



NOTE

Effects of Alanine Methyl Ester Hydrochlorides on Thermal Behaviour of Biodegradable Poly(L-lactic Acid)

YAN-HUA CAI*, QIANG XU, YING TANG, WEN LUO, SHEN-WEI ZHANG and HAI-TAO HAO

School of Materials and Chemical Engineering, Chongqing University of Arts and Sciences, Yongchuan, Chongqing-402160, P.R. China

*Corresponding author: E-mail: caiyh651@yahoo.com.cn

(Received: 4 November 2011;

Accepted: 29 September 2012)

AJC-12206

Alanine methyl ester hydrochlorides (AMEH) was synthesized to improve the crystallization of poly(L-lactic acid) (PLLA) and PLLA/AMEH was prepared by melt blending and hot-press forming process. The thermal behaviour of PLLA/AMEH was investigated by DSC. Non-isothermal crystallization showed that alanine methyl ester hydrochloride made the melt crystallization peak become much sharper in the cooling process and the crystallization enthalpy increases from 1.379 to 9.941 J g⁻¹ with the addition of 2 % alanine methyl ester hydrochloride at a cooling rate of 1 °C/min from melt. The melting behaviour of PLLA/2 % AMEH after at different crystallization temperature for 1 h confirmed that double-melting peak of PLLA/2 % AMEH resulted from melting-recrystallization, However, the high-temperature melting peak becomes smaller with increasing of crystallization temperature.

Key Words: Poly(L-lactic acid), Crystallization, Alanine methyl ester hydrochlorides, DSC.

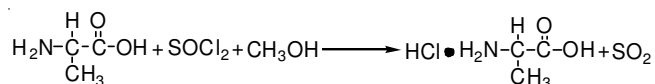
Poly(L-lactic acid) (PLLA) is a semi-crystalline polymer, used in the packaging materials, automotive interior and surgical sutures¹, due to lower energy consumption, biopolymer and non-toxic to the environment¹. Poly(L-lactic acid) has normally a slow crystallization rate. The thermal behaviour including crystallization behaviour of PLLA and its composites has been extensively studied. Usually, the crystallization behaviour of PLLA and its composites can be described by the stages of nucleation and crystal growth. Heterogeneous nucleation is used to improve the crystallization of PLLA. The heterogeneous nucleation can increase crystallization rate by foreign bodies within the molten phase and these foreign bodies are called nucleating agent. As to the nucleating mechanism, there existed two nucleating mechanism between polymer and nucleating agents, including the epitaxial nucleation and mechanisms of chemical².

In this paper, alanine methyl ester hydrochlorides (AMEH) was synthesized to improve the crystallization of poly(L-lactic acid) (PLLA) and PLLA/AMEH was prepared by melt blending and hot-press forming process. The thermal behaviour of PLLA/AMEH was investigated by DSC.

Poly(L-lactic acid) (2002D) was purchased from Nature Works LLC, USA. The other materials used in this study were of analytical grade (AR). Thionyl chloride and alanine were procured from Beijing Chemical Reagents Company and

Chengdu Kelong Chemical Reagents Company, respectively. Methyl alcohol was procured from Mianyang Rongshen Chemical Reagents Company.

Synthesis of alanine methyl ester hydrochloride (AMEH): alanine methyl ester hydrochloride was prepared as shown in **Scheme-I**. Thionyl dichloride in the presence of methyl alcohol was mixed with stirring for 1 h and the mixture was added slowly onto the mixture including alanine and refluxed for 1 h. After evaporation of thionyl dichloride and methyl alcohol in vacuum, the residue was AMEH.



Scheme-I: Synthesis of AMEH

Preparation of PLLA/AMEH sample: Preparation of PLLA/AMEH sample is similar to our method¹.

Fourier transform infrared spectra was recorded on a Bio-Rad FTS135 spectrophotometer from 4000-400 cm⁻¹. The non-isothermal crystallization behaviour of PLLA/2 % AMEH was measured by DSC Q2000 (TA Instruments-Waters LLC, USA). The temperature and heat flow at different heating rate were calibrated using an indium standard. The sample was heated to 190 °C 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 °C at different cooling rate. The melting behaviour with different condition was measured by DSC Q2000 instrument.

Structures of AMEH: In the FT-IR spectra, the peaks at 3419 cm^{-1} contributes to the absorption of N-H stretching vibration and the absorption peak at 2935 cm^{-1} belongs to O-H stretching vibration, the peak at 1741 cm^{-1} contributes to C=O stretching vibration. Then the absorption peak at 1273 cm^{-1} is mixed peak including C-N stretching vibration and N-H bending vibration absorption, the other absorption peaks are consistent with the literature³. Infrared spectrum analysis showed that alanine methyl ester hydrochlorides had been synthesized.

