Thermal Stability of Polyhydroxyalkanoates

F. Carrasco,[1] D. Dionisi,[2] A. Martinelli,[2] M. Majone[2]

[1]*Department of Chemical Engineering, University of Girona, Campus Montilivi, 17071 Girona, Spain*
[2]*Department of Chemistry, University of Rome "La Sapienza," Piazzale Aldo Moro 5, 00185 Rome, Italy*

Received 24 February 2005; accepted 26 September 2005
DOI 10.1002/app.23586
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, we examined the thermal decomposition of polyhydroxyalkanoates (PHAs) such as the homopolymer poly(3-hydroxybutyrate) and the copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate). They are biodegradable polymers that can replace plastics produced from nonrenewable resources, such as polypropylene. The biopolymers we analyzed were commercial PHAs [obtained by means of pure cultures, with hydroxyvalerate (HV) contents of 0 and 10.4 mol %] and biopolymers produced in our laboratories (by means of an enriched activated sludge at two different organic loads, 8.5 and 20 gCOD/L, with a HV content of 20 mol %). To process these biopolymers, it is important to know their thermal stability. For this reason, thermal degradation in air by means of dynamic thermogravimetry (TG) was carried out. The TG data were adjusted to the *n*th-order general analytical equation to evaluate the best order of the reaction, the temperatures of the onset and end of thermal decomposition, and the kinetic parameters. The latter were also calculated by means of other integral and differential methods and compared to those obtained by the general analytical solution. Finally, the influence of the preparation method (pure and mixed cultures and HV content within the biopolymer) on thermal stability was analyzed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2111–2121, 2006

Key words: biopolymers; kinetics (polym.); thermal properties; thermogravimetric analysis (TGA)

INTRODUCTION

Bioplastics can replace traditional plastics because they are biodegradable and can be formed from renewable resources. Among biodegradable plastics, polyhydroxyalkanoates (PHAs), in particular, the copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) [P(3-HB-*co*-3-HV)], are the most promising. P(3-HB-*co*-3-HV) has similar properties to polypropylene; it can be processed in the same way, and it could have the same wide application range.[1,2] However, until now, the production of P(3-HB-*co*-3-HV) has proven to be more costly than that of traditional oil-derived plastics, and this has hindered the further spread of its use.[3] Hence, there is a potential to widen the market for PHAs if their costs decrease.

The most relevant costs in the production of PHAs are the cost for the maintenance and growth of axenic cultures and the cost of the substrate.[1,4] The latter is usually a pure substrate [i.e., glucose and propionate for P(3-HB-*co*-3-HV) production]. Organic wastes (e.g., swine waste liquor, palm oil mill effluents, olive oil mill effluents, vegetable and fruit wastes) are being studied as alternative substrates for PHA production,[3,5–9] and mixed cultures, such as activated sludge instead of axenic cultures, are also being studied. On the other hand, these organic wastes are being used as raw materials to produce volatile fatty acids, fertilizers, methane, and edible mushrooms and in other applications.[5–7,10–15]

A new process[16] has been proposed for the production of biodegradable PHAs from wastes with a combination of anaerobic and aerobic steps. The process has three sequential steps. In the first step, acidogenic fermentation transforms a highly concentrated biodegradable waste into a mixture of organic acids. In the second step, an activated sludge process (with wholly aerobic conditions) is operated at a medium–high organic load by periodic feeding in a sequential batch reactor (SBR) to enrich and produce sludge with a high storage response. Indeed, the SBR periodic feeding creates alternating excess and lack of substrate that favors the growth of microorganisms most able to quickly store the substrate (during the feast phase) and reuse it for growth (during the famine phase).[17] The produced excess sludge has a high storage response, which is exploited in a third step, which is operated in batch but at quite a higher organic load than in the SBR to saturate the sludge storage capacity. Then, the PHA-rich sludge flows to the downstream processing, for PHA extraction, purification, and characterization. However, the question arises as to whether PHAs produced from mixed cultures have similar properties to PHAs produced from axenic cultures.

Dynamic thermogravimetry (TG; with a linear increase in heating rate) is widely used as a tool for

Correspondence to: F. Carrasco (felix.carrasco@udg.es).

studying the thermal stability of different polymeric materials, to determine the reaction order, and also to estimate other kinetic parameters, such as the activation energy (E), the frequency factor, and the rate of decomposition.[18] The advantages of determining kinetic parameters by nonisothermal methods rather than by isothermal studies are as follows:

1. The kinetics can be established over an entire temperature range in a continuous manner.
2. It is possible to obtain the required information with a single sample, which eliminates problems arising from the use of different samples.
3. When a sample undergoes considerable reactions as it is heated to the required temperature, the results obtained by isothermal methods are questionable because some decomposition may occur during the preheating period, particularly when the temperature at the onset of the reaction is considerably lower than the temperature of the isothermal trials.

Mathematical modeling of thermal decomposition reactions helps one to understand the processes being studied, to check the validity of the assumptions, and to arrive at quantitative conclusions from them.

The thermal stability of polymers is one of the fundamental properties that control their processing and application. It is widely believed that the thermal degradation of PHA occurs almost exclusively by a nonradical random chain-scission reaction. The thermal mechanism consists of a gradual decrease in the molecular weight. This type of process becomes significant only at temperatures above 200°C.[19]

The goal of this study was to examine, by means of dynamic TG, the thermal decomposition kinetics of biopolymers (i.e., PHAs) produced by enriched mixed cultures through the three-step process previously reported. Thermograms were used to determine the thermal stability of the biopolymers [with the temperature at which 5% of the mass was lost (T_5) and the temperature at which 95% of the mass was lost (T_{95})] and to evaluate the kinetic parameters of the thermal decomposition reaction [i.e., with the preexponential factor (A^*) and E]. On the other hand, two characteristic temperatures related to the thermal stability of the biopolymers were evaluated from the conversion and the temperature at the maximum decomposition rate.

