Study on the Performances of PLLA/CaSiO₃ Composites

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Abstract. In the current work, calcium silicate (CaSiO₃) was blended with the poly (L-lactic acid) (PLLA) to prepare the PLLA/CaSiO₃ composites, and the crystallization process, melting process and thermal decomposition behavior of PLLA/CaSiO₃ composites were studied. The promoting effect of CaSiO₃ on the crystallization of PLLA was proved by the melt-crystallization, and the CaSiO₃ content was a crucial factor to the crystallization behavior of PLLA. The crystallization temperature significantly affected the melting behavior of PLLA, and the double melting peaks degenerated into the single melting peak with the increasing of crystallization temperature from 90 °C to 130 °C. Additionally, for a given PLLA/CaSiO₃ sample, the different melting processes in heating after the melt-crystallization results from the different heating rates, and the appearance of the cold-crystallization peak indicated the medium nucleation capacity of CaSiO₃. The presence of CaSiO₃ decreased the onset thermal decomposition temperature of PLLA, and this effect depended on the competitive relationship of the poor compatibility of PLLA with CaSiO₃ and the content of CaSiO₃ with high thermal stability.

1 Introduction

Calcium silicate (CaSiO₃) has been large-scale application in traditional industries such as construction materials, insulation materials and refractory because of its unique physical and chemical properties and mineralogical characteristics [1]. In recent years, according to the excellent biological activity of CaSiO₃, the CaSiO₃ has attracted increasing attentions in fields of drug delivery and bone tissue engineering [2-4]. For example, Zhang et al employed 3D gel printing technology to prepare the porous CaSiO₃ scaffolds for bone tissue engineering, and the prepared CaSiO₃ power had the average particle size of about 5.119 μm. After sintering, the scaffolds had well-distributed designed voids and microporous with 62% porosity, and the compressive strength is up to about 16.52 MPa [5]. Additionally, on the basis of development of more in-depth works, CaSiO₃ with different morphologies of nanowires, nanobelts and hollow microspheres was successfully prepared using some methods such as solid-state synthesis, sol-gel method and chemical precipitation method [1], which promotes the CaSiO₃ to be used in more fields.

Poly(L-lactic acid) (PLLA) is a typical biodegradable polymer which has been applied in packaging [6], antibacterial materials [7], drug release [8] and agriculture [9] due to its inherent excellent performances like renewability, biodegradability, easy process, etc [10]. However, the PLLA also suffers from some defects of low

glass transition temperature, poor heat resistance, slow crystallization rate and low crystallinity [11]. To overcome slow crystallization speed of PLLA, many additives were selected or prepared to accelerate PLLA's crystallization, these typical additives for improving PLLA's crystallization were talc [12], TMC [13], inorganic salts [14]. For instance, Zhao et al synthesized N, N'-sebacic bis (hydrocinnamic acid) dihydrazide to accelerate the crystallization of PLLA, and the 1 wt% N, N'-sebacic bis (hydrocinnamic acid) dihydrazide could make the crystallization temperature increase to 131.6 °C, and the nucleation mechanism was proposed to be chemical nucleation [15].

In the current work, CaSiO₃ was added into PLLA resin to prepare the PLLA/CaSiO₃ composites, and the performances of melt-crystallization, melting behavior and thermal decomposition of PLLA/CaSiO₃ composites were studied via the relevant testing instruments, and this work may be beneficial to develop more bio-based polymer composites.

2 Experimental section

2.1 Materials

PLLA in this study was produced by Nature Works LLC of USA, and the CaSiO₃ was purchased from Chongqing Huanwei Chemical Company of China.

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2.2 Preparation of PLLA/CaCO₃

The dried PLLA and CaSiO₃ were firstly mixed according to the set mass ratio of PLLA and CaSiO₃ (99.7/0.3, 99.5/0.5, 99/1, 98/2, 97/3, 95/5), and then the mixture was melted on a torque rheometer to promote the CaSiO₃ to be further dispersed in PLLA matrix, and the melting temperature was set at 190 °C during blend, the rotation rate was 32 rpm. Finally, the mixture was hot pressed and cool pressed to form the resulting PLLA/CaSiO₃ composites.

2.3 Test

The melt-crystallization and melt processes of PLLA/CaSiO₃ composites were recorded by Q2000 DSC, and testing conditions were 5~7 mg testing sample, 50 ml/min nitrogen and indium standard calibration before testing. The thermal decomposition process curves of PLLA/CaSiO₃ composites were obtained by Q500 TGA under flowing air.

