Thermal Characterization of Polyethylene Blends with a Biodegradable Masterbatch Subjected to Thermo-Oxidative Treatment and Subsequent Soil Burial Test

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ABSTRACT: The viability of producing environment-friendly blends of HDPE and LDPE with a commercial biodegradable masterbatch containing starch and polyethylene was studied. The service life of these blends was simulated by means of a thermo-oxidative treatment, and their further disposal in landfill was modeled using an accelerated soil burial test. Characterization was carried out in terms of their calorimetric and thermogravimetric properties. Thermo-oxidative treatment causes an increase in the crystalline content of both components of the blends, and promotes a segregation of the crystallite sizes of polyethylene. The soil burial test leads to changes in the crystalline content of the biodegradable material, which is influenced by the polyolefinic matrix used. The kinetics of the thermal decomposition of these blends was studied using the Hirata and the Broido models. Thermogravimetric results reveal that the thermo-oxidative treatment causes a decrease in the activation energy of the thermal decomposition process of both components in the blends, regardless of the type of polyethylene used. The thermo-oxidative treatment mainly modifies the thermal properties of starch during the degradation process in soil, especially in the LDPE blends. Synergetic degradation of these blends is a complex process that is dependent on the polyolefinic matrix used and mainly causes morphological changes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2218–2230, 2007

Key words: calorimetric analysis; thermogravimetric analysis; polyethylene; degradation; thermo-oxidation

INTRODUCTION

It is well-known that plastics disposal has become a very important environmental problem. The development of degradable polymers offers an effective approach for minimizing plastics wastes.[1,2] Nowadays, most interest is focused on the use of degradable materials that can replace conventional synthetic polymeric materials, both in terms of the production cost and performance. In this sense, a viable solution that has been already employed by producers is to combine the different features and benefits of materials from both petroleum and natural resources, to produce useful blends that may satisfy both economical and environmental requirements.[3]

Conventional plastics like polyolefins are slowly degraded by the environment. However, their sensitivity to degradation can be enhanced by blending them with different commercial biodegradable masterbatches.[4–9] Such blends should be designed to guarantee suitable performance during service life and short degradation times during further disposal. Only an accurate characterization of the degradation process of these blends can validate their future applications.

The aim of this work is to simulate the service life and further disposal of high and low density polyethylene (LDPE) blends with a biodegradable masterbatch, to study their viability for future applications. Simulation of the degradative conditions, under which polymeric materials are exposed during their service life, can be done using many procedures, depending on the application of the studied material. These include reprocessing and thermo-oxidative treatments, among others.[10,11] In this work, the service life was modeled by means of a previous thermo-oxidative treatment in air atmosphere, and further disposal in landfill was simulated using an accelerated soil burial test.

In previous works, the biodegradation process under soil burial conditions of different polyolefin blends with commercial starch products has been characterized.[12,13] The important effect of a previous
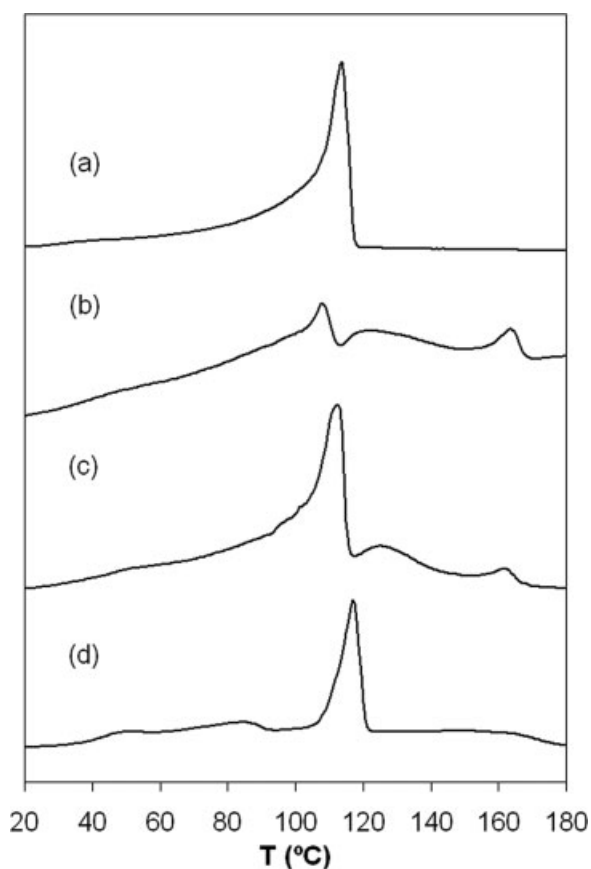
Figure 1 DSC thermograms of (a) LDPE, (b) Cornplast, (c) LDPE/Cornplast blend, and (d) LDPE/Cornplast blend subjected to thermo-oxidative treatment.

MATERIALS AND METHODS

Materials

LDPE 710 and high density polyethylene 10,062 (HDPE) supplied by Dow Chemical (Spain) were used as polymeric matrices.

Cornplast, produced by the National Corn Grower Association (USA), is a commercial biodegradable material with 20% of polyethylene and 80% of a promoter of biodegradation containing starch.

Samples

Two types of blends were prepared, consisting of a mixture of 50/50% by weight of polymeric matrix (either HDPE or LDPE) and Cornplast. The blends were prepared from the melt in a Brabender Plastic-Corder PL 2100 rheometer (Druisburg, Germany). The mixture was cut as nut coal and thereafter processed by compression molding into rectangular samples (68 mm × 12 mm × 1.8 mm), using a Carver M press (Wabash, IN).

thermo-oxidative treatment on the biodegradation process of polyethylene blends with enhanced biodegradability has also been reported in terms of their morphological changes.[14] As a continuation of the aforementioned studies, this work is focused on the assessment of the effect that different polyethylene types may have on the degradation process of these blends.

