

Thermal Analyses of Poly(3-hydroxybutyrate), Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), and Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

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ABSTRACT: Thermal analyses of poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(HB–HV)], and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(HB–HHx)] were made with thermogravimetry and differential scanning calorimetry (DSC). In the thermal degradation of PHB, the onset of weight loss occurred at the temperature (°C) given by $T_o = 0.75B + 311$, where B represents the heating rate (°C/min). The temperature at which the weight-loss rate was at a maximum was $T_p = 0.91B + 320$, and the temperature at which degradation was completed was $T_f = 1.00B + 325$. In the thermal degradation of P(HB–HV) (70:30), $T_o = 0.96B + 308$, $T_p = 0.99B + 320$, and $T_f = 1.09B + 325$. In the thermal degradation of P(HB–HHx) (85:15), $T_o = 1.11B + 305$, $T_p = 1.10B + 319$, and $T_f = 1.16B + 325$. The derivative thermogravimetry curves of PHB, P(HB–HV), and P(HB–HHx) confirmed only one weight-loss step change. The incorporation of 30 mol % 3-hydroxyvalerate (HV) and 15 mol % 3-hydroxyhexanoate (HHx) components into the polyester increased the various thermal temperatures T_o , T_p , and T_f relative to those of PHB by 3–12°C (measured at $B = 40$ °C/min). DSC measurements showed that the incorporation of HV and HHx decreased the melting temperature relative to that of PHB by 70°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 90–98, 2001

Key words: thermal analysis; poly(3-hydroxybutyrate); poly(3-hydroxybutyrate-co-3-hydroxyvalerate); poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); thermogravimetry

INTRODUCTION

Polyhydroxyalkanoates are natural polyesters produced by microorganisms as carbon and en-

ergy reserves. Their macroscopic properties are controlled by their chemical structure and composition.^{1–4} Poly(3-hydroxybutyrate) {[–COCH₂CH(CH₃)O–]_n; PHB}, and the random copolymers, such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) {[–COCH₂CH(CH₃)O–]_x[–COCH₂CH(CH₂CH₃)O–]_y; P(HB–HV)} and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) {[–COCH₂CH(CH₃)O–]_x[–COCH₂CH(CH₂CH₂CH₃)O–]_y; P(HB–HHx)}, are optically active, stereoregular polyesters. These polymers possess the physical properties and processability of conventional thermoplastics and yet are fully biodegradable

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when disposed of in a microbially active environment.^{5,6} They have applications in drug-delivery vehicles, orthopedic biomaterials, and surgical dressings.

In recent years, much effort has been spent optimizing the PHB bioproduction process and the blending of PHB and other polymers to reduce costs and improve the physical and mechanical properties of the product.^{7–15} PHB is a relatively stiff and brittle material because of its high crystallinity. Its melting point is about 180°C.^{3,16} On the other hand, the properties of P(HB–HV) and P(HB–HHx), including melting point, mechanical strength, and biodegradability, vary widely and depend on the molar percentage of 3-hydroxyvalerate (HV) or 3-hydroxyhexanoate (HHx) in the copolymer.^{17–23}

In this study, the thermal degradation of PHB, P(HB–HV) and P(HB–HHx) were investigated with dynamic thermogravimetry (TG). The effects of the heating rate (B) on the degradation temperature (T) and the effects of HV and HHx incorporation on the thermal properties of PHB were considered.

EXPERIMENTAL

Materials

Biosynthesized PHB and P(HB–HV) were obtained from Fluka (product numbers 81329 and 27819, respectively). P(HB–HHx) were biosynthesized at Tsinghua University in Beijing, China with bacterial strain *Pseudomonas stutzeri* 1317 in a glucose mineral-salt medium.²⁴ P(HB–HV) (70:30) stands for the statistically random copolymer with a molar ratio of HB:HV of 70:30, and P(HB–HHx) (85:15) stands for HB:HHx = 85:15. The weight-average molecular weight (M_w) of PHB and of P(HB–HV) were 400–700 kDa, according to the supplier. The exact M_w depended on the lot number. The M_w of P(HB–HHx) was about 750 kDa.

Measurements and Equipment

TG analyses were carried out with a PerkinElmer TG7 TG analyzer. The mass of each specimen was 5–6 mg, and the reaction environment was flowing nitrogen (45 mL/min). B ranged from 10 to 50°C/min. TG and derivative thermogravimetry (DTG) curves were recorded in the course of heating from room temperature to 500°C.

