Influence of Previous Annealing on First Stage of Degradation of Blends of Low-Density Polyethylene and Mater-Bi AF05H Aged in Soil: Comparative Thermal Analysis Study

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ABSTRACT: Samples of low-density polyethylene (LDPE) filled with a commercial biodegradable material (Mater-Bi AF05H) were subjected to an accelerated soil burial test in a culture oven. In addition, another series of these blends was subjected to thermal treatment and afterward buried in soil under the same conditions. Comparative studies of the changes in the thermal stability and the structural and morphological properties of the samples were carried out by means of differential scanning calorimetry, dynamic mechanical thermal analysis, and thermogravimetric analysis. The morphological properties under study were the melting temperature, the crystalline content, and the lamellar thickness distribution. The α_I relaxation zone of the mechanical spectra was characterized in terms of tan δ, whereas the α_{II} and relaxation zones were characterized in terms of E'' according to the Fuoss–Kirkwood equation and with the help of a deconvolution method. Finally, the kinetics of each thermodegradation process was studied using the Broido integral method. The Mater-Bi hindered the uniform growth of crystallites in PE and facilitate molecular motions, but the thermal treatment seemed to rearrange the crystallites in the crystalline phase of PE and promote segregation of the crystallite sizes. These molecular reorganizations affected the degradation process so that the degradation of the polymeric matrix seemed to be obstructed by the annealing during the first 120 days of aging in soil and only the Mater-Bi degradation could be observed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3359–3373, 2003

Key words: polyethylene; annealing; differential scanning calorimetry; mechanical properties; thermogravimetric analysis

INTRODUCTION

Biodegradation is considered to be the most desirable long-term future solution to the plastic waste disposal problem, among other alternatives such as incineration or recycling. However, further research is still necessary to take advantage of environmentally degradable polymers.

Different strategies have been developed in this respect, as reviewed by Albertsson and Karlsson.[1,2] One of them is to enhance the degradability of conventional inert polymers, such as polyethylene (PE), by introducing biodegradable components into the matrix. Several techniques in which starch is used as a biodegradable additive have been patented since the 1970s.[3,4] Biodegradation of the starch creates pores in the PE, leading to a weakened polymeric matrix. Thus, the susceptibility of PE to modification may increase as a result of the interaction of both biotic and abiotic processes.

In previous works,[5–9] blends of high-density PE, low-density PE (LDPE), or polypropylene with several starch products have been submitted to accelerated soil burial tests and analyzed mainly by different techniques of thermal analysis. In line with these studies, we present results here for blends of LDPE with Mater-Bi AF05H. Considering that the crystalline morphology strongly influences the degradation process,[10,11] a series of samples has been annealed prior to the soil burial test in order to improve their crystalline structure. Another series of such blends has been subjected directly to the soil burial test in order to compare both degradation processes.

The purpose of this work is to use thermal analysis to study the degradation process of blends of LDPE and Mater-Bi AF05H as biodegradable materials. The influence of annealing on the degradation process during the first stage of aging in soil has been analyzed.

EXPERIMENTAL

Materials

The LDPE (LDPE-585, $M_n = 16 \times 10^3$, $M_w = 75 \times 10^3$, $\rho = 0.9230$ g/cm^3) and Mater-Bi AF05H in the study

were supplied by Dow Chemical Iberica, S.A. (Tarragona, Spain) and Novamont North America, respectively. Mater-Bi AF05H is a biodegradable material commonly used as an additive. It contains thermoplastic starch that is heavily complexed with ethylene-vinyl alcohol copolymers.[4]

Sample preparation

A homogeneous mixture of 50/50 wt % LDPE and Mater-Bi AF05H was prepared from the melt in a Brabender Plasticorder (PL 2100) rheometer. The mixture was cut as nut coal and then processed by compression molding into rectangular samples (68 × 12 × 1.8 mm) by means of an M Carver press. Samples of pure LDPE were also compression molded from pellets. Untreated samples, both pure and blended, were taken apart to be used as controls.

Annealing

A series of both pure and blended samples (annealed samples) was subjected to a thermal treatment before aging in soil, whereas the other sample (nonannealed samples) was directly buried without any previous treatment.

The thermal treatment consisted of keeping the samples in a Hereaus UT6060 oven at 100 ± 1°C in an air atmosphere for 336 h. After annealing, the samples were immediately immersed in a ice-water bath at 0 ± 0.5°C. Again, samples of each type were taken apart to compare with the untreated samples and with annealed/aged samples.