It is well-established that thermal analysis allows the characterization of the degradation effects on the structure and on other important properties of the polymers. In this work, morphological changes of the different components of the blends have been monitored by Differential Scanning Calorimetry (DSC). Thermogravimetric analysis has been selected to provide information about the thermal stability and the kinetic parameters of the thermal decomposition process of these materials. These parameters are related to the breakdown of the molecular chains, as a result of degradation. Thus, the influence of both the thermo-oxidative treatment and the soil burial test on the properties loss of each type of polyethylene blends was able to be analyzed by means of these thermal analysis techniques.
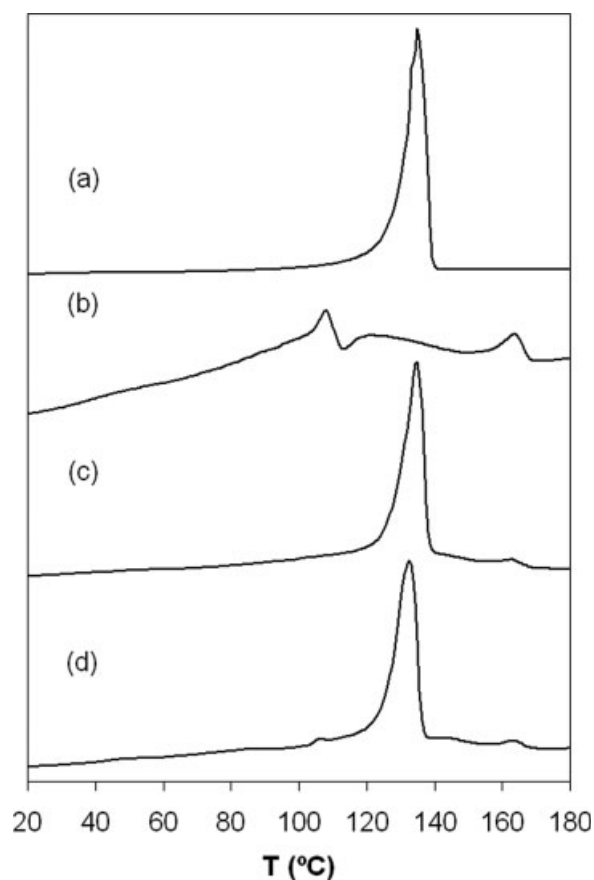

Figure 2 DSC thermograms of (a) HDPE, (b) Cornplast, (c) HDPE Cornplast blend, and (d) HDPE/Cornplast blend subjected to thermo-oxidative treatment.

TABLE I
Melting Temperatures of the Main Endotherm of the LDPE/Cornplast Blends

Exposure time in soil	LDPE/Cornplast blends T_m (°C)	LDPE/Cornplast blends with thermo-oxidative treatment T_m (°C)
0 Days	112.3	117.0
20 Days	112.6	116.5
2 Months	113.0	115.0
4 Months	112.0	116.1
6 Months	113.7	116.4

Thermo-oxidative treatment

A set of samples was subjected to a thermo-oxidative treatment, prior to the soil burial test. This was carried out in a Heraeus UT 6060 oven (Germany) at (100 ± 1)°C during 360 h in air atmosphere. Samples were then immediately quenched in a water and ice bath at 0°C.

Soil burial test

All samples (previously submitted to the thermo-oxidative treatment or not) were subjected to an accelerated soil burial test according to the DIN 53,739 standard norm.[15] Samples were buried for 6 months in biologically active soil in a plastic container, which was kept opened to ensure a fresh oxygen supply. The soil burial test was performed in a Heraeus B12 culture oven (Germany) at a constant temperature of (28 ± 0.5)°C. The soil was a 50/50% by weight mixture of a soil extract from a cultivated field and a soil typically used in pine tree nurseries. The pH of the soil measured in water was 6.75. Samples were removed periodically, cleaned with a soap solution, and dried, to stop the degradation process.

Differential scanning calorimetry

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.

Thermogravimetric analysis

Changes in the thermal properties of the samples were studied by Thermogravimetric Analysis (TGA). Measurements were carried out in a Mettler-Toledo

TGA/SDTA 851 module (Switzerland). Dynamic measurements were performed from 25 to 600°C at a heating rate of 10°C/min, under argon atmosphere (flow rate of 200 mL/min). Measurements were repeated to limit errors to ± 0.01°C for the peak temperatures.

RESULTS AND DISCUSSION

Calorimetric results

Calorimetric analysis was performed to study the morphological changes of the samples, as a consequence of the thermo-oxidative treatment and the degradation process in soil. The melting temperature, the total and partial crystalline contents, and the lamellar thickness distribution were analyzed.

Figures 1 and 2 show the DSC thermograms of pure LDPE, HDPE, and Cornplast, and their blends. The DSC thermogram of pure polyethylene consists of a main endotherm with a maximum around 113°C for LDPE and 130°C for HDPE. On the other hand, three endothermic peaks can be observed in the DSC thermogram of pure Cornplast. The first endotherm (around 108°C) could be assigned to the polyethylene present in the composition of this product. Cornplast also displays other overlapped peaks at higher temperatures: A broad peak located at about 122°C, and a narrower peak centered at 163°C, which can be associated to the starch present in Cornplast.[16,17] Different types of morphological structures have been proposed to describe the crystalline zone of starch,[18] basically organized as highly crystalline lamellae intermitted by less perfect crystalline regions, which could explain this complex melting behavior of starch.

The DSC thermogram of the LDPE/Cornplast blend shows three peaks that can be related to the two components of the blend (Fig. 1). The first one is a main peak around 112°C that can be originated by the carbonated chains of both the LDPE and the polyethylene contained in Cornplast. This thermo-

TABLE II
Melting Temperatures of the Main Endotherm of the HDPE/Cornplast Blends

Exposure time in soil	HDPE/Cornplast blends T_m (°C)	HDPE/Cornplast blends with thermo-oxidative treatment T_m (°C)
0 Days	134.7	132.5
20 Days	133.1	133.6
2 Months	132.3	133.9
4 Months	134.1	133.6
6 Months	131.6	133.1

TABLE III
Calorimetric Parameters of the LDPE/Cornplast Blends

Exposure time in soil	LDPE/Cornplast blends			LDPE/Cornplast blends with thermo-oxidative treatment			
	Area LDPE	Area cornplast	$l_{máx}$ (Å)	Area 1 HDPE	Area 2 LDPE	Area cornplast	$l_{máx}$ (Å)
0 Days	1.00	1.00	61	1.00	1.00	1.00	71
20 Days	0.84	–	61	1.06	2.01	–	70
2 Months	1.08	1.47	62	1.05	1.84	0.29	66
4 Months	0.93	1.06	59	1.08	2.00	0.20	70
6 Months	1.86	1.47	63	1.09	1.89	0.00	70

$l_{máx}$, relative partial areas and average lamellar thickness.

gram also clearly displays two small peaks at 122 and 163°C, which have already been observed in pure Cornplast. These two endotherms can therefore be related to the biodegradable material. Thus, the blending process does not seem to produce any interaction between the two components of the blend, since the different characteristic peaks of the blend correspond to the endothermic peaks of the pure components.

