Thermal Characterisation of Photo-Oxidized HDPE/Mater-BI and LDPE/Mater-BI Blends Buried in Soil

R. Moriana-Torró, L. Contat-Rodrigo, L. Santonja-Blasco, A. Ribes-Greus

Instituto de Tecnología de Materiales, Escuela Técnica Superior de Ingeniería del Diseño, Universidad Politécnica de Valencia, 46071 Valencia, Spain

ABSTRACT: Blends of high and low density polyethylene with a commercial biodegradable material (Mater-Bi) were subjected to an accelerated soil burial test. A set of samples was previously photo-oxidized to evaluate the effects of UV-irradiation on the degradation in soil process of these blends. Thermogravimetric as well as calorimetric analysis were performed to study the biodegradation, photo-degradation and their synergetic effects. Differential scanning calorimetry was carried out to analyze the morphological changes as a consequence of the photo-oxidation process. UV-irradiation slightly modifies the crystalline content of HDPE/Mater-Bi blends, increasing the heterogeneity of this blend. Criado master curves were plotted to analyses the degradation kinetic model. Broido and Coats-Redfern methods have been used for calculating the Ea of the thermal decomposition mechanisms. Thermogravimetric results reveal that noncomplexed starch is more affected by biodegradation than the polyethylene matrix and the starch/EVOH complexes chains from Mater-Bi. However, the effects of both photo-oxidation and biodegradation processes on the thermal decomposition of Mater-Bi is influenced by the polymeric matrix used. Previous photo-oxidation finds to slow down the degradative effects caused by the soil burial test on the HDPE/Mater-Bi blends. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1177–1188, 2008

Key words: thermogravimetric analysis; polyethylene; Mater-Bi; biodegradation; photo-oxidation

INTRODUCTION

The increasing problems posed by plastics waste management have stimulated the interest in developing different strategies to find out a solution to this environmental problem.[1–3] Among them, many efforts have been made these last years in promoting the development of degradable materials that could replace conventional synthetic polymers.[4–13] Although the contribution of such biodegradable polymers to the reduction of plastics waste is obvious, nowadays these materials still cannot compete from an economical point of view with conventional polymers.

A viable solution, already employed by producers, is to combine the different features and benefits of both synthetic and biodegradable materials to produce blends fulfilling the requirements of both good cost-performance ratio as well as being environmentally-friendly. This is the case of polyolefins that are still considered as one of the most important plastic materials due to their good mechanical properties and low cost but as it is well-known, they are resistant to microbial attack. Thus, blends of polyolefins with other commercial biodegradable polymers contain parts that may enhance their sensitivity to degradation. To assess the potential applications of these blends, their characterization, as well as the study of their degradation process must be performed. As it has already been shown in previous works.[14–17] Thermal Analysis can provide useful information about the irreversible changes in the properties of polymers caused by degradation in soil of polymeric materials.

In this study, blends of high and low density polyethylene with a commercial biodegradable material containing thermoplastic starch and ethylene vinyl alcohol were analyzed. Such blends were exposed to a soil burial test to study their degradation and to investigate the influence of the polyolefinic matrix. Some of these blends were subjected to photo-oxidation before the soil burial test to evaluate the effects of UV-irradiation on this biodegradation process. Thermogravimetric and calorimetric methods were used for this purpose, since they provide qualitative and quantitative information about the degradation processes of these materials. Biodegradation exhibits a complex mechanism, so that the interaction of different oxidative processes may produce a synergetic effect that may modify the biodegradation rate.

EXPERIMENTAL

Materials

Low-density polyethylene (LDPE 710) and high-density polyethylene (HDPE 10062) from Dow Chemical (Spain) were used as polymeric matrices. These polyolefins were blended with a commercial biodegradable material, Mater-Bi AF05H, supplied by Novamont North America (USA). This starch-based material contains about 60% of maize starch and natural additives, and 40% of [40/60 (mol/mol)] ethylene-vinyl alcohol copolymer (EVOH).[18]

Samples preparation

Homogeneous blends of 50/50 wt % of the corresponding polyethylene (LDPE 710 or HDPE 10062) and Mater-Bi AF05H were prepared from the molten state in a Brabender Plasti-Corder PL 2100 rheometer. The HDPE/Mater-Bi blends were processed at 170°C and the LDPE/Mater-Bi blends at 150°C. The processing time was 7 min for all the blends.

The samples for the burial test were prepared from the blends by compression molding with a Carver M press. The compression program consisted on decreasing temperature steps from 160 to 100°C for the LDPE 710/Mater-Bi blends, and from 125 to 90°C for the HDPE 10062/Mater-Bi blends. When the blends reached the final temperature a pressure step of 14 atm was applied. The resulting sheets were then submerged into cool water. Pure HDPE and LDPE samples were used as references. Finally all the samples were cut into rectangular bars with dimensions $68 \times 12 \times 1.8$ mm³.

Photo-oxidation test

A set of samples was subjected to an accelerated photo-oxidation test before the soil burial test. Pure and blended samples were irradiated in an Atlas XLS+ Suntest with UV-radiation. Samples were exposed to a total radiation of 138,000 kJ/m² during 98.7 h, while they were submerged in water at 38°C, continuously pumped around in close circuit.

Soil burial test

According to the DIN 53739 international Norm,[19] samples were buried in active soil contained in plastic rectangular boxes. The soil burial test was carried out during 6 months, periodically controlling the humidity, pH and temperature of the soil. Samples were taking out after different periods of time: 20 days, 2 months, 4 months, and 6 months. Pure samples were only removed at the end of the test. Once removed, samples were washed with a soap solution to stop the degradation process.

TGA measurements

Thermogravimetric measurements were performed using a Mettler Toledo TGA/SDTA 851 analyzer. Dynamic measurements were carried out from 25 to 600°C, at a heating rate of 10°C/min under Argon atmosphere with a flow rate of 200 mL/min. The initial sample mass was between 10 and 12 mg.

Differential scanning calorimetry measurements

The DSC measurements were carried out in a Perkin–Elmer DSC-4 Calorimeter (Norwalk, CT), previously calibrated with indium standard. Samples of 6–7 mg were placed in standard aluminum pans that were sealed, pierced and scanned from 0 to 200°C, at a heating rate of 10°C/min under nitrogen atmosphere. Measurements were repeated to limit errors to ± 0.01°C for the melting temperature and ± 0.05% for the crystalline content.

RESULTS AND DISCUSSION

Samples have been initially characterized by thermogravimetric analysis. Figures 1 and 2 show the differential thermogravimetric curves of pure HDPE and LDPE, respectively. The thermograms of both pure polyethylenes display a single weight-loss zone, centered at 486.7°C for HDPE and 483.5°C for LDPE.

