



Melting Behaviour of Poly(L-lactic acid)/Ethylene *bis*-Stearamide Composites

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Received: 4 September 2013;

Accepted: 11 December 2013;

Published online: 15 February 2014;

AJC-14725

The melting behaviour of poly(L-lactic acid)(PLLA)/ethylene *bis*-stearamide (EBS) composites were investigated by using differential scanning calorimetry. The melting behaviour of PLLA/EBS composites was affected significantly by EBS content, crystallization temperature and crystallization time and double-melting peak resulted from melting-recrystallization. With increasing of EBS content, the ratio of peak area between low-temperature melting peak and high-temperature melting peak has large difference. And increasing of crystallization time made the low-temperature melting peak shift to high temperature with increasing of crystallization time and the melting peak get sharper. However, the high-temperature melting peak hardly move with increasing of crystallization time. Increasing of crystallization temperature made the low-temperature melting peak and high-temperature melting peak shift to the opposite direction.

Keywords: Poly(L-lactic acid), Ethylene *bis*-stearamide, Melting behaviour, Composites.

INTRODUCTION

With development of green science and technology, poly(L-lactic acid) (PLLA), as a very important environment-friendly polymer, have been considered to apply in more and more industry due to its lower energy consumption, biopolymer and non-toxic to the environment¹. However, low crystallization rate often restricts its practical applications. Thus, more and more researcher have focused on improving the crystallization rate of PLLA. For example, Li *et al.*² studied the effect of N-aminophthalimide compound as nucleating agent on crystallization behaviour and morphology of PLLA. The results indicated that N-aminophthalimide compound showed obvious nucleating effect on isothermal crystallization above 120 °C and in non-isothermal crystallization after it is added in PLLA. Cai *et al.*³ reported that *N,N'*-*bis*(benzoyl) suberic acid dihydrazide was a novel nucleating agent for PLLA. Non-isothermal crystallization indicated that the presence of *N,N'*-*bis*(benzoyl) suberic acid dihydrazide accelerated the overall PLLA crystallization. The addition of *N,N'*-*bis*(benzoyl) suberic acid dihydrazide caused shorter crystallization time and faster overall crystallization rate, meaning advanced nucleation ability of *N,N'*-*bis*(benzoyl) suberic acid dihydrazide upon crystallization of PLLA. Upon the addition of 0.8 % *N,N'*-*bis*(benzoyl) suberic acid dihydrazide, the crystallization half-time of PLLA decreased from 26.5 to 1.4 min at 115 °C. In addition, many inorganic compounds such as CaCO₃, BaCO₃, TiO₂, SiO₂, *etc.*, been used to be as nucleating agent of PLLA⁴.

On the other hand, the melting behaviour of PLLA composites also often investigated during studying the crystallization behaviour of PLLA composites, the reason is that melting behaviour can strongly reflect the crystallization behaviour of PLLA composites. Thus, up to now, there exists many literature reported the melting behaviour of PLLA^{5,6} and double melting peaks are often found in PLLA isothermal or non-isothermal crystallization from melting. As to double melting peaks, there exist two melting mechanism including the melting of crystals of different stability and the melting recrystallization⁷.

In our previous work, we investigated the influence of ethylene *bis*-stearamide (EBS) on crystallization behaviour of PLLA, the EBS can accelerate the crystallization of PLLA and POM shows that EBS make the spherulite size of PLLA decrease dramatically and the spherulite number become large. In this paper, to further investigate the important role in PLLA matrix, the melting behaviour of PLLA/EBS composites under different conditions was studied.

EXPERIMENTAL

Poly(L-lactic acid) (M_w = 1.95 × 10⁵) 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 our previous paper³.

Characterization: The melting behaviour with different condition was measured by DSC Q2000 instrument.

RESULTS AND DISCUSSION

Usually, melting behaviour of polymer is affected by additive. Fig. 1 shows the melting behaviour of PLLA with different EBS content at heating rate of 10 °C/min after non-isothermal crystallization at cooling rate of 1 °C/min. It is clear that there exist double melting peaks. The double-melting behaviour of PLLA has been reported in literature⁸, the low-temperature melting peak is attributed to the primary crystallites and high-temperature melting peak reflect the relatively perfect lamella stacks results from recrystallization during the heating scan. Meantime, it is observed that the low-temperature melting peak hardly shift, but the high-temperature melting peak shifts to higher temperature with increasing of EBS content, the possible reason is that the more the content of EBS is, the easier EBS improves the crystallization of PLLA during the second heating scan and the crystallization of PLLA is more perfect. With increasing of EBS content, the ratio of peak area between low-temperature melting peak and high-temperature melting peak gets large, the increasing of peak area of low-temperature melting peak results from more EBS may improve the crystallization of PLLA during non-isothermal crystallization at cooling rate of 1 °C/min.

