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RESEARCH ARTICLE

Preparation and Physical Performance of Green Poly(L-lactic acid) Composition by Blending with Starch

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Abstract:

Objective:

To develop more green polymer composites and further know the performance of green composites, the composites based on green poly(L-lactic acid) (PLLA) and starch were fabricated by a counter-rotating mixer. And effect of starch on the fluidity and nucleating performance of PLLA was investigated using melt index instrument, optical depolarizer and wide angle X-ray diffraction instrument, respectively.

Method and Conclusion:

The fluidity of PLLA/starch composites showed that, compared to the neat PLLA, the addition of starch made the fluidity of PLLA increase significantly and the melt mass flow rate of PLLA/5%starch sample had the maximum value 13.36 g/10min. In addition, the introduction of starch could also increase the crystallization rate of PLLA through isothermal crystallization measurement and x-ray diffraction analysis, the maximum value of crystallization rate of PLLA/starch composites appeared in low crystallization temperature zone, and 10 wt% starch could make the t1/2 of PLLA decrease from 3999.4s to 421.4s.

Keywords: Poly(L-lactic acid), Starch, Green composites, Nucleating performance, Fluidity, Crystalization.

1. INTRODUCTION

It is well-known that Poly(L-lactic acid) (PLLA) is a very typical green thermoplastic polymer, and there exists many advantages such as biodegradable performance, biocompatibility, easy process, *etc* [1]. Thus, an increasing number of studies results based on PLLA were reported by scientists, and PLLA has been identified as a leader of biodegradable polymer materials. However, there are still some disadvantages to restrict the growing application of PLLA in industry and agriculture. Especially, materials based on PLLA often need to be modified by addition of functional additives to meet different application requirements. For example, Xiong *et al.* [2] introduced starch with surface hydrophobic modification using epoxidized itaconic acid or epoxidized cardanol to improve mechanical and thermal properties of PLA. The addition of modification starch made the tensile strength of PLA increase from about 35 MPa to over 50 MPa, and the crystallization ability of PLA was enhanced significantly. In order to reinforce the ultraviolet-resistance properties of PLA to meet outdoor application requirement, nanosilver was introduced into PLA to promote the ultraviolet-resistance properties and study the photochemical degradation. The experimental results showed that the neat PLA was more sensitive to photodegradation than PLA/nanosilver composites [3].

Starch is another important polymer material. Similarly, biodegradability is a significant feature of starch as PLLA. Many literatures have reported that starch can be added into thermoplastic polymer to improve the performance of polymers [4, 5]. Witono *et al.* investigated the water absorption and retention characteristics of cassava starch grafted

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with polyacrylic acid. The results showed that starch grafted with polyacrylic acid possessed very good initial absorption capacity, and this material could retain up to 63g H_2O/g under severe suction. The absorption kinetics indicated that polymer chain relaxations determined the rate of water penetration into the gel [6]. Though there existed many advantages of blending two different polymers, a few polymers were miscible with each other. Ferrira *et al.* added organoclay into polymer to improve the compatibility of blending materials; their experiment results indicated that the organoclay could significantly improve the compatibility between plasticized starch and polypropylene [7]. In addition, the literature reported that the starch also improves the hydrophilicity of PLA/starch/chitosan blends with antimicrobial function [8].

Both PLA and starch are very promising polymer materials, moreover, there is no doubt that PLA/starch blend materials should have more advantages. To further know more about performance of PLA/starch materials, in this paper, 2002D PLLA, purchased from Nature Works LLC and having M_w as $1.95 \cdot 10^5$, with different starch content blend materials were fabricated using melt blending technology. The thermal performance and fluidity of PLLA/starch composites were evaluated.

2. EXPERIMENT

2.1. Preparation of PLLA/Starch Composites

Blending of PLLA and starch dried in a vacuum oven for 48 h was performed on a counter-rotating mixer, and the similar details of the preparation process of PLLA/starch composites were described in our earlier work [9, 10].