As it has been previously mentioned, Mater-Bi AF05H is a starch-based material that contains starch and poly(ethylene-vinyl alcohol) copolymers (EVOH). This material is a blend with complex interactions between its components.[18] Because of the
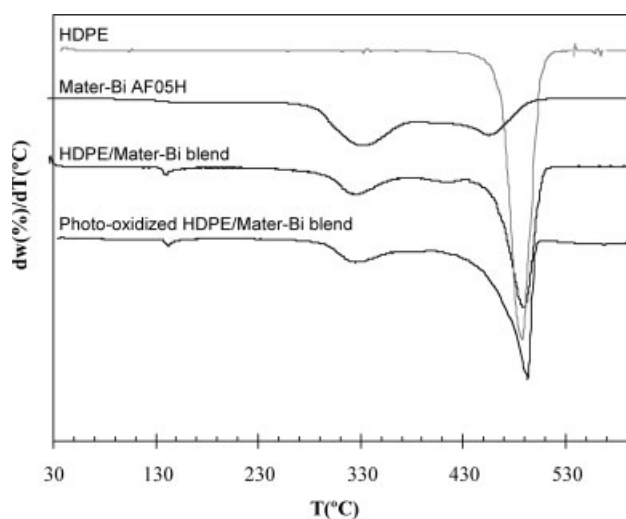

Figure 1 Differential thermogravimetric curves of pure HDPE, pure Mater-Bi AF05H, HDPE/Mater-Bi blend, and the photo-oxidized HDPE/Mater-Bi blend.
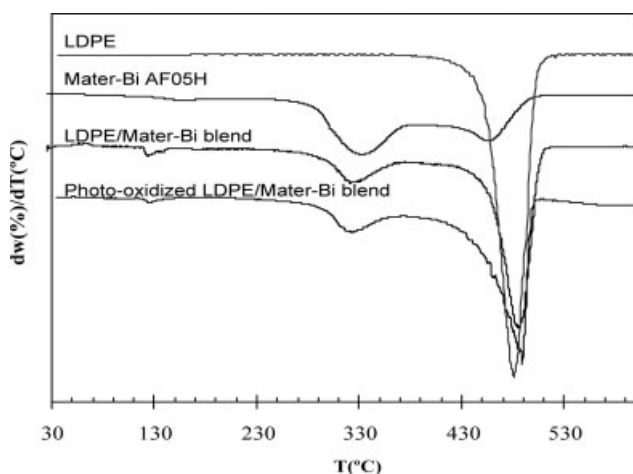
Figure 2 Differential thermogravimetric curves of pure LDPE, pure Mater-Bi AF05H, LDPE/Mater-Bi blend, and the photo-oxidized LDPE/Mater-Bi blend.

reported hydrophobic and hydrophilic interactions within starch, ethylene, and vinyl alcohol,[11,18] the differential thermogravimetric curve of this pure Mater-Bi displays multiple degradation zones (Figs. 1 and 2).

The first weight-loss region appears around 155°C and displays a mass loss of 4.6%. Such region can be attributed to the loss of low molecular weight molecules, like water absorbed by the starch or other compounds included in the Mater-Bi formulation.[4,10,20]

The second weight-loss zone appears around 260–360°C, with a peak at 331.1°C and a mass loss of 47.7%. This peak can be attributed to the pyrolysis of the starch present in the Mater-Bi, since this native polysaccharide shows a complex degradation in this temperature interval.[4,5,21,22]

The third weight-loss region is a complex zone with overlapped mechanisms that take place between 390 and 500°C. The main peak of this region appears around 455°C with a mass loss of 22.7%. Other authors related this peak to the pyrolysis of the synthetic component in Mater-Bi.[21,23,24]

According to its formulation, Mater-Bi AF05H contains 60% starch and 40% EVOH.[18] However, the experimental weight losses determined for these two components are inferior to those expected. A closer inspection of the differential thermogravimetric curve of pure Mater-Bi revealed the presence of various small shoulders overlapped to the second and third decomposition peaks, previously assigned to starch and to the synthetic component, respectively. To characterize this overlapped weight-loss region, a deconvolution method has been applied. Each individual contribution of the differential thermogravimetric curve has been fitted to the following equation:

$$y_i = A \left(\frac{1}{1 + \exp\left(\frac{-(x - x_c + \frac{w_1}{2})}{w_2} \right)} \right) \left(1 - \frac{1}{1 + \exp\left(\frac{-(x - x_c + \frac{w_1}{2})}{w_3} \right)} \right)$$

where x_c is a position parameter related to the curve maximum, A is an amplification parameter and w_1, w_2, w_3 describe the dispersion and symmetry of the curve.

This proposed deconvolution model considers that the measured value of $(dw(\%)/dT) = y$ is equivalent to $y = y_0 + \sum_{i=1}^{n} y_i$, where y_0 is the onset of each differential thermogravimetric curve and n is the total number of deconvoluted peaks.

Figure 3 shows the application of this deconvolution method for the differential thermogravimetric curve of pure Mater-Bi. Besides from displaying the two prominent peaks centered at 335°C and 455°C, which have been previously related to the pyrolysis of starch and the ethylene chains from the synthetic component (EVOH), the deconvolution also shows two small peaks at 393°C and 421°C. These small peaks may be assigned to the pyrolysis of the rest of more thermally stable starch chains and the vinyl alcohol chains, since literature shows that pure EVOH undergoes a complex thermal degradation under inert atmosphere.[25] EVOH pyrolysis consists of two partially overlapped peaks: the first peak that can be associated to the thermal degradation of vinyl alcohol chains appears in the 390–410°C interval at a heating rate of 10°C/min; the second peak at higher temperatures (450–455°C) can be assigned to thermal degradation of the ethylene chains. Thus, as the degradation in soil process undergoes and certain chain scission of starch occurs, the evolution of these small peaks (between 390 and 450°C) may be observed.
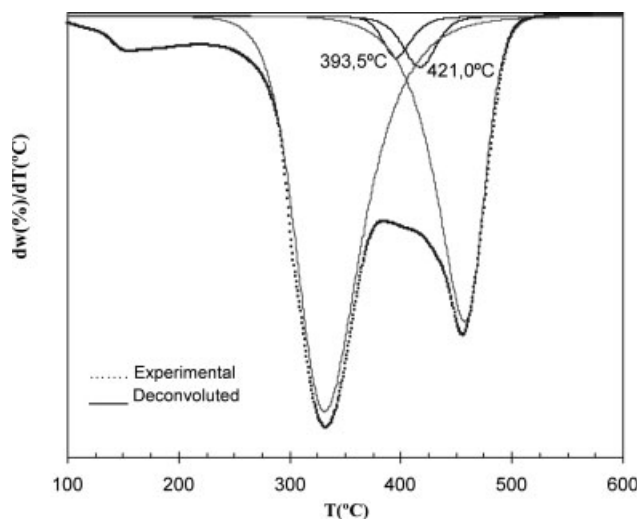

Figure 3 Deconvolution of the differential thermogravimetric curve of Mater-Bi AF05H.