Glass-transition temperature (T_g) and melting temperature (T_m) were measured by a Mettler Toledo DSC30 differential scanning calorimeter under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Thermal Degradation of PHB

Figures 1 and 2 show the TG and DTG curves from the thermal degradation of PHB at five different values of B . The TG curve is a smooth weight-loss curve. The DTG curve shows only a single rate of weight loss (dW/dt) peak. This indicates that the degradation consisted of one weight-loss step. With increases in B , the TG and DTG curves shift toward the high-temperature zone. The degradation behavior at all five B values was similar.

Figure 3 shows the effect of B on T . T_o is the temperature at the onset of weight loss. T_p is the temperature at the maximum dW/dt , the tip of the DTG curve peak, and T_f is the temperature at complete degradation. T_o and T_f were obtained from the TG curve with a bitangent method. The peak width of the DTG curve can be expressed as $T_f - T_o$.

It can be seen from Figure 3 that T increased with B , indicating that B was the main factor affecting T . These factors were related as follows:

$$T_o = 0.75B + 311$$

$$T_p = 0.91B + 320$$

$$T_f = 1.00B + 325$$

The thermal degradation temperature could be expressed more exactly as an equilibrium degradation temperature $T(0)$ when B approached zero: $T_o(0) = 311^\circ\text{C}$, $T_p(0) = 320^\circ\text{C}$, $T_f(0) = 325^\circ\text{C}$. The peak width $T_f - T_o = 0.25B + 14$ and increased with B .

Thermal Degradation of P(HB–HV) (70:30)

Figures 4 and 5 show the TG and DTG curves for the thermal degradation of P(HB–HV) (70:30) at five different values of B . Like that of PHB, the DTG curve of P(HB–HV) (70:30) consists of one peak.

Figure 6 illustrates that the thermal degradation temperature increased linearly with B . The equations are as follows:

$$T_o = 0.96B + 308$$

$$T_p = 0.99B + 320$$

$$T_f = 1.09B + 325$$

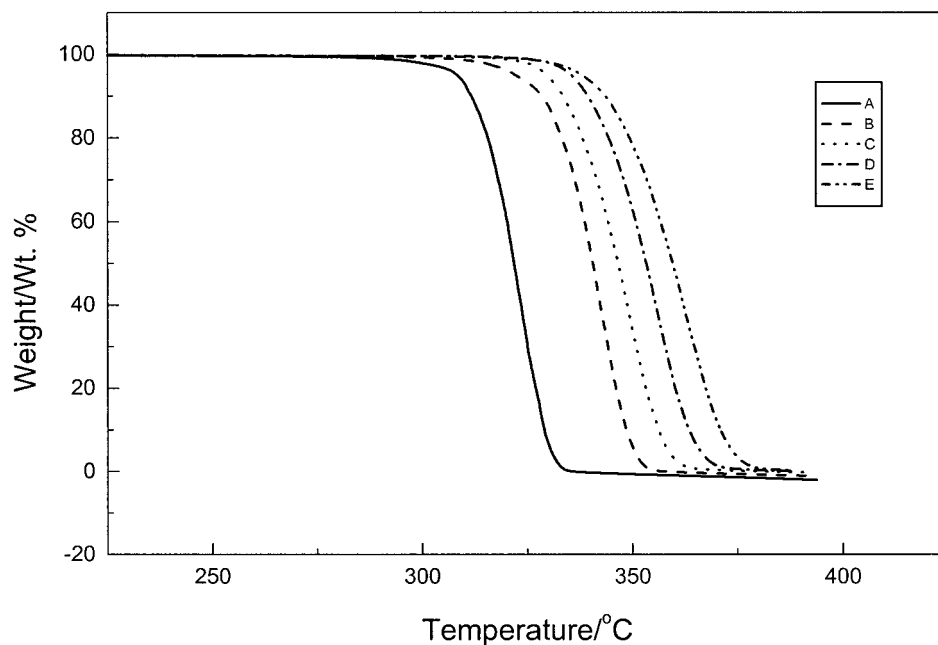


Figure 1 TG curves of PHB thermal degradation: (A) $B = 10^{\circ}\text{C}$, (B) $B = 20^{\circ}\text{C}$, (C) $B = 30^{\circ}\text{C}$, (D) $B = 40^{\circ}\text{C}$, and (E) $B = 50^{\circ}\text{C}$. The weight is expressed on the vertical axis as a percentage of the initial weight (wt %). The temperature ($^{\circ}\text{C}$) is expressed on the horizontal axis.

The equilibrium thermal degradation temperatures were $T_o(0) = 308^{\circ}\text{C}$, $T_p(0) = 320^{\circ}\text{C}$, and $T_f(0) = 325^{\circ}\text{C}$, respectively. The peak width could be expressed as $T_f - T_o = 0.13B + 17$, which increased with B .