Soil burial test

The accelerated soil burial test was performed following DIN 53739.[12] Samples were buried in biologically active soil contained in rectangular plastic boxes, which were kept open to ensure a fresh oxygen supply. A 20-mesh stainless wire cloth lined the bottom and sides of the box to lift the soil a little and ensure good air circulation.[13] The soil consisted of a 50/50 wt % mixture of a soil extract picked up from a culture field and a soil typically used in tree nurseries for growing pines. The boxes were kept in a Hereaus B12 culture oven at a constant temperature of 28 ± 0.5°C. The pH and water content of the soil were periodically controlled. During the test, the average pH value (measured in water) was 7.3 ± 0.1 and the average humidity was 65.0 ± 0.5%.

Blended samples were removed after different time periods of 20, 61, and 123 days for the previously annealed samples (annealed/aged blended samples) and 20, 61, 123, 179, and 255 days for the nonannealed samples (nonannealed/aged blended samples). Samples of pure LDPE were removed at the end of each test, carefully washed with a soap solution to stop the degradation process, and dried with a tissue.

Differential scanning calorimetry (DSC) measurements

DSC measurements were performed on a DSC 4 Perkin–Elmer calorimeter (Norwalk, CT) previously calibrated with indium standards. Each sample consisted of 6–7 mg of material that was accurately weighed in a standard aluminum pan. The pans were sealed, pierced, and heated from 0 to 200°C at a heating rate of 10°C/min under a nitrogen atmosphere. Measurements were repeated to assure errors of ±0.1°C for melting temperatures and ±0.5% for crystalline contents.

Dynamic mechanical thermal analysis (DMTA)

DMTA experiments were carried out using a Mark II dynamic mechanical thermal analyzer from Polymer Laboratories (Poole, U.K.). Deformation was applied in the cantilever double-clamping bending mode. Samples were heated from −80 to 120°C at a rate of 1°C/min at frequencies of 0.3, 1, 3, 10, and 30 Hz.

Thermogravimetric analysis (TGA)

TGA was carried out by means of an SDT 2960 module simultaneous differential thermal analyzer from TA Instruments (Surrey, U.K.). Samples of approximately 20 mg were scanned from 25 to 600°C at a heating rate of 20°C/min under an argon atmosphere (flow rate = 200 mL/min).

RESULTS AND DISCUSSION

DSC measurements

Calorimetric experiments were performed to study the changes occurring in the crystalline phase of the samples during annealing and aging in soil.

Figure 1 shows the DSC thermograms for pure LDPE, Mater-Bi AF05H, and a blended sample. The pure sample shows the typical DSC thermogram of a LDPE, consisting of a main endotherm with a maximum at around 111°C and a small shoulder at lower temperatures. The thermogram of Mater-Bi displays a broad plateau in the temperature range between 80 and 170°C. The blended sample displays the main peak at approximately 110°C, which is assigned to PE, and an overlapped small shoulder at higher temperatures, corresponding to Mater-Bi.

