 115℃.

Melting Behavior

Usually, melting behavior of polymer is affected by additive. Thus, studies on the melting behavior of polymer will help us investigate further the function and effect of additive. Fig. 5 presents the melting ednotherms of the PLLA/NA samples after different crystallization temperature for crystallization different time from melt. As seen in Fig. 5, there exists double-melting behavior after crystallization at 100℃ for 2h, The double-melting behavior of PLLA has been reported in literature [14], the low-temperature melting peak is attributed to the primary crystallites formed at crystallization temperature, and high-temperature melting peak reflects the relatively prefect lamella stacks results from recrystallization during the heating scan [15]. And it is observed in Fig. 5 that low-temperature melting peak does not move with increasing of NA content after crystallization at 100℃ for 2h. However, the high-temperature melting peak shifts to higher temperature with increasing of NA content, which may result from better nucleation effect of more NA content during the second heating, scan. At the same time, there exists only single melting peak after crystallization at 105℃ for 2h, which indicates full crystallization of PLLA. On the other hand, the melting peak shifts to higher temperature with the increasing of crystallization temperature, the reason may be that the crystallization of PLLA is more prefect at higher crystallization temperature. The melting peak of PLLA/0.8%NA is sharper than other PLLA/NA samples, this also confirm the most nucleation effect of 0.8%NA again [16].



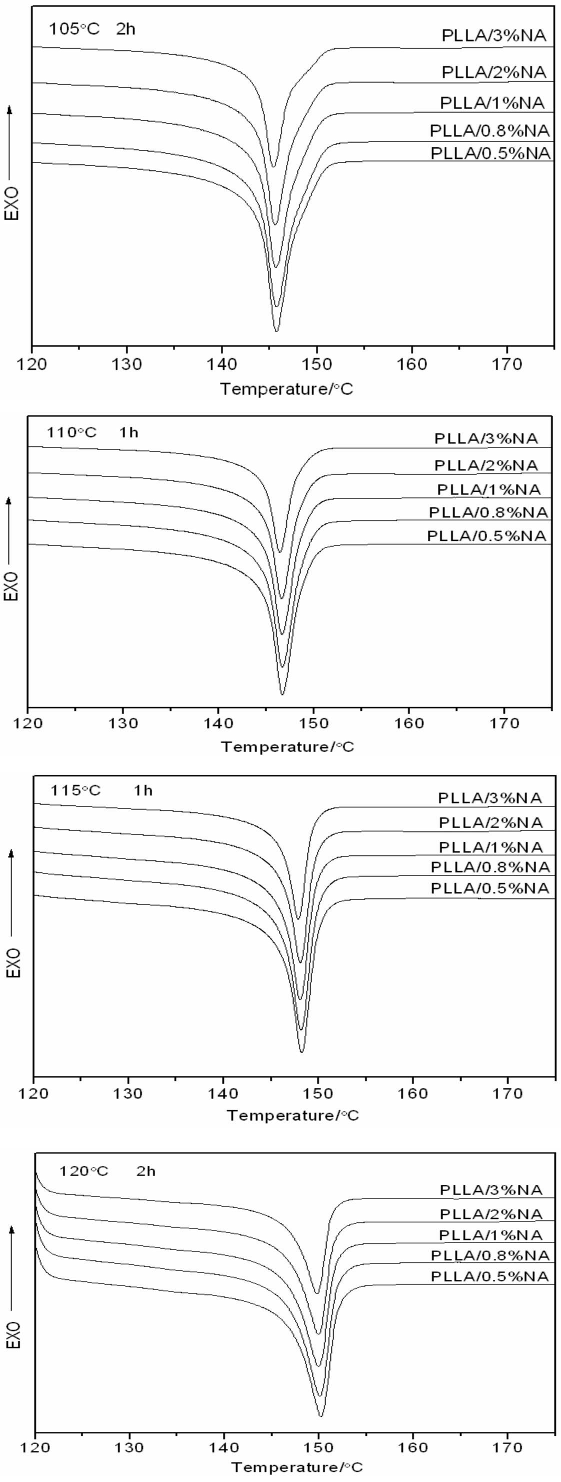
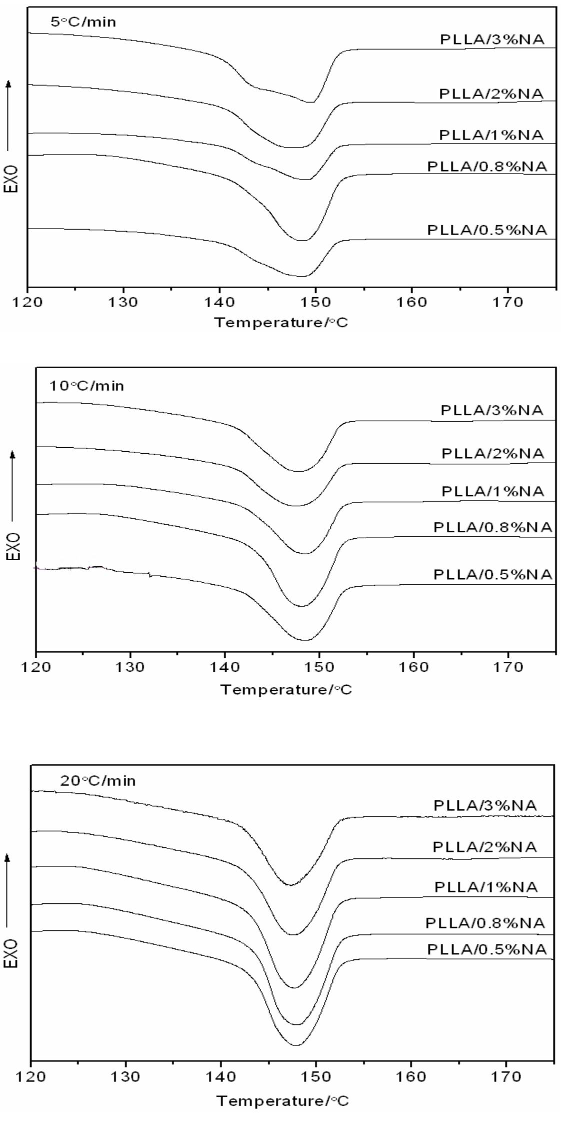