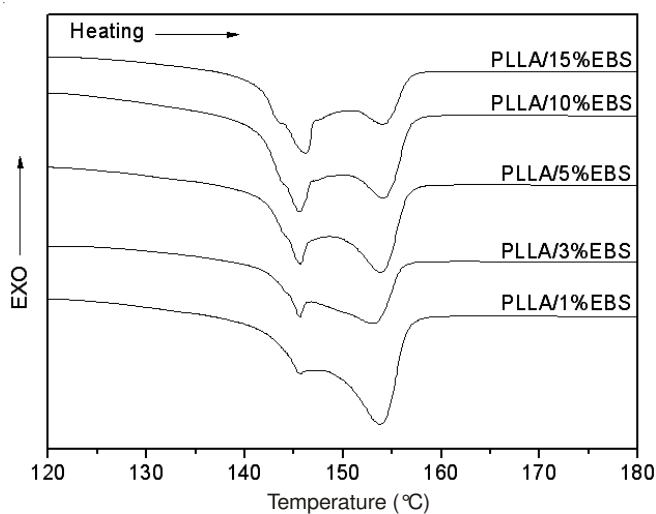


Fig. 1. Melting behaviour of PLLA with different EBS content at heating rate of 10 °C/min after non-isothermal crystallization at cooling rate of 1 °C/min

Melting behaviour of PLLA/1 % EBS composites after non-isothermal crystallization at different cooling rate:

Further investigate influence of cooling rate on the melting behaviour of PLLA/EBS composites. The melting behaviour of PLLA/1 % EBS composites after non-isothermal crystallization at different cooling rate was investigated. As shown in Fig. 2, with increasing cooling rate, the melting peak of primary crystallites formed during non-isothermal crystallization evidently decrease, the reason is that increasing of cooling rate make the reduction of crystallization degree of PLLA during non-isothermal crystallization from melt. On the other hand, Fig. 2 also show that the low-temperature melting peak shifts to lower temperature with increasing of cooling rate,

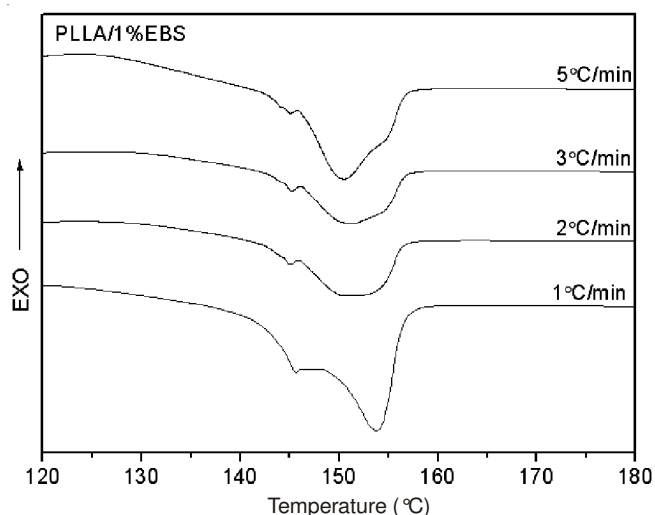


Fig. 2. Melting behaviour of PLLA/1 % EBS composites after non-isothermal crystallization at different cooling rate

resulting from the less perfect crystallization of PLLA. Similarly, the high-temperature melting peak also shifts to low temperature with increasing of cooling rate during non-isothermal crystallization.

Melting behaviour of PLLA/1 % EBS composites after isothermal crystallization for 1 h at 100 °C:

Fig. 3 shows the melting behaviour of PLLA/1 % EBS composites after isothermal crystallization for 1 h at 100 °C. As seen in Fig. 3, the low-temperature melting peak shifts to high temperature with increasing of crystallization time and the melting peak gets sharper, these results further confirm that EBS can improve the crystallization of PLLA and EBS makes the crystal of PLLA more perfect with increasing of crystallization time. However, the high-temperature melting peak hardly move with increasing of crystallization time and the area of melting peak also hardly change, the reason may be that the crystallization of PLLA is not enough at 100 °C for long time. The recrystallization of PLLA is similar at same heating rate during second heating scan.