2.2. Testing

Wide angle X-ray diffraction (WAXD): WAXD measurement of PLA/starch composites after different heating treatments was performed on a diffractometer (D/MAX2550, Rigaku, Japan) using Cu K_α radiation (wavelength, 1.54 Å) in the range of 2θ=10-80 ° with the scanning rate of 2 °/min.

Crystallization Measurement: Crystallization of PLLA/starch composites was investigated by GJY-IIIoptical depolarizer (Donghuang University, China) in the region from 100 °C to 120 °C.

Melt Index: The melt index instrument (Beijing Guance Testing Instrument Co., LTD, China) was used to measure the fluidity of melting PLLA/starch composites. The measurement parameters are as follows: the measurement temperature was 150 °C, and the load was 10 Kg.

3. RESULTS AND DISCUSSION

3.1. Fluidity of PLLA/Starch Composites

The fluidity of PLLA/starch composites was measured using melt index instrument, and the results are shown in (Fig. **1**). As shown in (Fig. **1**), the melt mass flow rate (MFR) of the neat PLLA is slow, which indicates that the fluidity of the neat PLLA is poor at 150 °C; the possible reason is that the low measurement temperature makes the fluidity of the neat PLLA poor. However, the data of (Fig. **1**) shows that addition of starch makes the fluidity of PLLA significantly increased, especially upon the 5 wt% starch, the MFR of PLLA/starch composites has the maximum value of 13.36 g/10min. Then, the value begins becoming small. This result indicates that 5 wt% starch makes the PLLA have the best fluidity, and the reason is that the starch would contribute to the fluidity of PLLA improvement, but too much starch also would block the movement of PLLA which affects the fluidity of PLLA. In addition, it is clear from (Fig. **1**) that the fluidity of PLLA/starch is better than that of PLLA at low temperature, which indicates that addition of starch would be effective to avoid the degradation of PLLA and additives with low decomposition temperature because of high processing temperature, and widen the application field of PLLA materials.

3.2. Crystallization of PLLA/Starch Composites

Influence of starch on the crystallization of PLA had been reported in literature [11, 12], and the research results showed that starch could serve as nucleating agent of PLA, improving the degree of crystallization and crystallization rate of PLLA. Similarly, the crystallization performance of PLLA with starch was investigated using optical depolarizer, and the rate of measurement is shown in (Fig. **2**). It is observed that the half-time of overall crystallization $t_{1/2}$ of PLLA is long, and the crystallization rate of neat PLLA appears to be maximum at value 115 °C. However, the addition of starch can increase the crystallization rate; this result is consistent with other literatures results [11, 12]. It is worth noting that the maximum value of crystallization rate of PLLA/starch composites appears in low crystallization temperature zone. This phenomenon suggests that the crystallization of PLLA/starch composites is significantly affected by starch and crystallization temperature, and the addition of starch makes the optimization crystallization temperature shift to low temperature zone. Compared to the neat PLLA, 10% starch can make the $t_{1/2}$ of PLLA decrease from 3999.4 s to 421.4 s.

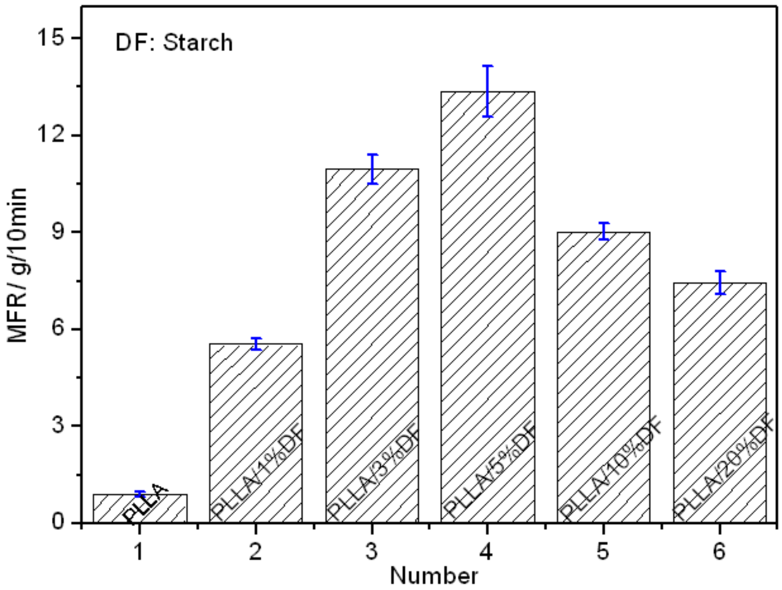

Fig. (1). The fluidity of PLLA/starch composites at 150 °C.

