

Reorganization behavior in low crystallinity poly(hydroxybutyrate-co-hydroxyhexanoate)

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Introduction

Structure and properties of PHAs

Polyhydroxyalkanoates (PHAs) are a class of biodegradable polymers which can be produced via bacterial synthesis. They have garnered interest due to their potential as a biodegradable alternative to petroleum-based plastics (Doi, *et al.* 1995). PHA molecules have been shown to have a helical morphology, which organize into spherulitic crystal structures. The most common, naturally occurring PHA, poly(3-hydroxybutyrate) (PHB), typically has a crystallinity of up to 75-85% in its homopolymer form (Xu *et al.* 2002). The resulting material is thus brittle and has a narrow processing window (Hu, *et al.* 2007). However, a broad range of mechanical properties has been achieved with the inclusion of varying quantities of 3-hydroxyhexanoate (HHx) units to form the polymer P(HB-*co*-HHx). Since the bulky propyl side-chains of the HHx unit disrupt packing of the helical chains, both average crystal size and overall crystalline content is reduced with increasing HHx content (Doi, *et al.* 1995). This results in lower melting points as well as an increased number and complexity of endothermic events between the crystallization and melting temperature.

Temperature-dependent FTIR studies of PHB-HHx

While FTIR spectra are sensitive to the conformational changes which occur around a phase change, the position of the peaks is affected by the temperature at which the measurement is taken. Thus, samples should ideally be measured at a constant temperature. However, P(HB-*co*-HHx) also exhibits crystallization when rapidly cooled to room temperature following partial melting (Figure 1). This rapid onset of crystallization is partially mitigated by the use of more HHx-rich material, which sterically disrupts the formation of crystals. In order to further reduce these secondary effects, however, the material was quenched to 0°C and allowed to equilibrate at room temperature.

Methods

Differential scanning calorimetry

P(HB-*co*-HHX) containing 20% hexanoate was allowed to crystallize at room temperature for seven days and serially heated at 10°C/min to final temperatures (T_f) 40-160°C. After equilibrating at T_f for ten minutes, the material was quenched at 0°C. Heat flow for each trial was normalized to the trace of completely amorphous material ($T_f = 160^\circ\text{C}$).

Fourier transform infrared spectroscopy

P(HB-co-HHX) containing 20% hexanoate was serially heated to $T_f = 40\text{-}140^\circ\text{C}$ for 10 minutes within a furnace and quenched in liquid nitrogen. The material was allowed to equilibrate at room temperature before the spectra was taken. Relative amorphous and crystalline content was calculated using using the relative area under the carbonyl peak (Xu *et al.* 2002). For fully amorphous material, the carbonyl peak occurs at 1740 cm^{-1} , while crystalline material includes an additional mode at 1720 cm^{-1} (Figure 2a). In order to estimate relative crystallinity, the peak from fully amorphous material was scaled to fit under the carbonyl peak for each spectra and subtracted from the area under the peak (Figure 2b).