Figure 2 shows the DSC thermograms for pure LDPE samples. When the annealed pure LDPE sample is compared to the untreated one, it can be noticed that the thermal treatment leads to a slight shift of the main
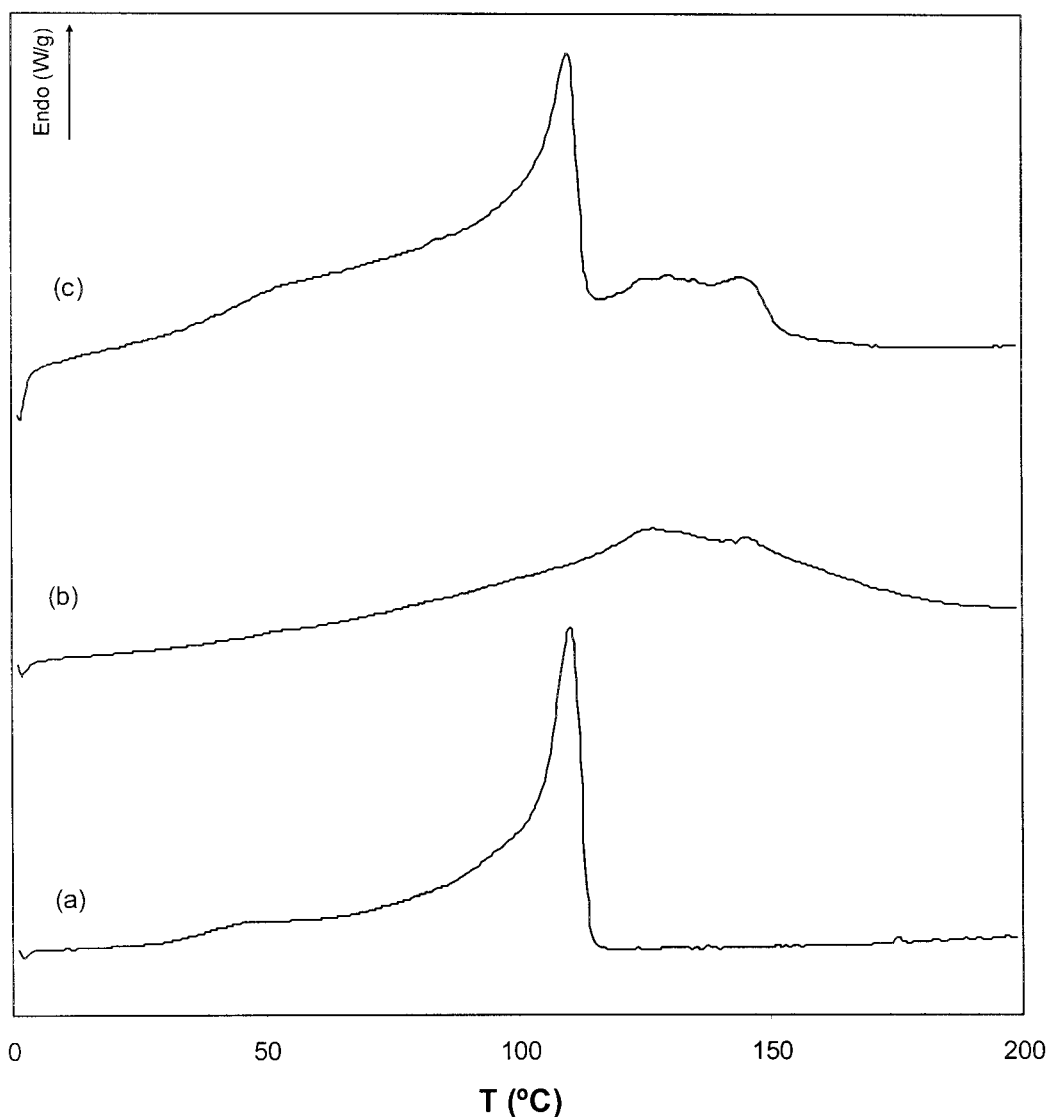
Figure 1 DSC thermograms for (a) pure LDPE, (b) Mater-Bi AF05H, and (c) 50/50 wt % LDPE/Mater-Bi AF05H blend.

endotherm to higher temperatures and the development of the shoulder at lower temperatures into two major peaks at 50 and 85°C. The burial test does not significantly affect the thermograms of pure LDPE samples (annealed or nonannealed.

Figures 3 and 4 show the DSC thermograms for nonannealed and annealed blended samples, respectively. The thermal treatment in blended samples causes the same effects in the main endotherm as those mentioned before for the pure samples: it promotes a shift to higher temperatures and the development of the shoulder into two major peaks.

With the aging time in soil, there are no changes observed in position or shape for the main endotherm in either nonannealed or annealed samples. However, the peak assigned to Mater-Bi broadens toward higher temperatures and develops into a narrow more resolved peak at approximately 160°C. This small peak

appears to be well resolved after 20 days of aging in soil for the nonannealed samples, whereas in annealed samples it is observed after 123 days in soil. These results seem to indicate that the peak corresponding to the Mater-Bi indicates more difficulties in being changed by the degradation in soil process in the previously annealed samples.

In order to analyze the obtained thermograms in detail, three different parameters have been studied: melting temperature, crystalline content, and lamellar thickness distribution.