KINETIC MODEL OF THERMAL DECOMPOSITION

The rate of weight loss in the process of thermal decomposition depends on weight and temperature according to complex equations. However, many heterogeneous decomposition reactions of polymers can be described by the model of pseudohomogeneous kinetics (i.e., nth-order reactions). According to Altofer,[20] some conditions have to be fulfilled to enable the ideal course of a reaction as represented by nth-order reaction kinetics; that is, one must have a well-defined, homogeneous sample temperature with no reverse reactions. The latter implies a negligible partial pressure of the decomposition gas. Therefore, a continuous flow of gas is recommended for the evacuation of volatilization products as they are formed. On the other hand, the constant rate with the temperature is generally accepted to be of the Arrhenius type because this relationship dominates physical and chemical phenomena.

If one considers the relationship between mass and conversion in addition to the previous considerations, a differential equation readily follows whose primitive form is a complex equation containing an infinite number of terms. The analytical solution is, therefore:[21]

$$-\ln(1-f) = \frac{A^*E}{\beta R}\left[\exp\left(-\frac{E}{RT}\right)\right] \times \sum_{i=1}^{\infty}(-1)^{i+1} i!\left(\frac{RT}{E}\right)^{i+1} \quad n = 1 \quad (1)$$

$$\frac{1-(1-f)^{1-n}}{1-n} = \frac{A^*E}{\beta R}\left[\exp\left(-\frac{E}{RT}\right)\right] \times \sum_{i=1}^{\infty}(-1)^{i+1} i!\left(\frac{RT}{E}\right)^{i+1} \quad n \neq 1 \quad (2)$$

where A^* is the preexponential factor, E is the activation energy, f is the degree of conversion, i is the iteration number, n is the reaction order, R is the gas constant, t is the time, T is the temperature, and β is the linear heating rate.

When the thermal energy (RT) is significantly less than activation, the sum can be truncated at the second term ($i = 2$). This case is often found for the thermal decomposition of solids. However, if RT tends to E (i.e., low E and/or high temperature), it is necessary to take a greater number of terms in the general analytical solution. Because the general analytical solution is an integral method, the values for the order of reaction have to be assumed ($n = 0, 1/2, 1, 3/2, 2$). The best order is chosen by means of an analysis of variance (ANOVA).

Conversion can be singled out from eqs. (1) and (2), from which the first and second conversion derivatives follow readily:

$$f = 1 - \exp\left(-\frac{A^*RT^2}{\beta E}\left[\exp\left(-\frac{E}{RT}\right)\right] \times \sum_{i=1}^{\infty}(-1)^{i+1} i!\left(\frac{RT}{E}\right)^{i-1}\right) n = 1 \quad (3)$$

$$f = 1 - \left[1 - (1-n)\frac{A^*RT^2}{\beta E}\left[\exp\left(\left(-\frac{E}{RT}\right)\right)\right.\right.$$
$$\left.\left.\times \sum_{i=1}^{\infty}(-1)^{i+1} i!\left(\frac{RT}{E}\right)^{i-1}\right]^{1/(1-n)} n \neq 1 \quad (4)$$

$$\frac{df}{dT} = \frac{A^*}{\beta}\left[\exp\left(-\frac{\mathrm{E}}{\mathrm{RT}}\right)\right](1-\mathrm{f})^{\mathrm{n}}\ \forall \mathrm{n} \quad (5)$$

$$\frac{d^2f}{dT^2} = \frac{df}{dT}\left(\frac{E}{RT^2} - \frac{n}{(1-f)}\frac{df}{dT}\right)\ \forall n \quad (6)$$

Because the maximum rate of decomposition is reached when $d^2f/dT^2 = 0$, E can be evaluated from eq. (6). The subindex m refers to the conditions at the maximum decomposition rate:

$$E = nRT_m^2\frac{\left(\frac{df}{dT}\right)_m}{(1-f_m)}\ \forall n \quad (7)$$

As indicated later, the thermal decomposition of PHA followed first-order kinetics, and RT was less than E (in this case, the sum could be truncated at $i = 2$). If one considers these findings, the conversion follows readily:

$$\ln[-\ln(1-f)T^2\left(1 - \frac{2RT}{E}\right) = \ln\left(\frac{A^*R}{\beta E}\right) - \frac{E1}{RT}\, n = 1\ i = 2 \quad (8)$$

The determination of the kinetic parameters (A^* and E) can be calculated from the linear regression of the following equation:

$$f = 1 - \exp\left[-\frac{A^*RT^2\left(1 - \frac{2RT}{E}\right)}{\beta E}\exp\left(-\frac{E}{RT}\right)\right] \quad n = 1\ i = 2 \quad (9)$$

Various methods (integral and differential) for the determination of the kinetic parameters were selected to compare the results so evaluated with those obtained by means of the general analytical solution. The equations used for the linear regression included equations from van Krevelen et al.[22]

$$\ln[-\ln(1-f)] = \ln\left[\frac{A^*}{\beta}\left(\frac{0.368}{T_m}\right)^{E/RT_m}\frac{1}{1 + \frac{E}{RT_m}}\right] + \left(1 + \frac{E}{RT_m}\right)\ln T \quad (10)$$

and Coats and Redfern[23]

$$\ln\left(\frac{f}{T^2}\right) = \ln\left(\frac{A^*R}{\beta E}\right) - \frac{E1}{RT} \quad (11)$$

and a differential equation:

$$\ln\left[\frac{\left(\frac{df}{dT}\right)}{(1-f)}\right] = \ln\left(\frac{A^*}{\beta}\right) - \frac{E1}{RT} \quad (12)$$

The values for temperature, conversion, and first conversion derivative at the maximum rate of decomposition are not generally known and must be estimated graphically from TG data. Thus, eq. (7) was useful for obtaining an approximate value of E. This estimate can serve as the initial value in iterative calculations and can lead to the determination of E through the general analytical solution.

To process plastics, it is absolutely necessary to know their thermal stability. For this reason, a series of temperatures must be defined. First, it is interesting to directly determine the experimental temperatures (from the TG curves) at which the thermal decomposition begins and ends: T_5 (i.e., the beginning of the thermal decomposition) and T_{95} (i.e., the end of the thermal decomposition).

