

# Thermal Analysis of High-Density Polyethylene and Low-Density Polyethylene with Enhanced Biodegradability

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**ABSTRACT:** The thermal properties of high-density polyethylene (HDPE) and low-density polyethylene (LDPE) filled with different biodegradable additives (Mater-Bi AF05H, Cornplast, and Bioeffect 72000) were investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The DSC traces of the additives indicated that they did not undergo any significant phase change or transition in the temperature region typically encountered by a commercial composting system. The TGA results showed that the presence of the additive led to a

thermally less stable matrix and higher residue percentages. The products obtained during the thermodegradation of these degradable polyolefins were similar to those from pure polyethylenes. The LDPE blends were thermally less stable than the HDPE blends. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 764–772, 2002

**Key words:** additives; biodegradable; differential scanning calorimetry (DSC); polyethylene (PE); thermogravimetric analysis (TGA)

## INTRODUCTION

The development of degradable polymers constitutes an important new approach in tackling the rapidly growing problem of plastic-based waste. Degradable plastics can be obtained either by the modification of inherently degradable polymers or by the incorporation, into nonbiodegradable polymers, of additives that increase their susceptibility to environmental degradation.<sup>1,2</sup> Polyolefins with enhanced biodegradability can be obtained with the latter method through the introduction of additives containing starch, in its granular or gelatinized form, into the polymeric matrix.<sup>3–10</sup>

Before an exploration of the application potential of these new biodegradable products, their thorough characterization, as well as an elucidation of the degradation, process must be undertaken. Because their processing and possible end uses will occur at elevated temperatures, the determination of their thermal properties is of prime importance. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are two widely used techniques in the study of the thermal properties of polymeric materials. TGA is used to probe the thermal stability of polymers and provides the kinetic parameters characterizing the decomposition process.<sup>11–13</sup> When a TGA analyzer is coupled to a mass spectrometer, it is also

possible to identify the chemical nature of the degradation products. Complimentary thermal data are provided by DSC, which provides information concerning transitions or phase changes exhibited by a sample.<sup>13</sup> Such structural and physical modifications lead to changes in the physical properties of the material, and if these occur at a temperature similar to that of degradation, these property changes may be wrongly attributed to the degradation process.<sup>14</sup> Therefore, the combination of these two thermal analysis techniques provides a complete overview of the thermal properties of a polymeric material. In this work, DSC and TGA were used to study the thermal properties of high-density polyethylene (HDPE) and low-density polyethylene (LDPE) filled with different commercial biodegradable additives.

## EXPERIMENTAL

### Materials

HDPE 10062 and LDPE 710, obtained from Dow Chemical (Tarragona, Spain), were chosen as representative polymeric matrices. Both polyethylenes have been previously characterized by infrared spectroscopy and size exclusion chromatography (Tables I and II).<sup>15,16</sup>

Three types of commercial biodegradable additives were incorporated into each of these matrices in the form of a master batch. The additives are marketed under the trade names Mater-Bi, Cornplast, and Bioeffect. The chemical compositions of these additives together with their suppliers are listed in Table III.

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**TABLE I**  
Branch, Double-Bond, and Carbonyl Contents of the Polyethylenes Expressed Either per 100 or per 1000 Methylene Units

Polyethylene	CH <sub>3</sub> /100 CH <sub>2</sub>	RHC=RHR'/ 1000 CH <sub>2</sub>	RCH=CH <sub>2</sub> / 1000 CH <sub>2</sub>	RRC=CH <sub>2</sub> / 1000 CH <sub>2</sub>	HC=O/ 1000 CH <sub>2</sub>	C=O/ 1000 CH <sub>2</sub>
HDPE 10062	0.21	—	0.38	—	—	—
LDPE 710	2.18	0.017	0.048	0.18	0.2	0.02

### Samples

Homogeneous mixtures (50/50 w/w) consisting of either HDPE or LDPE with each of these biodegradable additives were initially prepared from the melt in a Brabender Plasti-Corder PL 2100 rheometer. Samples for testing were subsequently prepared by compression molding with a Carver model M press. Samples of pure HDPE and LDPE and each additive were prepared in an identical manner and used as controls.

### Dsc

DSC measurements were carried out with a PerkinElmer DSC-4 calorimeter previously calibrated with indium. Each sample (5–6 mg) was weighed out in a standard aluminum pan. The sealed pan was scanned at a heating rate of 10°C/min from 0 to 200°C under a nitrogen atmosphere.

### Tga

TGA was performed with a Mettler-Toledo TGA/SDTA 851 analyzer. Dynamic measurements were performed from 25 to 600°C at a heating rate of 10°C/min under an argon atmosphere (flow rate = 200 mL/min). Sample masses were approximately 12 mg. The evolved gases were analyzed with a coupled Balzers Thermostat mass spectrometer. Products with molecular weights between 0 and 200 amu were determined.

