



Thermal Behaviour of Poly(L-lactic acid)/*N,N'*-Bis(benzoyl) Suberic Acid Dihydrazide with Crosslinking Agent

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Poly(L-lactic acid) (PLLA)/*N,N'*-bis(benzoyl) suberic acid dihydrazide (NA) with crosslinking agent 1,3,5-tri-2-propenyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TAIC) was prepared by melt blending and hot-press forming process and the thermal behaviour of PLLA/NA/TAIC was investigated by DSC and TGA. Non-isothermal crystallization behaviour shows that the TAIC addition leads to the shift of crystallization peak of PLLA to lower temperature indicating the decrease of crystallization temperature and crosslinking agent TAIC does not improve the crystallization of PLLA. Melting behaviour at different conditions shows that there existed double-melting peaks and TAIC addition makes the melting peak of PLLA/NA/TAIC samples locate in lower temperature. TGA shows that the decomposition temperature of PLLA/NA/TAIC is higher and PLLA/NA/TAIC decompose faster.

Key Words: Poly(L-lactic acid), Crystallization, Melting behaviour, Crosslinking agent.

INTRODUCTION

Poly(L-lactic acid) (PLLA) is very important biodegradable polymers and has gained considerable momentum in recent years due to its lower energy consumption, biopolymer and non-toxic to the environment¹⁻⁴. However, slow crystallization rate of PLLA is too weak to restrict its practical applications. Thus, there are 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, respectively. In previous work⁵, we had reported that *N,N'*-bis(benzoyl) suberic acid dihydrazide (NA) could improve the 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 min to 1.4 min at 115 °C. There existed some paper which reported that crosslinking also improve the crystallization of PLLA. Thus, in this work, we further investigate the thermal behaviour of PLLA/*N,N'*-bis(benzoyl) suberic acid dihydrazide (NA) with crosslinking agent 1,3,5-tri-2-propenyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TAIC).

EXPERIMENTAL

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

N,N-dimethylacetamide, thionyl dichloride and pyridine were procured from Mianyang Rongshen Chemical Reagents Company. TAIC was procured from Chengdu Kelong Chemical Reagents Company.

Synthesis of *N,N'*-bis(benzoyl) suberic acid dihydrazide (NA): Synthesis of *N,N'*-bis(benzoyl) suberic acid dihydrazide have described in previous work⁵.

Preparation of PLLA/NA and PLLA/NA/TAIC samples: Preparation of PLLA/0.8 %NA sample have described in our previous work⁵. Blending of PLLA/0.8 %NA and 1 % TAIC also was performed on a counter-rotating mixer and PLLA/0.8 %NA/1 %TAIC sample was cross-linked by electron beam.

Differential scanning calorimeter (DSC): The non-isothermal crystallization behaviour of PLLA/NA and PLLA/NA/TAIC 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.

Thermogravimetric analysis: Thermogravimetric analysis (TGA) 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 behaviour: Fig. 1 shows the DSC curves of non-isothermal crystallization of PLLA/NA/TAIC sample and PLLA/NA sample at the different cooling rate from melt. As seen in Fig. 1, there existed intensity crystallization peak of PLLA/NA sample at different cooling rate and the crystallization peak shifts to lower temperature with increasing of cooling rate. Similar results can be found in other systems such as PLLA/modified carbon black composites⁶. However, compared to the PLLA/NA, the TAIC addition leads to the shift of crystallization peak of PLLA/NA/TAIC sample to lower temperature indicating the decrease of crystallization temperature. On the other hand, crystallization peak for PLLA containing TAIC become much wider in the cooling process. Upon the cooling rate of 5 °C/min, the crystallization peak of PLLA/NA/TAIC sample can almost not be detected. These results indicate that crosslinking agent TAIC does not improve the crystallization of PLLA. In contrast, the TAIC addition decreases the nucleating effect of NA.

