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Yan-Hua Cai*, Li-Sha Zhao

Non-isothermal Crystallization, Thermal Stability, and Mechanical Performance of Poly(L-lactic acid)/Barium Phenylphosphonate Systems

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Abstract: The introduction of a nucleating agent in semi-crystalline polymers is a frequently utilized way to improve the crystallization performance, and the use of a nucleating agent has a very great effect on the performance of the polymer in other areas including thermal stability and mechanical properties. In this investigation, barium phenylphosphonate (BaP) was prepared as a crystallization accelerator for Poly(L-lactic acid) (PLLA), and the non-isothermal crystallization behavior, thermal stability, and mechanical properties of PLLA modified by BaP were investigated using differential scanning calorimetry (DSC), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and electronic tensile testing. Non-isothermal crystallization analysis showed that the BaP could significantly accelerate the crystallization of PLLA, and the non-isothermal crystallization peak shifted to a higher temperature with increasing concentration of BaP, however, the corresponding crystallization peak became wider. XRD results after non-isothermal crystallization confirmed the non-isothermal crystallization DSC results. Additionally, the addition of BaP did not change the crystal form of PLLA. A comparative study on thermal stability indicated that BaP decreased the onset decomposition temperature of PLLA, resulting from the formation of more tiny and imperfect crystals. Whereas the influence of BaP on the thermal decomposition profile of PLLA was negligible. In terms of mechanical properties, the tensile strength and elastic modulus of PLLA/BaP increased compared to the virgin PLLA, unfortunately, the elongation at break decreased.

Keywords: Poly(L-lactic acid), Barium phenylphosphonate, Non-isothermal crystallization, Thermal stability, Mechanical properties

1 Introduction

Among polyesters, poly(L-lactic acid) (PLLA) is an increasingly popular alternative for petroleum-based plastics because of its biodegradation, easy processability, excellent biocompatibility, *etc.* [1,2]. Additionally, environmental protection also requires the development of more environment-friendly materials such as PLLA, PBS, PCL, etc. Because of this, PLLA has been attracting increasing attention, and it has been widely employed in medical science [3-5], packaging [6,7], 3D printing [8], and the automobile [9]. However, it is a fact that the slow crystallization rate of PLLA results in low crystallinity and poor heat resistance during processing, which restricts seriously its usage in more industries. Thus, it is necessary to accelerate PLLA crystallization to increase its advantages compared to the commercial petroleum-based thermoplastics.

At present, the most effective and easiest way to accelerate PLLA crystallization is the incorporation of a nucleating agent, therefore many inorganic or organic compounds have been developed as nucleating agents for PLLA. The addition of silicates, such as talc [10], montmorillonite [11], halloysite [12], sepiolite [13], and mica [14], has shown a powerful accelerating effect for PLLA crystallization. For example, the half-time of overall crystallization of PLLA containing 1 wt% talc, in comparison to the virgin PLLA, decreases by an order of magnitude [15]. Additionally, some synthetic inorganic compounds including metal phenylphosphonates [16,17], metal phenylmalonates [18], nano whiskers [19,20],

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***Corresponding author: Yan-Hua Cai,** Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing-402160, P.R. China, E-mail: caiyh651@aliyun.com
Li-Sha Zhao: Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing-402160, P.R. China

etc., also exhibit advanced nucleating ability for PLLA. Recently, research about nucleating agents for PLLA has begun to focus on organic compounds because of their good compatibility with PLLA matrix and significant nucleating ability [21,22], and the development of organic nucleating agents is in the process of change from commercial functional additives to highly specific novel nucleating agents. For example, Wang et al. [23] reported the use of 1,3,5-trialkyl-benzenetricarboxylamide derivatives as nucleating agents for PLLA, and the results from the relevant measurements indicated that 1,3,5-tributyl-benzenetricarboxylamide exhibited the best nucleation ability for PLLA, and that all 1,3,5-trialkyl-benzenetricarboxylamide nucleated PLLA polymers had larger nucleation density and smaller spherulite size than virgin PLLA. In our previous studies [24,25], several benzoyl hydrazine derivatives exhibited powerful acceleration of crystallization for PLLA. In particular, the addition of only 0.8 wt% *N, N'*-bis(benzoyl) suberic acid dihydrazide decreased the crystallization half-time of the virgin PLLA from 26.5 min to 1.4 min at 115°C.

