

Thermal Stability of P(HB-co-HV) and Its Blends with Polyalcohols: Crystallinity, Mechanical Properties, and Kinetics of Degradation

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ABSTRACT: The thermal stability of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(HB-co-HV)] and its blends with poly(propylene glycol)s (PPGs) and castor oil (CO) is reported. The study includes the determination of the degradation kinetics of these materials and the analysis of the effects of the degradation on the mechanical properties and crystallization behavior. Spectroscopy (¹H-NMR, FTIR), differential scanning calorimetry (DSC), thermogravimetry, and tensile testing techniques are used for the experimental analysis. A chain-scission degradation mechanism is confirmed by the formation of vinyl groups. Two temperature ranges are investigated. In the range closest to the melting point, 100–200°C, where the blend does not exhibit weight reduction, a fast and sensible loss of molecular weight and tensile strength was detected. The second temperature range, 200–400°C, is characterized by mass loss by pyrolysis. In this range, different kinetic models of the degradation process are proposed. Polyalcohol addition produces opposite effects, while the addition of PPG enhances the degradation of P(HB-co-HV). When CO is added, the thermal stability of the blend increases. Mechanical properties of the blends before and after degradation were determined. The tensile modulus increases at the first step of degradation and decreases with the degradation time. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2889–2900, 2000

Key words: thermal stability; degradation; kinetics; polyhydroxyalkanoates; blends

INTRODUCTION

Poly(β -hydroxyalkanoate)s (PHAs) are named “green thermoplastics” because these materials

are naturally biodegradable thermoplastics.¹ Poly(β -hydroxybutyrate) (PHB) and its copolymer β -hydroxybutyrate/ β -hydroxyvalerate (PHB-co-HV) are principal types of PHAs. Although the properties of these biodegradable polymers are often compared with polypropylene,² PHAs have a very narrow processing window due to their poor thermal stability³ (the degradation interval starts close to the melting point) and to their very high viscosity. Moreover, the utility of these ma-

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terials is limited as a consequence of their relatively high melting point, which requires processing temperatures of at least of 190°C, and under these conditions, the molecular weight decreases rapidly.⁴ To reduce degradation risks, Holmes⁵ demonstrated that samples of P(3HB-co-3HV) could be injected, in practice, at a temperature below 165°C.

Polyalcohols are usually used as additives for thermoplastics in order to improve their processing behavior. However, the incorporation of this compound to P(HB-co-HV) copolymers could result in substantial changes in the surface and bulk properties of the polymer matrix. In principle, blending of PHB-co-HV with polyalcohol may provide a wide range of morphologies and physical properties determining a strong modification of characteristics and possible applications of the original polymer matrix.⁶

Some studies of the thermal degradation of PHAs have been reported; however, this topic has not been completely clarified yet. Kunioka and Doi⁷ studied the thermal degradation process of microbial copolyesters in the temperature range of 100–200°C by monitoring the time-temperature changes in the molecular weight of the melt samples. Two types of copolyester were used: P(3HB-co-3HV) and P(4HB-co-4HV). They found that all copolyesters are thermally unstable at temperatures above 170°C and their molecular weight decreases rapidly with time. The mechanism of chain scission at ester groups was investigated by NMR analysis of thermally degraded P(3HB) oligomers.

Grassie et al.⁸ studied the degradation of P(3HB) in the same temperature range and it was proved that the chain scission is completely random and no volatilization occurs during the thermal degradation of the copolyester samples. The rate constant of the random chain scission was not influenced by the composition of the copolyester but was strongly dependent upon the temperature.⁹ The activation energy of random chain scission was 212 kJ mol⁻¹ in the temperature range of 170–200°C. Figure 1 shows the six-member ring ester decomposition mechanism or β -CH hydrogen transfer involving the cleavage of the ester group.^{10,11}

Abate et al.¹² studied the thermal degradation of P(3HB), P(4HB), and P(3HB-co-4HB) copolymers containing 3–34% of 3HB units in the range of 180–200°C. They showed that P(4HB) shows lower depolymerization kinetics with respect to

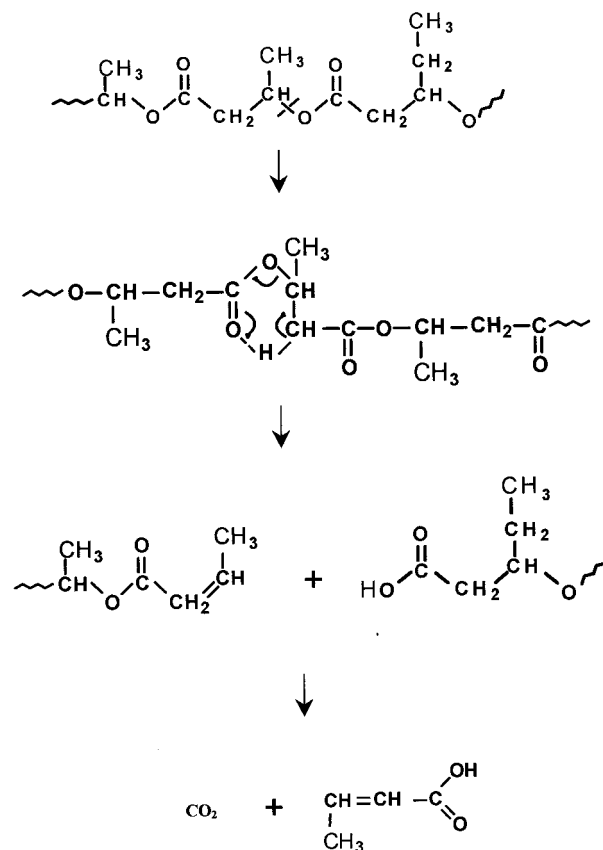


Figure 1 Chain-scission mechanism of degradation of biodegradable polyester at ester groups.

