



Crystallization and Melting Behavior of Biodegradable Poly(L-lactic acid)/Talc Composites

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Abstract: Crystallization and melting behavior of Poly(L-lactic acid)(PLLA)/Talc composites with different talc content were investigated in detail. The addition of talc can increase the overall crystallization rate of PLLA, 5%talc makes the melt-crystallization peak temperature of PLLA increase from 96.28 °C to 105.22 °C, and the crystallization enthalpy increases from 1.379 J·g⁻¹ to 28.99 J·g⁻¹. The melting behavior of PLLA/5%talc composites at a different heating rate during non-isothermal crystallization at different cooling rate shows that heating rate can affect the melting behavior of PLLA, with increasing of heating rate, the double melting peak degenerates to single melting peak. Melting behavior after isothermal crystallization and after cold isothermal crystallization and hot isothermal crystallization indicates that the double-melting peak of PLLA/5%talc composites results from melting-recrystallization.

Key Words: Poly(L-lactic acid); Talc; Crystallization; Melting behavior; Composites.

Introduction

Poly(L-lactic acid)(PLLA) is the most important biodegradable polymers, and has been applied in more and more industry due to its lower energy consumption, biopolymer and non-toxic to the environment^[1-3]. However, there exist many weakness such as slow crystallization rate, low crystalline degree and poor heat resistance, etc. Talc is often chosen as nucleating agent of PLLA, it was shown that talc nucleates the crystallization of polymers through an epitaxial mechanism^[4]. The crystallization behavior and the morphology of poly (L-lactide-co-meso-lactide) and poly (L-lactide-co-meso-lactide)/Talc composites shows that strong increase in nucleation density with addition of talc was found in poly (L-lactide-co-meso-lactide)^[5]. And the overall crystallization rate of PLLA increased with increasing content of talc^[6]. The addition of talc not only affects the crystallization behavior of PLLA in a significant manner but also has a strong effect on melting behavior. Double melting peaks are often reported in PLLA non-isothermal crystallization process from the melt^[7]. And there exist two mechanism of forming of double melting peaks^[7], including the melt-recrystallization mechanism and the melting of two populations of lamellae.

As to PLLA/talc composites, the melting behavior of PLLA/talc composites little is reported by literature. In this paper, crystallization and melting behavior of biodegradable Poly(L-lactic acid)/talc composites with different talc content were investigated in detail, and the mechanism of forming of double melting peaks was discussed.

Experimental Section

Materials

Poly(L-lactic acid) (2002D) was purchased from Nature Works LLC, USA. The talc was purchased from shanghai yuejiang titanium chemical manufacturer co., LTD.

Preparation of PLLA/Talc Composites

Blending of PLLA and talc was performed on a counter-rotating mixer, and the preparation process of PLLA/talc composites has described in our previous paper^[8].

Characterization

Differential Scanning Calorimeter (DSC): The non-isothermal crystallization behavior of PLLA/talc composites 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 °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 behavior with different condition was measured by DSC Q2000 instrument.

Results and discussion

Non-Isothermal Crystallization of PLLA/Talc Composites

Figure 1 shows the DSC curves of non-isothermal crystallization from melt of PLLA/talc composites with different talc content. As seen in figure 1, upon cooling rate at 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 talc, crystallization peak appears in the DSC cooling curve. Compared to the neat PLLA, talc addition leads to the shift of crystallization peak to high temperature indicating the increase of crystallization temperature, and the crystallization peak shifts to higher temperature with increasing of talc content. On the other hand, crystallization peak for PLLA containing talc becomes much sharper in the cooling process, this result shows that talc can serve as a nucleating agent for the crystallization, and increase the overall crystallization rate of PLLA^[8]. Compared to the other talc content, 5% talc makes the crystallization rate become fastest. **As seen in Table 1**, compared to the neat PLLA, with the addition of 5%talc, the crystallization temperature(T_o) increases from 105.88 °C to 109.91 °C, melt-crystallization peak temperature(T_{mo}) increases from 96.28 °C to 105.22 °C, and the crystallization enthalpy(ΔH_c) increases from 1.379 J·g⁻¹ to 28.99 J·g⁻¹. However, there existed the most crystallization enthalpy of PLLA/talc composites with the addition of 3%talc.