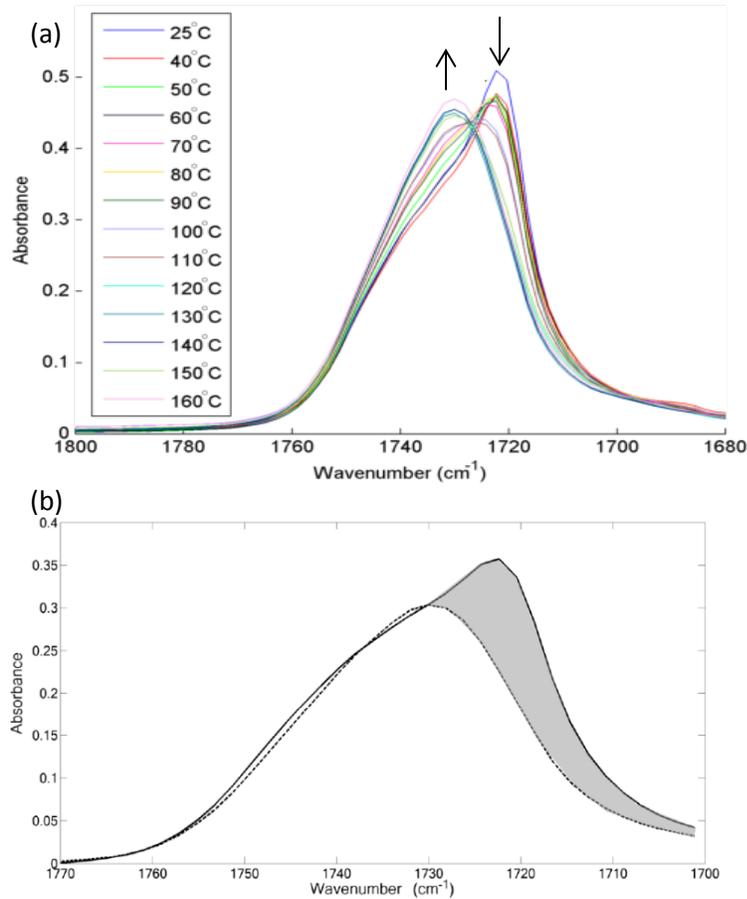
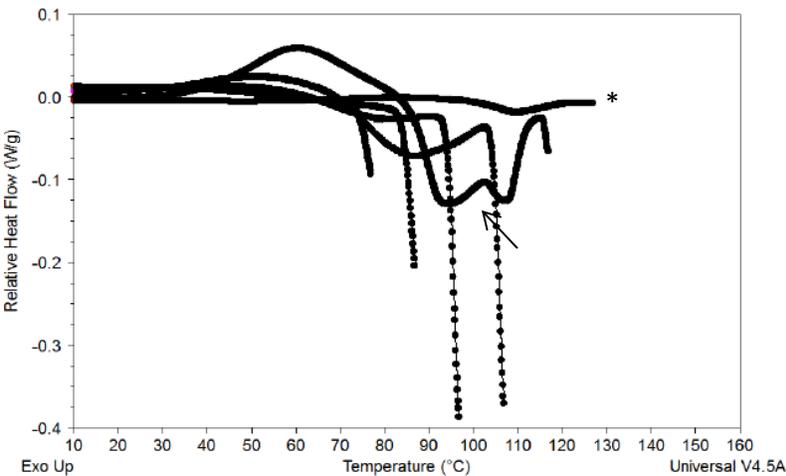
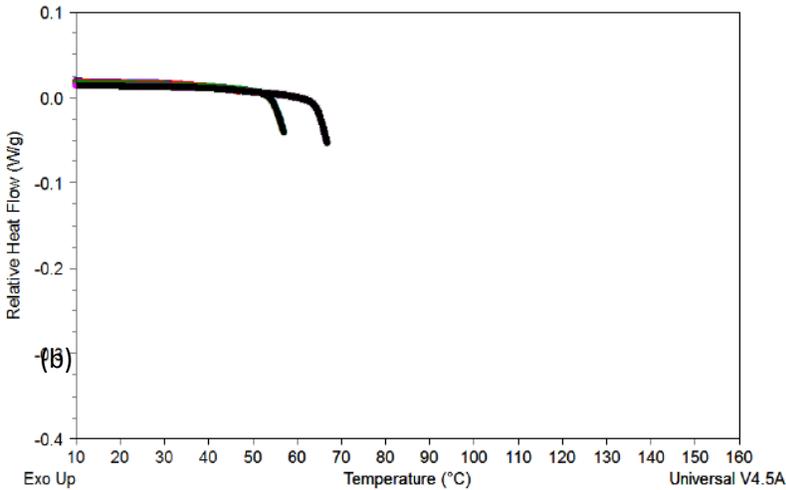


Figure 2: (a) Carbonyl peak for 20% HHx material. Arrows indicate how peak intensity changes with increasing temperature. Intensity at 1723 cm^{-1} can be seen with increasing temperature, which is used as an analog for decreasing crystalline content. (b) In order to approximate relative crystalline and amorphous content, the fully amorphous carbonyl peak ($T_f = 160^\circ\text{C}$) was scaled to fit under each peak and its area was approximate amorphous content, while the remaining area (shaded) was used to represent relative crystalline

Results and discussion

Phases of melting and recrystallization

Figure 3 highlights three primary regimes of crystallization and reorganizational behaviour within P(HB-co-HHX). In phase I (a), partial melting of secondary crystals (which form at room temperature during aging) can be observed, but minimal in-ramp crystallization (IRC) is seen. In phase II (b), both partial melting and IRC is shown to increase as T_f increases, until $T_f = 120^\circ\text{C}$ (indicated by a star), where endothermic activity appears to decrease during the ramping. On the subsequent heating, the material enters phase III (c), in which minimal (if any) melting occurs around 100°C , suggesting little presence of crystalline material. The trace after heating to 160°C is taken as representative of fully amorphous material.