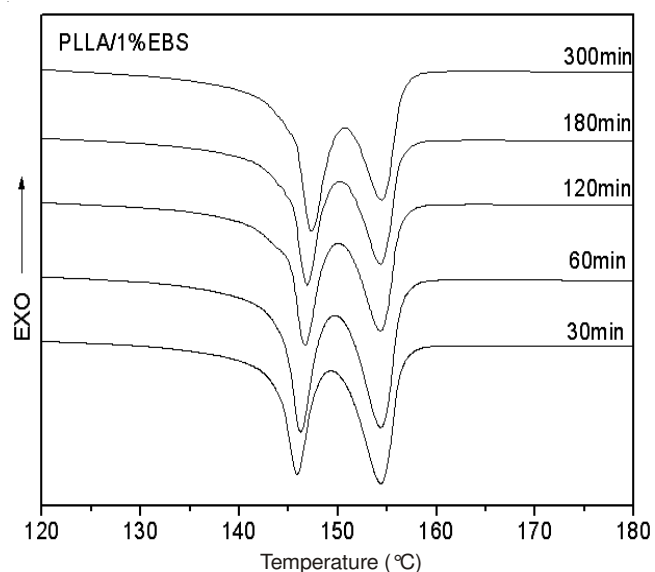


Fig. 3. Melting behaviour of PLLA/1 % EBS composites after isothermal crystallization for 1 h at 100 °C

Melting behaviour of PLLA/1 % EBS composites after isothermal crystallization for different time at different temperature: Fig. 4 shows the melting behaviour of PLLA/1 % EBS composites after isothermal crystallization for different time at different temperature. It is clear that low-temperature melting peak shifts to high temperature with increasing of crystallization temperature and the peak gets sharper, the melting peak shifts to higher temperature with the increasing of crystallization temperature, the reason may be that the crystallization of PLLA is more perfect at higher crystallization temperature. However, the high-temperature melting peak shifts to low temperature and the high-temperature melting peak hardly disappear at 105 °C for 1.5 h, these results indicate that the melting behaviour is affected by crystallization temperature and crystallization time.

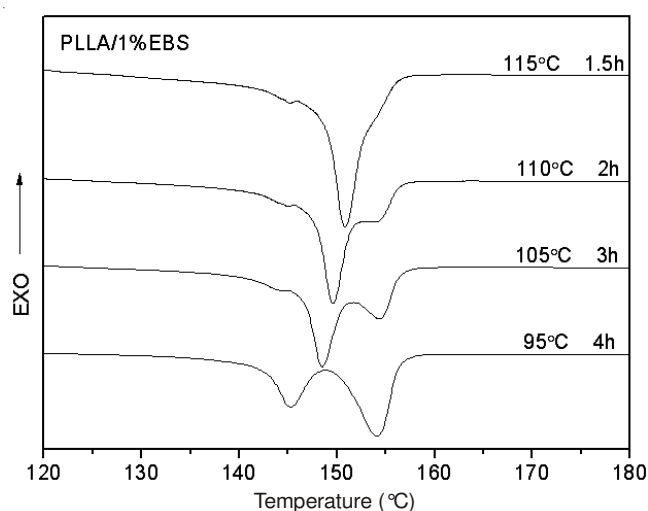


Fig. 4. Melting behaviour of PLLA/1 % EBS composites after isothermal crystallization for different time at different temperature

Conclusion

The melting behaviour of PLLA/EBS composites under different conditions were investigated. The results showed that the melting behaviour of PLLA/EBS composites was affected significantly by EBS content, crystallization temperature and crystallization time and the melting behaviour also indicated that double-melting peak of PLLA/EBS composites resulted from melting-recrystallization.

ACKNOWLEDGEMENTS

This work was supported by China Postdoctoral Science Foundation (project number 2013M531937), Natural Science Foundation Project of CQ CSTC (project number cstc2012jjA50001), Postdoctoral Science Foundation Project of Chongqing (project number XM20120035), Scientific and Technological Research Program of Chongqing Municipal Education Commission (project number KJ131202) and Chongqing University of Arts and Sciences (project number R2012CH10 and 2012PYXM04).

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