Metal phenylphosphonates as important inorganic/organic hybrid compounds have been widely applied in the chemical synthesis [26,27], catalysis [28], and functional additive fields [29,30]. As far as we know, the effects of some metal phenylphosphonates on PLLA have been reported in the literature [17,31,32]. However, the relevant studies mainly focused on the crystallization behavior of metal phenylphosphonate nucleated PLLA, moreover, not many categories of metal phenylphosphonates have been studied, especially when it comes to inexpensive metal phenylphosphonates. Thus, in the current work, an important and common metallic element – barium – was employed to prepare barium phenylphosphonate (BaP) as a functional additive for PLLA, and the influence of BaP on the non-isothermal crystallization, thermal stability, and mechanical properties of PLLA was investigated.

2 Experimental Section

2.1 Materials

2002D PLLA with 4.25 wt% D content was purchased from Nature Works LLC, USA. All analytical reagents used to prepare BaP, including phenylphosphinic acid, barium chloride, and sodium hydroxide, were obtained from Chongqing Huanwei Chemical Reagent Co., China.

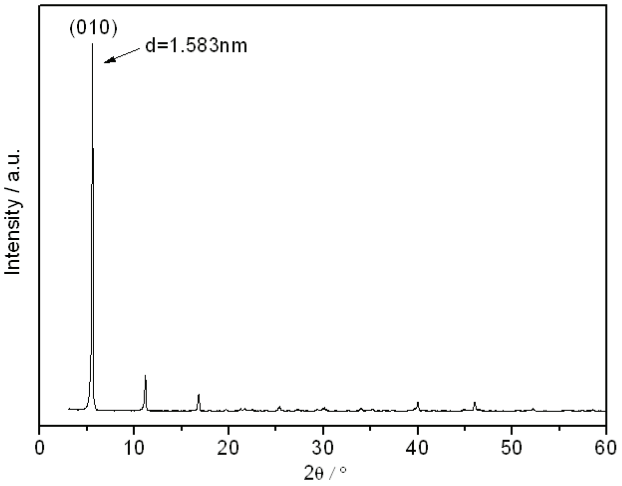

Figure 1: XRD pattern of BaP.

2.2 Synthesis of barium phenylphosphonate (BaP)

The barium phenylphosphonate (BaP) was prepared in the laboratory according to our previous similar work [17,33]. Typically, the barium chloride aqueous solution was slowly added into the phenylphosphinic acid solution with stirring, and then the PH of the mixed solution was adjusted to 5-6 using sodium hydroxide, followed by filtration, and the filtrate was stirred again to achieve full crystallization. The resulting solution was filtered and washed with deionized water to obtain the BaP.

The XRD pattern of the synthesized BaP is shown in Figure 1. The diffraction peaks, especially the strongest characteristic diffraction peak originating from (010) plane at 2θ=5.58°, are consistent with the reported XRD pattern [32]. In addition, the interlayer distance of BaP is also in good agreement with reported values of 1.582 nm [32].

2.3 Preparation of PLLA/BaP samples

PLLA samples containing various concentrations from 0.3 to 1.5 wt% BaP were obtained through melting blend and molding technology. The detailed operation is described as follows: the dried PLLA and BaP were mixed on a torque rheometer (Harbin Hapro Electric Technology Co., Ltd., China), and the blending temperature, blending time, and rotation speed were 180ºC, 32 rpm for 5 min, and 64 rpm for 5 min, respectively. Then the resulting mixture was hot pressed and cool pressed for 5 min and 7 min.

