Studies of Poly(L-lactic acid)/Hydroxyapatite Composites Through DSC and XRD

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Abstract: Poly(L-lactic acid) (PLLA) is important and biodegradable semi-crystalline polymer with promising application in industry. To estimate the effect of synthesized hydroxyapatite (HA) on the performance of PLLA, differential scanning calorimeter (DSC) and X-ray diffraction (XRD) were employed to investigate the crystallization of PLLA/HA composites. DSC showed that HA could accelerate the crystallization of PLLA, and the relationship between HA content and nucleation effect was not linear. However, 10 wt% HA had the best crystallization nucleation effect for PLLA. XRD analysis further confirmed the nucleation effect of HA, and there existed an interesting fact that the intensity of characteristic peak of PLLA/HA after isothermal became weak with an increase of HA content. XRD measurement for PLLA/0.5%HA after different isothermal temperatures showed that the crystallization temperature played important role in crystallization of PLLA.

1. Introduction

Hydroxyapatite (HA) is major inorganic component of bone tissue, and synthesized HA has prominent advantages such as excellent biocompatibility, good osteogenic activity[1], these characteristics make HA be widely employed in the biomedicine [2], in particular, in bone tissue engineering [3-4]. Poly(L-lactic acid) (PLLA), as a potential and important candidate for thermoplastic plastic based on petrochemical resources, has got rapid development according to its a large number of advantages, and its application has also broadened to more fields including medicine [5], food packaging [6], automotive interior [7], etc.. However, there exist some defects to restrict the development of PLLA industry, one of the major challenges in the field of PLLA application is slow crystallization rate. The effective way for improving crystallization is adding the nucleating agent [8], and many inorganic and organic, commercial and synthesized nucleating agents were introduced into PLLA matrix. The dilithium cis-4-cyclohexene-1, 2-dicarboxylate was synthesized to be as a novel nucleating agent for PLLA crystallization, Non-isothermal and isothermal crystallization behavior showed that dilithium cis-4-cyclohexene-1, 2-dicarboxylate could significantly accelerate the crystallization rate of PLLA, and the results indicated that the addition of more dilithium cis-4-cyclohexene-1, 2-dicarboxylate in PLLA matrix could lead to the faster crystallization rate [9]. Fu and his colleagues reported that tetramethylene-dicarboxylic dibenzoyl-hydrazide dissolved in PLA melt could formed fibrils upon cooling, and these fibrils played important role in accelerating the crystallization of PLA [10].

HA as crystallization accelerator for PLLA had been reported by the literature [11], and relevant results showed that HA could induce nucleation and accelerate the crystallization of PLLA. In this work, HA was firstly synthesized, and then the PLLA with different HA content were prepared using blending technology, and the focus is that the crystallization of HA for PLLA was further confirmed...
through other important testing technologies including X-ray diffraction (XRD) and differential scanning calorimeter (DSC). This work would be favorable for further understanding the physical performance of PLLA/HA materials.

2. Experimental Section

2.1 Materials
Poly(L-lactic acid) (PLLA) was provided by Nature Works LLC, USA. Other reagents used to prepare HA were obtained from Chongqing Chuandong Chemical Reagent Company, China.

2.2 Preparation of HA
The preparation procedure of HA was performed according to the literature [12]. The XRD curve of prepared HA was shown in Figure 1, and the relevant dates of all diffraction peaks are consistent with the results reported by literature [12], indicating that HA was successfully prepared.

![Figure 1: XRD curve of HA](image)

2.3 Blend of PLLA/HA sample
The detailed blending procedure of dried PLLA with dried different HA content was carried out according to our early work [13].

2.4 Characterization
**Differential Scanning Calorimeter (DSC):** The non-isothermal crystallization was performed by TA Instruments Q2000 DSC. And PLLA and PLLA/HA samples after melting at 190 °C for 3 min were cooled at a cooling rate of 1 °C/min under nitrogen with 50 ml/min.

**X-Ray Diffraction (XRD):** XRD test of HA, PLLA and PLLA/HA after different conditions were performed on a D/MAX2550 diffractometer using Cu Kα radiation (wavelength, 1.54 Å) at room temperature in the range of 2θ=5-60° with scanning rate of 2 °/min.