On the other hand, two theoretical characteristic temperatures were derived from the weight loss curves:

1. The temperature obtained from the TG curve at the value of the intercept between the locus of $f = 0$ and the tangent line at the maximum rate of decomposition (T_{c0}).
2. The temperature obtained from the TG curve at the value of the intercept of the locus $f = 1$ and the tangent line at the maximum rate of decomposition (T_{c1}).

After some mathematical rearrangement, these temperatures were evaluated from conversion and temperature at the maximum decomposition rate and the value of E (these characteristic temperatures were independent of n):

$$T_{c0} = T_m\left(1 - \frac{RT_m}{E}\frac{f_m}{(1-f_m)}\right) \quad (13)$$

$$T_{c1} = T_m\left(1 + \frac{RT_m}{E}\right) \quad (14)$$

EXPERIMENTAL

PHA samples

This study was conducted with two types of biopolymers:

TABLE I
SBR Operating Conditions for the Production of P(3-HB-*co*-3-HV)

SBR operating parameter	Run I	Run II
Overall influent concentration (gCOD/L)	8.5	20
Influent acetic acid concentration (gCOD/L)	3.4	8
Influent propionic acid concentration (gCOD/L)	1.7	4
Influent lactic acid concentration (gCOD/L)	3.4	8
Influent organic load rate (gCOD L^{-1} d^{-1})	8.5	20
Hydraulic residence time (d)	1	1
Feed mode (cycle/d)	12	12
Cycle length (min)	120	120
Feed length (min)	10	10
Fed volume (mL/cycle)	167	167
pH	7.5	7.5
T (°C)	25	25

1. PHAs produced by Sigma-Aldrich (Italy): poly(3-hydroxybutyrate) [P(3-HB); CAS number 29435-48-1] and P(3-HB-*co*-3-HV) (CAS number 80181-31-3) with a hydroxyvalerate (HV) content of 10.4% (molar basis). Both the homopolymer and the copolymer were produced with a pure culture of *Alcaligenes eutropha.*
2. PHAs produced in our laboratories with a mixed culture that was obtained by the enrichment of an activated sludge at two organic loads, 8.5 gCOD/L (run I) and 20.0 gCOD/L (run II), with a HV content, in both cases, of 20 mol % and a viscosimetric molecular weight of 5–8 $\times$ 10^5 Da.

A SBR (working volume = 2 L) was inoculated with activated sludge from the Roma Nord (Italy) full-scale plant and used under periodic feeding to culture and enrich the activated sludge of microorganisms most able to store PHAs. As shown in Table I, the SBR cycle consisted of feed (10 min), reaction (1 h 48 min), and final withdrawal (2 min) of the mixed liquor from the mixed vessel. No settling phase was performed, and all excess biomass was withdrawn with the mixed liquor (i.e., the biomass retention time was equal to the hydraulic retention time). The reactor was aerated by means of membrane compressors and stirred with a mechanical impeller at 900 rpm. The pH and temperature were maintained at 7.5 and 25°C, respectively. The SBR was fed by a mixture of acetic, lactic, and propionic acids, with an overall concentration of 8.5 gCOD/L (run I) and 20 gCOD/L (run II), and the organic load rates were 8.5 and 20 gCOD L^{-1} d^{-1}, respectively. The relative amounts of acetic, lactic, and propionic acids were 40, 40, and 20% on a COD basis. The hydraulic retention time was 1 day. The SBR feed also contained a typical mineral medium and thiourea (20 mg/L) to inhibit nitrification. To produce PHA, aerobic batch tests were performed with the excess sludge from the SBR. After a pseudo steady state had been reached in the SBR, the excess sludge was withdrawn at the end of a cycle, put in a smaller reactor (working volume = 500 mL with same temperature and pH as in the SBR), diluted to the chosen concentration, and then spiked with the substrate mixture. Before (at least 1 h) and during the test, the batch reactor was intermittently aerated by air bubbling (with care taken that oxygen concentration was never lower than 3 mg/L). The oxygen consumption rate was intermittently determined and used to monitor the substrate consumption. At evidence of substrate depletion, the test was interrupted, and the biomass containing the stored polymer was treated with HClO to interrupt any biological reactions. Then, the biomass was centrifuged for 10 min at 7000 rpm and washed twice with distilled water and twice with acetone. Then, the residual solids were separated from the surnatant and put in a vacuum oven to be dried at 30°C for 24 h.

PHA thermal decomposition as determined by TG

The thermal decomposition of the PHA samples was carried out in a Mettler T450 thermogravimetric analyzer (Italy), and the ISO/DIS 9225-1 method was applied. The operating conditions were as follows: heating rate = 5 K/min and sample weight = 4–5 mg (the presence of water and ash were almost negligible). Decompositions were conducted at atmospheric pressure, and gases produced by the decomposition were swept out by a continuous flow of air. Reproducibility trials showed that the maximum difference between the two thermograms was less than 0.6%.

RESULTS AND DISCUSSION

Figures 1 and 2 show, respectively, the variation of *f* with the temperature at a heating rate of 5 K/min for the Biopol biopolymers P(3-HB) and P(3-HB-*co*-3-HV) and the copolymers produced in our laboratories [P(3-HB-*co*-3-HV)] with the methodology reported previously (the fitted curves are analyzed later). The thermograms clearly indicated that there was only a decomposition reaction in a narrow temperature range. The thermograms corroborated that all of the samples contained only organic matter (no water and no inorganic residue were found). Because of the σ form of the TG curves, the thermal decomposition adjusted well to a kinetic model of *n*th-order reactions, as discussed later. The curves had the same shape, but the slopes were different. Therefore, the kinetic parameters and the thermal stability temperatures were dif-