Unlike the LDPE/Cornplast blend, the DSC thermogram of the HDPE/Cornplast blend exhibits only two peaks (Fig. 2). The main peak (around 130°C) is associated to the melting of the polyethylene chains. Concerning the Cornplast component, only its peak around 163°C can be observed. The other small peaks (around 108 and 122°C) cannot be distinguished, probably due to overlap with the polyethylene contribution.

The thermo-oxidative treatment modifies the DSC thermogram of the LDPE/Cornplast blend (Fig. 1). The endotherm assigned to the ethylene chains is divided into two peaks, suggesting a possible segregation of the crystalline zones. Furthermore, the endotherms related to starch develops into a single peak at 164°C. It has been reported for dry starch that a broad endotherm with a peak around 163°C is attributed to both the melting and recrystallization of the amylase and amylopectin components of starch.[19]

The thermo-oxidative treatment has different effects on the morphological behavior of both components of the HDPE/Cornplast blend, as compared

with the LDPE blend (Fig. 2). The main endotherm related to the ethylene chains shifts slightly to lower temperatures. Moreover, several small peaks related to the biodegradable material now can be distinguished. Thus, the thermo-oxidative treatment seems to provoke a diffusion of the molecular chains and a subsequent separation of the different heterogeneous components of the HDPE/Cornplast blend, highlighting the heterogeneity of this blend.

The main melting temperature of all the samples during the soil burial test is summarized in Tables I and II. This parameter scarcely changes with the exposure time in soil. Therefore, a study of the crystalline content and the lamellar thickness distribution has been performed as well, to more accurately characterize the degradation process of these blends.

Crystalline content

The total crystalline content of pure polyethylenes has been obtained using the equation:

$$X = \frac{(H_a - H_c)}{H_m}$$

where H_a and H_c are the enthalpies in the melt state and the crystalline state, respectively. Their difference is directly obtained from the thermogram. H_m is the change in the melting enthalpy of a perfect

TABLE IV
Calorimetric Parameters of HDPE Blends

Exposure time in soil	HDPE/Cornplast blends			LDPE/Cornplast blends with thermo-oxidative treatment			
	Area HDPE	Area cornplast	$l_{máx}$ (Å)	Area 1 HDPE	Area 2 HDPE	Area cornplast	$l_{máx}$ (Å)
0 Days	1.00	1.00	272	1.00	1.00	1.00	196
20 Days	1.07	2.09	211	0.75	2.00	0.46	228
2 Months	1.38	2.95	196	1.05	2.71	1.49	228
4 Months	1.19	2.00	248	0.78	0.29	1.05	228
6 Months	1.54	3.32	183	1.08	0.43	1.21	211

$l_{máx}$, relative partial areas and average lamellar thickness.

crystal of infinite size. For polyethylene, $H_m = 290.3$ J/g.[20] Crystalline contents of 0.48 for pure LDPE and 0.75 for pure HDPE have been found.

To study the evolution of the crystalline content of the blends during the soil burial test, a calculation method of partial areas has been used, which was already developed in previous works.[21,22] This method is based on the determination of the area of the main peaks, and the later subtraction of all the other contributions. After the peak separation, the area of each peak is calculated. This area is directly proportional to the necessary heat flow for the melting of this crystalline fraction. It can also be assumed that this heat flow is in turn directly proportional to the crystalline content. To obtain the relative partial area, the area of the corresponding peak of the original sample divides this area.

For the studied LDPE/Cornplast and HDPE/Cornplast blends, the area related to polyethylene has been evaluated, together with the area of the endotherm at higher temperatures assigned to the starch in Cornplast, because these are the endothermic peaks that persist in time. Tables III and IV list the values of the relative partial areas of all the samples.

A common increase of the areas of the two components can be observed for both blends after the thermo-oxidative treatment performed for the simulation of their service life. Thus, such treatment seems to lead to a recrystallization process, which results in an increase in the crystalline content. The area related to the starch in the LDPE/Cornplast blend exhibits the most significant increase. Concerning polyethylene, a segregation of its crystalline zones is observed in both types of polyethylene blends.

To simulate the further disposal of the LDPE/Cornplast and HDPE/Cornplast blends, these were submitted to a soil burial test. The area related to the biodegradable material of the LDPE/Cornplast blend under soil burial conditions does not change significantly (Table III). In contrast, the area related to polyethylene increases with the exposure time in soil.