Thermal Degradation of P(HB-HHx) (85:15)

Figures 7 and 8 show the TG and DTG curves for the thermal degradation of P(HB-HHx) (85:15) at five different values of B . Like that of PHB and

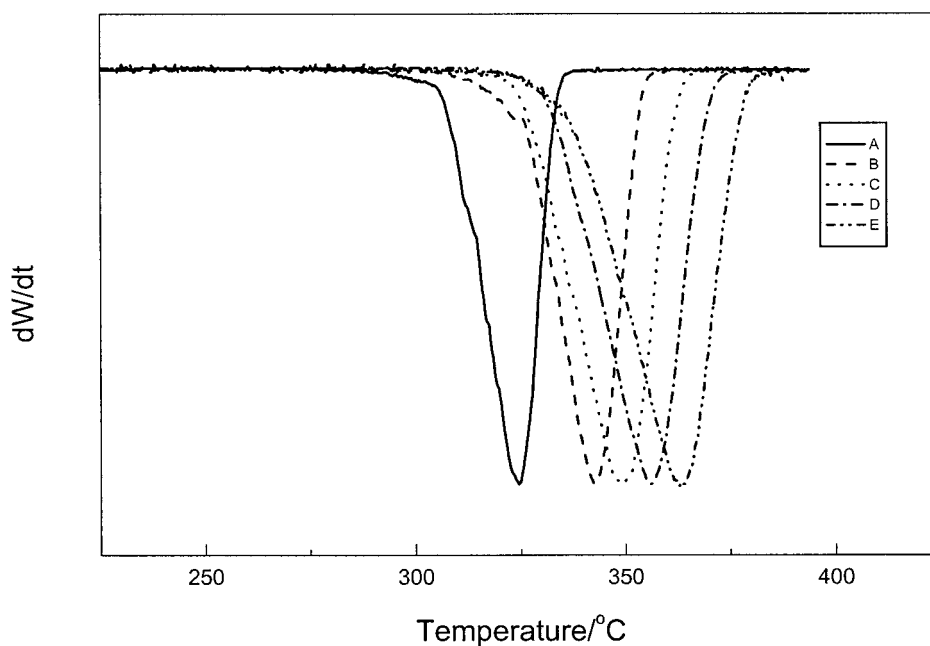


Figure 2 DTG curves of PHB thermal degradation: (A) $B = 10^{\circ}\text{C}$, (B) $B = 20^{\circ}\text{C}$, (C) $B = 30^{\circ}\text{C}$, (D) $B = 40^{\circ}\text{C}$, and (E) $B = 50^{\circ}\text{C}$. dW/dt is shown on the vertical axis. The temperature ($^{\circ}\text{C}$) is expressed on the horizontal axis.

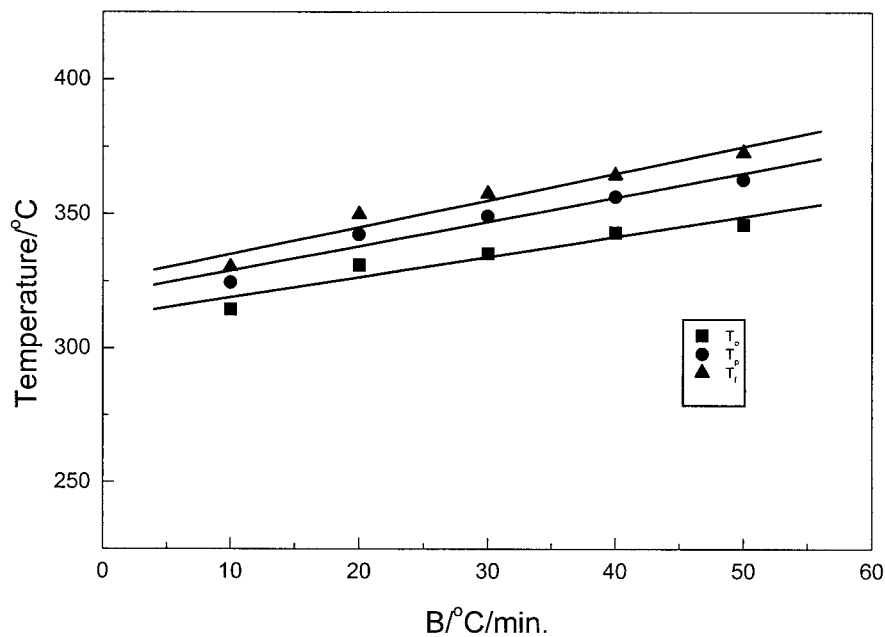


Figure 3 Relation of thermal degradation temperatures and B for PHB degradation.

