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Effect of cyanuric acid on the crystallization kinetics and morphology of biodegradable poly(L-lactide) as an efficient nucleating agent

Mengting Weng, Zhaobin Qiu*

State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

Biodegradable poly(L-lactide) (PLLA) and cyanuric acid (CA) composites were prepared via a solution and casting method at low CA loadings. The nonisothermal melt crystallization behavior, overall isothermal melt crystallization kinetics, spherulitic morphology, and crystal structure of neat PLLA and the PLLA/CA composites were investigated with various techniques. Relative to neat PLLA, the crystallization process of PLLA was accelerated obviously by the presence of CA under both nonisothermal and isothermal melt crystallization conditions, indicating that CA acted as an efficient nucleating agent for the crystallization of PLLA; however, CA did not change the crystallization mechanism and crystal structure of PLLA in the composites.

1. Introduction

As a biodegradable and biocompatible polyester, poly(L-lactide) (PLLA) has received more and more attention in the last two decades [1–5]. Because it may be produced from renewable resources, PLLA has recently become one of the most promising biodegradable polyesters [6–9]. It should be noted that the following disadvantages, including relatively high cost, unsatisfied mechanical properties, slow degradation rate, and slow crystallization rate must be solved for the wider practical application of PLLA. Among them, a slow crystallization rate has seriously restricted the practical application of PLLA-based materials from a viewpoint of polymer processing, because PLLA crystallizes very slowly or even does not crystallize under some practical processing conditions. The utilization of nucleating agent is one of the most effective ways to accelerate the crystallization process of PLLA, which is very essential for its practical melt processing, such as injection molding, film blowing and melting spinning. Some kinds of nucleating agents have been found and developed to enhance the crystallization rate and improve the processability of PLLA, such as polyglycolide, layered metal phosphonate, multi-walled carbon nanotubes (MWCNTs), polyhedral oligomeric silsesquioxanes (POSS), orotic acid (OA), graphene oxide (GO), graphene, uracil and xylan esters [10–23]. Through melt compounding or solution and casting methods, different nucleating agents have been introduced into the PLLA matrix; moreover, the presence of nucleating agents has enhanced the nonisothermal melt crystallization peak temperature, reduced the crystallization half-time, and increased the nucleation density of PLLA spherulites, compared with those of neat PLLA [10–23].

Pan et al. have recently found that cyanuric acid (CA) may act as an efficient nucleating agent for the crystallization of bacterial poly(3-hydroxybutyrate) (PHB) and its copolyesters, including poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH) [24]. PHBV and PHBH did not crystallize during the nonisothermal melt crystallization process at a cooling rate of 10 °C/min, while they were able to complete crystallization under the same condition in the presence of 1 wt% CA, indicative of its strong heterogeneous nucleating agent effect; however, the authors did not discuss the nucleation mechanism of CA for the crystallization of PHB and its copolyesters [24]. It is of great interest to investigate whether CA may also be an efficient nucleating agent for the crystallization of PLLA, because a slow crystallization rate is one of its main drawbacks from a viewpoint of polymer processing. To the best of our knowledge, such research has not been reported in literature till now.

The aims of this work are to study whether CA may act as an efficient nucleating agent for the crystallization of PLLA and to discuss the possible nucleation mechanism. In this work, we prepared the PLLA/CA composites at low CA loadings via a solution and casting method. The nonisothermal melt crystallization behavior, overall

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* Corresponding author. Tel.: +86 10 64413161; fax: +86 10 64413161.
E-mail addresses: qiuzb@mail.buct.edu.cn, zbqiu99@yahoo.com (Z. Qiu).

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isothermal melt crystallization kinetics, spherulitic morphology, and crystal structure of PLLA/CA composites were studied in detail with various techniques and compared with those of neat PLLA. It is found that CA may act as an efficient nucleating agent for the crystallization process of PLLA under both nonisothermal and isothermal melt crystallization conditions, which is of great importance and help for its wider application from both academic and industrial viewpoints.

2. Experimental details

PLLA ($M_w = 1.53 \times 10^5$ g/mol) was kindly supplied by Biomer Company, Germany. CA was bought from Sigma–Aldrich (Shanghai) Trading Co., Ltd. and used as received.

Neat PLLA and the PLLA/CA composites containing 0.3 wt% and 1 wt% CA contents were prepared via a solution and casting method. The preparation of a PLLA/CA composite containing 1 wt% CA is described as follows. 0.01 g of CA was first placed into 20 mL ethanol and then sonicated with a KQ 3200E ultrasonic generator for 90 min. 0.99 g of PLLA was added into 30 mL chloroform and stirred for 90 min at room temperature. Then, the two solutions were mixed together and followed by stirring for 4 h. The mixture was poured into a dish to evaporate the solvent at room temperature for 12 h, and a film was obtained. The film was further dried in a vacuum oven at 80 °C for 3 days to remove the solvent completely. For brevity, the PLLA/CA composites containing 0.3 wt% and 1 wt% CA were abbreviated as PLLA/CA0.3 and PLLA/CA1, respectively, in this work.

Both the nonisothermal melt crystallization behavior and overall isothermal melt crystallization kinetics of neat PLLA and the PLLA/CA composites were investigated by a TA Instruments differential scanning calorimeter (DSC) Q100 with a Universal Analysis 2000. For the nonisothermal melt crystallization behavior study, the samples were heated to 190 °C at 20 °C/min, held for 3 min to erase any thermal history, and then cooled from the melt at a cooling rate of 5 °C/min. For the overall isothermal melt crystallization kinetics study, the samples were heated to 190 °C at 20 °C/min, held for 3 min to erase any thermal history, cooled to the chosen crystallization temperature (T_c) at 60 °C/min, and held for a period of time until the isothermal crystallization was complete. The exothermal traces were recorded for the later data analysis.