In the LDPE/Cornplast blend subjected to both the thermo-oxidative treatment and the soil burial test, the area associated to the biodegradable material tends to disappear as the exposure time in soil increases (Table III). Moreover, both areas related to polyethylene increase with the degradation time in
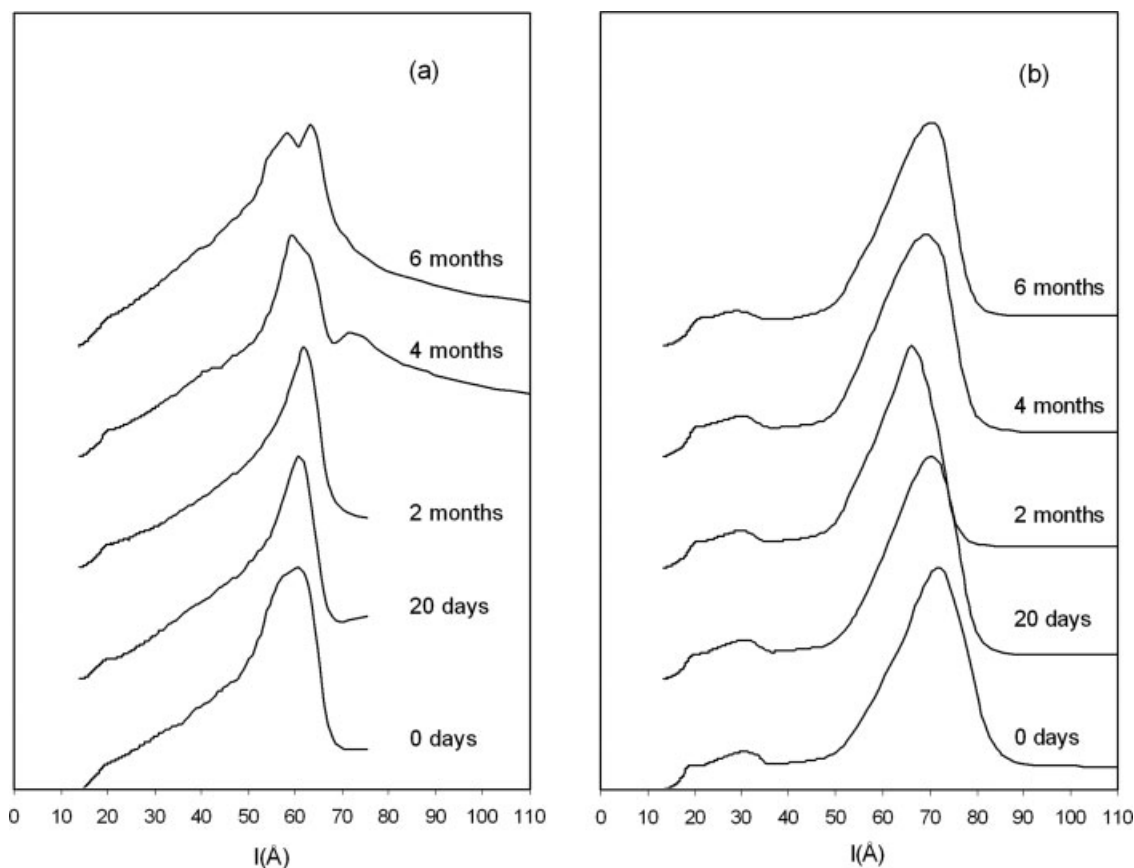

Figure 3 Evolution with the exposure time of the lamellar thickness distribution of the (a) LDPE/Cornplast blends and (b) LDPE/Cornplast blends subjected to thermo-oxidative treatment.

soil. These results may indicate that the thermo-oxidative treatment mainly modifies the degradation process in soil of the starch.

On the other hand, for the HDPE/Cornplast blends that were submitted to the burial soil test, it has been found that the areas related to both the biodegradable material and polyethylene increase with the exposure time in soil (Table IV).

Concerning the HDPE/Cornplast blends subjected to both the thermo-oxidative treatment and the soil burial test, a similar evolution of the two polyethylene areas and the Cornplast area is observed (Table IV). This consists of an initial increase followed by a later decrease of these areas as a function of the exposure time in soil. Comparing with the HDPE blends directly buried in soil, these results suggest that the thermo-oxidative treatment accelerates the degradation process in soil. This could be probably due to the fact that the thermo-oxidative treatment has promoted heterogeneity of these blends.

Thus, from the analysis of the crystalline content it can be stated that the thermo-oxidative treatment has a different effect on both types of blends. Whereas in the LDPE/Cornplast blends, starch is affected to a greater extent, in the HDPE/Cornplast blends both components are significantly modified by such treatment.

These results reveal that degradation is a complex process into which a great variety of molecular mechanisms are involved, such as crystallization and segregation processes. To analyze in more detail the changes taking place in the crystalline zone, the lamellar thickness distributions of the polyethylene contributions have also been calculated.

Lamellar thickness distribution

The lamellar thickness distribution of polyethylene was determined for each sample, using the method proposed by Wlochowicz and Eder,[23] based on the Thompson equation:

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta h_m l}\right)$$

where T_m is the observed melting point of lamellae of thickness l, σ_e is the surface free energy of the basal plane, Δh_m is the melting enthalpy per unit volume, and T_m^0 is the equilibrium melting point of an infinite crystal. These parameters have the following values for polyethylene: $T_m^0 = 414.6$ K,[23] $\sigma_e = 60.9 \times 10^{-3}$ J/m²,[24] and $\Delta h_m = 2.88 \times 10^8$ J/m³.[24]

The lamella thickness corresponding to each melting temperature can be calculated by means of the
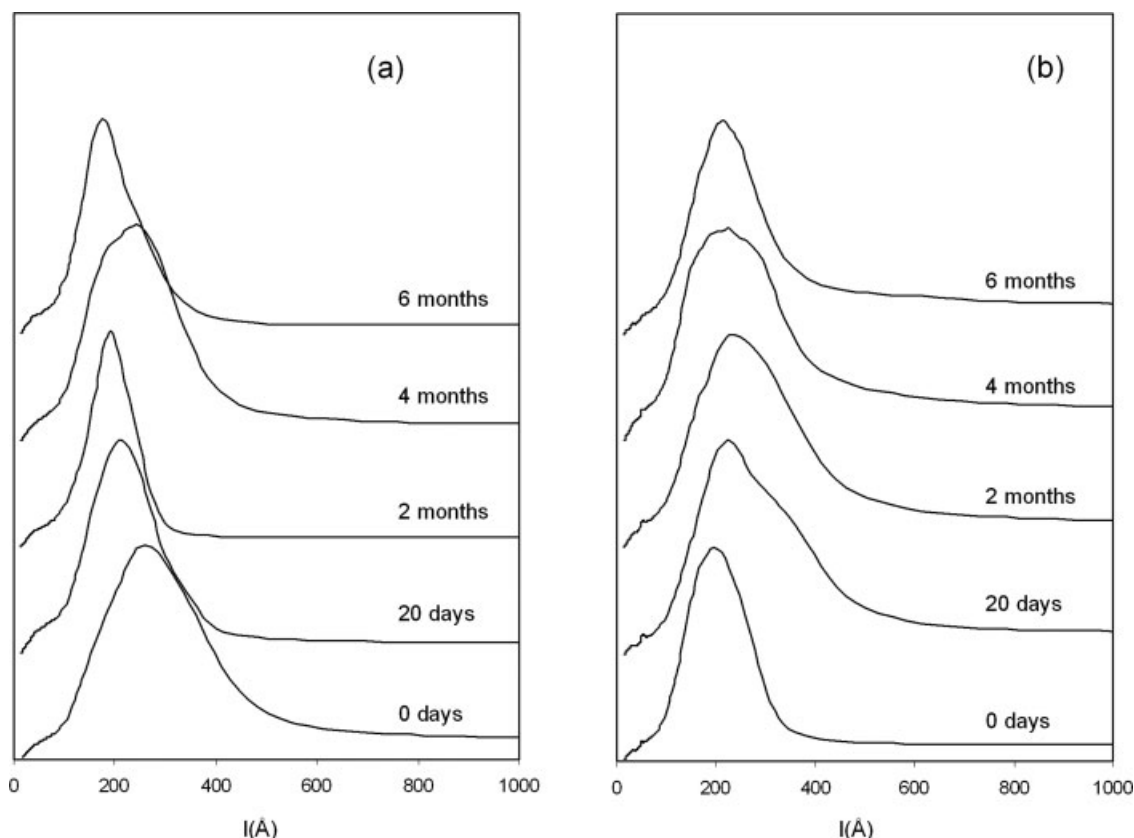

