



Influence of Ethylene *bis*-Stearamide on Crystallization Behaviour of Poly(L-lactide)

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The crystallization behaviour of poly(L-lactide) (PLLA)/ethylene *bis*-stearamide (EBS) composites with different content of EBS has been investigated by differential scanning calorimetry (DSC), polarization optical microscopy (POM) and thermogravimetric analysis. Ethylene *bis*-stearamide can accelerate the crystallization of PLLA upon the addition of 1 % EBS, the crystallization peak is most obvious and sharp, which indicates the best effect of crystallization at 1 % EBS. Cooling rate affect the process of crystallization of PLLA, with increasing of the cooling rate, the crystallization peak becomes wider and shifts to a lower temperature. Polarization optical microscopy shows that EBS make the spherulite size of PLLA decrease dramatically and the spherulite number become large. And the decomposition temperature of PLLA/EBS is slightly lower than that of neat PLLA.

Key Words: Poly(L-lactic acid), Crystallization, Sodium alginate, Nucleating effect.

INTRODUCTION

Poly(L-lactide) (PLLA) is very importance environmentally friendly polymer and has been the subject of many researches because of the producibility from renewable resources. However, slow crystallization rate, low crystalline degree and poor heat resistance of PLLA, which results from amorphous state by quenching from the melt to temperatures below the glass transition temperature, restrict its practical applications.

Thus, the study on the thermal behaviour, crystallization behaviour especially, of PLLA and its composites is of great important not only from academic interest but also from the engineering viewpoint, because, PLLA with high crystalline degree can be produced in a short period of time at a reduced cost. Up to now, there existed four routes to increase crystallization rate, including minimizing the amount of D-lactide isomers in the L-lactide, adding nucleating agent, adding plasticizer and playing with the molding conditions. And the most viable method to increase the overall crystallization rate is the blending with nucleating agent. The inorganic fillers are widely used to be as nucleating agent of PLLA¹⁻³ and has obtained many useful research result, but the inorganic fillers are not always the most efficient when compared with organic nucleating agents. Thus, to further improve the crystallization of PLLA and develop more nucleating agents of PLLA, the attention of nucleating agent has focused on organic compounds. The literatures⁴ showed that ethylene *bis*-stearamide (EBS) was very effective on the enhancement of crystallization of

PLLA. However, their work did not research crystallization behaviour in detail. In this paper, EBS is used to be as accelerator of crystallization of PLLA and the crystallization behaviour of PLLA/EBS composites were investigated by differential scanning calorimetry and depolarized-light intensity measurement.

EXPERIMENTAL

Poly(L-lactide) ($M_w = 1.95 \times 10^5$) was purchased from Nature Works LLC, USA. EBS was purchased from Chengdu Kelong Chemical Reagents Company, Sichuan, China.

Preparation of PLLA/EBS composites: Blending of PLLA and EBS was performed on a counter-rotating mixer and the preparation process of PLLA/EBS composites is similar to that of previous paper⁵.

For the thermal properties, the PLLA and its composites were first heated to 190 °C at a rate of 100 °C/min and held at the same temperature for 5 min, then were cooled at the same speed to 20 °C and held for another 5 min. Finally, the samples were scanned again to 180 °C at 10 °C/min.

The spherulite growth in the films was observed using an XPN-203E (Changfang Optical instrument Co., Ltd. Shanghai, China) equipped with a Canon Powershot- A610 camera and a Programmable temperature controller KEL-XMT-3100A (Chaoyang instrument Co., Ltd. Nanjing, China).

Thermogravimetric analysis was performed using a thermal analysis Q500 from TA Instruments-Waters LLC with a heating ramp of 20 °C/min under air flow (60 mL/min) from room temperature to 500 °C.

RESULTS AND DISCUSSION

Non-isothermal crystallization of PLLA/EBS composites: Fig. 1 shows the DSC curves of non-isothermal crystallization of PLLA/EBS composites from melt at a cooling rate of 1 °C/min. As seen in Fig. 1, upon cooling rate of 1 °C/min, the crystallization peak of PLLA can almost not be detected, which shows that the crystallization of neat PLLA is very slow. With addition of EBS, crystallization peak appears in the DSC cooling curve. Compared to the neat PLLA, EBS addition leads to the shift of crystallization peak to higher temperature indicating the increase of crystallization temperature. On the other hand, crystallization peak for PLLA containing EBS becomes much sharper in the cooling process. This result shows that EBS can increase the overall crystallization rate of PLLA. However, it is clear that the crystallization peak becomes weak with increasing addition of EBS, which indicates that there existed optimized content of EBS as accelerator of crystallization of PLLA. As shown in Fig. 1, upon the addition of 1 % EBS, the crystallization peak is most obvious and sharp, which indicates the best effect of crystallization at 1 % EBS.