Non-isothermal crystallization of PLLA/2 % AMEH:

Fig. 1 shows the DSC curves of non-isothermal crystallization from melt. The crystallization of neat PLLA is very slow. Upon cooling at 1 °C/min, the crystallization peak is not detected. On addition of 2 % AMEH, crystallization peak appears in the DSC cooling curve. Compared to the neat PLLA, AMEH makes the melt crystallization peak become much sharper in the cooling process, the result shows that AMEH could increase the overall crystallization rate and serve as a nucleating agent for the crystallization of PLLA. However, the crystallization peak of PLLA/AMEH is not detected at cooling rate of 2 °C/min, which shows that cooling rate is very important to crystallization of PLLA. With the addition of 2 % AMEH, as seen in Table-1, the crystallization temperature (T_o) decreases from 105.88-102.94 °C, melt-crystallization peak temperature (T_{mo}) decreases from 96.28 to 92.70 °C and the crystallization enthalpy (ΔH_c) increases from 1.379 to 9.941 J g^{-1} at a cooling rate of 1 °C/min from melt.

Melting behaviour of PLLA/2 % AMEH: Fig. 2 shows the melting behaviour of PLLA/2 % AMEH sample at different crystallization temperature for 1 h. All DSC curves show the

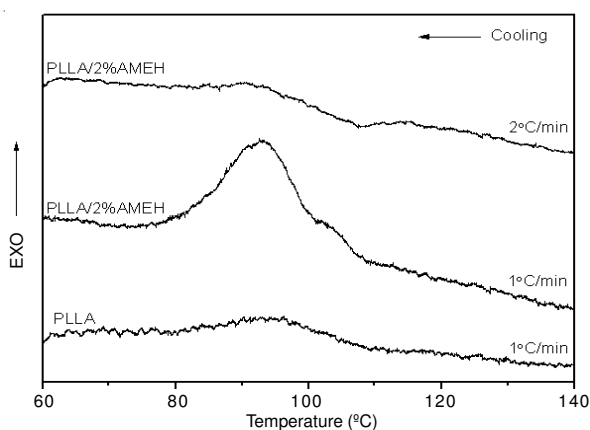


Fig. 1. DSC of PLLA and PLLA/2 % AMEH crystallized from melt at different cooling rate

TABLE-1
DSC DATE OF PLLA/2 % AMEH CRYSTALLIZED FROM MELT AT DIFFERENT COOLING RATE

Sample	T_o (°C)	T_{mo} (°C)	ΔH_c (J g^{-1})
PLLA (1 °C/min)	105.88	96.28	1.379
PLLA/2 % AMEH (1 °C/min)	102.94	92.70	9.941
PLLA/2 % AMEH (2 °C/min)	101.93	93.13	1.290

double melting peak, the low-temperature melting peak belongs to melting peak of crystal after isothermal crystallization at different cryatllization temperature and the high-temperature melting peak belongs to melting peak of crysatl at second heating process, which indicates that PLLA undergo a melt recrystallization-remelting process upon heating. From the Fig. 2 it is clear that the increasing of crystallization temperature leads to the shift of melting peak to higher temperature and the low-temperature melting peak become sharper, the reason may be that the increasing of crystallization temperature makes the degree of recrystallization of imperfect crystal increase. However, with increasing of crystallization temperature, the high-temperature melting peak becomes smaller, which indicates that the crystallization decrease at second heating process and which further confirms that double-melting peak result from melting-recrystallization.

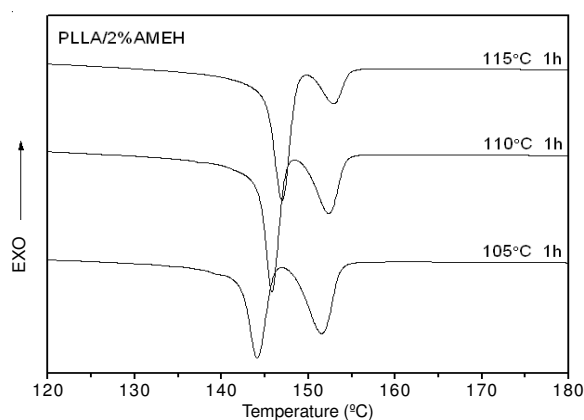


Fig. 2. Melting behaviour of PLLA/2 % AMEH sample at different crystallization temperature for 1 h

Conclusion

AMEH was synthesized by liquid phase reaction to improve the crystallization of PLLA. The thermal behaviour of PLLA/AMEH showed that AMEH made the melt crystallization peak become much sharper in the cooling process and the crystallization enthalpy increases from 1.379 - 9.941 J g^{-1} with the addition of 2 % AMEH at a cooling rate of 1 °C/min from melt. And the melting behaviour of PLLA/2 % AMEH after at different crystallization temperature for 1 h confirmed that double-melting peak of PLLA/2 % AMEH resulted from melting-recrystallization.

ACKNOWLEDGEMENTS

This work was supported by The Ministry of Science and Technology of the P.R. China (Project No. 2007BAE42B00), Natural Science Foundation Project of CQ CSTC (Project No. cstc2012jjA50001) and Chongqing University of Arts and Sciences (Project No. 2012PYXM04 and Z2011CL11).

REFERENCES

- Y.H. Cai, S.F. Yan, J.B. Yin, Y.Q. Fan and X.S. Chen, *J. Appl. Polym. Sci.*, **121**, 1408 (2011).
- P.J. Pan, Z.C. Liang, A. Cao and Y. Inoue, *ACS Appl. Mater. Interf.*, **1**, 402 (2009).
- X. Song, C. Min and L. Sun, *Huaxue Shiji*, **29**, 687 (2007).