Figure 4 Evolution with the exposure time of the lamellar thickness distribution of the (a) HDPE/Cornplast blends and (b) HDPE/Cornplast blends subjected to thermo-oxidative treatment.
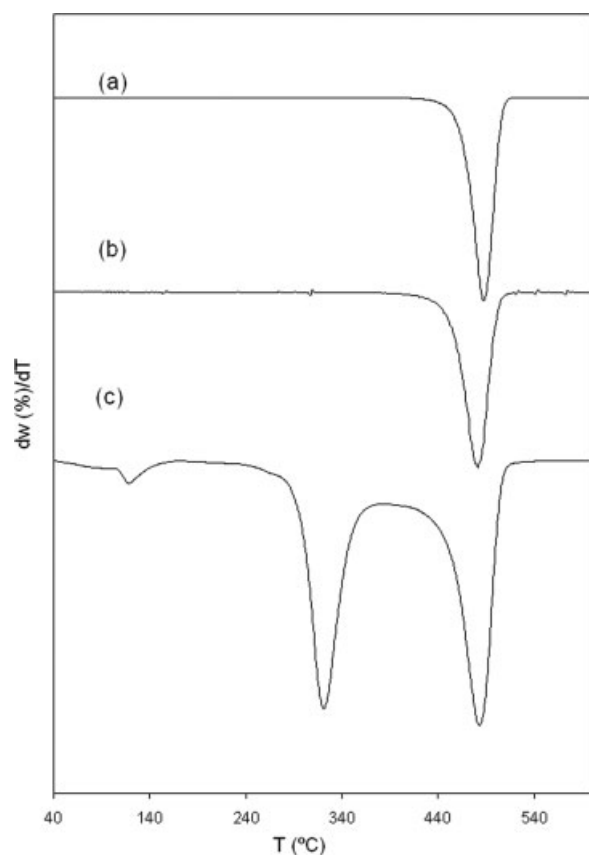
Figure 5 DTG thermograms of pure components. (a) LDPE, (b) HDPE, and (c) Cornplast.

Thomson equation and the earlier parameters. This method leads to the distribution curves of lamellae thicknesses. The lamellar thickness distribution of all the samples is plotted in Figures 3 and 4. The average lamellar values, corresponding to the maximum of each distribution, are listed in Tables III and IV.

The thermo-oxidative treatment leads to a shift towards higher values of the average lamellar thickness of the LDPE/Cornplast blends. Furthermore, a segregation of lamellae with very small thicknesses is also observed (Fig. 3).

Figure 3 reveals that the previous thermo-oxidative treatment leads to a different evolution of the lamellar thickness distribution of the LDPE/Cornplast blends during the soil burial test. The blends that were not subjected to the thermo-oxidative treatment exhibit two evolution stages as a function of the ex-

posure time in soil. In a first stage, the distribution tends to become more homogeneous. In a second stage, a segregation of the crystallite sizes is observed. This phenomenon indicates a rearrangement of the crystalline phase, maybe promoted by the diffusion of the chains of the interspherulitic zone to the crystalline region. However, in the LDPE/Cornplast blends previously subjected to the thermo-oxidative treatment, the shape of their distribution does not change with the exposure time in soil. A slight decrease of the average lamellar thickness can also be observed in these blends (Table III).

The morphological behavior of the HDPE/Cornplast blends is different from that observed for the LDPE/Cornplast blends, regardless if they were subjected to the thermo-oxidative treatment or not (Fig. 4). For the HDPE/Cornplast blends directly buried in soil, the average lamellar thickness shifts to lower values with the exposure time in soil (Table IV). However, the average lamellar thickness of the HDPE/Cornplast blends subjected to the thermo-oxidative treatment first increases and finally tends to decrease with the exposure time in soil.

The lamellar thickness distribution of the HDPE/Cornplast blends that were directly buried in soil tends to become more homogeneous as the exposure time in soil increases. In contrast, in the HDPE blends that were previously subjected to the thermo-oxidative treatment, a broadening of their lamellar thickness distribution can be noted as a function of the exposure time in soil. This could probably be due to the heterogeneity promoted by the thermo-oxidative treatment in the HDPE/Cornplast blend.

These results confirm that degradation of the studied blends is a complex process involving various molecular mechanisms, such as homogeneity and segregation of the crystalline sizes. These are competitive processes that can occur simultaneously during degradation. Many factors like moisture, morphology of the blends, etc., may provoke one process prevailing over the others.

