

Thermogravimetric Analysis of Poly(3-hydroxybutyrate) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

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ABSTRACT: The thermal degradation of poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(HB-HV)] was studied using thermogravimetry (TG). In the thermal degradation of PHB, the temperature at the onset of weight loss (T_o) was derived by $T_o = 0.97B + 259$, where B represents the heating rate ($^{\circ}\text{C}/\text{min}$). The temperature at which the weight loss rate was maximum (T_p) was $T_p = 1.07B + 273$, and the final temperature (T_f) at which degradation was completed was $T_f = 1.10B + 280$. The percentage of the weight loss at temperature T_p (C_p) was $69 \pm 1\%$ whereas the percentage of the weight loss at temperature T_f (C_f) was $96 \pm 1\%$. In the thermal degradation of P(HB-HV) (7:3), $T_o = 0.98B + 262$, $T_p = 1.00B + 278$, and $T_f = 1.12B + 285$. The values of C_p and C_f were 62 ± 7 and $93 \pm 1\%$, respectively. The derivative thermogravimetric (DTG) curves of PHB confirmed only one weight loss step change because the polymer mainly consisted of the HB monomer only. The DTG curves of P(HB-HV), however, suggested multiple weight loss step changes; this was probably due to the different evaporation rates of the two monomers. The incorporation of 10 and 30 mol % of the HV component into the polyester increased the various thermal temperatures (T_o , T_p , and T_f) by 7–12 $^{\circ}\text{C}$ (measured at $B = 20^{\circ}\text{C}/\text{min}$). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2237–2244, 2001

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

INTRODUCTION

Polyhydroxyalkanoates (PHAs) are natural polyesters produced by microorganisms as carbon and energy reserves. Various PHAs can be produced, depending on the bacterial strain and

the cultivation conditions. The macroscopic properties of PHAs are controlled by the chemical structure and composition.^{1–4} Poly(3-hydroxybutyrate) {PHB; $[-\text{COCH}_2\text{CH}(\text{CH}_3)\text{O}-]_n$ } and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(HB-HV)] random copolymer $\{[-\text{COCH}_2\text{CH}(\text{CH}_3)\text{O}-]_x[-\text{COCH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{O}-]_y\}$, which belong to the PHA family, are optically active, stereoregular polyesters. These polymers possess the physical properties and processability of conventional thermoplastics yet are fully biodegradable when disposed of in a microbially active environment.^{5,6} They are found in an increasing number of applications in packaging and waste management.

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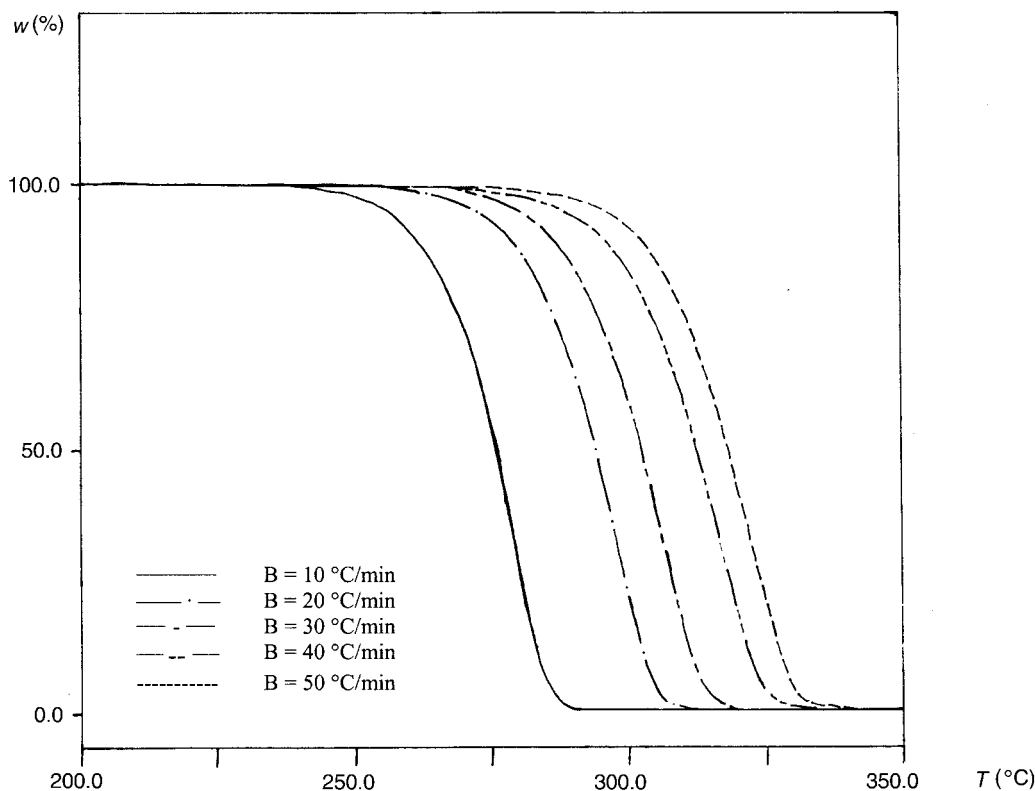