## RESULTS AND DISCUSSION

### Dsc

The additives Mater-Bi, Cornplast, and Bioeffect were characterized with DSC, and the traces are shown in Figure 1. Their principal features are several overlapping melting endotherms between 100 and 170°C. No

**TABLE II**  
Weight-Average Molecular Weight ( $M_w$ ), Number-Average Molecular Weight ( $M_n$ ), and Polydispersity ( $M_w/M_n$ ) of the Polyethylenes

Polyethylene	$M_w$	$M_n$	$M_w/M_n$
HDPE 10062	62,700	18,000	3.48
LDPE 710	47,600	7,530	6.32

clear glass transition is exhibited by any of the additives in the temperature range of interest. The broad, weak transitions occurring around 40–60°C for Cornplast and Bioeffect are attributed to the melting of the smallest crystallites of LDPE contained in these additives. Therefore, the biodegradable additives do not undergo any significant phase change or transition at the temperatures experienced by a commercial composting system (60–70°C).

The DSC trace of Mater-Bi displays a broad peak between 80 and 170°C (Fig. 1). This peak is made up of at least two overlapping endotherms, with maxima at 127 and 145°C, respectively.

The DSC trace obtained for Cornplast contains a sharp endothermic peak at about 164°C and a broader one located at about 122°C. An endotherm at about 108°C is also observed, which has been attributed to the polyethylene present in its composition.

The DSC curve of Bioeffect is more similar to that of Cornplast than to that of Mater-Bi. It contains a peak at about 119°C and a smaller one at about 138°C. Bioeffect also displays an endotherm around 106°C, which has been assigned to the LDPE included in its formulation.

### Tga

The thermal stability of all the samples was studied with TGA. Figure 2 shows the mass-loss behavior as a function of temperature for the pure HDPE and LDPE control samples. Both polyethylenes display similar thermograms with a single mass-loss zone centered around 465°C for HDPE and around 460°C for LDPE (Table IV).

The thermogravimetry (TG) curves of HDPE and LDPE blended with the biodegradable additives are plotted in Figures 3 and 4, respectively. Small differences can be seen in the shapes of the thermograms according to the additive used, but common features are apparent in these traces. We have seen already that HDPE and LDPE exhibit a single degradation zone (Fig. 2), but polyethylenes filled with biodegradable additives display three weight-loss zones, regardless of the type of polymeric matrix and additive used. The characteristic parameters of the degradation zones of each sample are summarized in Table IV.

The first weight-loss region is centered around 133–136°C for the HDPE blends and around 115–120°C for the LDPE blends and accounts for less than 2% of the