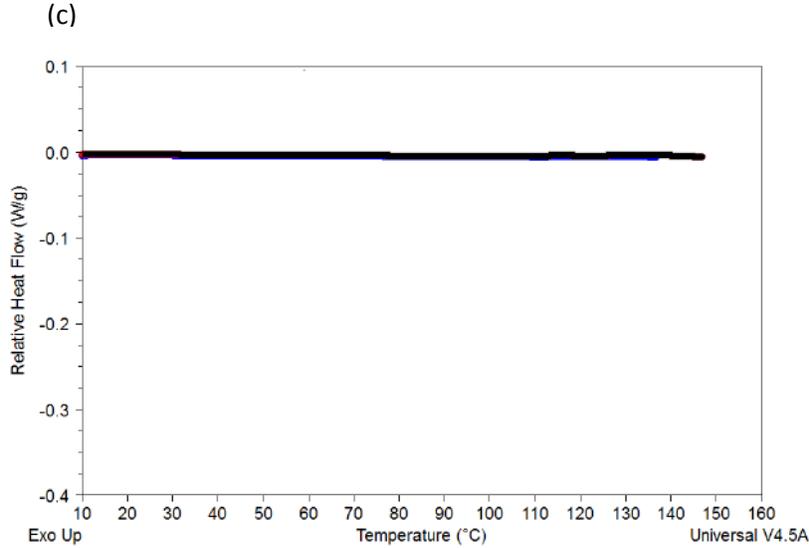


Figure 3: DSC traces of 20% P(HB-*co*-HHx) serially heated to $T_f = 40$ -160°C. (a) Partial melting of material crystallized at room temperature is observed with minimal IRC. (b) IRC increases with T_f , reaching a maximum at $T_f = 110^\circ\text{C}$, where the material can be seen undergoing two overlapping thermal events from 90-110°C, indicated by the arrow. At $T_f = 120^\circ\text{C}$ (star), both IRC and melting around 100°C are dramatically decreased, indicated. (c), in Minimal IRC and melting around 100°C, suggesting mostly amorphous material.

FTIR shows changes in relative amorphous and crystalline content

Figure 4 shows the ratio of amorphous to crystalline materials approximated by the carbonyl peak in the FTIR spectra.

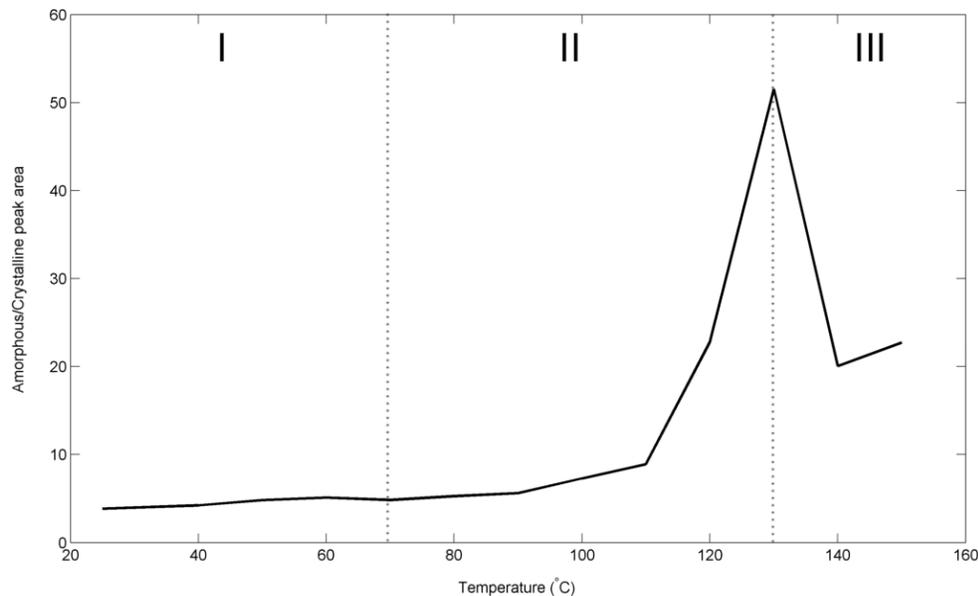


Figure 4: Peak area ratios between amorphous and crystalline peaks. For $T_f < 110^\circ\text{C}$, the peak area ratios remain relatively stable, suggesting limited melting of new material despite strong endothermic activity in the DSC.

These data suggest that P(HB-co-HHX) exhibits both melting in crystalline structure and changes in crystal perfection during heating. The melting observed in phase I is hypothesized to be material produced through secondary (room temperature) crystallization which produces crystals with a greater degree of defects, and thus, melt at a lower temperature. This results in an accumulation of amorphous material within the microstructure. During phase II, partially melted primary crystals may serve of nucleation sites for crystallization of the amorphous material formed during phase I. This is supported by observed increases in IRC as well as increases in melting temperatures after each heating cycle, suggesting that both the quantity of crystals and the degree of crystal perfection is increasing. However, despite strong endothermic activity between 80°C and 110°C , FTIR spectra do not suggest significant increases in the ratio of amorphous to crystalline material. In addition, when material is heated to 120°C , DSC traces (Figure 3b) appear to suggest two distinct, but overlapping thermal events that occur between 90 - 110°C . This suggests that one of these events may not be associated with the melting of crystalline material, but rather the some form of recovery in which secondary crystalline lamellae are reorganized and incorporated into the primary lamellae in the helical structure. When primary crystals are allowed to melt fully or near-fully at $T_f = 130^\circ\text{C}$, subsequent crystallization is significantly obstructed due to the lack of nucleation sites to promote growth in the amorphous material.

References

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