Fig. 5: The melting ednotherms of the PLLA/NA samples after different crystallization temperature for crystallization different time from melt.

Fig. 6 shows the melting behavior of PLLA/NA samples at heating rate of 10℃/min after cooling process at different cooling rate from melt. Increasing of cooling rate makes the low-temperature melting peak of PLLA/NA samples disappear, and the double-melting peak of PLLA/NA samples becomes the single-melting peak. The reason is that there exists crystallization process at cooling rate of 5℃/min, but the melting crystallization almost do not occure at higher cooling rate, which also confirms the important effect of cooling rate on the crystallization of PLLA. What is more, it is obvious that the high-temperature melting peak of PLLA/NA samples do not move at heating rate of 10℃/min after cooling process at different cooling rate from melt, this result indicates that the melting behavior results from recrystallization during the heating scan.



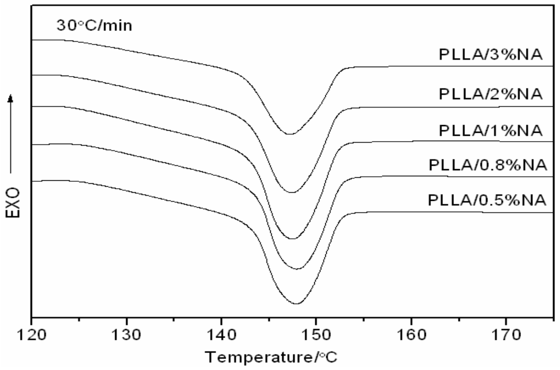


Fig. 6: The melting behavior of PLLA/NA samples at heating rate of 10℃/min after cooling process at different cooling rate from melt

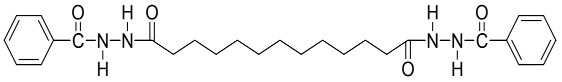
Experimental

Materials

Poly(L-lactic acid) (2002D) was purchased from Nature Works LLC, USA. The other materials used in this study were of analytical grade (AR). Benzoyl hydrazine and tridecanedioic acid were purchased from Beijing Chemical Reagents Company (Beijing, Chian) and Chengdu Kelong Chemical Reagents Company respectively (Sichuan Province, China); Thionyl dichloride, *N*, *N*-dimethylacetamide and Pyridine were procured from Mianyang Rongshen Chemical Reagents Company (Sichuan Province, China).

