

Thermal Degradation of Poly(3-hydroxybutyrate) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) as Studied by TG, TG-FTIR, and Py-GC/MS

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ABSTRACT: The thermal degradation kinetics of poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [poly(HB-HV)] under nitrogen was studied by thermogravimetry (TG). The results show that the thermal degradation temperatures (T_o , T_p , and T_f) increased with an increasing heating rate (B). Poly(HB-HV) was thermally more stable than PHB because its thermal degradation temperatures, $T_o(0)$, $T_p(0)$, and $T_f(0)$ —determined by extrapolation to $B = 0^\circ\text{C}/\text{min}$ —increased by 13°C – 15°C over those of PHB. The thermal degradation mechanism of PHB and poly(HB-HV) under nitrogen were investigated with TG-FTIR and Py-GC/MS. The results show that the degradation

products of PHB are mainly propene, 2-butenic acid, propenyl-2-butenic acid and butyric-2-butenic acid; whereas, those of poly(HB-HV) are mainly propene, 2-butenic acid, 2-pentenic acid, propenyl-2-butenic acid, propenyl-2-pentenic acid, butyric-2-butenic acid, pentanoic-2-pentenic acid, and CO_2 . The degradation is probably initiated from the chain scission of the ester linkage. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1530–1536, 2003

Key words: thermal stability; thermal degradation; TG; TG-FTIR; Py-GC/MS; poly(3-hydroxybutyrate); poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

INTRODUCTION

Polyhydroxyalkanoate (PHA) is a family of intracellular biopolymers synthesized by many bacteria as intracellular carbon and energy storage granules under conditions of restricted growth.^{1–4} Poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [poly(HB-HV)] are the most commonly found members of the PHA family. PHAs are hydrolyzed by extracellular depolymerases, which are secreted by many bacteria in microbially active environments.⁵ All PHA depolymerases are comprised of an N-terminal catalytic domain, a C-terminal substrate binding domain, and a linkage region connecting the two domains. The first step in enzymatic degradation

is adsorption of the PHA depolymerase on the biopolymer surface by the substrate binding domain of the enzyme; the second step is hydrolysis of the polymer chains by the active site (catalytic domain) of the enzyme into water-soluble products.⁶ The enzymatic hydrolysis of PHB produces HB dimers as the major product, along with a mixture monomers and oligomers. The oligomers are hydrolyzed to monomers by oligomer hydrolases.^{5–8} Enzymatic degradation of PHA requires the presence of a crystalline phase because depolymerases do not bind well with the mobile amorphous phase to induce hydrolysis.^{9–11}

Attempts have been made to produce PHA as an environmental friendly thermoplastic because of its biodegradability and thermoplastic-like properties.^{12–16} Much effort has also been spent to optimize PHB bioproduction and to blend PHB with other polymers to improve the physical and mechanical properties.^{17–26} PHB is a relatively stiff and brittle material, and its melting point is about 180°C .^{27,28} On the other hand, the properties of poly(HB-HV), including melting point, mechanical strength, and biodegradability, vary widely depending on the mole percentage of HV in the copolymer.^{29–35} PHB has a narrow thermal processing window, and so it is important to know the thermal properties in order to improve the thermal processing of these biopolymers.

The objective of the present research was to investigate the thermal degradation of PHB and poly(HB-

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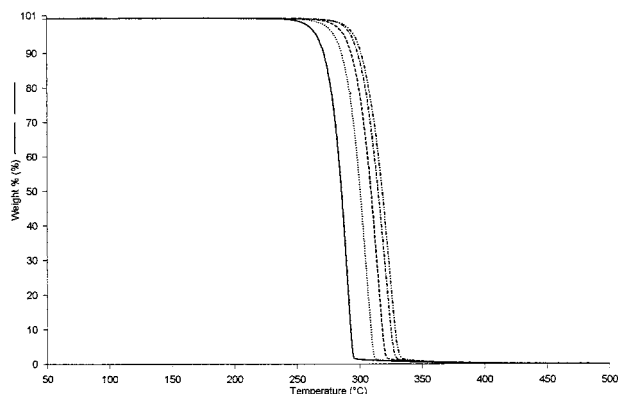


Figure 1 TG curves of PHB thermal degradation:

HV) with dynamic thermogravimetry (TG), thermogravimetry–Fourier transform infrared spectroscopy (TG–FTIR), and pyrolysis–gas chromatography/mass spectroscopy (Py–GC/MS). The kinetics and mechanism of thermal degradation of PHB and poly(HB–HV) have also been considered.