Figure 1 The TG curves of PHB thermal degradation. The weight (w) is expressed on the vertical axis as a percentage of the initial weight. The temperature is expressed on the horizontal axis ($^{\circ}\text{C}$).

In recent years, much effort has been spent on optimizing the PHB bioproduction process and blending of PHB and other polymers to reduce costs and to 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), including the melting point, mechanical strength, and biodegradability, vary widely and depend on the mole percent of HV in the copolymer.¹⁷⁻²³

In this work, the thermal degradations of PHB and P(HB-HV) were investigated using dynamic thermogravimetry (TG). The effects of the heating rate (B) on the degradation temperature (T) and weight loss percentage (C) and the effects of HV incorporation on the thermal degradation of PHB were considered.

EXPERIMENTAL

Biosynthesized PHB and P(HB-HV) were obtained from Fluka (Sigma-Aldrich). P(HB-HV) (9

: 1) stands for the statistically random copolymer with a HB:HV molar ratio of 9 : 1, and P(HB-HV) (7 : 3) stands for a HB:HV of 7 : 3. The TG analyses were carried out with a Perkin-Elmer TG7 TG analyzer. The mass of each specimen was 5–6 mg, and the reaction environment was flowing nitrogen (45 mL/min). The heating rate ranged from 10 to $50^{\circ}\text{C}/\text{min}$. TG and derivative TG (DTG) curves were recorded in the course of heating from room temperature to 400°C .²⁴

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 heating rates B . The TG curve was a smooth weight loss curve. The DTG curve showed only a single rate of weight loss (dw/dt) peak. This indicated that the degradation consisted of one weight loss step. This was not surprising because the polymer was made up of HB monomers only.