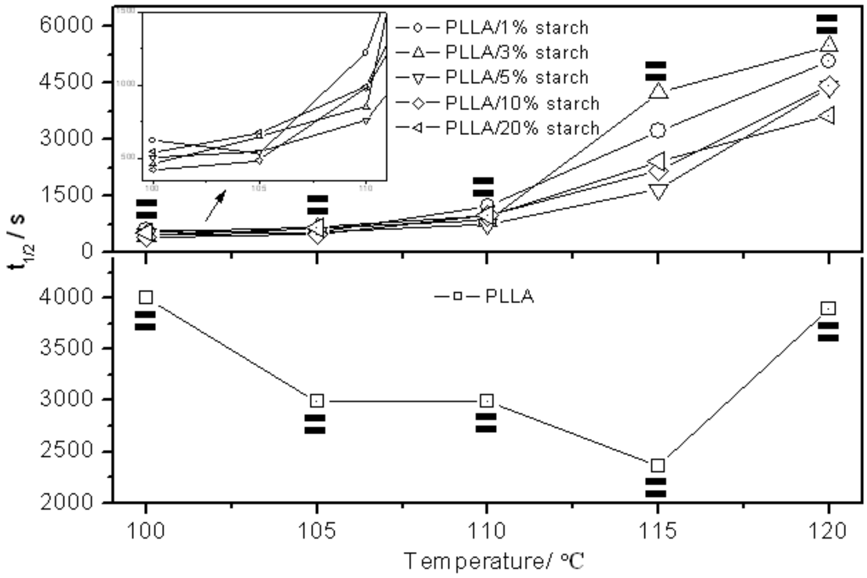

Fig. (2). The effect of temperature and starch on crystallization of PLLA.

Meantime, Avrami equation is used to describe the kinetics of crystallization behavior of PLLA/starch composites, and the Avrami plots of PLLA/starch composites are shown in Fig. (**3**); it is clear from Fig. (**3**) that the relationship of log[−ln(1−X_t)] versus logt is linear, which indicates that Avrami equation may be feasible to describe the crystallization behavior of PLLA/starch composites.

In addition, the crystallization of PLLA/starch composites was also investigated by WAXD. Fig. (**4**) shows the XRD curves of PLLA and PLLA/starch samples without heating treatment, in which it can be observed that the trend of XRD curves of PLLA and PLLA with different starch contents is similar, and the peaks are very wide, which indicates that the degree of crystallization of all samples is low, and this low degree of crystallization results from rapid cooling molding.