P(HB-HV), the DTG curve of P(HB-HHX) (85:15) consists of only one peak.

Figure 9 illustrates that the thermal degradation temperature increased linearly with B . The equations are as follows:

$$T_o = 1.11B + 305$$

$$T_p = 1.10B + 319$$

$$T_f = 1.16B + 325$$

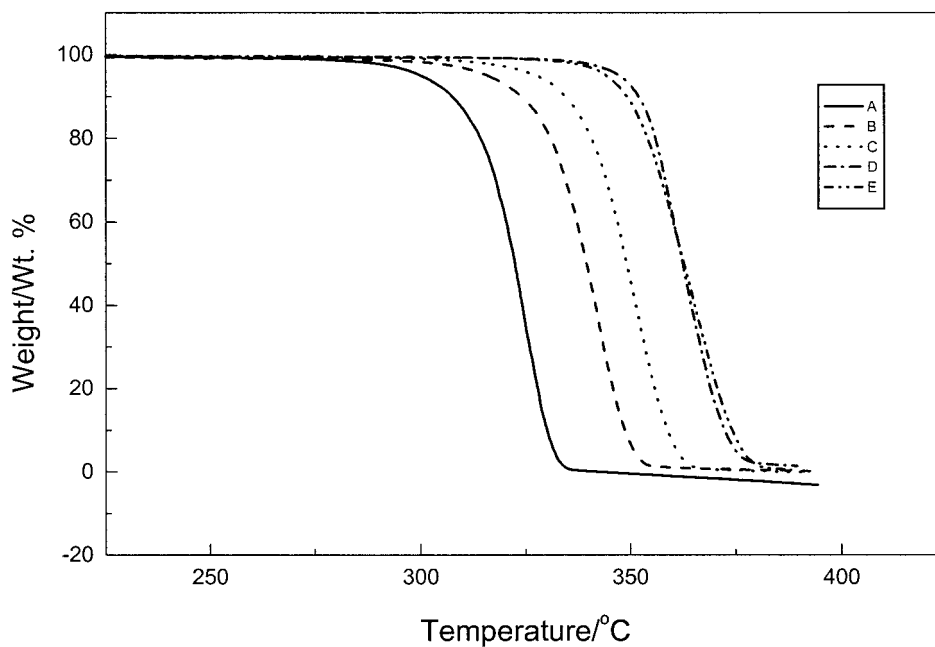


Figure 4 TG curves of P(HB-HV) (70:30) thermal degradation: (A) $B = 10^\circ\text{C}$, (B) $B = 20^\circ\text{C}$, (C) $B = 30^\circ\text{C}$, (D) $B = 40^\circ\text{C}$, and (E) $B = 50^\circ\text{C}$. The weight is expressed on the vertical axis as a percentage of the initial weight (wt %). The temperature ($^\circ\text{C}$) is expressed on the horizontal axis.