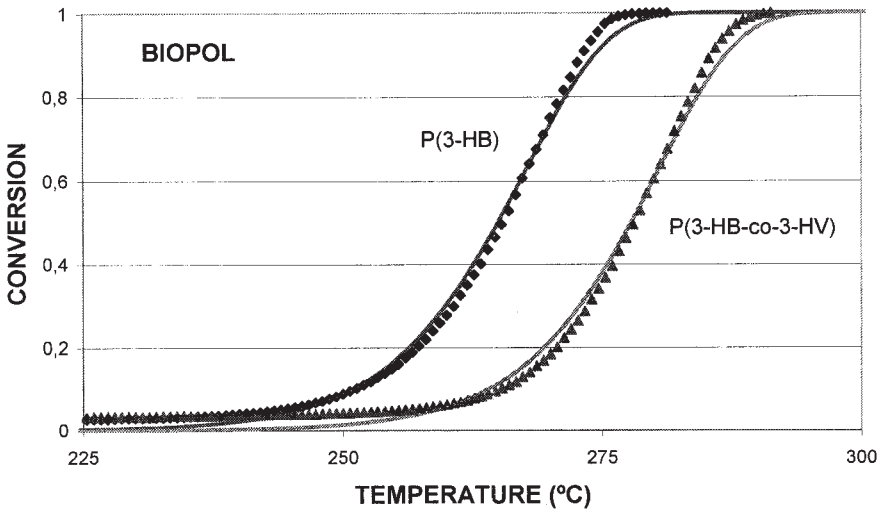

Figure 1 Variation of conversion as a function of temperature for the Biopol biopolymers P(3-HB) and P(3-HB-*co*-3-HV).

ferent for each type of polymer. For the Biopol biopolymers, the presence of HV was responsible for a higher thermal stability because the TG curves were shifted toward higher temperatures. Two temperatures related to the thermal stability of the polymers were determined from TG data: T_5 and T_{95}. In fact, T_5 provided a good idea of the thermal stability of the polymer (i.e., the beginning of the thermal decomposition). T_5 values for the Biopol biopolymers were 246.3 and 260.4°C for P(3-HB) and P(3-HB-*co*-3-HV), respectively. This indicated that the presence of HV within the copolymer led to a thermally more stable material (i.e., an increase of 14.1°C). For our biopolymers, these temperatures were 247.1 and 253.0°C for run I (organic load = 8.5 gCOD/L) and run II (organic load = 20 gCOD/L), respectively, thus indicating that the biopolymer produced at a higher organic load was slightly more stable. In this case, the T_5 difference was less important because, in both runs, the copolymer contained approximately the same HV content (19–20 mol %). Again, the difference in thermal stability could be attributed to different copolymer structure or/and molecular weights due to the different organic load used. A previous work[24] reported that the molecular weight of the polymers greatly influenced their thermal behaviors. The T_5 for polystyrene greatly varied as a function of its molecular weight (from 280 to 340°C for molecular weights from 517 to 7829 g/mol).[24] On the other hand, these temperatures were high, thus indicating an important thermal stability. The difference in thermal stability found between the Biopol biopolymers and our biopolymers (with HV

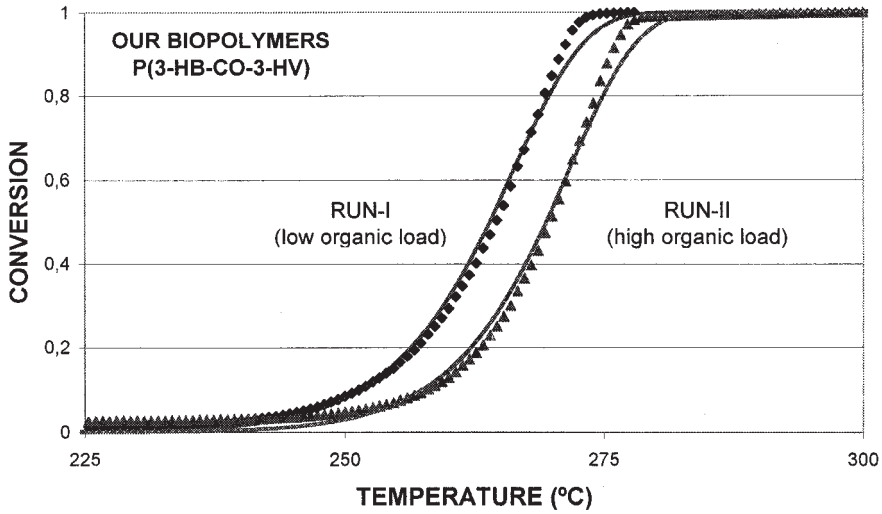

Figure 2 Variation of conversion as a function of temperature for our biopolymers obtained at various organic loads: 8.5 gCOD/L (run I) and 20 gCOD/L (run II).

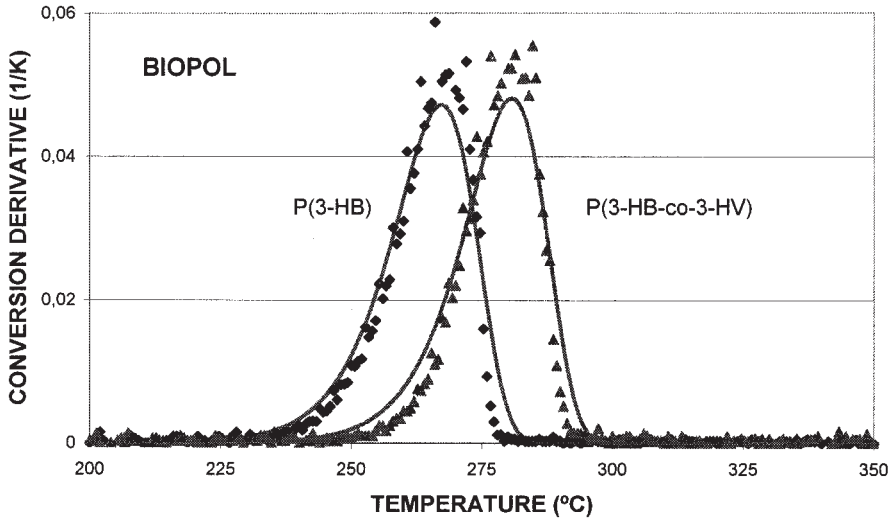

Figure 3 Variation of the conversion derivative (i.e., thermal decomposition rate) for the Biopol biopolymers P(3-HB) and P(3-HB-*co*-3-HV).

contents of 10.4 and 20 mol %, respectively) were attributed to different copolymer structures and molecular weights. One must consider that the Biopol biopolymers were produced with a pure culture and different operating conditions that those applied to the production of our biopolymers (with a mixed culture). There was no a clear trend of variation between the onset of thermal decomposition and HV content or production method.