EXPERIMENTAL

Materials

Biosynthesized PHB and poly(HB–HV) were purchased from Fluka (product numbers 81329 and 27819, respectively). The molar ratio of HB to HV in poly(HB–HV) was 70:30. The weight-average molecular weights (M_w) of PHB and poly(HB–HV) are about 400,000–700,000 g/mol.

TG analysis

TG was performed on a Perkin–Elmer TGA-7 thermal gravimetric analyzer. The mass of each sample was about 5–6 mg. The carrier gas was nitrogen with a flow rate of 50 mL/min. The temperature was raised from 50°C to 500°C at several heating rates: 10°C/min, 20°C/min, 30°C/min, 40°C/min, and 50°C/min. The

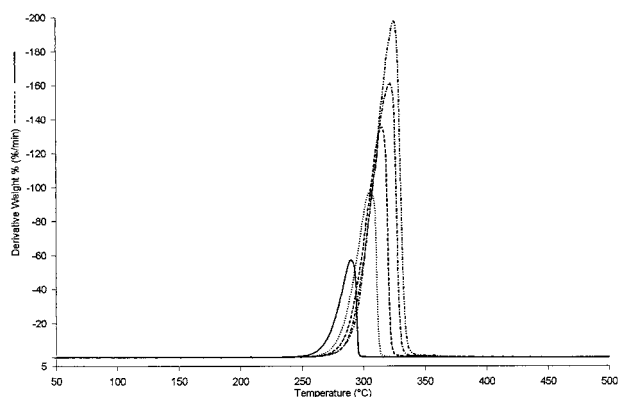


Figure 2 DTG curves of PHB thermal degradation.

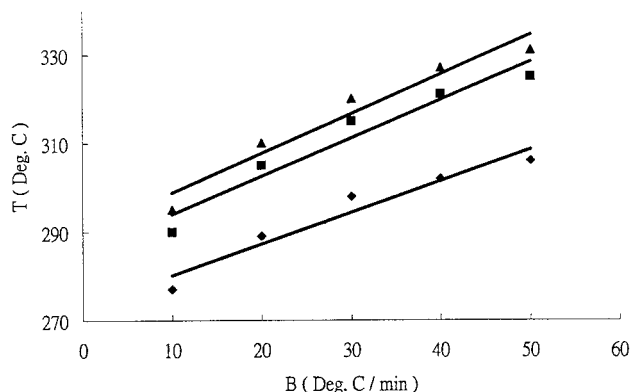


Figure 3 Relation of B and T for PHB thermal degradation.

thermogravimetric (TG) curves and derivative thermogravimetric (DTG) curves were recorded.

TG/FTIR analysis

TG was performed under a nitrogen environment at a heating rate of 40°C/min over a range of 50°C–500°C. The TG outlet was coupled on-line with the spectrometer through a gas cell, which was warmed up to 230°C and stabilized for 2 h before the running of TG. Subsequently, the stack plots of the TG–FTIR spectra were recorded.

Py–GC/MS analysis

Py–GC/MS experiments were carried out with a Japan Analytical Industry JHP-3S Curie point pyrolyzer coupled to a HP6890 gas chromatograph linked to a 5973 quadrupole mass spectrometer. The samples were pyrolyzed at 590°C for 10 s. The carrier gas was high-purity nitrogen at a flow rate of 50 mL/min. The GC column was a HP-5 fused silica capillary column. The GC column temperature was initially held at 50°C for 2 min; then, at a rate of 5°C/min, it was raised to 280°C and held there for 30 min. The GC–MS interface was set at 230°C. Mass spectra were recorded under an electron impact ionization energy of 70 eV. The total flow was split at a ratio of 50:1. The mass of each sample was 0.10–0.20 mg.