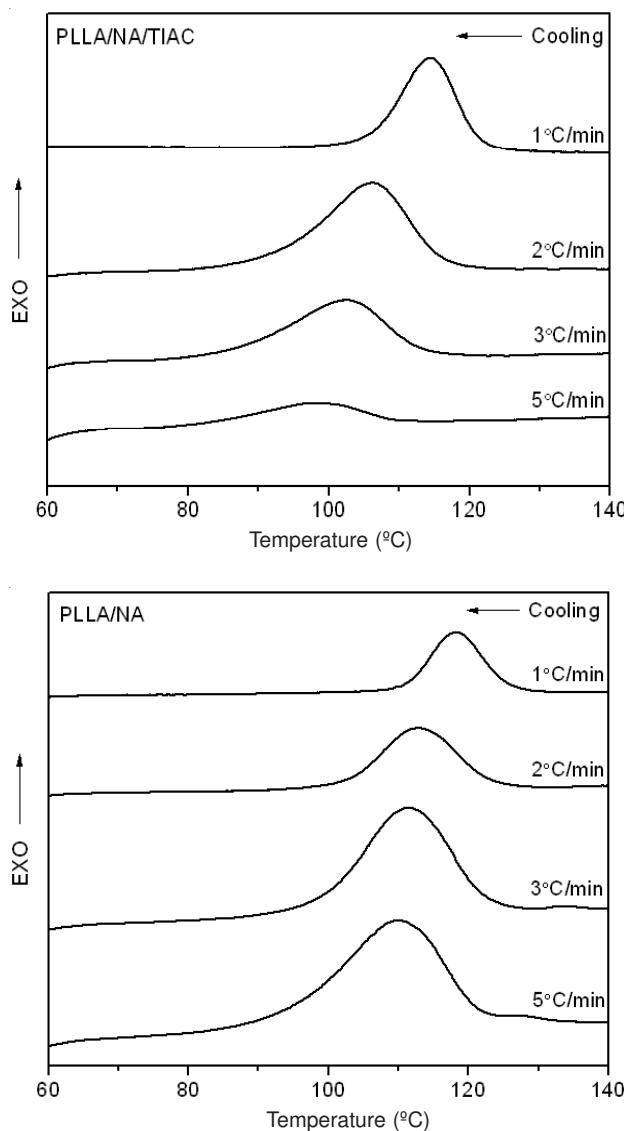


Fig. 1. DSC curves of non-isothermal crystallization of PLLA/NA/TAIC sample and PLLA/NA sample at the different cooling rate from melt

Melting behaviour

Melting behaviour at different heating rate after isothermal crystallization for 1 h at 100 °C: Fig. 2 shows the DSC of PLLA/NA/TAIC and PLLA/NA samples at a different heating rate during isothermal crystallization for 1 h at 100 °C. With increasing of heating rate, the double melting peak degenerate to single melting peak and the high-temperature melting peak existed in the form of pulse. From the Fig. 2 it is clear that the low-temperature melting peak of PLLA/NA/TAIC sample does not shift to lower temperature as that of PLLA/NA sample with increasing of heating rate. On the other hand, the high-temperature melting peaks of PLLA/NA and PLLA/NA/TAIC samples shift to low temperature with increasing of heating rate, the reason may be that the increasing of heating rate made the degree of recrystallization of imperfect crystal decrease, which confirmed that double-melting peak of PLLA/NA/TAIC and PLLA/NA samples result from melting-recrystallization.