TABLE I
Thermogravimetric Parameters of the HDPE/Mater-Bi Blends as a Function of the Exposure Time in Soil

	HDPE/Mater-Bi blends							
	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)
0 days	2.0	142.0	24.7	328.0	6.6	398.0	66.0	489.0
20 days	–	–	13.0	324.0	8.7	396.0	70.0	490.0
2 months	–	–	6.0	320.0	14.7	391.0	75.1	489.0
4 months	–	–	–	–	18.0	392.6	77.0	489.0
6 months	–	–	–	–	18.0	392.0	77.2	487.2

Figures 1 and 2 also show the differential thermogravimetric curves of HDPE/Mater-Bi and LDPE/Mater-Bi blends that display several decomposition regions, which can consequently be attributed to both PE and Mater-Bi components.

As in pure Mater-Bi, the first weight loss region (around 140°C), can be assigned to the thermal decomposition of the low molecular weight compounds present in this material.

The second weight-loss (between 275°C and 435°C) is a complex region also associated to Mater-Bi contributions. For the differential thermogravimetric curves of LDPE/Mater-Bi blends only one peak centered at 328°C can be distinguished. For the HDPE/Mater-Bi blends, two peaks can be observed in this region. The first one (275–360°C) is a prominent peak, which can be attributed to the thermal degradation of most part of the starch. The second peak (360–435°C) appears as a very small shoulder that may have the origin in the pyrolysis of the more thermally stable starch chains and the vinyl alcohol chains.

The third weight-loss is located between 435 and 530°C and is the main decomposition region. Since differential thermogravimetric curves of both HDPE/Mater-Bi and LDPE/Mater-Bi blends display a single peak in this region, they must include two contributions overlapped; one of them assigned to the thermal decomposition the backbones chains of pure polyethylenes and the other to ethylene chains of Mater-Bi.

Thermogravimetric parameters of these blends are summarized in Tables I and II, respectively. The blending process does not modify the thermogravimetric parameters of both pure components. This may be an indication of the heterogeneity of polyethylenes/Mater-Bi blends.

Figures 1 and 2 also show the differential thermogravimetrics curves of photo-oxidized HDPE/Mater-Bi and LDPE/Mater-Bi blends. The thermogravimetric parameters of these photo-oxidized blends are summarized in Tables III and IV, respectively. These results show that photo-oxidation does not modify the initial weight loss region, which has been associated to the thermal decomposition of the low molecular weight compounds. However, photo-oxidation affects the pyrolysis of both Mater-Bi and the polyethylene components of the blends.

When HDPE/Mater-Bi and LDPE/Mater-Bi blends are subjected to photo-oxidation, the main thermogravimetric peak overlaps with the small shoulders at 360–435°C related to the more thermally stable starch and vinyl alcohol chains. Furthermore, an increase of the thermal stability of both blends types has been observed. In contrast, the thermal stability of the starch slightly decreases for the HDPE/Mater-Bi blend, and remains unmodified for the LDPE/Mater-Bi. These results suggest that the behavior of the starch during photo-oxidation depends on the polyolefinic matrix used.

On the other hand, derivative thermogravimetric curves of the HDPE/Mater-Bi blends and the LDPE/Mater-Bi blends subjected to the soil burial test are plotted in Figures 4 and 5. Substantial modifications appeared in the region associated to Mater-Bi (275–435°C). Thus, a careful study of the degradation in soil of pure Mater-Bi is very important to understand the degradation in soil of these blends.

TABLE II
Thermogravimetric Parameters of the LDPE/Mater-Bi Blends as a Function of the Exposure Time in Soil

	LDPE/Mater-Bi blends							
	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)
0 days	2.3	125.3	22.2	325.0	–	–	64.5	485.6
20 days	1.0	125.0	14.0	325.0	10.0	399.0	69.2	486.0
2 months	0.8	125.0	8.0	327.0	13.0	397.0	75.0	485.3
4 months	0.9	121.5	8.1	323.4	13.0	397.6	75.0	485.3
6 months	0.8	120.2	8.2	324.0	13.0	397.5	75.1	486.7

TABLE III
Thermogravimetric Parameters of the Photo-Oxidized HDPE/Mater-Bi Blends as a Function of the Exposure Time in Soil

	Photo-oxidized HDPE/Mater-Bi blends							
	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)
0 days	1.0	142.1	21.3	325.6	–	–	69.5	493.0
20 days	1.0	141.0	13.0	322.5	8.0	388.0	70.9	495.0
2 months	0.2	142.6	7.0	322.5	12.0	385.6	73.6	492.5
4 months	–	–	–	–	20.0	387.0	75.6	493.2
6 months	–	–	–	–	20.2	389.2	75.0	494.5

TABLE IV
Thermogravimetric Parameters of the Photo-Oxidized LDPE/Mater-Bi Blends as a Function of the Exposure Time in Soil

	Photo-oxidized LDPE/Mater-Bi blends							
	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)
0 days	1.8	125.0	24.3	324.7	–	–	66.0	489.0
20 days	1.2	123.5	17.8	319.4	–	–	74.0	493.2
2 months	0.2	126.7	7.9	327.0	14.0	400,0	71.5	492.7
4 months	0.1	127.0	5.7	323.5	16.6	402,4	72.4	492.4
6 months	0.4	128.0	6.7	320.4	14.0	401,7	73.1	493.9

Figure 6 shows differential thermogravimetric curve of the pure Mater-Bi submitted to the burial soil test. Table V displays the thermogravimetric parameters related to the decomposition zones of pure Mater-Bi. These plots show that substantial changes are related to the thermal decomposition of starch.

Figure 6 also displays the deconvolution method of the differential thermogravimetric curves of the biodegraded Mater-Bi, to characterize this complex zone. The original contribution at 331°C, attributed to thermal degradation of starch chains, is continuously reduced as the degradation time increases.

These results confirm the degradation of most of starch by the biodegradation process in soil.

Furthermore, as the degradation test in soil progresses, the small shoulders in the 360–435°C interval that above have been related to the remaining more thermally stable starch chains and vinyl alcohol chains, considerably develop into a single and main contribution. After 20 days of exposure time in soil, this single contribution is centered at 391°C. As the degradation time increases, this peak slightly shifts towards lower temperatures (386°C).