**TABLE III**  
**Commercial Biodegradable Additives Used in this Study**

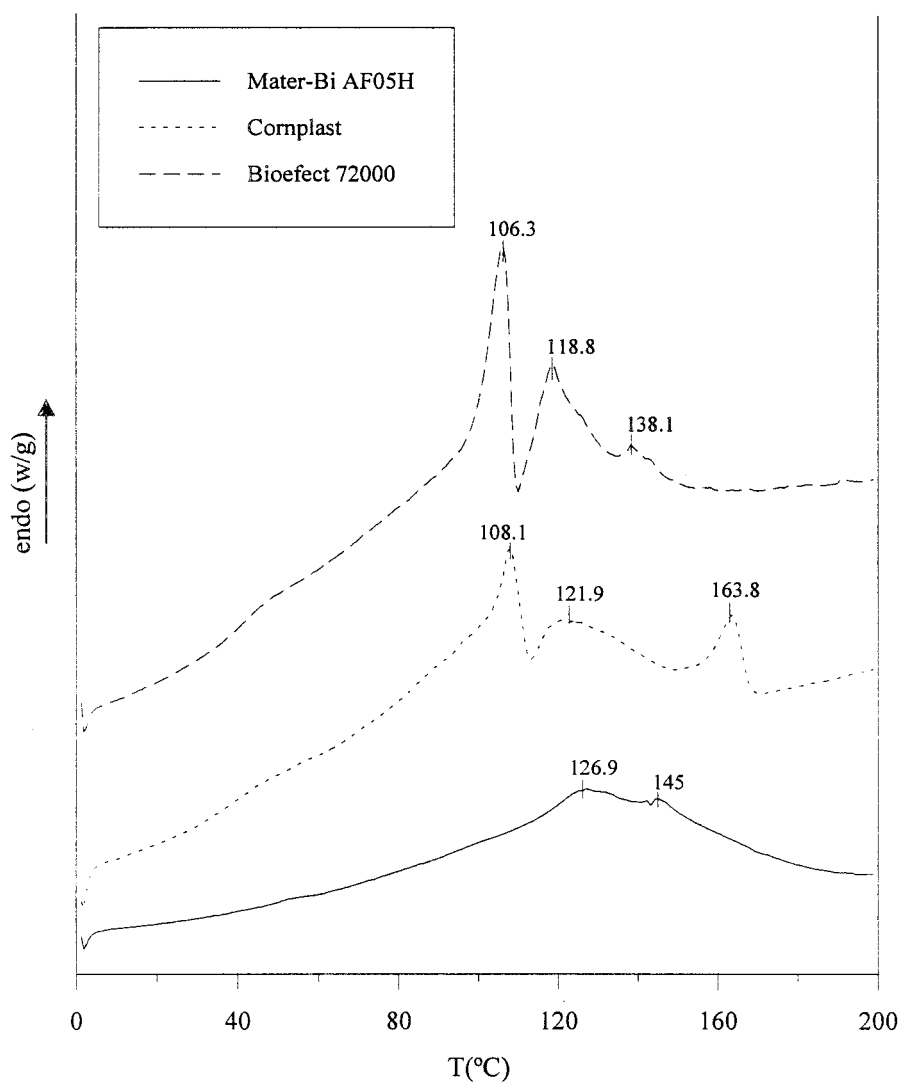
Additive	Code	Composition	Supplier
Mater-Bi AF05H	MB	Thermoplastic starch/ethylene-vinyl alcohol copolymers	Novamont (United States)
Cornplast	C	20% polyethylene + 80% product containing starch	National Corn Grower Association (United States)
Bioefect 72000	B	75% LDPE + 20% starch + 5% prooxidants containing fatty acids	Proquimaq Color, S.L. (Spain)

total mass loss for each sample (Table IV). It is well known that starch strongly absorbs water,<sup>3,4</sup> and so this weight loss may be attributed to the loss of absorbed water. This view is supported by the analysis of the evolved gases with mass spectroscopy. Specifically, fragments with a molecular weight of 18 are detected.

The second weight-loss region is located around 300–310°C for all the samples. This degradation zone, which was not observed in the thermograms of the

pure polyethylenes, is essentially identical for the blends containing the same additive, regardless of the polymeric matrix. This strongly suggests that this decomposition process is associated with the thermal degradation of the additive. Indeed, in this temperature range, starch is known to pyrolyze.<sup>3</sup> Weight losses of 11–13% occur for all the samples in this region (Table IV).

The third weight-loss zone seen for the polyethylene blends is associated with the greatest mass loss and is



