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Synthesis, Thermal Properties and Nucleating Effect of *N, N, N, N′*-Tetra(benzoyl) Ethylene Diamine Tetraacetic Acid Dihydrazide as Nucleating Agent of Poly(L-lactic acid)

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ABSTRACT: *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide as nucleating agent of Poly(L-lactic acid) (PLLA) was synthesized from benzoyl hydrazine and tetraacetic acid by acylation and ammoniation. and the structure of this novel tetraamide compound had been characterized by FT-IR. The thermal stability of *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide was investigated by TGA thermal analyzer. The result showed good thermal stability of *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide under 170℃. *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide modified PLLA sample was prepared by a melt-mixing technique. With incorporation of 0.5% *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide, Non-isothermal crystallization behavior at different cooling rate showed the crystallization peak of PLLA became sharper and shift to higher temperature, and indicated that the presence of *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide accelerated the overall PLLA crystallization.

Keywords: Benzoyl hydrazine; Poly(L-lactic acid); Tetraacetic acid; Thermal stability; Crystallization.

Introduction

Poly(L-lactic acid) is a very important gree polymer due to its low energy consumption, biodegradable properties and non-toxic to the environment[1-5]. However, slow crystallization rate of PLLA is too weak for practical application [6]. Thus, it is necessary to increase crystallization rate of PLLA to make it fully competitive with commercial thermoplastics. Now, the most viable method to increase the overall crystallization rate is the blending with nucleating agent. It has been reported that amides could be used to improve the crystallization rate of PLLA as nucleating agent [7]. For example, the importance of the amides in PLLA has been recently highlighted in our previous paper [6]. In that paper, it is reported that 0.8%*N,N′*-bis(benzoyl) suberic acid dihydrazide make the crystallization half-time of PLLA decrease from 26.5 min to 1.4 min at 115°C, and nucleating mechanism belongs to the mechanisms of chemical. Finally, we presume that hydrogen bonding come into being between PLLA and *N,N'*-bis(benzoyl) suberic acid dihydrazide according to their functional groups analysis. Thus, in this paper, *N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide including more amide functional groups was synthesized to improve crystallization of Poly(L-lactic acid), and we fabricated the PLLA/0.5%*N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide samples by melt-mixing technique. The thermal properties and nucleating effect of *N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide on PLLA was investigated.

Experimental Section

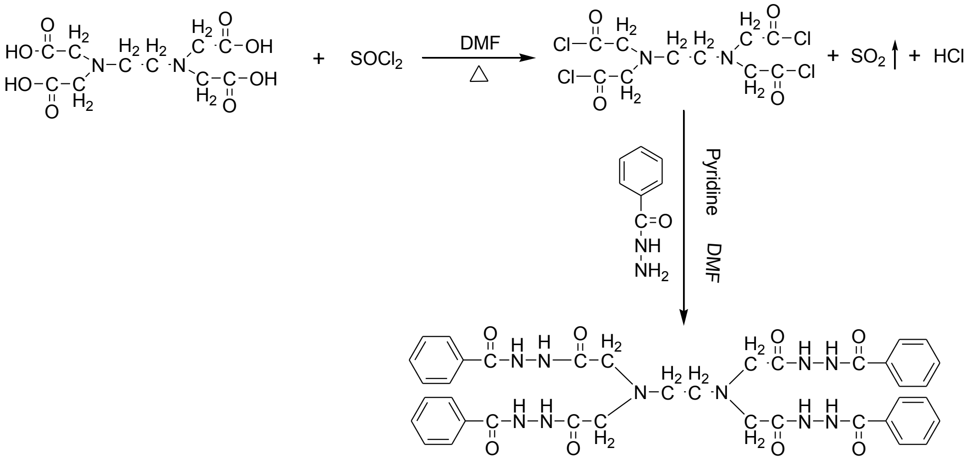
Materials

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

Synthesis procedure of N, N, N, N'-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide (NA)

N, N, N, N'-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide was prepared as shown in Scheme 1: tetraacetic acid, Thionyl dichloride of 60 mL in the presence of *N, N*-dimethylacetamide as catalyst was mixed, and the mixture was heated up to 78°C, and held at 78°C for 10 h with stirring. After cooling to room temperature and evaporation of thionyl dichloride in vacuum, the residue was tetrachloride.

Benzoic hydrazide and *N, N*-dimethylacetamide of 70 mL were mixed, and the mixture was purged under nitrogen atmosphere. Tetrachloride was added slowly onto the mixture, followed by adding pyridine of 0.073 mol, and the mixture was heated up to 70°C, and held at 70°C with stirring. Reaction mixture was poured onto water of 350 mL and stirred, followed by filtrating. Obtained crude product was washed four times by water of each 350 mL at room temperature, and then washed by methanol of 250 mL at 50°C to eliminate raw materials and by-products, the resulting product was dried in a vacuum at 60°C.