Figure 6 also displays that the weight-loss peak associated with the ethylene chains of poly(vinyl
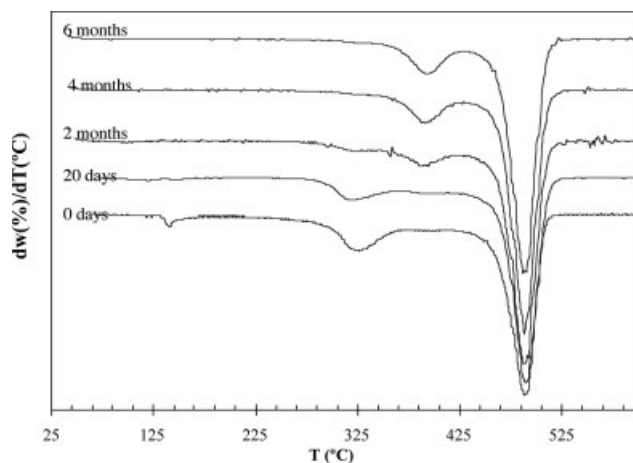

Figure 4 Differential thermogravimetric curves of the HDPE/Mater-Bi blends as a function of the exposure time in soil.
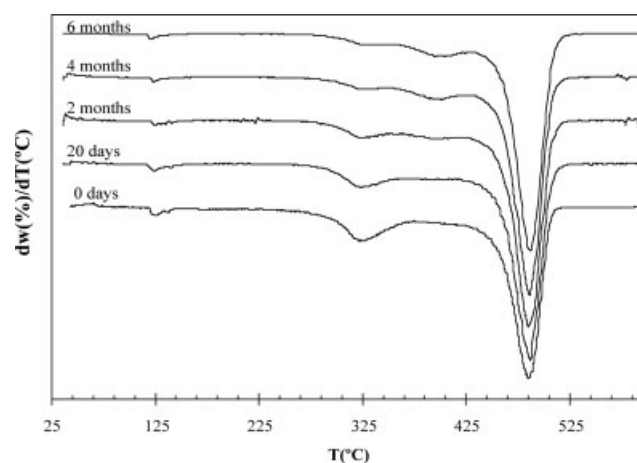

Figure 5 Differential thermogravimetric curves of the LDPE/Mater-Bi blends as a function of the exposure time in soil.
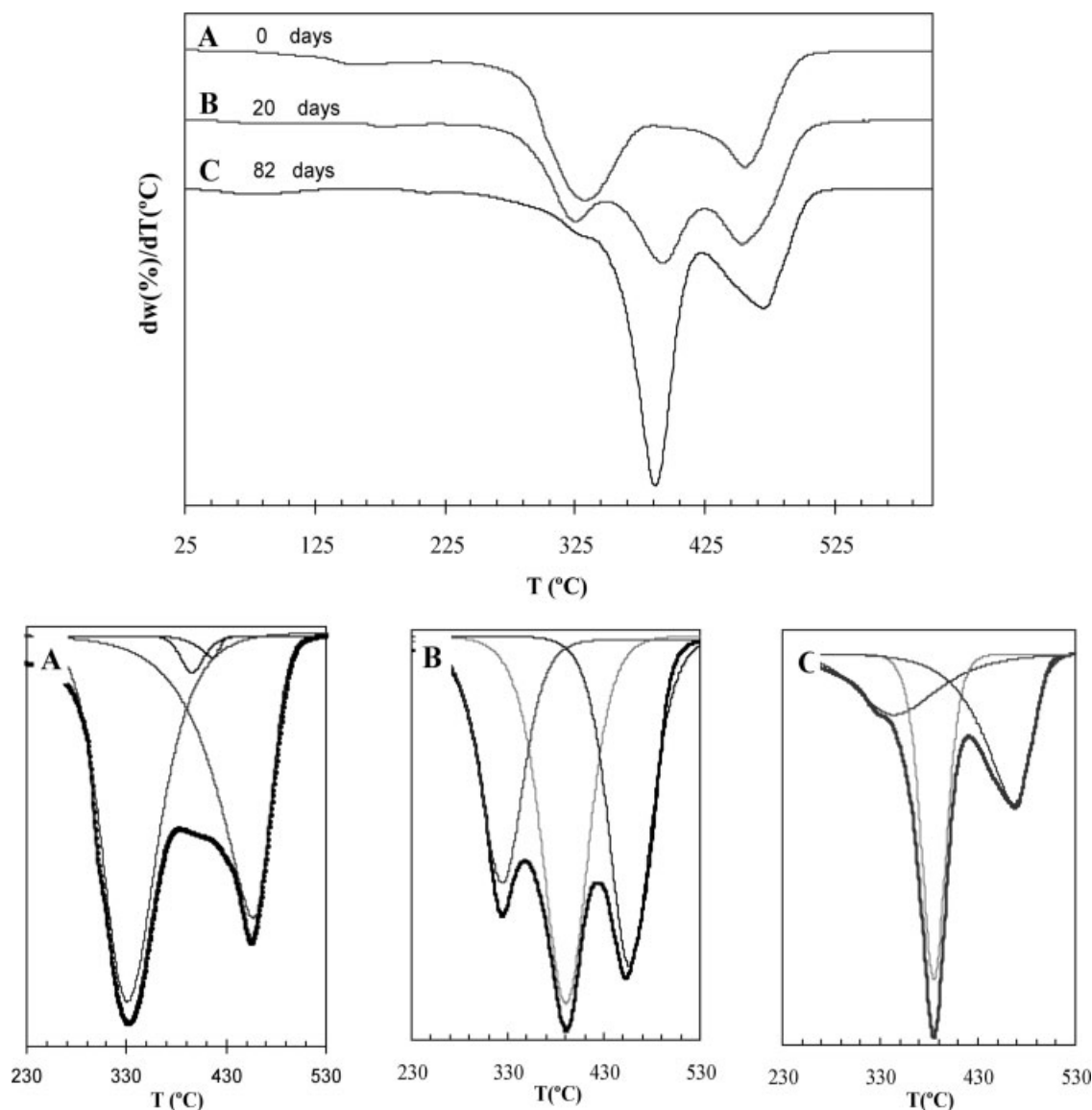
Figure 6 Differential thermogravimetric curves of Mater-Bi AF05H as a function of the exposure time in soil. (A) deconvolution of the DTG curve of Mater-Bi AF05H (B) deconvolution of the DTG curve after 20 days and (C) after 82 days of exposure time in soil.

alcohol) is not significantly modified as a result of the biodegradation process in soil; a shift of that peak towards higher temperatures (468°C) is only noted as the degradation time increases.