TABLE I
Relation between Heating Rate (B) and Weight Loss Percentage (C) for PHB and Poly (HB–HV) Degradation

B (°C/min)	PHB		Poly (HB–HV)	
	C_p (%)	C_f (%)	C_p (%)	C_f (%)
10	80.1	100.0	71.8	99.6
20	79.4	99.5	75.0	98.7
30	79.8	99.1	70.6	99.1
40	80.3	99.3	70.2	98.9
50	80.5	99.5	70.4	99.1
Average	80.0 ± 0.6	99.5 ± 0.5	71.6 ± 3.4	99.1 ± 0.5

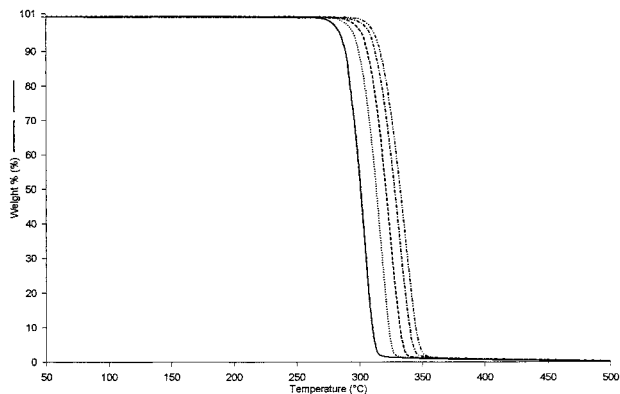


Figure 4 TG curves of poly(HB-HV) thermal degradation.

Data processing

The reaction kinetic parameters were obtained by the processing of TG data through the Coats-Redfern integral method.³⁶ Integrating the reaction kinetic equation

$$d\alpha/dt = k(1 - \alpha)^n \tag{1}$$

and using the Arrhenius equation

$$k = Ae^{-E/RT} \tag{2}$$

the following equations can be obtained:

$$\ln\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\} = \ln[(1 - 2RT/E)AR/BE] - E/RT \quad (n \neq 1) \tag{3}$$

and

$$\ln[-\ln(1 - \alpha)/T^2] = \ln[(1 - 2RT/E)AR/BE] - E/RT \quad (n = 1) \tag{4}$$

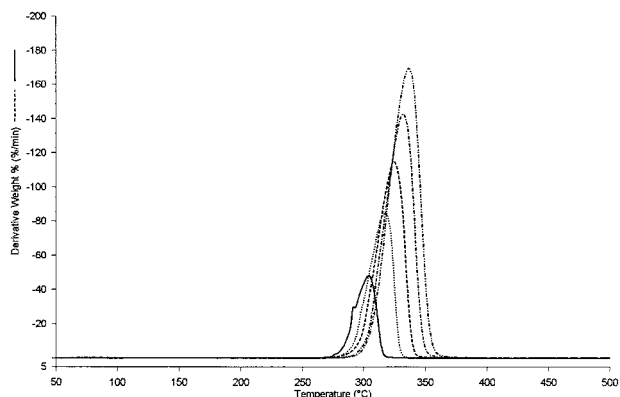


Figure 5 DTG curves of poly(HB-HV) thermal degradation.

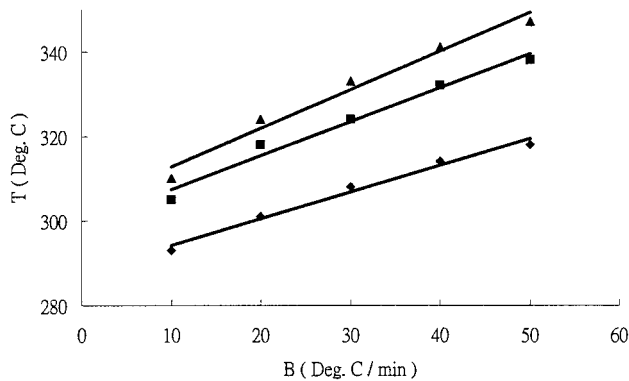


Figure 6 Relation of *B* and *T* for poly(HB-HV) thermal degradation.