Melting temperature

The melting temperature (T_m) of the main endotherm has been determined in each case as the maximum of this peak, and they are listed in Table I. It is worthwhile to mention that the T_m for blended samples is
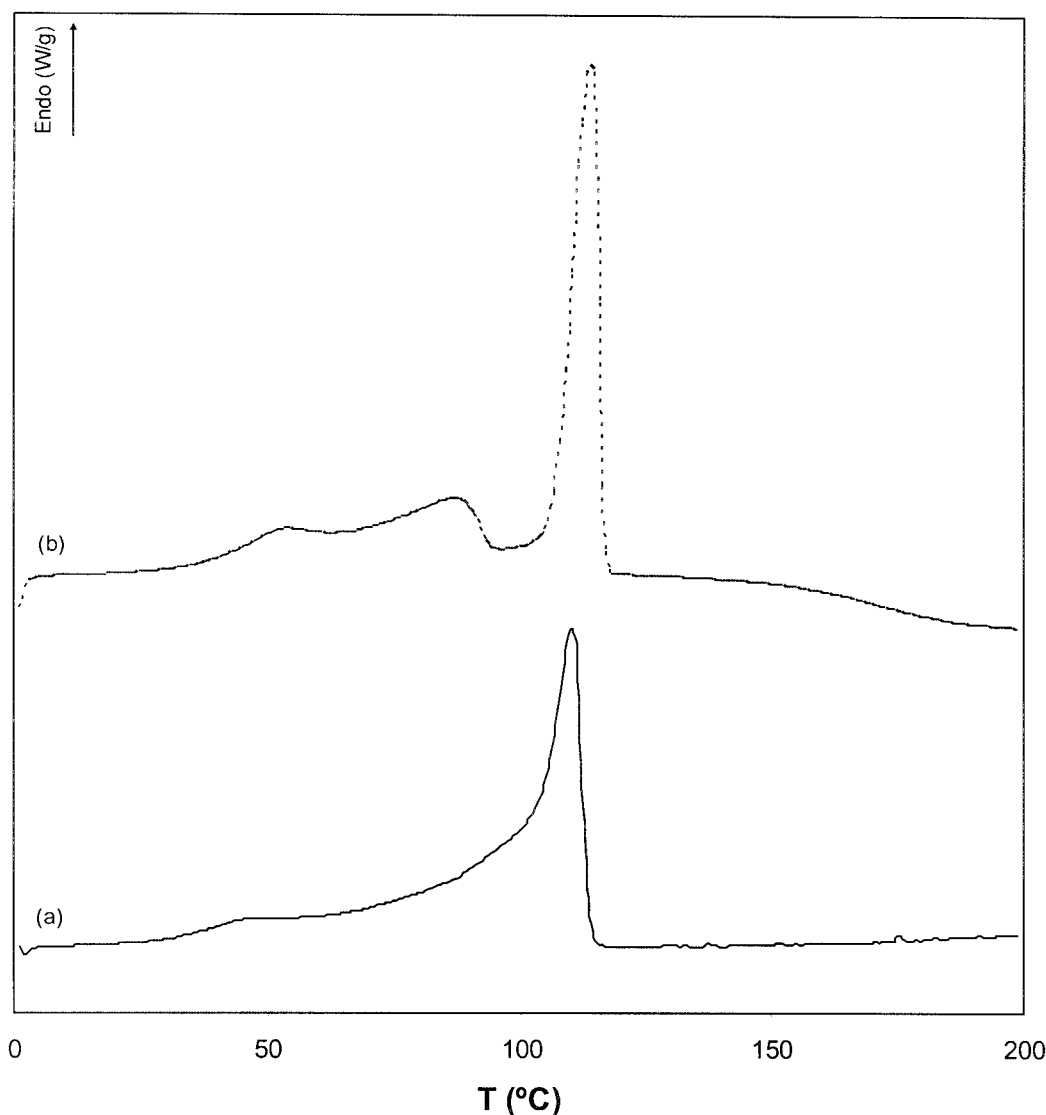
Figure 2 DSC thermograms for pure LDPE (a) untreated and (b) annealed samples.

generally slightly lower than those of pure samples. The thermal treatment increases the T_m about 4°C in both pure and blended samples. This parameter scarcely changes during the soil burial test.

Crystalline content

A method of calculation of partial areas, which was developed in previous work,[5,8,9] was applied in order to study the evolution of the crystalline content of PE and Mater-Bi separately during the degradation process. This method is based on the determination of the peaks corresponding to PE and Mater-Bi in each thermogram and the subtraction of all the other contributions.

After separating the peaks, the area of each peak is calculated. This area is then divided by the area of the corresponding peak for the untreated sample in order to obtain the relative partial areas. No changes were observed for the pure samples after the annealing and/or the soil burial test. Figure 5(A,B) shows the obtained results for the relative partial areas (a_r) for PE and Mater-Bi in both annealed and nonannealed blended samples.

The relative partial areas assigned to Mater-Bi decrease with the aging time in soil. However, this evolution seems to be delayed by thermal treatment. Concerning the relative partial areas of PE in blended samples, the increase during the first 120 days of exposure in soil has been found to be more pronounced in the nonannealed samples, in spite of the initial increase of crystallinity in the annealed samples caused by the thermal treatment.