**Figure 1** DSC traces of the biodegradable additives Mater-Bi AF05H, Cornplast, and Bioefect 72000.

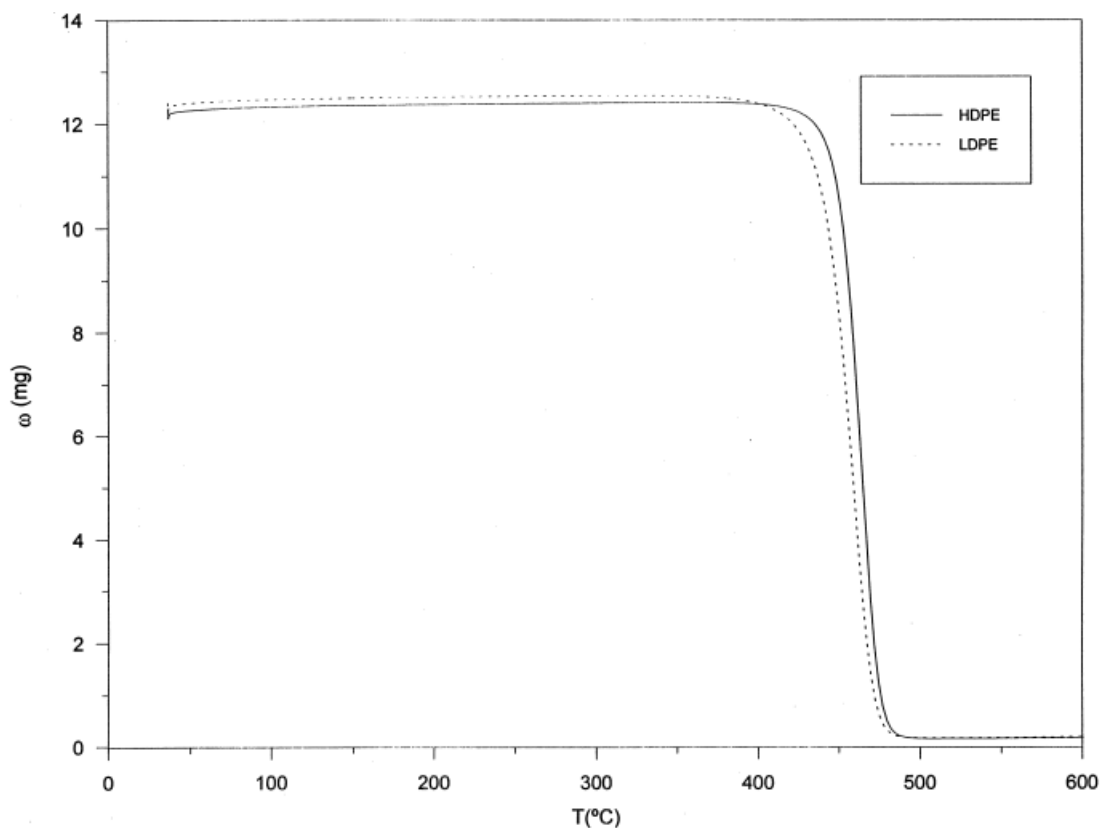


Figure 2 TG thermograms of pure HDPE and LDPE.

termed, therefore, the *main stage*. The parameters associated with this weight-loss region are similar to those observed in the TG of pure HDPE and LDPE (Table IV). Therefore, this mass loss has been attributed to the complete thermodegradation of the polyethylene backbones. The residue percentages, however, are considerably greater for the blends than for the pure polyethylenes (Table IV); this indicates that the origin of the residue may be the additives.

For a closer analysis of these thermogravimetric data, the kinetics of each degradation process were studied with the Broido integral method.<sup>17</sup> The kinetics of a system undergoing chemical changes are usually expressed in the following form:

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \quad (1)$$

where the rate of the change of the conversion  $\alpha$ , with respect to time  $t$ , is equated to separable functions of  $\alpha$  and the absolute temperature  $T$ .

The conversion or reacted fraction  $\alpha$  can be defined as the weight loss at time  $t$  divided by the weight loss at infinite time or total weight loss:

$$\alpha = \frac{\omega_0 - \omega}{\omega_0 - \omega_\infty} \quad (2)$$

TABLE IV  
TG Results

Sample	$T$ peak (°C)	Mass loss (%)	$T$ peak (°C)	Mass loss (%)	$T$ peak (°C)	Mass loss (%)	Residue (%)
HDPE	465	99.4	—	—	—	—	0.6
HDPE-B	460	75.7	300	12.5	133	0.8	6.2
HDPE-C	466	66.3	301	13.5	136	0.6	5.5
HDPE-MB	466	56.9	308	11.6	137	0.6	4.8
LDPE	459	98.7	—	—	—	—	0.7
LDPE-B	458	76.9	302	11.4	116	1.3	5.4
LDPE-C	463	65.7	302	13.5	116	0.8	5.4
LDPE-MB	464	55.8	310	11.2	121	0.7	5.0