P(3HB), while the P(3HB-co-4HB) sample has an intermediate rate of depolymerization. This behavior, contrary to the earlier reports of Kunioka and Doi,⁷ clearly shows that the k_d value of random chain scission is influenced by the copolymer composition. They also indicated that the P(3HB-co-4HB) copolymers undergo thermal degradation by two competitive random chain-scission mechanisms: a β -CH hydrogen transfer at the 3HB units and an ester exchange cyclation at the 4HB units.

Kopinke et al.¹³ studied the thermal decomposition of PHB using several thermoanalytical techniques: thermogravimetry (TGA), differential scanning calorimetry (DSC), and pyrolysis with gas chromatography. The temperature range studied was 200–400°C at a heating rate of 10°C min⁻¹. The authors proposed an n th-order reaction for the global kinetic model of the degradation of the PHB homopolymer.

If the weight loss during degradation is associated to the depolymerization reaction, the degree of depolymerization can be defined as

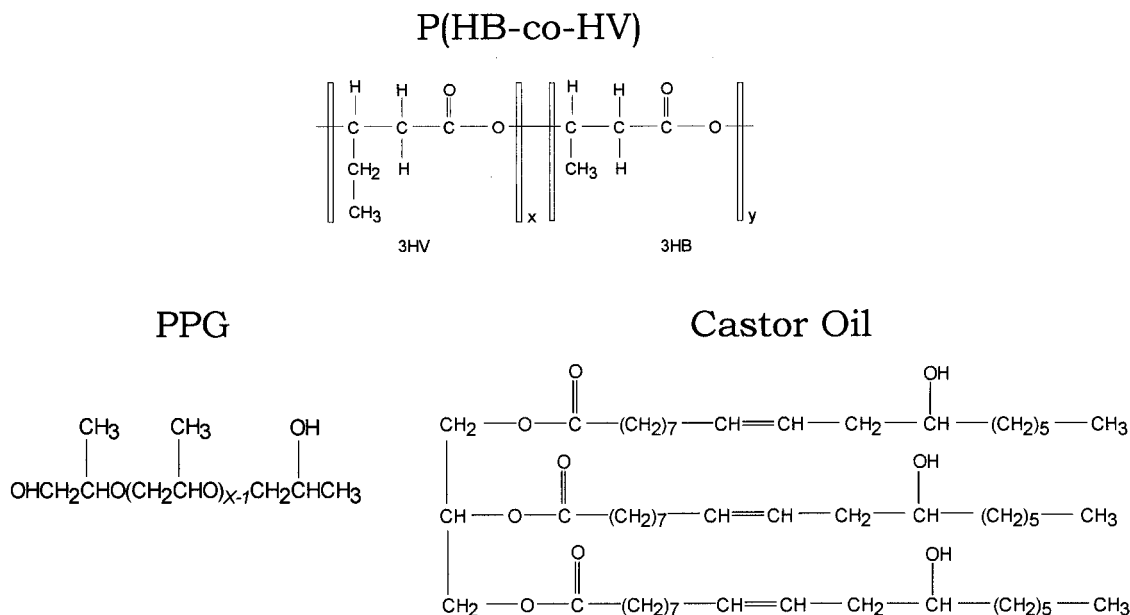


Figure 2 Chemical structure of P(HB-co-HV), PPG, and CO.

$$\alpha = (\omega_0 - \omega) / (\omega_0 - \omega_f) \quad (1)$$

where ω_0 is the initial mass; ω , the weight at any time; and ω_f , the weight at the end of the TGA run. Then, the n th-order degradation kinetic equation is defined as follows:

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right) (1 - \alpha)^n \quad (2)$$

where k_0 is the preexponential factor; E_a , the apparent activation energy; and n , the apparent reaction order. Kopinke et al. obtained values of $E_a = 380$ kJ/mol and $n = 1.5$ for PHB degradation. From the DSC experiments, they reported an activation energy of 235 kJ/mol; however, during the DSC experiments, volatilization of the sample occurs and the mass and thermal capacity of the material is continuously changing during the run. For this reason, this result cannot be compared with the one obtained from the TGA tests.

Galego and Rozsa¹⁴ also studied the thermal decomposition of PHB and its copolymers. The thermal stability of PHB copolymers slightly decreases with an increasing fraction of the 3HV comonomer. The results obtained in the dynamic thermogravimetric experiments are consistent with the n th-order reaction reported by Kopinke

et al.¹³ Moreover, they found that the activation energy changes with the composition of the comonomers, from the PHB homopolymer to the PHB-co-24%HV (296 to 233 kJ/mol), in agreement with results reported by Abate et al.¹²

Yoon et al.¹⁵ performed a theoretical calculation of the number-average molecular weight and of the polydispersity of microbial polyesters as they degrade by random chain scission and compared their findings with the experimental data reported by Kunioka and Doi⁷ and Lauzier et al.¹⁶

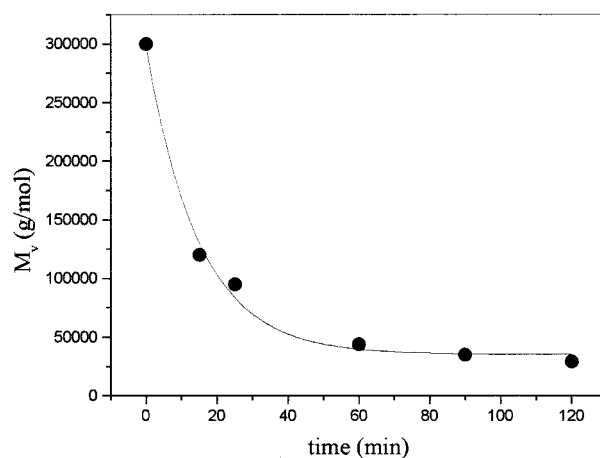


Figure 3 Viscosity-average molecular weight, M_v , as a function of the degradation time at 175°C.