With the conversion versus temperature data, it was possible to calculate the derivative of the conversion with the temperature with finite differences (i.e., $df/dT \approx \Delta f/\Delta T$) between two consecutive conversions (temperature difference = .67°C). In this way, it was possible to evaluate the temperature, conversion, and conversion derivative at the maximum rate of decomposition. Figures 3 and 4 illustrate the variation of the rate of decomposition with increasing temperature (in terms of the conversion derivative with respect to the temperature) for the Biopol biopolymers and our biopolymers, respectively, for both experimental points and fitted curves (the latter are analyzed later). This type of graph is highly useful because the temperature at the maximum rate of decomposition can be determined with a good degree of precision. Again, in the Biopol biopolymers, the presence of HV led to a shift of the peak toward a higher temperature. Table II shows the experimental values of the temperature, conversion, and conversion derivative at the maximum rate of decomposition (these values were evalu-

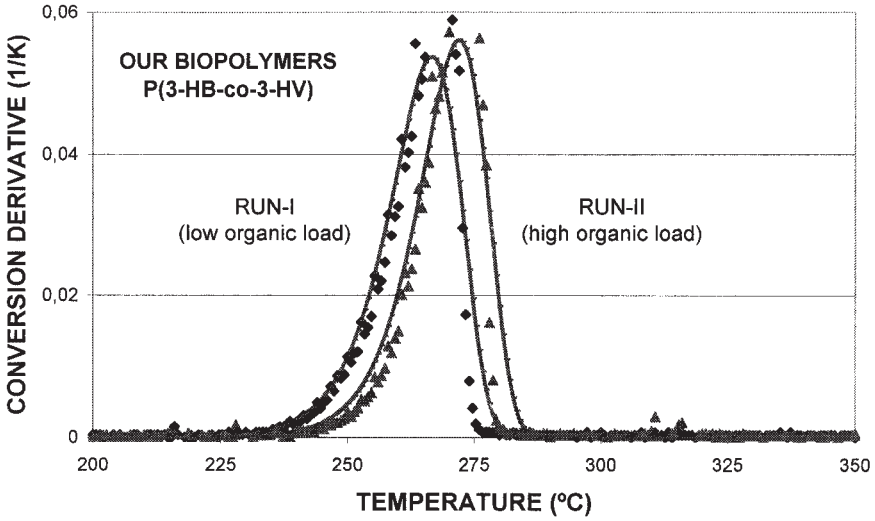

Figure 4 Variation of the conversion derivative (i.e., thermal decomposition rate) for our biopolymers obtained at various organic loads: 8.5 gCOD/L (run I) and 20 gCOD/L (run II).

TABLE II
Experimental Values of Thermal Stability and Kinetic Parameters, as Obtained from TG Data

	T_5 (°C)	T_{95} (°C)	T_m (°C)	f_m	$(df/dT)_m$ (K^{-1})	E (kJ/mol)
Biopol P(3-HB)	246.3	275.0	267.3	0.608	6.12×10^{-2}	378.8
Biopol P(3-HB-*co*-3-HV)	260.4	287.7	282.0	0.720	6.35×10^{-2}	580.3
P(3-HB-*co*-3-HV), run I	247.1	273.8	266.7	0.633	6.99×10^{-2}	461.2
P(3-HB-*co*-3-HV), run II	253.0	278.9	273.3	0.738	6.75×10^{-2}	639.5

ated from TG data at the point of the maximum conversion derivative, as calculated by a finite difference). As for the Biopol biopolymers, the melting temperature (T_m) increased from 267.3 to 282.0°C (i.e., an increase of 14.7°C) when the biopolymer contained HV units, but the decomposition rate was approximately the same (mean value = 6.2% K^{-1}). In the case of our copolymers, the T_m values were 266.7 and 273.3°C for run I (organic load = 8.5 gCOD/L) and run II (organic load = 20 gCOD/L; i.e., a difference of 6.6°C); both temperatures were lower than that of the Biopol copolymer. This behavior was also found with the thermal stability (T_5). The decomposition rate of our copolymers was quite constant for both experimental procedures (mean value = 6.9% K^{-1}, which was slightly higher than that found for the Biopol biopolymers). The values for E were calculated with eq. (7) for $n = 1$ with the conditions existing in the peak (i.e., maximum rate of decomposition). These values were subject to error because the derivative was calculated with finite differences, which introduced a significant imprecision because, in the environs of the point of the maximum rate of decomposition, conversion varies very quickly. In any case, these values served to initialize the iterative process required for the calculation of E, as we explain later.

With the aim of determining the kinetic parameters of the decomposition reactions, we used eqs. (1) and (2). Because the order of reaction was not known, we performed an ANOVA of the regression. The results obtained for F value indicate that the best order of reaction corresponded to first order. Adjustment to eq. (1) requires an iterative procedure due to the presence of the $1 - 2RT/E$ term. Hence, the iteration was begun with the value for E previously calculated by an approximate procedure (see Table II). The value for E evaluated from the slope was then used in the following iteration until convergence took place. Equation (1) contains a summation with an infinite number of terms. In any case, we verified that when we took just two terms ($i = 2$), the errors occurring were negligible. In our case, RT was approximately 1% of E. The kinetic parameters (A^* and E) obtained by adjustment of the experimental points of first-order kinetics and the summation, shortened to two terms, are shown in Table III. The adjustments were excellent ($r^2 = 0.99$) for all of the biopolymers through the entire conversion range (f = 5–95%), as shown in Figure 5 for P(3-HB-*co*-3-HV) in run I (organic load = 8.5 gCOD/L). This excellent adjustment to first-order kinetics for a polymeric material, within the entire range of conversion, is not always observed for other solids. This finding indicates that the thermal decomposition of PHA occurred through a simple reaction mechanism, which supported the hypothesis that the controlling step is the depolymerization of macromolecular chains. The results clearly indicated an increase in E with increasing HV content (304.1, 325.4, and 344.3–367.4 kJ/mol for biopolymers containing 0, 10.4, and 20% HV, respectively). Moreover, the organic load used in our experiments also showed an influence on this kinetic parameter (344.3 and 367.4 kJ/mol for the lower and higher organic loads, respectively). The confidence interval for E, as shown in Table III, was as low as 1.2–2.5 kJ/mol (i.e., 0.4–0.7% of E), which indicated that the experimental points were well explained by the first-order kinetics equation. Lee et al.[19] reported values of E of 296 kJ/mol for P(3-HB) and 310 kJ/mol for P(3-HB-*co*-3-HV), when the biopolymers were obtained by means of pure cultures and with a heating rate of 20 K/min (the heating rate was 5 K/min in this study, which reduced heat-transfer limitations). With regard to E, great variations are mentioned in the literature[21] for a given polymeric material. These differences depend on several factors:

1. The preparation method of the polymer. The use of different substrates (glucose and organic acids, among others) and various microorganisms (pure or mixed cultures) influence the chemical configuration of the polymer, its molecular weight, and thus, its thermal stability. The presence of lattice defects, weak links, and impurities are other influencing factors.
2. Experimental techniques and operating conditions (e.g., sample weight, sample particle size, heating rate, mass flow and type of gas, thermal contact between the sample and sample holder).
3. Mathematical treatment of data with different kinetic models and methods (integral, differential, and special).

In this study, points 2 and 3 had no influence on the determination of E because they were the same for all

TABLE III
Calculated Values of of Kinetic Parameters as Obtained from Linear Regression

	General analytical solution			van Krevelen et al.[22]			Coats and Redfern[23]			Differential		
	A^* (s^{-1})	E (kJ/mol)	r^2	A^* (s^{-1})	E (kJ/mol)	r^2	A^* (s^{-1})	E (kJ/mol)	r^2	A^* (s^{-1})	E (kJ/mol)	r^2
Biopol P(3-HB)	2.50×10^{27}	304.1±1.2	0.992	1.86×10^{28}	313.4	0.993	1.98×10^{20}	234.3	0.996	2.03×10^{34}	374.8	0.989
Biopol P(3-HB-*co*-3-HV)	5.40×10^{28}	325.4±1.8	0.984	5.74×10^{29}	336.5	0.986	3.52×10^{21}	253.0	0.991	1.10×10^{39}	433.5	0.995
P(3-HB-*co*-3-HV), Run-I	2.61×10^{31}	344.3±1.7	0.991	2.22×10^{32}	354.0	0.993	3.01×10^{23}	265.9	0.998	3.67×10^{38}	417.1	0.968
P(3-HB-*co*-3-HV), Run-II	2.10×10^{33}	367.4±2.5	0.985	2.48×10^{34}	378.7	0.987	2.52×10^{25}	288.3	0.996	1.10×10^{44}	478.0	0.988

of the samples. Therefore, the different values of E were due to the preparation method of the biopolymer and the content of HV.

When thermal decomposition takes place, the diffusion of heat and/or the gases of decomposition has to be considered as a process that is taking place simultaneously with the chemical reaction. The endothermal/exothermal reaction induces an inhomogeneous temperature distribution. On the other hand, although the constancy of the heating rate in TG is generally assumed when a linear heating program is used, this constancy is slightly affected as the reaction takes place. Smaller samples and lower heating rates (i.e., ideal conditions) reduce this influence.[25] For this reason, we chose small samples (4–5 mg) and a relatively low heating rate (5 K/min) in this study.

Table III also contains the kinetic parameters obtained by means of other methods. Only the van Krevelen et al.[22] method led to quite similar E values [range = 313–379 kJ/mol, compared to 304–367 kJ/mol obtained by means of the general analytical equation (i.e., relative error as low as 3%)]. The Coats and Redfern[23] method (to be applied when $RT \leq E$) underevaluated E (range = 234–288 kJ/mol; relative error = 22%), whereas the differential method led to overevaluations (range = 375–478 kJ/mol; the relative error as high as 30%). Methods based on the second conversion derivative (e.g., the Freeman and Carroll[26] and Vachuska and Voboril[27] methods) led to very poor fitting by linear regression.

On the other hand, A^* was lower for the homopolymer P(3-HB) with respect to the P(3-HB-*co*-3-HV) copolymers. There was a compensation factor between A^* (in logarithmic form) and E:

$$\ln A\ (s^{-1}) = -6.2423 + 0.2256E\ (\text{kJ/mol})\ r^2 = 0.997 \quad (15)$$

This equation clearly indicated that A^* decreased when E increased.

Once A^* and E were evaluated, the conversion and conversion derivative were calculated by means of eqs. (8) and (5) and are plotted as curves in Figures 1 and 2, respectively. From these curves, it was possible to recalculate the conversion and conversion derivative at conditions of the maximum decomposition rate (see Table IV). The conversion at the maximum decomposition rate was approximately the same for all of the polymers (i.e., $f = 64\%$), and the maximum rate was 4.7–5.6% K^{-1}. The calculated T_m values were quite similar to the experimental values (differences $< 0.5\%$). Figures 1–4 represent the thermal fingerprints of the biopolymers. The conversion experimental data fitted well to the theoretical curve. However, as expected, a certain disparity became visible for the derivative. For this reason, the application of methods