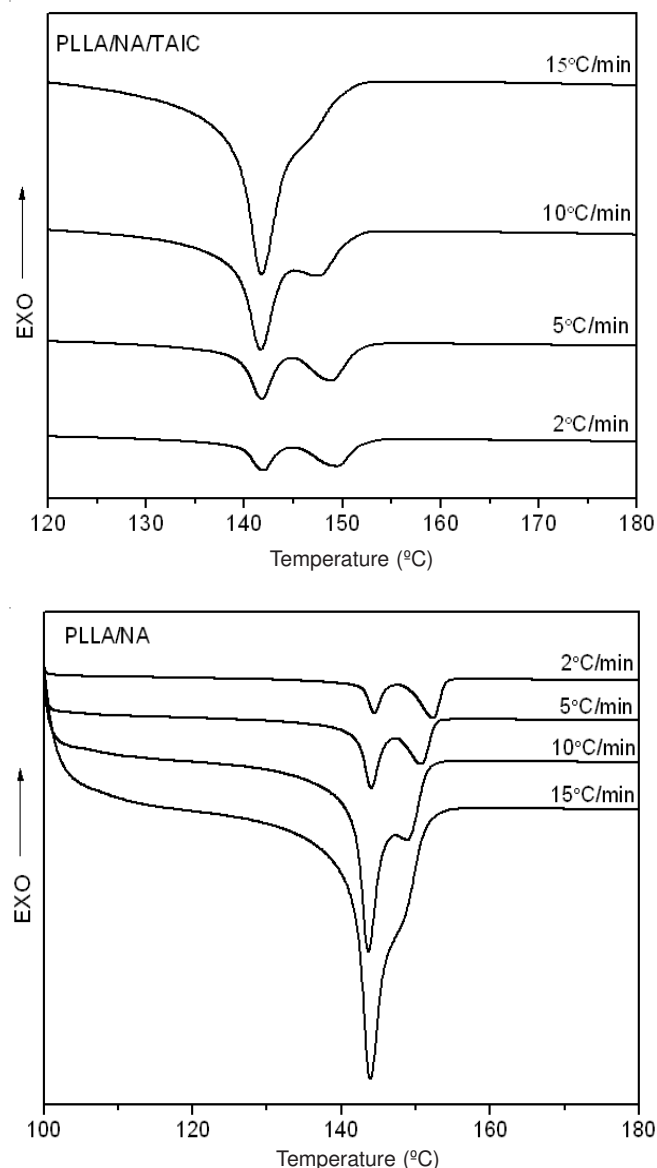


Fig. 2. DSC of PLLA/NA/TAIC and PLLA/NA sample at a different heating rate during isothermal crystallization for 1 h at 100 °C

Melting behaviour at the heating rate of 10 °C/min after different isothermal crystallization time: Fig. 3 shows the DSC of PLLA/NA/TAIC and PLLA/NA samples at the heating rate of 10 °C/min after different isothermal crystallization time. As shown in Fig. 3, The high-temperature melting peak of PLLA/NA and PLLA/NA/TAIC samples existed in the form of pulse with increasing of isothermal crystallization time. At the same time, the low-temperature melting peak shifts to higher temperature and the high-temperature melting peak shifts to lower temperature. Compared to PLLA/NA, the double melting peaks of PLLA/NA/TAIC samples are located in lower temperature, which indicates that the crystallization perfect of PLLA/NA/TAIC sample is worse than that of PLLA/NA sample and TAIC reduce the crystallization of PLLA. However, the trend of melting behaviour of PLLA/NA and PLLA/NA/TAIC samples is similar.