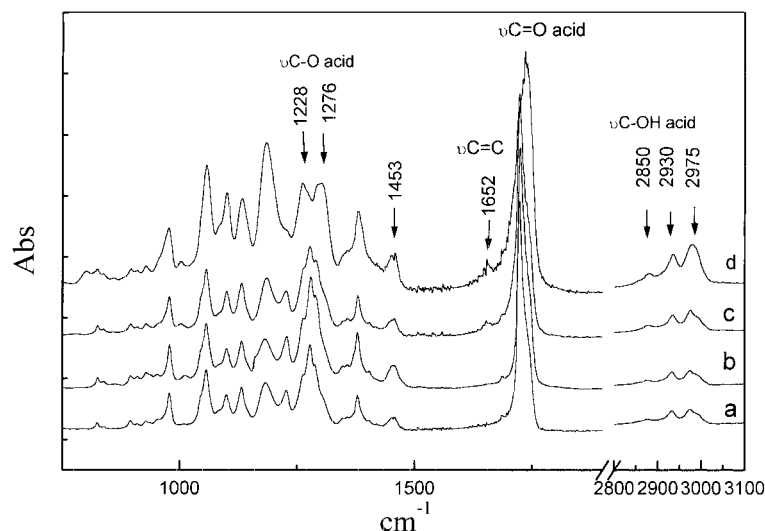


Figure 4 FTIR spectra of P(HB-*co*-HV): (a) before degradation; (b) after heating at 175°C for 30 min; (c) after heating at 175°C for 120 min; (d) after heating at 240°C for 12 min.

They showed that the major portion of polydispersity changes occur during the early stage of the isothermal degradation of the polymer. The polydispersity index will reach the value of 2 after degradation at a low-temperature range. However, as the degradation reaches the final stage and the polymer degrades completely to a monomeric species, the polydispersity index should approach 1.

The effect of the hydrolytic and biodegradation time and temperature on the crystallizing conditions and nucleation density on the resultant structure in PHB was studied by several authors.^{16–19} However, the effects of the degradation on the crystallinity and mechanical properties of the copolymers PHB-*co*-HV and of their blends with polyalcohols were not studied.

The objective of our study was the analysis of the thermal stability of the copolymer PHB-*co*-HV and of its blends with poly(propylene glycol) (PPG) and castor oil (CO). These kinds of polyalcohols could be used as processing additives to reduce the viscosity of the copolymer. However, it would be very important to assess the eventual exposure to degradation conditions during melt extrusion. During the extrusion processing, the material can be exposed at high temperature and the knowledge of the thermal stability of this compound is very important for choosing the material. If the material is exposed at low temperature or a short time, only the break of the chain

can occur. Besides, if the exposure of the copolymer is for more time or temperature, the volatilization of part of the blend is possible. The studied range of temperatures will be from the melting point up to very high degradation temperatures characterized by high and fast mass loss. The effects of the degradation on the mechanical properties and their relationship with the structure of the materials studied were also analyzed.

EXPERIMENTAL

Materials

A poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) copolymer [P(HB-*co*-HV)], containing 8% wt of HV purchased from Aldrich (USA), was used ($M_w = 296,000$) as the main constituent of the blends. Two types of polyalcohols were used for the blend preparation: CO from Pharmos S.A. (BsAs, Argentina), with a hydroxyl equivalent weight of 340 g/equiv, and two types of PPG, PPG400 and PPG1000, supplied by Noren Plast S.A. (BsAs, Argentina) with average molecular weights of 400 and 1000, respectively. Both glycols are liquid at room temperature.

The chemical structure of P(HB-*co*-HV) and the polyalcohols are shown in Figure 2. It should be noticed that CO is typically said to be 80 or 90% pure; this value refers to the purity of the total