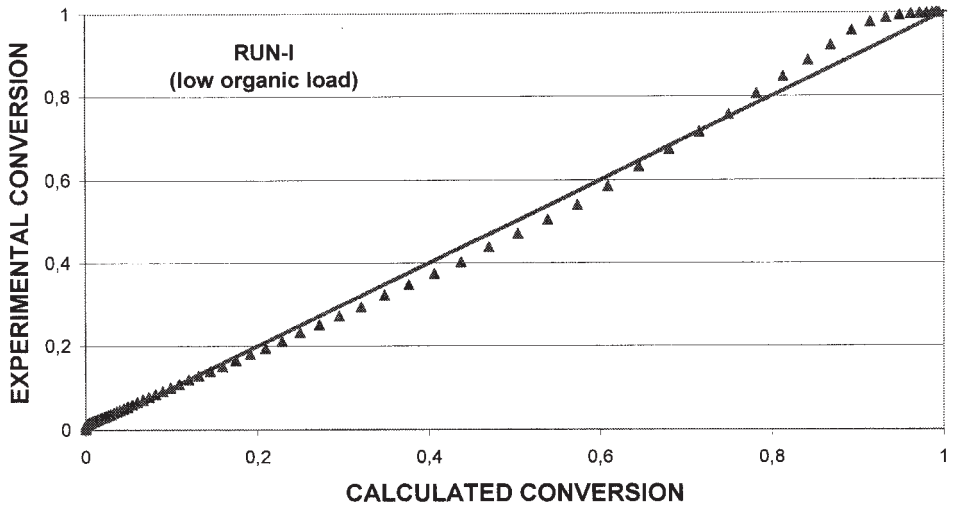

Figure 5 Comparison of the experimental values of the conversion and the values obtained by adjustment of the kinetic model for our biopolymer P(3-HB-*co*-3-HV) for run I (organic load = 8.5 gCOD/L).

based on derivatives can generate imprecise kinetic parameters.

The calculation of the characteristic temperatures of the decomposition reaction was carried out by means of eqs. (13) and (14), with calculated values (T_m and E), obtained through linear regression. These characteristic temperatures represent the temperatures at which the thermal decomposition reaction began and ended. In addition, because they were calculated with values obtained from the kinetic model that considers the set of experimental points, they offered a great deal of precision. The T_{c0} values for the Biopol biopolymers were 253.6 and 266.9°C for P(3-HB) and P(3-HB-*co*-3-HV), respectively. This indicated that the presence of HV within the copolymer led to a thermally more stable material (i.e., an increase of 13.3°C). For our biopolymers, these temperatures were 253.9 and 259.9°C for run I (organic load = 8.5 gCOD/L) and run II (organic load = 20 gCOD/L), respectively. In this case, the T_{c0} difference was less important because, in both runs, the copolymer contained approximately the same HV content (only a different chemical configuration may have been present). Because our biopolymers were stable up to 254–260°C, these plastics could be industrially processed. On the other hand, T_{c1} values for the Biopol biopolymers were 276.1 and 288.5°C for P(3-HB) and P(3-HB-*co*-3-HV), respectively (i.e., an increase of 12.4°C). For our biopolymers, these temperatures were 273.7 and 278.8°C for run I (organic load = 8.5 gCOD/L) and run II (organic load = 20 gCOD/L), respectively. Again, the T_{c1} difference was less important because, in both runs, the copolymer contained approximately the same HV content. The theoretical characteristic temperatures were quite similar to experimental temperatures of thermal stability. Indeed, T_5 values were 3% lower than T_{c0}, and T_{95} values were 0.5% higher than T_{c1}. The entire thermal decomposition took place in a narrow temperature interval (mean value = 20°C). With the same operating conditions, the temperature interval was considerably higher for the thermal decomposition of polystyrene ($\Delta T_{c1} - T_{c0} = 65$°C).[25]

Because of the approximate constancy of terms between brackets in eqs. (13) and (14), a relationship between characteristic temperatures and the temperature at the maximum decomposition rate for all of the biopolymers, independently of their preparation method, was obtained:

$$T_{c0}\,(°C) = 0.9756 T_m\,(°C) \quad (16)$$

$$T_{c1}\,(°C) = 1.0136 T_m\,(°C) \quad (17)$$

When eqs. (16) and (17) were considered, the temperature interval for the thermal decomposition followed

TABLE IV
Calculated Values of Variables at the Maximum Decomposition Rate and Characteristic Temperatures

	f_m	$(df/dT)_m$ (K^{-1})	T_m (°C)	T_{c0} (°C)	T_{c1} (°C)	ΔT_c (°C)
Biopol P(3-HB)	0.644	4.73×10^{-2}	268.0	253.6	276.1	22.5
Biopol P(3-HB-*co*-3-HV)	0.636	4.82×10^{-2}	280.7	266.9	288.5	21.6
P(3-HB-*co*-3-HV), run I	0.645	5.37×10^{-2}	266.7	253.9	273.7	19.8
P(3-HB-*co*-3-HV), run II	0.644	5.61×10^{-2}	272.0	259.9	278.8	18.9

readily, and it was approximately 26 times lower than T_m, which indicated again that the PHA decomposition took place within a narrow interval of temperatures.

CONCLUSIONS

Two types of biopolymers were used: (1) commercial biopolymers (Biopol) produced by means of pure cultures with HV contents of 0 and 10.4 mol % and (2) our biopolymers produced with an enriched activated sludge and a substrate containing organic acids (acetic, lactic, and propionic acids) at two organic loads (8.5 and 20 gCOD/L) with HV contents in both cases of 20 mol %. Thermograms clearly indicated that was only a decomposition reaction in a narrow temperature range (i.e., 20°C) in all cases. The thermograms corroborated that all of the samples contained only organic matter (no water and no inorganic residue were found). Two experimental temperatures related to the thermal stability of the polymers were determined from the TG data: T_5 (i.e., the onset of degradation) and T_{95} (i.e., end of degradation). The T_5 values for Biopol biopolymers were 246.3 and 260.4°C for P(3-HB) and P(3-HB-*co*-3-HV), respectively. This indicated that the presence of HV within the copolymer led to a thermally more stable material (with an increase of 14.1°C). For our biopolymers, these temperatures were 247.1 and 253.0°C for run I (organic load = 8.5 gCOD/L) and run II (organic load = 20 gCOD/L), respectively, which indicated that the biopolymer produced at a higher organic load was slightly more stable. In this case, the T_5 difference was less important because, in both runs, the copolymer contained approximately the same HV content. The difference in thermal stability was attributed to a different macromolecular configuration or/and molecular weight. On the other hand, two theoretical characteristic temperatures were evaluated: T_{c0} and T_{c1}. The values obtained were quite close to the experimental T_5 and T_{95} values. On the other hand, the temperature at the maximum decomposition rate also depended on the PHA preparation method. As for the Biopol biopolymers, T_m increased from 268.0 to 280.7°C (i.e., an increase of 12.7°C) when the biopolymer contained HV units, but the decomposition rate was approximately the same (mean value = 6.2% K^{-1}). In the case of our copolymers, the T_m values were 266.7 and 272.0°C, respectively, for runs I and II (organic loads = 8.5 and 20 gCOD/L; i.e., a difference of 5.3°C), with both temperatures slightly lower than those of the Biopol copolymers. The decomposition rate of our copolymers was quite constant for both experimental procedures (mean value = 6.9% K^{-1}).