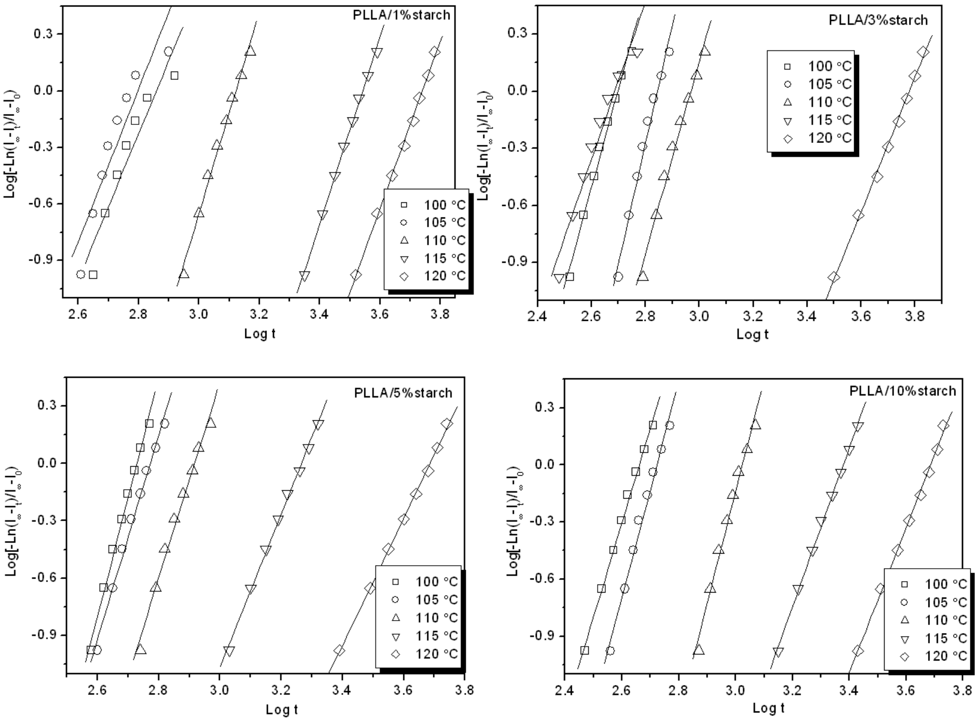

Fig. (3). Avrami plots for PLLA/starch composites at different temperature.

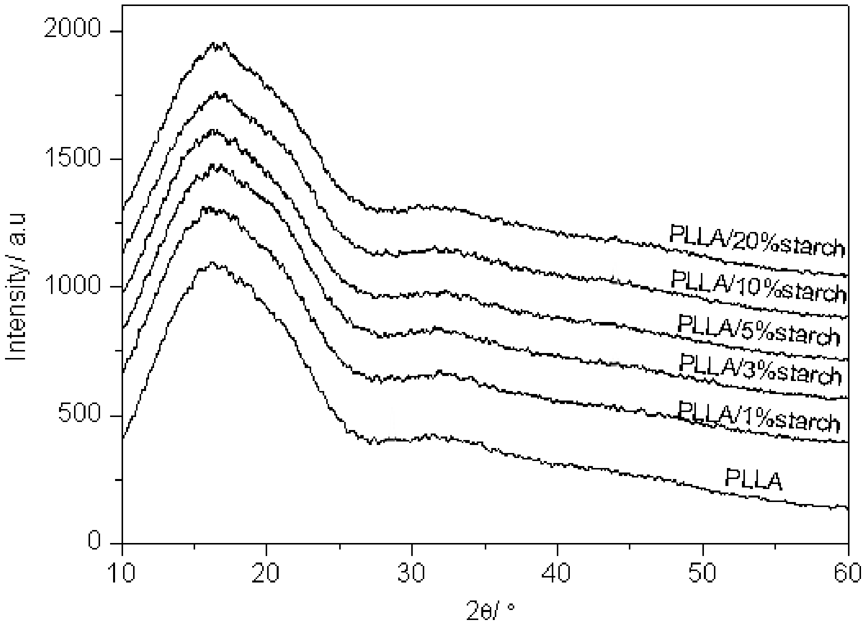

Fig. (4). XRD curves of PLLA and PLLA/starch without heating treatment.

However, the XRD curves of PLLA and PLLA/starch after isothermal crystallization at 100 °C for 5 min are very different. As shown in Fig. (**5**), the neat PLLA only exhibits a peak at 2θ= 16.6 ° due to diffraction from (110) plane, and the intensity of (110) plane diffraction peak is very weak. These results indicate that the crystal of the neat PLLA after isothermal crystallization at 100 °C for 5min is not perfect. However, all PLLA/starch samples exhibit peaks not only at 2θ= 16.6 °, but also at 2θ=14.7 °, 18.9 ° and 22.2 ° occurring from the (010) plane, (203) plane and (205) plane, respectively [13].Moreover, the intensity of diffraction peak is very strong, resulting from the nucleating effect of starch. With increasing of crystallization time, it is clear from Fig. (**6**) that the diffraction peak of the neat PLLA further strengthens because of increasing crystal perfection of the neat PLLA. However, compared to the diffraction peaks of PLLA/starch after isothermal crystallization at 100 °C for 5 min, the diffraction peaks of PLLA/starch composites after isothermal crystallization at 100 °C for 15 min strengthen slightly, which indicates that the crystal of PLLA/starch after isothermal crystallization at 100 °C for 5 min has become relatively perfect.