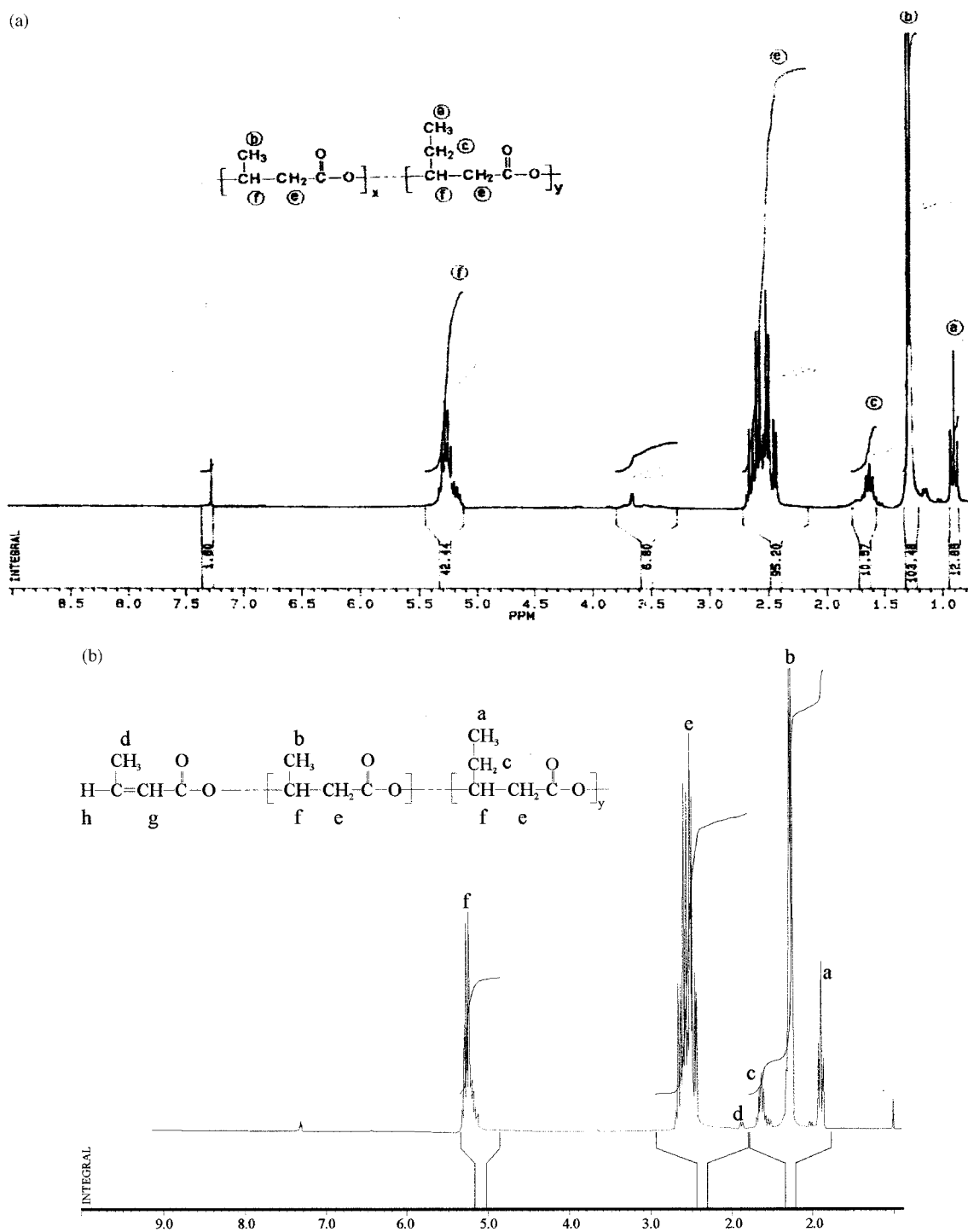


Figure 5 $^1\text{H-NMR}$ spectra of P(HB-co-HV): (a) before degradation; (b) after heating at 175°C for 30 min.

acid components composing triglyceride and does not mean that, for instance, CO is 90% pure triglyceride of ricinoleic acid. Thus, CO contains mostly triricinoleic and diricinoleic.²⁰

Blends of the P(HB-co-HV) copolymer and different polyalcohols (50% wt/wt) were prepared by casting from a chloroform solution (10% wt/v) at room temperature. The films were

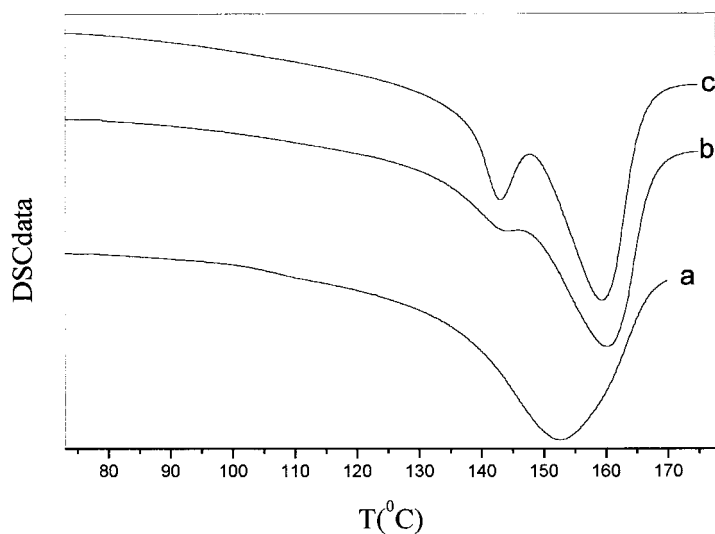


Figure 6 Dynamic DSC thermograms at 10°C/min of degraded samples of P(HB-co-HV) copolymer held at 175°C at different degradation times: (a) $t = 0$; (b) $t = 30$ min; (c) $t = 60$ min.

dried at room temperature to allow the evaporation of the solvent and kept at room temperature more than 15 days to allow the final crystallinity to develop.²¹ Film thickness was close to 0.2 mm.

Methods

Viscosity-average molecular weight measurements were carried out with an Ubbelohde capillary viscometer at $30^\circ \pm 0.01^\circ$ in a chloroform solution ($a = 0.78$ and $K = 11.8 \times 10^{-5}$ dL/g).¹⁶ Thermogravimetric analysis (TGA) was performed with a Mettler TA 4000 thermogravimeter. Dynamic tests were performed at 10°C/min in the temperature interval of 25–500°C. Sample weight was 3–7 mg. Kinetic runs for the P(HB-co-HV) copolymer were performed in an isothermal mode and a dynamic mode under a nitrogen atmosphere.

Spectrometric ¹H-NMR tests were carried out at 300 K using a Brücker AC 250F spectrometer at 250 MHz (¹H). Samples were analyzed in 5-mm tubes in chloroform- δ . The spectra were referenced to internal TMS.

A Shimadzu DSC-50 was used for the DSC. After isothermal tests were conducted at different times, the sample was quenched in dry ice and then a dynamic run was performed from 25 to 190°C at a heating rate of 10°C/min under a nitrogen atmosphere.