2.4 Characterization and testing

XRD measurements of BaP itself and PLLA/BaP samples after non-isothermal crystallization were performed on a diffractometer (XRD6000, Shimadzu, Japan) using Cu K_α radiation (wavelength, 1.54 Å) at room temperature with scanning rate of 2º/min. The non-isothermal crystallization behavior of the virgin PLLA and PLLA/BaP samples from the melt at a cooling rate of 1ºC/min were measured using a differential scanning calorimeter (DSC, Q2000, TA instrument, USA) with 50 mL/min nitrogen flow. Before testing, the temperature and heat flow were calibrated using an indium standard; then the data from melt-crystallization were recorded . The thermal stability of the virgin PLLA and PLLA/BaP samples were characterized by thermogravimetric analysis (TGA, Q500, TA instrument, USA) under 60 mL/min air flow, and the testing temperature ranged from room temperature to 650ºC. The mechanical properties tests were conducted on a UTM4103S electronic tensile tester (Shenzhen Suns Technology Stock Co., Ltd,. China) at the speed of 50 mm/min at room temperature, all samples were cut into tension test specimens with effective dimensions of 25 mm × 6 mm × 0.4 mm by a dumbbell shaped die. The tensile strength, elongations at break and elastic modulus were obtained by averaging over three specimens.

Ethical approval: The conducted research is not related to either human or animals use.

3 Results and discussion

3.1 Non-isothermal crystallization

Firstly, we evaluated the effect of BaP on the non-isothermal crystallization of PLLA to determine the role of BaP in the PLLA matrix. Figure 2 displays the DSC curves of the non-isothermal crystallization of the virgin PLLA and PLLA/BaP samples from the melt at a cooling rate of 1ºC/min. It is clearly observed that the virgin PLLA has almost no non-isothermal crystallization peak, that is, the virgin PLLA cannot form a crystal when cooling through the homogeneous nucleation of PLLA itself. In contrast, all BaP containing PLLA samples show obvious non-isothermal crystallization peaks, indicating that BaP as a heterogeneous nucleating agent promotes the crystallization of PLLA in the same way as other metal phenylphosphonates [32,34]. Moreover, the non-isothermal crystallization peak shifts to a higher temperature with increasing concentration of BaP (from 0.3 wt% to 1.5 wt%), indicating the BaP concentration dependence of non-isothermal crystallization behavior. On the other hand, a large amount of BaP can cause the PLLA to crystallize at higher temperature because of the higher nucleating density in the PLLA matrix and the greater induced-crystallization effect. However, excessive BaP may also impede the motility of the PLLA molecular chain, which results in the outcome that PLLA/1%BaP exhibits the largest non-isothermal crystallization enthalpy 33.4 J/g compared to other PLLA/BaP samples. Additionally, it is noted that the non-isothermal crystallization peak becomes wider with an increase of BaP content, resulting from the competition of the crystallization promoting and impeding effect of more BaP in PLLA matrix. That is, more BaP can provide larger nucleating density, but more BaP also impede the crystal growth of PLLA, forming various crystals with different levels of perfection upon cooling.

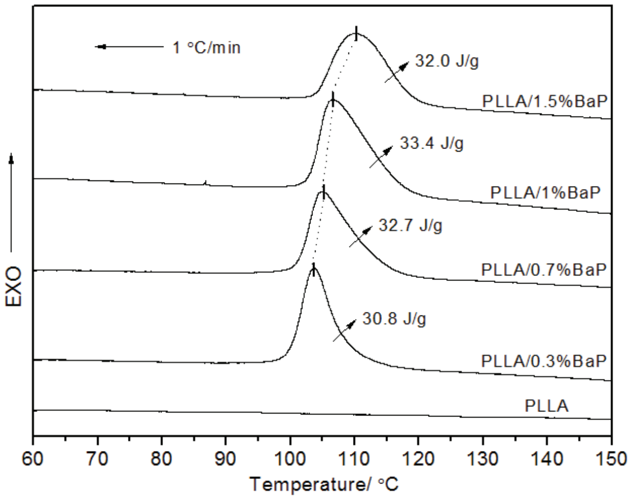

Figure 2: DSC curves of the non-isothermal crystallization of the virgin PLLA and PLLA/BaP samples from the melt at a cooling rate of 1 ºC/min.

