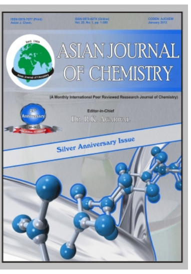
Asian Journal of Chemistry; Vol. 25, No. 4 (2013), 2170-2172

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13381



Effects of Barium Sulphate on Thermal Behaviour of Poly(L-lactic Acid)

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(*Received*: 4 January 2012; *Accepted*: 17 October 2012) AJC-12305

Poly(L-lactic acid)(PLLA)/barium sulphate ($BaSO_4$) composites were fabricated by melt blending and hot-press forming process. The thermal behaviour of PLLA/$BaSO_4$ composites with different amount of $BaSO_4$ has been investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and thermogravimetric analysis (TGA). Barium sulphate is effective nucleating agent for the crystallization and can increase the overall crystallization rate of PLLA. With the addition of 2 % $BaSO_4$, the crystallization temperature (T_o) increase from 105.88-117.03 ºC and the crystallization enthalpy (ΔH_c) increase from 1.379-39.39 J g^{-1}. Polarized optical microscopy shows that $BaSO_4$ makes the spherulite size decrease dramatically and the spherulite number become large. With increasing of cooling rate, the crystallization peak of PLLA/$BaSO_4$ shifts to lower temperature and the crystallization peak becomes wider. TGA analysis shows that the decomposition temperature of PLLA/$BaSO_4$ composites is slightly higher than that of neat PLLA.

Key Words: Poly(L-lactic acid), Crystallization, Barium sulphate, Nucleating effect.

INTRODUCTION

Over the past decade, there has been a increasing attention on poly(L-lactic acid) (PLLA) derived from renewable sources. The poly(L-lactic acid) has been widely used in medical and commercial applications, becsause of its biodegradable, biocompatible and non-toxic to the environment[1-3]. Usually, the processing of PLLA is carried out by melt blending and hot-press forming. This method involves heating the polymer above its melting point and cooling to stabilize its dimensions. Thus, the thermal behaviour is very important aspect of the physical properties of PLLA. However, PLLA has many weakness such as slow crystallization rate, low crystalline degree and poor heat resistance[4], *etc*. Many literatures[5,6] have reported the thermal behaviour of PLLA and its composites, especially for improving its crystallization rate. There exist 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. Adding nucleating agent is the easiest way to increase crystallization rate of PLLA.

Barium sulphate ($BaSO_4$) is very important inorganic compound and compared to calcium carbonate, $BaSO_4$ is little used to be as nucleating agent of polymer. In this paper, barium sulphate as effective nucleating agent for PLLA is used to improve the crystallization of PLLA and the thermal behaviour of PLLA/$BaSO_4$ composites was investigated.

EXPERIMENTAL

Poly(L-lactic acid) (2002D) was purchased from Nature Works LLC, USA. The barium sulphate was prepared by solution reaction and the SEM images of barium sulphate is shown in Fig. 1.

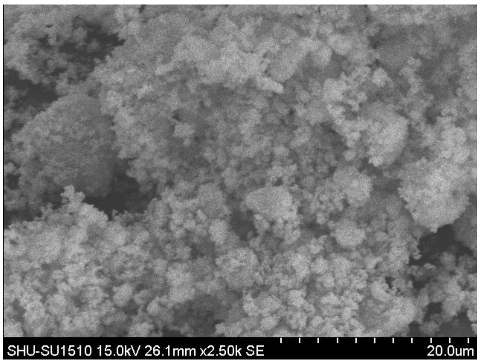

Fig. 1. SEM of barium sulphate

Preparation of PLLA/$BaSO_4$ sample: Blending of PLLA and $BaSO_4$ was performed on a counter-rotating mixer and the preparation process of PLLA/$BaSO_4$ composites has described in our previous paper[4].

Characterization

Differential scanning calorimeter (DSC): The non-isothermal crystallization behaviour of PLLA/2 % $BaSO_4$ was measured by DSC Q2000 (TA Instrumrnts-Waters LLC, USA). The temperature and heat flow at different heating rate were calibrated using an indium standard. The sample was heated to 190 ºC and maintained at that temperature for 5 min to make sure that the polymer crystals were melted completely. Then the samples were cooled from the melt state to 20 ºC at different cooling rate.

Environmental scanning electron microscopy (SEM): The morphologies of the fracture surfaces of samples were examined by XL-30 ESEM FEG, Philips, in 15-20 kV accelerating voltage (Tungsten filament). The samples were fractured and covered by gold vapors.