where *n* is the reaction order, α is the reaction degree, *T* is the absolute temperature, *B* is the heating rate, *E* is the reaction activation energy, *R* is the gas constant, and *A* is the frequency factor. Where $n \neq 1$, a line can be obtained from the plot of $\ln\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\}$ versus $1/T$, of which the slope is $-E/R$, and the intercept is $\ln[(1 - 2RT/E)AR/BE]$. Where $n = 1$, a line can be obtained from the plot of $\ln[-\ln(1 - \alpha)/T^2]$ versus $1/T$, of which the slope is $-E/R$, and the intercept is $\ln[(1 - 2RT/E)AR/BE]$. Adopting the least-squares fitting method with different values of *n*, the *n* with the maximum correlated coefficient (*r*) is the reaction order, and the corresponding *E* is the apparent activation energy.

RESULTS AND DISCUSSION

Figures 1 and 2 show the TG and DTG curves from the thermal degradation of PHB at five heating rates. The TG curve is a smooth weight loss curve, and the DTG curve shows only a single rate of weight loss (*dw/dt*) peak at 250°C–350°C. The TG and DTG curves shift toward higher temperatures with an increasing heating rate.

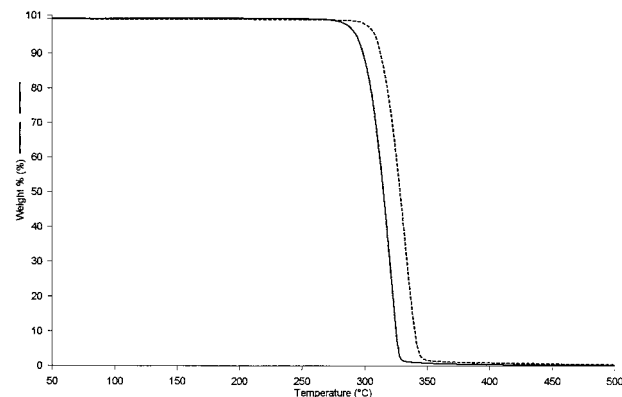


Figure 7 TG curves of PHB and poly(HB-HV).

TABLE II
Reaction Order and Activation Energy for PHB Degradation

	<i>B</i> (°C/min)				
	10	20	30	40	50
<i>n</i>	0.7	0.6	0.7	0.8	0.7
<i>E</i> (kJ/mol)	307	303	300	299	298
<i>A</i> × 10 ⁻²³	443	50.4	17.4	9.42	0.481

Figure 3 shows the effect of *B* on degradation temperatures *T*_o, *T*_p, and *T*_f. *T*_o is the temperature at the onset of weight loss, *T*_p the temperature at the tip of the DTG curve peak, and *T*_f the temperature of complete degradation. *T*_o, *T*_p, and *T*_f increase linearly with *B*, and by linear regression of the plots in Figure 3:

$$T_o = 0.72B + 273 \quad T_p = 0.87B + 286$$

$$T_f = 0.89B + 290 \quad (5)$$

The results shown in Figures 1–3 are similar to those in our previous published reports.^{37,38} The peak width of the DTG curve may be expressed as (*T*_f – *T*_o) = 17 + 0.17*B*.

Table I shows the correlation between the heating rate and the thermal degradation weight loss percentages of PHB and poly(HB–HV). The *C*_p and *C*_f are the thermal degradation weight losses that correspond to *T*_p and *T*_f, respectively. *C*_p is the weight loss percentage at *T* = *T*_p, and *C*_f is the weight loss percentage at *T* = *T*_f. *C*_p and *C*_f are not significantly affected by the heating rate. The average *C*_p and *C*_f of PHB are 80.0% ± 0.6% and 99.5% ± 0.5%, respectively. The thermal degradation of PHB under nitrogen may be regarded as complete degradation.