Thus, the thermal treatment leads to different morphological effects on the studied blends, depending on the polyethylene type. In the LDPE/Cornplast blends, the thermo-oxidative treatment promotes the degradation in soil of the biodegradable material, but it increases the crystalline zone of polyethylene and apparently hinders the degradation in soil of

TABLE V
Thermogravimetric Parameters of Pure LDPE, HDPE, and Cornplast

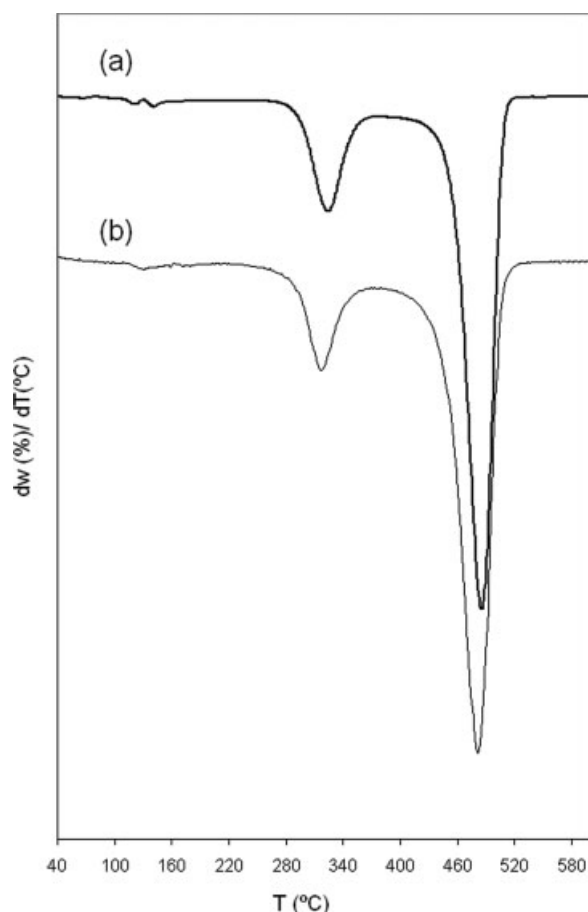| Exposure time in soil	LDPE		HDPE		CORNPLAST		
	T peak (°C)	Residue (%)	T peak (°C)	Residue (%)	T peak starch (°C)	T peak carbonated chains (°C)	Residue (%)
0 Days	483.5	1.6	486.7	0.36	322.0	484.0	7.0

Figure 6 DTG thermograms of (a) LDPE/Cornplast blend and (b) LDPE/Cornplast blend subjected to thermo-oxidative treatment.

for HDPE. These values agree with those reported in the literature for the thermal decomposition of the carbonated chains of these types of polyethylenes.[25,26] The amount of residue for both polyethylenes is less than 2% (Table V).

The thermogram of pure Cornplast displays two degradation steps (Fig. 5). The first one that appears at 321°C has been associated with the pyrolysis of starch.[27,28] The second step is centered on 482°C, and appears in the same temperature range as pure LDPE. Thus, this step has been related to the thermal decomposition of the polyethylene present in Cornplast. The amount of residue for pure Cornplast is 7% (Table V).

The thermograms of the LDPE/Cornplast and HDPE/Cornplast blends are displayed in Figures 6 and 7, respectively. The values of the residue and the peak temperature, corresponding to the temperature of the maximum rate of the thermal decomposition, are reported for these blends in Tables VI and VII, respectively. Three well-defined mass loss stages can be observed in both types of blends. The first mass loss is located around 130°C. It is well-known this component. In contrast, in the HDPE blends, the main modification is observed in the crystalline zone related to polyethylene. The thermo-oxidative treatment enhances the segregation of different lamellar thickness under soil burial conditions.

To analyze the occurrence of possible scissions of the molecular chains as result of the degradation process, and to confirm the different behavior of both polyethylene types, thermogravimetric measurements have also been performed.

TGA results

All the samples have been analyzed using TGA to study their thermal stability and to obtain their kinetic parameters. The latter allows the characterization of the thermal decomposition process of these blends, since these parameters may reveal the changes that occur in the molecular chains as a result of the degradation process.

The thermogram of pure polyethylenes can be observed in Figure 5. It displays a single degradation zone, which appears at 483°C for LDPE and 487°C
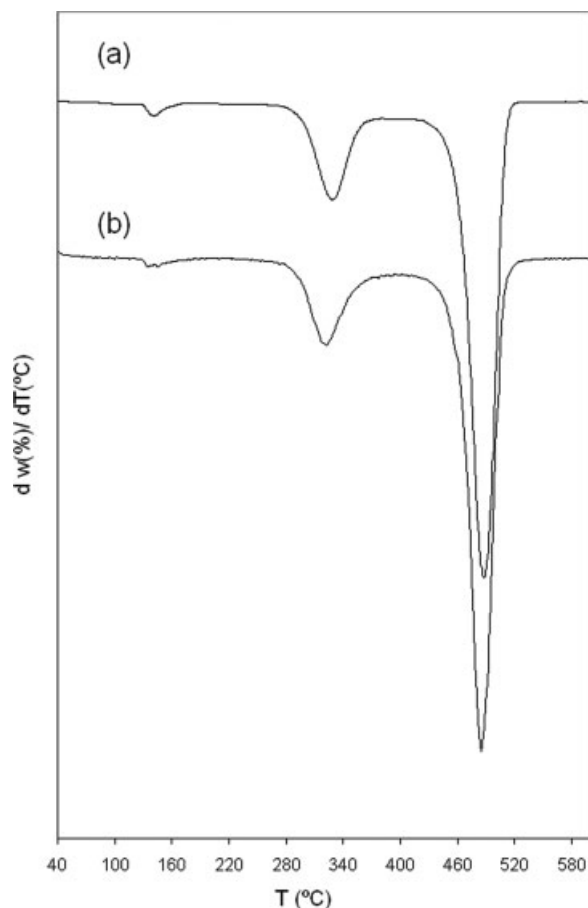

Figure 7 Thermograms of (a) HDPE/Cornplast blend and (b) HDPE/Cornplast blend subjected to thermo-oxidative treatment.

TABLE VI
Thermogravimetric Parameters of the LDPE/Cornplast Blends

Exposure time in soil	LDPE/Cornplast blends			LDPE/Cornplast blends with thermo-oxidative treatment		
	T peak secondary stage (°C)	T peak main stage (°C)	Residue (%)	T peak secondary stage (°C)	T peak main stage (°C)	Residue (%)
0 Days	324.1	485.6	5.3	316.0	481.3	6.2
20 Days	324.4	485.7	5.4	318.0	482.0	6.3
2 Months	326.2	485.9	4.7	317.0	481.2	6.1
4 Months	327.0	485.2	5.5	318.0	482.0	6.1
6 Months	329.6	485.5	4.9	319.0	482.0	6.0

that the loss of water retained by starch takes place in this temperature range. Thus, this stage can be attributed to the water absorbed by the starch present in Cornplast. This mass loss does not represent in any case more than 2%.[7]

The second mass loss appears around 323°C, regardless of the polyolefinic matrix used. Because this peak does not appear in the thermograms of pure LDPE and HDPE, it can be assigned to the thermal decomposition of Cornplast. Moreover, because the thermogram of pure Cornplast exhibits the pyrolysis of starch in this temperature interval, this stage can be associated with the thermal decomposition of the starch present in this biodegradable product.