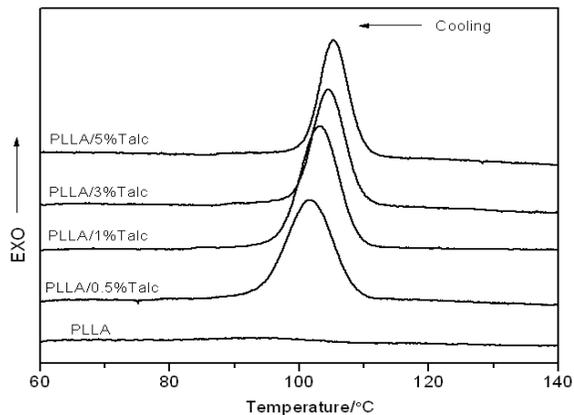


Figure 1. DSC curves of non-isothermal crystallization from melt of PLLA/Talc composites with different talc content.

Table 1. DSC data of PLLA/talc composites crystallized from melt at cooling of 1 °C/min.

Sample	$T_o/^\circ\text{C}$	$T_{m0}/^\circ\text{C}$	$\Delta H_c/\text{J}\cdot\text{g}^{-1}$
PLLA	105.88	96.28	1.379
PLLA/0.5%talc	108.56	101.85	28.52
PLLA/1%talc	108.90	103.24	28.68
PLLA/3%talc	109.67	104.56	29.54
PLLA/5%talc	109.91	105.22	28.99

Melting Behavior of PLLA/5% Talc at Different Heating Rate after Non-isothermal Crystallization at Different Cooling Rate

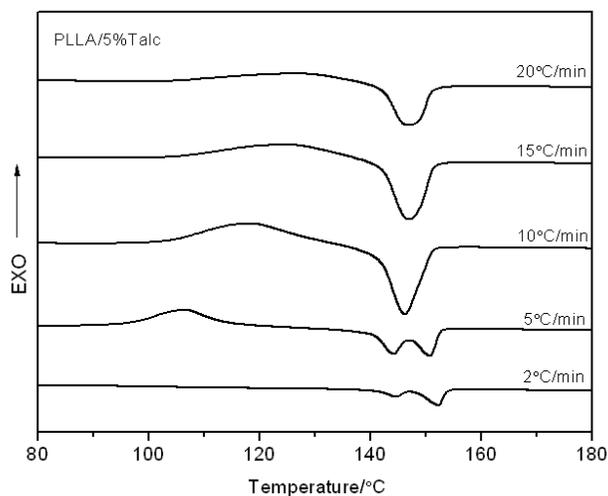


Figure 2. Melting behavior of PLLA/5%talc composites at a different heating rate during non-isothermal crystallization at different cooling rate.

Figure 2 shows the melting behavior of PLLA/5%talc composites at a different heating rate during non-isothermal crystallization at different cooling rate. With increasing of heating rate, the double melting peak degenerates to single melting peak. It is clear that the high-temperature melting peak of PLLA/5%talc composites shifts to low-temperature with increasing of heating rate, the reason is that the increasing of heating rate makes the crystallization of PLLA to be incomplete, and the prefect of spherulite becomes worse. However, the low-temperature melting peak shifts to high-temperature. Meantime, there exist obvious second crystallization process with increasing of heating rate, this is due to incomplete of crystallization of PLLA with increasing of heating rate. According to the other literature^[9], The double-melting behavior of PLLA assigns to melting-recrystallization, the low-temperature melting peak is attributed to the primary crystallites formed at T_c , and high-temperature melting peak reflect the relatively prefect lamella stacks resulted from recrystallization during the heating scan.