The scission of the molecules of the amorphous region allows the crystallization to proceed to a higher extent. Thus, the increase in crystallinity observed for

the PE in the blends during the soil burial test could be understood as a sign of degradation.[14]

Lamellar thickness distribution

Next, the lamellar thickness distribution of PE was determined for each sample. According to the method proposed by Wlochowicz and Eder,[15] it was assumed that the rate of heat consumption at a given temperature is directly proportional to the fraction of melting lamellae whose thickness is given by the Thomson equation, from where it can be deduced that
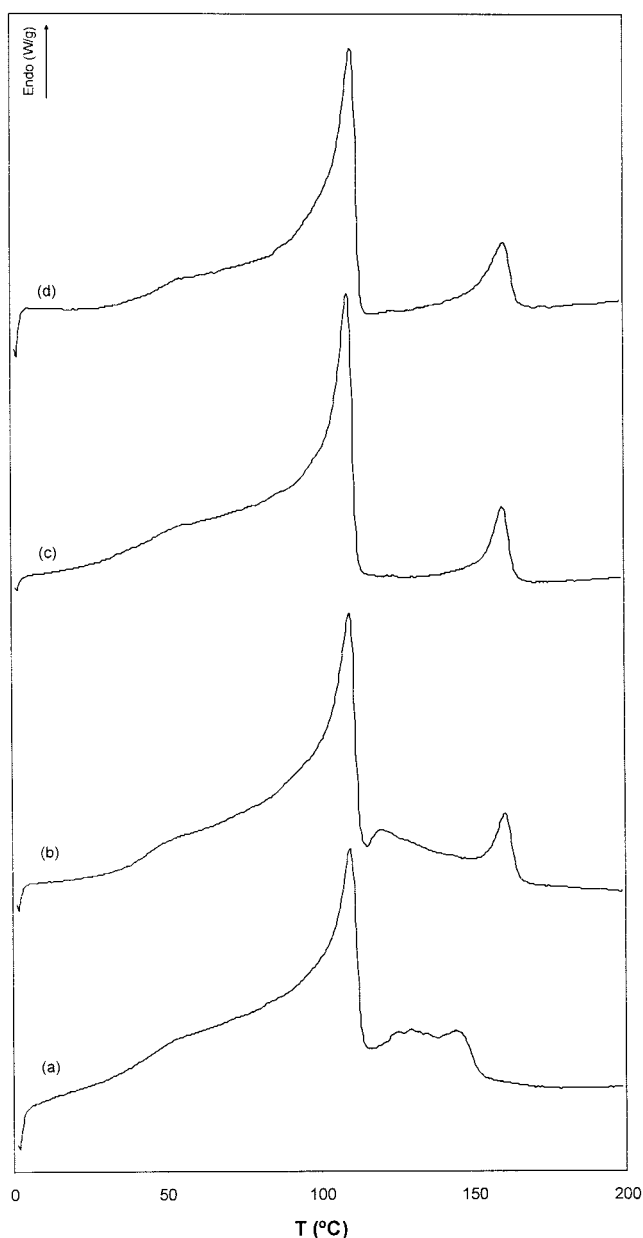