With the aim of determining the kinetic parameters of the decomposition reactions, we used the general analytical solution. By performing an ANOVA, we obtained results for F that indicated that the best order of reaction corresponded to the first order. The adjustments were excellent (r^2 = 0.97–0.99) for all of the biopo1ymers through the entire conversion range (f = 5–95%). This finding indicated that the thermal decomposition of PHA occurred through a simple reaction mechanism; this supported the hypothesis that the controlling step was the depolymerization of the macromolecular chains. The results clearly indicate an increase in E with increasing HV content (304.1, 325.4, and 344.3–367.4 kJ/mol for biopolymers containing 0, 10.4, and 20% HV, respectively). Moreover, the organic load used in our experiments also showed an influence on this kinetic parameter (344.3 and 367.4 kJ/mol for lower and higher organic loads, respectively). The confidence interval for E was as low as 1.2–2.5 kJ/mol (i.e., 0.4–0.7% of E). The kinetic parameters were also evaluated by means of other methods. The van Krevelen et al.[22] method led to quite similar E values (313–379 kJ/mol) compared to those obtained by means of the general analytical solution (304–367 kJ/mol; i.e., relative error as low as 3%). The Coats and Redfern[23] method underevaluated E (range = 234–288 kJ/mol; i.e., relative error of 22%), whereas the differential method led to overevaluations (range = 375–478 kJ/mol; i.e., relative error as high as 30%). Methods based on the second conversion derivative (e.g., the Freeman and Carroll[26] and Vachuska and Voboril[27] methods) led to very poor fitting by linear regression.

One of the authors (F.C.) thanks the Ministry of Education, Culture and Sport of the Spanish government for financing his research visit to the Department of Chemistry of the University of Rome "La Sapienza."

References

1. Lee, S. Y. Biotechnol Bioeng 1996, 49, 1.
2. Carrasco, F.; Dionisi, D.; Majone, M.; Petrangeli Papini, M.; Carucci, G.; Beccari, M. Ing Quim (Madrid) 2004, 36(414), 244.
3. Salehizadeh, H.; van Loosdrecht, M. C. M. Biotechnol Adv 2004, 22, 261.
4. Choi, J.; Lee, S. Y. Appl Microbiol Biotechnol 2000, 53, 646.
5. Hassan, M. A.; Shirai, Y.; Kusubayashi, N.; Abdul Karim, M. I.; Nakanishi, K.; Hashimoto, K. J Ferment Bioeng 1996, 82, 151.
6. Hassan, M. A.; Shirai, Y.; Kusubayashi, N.; Abdul Karim, M. I.; Nakanishi, K.; Hashimoto, K. J Ferment Bioeng 1997, 83, 485.
7. Hassan, M. A.; Shirai, Y.; Umeki, H.; Abdul Karim, M. I.; Nakanishi, K.; Hashimoto, K. Biosci Biotechnol Biochem 1997, 61, 1465.
8. Meesters, K. H. P., Report of the Technical University of Delft, Delft (The Netherlands), 1998. Production of Poly(3-hydroxyalcanoates) from Waste Streams.
9. Dionisi, D.; Carucci, G.; Petrangeli Papini, M.; Riccardi, C.; Majone, M.; Carrasco, F. Water Res, 2005, 39, 2076.
10. Ugoj, E. O. Renewable Energy 1997, 10, 291.
11. Carucci, G.; Carrasco, F.; Trifoni, K.; Majone, M.; Beccari, M. J. Environ Eng 2005, 131, 1037.
12. Beccari, M.; Bonemazzi, F.; Majone, M.; Riccardi, C. Water Res 1996, 30, 183.

13. Beccari, M.; Carucci, G.; Majone, M.; Torrisi, L. Environ Technol 1999, 20, 105.
14. Zervakis, G.; Yiatras, P.; Balis, C. Int Biodeter Biodegrad 1996, 38, 237.
15. Ahmad, A. L.; Ismail, S.; Bhatia, S. Desalination 2003, 157, 87.
16. Dionisi, D.; Majone, M.; Papa, V.; Beccari, M. Biotechnol Bioeng 2004, 85, 569.
17. Majone, M.; Dircks, K.; Beun, J. J. Water Sci Technol 1999, 39, 61.
18. Dickens, B. Polym Degrad Stab 1980, 2, 249.
19. Lee, M. L.; Lee, T. S.; Park, W. H. Macromol Chem Phys 2001, 202, 1257.
20. Altofer, R. Thermochim Acta 1978, 24, 17.
21. Carrasco, F. Thermochim Acta 1993, 213, 115.
22. van Krevelen, D. W.; van Heerden, C.; Huntjens, F. J. Fuel 1951, 30, 253.
23. Coats, A. W.; Redfern, J. P. J Polym Sci Part B: Polym Lett 1965, 3, 917.
24. Heitz, M.; Carrasco, F.; Chornet, E.; Overend, R. P. Thermochim Acta 1989, 142, 83.
25. Carrasco, F.; Pages, P. J Appl Polym Sci 1996, 61, 187.
26. Freeman, E. S.; Carroll, B. J Phys Chem 1958, 62, 394.
27. Vachuska, J.; Voboril, M. Thermochim Acta 1971, 2, 379.