These results seem to indicate that the starch chains exhibit diverse behavior when Mater-Bi is subjected to degradation in soil. Most of the more labile, easily accessible and biodegradable starch chains in Mater-Bi, disappear. The rest of the more thermally stable and/or less accessible starch remains, probably for the influence of the vinyl alcohol.[26] These results may be understood taking into

TABLE V
Thermogravimetric Parameters of Mater-Bi AF05H as a Function of the Exposure Time in Soil

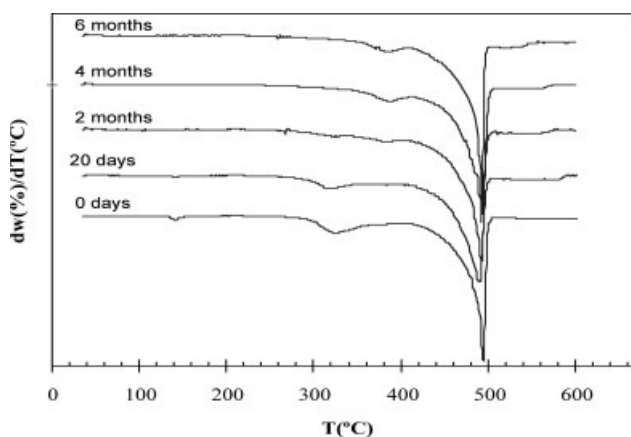|	Mater-Bi AF05H							
	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)	Weight loss (%)	T Peak (°C)
0 days	4.6	155.0	47.7	331.1	–	–	22.7	456.5
20 days	1.6	176.5	35.0	325.6	35.0	391.2	24.7	453.7
80 days	–	–	–	–	55.5	385.5	24.5	469.7

Figure 7 Differential thermogravimetric curves of the photo-oxidized HDPE/Mater-Bi blends as a function of exposure time in soil.

consideration previous studies made by Bastioli et al.[11,18]; they have proposed a model considering large individual amylopectine molecules, interconnected at several points per molecule, as a result of hydrogen bonds and entanglements, by chains of amylose/EVOH complexes. Thus, Mater-Bi AF05H adopts a complex droplet structure, with a core of an almost amorphous amylopectine surrounded by amylose/EVOH complexes that make amylopectine unsoluble. The droplets can interact by means of hydrogen bonds, producing a gel-like structural skeleton. During the soil burial test, the droplets structure core and the ethylene chains of Mater-Bi should be degraded slower than the noncomplexed starch.[27]

For the HDPE/Mater-Bi and LDPE/Mater-Bi blends submitted to degradation in soil, the same behavior as the one described for the pure Mater-Bi is observed in the region between 275 and 435°C. The thermogravimetric parameters are showed at Tables I–IV from both kinds of blends.

Derivative thermogravimetric curves of the HDPE/Mater-Bi and LDPE/Mater-Bi blends subjected to both the photo-oxidation and the soil burial tests are displayed in Figures 7 and 8. Their parameters are also showed at Tables I–IV. As it has been previously stated, the small shoulders in the 360–435°C interval, which may be related to the core of droplets structure, cannot be identified when these blends are photo-oxidized, since they overlap with the main decomposition zone associated to polyethylene chains. However, as the exposure time in soil increases, the main peak becomes narrower, and the development of small shoulder associated to Mater-Bi can be distinguished.

To analyze in more detail the thermogravimetric results and assessed the mechanisms involved, the kinetic behavior of all the blends has been studied. Criado method[28] was employed to analyze the decomposition mechanism of the ethylene chains in the HDPE/Mater-Bi and LDPE/Mater-Bi blends. Criado equation allows obtaining reduced master curves, which are used to assess the kinetic model that describes the studied thermal decomposition process.

$$\frac{z(\alpha)}{z(0,5)} = \frac{f(\alpha)g(\alpha)}{f(0,5)g(0,5)} = \left(\frac{T}{T_{0,5}}\right)^2 \frac{(d\alpha/dt)}{(d\alpha/dt)_{0,5}}$$

where $\frac{d\alpha}{dt}$ is the rate equation, T is the absolute temperature, α is the degree of degradation or conversion, $f(\alpha)$ is the differential conversion function and $g(\alpha)$ is the integral conversion function.

The left side of this equation is a reduced theoretical curve, where the digit 0.5 refers to the conversion of 0.5. This side of equation is characteristic for each reaction mechanism, whereas the right side of the equation can be obtained from experimental data. Different algebraic expressions for $f(\alpha)$ and $g(\alpha)$ have been used to describe the employed kinetics models.[29]

Figure 9 displays the reduced master curves of HDPE/Mater-Bi and LDPE/Mater-Bi blends, proving that the thermodegradation mechanism of the ethylene chains of the blends follows a kinetic model of $f(\alpha) = (1-\alpha)^n$, being $n = 1$.

The Broido method[30] has also been used for the kinetic analysis of the main thermal decomposition process for the both kind of blends as has already been successfully applied in previous works for polyolefins.[15–17] Broido equation could be used to calculate the activation energy.

$$\ln\ln\left(\frac{1}{x}\right) \cong -\frac{E_a}{RT} + \text{constant}$$

where R is the gas constant, T is the absolute temperature, E_a is the activation energy and x is the
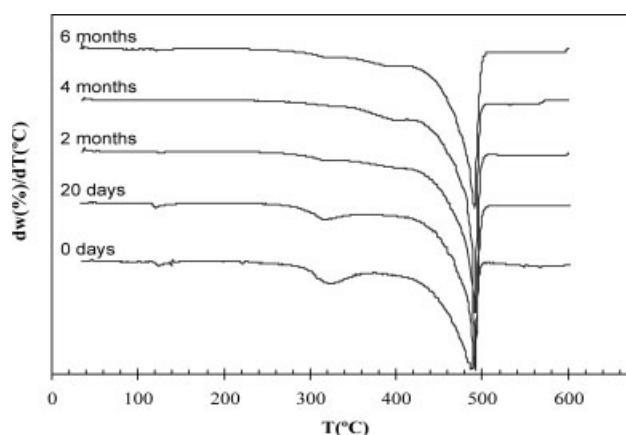

Figure 8 Differential thermogravimetric curves of the photo-oxidized LDPE/Mater-Bi blends as a function of exposure time in soil.
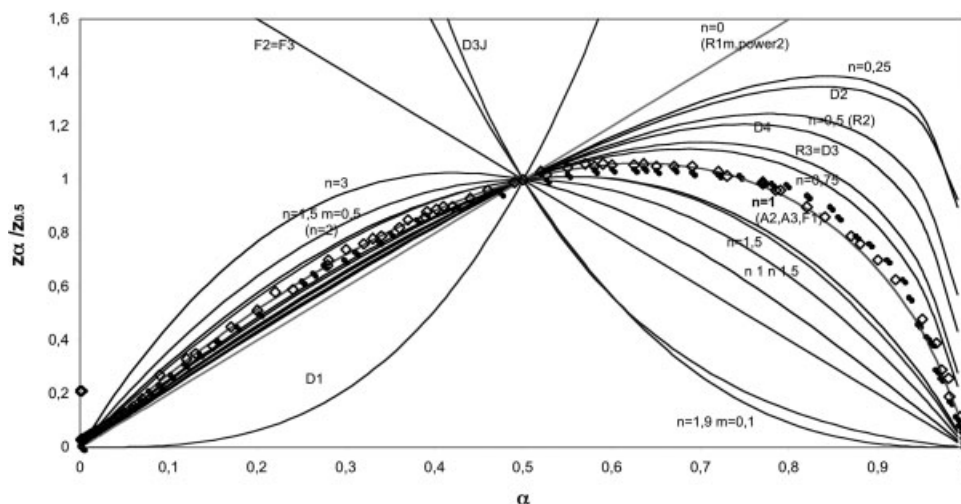
Figure 9 Reduced master curves of different kinetic models and experimental data for the main thermal decomposition processes of the (●) HDPE/Mater-Bi and the (◇) LDPE/Mater-Bi blends.

residual fraction, calculated as $(w-w_\infty)/(w_0-w_\infty)$, where w_0 is the initial mass, w is the sample mass at time t and w_∞ is the final mass.