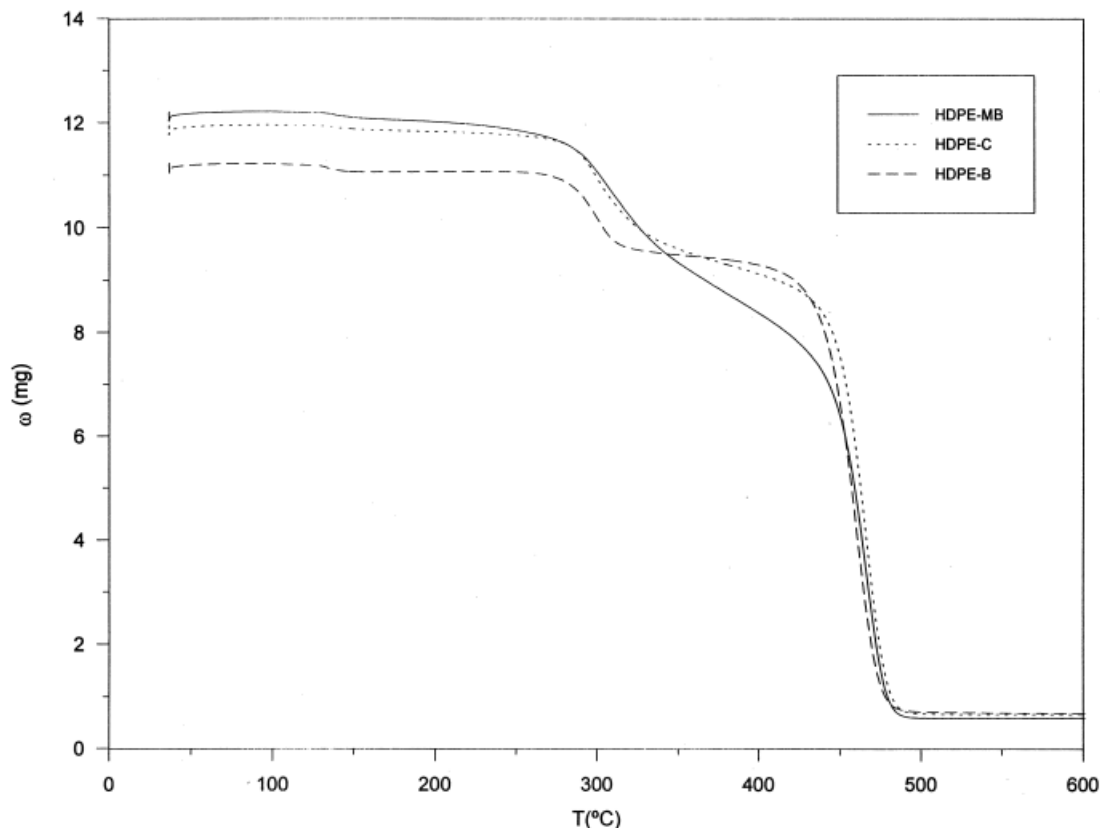


Figure 3 TG thermograms of the HDPE blends with Mater-Bi (HDPE-MB), Cornplast (HDPE-C), and Bioeffect (HDPE-B).

where  $\omega_0$ ,  $\omega$ , and  $\omega_\infty$  are the sample weight initially, at time  $t$ , and at infinite time, respectively.

Polymer degradation often involves a series of reactions. Therefore,  $f(\alpha)$  represents the net result of a number of elementary steps. Each elementary step has its own activation energy, and so the rate constants of each have different temperature dependencies.

The temperature dependence of the rate of reaction is generally expressed with the Arrhenius equation:

$$k(T) = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $E$  is the activation energy, and  $A$  is the pre-exponential factor.

The simplest model used to describe the kinetic function  $f(\alpha)$  is

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

where  $n$  is the apparent order of reaction.

Therefore, substituting the expression for  $f(\alpha)$  and  $k(T)$  into eq. (1) gives

$$\frac{d\alpha}{dt} = (1 - \alpha)^n A \exp\left(\frac{-E}{RT}\right) \quad (5)$$

The initial condition of  $\alpha = 0$  at  $T = T_0$  leads to the following integral form:

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \quad (6)$$

where  $\beta$  is the heating rate used in TGA ( $\beta = dT/dt$ ).

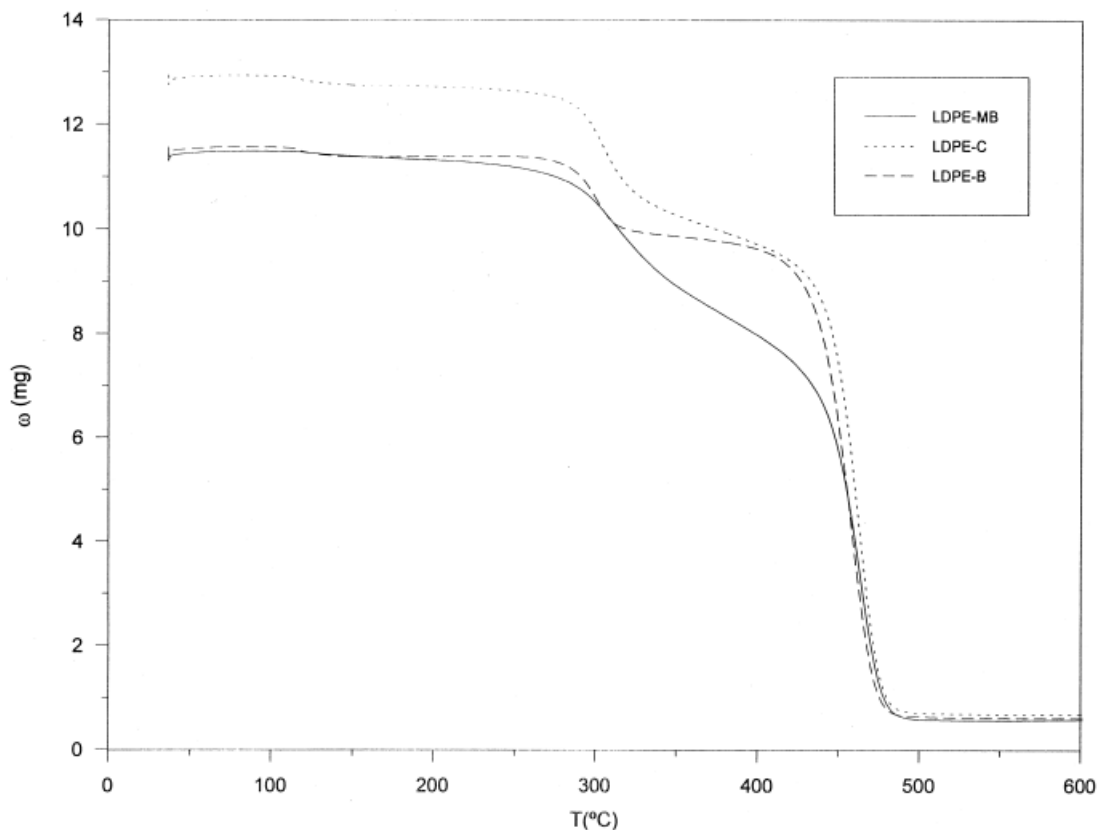
The integral methods are based on eq. (6). The one proposed by Broido<sup>17</sup> has been chosen for an analysis of the kinetics of the degradation stages in terms of their activation energy:

$$\ln\left[\ln\left(\frac{1}{x}\right)\right] \cong -\frac{E}{RT} + \text{const} \quad (7)$$

where  $x$  is the residual fraction defined as

$$x = 1 - \alpha = \frac{\omega - \omega_\infty}{\omega_0 - \omega_\infty} \quad (8)$$

According to the Broido equation, the plot of  $\{\ln[\ln(1/x)]\}$  against the reciprocal of temperature should give a straight line for each chemical process. From the slope of this straight line, the activation energy of the process can be calculated.



**Figure 4** TG thermograms of the LDPE blends with Mater-Bi (LDPE-MB), Cornplast (LDPE-C), and Bioeffect (LDPE-B).

Figures 5 and 6 show estimations of the activation energy of the different processes involved in the thermodegradation of the HDPE samples and the LDPE samples, respectively. The activation energies calculated for each sample are listed in Table V. The process related to the thermal degradation of the polyethylene chains (400–500°C) exhibits the highest activation energies. For this stage, higher activation energies are found for pure HDPE and LDPE than for their blends with the biodegradable additives. The presence of the additive may have hindered the crystallization of the polymeric matrix, thereby leading to a thermally less stable matrix.

The stages related to the thermodegradation of the starch contained in the additive (265–335°C) exhibit lower activation energies. In general, for the same additive, similar values have been obtained. Samples containing Cornplast and Bioeffect, two polyethylene-based additives, display activation energies around 30 kcal/mol for this process. Samples containing Mater-Bi, a starch-based additive made up of gelatinized starch,<sup>4</sup> exhibit lower activation energies of about 20 kcal/mol. At the root of these differences are the different chemical compositions of the additives.

Relatively high activation energies (60 kcal/mol) are found for the loss of the absorbed water present in samples containing Mater-Bi. This indicates that water is strongly bonded to the starch/ethylene-vinyl alco-