Infrared measurements were carried out with a Brüker IFS25 spectrometer. All reported spec-

tra were baseline-corrected. A total of 100 scans were recorded for each sample. Thin-film copolymers and their blends were cast from 10 mg/mL solutions in CHCl₃ on a NaCl window. The films

Table I DSC Results on the Crystallization Behavior of PHB-co-HV and Its Blends with PPG and CO

Time (min)	T_g (°C)	ΔH_f (J/g)	ΔT (°C)
PHB-co-HB			
0	152.6	64.6	53
30	160.2	61.1	40
60	159.3	61.4	32
120	154.8	61.3	30
PHB-co-HV/PPG400			
0	150.6	71.7	46
15	144.7	59.9	39
60	141.6	61.0	33
90	139.8	55.9	31
120	138.9	53.4	29
PHB-co-HV/PPG1000			
0	153.4	77.7	58
15	147.4	60.3	40
60	143.2	51.8	33
90	140.9	46.6	29
120	136.9	37.9	28
PHB-co-HV/CO			
0	150.2	74.5	50
25	156.9	67.4	30
60	154.6	66.8	27
90	152.5	65.2	24
120	149.2	62.0	24

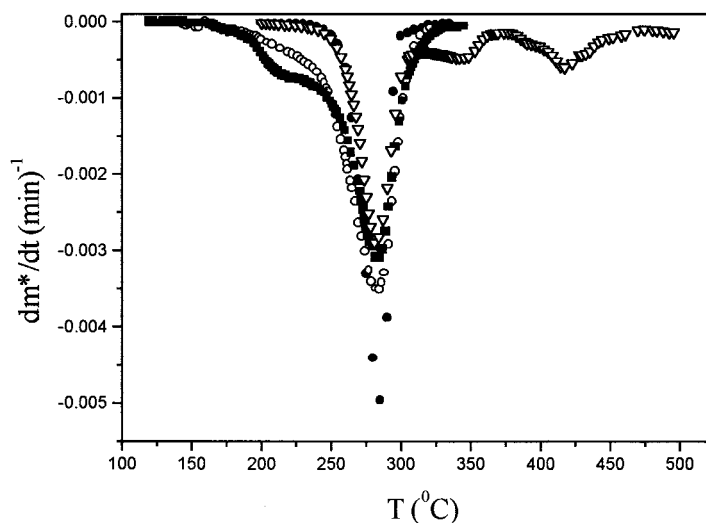


Figure 7 Dynamic TGA thermograms at 10°C/min of P(HB-co-HV) and its blends with polyalcohols: (●) P(HB-co-HV); (■) P(HB-co-HV)/PPG400; (□) P(HV-co-HB)/PPG1000; (▽) P(HB-co-HV)/CO.

were dried at room temperature. Complete removal of CHCl_3 was confirmed by FTIR.

Tensile properties were determined from cut bone-shaped films (25 × 3mm) in an Instron 4467 dynamometer at a testing speed of 10 mm/min. Stress values were calculated using the initial thickness and width of each sample.

RESULTS AND DISCUSSION

Thermal Stability of the Copolymer (PHB-co-HV)

Thermal degradation studies on the neat copolymer P(HB-co-HV) were carried out for different times at 175°C, a temperature where no mass loss was detected by the TGA experiments. Different experimental determinations were carried out on the degraded samples as a function of the degradation time. Results of the viscosity-average molecular weight, M_v , determined as a function of the degradation time and reported in Figure 3, demonstrate that a high decrease of the molecular weight is produced during the first 15 min.

Samples degraded for 30 min at 175 and 240°C were analyzed by FTIR. Figure 4 shows the spectrum of the degraded sample at 240°C where carbonyl and double-bond peaks are shown. The peak of the double bonds did not appear in the sample treated for 30 min at 175°C. However, it does appear if the time is longer, as can be seen in

Figure 4. The carbonyl peak is shifted to lower cm^{-1} because the ester $\text{C}=\text{O}$ is conjugated with $\text{C}=\text{C}$ groups. The $^1\text{H-NMR}$ spectrum of the degraded sample at 175°C, reported in Figure 5, shows a signal at 2.9 ppm that is attributed to the methylic protons in the ending vinyl group (called *d*). The low signal intensity is due to the small quantity of vinyl protons in the macromolecule. The FTIR and $^1\text{H-NMR}$ results confirm that the mechanism of degradation can be explained in terms of chain scission of the ester linkages, which leads to the formation of crotonic acid (see Fig. 1).

Table II TGA Results on the Thermal Decomposition of P(HB-co-HV) and Its Blends with PPG400, PPG100, and CO

Sample	T_{max} (°C)	T_{onset} (°C)	E_a (kJ/mol)
P(HB-co-HV)	284	235	310
P(HB-co-HV)/PPG400	282 191	158	150
P(HB-co-HV)/PPG1000	283 207	163	131
P(HB-co-HV)/CO	280 345 417	227	223

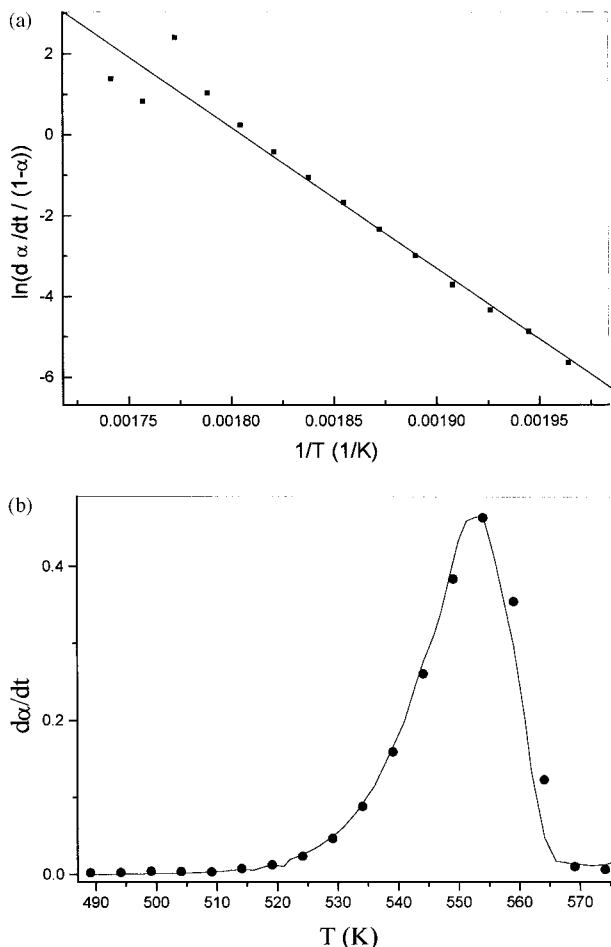


Figure 8 Application of the order 1 model to the degradation of P(HB-co-HV) copolymer: (a) determination of the preexponential factor and the activation energy values; (b) (—) comparison of model predictions and (●) experimental results.