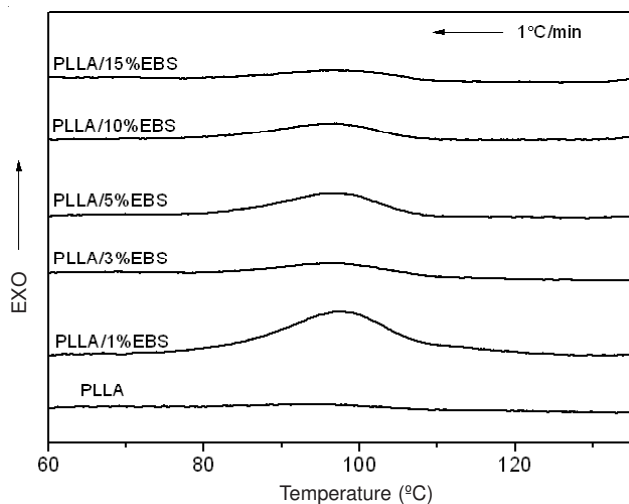
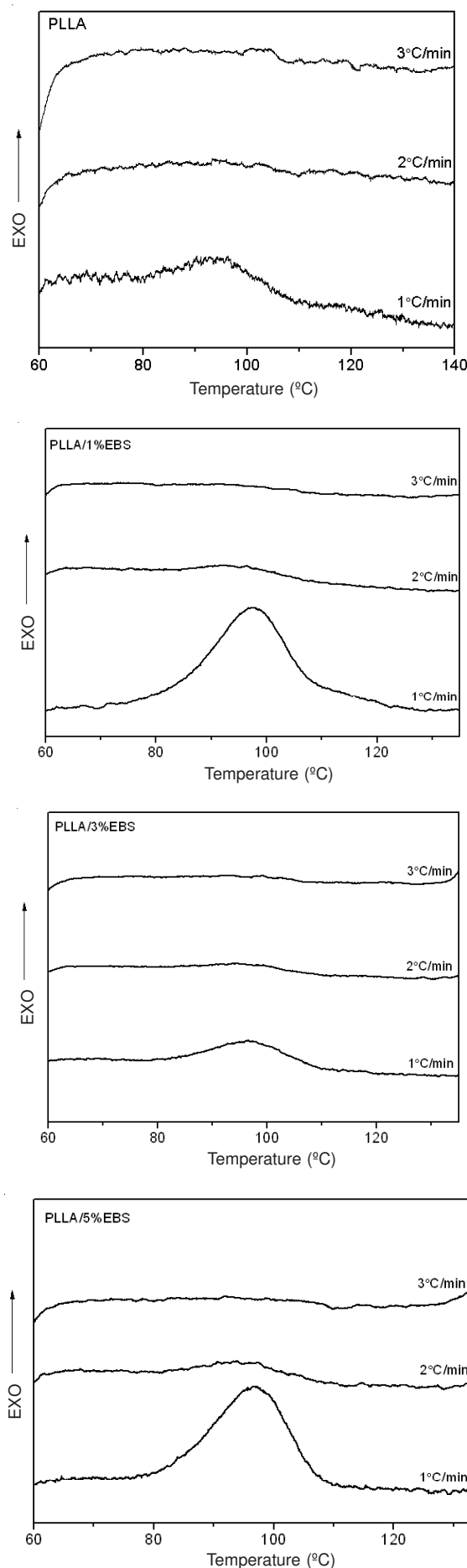


Fig. 1. DSC of PLLA and PLLA/EBS composites crystallized from melt at a cooling of 1 °C/min

The non-isothermal crystallization exotherms of PLLA and PLLA/EBS samples from the melt at different cooling rates are shown in Fig. 2. With increasing of the cooling rate, the crystallization peak becomes wider and shifts to a lower temperature. At the same cooling rate, the crystallization onset temperature and crystallization exotherms of PLLA/EBS are higher than those of PLLA. These results further confirm that EBS can accelerate the crystallization of PLLA.

Polarization optical microscopic (POM) analysis of PLLA/EBS samples: The spherulite morphology of PLLA/1 % EBS was compared with that of the neat PLLA by polarization optical microscopy (POM). Fig. 3 presents the POM photographs of neat PLLA and PLLA/1 % EBS sample isothermal melt-crystallizing at 105 °C for 90 and 40 min, respectively. Neat poly(L-lactide) has typical spherulite structure that can be seen clearly in POM images (Fig. 3). The spherulite size is large and the spherulite number is small. With the addition of 1 % EBS, the spherulite size decrease dramatically and the