The activation energy values of the pyrolysis process of the ethylene chains as a function of the soil burial time can be observed in Table VI. Similar activation energy values have been obtained for the HDPE/Mater-Bi and LDPE/Mater-Bi blends in the same temperature interval. It is noted that the activation energy increases in both types of blends with the exposure time in soil, but the increase is higher in the HDPE/Mater-Bi blend (85 kJ/mol) than in the LDPE/Mater-Bi blend (54 kJ/mol).

Photo-oxidation leads to the decrease of the activation energies for both polyethylenes/Mater-Bi blends. This decrease in the activation energy affects to a higher extent the HDPE/Mater-Bi blends (42 kJ/mol) than the LDPE/Mater-Bi blends (17 kJ/mol). When these previous photo-oxided blends were submitted to soil burial test, the activation energy values of the pyrolysis process of the ethylene chains also increase, but the effects caused by the soil burial test are slowed down. These results

may indicate that some changes in the morphology of these blends may be produced during the photo-oxidative process.[31]

To analyze these possible morphological changes as a consequence of both the photo-oxidative treatment and the degradation process in soil, calorimetric measurements have also been performed. In previous studies,[16,17,32] the melting temperature were directly determined from the thermogram as the value of the maximum of each endothermic peak. Pure polyethylenes showed their typical thermogram, with a main endothermic peak around 113°C for LDPE and 130°C for HDPE. Two endothermic peaks around 133 and 156°C can be observed in the DSC thermogram of pure Mater-Bi: the low temperature peak is associated to the crystalline phase of starch and the high temperature peak is related to the crystalline phase of EVOH.

Figures 10 and 11 display the calorimetric thermograms of HDPE/Mater-Bi and LDPE/Mater-Bi blends, respectively. The synergetic effects caused by the previous photo-oxidation process on the calorimetric thermograms have also displayed in the same

TABLE VI
Activation Energies of the HDPE/Mater-Bi and LDPE/Mater-Bi Blends as a Function of the Exposure Time in Soil Calculated Using Broido Method

	HDPE/Mater-Bi blends		LDPE/Mater-Bi blends	
	Non photo-oxidized	Photo-oxidized	Non photo-oxidized	Photo-oxidized
	E_a (kJ/mol) 475–490°C	E_a (kJ/mol) 475–490°C	E_a (kJ/mol) 475–490°C	E_a (kJ/mol) 475–488°C
0 days	218	176	222	205
20 days	254	189	240	181
2 months	277	202	261	202
4 months	297	195	278	202
6 months	304	201	277	196

Figure 10 (A) DSC thermograms of the HDPE/Mater-Bi blend as a function of the exposure time in soil. (B) DSC thermograms of the photo-oxidized HDPE/Mater-Bi blend as a function of the exposure time in soil.

figures. The calorimetric thermograms of HDPE/Mater-Bi blends exhibit a prominent endothermic peak assigned to the polyethylene chains. Other small endothermic peaks associated to the Mater-Bi components cannot be distinguished, probably due to their overlapping with the ethylene contribution.
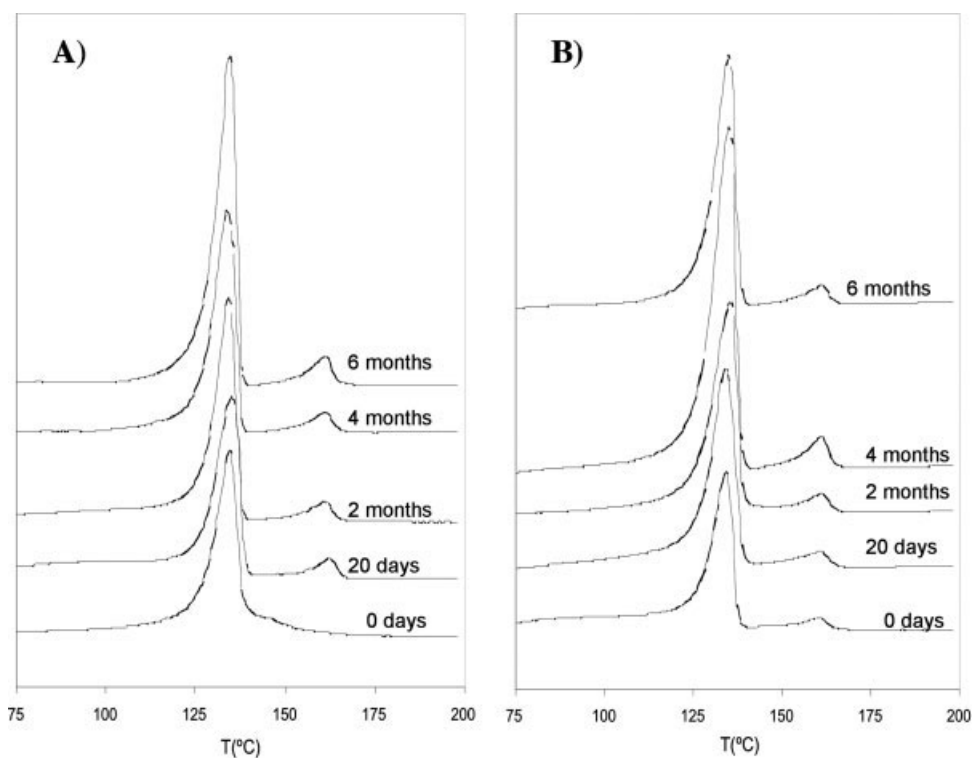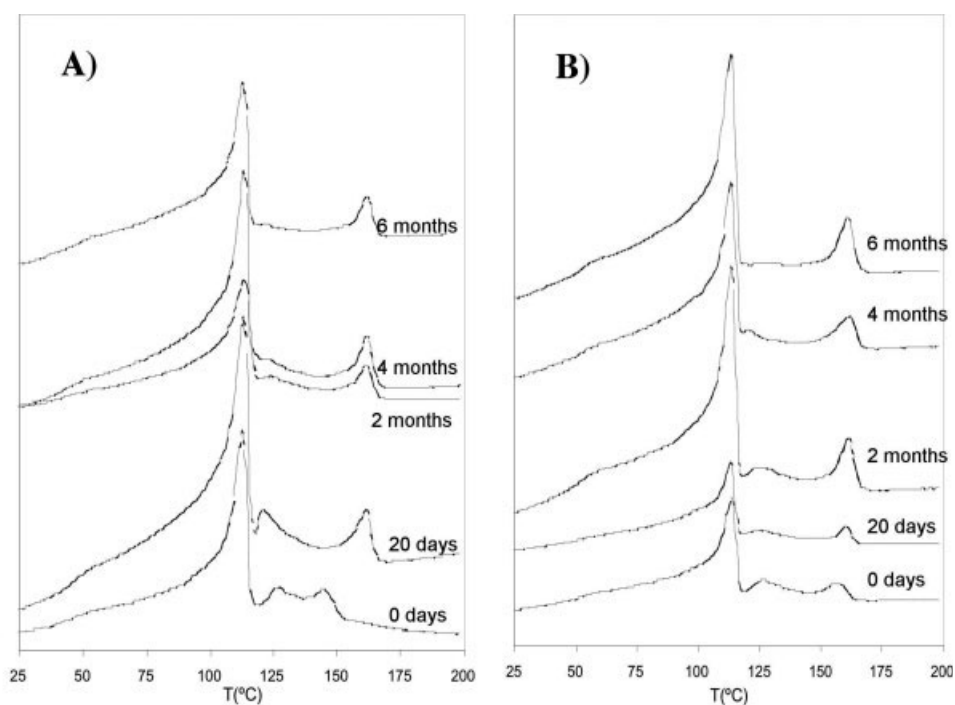