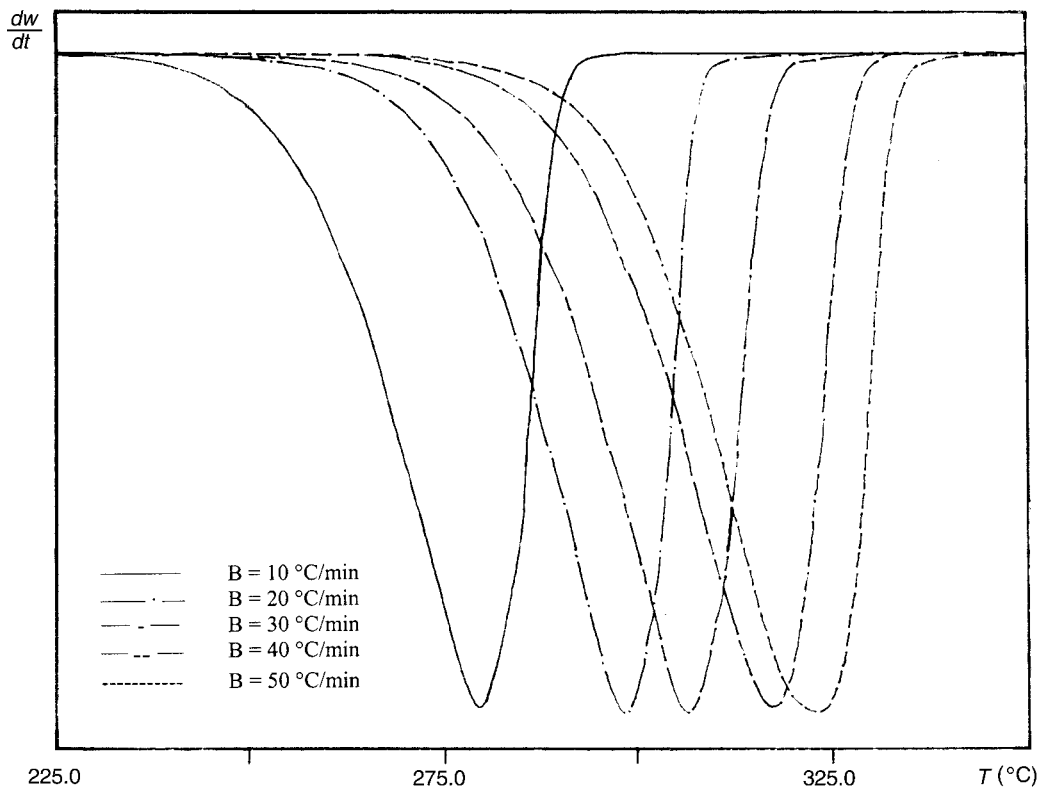


Figure 2 The DTG curves of PHB thermal degradation. The rate of change in the weight (dw/dt) or the weight loss rate is shown on the vertical axis. The temperature is expressed on the horizontal axis ($^{\circ}\text{C}$).

With increases in the heating rate, the TG and DTG curves shifted toward the high-temperature zone. The degradation behavior at all five heating rates was similar.

Figure 3 shows the effect of the heating rate B on the degradation temperature T . The temperature at the onset of weight loss (T_o) and the temperature of complete degradation (T_f) were obtained from the TG curve using a bitangent

method. The temperature at the maximum rate of weight loss (T_p), the tip of the DTG curve peak, is shown. The peak width of the DTG curve can be expressed as $T_f - T_o$.

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

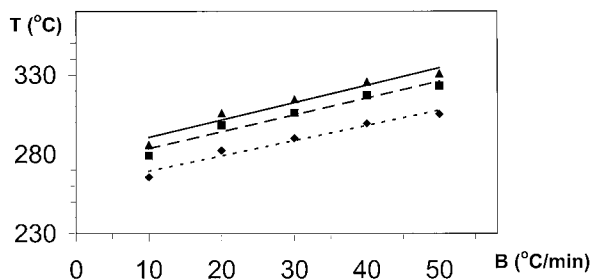


Figure 3 The relation of the thermal degradation temperatures and heating rates (B) for PHB degradation: (\blacktriangle) T_p , (\blacksquare) T_o , and (\blacklozenge) T_f .

$$T_o = 0.97B + 259$$

$$T_p = 1.07B + 273$$

$$T_f = 1.10B + 280$$

The thermal degradation temperature increase with increasing heating rate was caused by heat hysteresis. The thermal degradation temperature can be expressed more exactly as an equilibrium degradation temperature $T(0)$ when the heating rate approaches zero: $T_o(0) = 259^{\circ}\text{C}$, $T_p(0)$

Table I Relation between Heating Rate (B) and Weight Loss Percentages (C_p , C_f) for PHB and P(HB-HV) (7 : 3) Degradation

B ($^{\circ}\text{C}/\text{min}$)	PHB		P(HB-HV) (7 : 3)	
	C_p (%)	C_f (%)	C_p (%)	C_f (%)
10	68	95	63	93
15			66	92
20	69	97		
25			59	94
30	68	96		
35			69	93
40	70	96		
45			55	93
50	71	96		
Average	69 ± 1	96 ± 1	62 ± 7	93 ± 1

The C_p and C_f are the percentages of thermal degradation that correspond to T_p and T_f , respectively. T_p is the temperature at which the weight loss rate has peaked, and T_f is the temperature at which degradation is completed.

= 273°C , and $T_f(0) = 280^{\circ}\text{C}$. The peak width was $T_f - T_o = 21 + 0.13B$ and it increased with the heating rate.