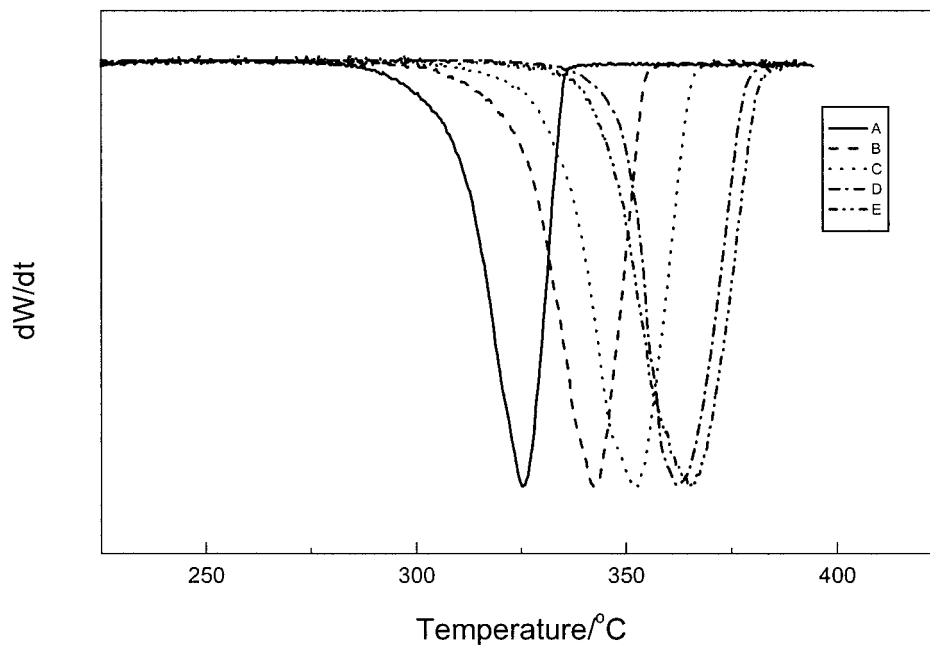


Figure 5 DTG curves of P(HB-HV) (70:30) thermal degradation: (A) $B = 10^\circ\text{C}$, (B) $B = 20^\circ\text{C}$, (C) $B = 30^\circ\text{C}$, (D) $B = 40^\circ\text{C}$, and (E) $B = 50^\circ\text{C}$. dW/dt is shown on the vertical axis. The temperature ($^\circ\text{C}$) is expressed on the horizontal axis.

The equilibrium thermal degradation temperatures were $T_o(0) = 305^\circ\text{C}$, $T_p(0) = 319^\circ\text{C}$, and $T_f(0) = 325^\circ\text{C}$, respectively. The peak width could be expressed as $T_f - T_o = 0.05B + 20$, which increased with B .

Effects of HV and HHx Incorporation on the Thermal Properties of PHB

Figures 10 and 11 show the TG and DTG curves of PHB, P(HB-HV) (70:30), and P(HB-HHx) (85:15)

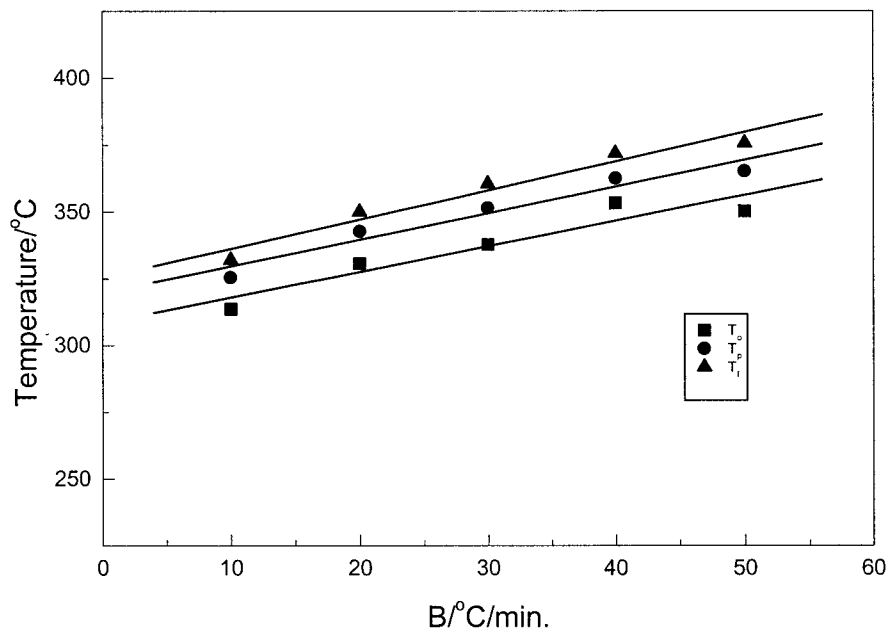


Figure 6 Relation of thermal degradation temperatures and B for P(HB-HV) (70:30) thermal degradation.