Figure 11 (A) DSC thermograms of the LDPE/Mater-Bi blend as a function of the exposure time in soil. (B) DSC thermograms of the photo-oxidized LDPE/Mater-Bi blend as a function of the exposure time in soil.

TABLE VII
Activation Energies of Mater-Bi as a Function of the Exposure Time in Soil

		Mater-Bi AF05H				
	T (°C)	E_a (kJ/mol)	T (°C)	E_a (kJ/mol)	T (°C)	E (kJ/mol)
0 days	300–360	65	–	–	450–490	50
20 days	285–335	72	350–420	45	450–490	51
82 days	285–335	49	365–402	114	450–490	55

However, LDPE/Mater-Bi blends exhibited three peeks, which could be assigned to both polyethylene and Mater-Bi components.

The photo-oxidative treatment modifies more the calorimetric thermograms of the HDPE/Mater-Bi (Fig. 10) than the LDPE/Mater-Bi blends (Fig. 11). The endothermic peaks assigned to Mater-Bi in the HDPE/Mater-Bi blends appear as a small and a broad peak separated by the ethylene contribution. This fact suggests that photo-oxidative treatment may cause chain scission, enhancing the crystallization and segregation of the different components of the HDPE/Mater-Bi blends, and thus increasing the heterogeneity of these blends. These calorimetric results are in agreement with the activation energy values determined for the thermal decomposition process of the ethylene chain. In general, photo-oxidation enhances the degradation in soil by means of chain scission reactions, but at the same time crystallization processes may be caused, which slow down the biodegradation effects caused by the soil burial test.

No significant changes can be observed in the endotherms associated with the Mater-Bi. Thus, a careful analysis of this region in the derivative thermogram by means of kinetic analysis is very important to understand the degradation of this Mater-Bi in the blends.

In previous studies,[33] the decomposition mechanisms of the different thermal degradation processes of pure Mater-Bi were calculated using Criado method. It has been assessed that at least two mechanisms coexist, and the main thermal decomposition processes follow an Rn type mechanism, being the algebraic expression $f(\alpha) = 3(1 - \alpha)^{2/3}$. The activation energies of the two main thermal decomposition processes of pure Mater-Bi could not be calculated by Broido method, since this method is proposed for reaction order equal to one. Thus, they were calculated using Coats-Redfern method.[34]

Table VII shows also the activation energy values for degraded pure Mater-Bi as the degradation process in soil undergoes. Two different behaviors have been observed when the exposure time in soil increases: (i) the activation energy of the thermal decomposition of the noncomplex starch and more accessible and biodegradable starch diminishes and (ii) the activation energy related to the less accessible to microorganisms complex starch with vinyl alcohol (complex droplet structure) increases. Moreover, the activation energy associated to the thermal decomposition of ethylene chains scarcely is modified. These results agree with the biodegradation mechanisms suggested by Bastioli et al.,[11] who proposed that starch is first hydrolyzed by extracellular enzymes, whereas the synthetic component is biodegraded by surface erosion by the microorganisms. This surface adsorption is enhanced by the increase of available surface area during the hydrolysis of the natural component.

Tables VIII and IX show the activation energy values of thermal decomposition of noncomplex and more accessible starch, the complex starch with vinyl alcohol chains of HDPE/Mater-Bi, LDPE/Mater-Bi blends and the previous photo-oxidized blends, respectively, as a function of the soil burial time.

The differences obtained between the activation energy values from both kinds of PE/Mater-Bi blends suggest that the degradation in soil of Mater-Bi can be conditioned by the matrix used. In the

TABLE VIII
Activation Energies of the HDPE/Mater-Bi Blends as a Function of the Exposure Time in Soil Using Coats-Redfern Method

	HDPE/Mater-Bi blends							
	Non photo-oxidized				Photo-oxidized			
	T (°C)	E_a (kJ/mol)	T (°C)	E_a (kJ/mol)	T (°C)	E_a (kJ/mol)	T (°C)	E_a (kJ/mol)
0 days	296–321	69	–	–	280–341	102	–	–
20 days	290–328	173	–	–	250–320	117	–	–
2 months	315–328	185	354–390	73	283–321	120	350–410	48
4 months	–	–	350–390	111	–	–	350–410	75
6 months	–	–	349–392	117	–	–	350–410	75

TABLE IX
Activation Energies of the LDPE/Mater-Bi Blends as a Function of the Exposure Time in Soil Using Coats-Redfern Method

	LDPE/Mater-Bi blends							
	Non Photo-oxidized				Photo-oxidized			
	T (°C)	E_a (kJ/mol)	T (°C)	E_a (kJ/mol)	T (°C)	E_a (kJ/mol)	T (°C)	E_a (kJ/mol)
0 days	299–340	64	–	–	295–309	66		–
20 days	233–340	83	–	–	260–317	75		–
2 months	265–340	129	352–429	50	264–317	110	335–416	42
4 months	268–340	97	356–429	48	290–346	83	351–419	61
6 months	267–333	119	356–429	53	267–317	104	351–411	51

HDPE/Mater-Bi blends, the noncomplex starch disappears in less time than in the LDPE/Mater-Bi blends. When PE/Mater-Bi blends are submitted to both degradation in soil and photo-oxidation, differences in the activation energy profiles can be observe. In the HDPE/Mater-Bi blends, kinetic parameters seem to indicate that photo-oxidation slows down the changes caused during the soil burial test. In the LDPE/Mater-Bi blends, photo-oxidation faintly modifies the activation energy during biodegradation.