Thermal Stability of the Blends

The thermal stability of the copolymer and its blends was also analyzed by DSC. In a previous work,⁶ it was already shown that the blends are immiscible as a result of the independence of the melting point and glass transition temperature values of the blends from the polyalcohol content. Dynamic DSC tests were carried out on isothermally degraded samples at 175°C (see Fig. 6). The peak observed at higher temperature, T_p , corresponds to crystal melting, while the second peak that starts to appear in the thermograms obtained after a certain degradation time can be attributed to a secondary crystallization melting peak. The peak temperature, T_p , the melting en-

thalpy, ΔH_f (J/g copolymer), and the distribution of the lamella thickness²² were analyzed. The distribution of the lamella thickness can be represented by $\Delta T = T_p - T_{m0}$, where T_p is the melting point of crystallites with a determined lamella thickness and T_{m0} is the onset value which corresponds to the melting of crystallites with a smaller lamella thickness.

Results obtained on the effects of the degradation time on the crystallization behavior of the different materials studied are reported in Table I. The melting enthalpy of the samples crystallized after isothermal degradation decreases with the degradation time. In all the cases, polyalcohol addition increases the reduction of the melting enthalpy of the PHB-co-HV. The highest decrease, associated with the lowest value of crystallinity, was obtained for PPG1000 and PPG400. On the other hand, CO blends showed the opposite behavior with a slight increase of the melting enthalpy. The melting point also decreased in almost all the cases, except for the neat PHB-co-HV, which shows a maximum of the melting point at short degradation times. In this case, it can be assumed that the first stage of the degradation process is characterized by random scission of the ester links that not only reduces the molecular weight, but also reduces entanglements, allowing the reorganization of the lamella morphology. The highest value of the melting temperature, T_p (at 120 min and 175°C), obtained for the P(HB-co-HV)/CO blend could be related to its higher molecular weight compared with PPG1000 or PPG400.

Degradation Kinetics

The thermal decomposition of the blends was also studied by thermogravimetry. Dynamic TGA thermograms obtained at 10°C/min for P(HB-co-HV) and their blends with polyalcohols are shown in Figure 7. Thermogravimetric results are shown in Table II in terms of the onset temperature (T_{onset}) and the maximum temperature (T_{max}) of the degradation peaks. From Table II, it can be concluded that the PPG addition produces a shift of the degradation interval to lower temperatures with respect to the neat P(HB-co-HV), while the addition of CO produces the opposite effect, leading to a more thermally stable blend.

To compare our results with those reported in the literature, the degradation reaction was modeled with a global kinetic expression similar to

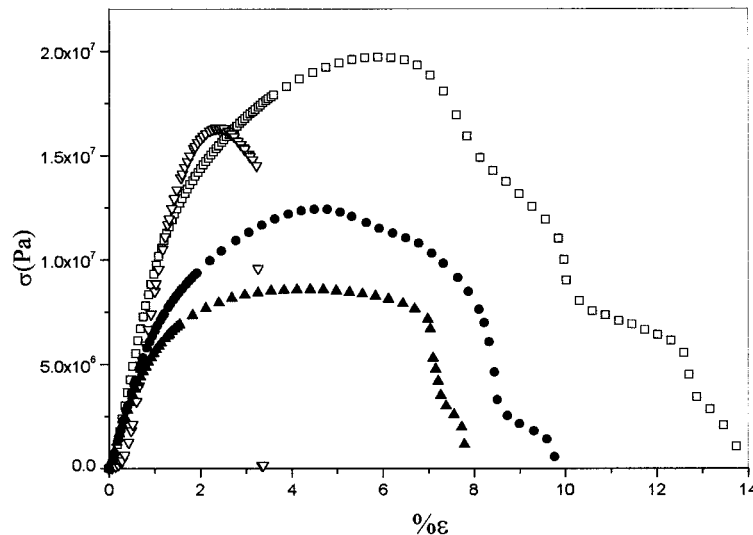


Figure 9 Tensile test results for the degraded copolymer P(HB-co-HV) samples for 10 min at different temperatures: (□) without degradation; (▽) 175°C; (●) 184°C; (▲) 190°C.

the one proposed by Kopinke et al.¹³ Then, the following expression was used for an order 1 degradation reaction:

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right) (1 - \alpha) \quad (3)$$

The values of the calculated apparent activation energy corresponding to eq. (3) of all the materials studied are reported in Table II. The determina-

tion of the activation energy and the comparison of experimental and model results for P(HB-co-HV) are shown in Figure 8. To compare the effects of blending on the apparent activation energy, only the peak of P(HB-co-HV) was taken into account for modeling purposes.

Typical values of the apparent activation energy of gas-phase pyrolysis are in the range of 175–200 kJ/mol². Then, it can be concluded that the values of the apparent activation energy of

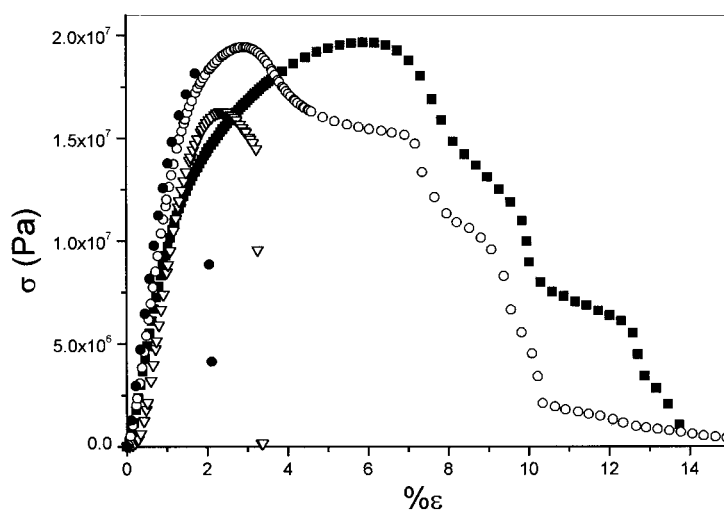


Figure 10 Tensile test results for degraded samples at 175°C and different times: *t* = (■) 0 min, (○) 5 min, (▽) 10 min, and (●) 15 min.