Figures 4 and 5 show the TG and DTG curves of poly(HB–HV). Like that of PHB, the DTG curve of poly(HB–HV) consists of one peak at 270°C–370°C. Figure 6 shows that *T*_o, *T*_p, and *T*_f increase linearly with *B*:

$$T_o = 0.64B + 288 \quad T_p = 0.80B + 299$$

$$T_f = 0.91B + 304 \quad (6)$$

TABLE III
Reaction Order and Activation Energy for Poly (HB–HV) Degradation

	<i>B</i> (°C/min)				
	10	20	30	40	50
<i>n</i>	1.3	1.2	1.3	1.3	1.4
<i>E</i> (kJ/mol)	374	373	371	370	368
<i>A</i> × 10 ⁻³¹	45900	184	0.947	0.0558	0.0280

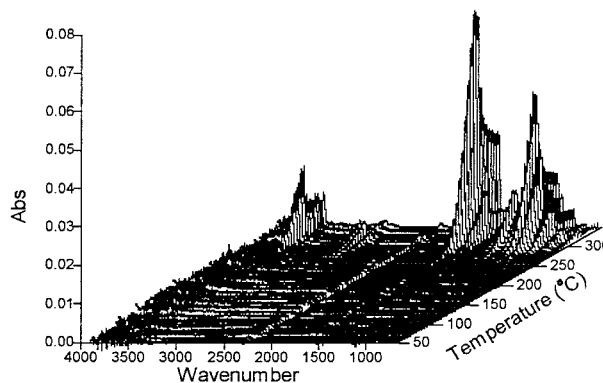


Figure 8 TG-FTIR stack plots for PHB.

The peak width may be expressed as (*T*_f – *T*_o) = 16 + 0.27*B*. The average *C*_p and *C*_f of poly(HB–HV) are 71.6% ± 3.4% and 99.1% ± 0.5%, respectively.

Figure 7 shows a comparison of the TG curves of PHB and poly(HB–HV) at *B* = 40°C/min. Poly(HB–HV) is more stable than PHB. At *B* = 0°C/min, the *T*_o(0), *T*_p(0), and *T*_f(0) of poly(HB–HV) increase 13°C–15°C more than PHB, and *C*_p decreases from 80.0% ± 0.6% to 71.6% ± 3.4%.

Table II shows the kinetic parameters in PHB degradation. The mean value of all *n* values measured at different values of *B* is 0.7. The frequency factor, *A*, and activation energy, *E*, decrease linearly with the increment of *B*. By the linear regression least-squares method, *E* = 308 – 0.22*B*, and the apparent activation energy, *E*_o, at *B* = 0°C/min is 308 kJ/mol. Table III shows the kinetics parameters in the thermal degradation of poly(HB–HV). The mean value of *n* is 1.3, *E* = 376 – 0.15*B*, and *E*_o is 376 kJ/mol. However, too much physical significance should not be attached to the differences in *A*, *E*_o and *n* because the solid-state reaction rate kinetic parameters obtained from linear

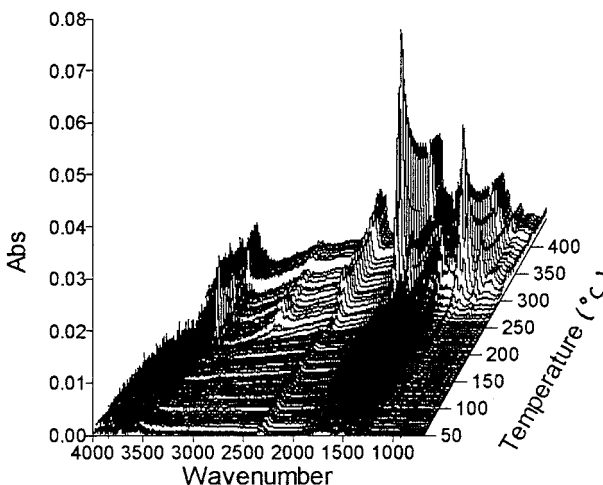


Figure 9 TG-FTIR stack plots for poly(HB–HV).