Table I shows the relationship between the heating rate and the thermal degradation loss C in the degradation of PHB. The C_p and C_f are the

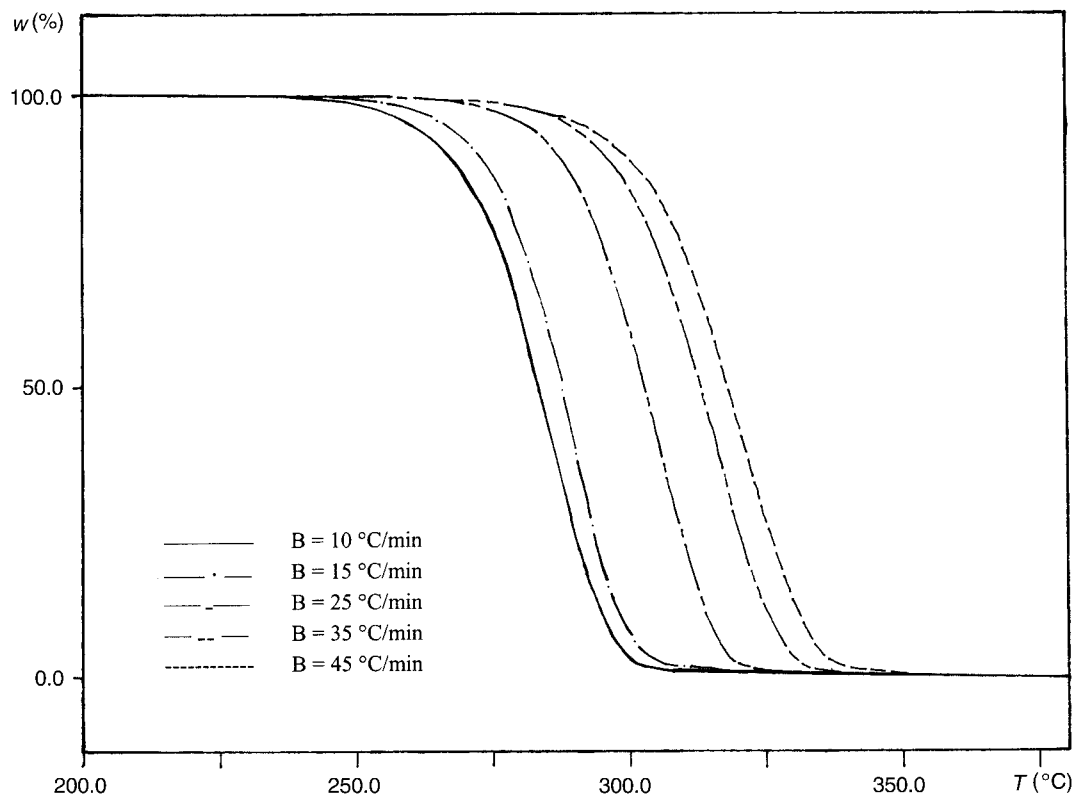


Figure 4 The TG curves of P(HB-HV) (7:3) thermal degradation. The weight (w) is expressed on the vertical axis as a percentage of the initial weight. The temperature is expressed on the horizontal axis ($^{\circ}\text{C}$).