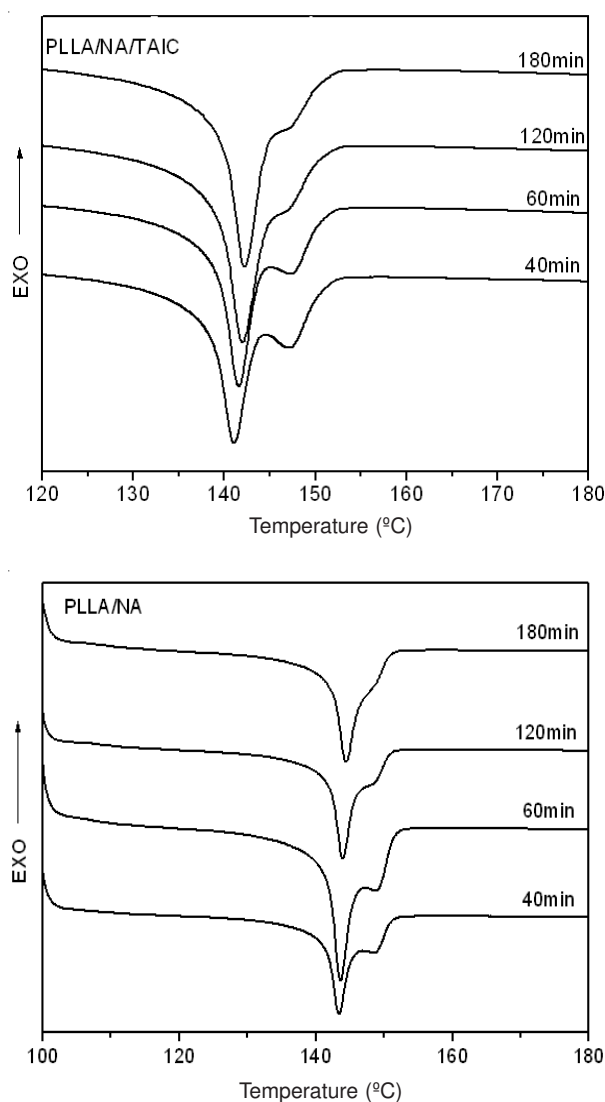


Fig. 3. DSC of PLLA/NA/TAIC and PLLA/NA samples at the heating rate of 10 °C/min after different isothermal crystallization time

Thermogravimetric analysis: Fig. 4 shows TGA curve of NA, PLLA, PLLA/NA and PLLA/NA/TAIC samples decomposition at heating rate of 20 °C/min, respectively. As seen in Fig. 4, the NA starts to decompose above 200 °C and in a

broad temperature range. 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 ketene⁷. The decomposition temperature of PLLA/NA is lower than that of PLLA/NA/TAIC sample, which indicates that TAIC addition improve the decomposition temperature of sample. However, PLLA/NA/TAIC decomposes faster than PLLA/NA. In addition, the decomposition temperatures of PLLA/NA and PLLA/NA/TAIC are lower than that of PLLA, this is due to low decomposition temperature of NA and TAIC.

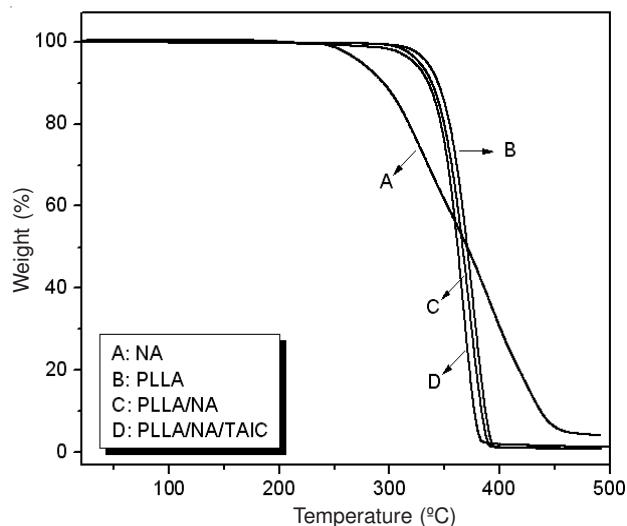


Fig. 4. TGA curve of NA, PLLA, PLLA/NA and PLLA/NA/TAIC samples decomposition at heating rate of 20 °C/min

Conclusion

TAIC was filled to PLLA/NA sample and the thermal behaviour of PLLA/NA/TAIC was investigated by DSC and TGA. The results showed that TAIC did not improve the crystallization of PLLA and TAIC made the double melting peaks of PLLA/NA/TAIC samples locate in lower temperature. TGA showed that decomposition temperature of PLLA/NA/TAIC was higher and PLLA/NA/TAIC decomposed faster.

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