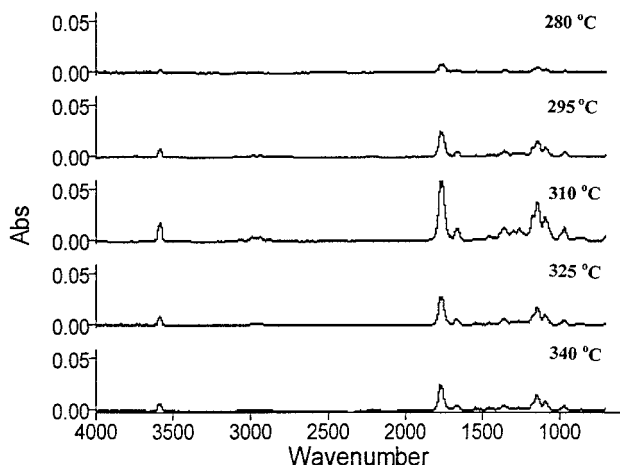


Figure 10 FTIR spectra of gases evolved from PHB degradation at various temperatures.

regression are very sensitive to the conditions surrounding the solid samples.³⁹

The thermal degradation phenomena of PHB and poly(HB-HV) can be observed directly from the stack plot of the coupling TG and FTIR measurements by analyzing the gas spectra from the thermal degradation of the polymers.^{40,41} Figures 8 and 9 show the stack plots of TG-FTIR for PHB and poly(HB-HV), respectively, under nitrogen at a heating rate of 40°C/min. The horizontal axis represents the FTIR wave numbers of released gas from the TG furnace, the vertical axis the intensity of the absorption from the released gas, and the third axis the temperatures of the TG furnace.

Absorptions at 3585 and 965 cm^{-1} are of —OH vibration in the carboxyl group, those at 1770 and 1760 cm^{-1} are of —C=O stretching vibration in unsaturated ester and unsaturated carboxyl acid. Absorption at 1655 cm^{-1} is of —C=C— stretching vibration, and absorptions at 1150 and 1095 cm^{-1} are of —C—O—

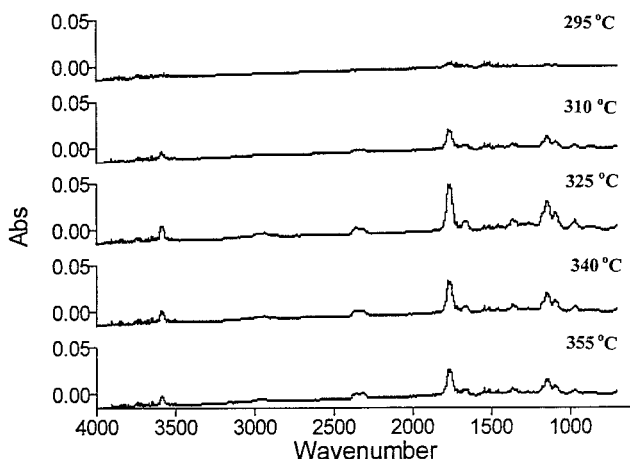


Figure 11 FTIR spectra of gases evolved from poly(HB-HV) degradation at various temperatures.

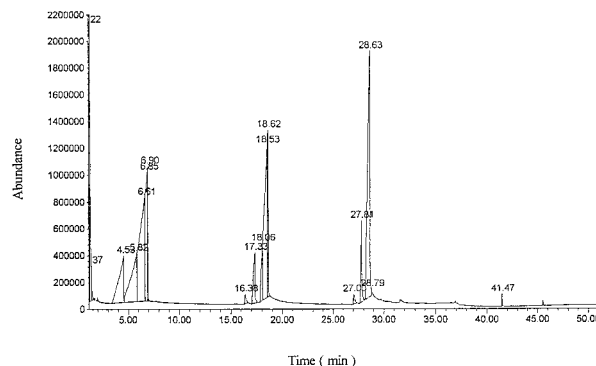


Figure 12 Chromatograms of products from pyrolysis of PHB.

stretching vibration in esters. Figures 10 and 11 show the FTIR spectra of gases evolved from these samples at various temperatures. Figure 10 shows that there are many chemical groups, especially the C=O group, at 295°C in PHB degradation products. At 310°C, the absorbance of —C=C— , —C=O , —C—O— , and —OH reach maximum. After 310°C the absorbance of the above groups decrease. So the products of PHB degradation should be unsaturated esters and unsaturated carboxylic acids.