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

RESULTS AND DISCUSSION

Crystallization behaviour of PLLA/$BaSO_4$ samples: Fig. 2 shows the DSC curves of non-isothermal crystallization of PLLA/$BaSO_4$ composites with different $BaSO_4$ content from melt at a cooling rate of 1 ºC/min. As seen in Fig. 2, Upon cooling at 1 ºC/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 $BaSO_4$, crystallization peak appears in the DSC cooling curve. Compared to the neat PLLA, $BaSO_4$ addition makes crystallization peak for PLLA become sharp in the cooling process, this result shows that $BaSO_4$ can serve as a nucleating agent for the crystallization and increase the overall crystallization rate of PLLA. Upon cooling at 1 ºC/min, as shown in Fig. 2, with increasing $BaSO_4$ content, crystallization peak for PLLA become much sharper, upon the addition of 2 % $BaSO_4$, the crystallization peak is the sharpest, which indicates the best effect of crystallization at 2 % $BaSO_4$. When the $BaSO_4$ content is larger than 2 %, the crystallization peak becomes wide, the reason may be that it is difficult to disperse excessive $BaSO_4$ homogeneously in PLLA matrix and reduce nucleating effect of nucleating agent $BaSO_4$. Compared to the neat PLLA, with the addition of 2 % $BaSO_4$, the crystallization temperature (T_o) increase from 105.88 to 117.03 ºC and the crystallization enthalpy (ΔH_c) increase from 1.379 to 39.39 J g^{-1}.

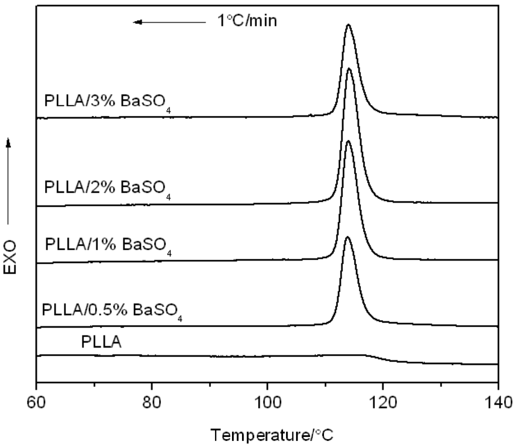

Fig. 2. DSC of PLLA and PLLA/$BaSO_4$ crystallized from melt at a cooling of 1 ºC/min

The spherulite morphology of $BaSO_4$-containing PLLA was observed by POM. Fig. 3 shows the POM image of PLLA and PLLA/2 % $BaSO_4$ sample after isothermal crystallization process at 115 ºC. PLLA and PLLA/2 % $BaSO_4$ samples have typical spherulite structure that can be seen clearly in POM images of Fig. 3. As for neat PLLA, the spherulite size is large and the spherulite number is small. With the addition of 2 % $BaSO_4$, the spherulite size decrease dramatically and the spherulite number become large, which further confirms that $BaSO_4$ is very effective on the enhancement of crystallization of PLLA.

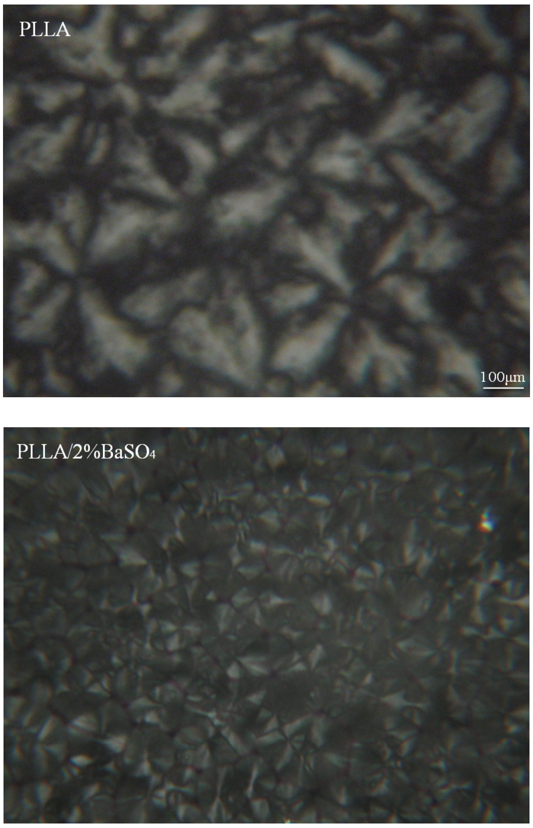

Fig. 3. Polarized optical microscopy of PLLA and PLLA/2 % $BaSO_4$ after isothermal crystallization at 115 ºC

Crystallization behaviour of PLLA/2 % $BaSO_4$ sample at different cooling rate: Cooling rate significantly affects the crystallization of polymer, thus, we investigate the crystallization behaviour of PLLA/2 % $BaSO_4$ sample at different cooling rate. Fig. 4 shows the crystallization behaviour of PLLA/2 % $BaSO_4$ sample at different cooling rate, as shown in Fig. 4, the crystallization peak of PLLA/2 % $BaSO_4$ sample shifts to lower temperature with increasing of cooling rate and the crystallization peak becomes wider. Similar results can be found in other systems such as PLLA/modified carbon black composites[7], this is may be that the crystallization of PLLA is slower than the reduction of cooling rate. However, Upon 1 ºC/min or 5 ºC/min of cooling rate, there exist significantly crystallization peak, which indicates that $BaSO_4$ can significantly improve the crystallization rate of PLLA.