The third mass loss corresponds to the main stage, which appears at 486°C for LDPE and at 489°C for HDPE, and can be associated to the overlapped thermal decomposition of the carbonated chains of both polyethylene and Cornplast. The temperature of this peak increases slightly as compared with their corresponding pure polyethylenes. This suggests that these blends have a thermal stability similar to that of pure polyethylene.

Regardless of the polyethylene used, all blends exhibit a similar amount of residue (6%). The fact that the residue of pure LDPE and HDPE is less than 2% and that of Cornplast is 7%, indicates that the origin of the residue in the blends may be mainly due to Cornplast.

To simulate the service life of the LDPE/Cornplast and HDPE/Cornplast blends, they were submitted

to a previous thermo-oxidative treatment. The thermograms of these blends are displayed in Figures 6 and 7, and their thermogravimetric parameters are summarized in Tables VI and VII. It can be observed that the thermo-oxidative treatment causes a slight decrease of the peak temperature of starch in both types of blends. However, the peak temperature of the polyethylene chains changes slightly as a consequence of the thermo-oxidative treatment. These thermogravimetric results also show that the thermo-oxidative treatment increases the residue percentage in the same proportion for both types of blends.

The further disposal in landfill of the LDPE/Cornplast and HDPE/Cornplast blends was modeled with a soil burial test. It is observed for both blends that the peak temperature of the polyethylene backbones does not change significantly with the exposure time in soil, regardless of whether the blends were previously subjected to the thermo-oxidative treatment or not (Figs. 6 and 7). This indicates that the polyethylene chains of all the components of the blends are basically not modified during the degradation process in soil, regardless of thermo-oxidative treatment. However, a slight increase in the peak temperature of starch is noted, regardless of the polymeric matrix used.

Furthermore, the soil burial test leads to a slight decrease in the amount of residue in both blends, regardless of thermo-oxidative treatment (Tables VI

TABLE VII
Thermogravimetric Parameters of the HDPE/Cornplast Blends

Exposure time in soil	HDPE/Cornplast blends			HDPE/Cornplast blends with thermo-oxidative treatment		
	T peak secondary stage (°C)	T peak main stage (°C)	Residue (%)	T peak secondary stage (°C)	T peak main stage (°C)	Residue (%)
0 Days	328.3	488.6	5.5	322.0	485.6	6.6
20 Days	324.1	488.5	5.4	323.0	486.4	6.0
2 Months	324.5	488.7	4.4	324.9	485.2	6.2
4 Months	329.0	488.0	4.6	325.7	486.4	6.3
6 Months	331.4	488.7	5.4	326.0	486.0	6.1

TABLE VIII
Activation Energies (Ea) of Pure LDPE, HDPE, and Cornplast

	LDPE		HDPE		CORNPLAST			
	Ea (kJ/mol)		Ea (kJ/mol)		Ea (kJ/mol)			
	Broido	Hirata	Broido	Hirata	Broido		Hirata	
Exposure time in soil	(475–505°C)	(450–485°C)	(475–505°C)	(450–485°C)	(300–330°C)	(475–485°C)	(290–315°C)	(450–485°C)
0 Days	399.5	405.8	518.8	502.0	132.2	199.1	214.2	265.6

and VII). Because the residue has been attributed to the presence of Cornplast, this decrease in the amount of residue may indicate the degradation of Cornplast. As Cornplast is mainly made up of starch and this degradation is expected to be related to the degradation of the starch.

Because the temperature of the maximum rate of the thermal decomposition scarcely changes, a kinetic analysis was performed as well. This has allowed the calculation of the activation energy, to more accurately characterize the degradation process.

The activation energies of all thermal decomposition zones have been determined using the Broido integral method and the Hirata differential method. In previous works, it was concluded that the integral methods seem to better define the thermal decomposition stages at high temperatures when there are several overlapped processes, because these methods provide an average activation energy value.[13] On the other hand, the differential methods seem to better describe the low-temperature stages, since they allow the identification of different stages taking place in the same thermal decomposition process.

The Broido model[29] is based on the equation:

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

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

sidual fraction defined as $x = \frac{\omega_0 - \omega}{\omega_0 - \omega_\infty}$, where ω_0, ω_∞, and ω are the initial, residual, and actual mass, respectively.

The activation energy values estimated with the Broido model for the different processes involved in the thermal decomposition of all the samples are shown in Tables VIII, IX, and XI.

The Hirata model[30] is directly deduced from a kinetic function in its derivative form. This method describes the kinetics of a system undergoing chemical changes in terms of the weight of the sample ω at time t. The Hirata model is based on the equation:

$$\ln\left(-\frac{d\omega}{dt}\right) - \ln(\omega) = \ln A - \frac{E_a}{RT}$$

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

The activation energies calculated with the Hirata model for the pure components and their blends are summarized in Tables VIII, X, and XII.

The results obtained with the Broido and the Hirata methods lead to the same decomposition stages. Nevertheless, the Hirata method allows the identification of more differences between the activation energy associated with each type of degradation.

As it has been previously mentioned, the thermal decomposition of pure LDPE and HDPE takes place in a single stage, which can be associated to the

TABLE IX
Activation Energies (Ea) of the LDPE/Cornplast Blends Calculated with the Broido Model

	LDPE/Cornplast blends		LDPE/Cornplast blends with thermo-oxidative treatment	
	Ea (kJ/mol)		Ea (kJ/mol)	
	P2[a]	P1[b]	P2[a]	P1[b]
Exposure time in soil	(300–330°C)	(475–505°C)	(290–330°C)	(475–505°C)
0 Days	118.8	297.4	118.8	255.2
20 Days	131.7	297.4	92.8	261.5
2 Months	117.9	304.6	88.2	268.6
4 Months	123.0	300.8	82.8	274.0
6 Months	112.1	302.0	84.5	271.1

[a] Related to the starch.
[b] Related to the carbonated chains.