3. Results and discussion

3.1 DSC analysis
Figure 2 is the DSC curves of non-isothermal crystallization behavior of PLLA and PLLA/HA samples from melt at a cooling rate of 1 °C/min. As shown in Figure 2, PLLA can almost not have the non-isothermal crystallization peak. However, all PLLA/HA samples exhibit obvious and sharp non-isothermal crystallization peak under the same condition. Moreover, With an increase of HA content, the non-isothermal crystallization peak exhibits different phenomenon, and the influences of HA content on non-isothermal crystallization are concluded into two types. For the first type, the HA content is in the range from 0.5 wt% to 3 wt%, the non-isothermal crystallization peak shifts to the lower temperature with the increasing of HA content, indicating that the inhibition effect of HA on the movement ability of PLLA molecular segment is predominant comparing with the nucleation effect. In
contrast with the first type, the HA content is from 3 wt% to 10 wt%, the non-isothermal crystallization peak moves to the higher temperature with an increase of HA, showing that the nucleation effect is predominant. Additionally, it is clear that 10 wt% HA makes the non-isothermal crystallization peak shift to the highest temperature and exhibit the sharpest crystallization peak. The result indicates that 10 wt% HA has the best nucleation effect for PLLA.

![DSC curves of non-isothermal crystallization of PLLA and PLLA/HA](image)

**Figure. 2** DSC curves of non-isothermal crystallization of PLLA and PLLA/HA

### 3.2 XRD analysis

Figure. 3 is XRD curves of PLLA and PLLA/HA samples without heat treatment, it is obvious that the characteristic diffraction peaks of the neat PLLA and PLLA/HA samples are very wide, indicating that amorphous is predominant in PLLA/HA samples after fast cooling. Meantime, it is found that the characteristic diffraction peaks of HA become more obviously with increasing of HA content.

![XRD curves of the neat PLLA and PLLA/HA without heat treatment](image)

**Figure. 3** XRD curves of the neat PLLA and PLLA/HA without heat treatment

Figure.4 is the XRD curves of the neat PLLA and PLLA/HA samples after isothermal at 110 ºC for 5 min. Compared to the samples without heat treatment, all samples after isothermal appear obvious diffraction peaks, and PLLA containing HA has the stronger diffraction peak than the neat PLLA, which confirms the nucleation effect of HA for PLLA again. For the PLLA with different HA content, the intensity of characteristic diffraction peak gradually becomes weak with an increase of HA content, this result is different from the aforementioned DSC results, directly showing the testing difference because of different testing equipment. But this phenomenon is very interesting for further understanding the role of HA in PLLA matrix. Increasing of isothermal crystallization time makes the intensity of characteristic diffraction peak further increase (See Figure.5), moreover, PLLA with high HA content has a faster increase of diffraction intensity than PLLA with low HA content.
According to aforementioned XRD results, PLLA/0.5%HA has the strongest characteristic diffraction peak. Thus, the XRD analysis of PLLA/0.5%HA after different isothermal temperature for 5 min was discussed (See Figure. 6). It is found that the characteristic diffraction peak at the range from 100 ºC to 110 ºC has larger intensity than that at the range from 115 ºC to 120 ºC, furthermore, the intensity of characteristic diffraction peak at 115 ºC to 120 ºC is very weak, indicating the higher crystallization temperature is not favorable for crystallization for PLLA/0.5%HA, the probable reason is that a small amount of HA can not provide more effective nuclear for molecular chain segment with excellent movement ability in high temperature. This result also shows that crystallization temperature is crucial factor for PLLA crystallization.

Figure. 6  XRD of PLLA/0.5%HA after different isothermal temperature for 10 min

4. Conclusion
In this work, the crystallization of PLLA/HA composites prepared using melt blending technology was evaluated using DSC and XRD in detailed. The non-isothermal crystallization results further confirmed the nucleation effect of HA for PLLA, and 10 wt% HA had the best crystallization nucleating effect for PLLA. However, XRD analysis showed that PLLA/0.5%HA had the strongest characteristic diffraction peak after isothermal, as well as the crystallization temperature significantly affected the crystallization of PLLA.
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