Table III Mechanical Properties of the Copolymer P(HB-co-HV) and Its Blends with PPG1000, PPG400, and CO Before and After Degradation at 175°C

Sample	Elongation at Break (%)	Tensile Modulus (MPa)
P(HB-co-HV)	11.4 ± 3.0	1009 ± 22
P(HB-co-HV) 175°C, 10 min	3.4 ± 0.3	1017 ± 163
P(HB-co-HV)/PPG1000 (30%)	10.0 ± 2.3	511 ± 34
P(HB-co-HV)/PPG1000 (30%) 175°C, 10 min	7.4 ± 2.1	659 ± 84
P(HB-co-HV)/PPG400 (30%)	6.4 ± 0.8	493 ± 65
P(HB-co-HV)/PPG400 (30%) 175°C, 10 min	3.9 ± 1.2	599 ± 99
P(HB-co-HV)/CO (30%)	4.8 ± 0.4	390 ± 55
P(HB-co-HV)/CO (30%) 175°C, 10 min	4.0 ± 0.4	416 ± 17

P(HB-co-HV) reported here are similar to those reported in the literature for the random chain scission. The mechanism of degradation is the same shown in Figure 1: A chain scission mechanism produces lower molecular weight compounds that can volatilize. The apparent activation energy decreases with the addition of polyalcohols. However, the CO blend presents a higher apparent activation energy than that of the PPG blends, confirming its higher thermal stability.

Effects of Degradation on Mechanical Properties

The degradation process is accompanied by the loss of mechanical properties. Figure 9 shows the tensile stress-displacement curves for degraded and undegraded films at different temperatures. The elongation at break of P(HB-co-HV), which decreases during the first stage of the degradation, may be due to a higher degree of crystallinity. In the studied range, the maximum stress at break decreases with degradation time. Figure 10 shows the influence of the degradation kinetic on the mechanical properties. Table III shows a summary of the mechanical properties of the copolymer and its blends before and after 10 min of degradation at 175°C. The blend with CO was the more stable, confirming previous results in TGA.

Kinetic Analysis for Dynamic and Isothermal Runs

A simple order 1 kinetic model is not able to represent the degradation of the P(HB-co-HV) copolymer in isothermal and dynamic modes. In

fact, the degradation process is more complex than is the simple order 1 reaction assumed. Then, the pyrolysis of different compounds with different decomposition rates should be considered: (i) saturated ester in the original copolymer, (ii) an ester chain with an unsaturated ester as end group, and (iii) an ester chain with a carboxylic acid as the end group.¹² When the concentration of terminal chain ends with acid termination increases in the bulk, a higher rate may be found accordingly with an autocatalytic reaction where acid end groups catalyse the ester cleavage. Then, the following autocatalytic model of the degradation process is proposed:

$$d\alpha/dt = k(T)(1 - \alpha)^n \alpha^m \quad (4)$$

where α is the degree of depolymerization, and $k(T)$, the Arrhenius constant given by $k(T) = k_0 \cdot \text{Exp}(E_a/RT)$ and n and m are kinetic parameters. Figure 11(a,b) shows the determination of the kinetic parameters. Figure 11(a) shows the plot of $d\alpha/dt$ (min^{-1}) as a function of the degree of depolymerization for an isothermal TGA at 245°C for P(HB-co-HV), by determination of the preexponential factor and the n and m of the autocatalytic degradation model. Also, Figure 11(b) shows the Arrhenius plot fitting of the apparent rate constant (k) with temperature by determination of the preexponential factor k_0 and the activation energy values of the autocatalytic degradation model.

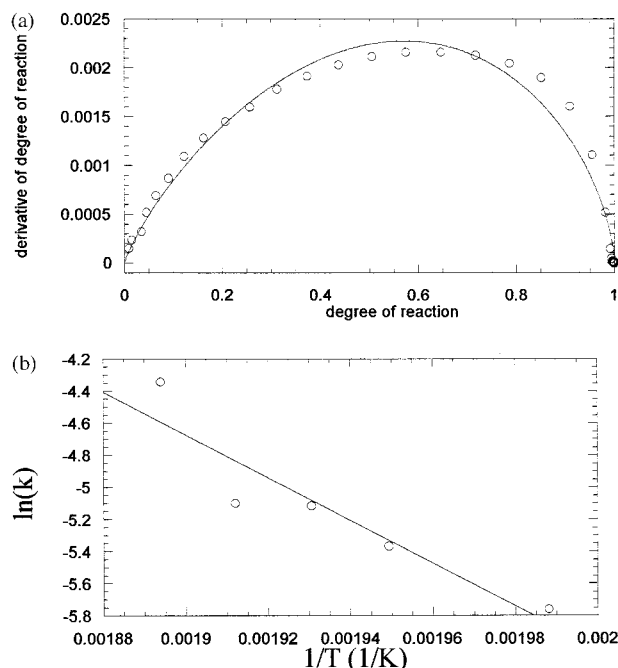


Figure 11 (a) $d\alpha/dt$ (min^{-1}) in function of degree of depolymerization for an isothermal TGA at 245°C for P(HB-co-HV). (b) Arrhenius plot fitting of the apparent rate constant (k) with temperature.