TABLE X
Activation Energies (Ea) of the LDPE/Cornplast Blends Calculated with the Hirata Model

Exposure time in soil	LDPE/Cornplast blends		LDPE/Cornplast blends with thermo-oxidative treatment	
	Ea (kJ/mol)		Ea (kJ/mol)	
	P2	P1	P2	P1
	(290–315°C)	(450–485°C)	(290–315°C)	(450–480°C)
0 Days	200.8	389.1	178.6	300.4
20 Days	196.6	401.6	131.3	301.2
2 Months	193.0	402.2	119.2	306.2
4 Months	184.0	414.6	99.1	309.6
6 Months	167.3	408.7	107.9	313.8

decomposition of their carbonated chains. Table VIII displays the activation energies assigned to this stage, calculated according to the Broido and the Hirata methods. It is well-known that the activation energy of the thermal decomposition process of LDPE is lower than that of HDPE.

The characteristic activation energies of the thermal decomposition process of pure Cornplast have also been determined (Table VIII). These correspond to the two thermal decomposition processes that were previously identified, related to starch and the polyethylene chains in the biodegradable material.

Activation energies for the LDPE/Cornplast and the HDPE/Cornplast blends are shown in Tables IX and X, and Tables XI and XII (where P2 is related to the starch and P1 to the carbonated chain), respectively. In general, kinetic results show that the LDPE/Cornplast blends have slightly lower activation energy values for all the thermal decomposition stages than the HDPE/Cornplast blends.

In contrast, the thermo-oxidative treatment causes a decrease in the activation energies of the thermal decomposition process of both the starch and the carbonated chains, regardless of the polyethylene type. However, this effect is more pronounced for the decomposition process of the polyethylene chains.

Therefore, it can be established that the thermo-oxidative treatment affects the carbonated chains of polyethylenes to a greater extent. These results are in good agreement with the previous calorimetric results.

Concerning the LDPE/Cornplast and HDPE/Cornplast blends subjected to the soil burial test, a slight decrease of the activation energy of the starch has been noted, and is most significant in the HDPE/Cornplast blends. In contrast, the activation energy of both polyolefins tends to increase slightly with the exposure time in soil. Hence, degradation in soil affects the starch more significantly than the polyethylene chains. Moreover, the starch seems to degrade faster in the HDPE/Cornplast blends.

Finally, it can also be observed that the thermo-oxidative treatment accelerates the decrease of the activation energy of the decomposition of starch, when the blends are later submitted to the soil burial test. Furthermore, this effect is more significant in the LDPE/Cornplast blends, in contrast to what was noted in the LDPE blends directly buried in soil. These results are also in good agreement with the calorimetric results that have shown that in the LDPE/Cornplast blends, the area associated with the biodegradable material tends to disappear with the exposure time in soil. On the other hand, the

TABLE XI
Activation Energies (Ea) of the HDPE/Cornplast Blends Calculated with the Broido Model

Exposure time in soil	HDPE/Cornplast blends		HDPE/Cornplast blends with thermo-oxidative treatment	
	Ea (kJ/mol)		Ea (kJ/mol)	
	P2	P1	P2	P1
	(300–330°C)	(475–490°C)	(290–330°C)	(470–505°C)
0 Days	149.3	305.4	216.0	256.4
20 Days	128.8	310.8	121.3	261.9
2 Months	115.0	330.1	126.7	266.5
4 Months	115.4	336.3	117.1	264.8
6 Months	140.5	324.2	112.9	273.6

TABLE XII
Activation Energies (Ea) of the HDPE/Cornplast Blends Calculated with the Hirata Model

Exposure time in soil	HDPE/Cornplast blends		HDPE/Cornplast blends with thermo-oxidative treatment	
	Ea (kJ/mol)		Ea (kJ/mol)	
	P2	P1	P2	P1
	(290–315°C)	(450–485°C)	(290–315°C)	(450–480°C)
0 Days	213.3	397.4	186.6	364.8
20 Days	184.9	442.6	193.7	374.8
2 Months	186.6	442.2	179.0	370.2
4 Months	140.5	447.6	171.5	369.4
6 Months	129.7	449.7	161.0	369.8

thermo-oxidative treatment does not seem to affect significantly the thermal behavior of the polyethylene chains under soil burial conditions.

It could then be suggested that the thermo-oxidative treatment accelerates the degradation process in soil of the starch, especially in the LDPE/Cornplast blends. However, degradation in soil of the polyethylene chains seems not to be so influenced by the thermo-oxidative treatment.

CONCLUSIONS

Mixtures of high and LDPEs and a commercial biodegradable masterbatch containing starch (Cornplast) allow the production of heterogeneous blends with high thermal stability. The heterogeneity of the LDPE/Cornplast and HDPE/Cornplast blends has been demonstrated in the DSC thermograms where it is possible to distinguish the endotherm attributed to polyethylene from those associated with Cornplast.

For both types of blends, the thermo-oxidative treatment mainly affects the morphological and thermal properties of polyethylene. However, the degradation process in soil modifies to a greater extent the morphological and thermal behavior of the starch contained in the biodegradable material, which seems to degrade faster in the HDPE/Cornplast blends.

Synergetic degradation of the LDPE/Cornplast and HDPE/Cornplast blends has proved to be a complex process, in which a great variety of competitive processes are involved that mainly originate morphological changes in both components, especially in polyethylene. During the degradation process of these blends, a simultaneous tendency towards homogeneity and segregation of the crystallite sizes of polyethylene takes place.

In the LDPE/Cornplast blends, the thermo-oxidative treatment promotes the degradation of the biodegradable material under soil burial conditions. However, it also increases the crystalline zone of polyethylene, which apparently hinders its degradation in soil.

In the HDPE/Cornplast blends, the thermo-oxidative treatment promotes its heterogeneity and mainly modifies the crystalline zone of polyethylene. As a consequence, the segregation of different lamellar thicknesses of polyethylene during the soil burial test is enhanced.

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