Melting Behavior at Different Heating Rate after Isothermal Crystallization for 1h at 10 °C

Figure 3 shows the DSC of PLLA/5%talc composites at different heating rate during isothermal crystallization for 1h 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. And the low-temperature melting peak of PLLA/5%talc composites does not shift with increasing of heating rate. However, the high-temperature melting peak shifts to low temperature with increasing of heating rate, the reason may be that the increasing of heating rate makes the degree of recrystallization of imperfect crystal decrease, which confirmed that double-melting peak of PLLA/5%talc composites result from melting-recrystallization.

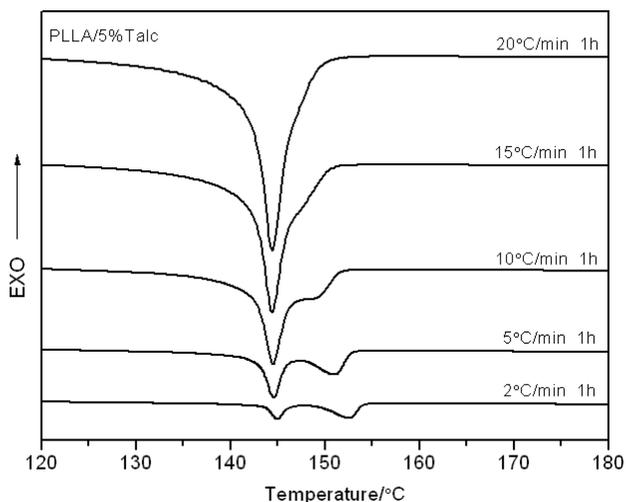


Figure 3. Melting behavior of PLLA/5%talc composites at different heating rate during isothermal crystallization for 1h at 100°C.

Melting Behavior of PLLA/5% Talc Composites after Cold Isothermal Crystallization and Hot Isothermal Crystallization

Figure 4 shows the melting behavior of PLLA/5%talc composites after cold isothermal crystallization and hot isothermal crystallization. As seen in Figure.4, the melting temperature of PLLA/5%talc increases with increasing of isothermal temperature, the reason

is that high crystallization temperature makes the crystal of PLLA/5%talc composites to be more perfect, and the spherulite is bigger. And the melting temperature of PLLA/5%talc through hot isothermal crystallization is higher than that through cold isothermal crystallization, which indicates that cold isothermal crystallization process can improve the crystallization of PLLA, but the perfect of spherulite become worse.

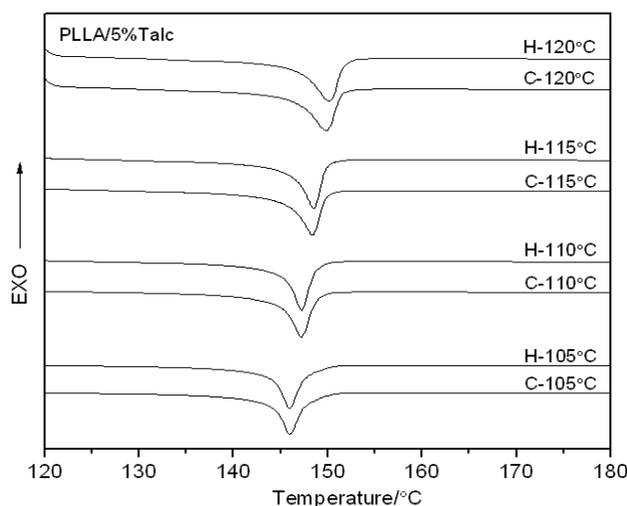


Figure 4. Melting behavior of PLLA/5%talc composites after cold isothermal crystallization and hot isothermal crystallization.

Conclusion

Crystallization and melting behavior of PLLA/Talc composites with different talc content were investigated in detail. The addition of 5%talc makes the melt-crystallization peak temperature of PLLA increase from 96.28°C to 105.22°C, and the crystallization enthalpy increases from 1.379 J•g⁻¹ to 28.99 J•g⁻¹. The melting behavior of PLLA/5%talc composites shows that heating rate can affect the melting behavior of PLLA, with increasing of heating rate, the double melting peak degenerates to single melting peak. And the double-melting peak of PLLA/5%talc composites results from melting-recrystallization.

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