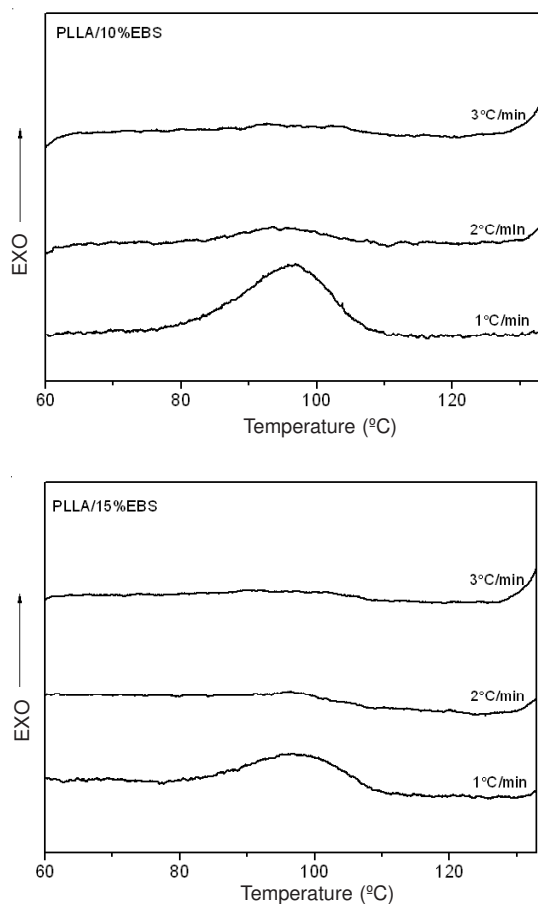


Fig. 2. DSC curves of PLLA, PLLA/EBS crystallization from melt at various cooling rates

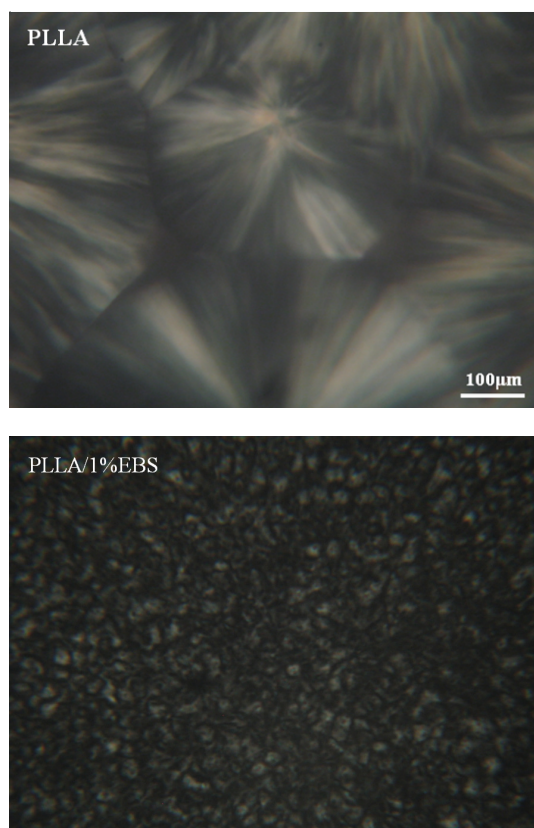


Fig. 3. POM images of PLLA and PLLA/1 % EBS after isothermal crystallization at 105 °C

spherulite number become large, which further confirms that EBS is very effective on the enhancement of crystallization of PLLA.

TGA analysis of PLLA/EBS samples: Thermogravimetric curves of thermal degradation for PLLA and PLLA/EBS composites at heating rates of 10 °C/min are presented in Fig. 4, PLLA decomposes fast and completely in one stage above 300 °C, the main degradation products of PLLA are oligomers together with some lactide, but there are also other volatile products such as acetaldehyde, carbon dioxide, carbon monoxide and ketene⁶. As shown in Fig. 4, compared to neat PLLA, the decomposition temperature of PLLA/EBS is slightly lower than that of neat PLLA, this is due to low decomposition temperature of EBS. What is more, the decomposition temperature of PLLA/EBS composites decrease with increasing of EBS content.

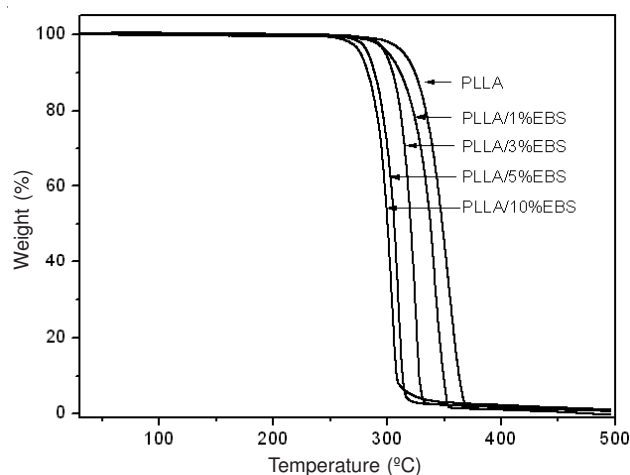


Fig. 4. TGA curves of for PLLA and PLLA/EBS composites

Conclusion

The crystallization behaviour of PLLA/EBS composites were investigated by DSC, POM and TGA in detailed. EBS is accelerate agent of the crystallization of PLLA and make the spherulite size of PLLA decrease dramatically and the spherulite number become large. TGA shows that the decomposition temperature of PLLA/EBS is slightly lower than that of neat PLLA.

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