In order to further analyse the effect of BaP on non-isothermal crystallization of PLLA, PLLA/BaP samples after non-isothermal crystallization were tested using XRD. Figure 3 shows the XRD curves of PLLA/BaP samples without non-isothermal crystallization procedure, it is clear that intensity of characteristic diffraction peaks of BaP strengthens with increasing of BaP concentration, but the PLLA matrix exhibits very wide diffraction peak, indicating that most of the PLLA matrix is amorphous. However, PLLA/BaP samples after non-isothermal crystallization display completely different XRD curves (See Figure 4). The BaP nucleated PLLA exhibits the characteristic diffraction peaks of α form PLLA at 2θ= 16.7°, 19.1° and 22.3° occurring from the (110) plane, (203) plane, and (205) plane respectively [35], implying that the addition of BaP does not change the crystal form. However, the intensities of the diffraction peaks of PLLA/0.3%BaP are the strongest, indicating that the PLLA/0.3%BaP sample may have more perfect crystals, because a sharp non-isothermal crystallization peak may indicate a smaller difference in crystals (see aforementioned non-isothermal crystallization section). In addition, a weak peak appears at 2θ= 14.8° due to diffraction from (010) plane [36] in XRD pattern of other PLLA/BaP samples. However this peak does not occur with the PLLA/1%BaP sample.

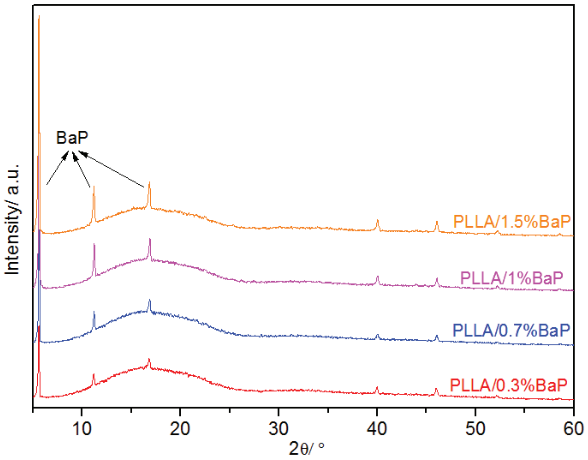

Figure 3: XRD curves of PLLA/BaP samples without crystallization process.

3.2 Thermal stability

The thermal stability of polymers directly determines their working temperatures, thus it is necessary to obtain the relevant thermal decomposition parameters to estimate a potential application. Here, TGA was used to investigate the thermal stability of the virgin PLLA and PLLA/BaP samples. TGA curves of the virgin PLLA and PLLA/BaP samples at a heating rate of 5ºC/min from room temperature to 650ºC are displayed in Figure 5. As shown in Figure 5, the virgin PLLA and all PLLA/BaP samples exhibit only one decomposition stage, which is probably attributed to the thermal decomposition of the main chain and loss of ester groups [37]. And it is clear that the addition of BaP does not change the thermal decomposition profile of PLLA. However, the effect of BaP on the onset decomposition temperature (T_o) of PLLA is not negligible, overall, the T_o is decreased with an increase of BaP concentration in PLLA matrix. For the virgin PLLA, PLLA/0.3%BaP, PLLA/0.7%BaP, PLLA/1%BaP, and PLLA/1.5%BaP, the T_o are 341.3°C, 336.2°C, 335.7°C, 334.7°C, 334.9°C, respectively. Through analysis of TGA data, it is found that the T_o of PLLA lowers slightly with increasing BaP concentration from 0.3 wt% to 1.5 wt%, and the T_o of all PLLA/BaP samples are smaller than that of the virgin PLLA. This might be because, for PLLA/BaP samples, the number of crystals formed is almost the same under the same circumstances. However, compared to the virgin PLLA, the presence of the crystallization promoting agent BaP causes the PLLA to form more tiny and imperfect crystals, resulting in the thermal decomposition of PLLA/BaP samples starting at lower temperature. Similar results were reported with other polymers such as the PLA/NPCC system and the PLA/CsNP system [37,38].

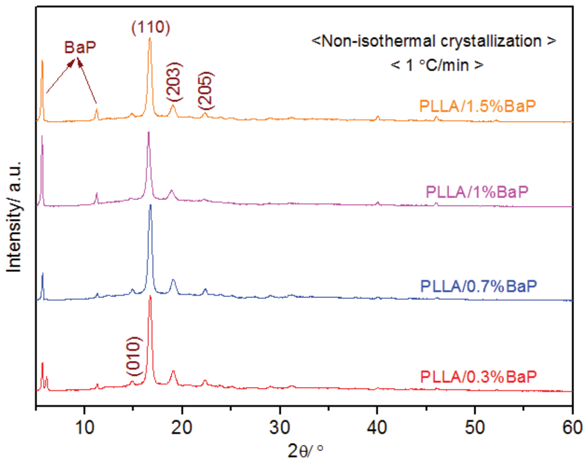

Figure 4: XRD curves of PLLA/BaP samples after non-isothermal crystallization.