Synthesis of N, N'-Bis(benzoyl) terephthalic acid dihydrazide (NA)

The chemical structure of *N*, *N'*-Bis(benzoyl) tridecanedioic acid dihydrazide was shown in Scheme-1. And the synthesis process of *N*, *N'*-Bis(benzoyl) tridecanedioic acid dihydrazide has described in our previous paper [5]. IR (KBr) υ: 3439、3221.3、2920.9、2850、1642.9、1604.8、1574.3、1503.2、1468.4、1407.8、1382.9、1358.1、1266.9、1158.7、1072.5、997、951.2、861.4、711.1、691.6、636.4、548.3、522.9、449.8 cm^{-1}; ^{1}H NMR (DMSO, 500 MHz) δ: ppm; 10.28 (s, 1H, NH), 9.83 (s, 1H, NH), 7.48 ~ 7.88 (m, 5H, Ar), 2.16 ~ 2.19 (t, 2H, CH_2), 1.54 ~ 1.55 (d, 2H, CH_2), 1.21 ~ 1.27 (d, 2H, CH_2).



Scheme-1: Structure of *N*, *N'*-Bis(benzoyl) tridecanedioic acid dihydrazide.

Preparation of PLLA/NA samples

PLLA was dried at 50 ℃ under vacuum to remove residual water in PLLA. Blending of PLLA and NA was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 5 min, then at 64 rpm for 5 min. The processing temperature was 185℃. PLLA/NA samples were hot pressed at 180℃ under 20 MPa for 4 min, then were cooled down to room temperature by being compressed at room temperature under 20 MPa for 10 min.

Test

The non-isothermal crystallization behavior of PLLA was measured by DSC Q2000 (TA Instruments-Waters LLC, USA). The temperature and heat flow at different heating rate were calibrated using an indium standard. The sample was heated to 190℃ and maintained at that temperature for 5 min to make sure that the polymer crystals were melted completely. Then the samples were cooled from the melt state to 40℃ at different cooling rate. At last, the samples were reheated to 190℃ at the heating rate of 10℃/min to observe the melting behavior. The sample was quenched from melt to the crystallization temperature T_c (100, 105, 110, 115, 120℃), held at that temperature for at least 60 min to ensure crystallization. Then, the samples were reheated to 190℃ at the heating rate of 10 ℃/min to observe the melting behavior.

The spherulite of PLLA/NA sample was observed using an XPN-203E (Changfang Optical instrument Co., Ltd. Shanghai, China) equipped with a Canon Powershot-A610 camera and a Programmable temperature controller KEL-XMT-3100A (Chaoyang instrument Co., Ltd. Nanjing, China).

Wide angle X-ray diffraction (WAXD) experiments were performed on a diffractometer (D/MAX2550, Rigaku, Japan) using Cu K_α radiation (wavelength, 1.54 Å) at room temperature in the range of 2θ=5-70° with scanning rate of 2 °/min.

A Fourier transform infrared spectrum was recorded on a Bio-Rad FTS135 spectrophoto meter from 4000 to 400 cm^{-1}. The NA sample was mixed with KBr powders and pressed into a disk suitable for IR measurement.

The ^1H nuclear magnetic resonance was recorded on Brucker AVANCE 300 spectrometers. The solvent was dimethyl sulphoxide (DMSO).

Conclusions

The nucleation effect and melting behavior of PLLA/NA with different NA content were investigated. These results showed that NA could significantly improve the crystallization of PLLA.Upon the addition of 0.8% NA, the crystallization peak temperature increased from 96.28 ℃ to 113.58 ℃, and the crystallization enthalpy increased from 1.379 $J{\cdot}g^{-1}$ to 30.51 $J{\cdot}g^{-1}$. The melting behavior at different conditions showed that the melting behavior of PLLA/NA samples was affected significantly by crystallization time, crystllization temperature and cooling rate.

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