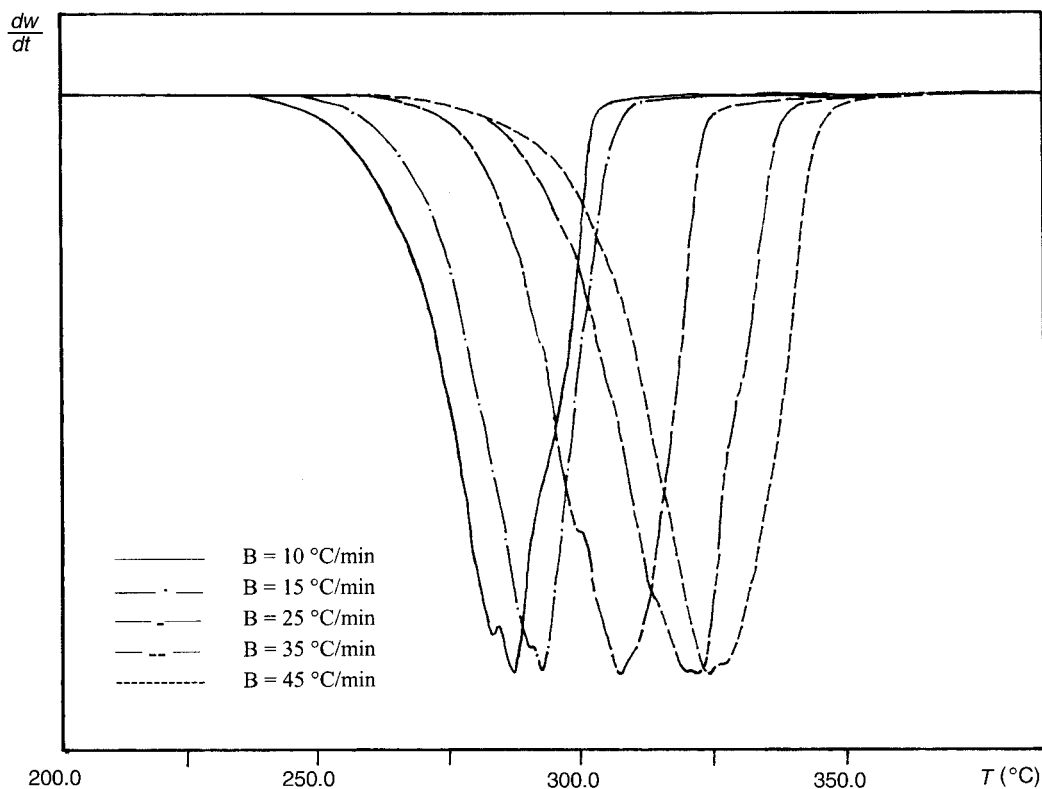


Figure 5 The DTG curves of P(HB-HV) (7:3) thermal degradation. The rate of change in the weight (dw/dt) or the weight loss rate is shown on the vertical axis. The temperature is expressed on the horizontal axis ($^{\circ}\text{C}$).

thermal degradation losses that correspond to T_p and T_f , respectively. The C_p is the thermal degradation loss at $T = T_p$, and $C_p = 100\%$ – the weight percent of residue at T_p . The C_f is the thermal degradation loss at $T = T_f$ and $C_f = 100\%$ – the weight percent of residue at T_f . The values of C_p and C_f were not significantly affected by the heating rate. The C_p and C_f were 69 ± 1 and $96 \pm 1\%$, respectively. The thermal degradation of PHB proceeded to completion.

Thermal Degradation of P(HB-HV) (7:3)

Figures 4 and 5 show the TG and DTG curves for the thermal degradation of P(HB-HV) (7:3) at five different heating rates. Unlike that of PHB, the DTG curve of P(HB-HV) (7:3) consisted of mainly two overlapping peaks. The products of thermally degraded P(HB-HV) (7:3) might be HB and HV monomers, and the overlapping peaks might have been caused by the different evaporation rates of the two monomers.

Figure 6 illustrates that the thermal degradation temperature was linearly increased with the heating rate. The equations were as follows:

$$T_o = 0.98B + 262$$

$$T_p = 1.00B + 278$$

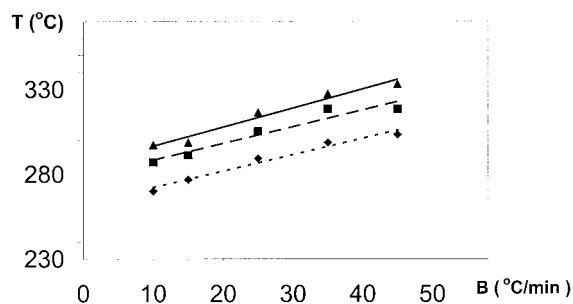


Figure 6 The relation of the thermal degradation temperatures and heating rates (B) for P(HB-HV) (7:3) degradation: (\blacktriangle) T_p , (\blacksquare) T_p , and (\blacklozenge) T_o .