There are absorption peaks at 3585, 2360, 1770, 1760, 1655, 1150, 1095, and 965 cm^{-1} in the TG-FTIR spectra of poly(HB-HV), which are similar to those of PHB. The maximum absorbance is at 325°C. The small absorption at 2360 cm^{-1} is the characteristic absorption of CO_2 . So the products of poly(HB-HV) degradation should be unsaturated esters and unsaturated carboxylic acids and a small amount of CO_2 .

Figures 12 and 13 show the gas chromatograms of the pyrolysis products of PHB and poly(HB-HV) in nitrogen at 590°C. Table IV shows the identification of the products in the Py-GC/MS of PHB and poly(HB-HV). In the pyrolysis of PHB, the major pyrolysates

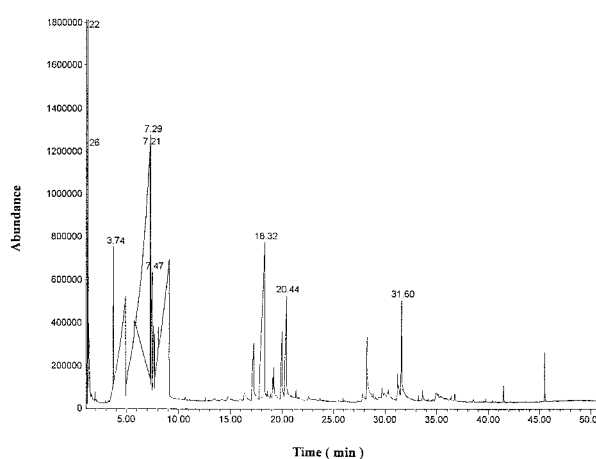


Figure 13 Chromatograms of products from pyrolysis of poly(HB-HV).

TABLE IV
Identification of the Products in the Py-GC/MS of PHB and Poly (HB-HV) at 590°C in N₂

Retention time (min)	Compound	Molecular formula	Molecular weight	Content (%)
PHB				
1.23	Propene	C ₃ H ₆	42	6.73
6.85	2-Butenoic acid	C ₄ H ₆ O ₂	86	45.78
18.62	Propenyl-2-butenate	C ₇ H ₁₀ O ₂	126	24.66
28.63	Butyric-2-butenate	C ₈ H ₁₂ O ₄	172	21.73
Poly (HB-HV)				
1.22	Propene	C ₃ H ₆	42	6.20
7.29	2-Butenoic acid	C ₄ H ₆ O ₂	86	45.47
8.71	2-Pentenoic acid	C ₅ H ₈ O ₂	100	25.81
18.31	Propenyl-2-butenate	C ₇ H ₁₀ O ₂	126	11.57
20.44	Propenyl-2-pentenoate	C ₈ H ₁₂ O ₂	140	5.39
28.25	Butyric-2-butenate	C ₈ H ₁₂ O ₄	172	1.93
31.60	Pentanoic-2-pentenoate	C ₁₀ H ₁₆ O ₄	200	2.31

were propene (6.73%), 2-butenic acid (45.78%), propenyl-2-butenate (24.66%), and butyric-2-butenate (21.73%). In the pyrolysis of poly(HB-HV), the major

pyrolysates were propene (6.20%), 2-butenic acid (45.47%), 2-pentenoic acid (25.81%), propenyl-2-butenate (11.57%), propenyl-2-pentenoate (5.39%), butyric-2-butenate (1.93%), and pentanoic-2-pentenoate (2.31%).