TGA analysis of PLLA/$BaSO_4$ samples: Thermogravimetric TG curves of thermal degradation for PLLA, $BaSO_4$ and PLLA/$BaSO_4$ composites at heating rates of 10 ºC/min

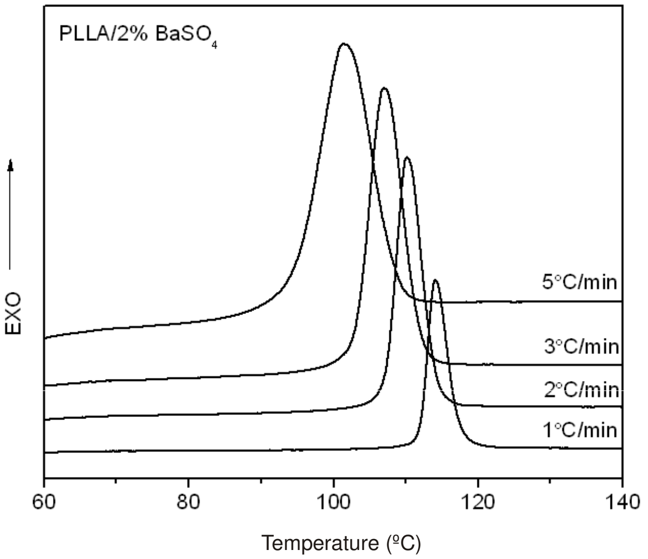

Fig. 4. Crystallization behaviour of PLLA/2 % $BaSO_4$ sample at different cooling rate

are presented in Fig. 5, PLLA decomposes fast and completely in one stage above 300 ºC, 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 ketene[8]. As shown in Fig. 5, amostly, $BaSO_4$ does not degradate during room temperature to 500 ºC and compared to neat PLLA, the decomposition temperature of PLLA/$BaSO_4$ is slightly higher than that of neat PLLA, this is due to high decomposition temperature of $BaSO_4$. However, the decomposition temperature of PLLA/$BaSO_4$ composities does not increase with increasing of $BaSO_4$ content, this is may be that there existed non-uniformly dispersion in PLLA matrix.

Conclusion

PLLA/$BaSO_4$ composites were fabricated by melt blending technology and the thermal behaviour of PLLA/$BaSO_4$ composites were investigated in detail. Crystallization behaviour showed that $BaSO_4$ was effective nucleating agent for the crystallization and could increase the overall crystallization rate of PLLA. With increasing of cooling rate, the crystallization peak of PLLA/$BaSO_4$ shifted to lower temperature and became wider. And the decomposition temperature of PLLA/$BaSO_4$ composites was slightly higher than that of neat PLLA.

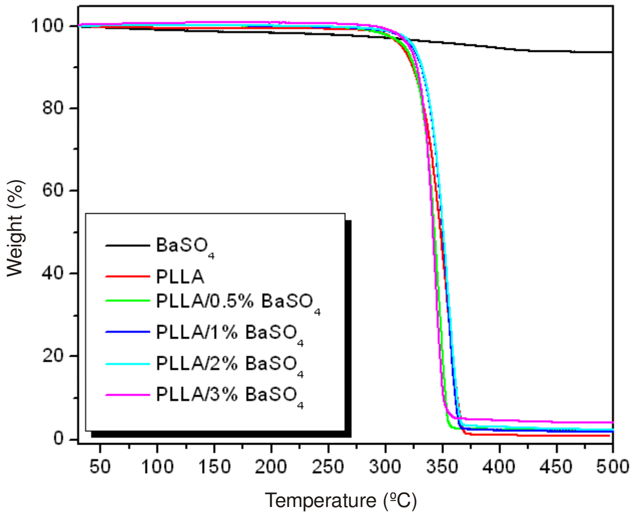

Fig. 5. TGA curves of for PLLA, $BaSO_4$ and PLLA/$BaSO_4$ composites

ACKNOWLEDGEMENTS

This work was supported by Natural Science Foundation Project of CQ CSTC(project number cstc2012jjA50001) and Chongqing University of Arts and Sciences (Project Number 2012PYXM04 and Z2011CL11).

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