Scheme 1. Synthesis of *N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide.

Preparation of PLLA/NA sample

PLLA was dried over night at 45°C under vacuum respectively to remove residual water. Blending of PLLA and NA was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 4 min, then at 64 rpm for 4 min. The processing temperature was set at 175°C but it increased to 180°C upon mixing. Products were hot pressed at 175°C under 20 MPa for 4 min to prepare sheets. The sheets were then cooled down by being compressed at room temperature under 20 MPa for 10 min.

Characterization

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

The thermal stability of *N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide was measured by Thermogravimetric Analysis (TGA). TGA was performed using a thermal analysis Q500 from TA Instruments-Waters LLC with a heating ramp of 20°C /min under air flow (60 ml/min) from room temperature to 450°C.

The nucleating effect of NA for PLLA was measured by Differential Scanning Calorimeter (DSC). The PLLA and PLLA/0.5%NA samples were first heated to 190°C and held at the same temperature for 5 min, then were cooled at a different cooling rate from melt.

Results and discussion

Structures of NA

The FT-IR spectra of NA was shown in Fig.1. In the spectra, the peaks at 3420.2 cm^{-1} and 907.6 cm^{-1} contribute to the absorption of N-H stretching vibration and the plane bending vibration, and the absorption peak at 1740.3 cm^{-1} contribute to C=O stretching vibration of the amide group. Owing to conjugated effect between carbonyl and benzene, carbonyl absorption move to lower frequency. Thus, the absorption peak at 1655.8 cm^{-1} contribute to C=O stretching vibration of benzoyl hydrazine. Then the absorption peaks at 1577 cm^{-1}, 1522.8 cm^{-1}, 1482.5 cm^{-1} proved the existence of a benzene. The absorption peak at 1273.5 cm^{-1} was mixed peak including C-N stretching vibration and N-H bending vibration absorption, the absorption peak at 1380.7 cm^{-1}, 790.5 cm^{-1}, 700.7 cm^{-1} belongs to C-H stretching vibration. Infrared spectrum analysis showed *N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide had been synthesised.

Thermal properties of NA

Figure.2 shows the TGA curves of *N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide with a heating ramp of 1, 2.5, 5, 15, 20°C /min under nitrogen flow from room temperature to 450°C. As seen in figure.2, *N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide begin to decomposition above 170°C, which can suggest that *N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide has good thermal stability during application temperature of polymer. With the increasing of heating rate, the decomposition temperature increases, the reason is that rapid heating rate make decomposition of *N, N, N, N'*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide not achieve at set temperature, at the same time, the temperature has get into the following set temperature, resulting in decomposition achieving at higher temperature. This result is consistent with that of other decompositon compound [8-9].

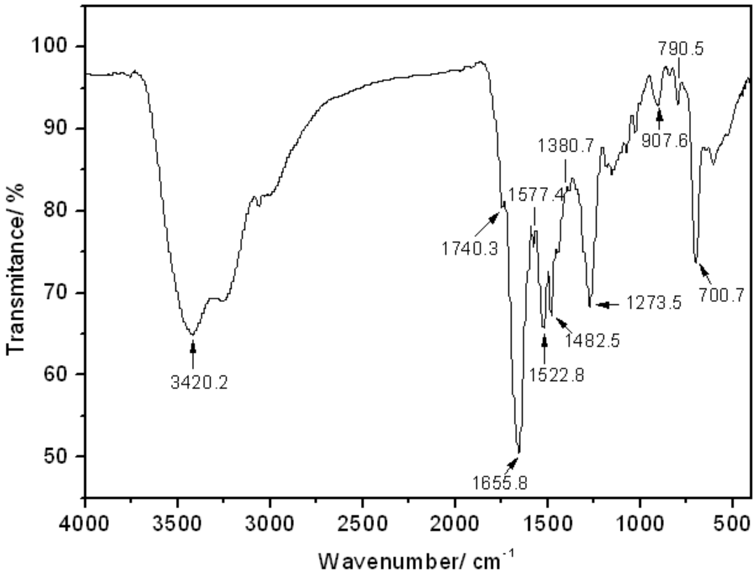


Figure 1. The FTIR spectra of *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide.