3 Results and discussion

3.1 Melt-crystallization

Figure.1 is the melt-crystallization process DSC curves of the pure PLLA and PLLA/CaSiO₃ composites at a cooling rate of 1 °C/min. As reported, the DSC curve of the pure PLLA can almost not observe any peak, meaning that the crystals cannot form in cooling. Although the presence of CaSiO₃ leads to the appearance of the melt-crystallization peak, the effect of the CaSiO₃'s content on the melt-crystallization process of PLLA is irregular as shown in Fig.1. When the CaSiO₃ is 0.3 wt% ~ 1 wt%, the CaSiO₃ exhibits a negative influence on the crystallization process of PLLA, that is to say, the crystallization occurs at the lower temperature with an increase of CaSiO₃ content. In particular, when the CaSiO₃ is 1 wt%, only few crystals are formed in DSC curves, showing the 1 wt% CaSiO₃ has the minimum promoting effect for PLLA's crystallization. Whereas the crystallization occurs at the higher temperature when increasing CaSiO₃ content from 1 wt% to 5 wt%, and the PLLA/5%CaSiO₃ sample has the sharpest melt-crystallization peak located in the highest temperature comparing with the other PLLA/CaSiO₃ sample, indicating that 5 wt% CaSiO₃ is the optimum concentration in this study. Overall, the addition of CaSiO₃ promotes the melt-crystallization of PLLA, because the CaSiO₃ as a heterogeneous nucleus plays an important role in increasing the nucleation speed in PLLA composites; but the irregular variation of crystallization behavior with increasing of CaSiO₃ content displays the complex crystallization process.

Fig 1. Melt-crystallization process of the pure PLLA and PLLA/CaSiO₃ at 1 °C/min

3.2 Melting process

Figure.2 is the melting process of PLLA/2%CaSiO₃ sample after crystallization at different temperatures for 180 min. It is observed that, with increasing of crystallization temperature, the low temperature melting peak shifts to the higher temperature, and the high temperature melting peak moves toward the low temperature. As a result, the double melting peaks gradually degenerated into the single melting peak. This result showed that the melting behavior of PLLA/CaSiO₃ samples significantly depends on the crystallization temperature, in addition, although that the crystallization time is very enough, the crystallization in the low temperature region cannot still be completed, resulting in that the recrystallization behavior occurs in heating. Furthermore, the lower the crystallization temperature is, the more the number of crystals reformed in heating is. When the crystallization temperature is 130 °C, the PLLA/2%CaSiO₃ sample only exhibits the single melting peak, the reason is that, in the high temperature region of 130 °C, the mobility of PLLA molecular segment is very high, leading to the difficulty in reforming the crystals.

Fig 2. Melting process of PLLA/2%CaSiO₃ at a heating rate of 10 °C/min after crystallization

Additionally, the melting process of PLLA/2%CaSiO₃ sample at different heating rates after

cooling of 1 °C/min was further investigated by DSC. The low temperature melting peak becomes more obvious with increasing of the heating rate, and the peak area ratio of high temperature melting peak and low temperature melting peak also becomes smaller. It is noted from Fig.3 that the cold-crystallization significantly occurs, when the heating rate is 3 °C/min and 5 °C/min. This result implied that the crystallization cannot be completed after cooling of 1 °C/min. Meantime, when the heating rate is lower than 5 °C/min, the high temperature melting peak shifts toward the low temperature with increasing of the heating rate, the reason is that the high temperature melting peak results from the melt of the reformed crystals in heating, and the slower heating rate can provide more time to form the more perfect crystals in heating. However, an enough fast heating rate can make the melting peak appear in the high temperature region because of the thermal inertia.

Fig 3. DSC curves of PLLA/2%CaSiO₃ sample at different heating rates after melt-crystallization

3.3 Thermal decomposition

Figure.4 is the TGA curves of the pure PLLA and PLLA/CaSiO₃ samples at a heating rate of 5 °C/min. As shown in Fig.4, a higher CaSiO₃ loading can cause the onset decomposition temperature (Tod) to decrease in the concentration range of 0.3 wt% to 2 wt%, because the compatibility of PLLA with CaSiO₃ is very poor, which results in the more defect of PLLA/CaSiO₃ composites, and these defects can be firstly destroyed in heating. However, further increasing the CaSiO₃ content can elevate the Tod, resulting from the high decomposition temperature of CaSiO₃. In a word, the Tod depends on the negative effect of poor compatibility of PLLA with CaSiO₃ and positive effect of CaSiO₃ with high decomposition temperature. Additionally, the only one thermal decomposition stage in TGA curve shows that the CaSiO₃ content in this study cannot change the thermal decomposition profile of PLLA.

Fig 4. Thermal decomposition of the pure PLLA and PLLA/CaSiO₃ samples

4 Conclusions

PLLA/CaSiO₃ composites was prepared via the melting blend technology, and the thermal properties of the composites were investigated by DSC and TGA. CaSiO₃ as a heterogeneous nucleus could accelerate the crystallization of PLLA, and 5 wt% CaSiO₃ exhibited the best promoting effect for PLLA's crystallization, but the crystallization process was complex. Both crystallization temperature and heating rate could significantly affected the melting processes of PLLA/CaSiO₃ composites, and the thermal stability of the composites was decreased due to the introduction of CaSiO₃.

Acknowledgments

This work was supported by Foundation of Chongqing Municipal Science and Technology Commission (cstc2017shmsA20021 and cstc2019jcyj-msxmX0876), Scientific and Technological Research Program of Chongqing Municipal Education Commission (project number KJQN201801319).

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