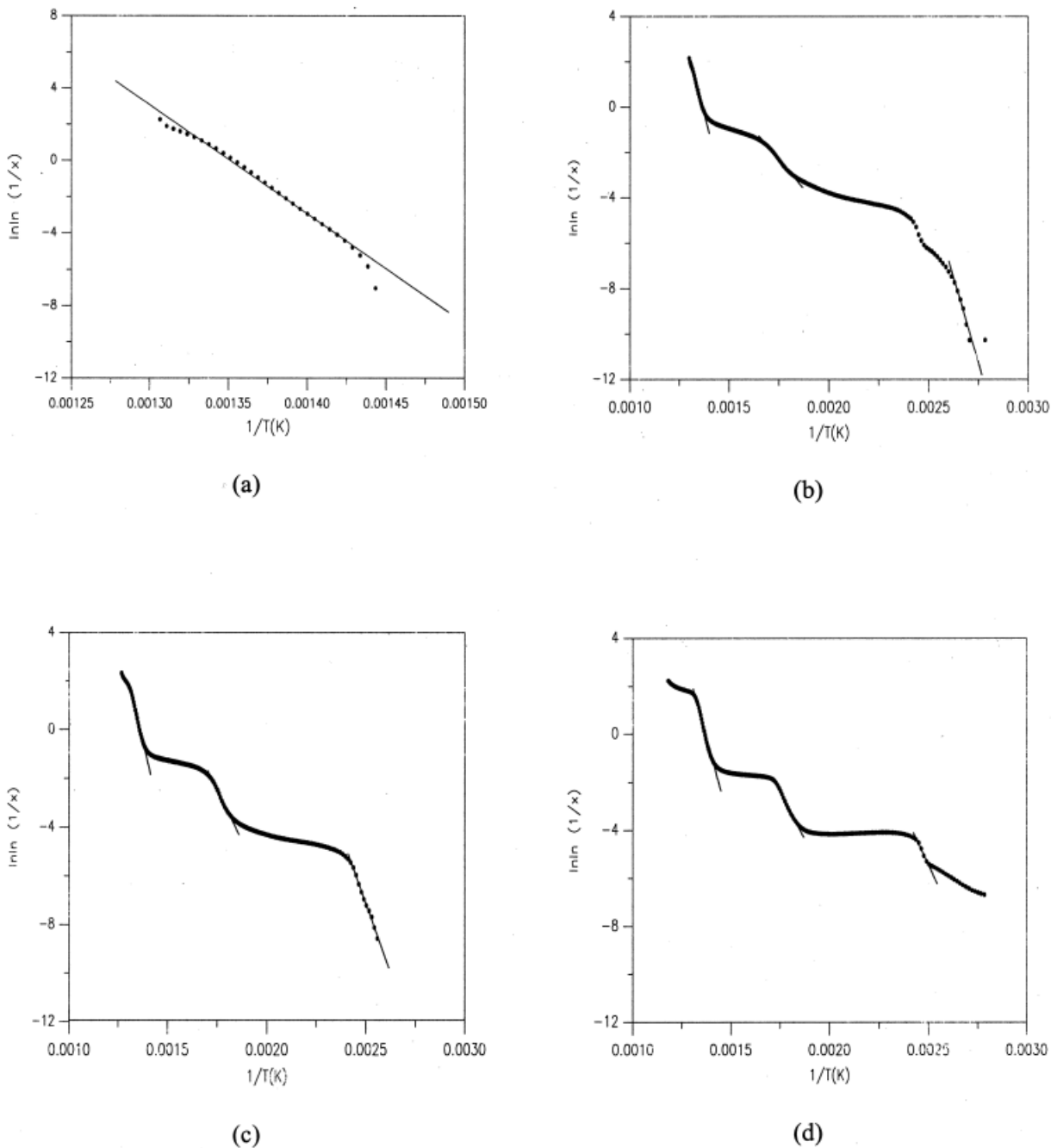
hol complex, probably by means of hydrogen bonds. Samples containing Cornplast and Bioeffect display lower activation energies for this process (35–50 kcal/mol).

In general, the LDPE blends display lower activation energies than the corresponding HDPE blends. This may be due to the fact that LDPE has a higher branch content than HDPE (Table I), and branches reduce the thermal stability of a polymeric material because they are more labile sites for degradation.<sup>18–20</sup>

The volatile products of the thermal degradation of the samples were characterized with mass spectrometry, which revealed essentially complete thermodegradation of all the samples because only fragments with low molecular weights were detected. These included the combustion products water, carbon monoxide, and carbon dioxide and the possible molecular fragments  $\text{CH}_3 \cdot$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_3\text{H}_4$ , and  $\text{C}_2\text{H}_4\text{O}$ ; the peak at 44 amu was detected only for the LDPE blends. Therefore, the behavior of the blends is similar to that observed for pure polyethylenes.<sup>19</sup> This could suggest that depolymerization reactions have been favored, instead of transfer reactions.

## CONCLUSIONS

The DSC thermograms of the pure additives indicate that they do not undergo any significant phase change



**Figure 5** Calculation of the activation energy according to the Broido integral method for (a) pure HDPE and (b–d) HDPE samples with (b) Mater-Bi, (c) Cornplast, and (d) Bioeffect.