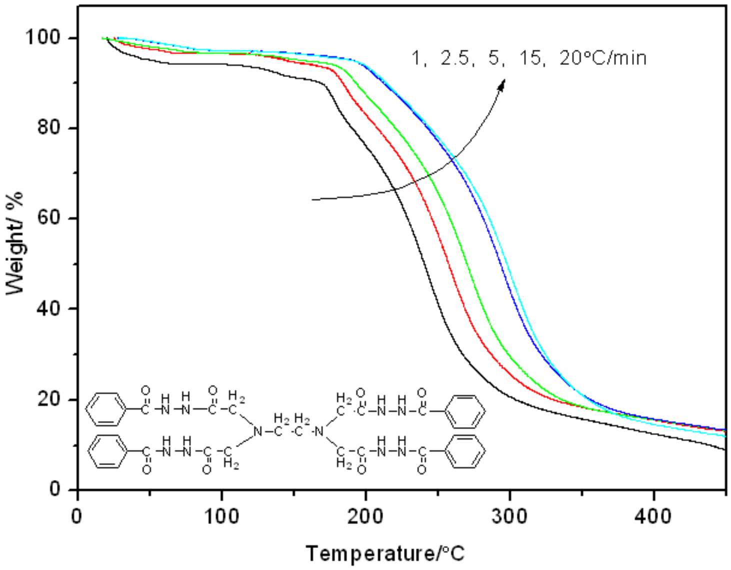


Figure 2. TGA curves of *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide.

Nucleating effect of NA

Non-isothermal crystallization behavior is of very practical interesting, This is because polymers are usually processed under non-isothermal cycles. Figure 3 shows the DSC curves of non-isothermal crystallization from melt at a different cooling rate. The crystallization of neat PLLA is very slow. Upon cooling at 1 °C/min, the crystallization peak is not detected. With addition of 0.5%NA, crystallization peak appears in the DSC cooling curve. Compared to the neat PLLA, NA made the melt crystallization peak of PLLA shift to higher temperature, which indicated that NA could increase the crystallization temperature of PLLA, On the other hand, NA made the melt crystallization peak becomes much sharper in the cooling process, the result shown NA could increase the overall crystallization rate, and serve as a nucleating agent for the crystallization of PLLA. As showed in Figure 3, the melt crystallization peak of PLLA/0.5% NA shifts to lower temoeråture and becomes wider with increasing of cooling rate. Similar results can be found in other systems such as PLLA/ modified carbon black composites [10]. with the addition of 0.5% NA, the crystallization temperature (T_o) increase from 105.88°C to 116.12°C, and the crystallization enthalpy(ΔH_c) increase from 1.379 J•g^{-1} to 41.41 J•g^{-1} at a cooling rate of 1°C/min from melt.

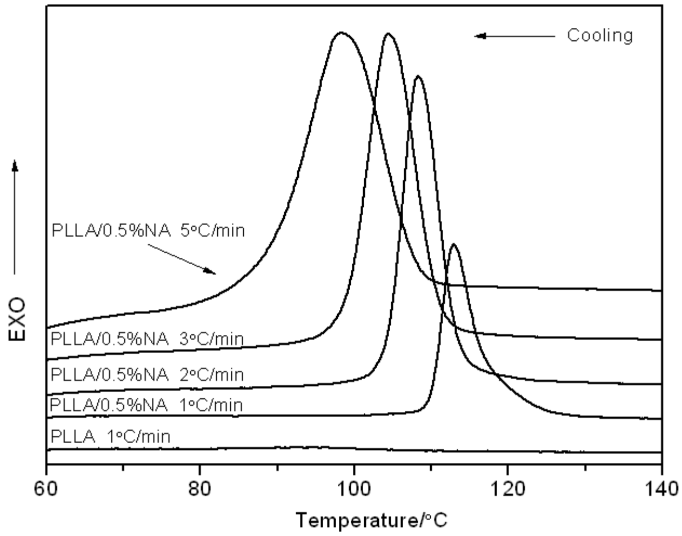


Figure 3. DSC of PLLA and PLLA/0.5%NA crystallized from melt at a different cooling rate.

Conclusions

N, N, N, N′-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide as nucleating agent of PLLA was synthesized from benzoyl hydrazine and tetraacetic acid by acylation and ammoniation. Investigations on the Thermal properties and nucleating effect of *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide were carried out by TGA and DSC respectively. The TGA result showed good thermal stability of *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide as functional agents of polymer. Non-isothermal crystallization behavior indicated that NA as a kind of heterogeneous nucleation agent can accelerate the overall PLLA crystallization. Upon the addition of 0.5% *N, N, N, N′*-Tetra(benzoyl) ethylene diamine tetraacetic acid dihydrazide, the crystallization temperature increased from 105.88°C to 116.12°C, and the crystallization enthalpy increased from 1.379 J•g^{-1} to 41.41 J•g^{-1} at a cooling rate of 1°C/min from melt.

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