The following kinetic parameters of the autocatalytic model were calculated: $m = 0.8$, $n = 1$, $\ln k_0 = 20.6$, and $E_a = 111$ kJ/mol. A good agreement between the experimental results and the model predictions is shown in Figures 12 and 13 for isothermal and dynamic runs, respectively. These results confirm the ability of the autocatalytic model as a good general model for the degradation process of P(HB-co-HV) and its blends.

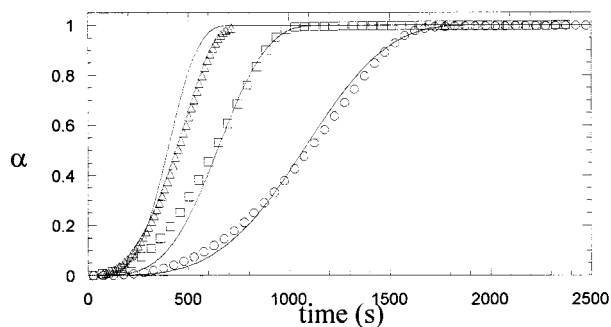


Figure 12 Comparison of (—) autocatalytic model predictions and experimental TGA results for the isothermal degradation of P(HB-co-HV) at different temperatures: (a) (○) 230°C ; (b) (□) 240°C ; (c) (△) 250°C .

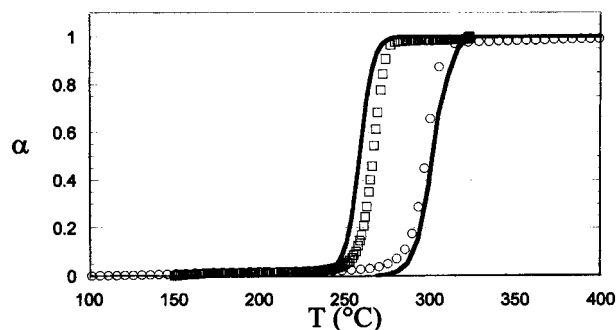


Figure 13 Comparison of (—) autocatalytic model predictions and experimental TGA results for the dynamic degradation of P(HB-co-HV) at different heating rates: (a) (○) $5^\circ\text{C}/\text{min}$; (b) (□) $30^\circ\text{C}/\text{min}$.

CONCLUSIONS

The thermal stability of the P(HB-co-HV) copolymer and its blends with polyalcohols was analyzed. While the addition of PPGs produces a reduction of the thermal stability of P(HB-co-HV), a small increase was observed in the CO-copolymer blend. Similar effects are observed in the changes of the mechanical properties as a function of the degradation time.

A *cis*-elimination mechanism is assumed as a representative of the degradation process. When a simple order 1 kinetic model was applied to the degradation process, similar activation energy values to those reported in the literature were obtained. However, to represent better the experimental results obtained under isothermal and dynamic thermal conditions, an autocatalytic kinetic model must be assumed, suggesting a catalytic action of the chain-scission products.

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REFERENCES

1. Lupke, T.; Joachim, H.; Metzner, K. *Macromol Symp* 1998, 127, 227–240.
2. Doi, Y. In *Microbial Polyesters*, VCH: New York, 1990.
3. Hammond, T.; Liggett, J. J. In *Degradable Polymers, Principles and Applications*, 1st ed.; Scott,

- G.; Gilead, D., Eds.; Chapman and Hall: Cambridge, UK, 1995; Chapter 5.
4. Resntard, R.; Karlsson, S.; Albertsson, A. C. *Macromol Symp* 1998, 127, 241–249.
 5. Holmes, P. A. In *Developments in Crystalline Polymers-2*; Bassett, D. C., Ed.; Elsevier: London, 1988; Chapter 1.
 6. Cyras, V. P.; Galego Fernández, N.; Vázquez, A. *Polym Int* 1999, 48, 705.
 7. Kunioka, M.; Doi, Y. *Macromolecules* 1990, 23, 1930–1936.
 8. Grassie, N.; Murray, E. J.; Holmes, P. A. *Polym Degrad Stab* 1984, 6, 95.
 9. Jellinek, H. H. G. In *Degradation of Vinyl Polymers*; Academic: New York, 1955.
 10. Grassie, N.; Murray, E. J.; Holmes, P. A. *Polym Degrad Stab* 1984, 6, 127.
 11. Morikawa, H.; Marchessault, R. H. *Can J Chem* 1981, 59, 2306.
 12. Abate, R.; Ballistreri, A.; Montaudo, G.; Giuffrida, M.; Impallomeni, G. *Macromolecules* 1995, 28, 7911–7916.
 13. Kopinke, F. D.; Remmler, M.; Mackenzie, K. *Polym Degrad Stab* 1996, 52, 25–38.
 14. Galego, N.; Rozsa, Ch. *Polym Int* 1999, 48, 1202.
 15. Yoon, J.-S.; Chin, I.-J.; Kim, M.-N.; Kim, C. *Macromolecules* 1996, 29, 3303–3307.
 16. Lauzier, C.; Revol, J.-F.; Debzi, E.-M.; Marchessault, R. H. *Polymer* 1994, 35, 4156–4162.
 17. Satoh, H.; Yoshie, N.; Inoue, Y. *Polymer* 1994, 35, 286–290.
 18. Timmins, M. R.; Lenz, R. W.; Clinton Fuller, R. *Polymer* 1997, 38, 551–562.
 19. Tomasi, G.; Scandola, M.; Briese, B. H.; Jendrossek, D. *Macromolecules* 1996, 29, 507–513.
 20. Barret, L. W.; Ferguson, G. S.; Sperling, L. M. *J Polym Sci Polym Chem* 1993, 31, 1287.
 21. Bloembergen, S.; Holden, D. A.; Hammer, G. K.; Bluhm, T. L.; Marchessault, R. H. *Macromolecules* 1986, 19, 2865.
 22. Msuya, W. F.; Yue, C. Y. *J Mater Sci Lett* 1989, 8, 1266–1286.