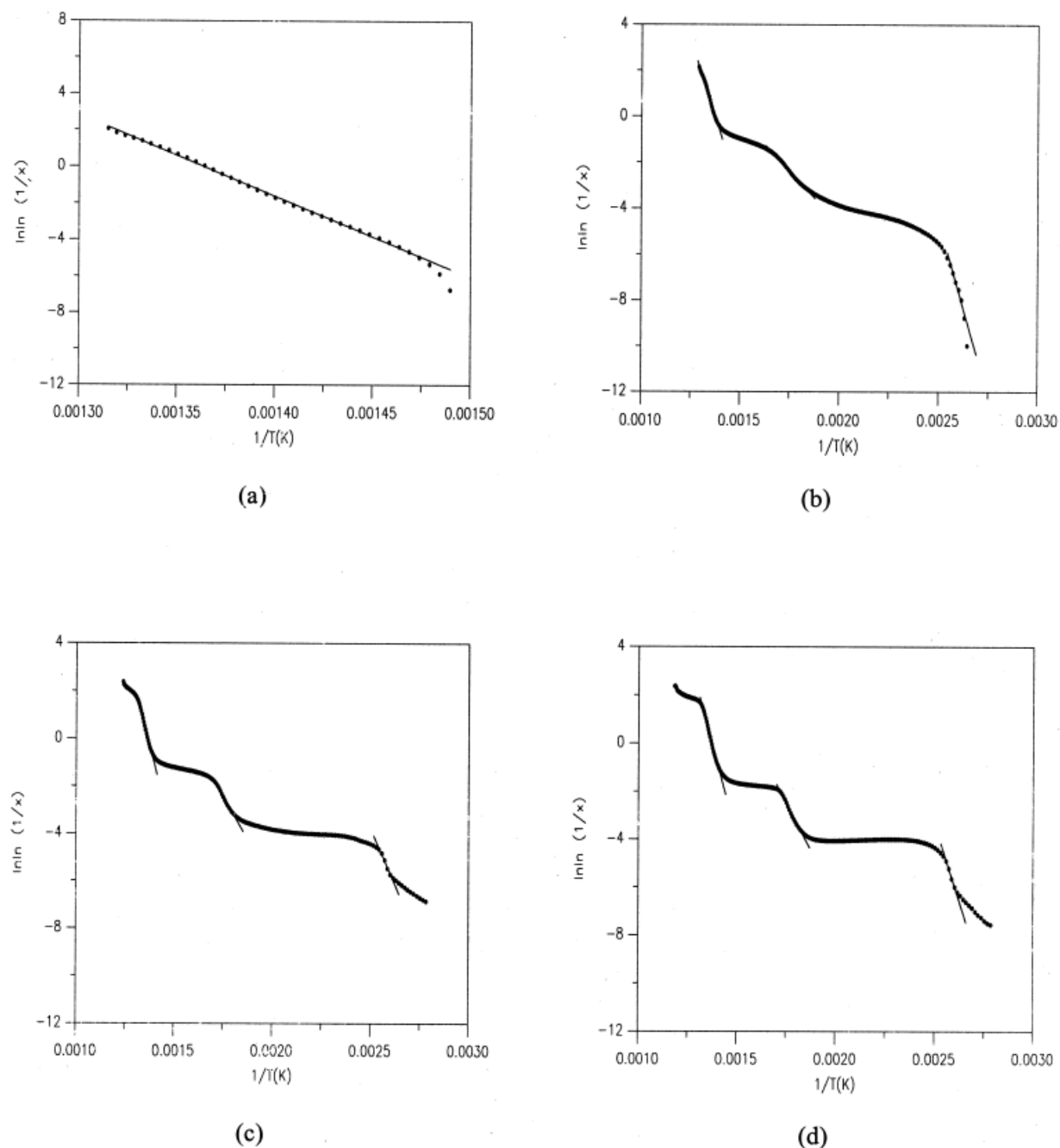
or transition in the temperature region encountered by a commercial composting system (60–70°C). Therefore, changes detected in these biodegradable additives or in their blends with HDPE and LDPE during composting can be attributed to degradation.

For all the samples, the main stage of their thermodegradation corresponds to the complete decomposition of the polyethylene chains. However, the presence of the additive leads to a thermally less stable matrix, with decreased activation energies for the decomposition processes, in comparison with pure

HDPE and LDPE. The additive used determines the residue percentage, which is higher in the blends than in the pure matrices.

The LDPE blends are thermally less stable than the corresponding HDPE blends, as indicated by their lower activation energies in all the thermodegradation stages, and this is attributed to the higher branch content.

In general, the thermal degradation of these degradable polyethylenes leads to products similar to those obtained for pure polyethylenes.



**Figure 6** Calculation of the activation energy according to the Broido integral method for (a) pure LDPE and (b–d) LDPE samples with (b) Mater-Bi, (c) Cornplast, and (d) Biofect.

**TABLE V**  
Activation Energies Calculated with the Broido Integral Method

Sample	T range (°C)	Activation energy (kcal/mol)	T range (°C)	Activation energy (kcal/mol)	T range (°C)	Activation energy (kcal/mol)
HDPE	427–485	119.9	—	—	—	—
HDPE-MB	456–495	65.5	274–322	20.6	97–105	59.4
HDPE-C	448–485	68.0	276–307	33.0	118–137	45.5
HDPE-B	427–483	59.9	267–303	32.3	127–135	35.3
LDPE	405–483	88.1	—	—	—	—
LDPE-MB	444–499	53.5	267–334	18.3	86–81	60.2
LDPE-C	446–485	64.1	279–312	29.2	84–87	37.9
LDPE-B	432–483	60.5	272–310	31.4	111–118	51.3



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