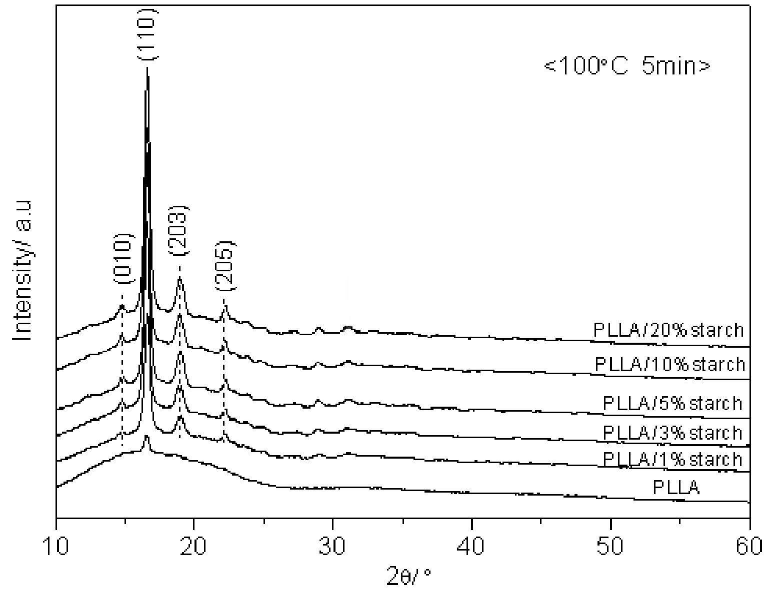

Fig. (5). XRD curves of PLLA and PLLA/starch after isothermal crystallization at 100 °C for 5 min.

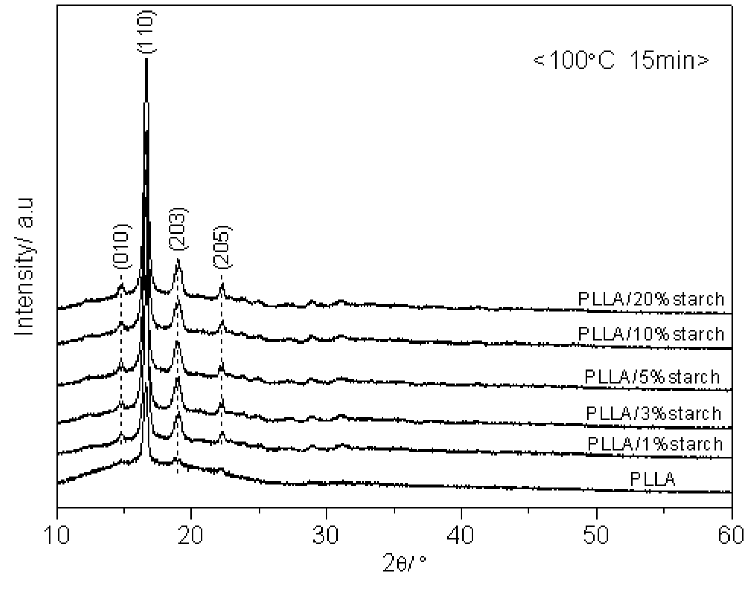

Fig. (6). XRD curves of PLLA and PLLA/starch after isothermal crystallization at 100 °C for 15 min.

CONCLUSION

Green PLLA/starch composites were fabricated by melt blending, and the fluidity and crystallization behavior of PLLA/starch were investigated; the kinetics of the isothermal crystallization of PLLA/starch composites was described using Avrami equation. The measurement results showed that the addition of starch could increase the fluidity and crystallization rate of PLLA significantly.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No Animals/Humans were used for studies that are base of this research.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The author declares no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS

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