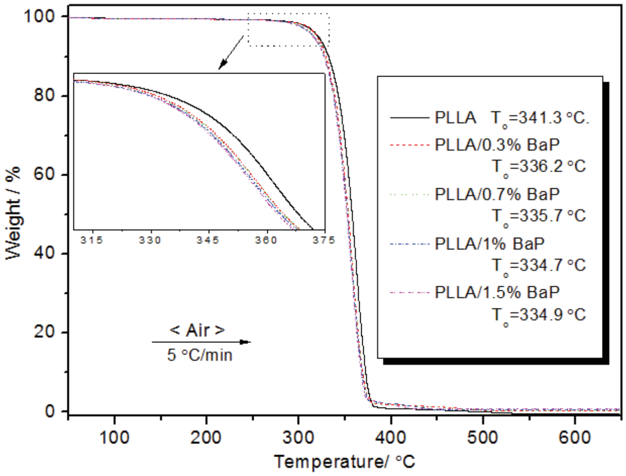

Figure 5: TGA curves of the virgin PLLA and PLLA/BaP samples.

Table 1: Mechanical properties of the primary PLLA and PLLA/BaP samples.

Sample	Tensile strength (MPa)	Elastic Modulus (GPa)	Elongation at break (%)
PLLA	71.0	0.5	5.1
PLLA/0.3%BaP	73.1	0.8	4.9
PLLA/0.7%BaP	75.0	1.2	4.7
PLLA1%BaP	80.8	1.0	4.1
PLLA/1.5%BaP	90.7	1.1	3.7

3.3 Mechanical properties

For semicrystalline polymers, the mechanical properties depend directly on the crystallization condition of polymers. In the non-isothermal crystallization section, we showed that BaP exhibited an excellent crystallization accelerating effect for PLLA. Therefore, the mechanical properties of PLLA must be affected by the addition of BaP. In this study, the virgin PLLA and PLLA/BaP samples for mechanical property testing were obtained directly after melting blend and compression molding. Table 1 lists the tensile strength, elastic modulus, and elongation at break of the virgin PLLA and PLLA/BaP samples. The data from Table 1 show that BaP can improve the tensile strength and elastic modulus of PLLA, furthermore, the tensile strength increases with increasing of BaP concentration. The probable reason is that more BaP will promote the crystallization of PLLA at a high cooling rate, as BaP has a higher concentration in the PLLA matrix. However, PLLA/0.7%BaP possesses a maximum value of elastic modulus, showing a complicated effect of BaP on the mechanical properties of PLLA. Compared to the virgin PLLA, the enhancement of the tensile strength and modulus of PLLA/BaP samples is due to the increasing crystallinity [39]. Whereas it is also very clear that the addition of BaP decreases the elongation at break of PLLA, implying that modified PLLA materials become brittle due to the crystallinity.

4 Conclusion

The influence of BaP on the non-isothermal crystallization, thermal stability, and mechanical properties of PLLA was evaluated through relevant testing technologies including DSC, XRD, TGA, and an electronic tensile tester. The results indicated that the addition of BaP accelerated significantly the crystallization of PLLA in cooling, and 1 wt% BaP made the non-isothermal crystallization enthalpy of PLLA increase from 0.1 J/g to the maximal value 33.4 J/g. Additionally, XRD results further confirmed the crystallization accelerating role of BaP, and the addition of BaP did not change the crystal form of PLLA. The virgin PLLA and PLLA/BaP systems exhibited a similar thermal decomposition process. However, through analysis of T_o data, it was shown that the incorporation of the BaP decreased slightly the thermal stability of PLLA, and among PLLA/BaP systems, the T_o only marginally depended on the BaP concentration. Mechanical properties measurements showed that BaP could enhance the tensile strength and modulus of PLLA, in contrast, the elongation at break of PLLA decreased resulting from the change of crystallinity of PLLA/BaP.

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Conflict of interest: Authors state no conflict of interest

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