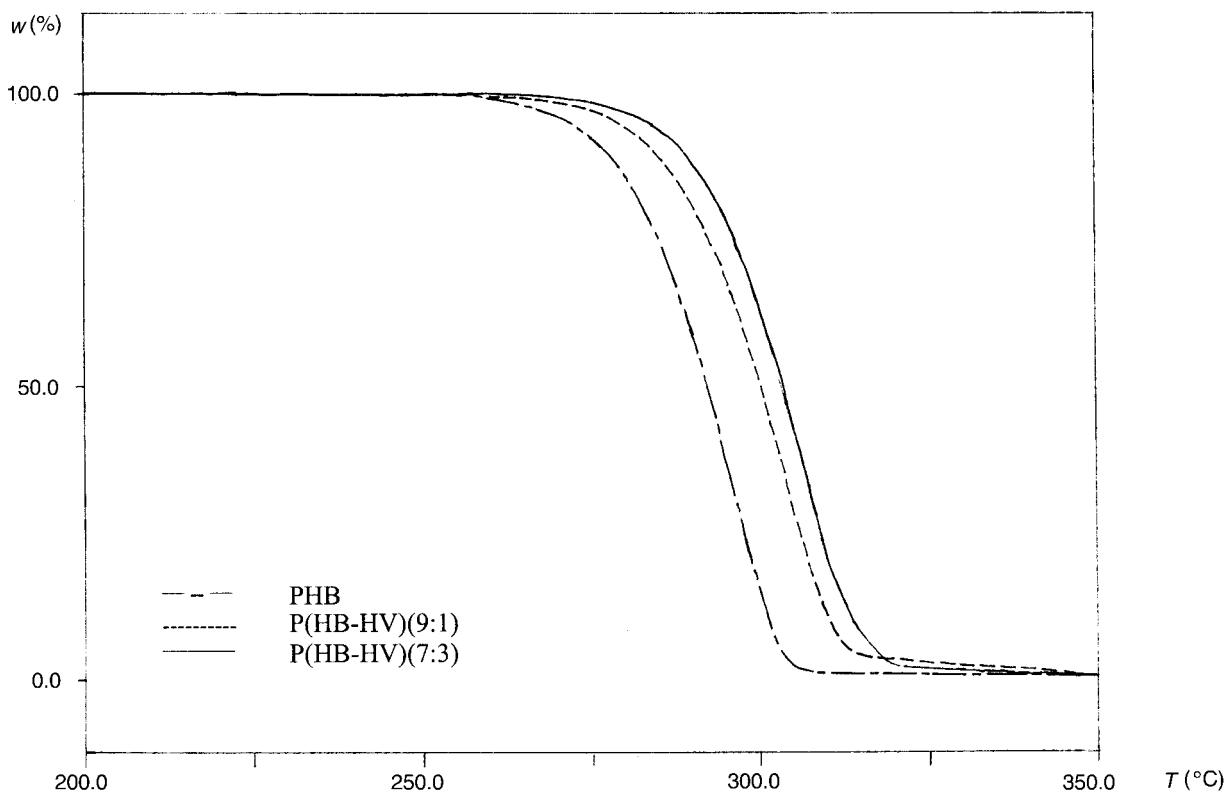


Figure 7 The TG curves of PHB and P(HB-HV) thermal degradation at 20°C/min. The weight (w) is expressed on the vertical axis as a percentage of the initial weight. The temperature is expressed on the horizontal axis (°C).

$$T_f = 1.12B + 285$$

The equilibrium thermal degradation temperatures were $T_o(0) = 262^\circ\text{C}$, $T_p(0) = 278^\circ\text{C}$, and $T_f(0) = 285^\circ\text{C}$, respectively. The peak width can be expressed as $T_f - T_o = 23 + 0.14B$, which increased with the heating rate. Table I shows that the thermal degradation loss in P(HB-HV) (7:3) fluctuated with the heating rate and the average value of the C_p was $62 \pm 7\%$. The C_f reached $93 \pm 1\%$. The reason for the greater fluctuations of C_p in P(HB-HV) (7:3) than in PHB was that the relative weight loss rate between the overlapping peaks changed with the heating rate. The DTG curve of PHB was a smooth single peak because the degraded product consisted of only HB monomer.