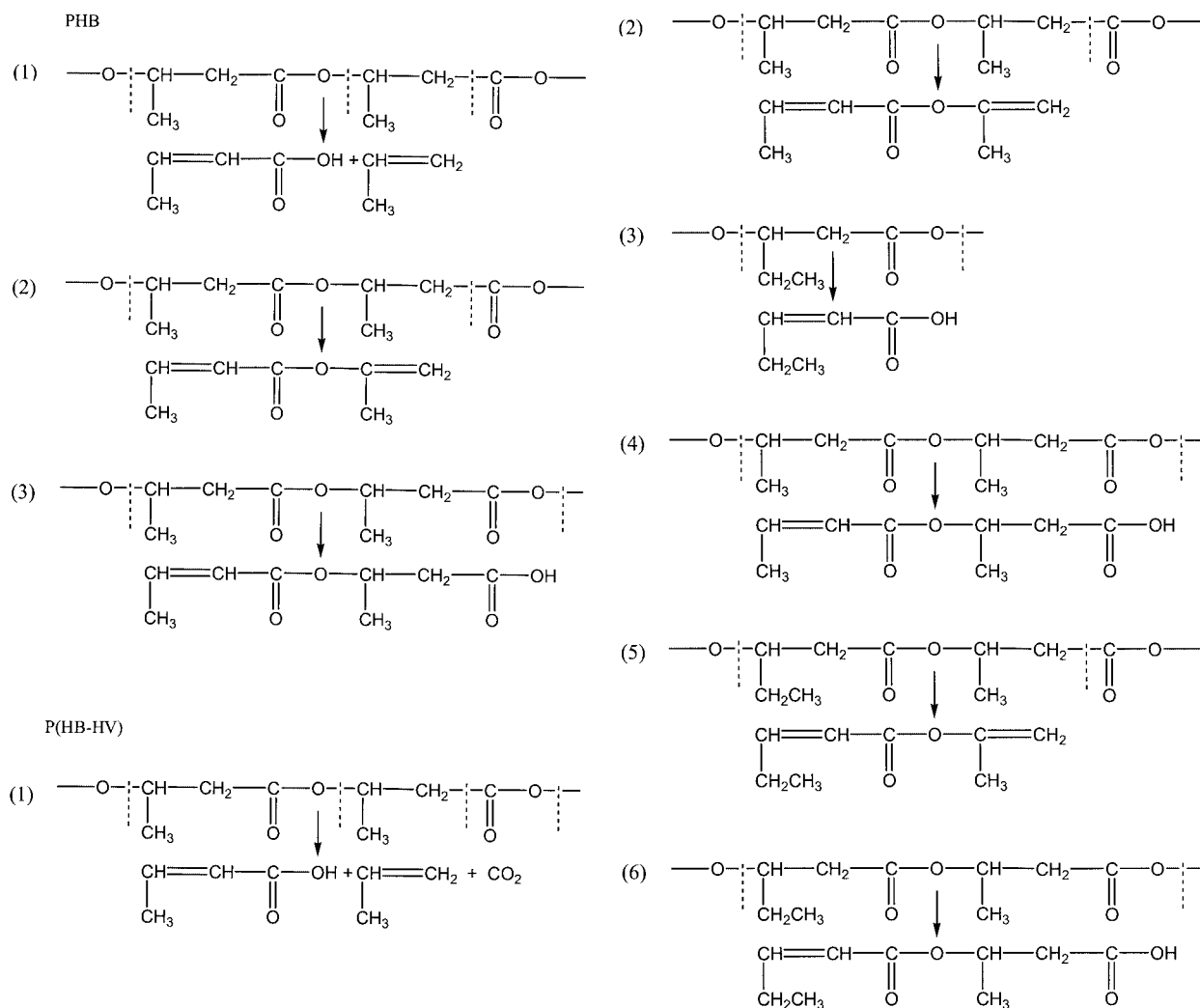


Figure 14 Major products from thermal degradation of PHB and poly(HB-HV) under N₂.

Analyses of the FTIR and GC/MS data show that the thermal degradation products of the two biopolymers were slightly different: the PHB yielded mainly four-carbon unsaturated carboxyl acids and unsaturated esters, whereas the poly(HB–HV) yielded mainly five-carbon unsaturated carboxyl acids and unsaturated esters. The above results suggest that the thermal degradation of PHB and poly(HB–HV) begins with chain scission of the ester linkages by *cis* elimination, which leads to the formation of unsaturated carboxyl acids and unsaturated esters (see Fig. 14).^{42,43}

CONCLUSIONS

PHB and poly(HB–HV) were thermally degraded at 250°C–400°C in nitrogen. Poly(HB–HV) was more thermally stable than was PHB. The degradation products of PHB were mainly propene, 2-butenic acid, and propenyl-2-butenate. The degradation products of poly(HB–HV) were mainly propene, 2-butenic acid, 2-pentenoic acid, propenyl-2-butenate, butyl-2-butenate, and CO₂. The degradation was probably initiated from chain scission of the ester linkage.

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