CONCLUSIONS

The thermal decomposition process of blends of polyolefins (HDPE and LDPE) and Mater-Bi AF05H, a starch-based material that contains starch and poly(ethylene-vinyl alcohol) copolymers is a complex degradation that results from its complex structure. Several decomposition regions are displayed in the differential thermogravimetric curves of HDPE/Mater-Bi and LDPE/Mater-Bi blends display, which can therefore be attributed to both PE and Mater-Bi components.

A deconvolution method has been applied to characterize each individual contribution from the differential thermogravimetric curves of all the studied samples. The thermal decomposition mechanism of the ethylene chains of HDPE/Mater-Bi and LDPE/Mater-Bi blends was proved to follow a kinetic function of order 1 $f(\alpha) = (1 - \alpha)$. On the other hand, the two main thermal decomposition mechanisms of pure Mater-Bi were proved to follow a Rn type kinetic model mechanism, $f(\alpha) = 3(1 - \alpha)^{2/3}$.

Photo-oxidized blends of HDPE/Mater-Bi and LDPE/Mater-Bi exhibit the same weight-loss regions than non photo-oxidized blends. Previous photo-oxidation enhances the thermal stability and decrease the activation energy of the pyrolysis process of the ethylene chains in both types of blends. However, the effect of the photo-oxidation on the thermal decomposition of the starch chains depends on the polyolefinic matrix used. HDPE/Mater-Bi blends are more affected by photo-oxidation than LDPE/Mater-Bi blends.

Degradation in soil, on the other hand, mainly affects the noncomplexed starch in both blends; ethylene chains from Mater-Bi and polyethylene prove to be more resistant to biodegradation. The behavior of noncomplexed starch in the blends during the soil burial test is influenced by the used polymeric matrix, being faster in HDPE/Mater-Bi blends than in the LDPE/Mater-Bi blends.

The synergetic effects caused by both degradation processes, the photo-oxidation and the degradation in soil on both types of PE/Mater-Bi blends can be monitorized by the activation energy parameters. In the HDPE/Mater-bi blends seems that the previous photo-oxidation slow down the effects caused by the soil burial test in all thermal decomposition regions.

References

1. La Mantia, F. Handbook of Plastics Recycling; Rapra Technology: Shawbury, 2002.
2. Albertsson, A.-C.; Huang, S. J., Eds. Degradable Polymers, Recycling and Plastics Waste Management; Marcel Dekker: New York, 1995.
3. Smits, M. Polymer Products and Waste Management; Marcel Dekker: New York, 1995.
4. Griffin, G. J. L., Ed. Chemistry and Technology of Biodegradable Polymers; Blackie: Glasgow, 1994.
5. Chandra, R.; Rustgi, R. Polym Degrad Stabil 1997, 56, 185.
6. Erlandsson, B.; Karlsson, S.; Albertsson, A.-C. Polym Degrad Stabil 1997, 55, 237.
7. Albertsson, A.-C.; Erlandsson, B.; Hakkarainen, M.; Karlsson, S. J Environ Polym Degrad 1998, 6, 187.
8. Scott, G. Degradable Polymers; Kluwer Academic: Netherlands, 2002.
9. Clarinval, A.; Halleux, J. In Biodegradable Polymers for Industrial Applications; Smith, R., Ed.; Woodhead Publishing: London, 2005.
10. Bastioli, C. Polym Degrad Stabil 1998, 59, 263.
11. Bastioli, C. Handbook of Biodegradable Polymers. Rapra Technology: Shrewsbury, 2005.
12. Mohanty, A. K.; Misra, M.; Drzal, T. D., Eds. Natural Fibers, Biopolymers and Biocomposites; Taylor & Francis: Boca Raton, 2005.
13. Marcelo, A. V.; Edwin, L. T.; Amstrong, R. C. Polymer 1995, 36, 1869.

14. Contat-Rodrigo, L.; Ribes-Greus, A. J Appl Polym Sci 2000, 78, 1707.
15. Contat-Rodrigo, L.; Ribes-Greus, A.; Día-Calleja, R. J Appl Polym Sci 2001, 82, 2174.
16. Contat-Rodrigo, L.; Ribes-Greus, A. J Appl Polym Sci 2002, 83, 1683.
17. Contat-Rodrigo, L.; Ribes-Greus, A.; Imrie, CT. J Appl Polym Sci 2002, 86, 764.
18. Bastioli, C.; Belloti, V.; Rallis A. Rheologica Acta 1994, 33, 307.
19. DIN 53739 Testing of Plastics. Influence of Fungi and Bacteria. Visual Evaluation. Change in Mass and Physical Properties, November 1984.
20. Contat-Rodrigo, L.; Ribes-Greus, A.; Imrie, C. T. J Appl Polym Sci 2002, 86, 174.
21. Jiang, W.; Qiao, X.; Sun. K. Carbohydr Polym 2006, 65, 139.
22. Wang, X.-L.; Yang, K.-K.; Wang, Y.-Z.; Wu, B.; Liu, Y.; Yang, B. Polym Degrad Stabil 2003, 81, 415.
23. Mano, F.; Koniarova, D.; Reis, R. L. J Mater Sci Mater Med 2003, 14, 127.
24. Cabedo, L.; Jiménez, E.; Lagaron, J. M.; Gavara, R.; Saura, J. J Polym 2004, 45, 5233.
25. Alvarez, V. A.; Ruseckaite, R. A.; Vázquez, A. J Appl Polym Sci 2003, 90, 3157.
26. Aráujo, M. A.; Cunha, A. M.; Mota, M. Biomaterials 2004, 25, 2687.
27. Simmons, S.; Thomas, E. L. J Appl Polym Sci 1995, 58, 2259.
28. Criado, J. M. Thermochim Acta 1978, 24, 86.
29. Vayazovkin, S. Int Rev Phys Chem 2000, 19, 45.
30. Broido, A. J Polym Sci Part A-2: Polym Phys 1969, 7, 1761.
31. Scott, G. Mechanisms of Polymer Degradation and Stabilisation; Elsevier: New York, 1990.
32. Santonja-Blasco, L.; Contat-Rodrigo L.; Moriana-Torró, R.; Ribes-Greus A. J Appl Polym Sci 2007, 106, 2218.
33. Ramis, X.; Cadenato, A.; Salla, J. M.; Morancho, J. M.; Valles, A.; Contat, L.; Ribes, A. Polym degrad Stabil 2004, 86, 483.
34. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 68.