Effect of HV Content on Thermal Degradation of PHB and P(HB-HV)

Figures 7 and 8 show the TG and DTG curves of PHB, P(HB-HV) (9:1), and P(HB-HV) (7:3) at a

heating rate of 20°C/min. Table II lists the thermal degradation temperatures T_o , T_p , and T_f for the three polyesters. It is obvious from the figures and table that the thermal stability of the polyesters increased with increasing HV content as indicated by the increase in the thermal degradation temperatures. Furthermore, we learned from the literature that P(HB-HV) has a lower degree of crystallinity and a lower melting temperature^{3,16,21} but only a slightly lower mechanical strength than PHB. Therefore, from the perspective of polymer processing and higher thermal stability, P(HB-HV) is preferable to PHB.

CONCLUSIONS

The weight loss of PHB due to thermal degradation was a one-step process whereas that of P(HB-HV) was mainly a two-step process. The thermal degradation temperatures of the polymers increased with increasing heating rate. The peak

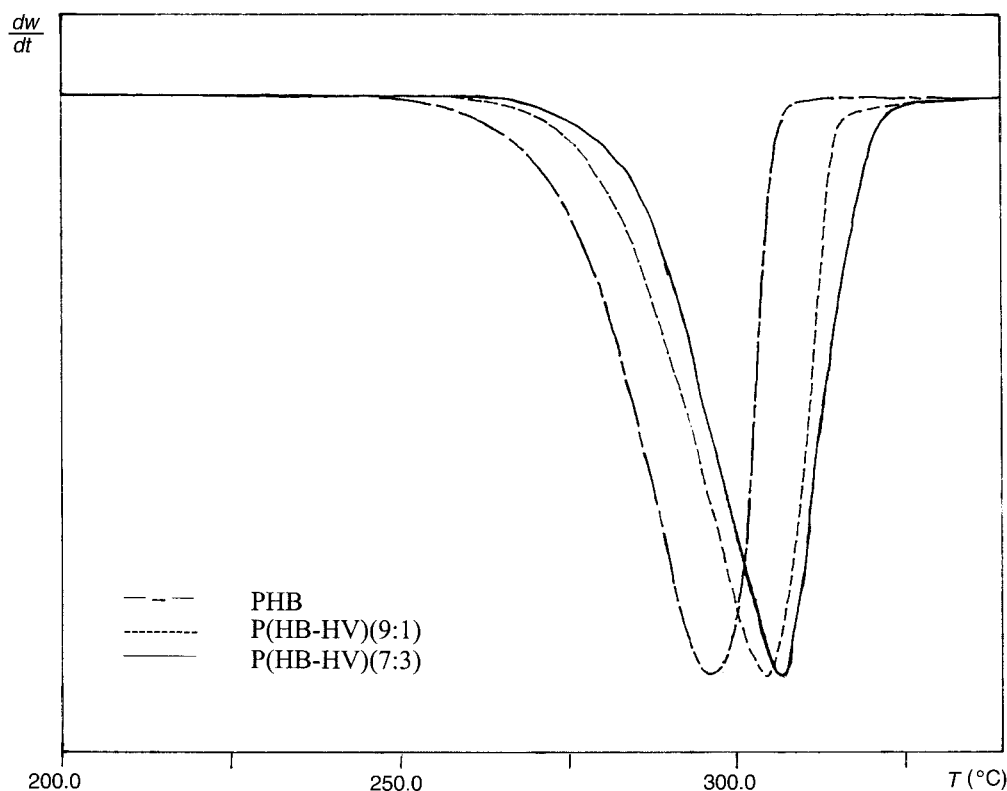


Figure 8 The DTG curves of PHB and P(HB-HV) thermal degradation at 20°C/min. The rate of change in the weight (dw/dt) or the weight loss rate is shown on the vertical axis. The temperature is expressed on the horizontal axis (°C).

width of the DTG curves increased with the heating rate. The thermal degradation weight loss percentages were not affected by the heating rate. The thermal degradation temperatures of the polyesters increased with increasing HV content. The incorporation of HV into the polyester improved the thermal stability.

Table II Thermal Degradation Temperatures of PHB and P(HB-HV) at Heating Rate of 20°C/min

	PHB	P(HB-HV) (9 : 1)	P(HB-HV) (7 : 3)
T_0 (°C)	282	289	293
T_p (°C)	296	304	307
T_f (°C)	303	312	315
HV (mol %)	0	10	30

The T_0 is the temperature at the onset of weight loss; T_p is the temperature at which the weight loss rate has peaked, and T_f is the temperature at which degradation is completed.

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