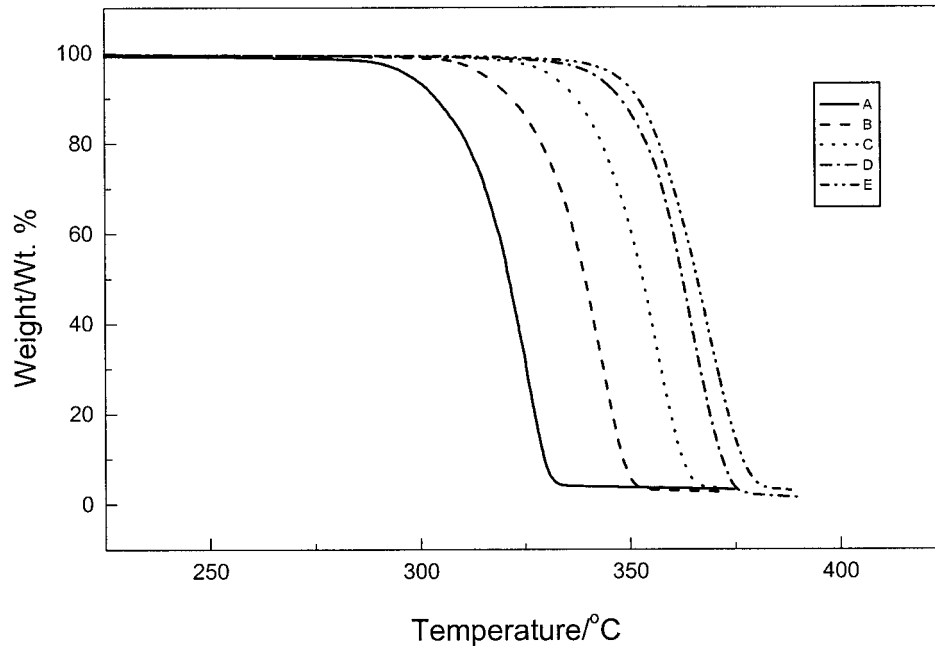


Figure 7 TG curves of P(HB-HHX) (85:15) thermal degradation: (A) $B = 10^\circ\text{C}$, (B) $B = 20^\circ\text{C}$, (C) $B = 30^\circ\text{C}$, (D) $B = 40^\circ\text{C}$, and (E) $B = 50^\circ\text{C}$. The weight is expressed on the vertical axis as a percentage of the initial weight (wt %). The temperature ($^\circ\text{C}$) is expressed on the horizontal axis.

at $B = 40^\circ\text{C}/\text{min}$. Table I lists the thermal degradation temperatures T_o , T_p , and T_f for the three polyesters. The molecular weights of the polymers

were of the same order of magnitude. Therefore, it is obvious from the figures and Table I that the thermal stability of the polyesters increased with

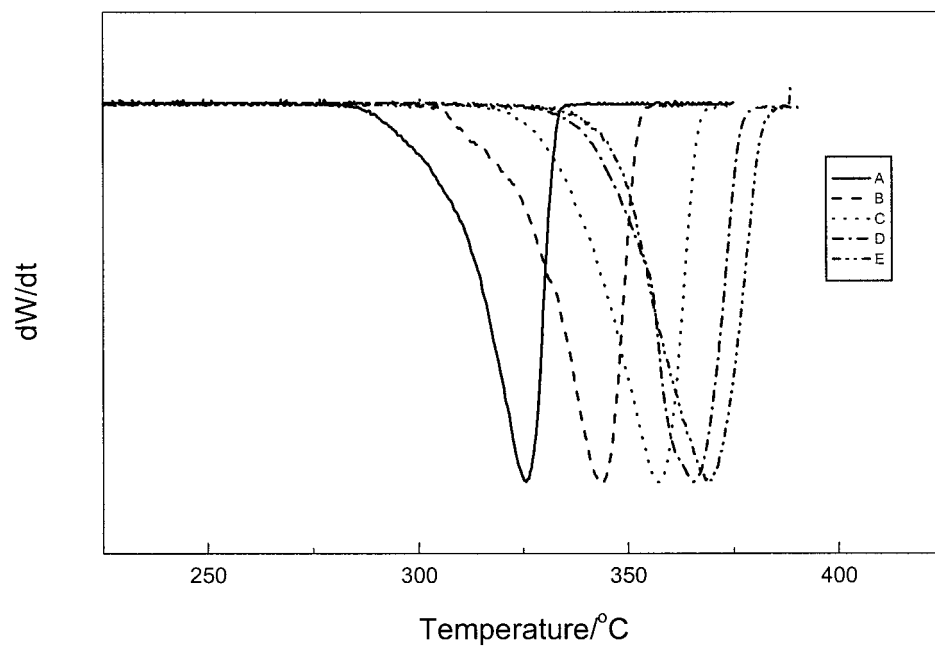


Figure 8 DTG curves of P(HB-HHX) (85:15) thermal degradation: (A) $B = 10^\circ\text{C}$, (B) $B = 20^\circ\text{C}$, (C) $B = 30^\circ\text{C}$, (D) $B = 40^\circ\text{C}$, and (E) $B = 50^\circ\text{C}$. dW/dt is shown on the vertical axis. The temperature ($^\circ\text{C}$) is expressed on the horizontal axis.