The spherulitic morphology of neat PLLA and the PLLA/CA composites was observed with an optical microscope (POM) (Olympus BX51) equipped with a temperature controller (Linkam THMS 600).

The crystal structures of neat PLLA and the PLLA/CA composites were studied using a Rigaku D/Max 2500 VB2t/PC X-ray diffractometer at 40 kV and 200 mA. Wide-angle X-ray diffraction (WAXD) experiments were performed with a scanning rate of 5°/min in the range of 5–40°. The samples were first pressed into films with a thickness of around 1 mm on a hot stage at 190 °C and then transferred into a vacuum oven at 130 °C for 3 days.

3. Results and discussion

3.1. Effect of CA on the nonisothermal melt crystallization behavior and overall isothermal melt crystallization kinetics of PLLA in the PLLA/CA composites

It is of interest to investigate the effect of CA on the nonisothermal melt crystallization behavior of PLLA, because most polymer processing operations are performed under nonisothermal crystallization conditions. As introduced in the Experimental section, the nonisothermal melt crystallization behavior of neat PLLA and its composites was studied with DSC at 5 °C/min. Fig. 1 illustrates the DSC cooling traces of neat PLLA and its two composites, from which the crystallization exotherms are more easily observed in the composites than in neat PLLA. Neat PLLA had a nonisothermal melt crystallization peak temperature (T_p) of 97.2 °C with a crystallization enthalpy (ΔH_c) of 5.1 J/g. In the case of PLLA/CA0.3, it showed a T_p at 111.5 °C with a ΔH_c of 30.1 J/g, indicating that the nonisothermal melt crystallization of PLLA was enhanced apparently by a small amount of CA. With further increasing the CA content, PLLA/CA1 showed a T_p at 113.1 °C with a ΔH_c of 39.1 J/g. It is interesting to compare the effect of CA as a novel nucleating agent on the enhancement of T_p of PLLA with some other nucleating agents. When the same nucleating agent concentration of 0.3 wt% and the same cooling rate of 5 °C/min were used, the values of T_p were increased by around 14 and 30 °C in the presence of CA and OA [17], respectively, indicating that OA should be more efficient as a nucleating agent than CA. However, the values of T_p were increased only by around 5 °C in the presence of MWCNTs or GO [6,19] and about 15 °C in the presence of POSS or CA [14], when the same nucleating agent concentration of 1 wt% and the same cooling rate of 5 °C/min were used, suggesting that the nucleating agent effect of CA may be comparable to that of POSS and better than those of MWCNTs and GO. In addition, the values of degree of crystallinity (W_c) were estimated to be 5.5%, 32.5%, and 42.5% for neat PLLA, PLLA/CA0.3, and PLLA/CA1, respectively, on the basis of the heat of fusion of 100% crystalline (ΔH°_m) PLLA (93 J/g) [25]. In brief, incorporating a small amount of CA had enhanced significantly the nonisothermal melt crystallization of PLLA, because the values of T_p, ΔH_c, and W_c were increased remarkably in the PLLA/CA composites relative to neat PLLA, indicating that CA acted as an efficient nucleating agent for the nonisothermal melt crystallization of PLLA.

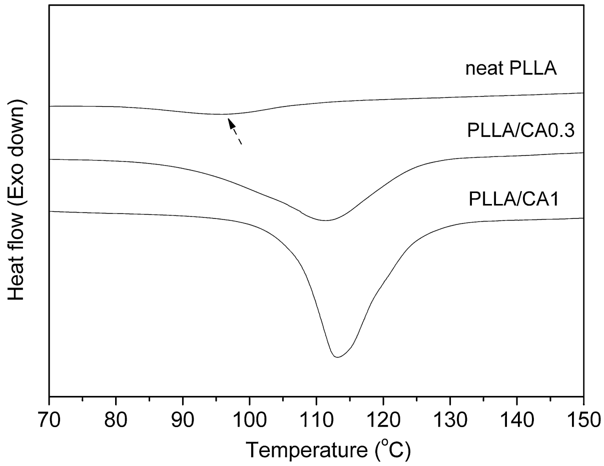

Fig. 1. DSC cooling traces of neat PLLA and its composites at 5 °C/min.

As introduced in the Experimental section, the overall isothermal melt crystallization kinetics study of neat PLLA and its two composites was further investigated with DSC in a wide T_c range from 120 to 140 °C. Fig. 2 shows the development of degree of relative crystallinity with crystallization time and the corresponding Avrami plots for neat PLLA and its two composites crystallized at 130 °C as an example. As shown in Fig. 2a, it took neat PLLA around 69 min while only around 14.2 and 7.6 min for the PLLA/OA0.3 and PLLA/CA1 samples to finish crystallization completely, indicating that the overall isothermal melt crystallization process of PLLA was accelerated significantly by the presence of a small amount of CA. The well-known Avrami equation was further used to analyze the overall isothermal melt crystallization kinetics of neat PLLA and its two composites. According to the Avrami equation, the relative degree of crystallinity (X_t) develops with crystallization time (t) as.

$$1 - X_t = \exp(-kt^n) \qquad (1)$$