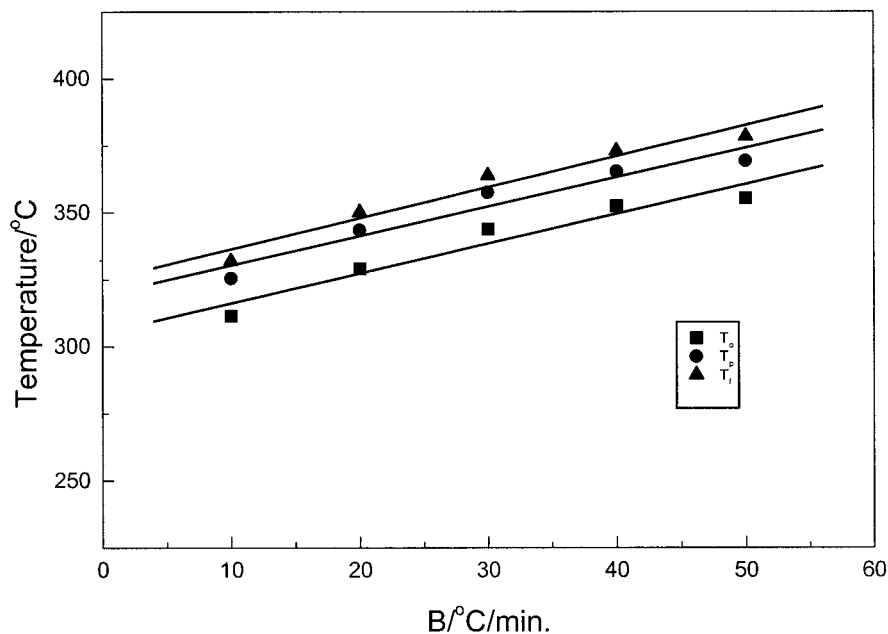


Figure 9 Relation of thermal degradation temperatures and B for P(HB-HHx) (85:15) thermal degradation.

increasing number of structural carbon units in the polymers. Table II lists T_g and T_m for the three polyesters. It is obvious from Table II that P(HB-HV) and P(HB-HHx) had a lower T_g and

T_m than PHB. Furthermore, the literature shows that P(HB-HV) has a lower degree of crystallinity and a lower T_m ^{3,16,21} but only a slightly lower mechanical strength than PHB. It is also known

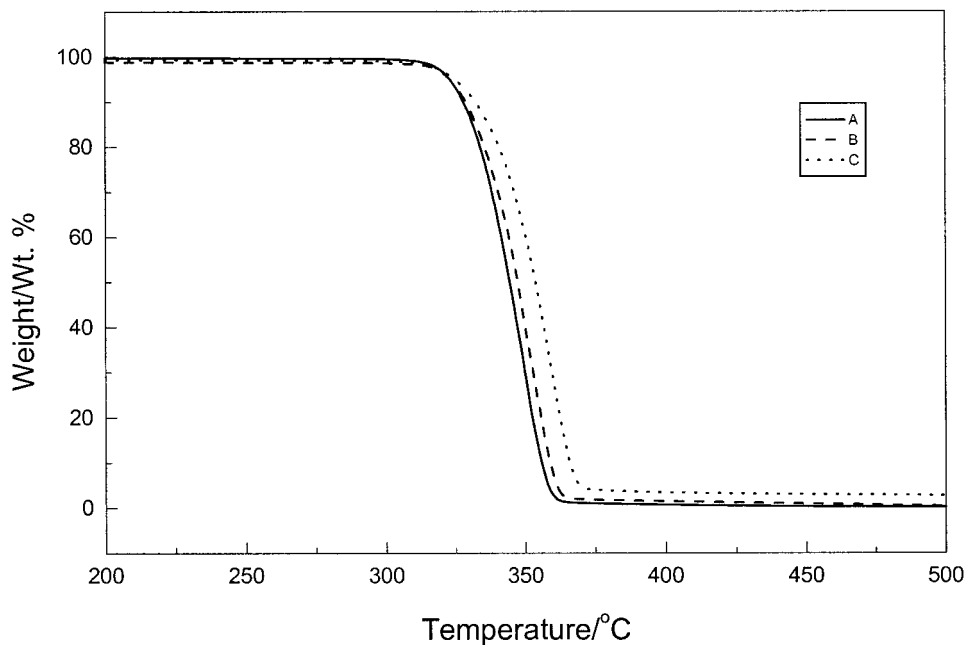


Figure 10 TG curves of (A) PHB, (B) P(HB-HV), and (C) thermal degradation at 40°C/min: (A) PHB, (B) P(HB-HV), and (C) P(HB-HHx). The weight is expressed on the vertical axis as a percentage of the initial weight (wt %). The temperature (°C) is expressed on the horizontal axis.

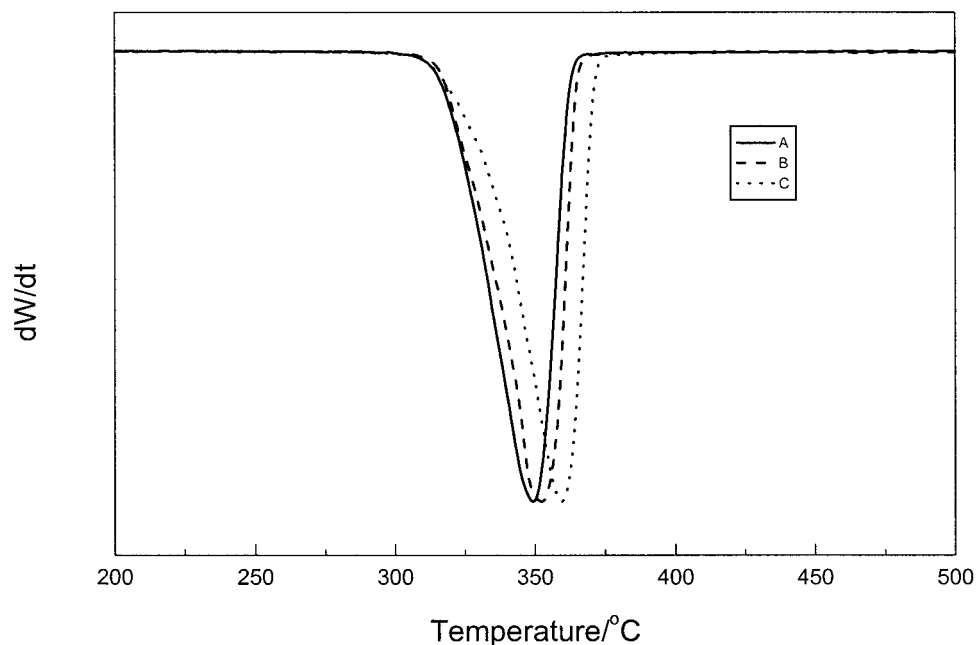


Figure 11 DTG curves of (A) PHB, (B) P(HB–HV), and (C) P(HB–HHx) thermal degradation at 40°C/min: (A) PHB, (B) P(HB–HV), and (C) P(HB–HHx). dW/dt is shown on the vertical axis. The temperature (°C) is expressed on the horizontal axis.

from the literature that the homopolymer PHB is thermally unstable at temperatures just slightly above a melting point of about 180°C. It has been reported that a PHB sample stored at 190°C for 1 h degraded to half its original molecular weight.²⁵ It is unfavorable for the processing of polymers when T_m and T_p are very close. PHB is limited to a narrow melt-process window of short residence times, and stabilizers have had little effect.²⁶ Incorporating HV units in 10–50 mol % reduces the melting point to 150–100°C, respectively.³ This study showed that the copolymers have higher thermal degradation temperatures relative to PHB at any given nonzero B . Extrapolating back to zero B allows us to calculate the peak width at zero B , $T_f(0) - T_o(0)$, which gives us an index of how thermally stable the polymers are. The peak widths at zero B for PHB, P(HB–

HV), and P(HB–HHx) were 14, 17, and 20°C, respectively. It was clear that the copolymers degraded slower than the homopolymer.

CONCLUSIONS

The weight loss of PHB, P(HB–HV), and P(HB–HHx) caused by thermal degradation was a one-step process. The thermal degradation temperatures of the polymers increased with increasing B . The peak width of the DTG curves increased with B . The peak widths at zero B , $T_f(0) - T_o(0)$, for PHB, P(HB–HV), and P(HB–HHx) were 14, 17,

Table I Thermal Degradation Temperatures of PHB, P(HB–HV), and P(HB–HHx) at a B of 40°C/min

	PHB	P(HB–HV) (70 : 30)	P(HB–HHx) (85 : 15)
T_o (°C)	331	334	339
T_p (°C)	349	352	359
T_t (°C)	358	364	369

Table II T_g and T_m of PHB, P(HB–HV), and P(HB–HHx)

	PHB	P(HB–HV) (70 : 30)	P(HB–HHx) (85 : 15)
T_g (°C)	5.73	2.11	3.22
T_m (°C)	179	111	109

T_g : the samples (30 mg) were heated from room temperature to 200°C at a 20°C/min under N_2 gas flow; after 2 min, the melted samples were rapidly cooled to –50°C by liquid N_2 , and then the frozen samples were heated at a constant scanning rate of 10°C/min under a N_2 purge. T_m : the samples (10 mg) were heated from room temperature to 200°C at a constant scanning rate of 10°C/min under N_2 atmosphere.

and 20°C, respectively. The incorporation of HV and HHx into the homopolymer rendered the polymer chain more flexible, as indicated by the decrease in T_g and T_m ; therefore, P(HB–HV) and P(HB–HHx) were more thermally stable than PHB.

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