Figure 3 DSC thermograms for nonannealed blended samples aged in soil for (a) 0 (untreated), (b) 20, (c) 123, and (d) 255 days.
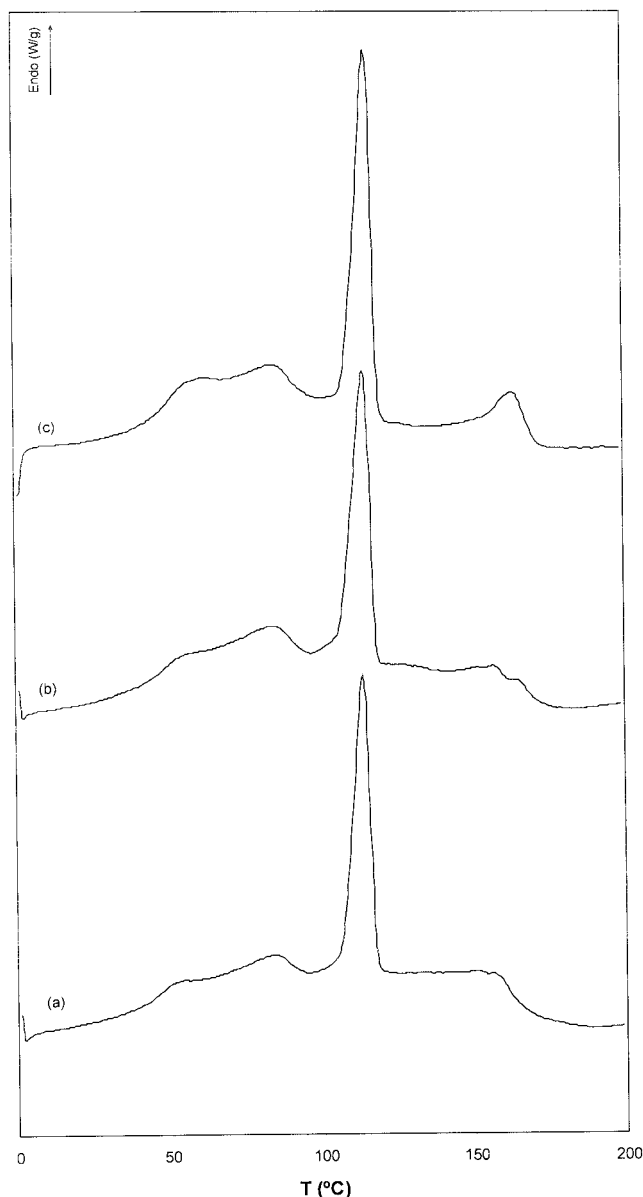

Figure 4 DSC thermograms for annealed blended samples aged in soil for (a) 0, (b) 20, and (c) 123 days.

$$l = \frac{2\sigma_e}{\Delta Hi\left(1 - \dfrac{T_m}{T_m^o}\right)} \qquad (1)$$

where T_m is the observed melting point of lamellae of thickness l, T_m^o is the equilibrium melting point of an infinite crystal, σ_e is the surface free energy of the basal plane, and ΔH is the enthalpy of melting per unit volume. Considering the values of these parameters for PE, which are $T_m = 414.6$ K,[16] $\sigma_e = 60.9 \times 10^{-3}$ J/m^2,[15] and $H = 2.88 \times 10^8$ J/m^3,[15] the lamella thickness corresponding to each melting temperature can be calculated. This method yields the distribution curves of lamellae thicknesses.

TABLE I
Melting Temperature of Main Endotherm (T$_m$) for Annealed and Nonannealed Pure and Blended Samples

Sample	Soil Exposure Time (days)	T$_m$ (°C)
Nonannealed		
Pure LDPE	—	*110.3*
	255	110.7
LDPE/Mater-Bi blend	—	*109.8*
	20	109.9
	61	109.4
	123	109.4
	179	110.0
	255	109.7
Annealed		
Pure LDPE	—	114.0
	123	116.0
LDPE/Mater-Bi blend	—	113.8
	20	114.4
	61	114.4
	123	115.4

Figure 6(A) shows the lamellar thickness distribution for pure LDPE samples. For the untreated pure samples the distribution extends from approximately 15 to 65 Å, and the maximum is at approximately 55 Å. After the aging in soil, the distribution maintains a similar shape. The annealing causes a shift of the distribution to larger thicknesses and the development of the distribution into two distinguished zones: the main peak from 45 to 75 Å and a small shoulder from 15 to 40 Å. After aging in soil, a slight broadening was observed for the annealed samples.

The respective curves for blended samples are displayed in Figure 6(B). The untreated blended sample shows a maximum at a lamellar thickness similar to that of the untreated pure sample but the curve shape is smoother, suggesting that the carbonated chains of the vinyl alcohol and the other components that compose Mater-Bi make the growth of crystallites in PE difficult. The thermal treatment also causes a shift of the distribution to higher thicknesses and the development of the distribution into two distinguished zones as for pure samples, but it is more significant for pure than for blended samples. Thus, the carbonated chains in the Mater-Bi seem to obstruct the segregation of the crystallite sizes.

For the nonannealed blended samples, only small changes throughout the degradation process are noted, consisting basically of successive broadenings and narrowings. On the other hand, only a slight displacement to higher crystallite sizes and broadening of the main peak can be noticed in annealed blended samples during the soil burial test.

In general, in both annealed and nonannealed samples, the small changes underwent by the lamellar thickness distribution indicate that degradation has little affect on PE, and the effects of the aging in soil

seem to be attributed exclusively to the Mater-Bi. In fact, from the evolution of Mater-Bi with the exposure time in soil, it can be assumed that degradation starts in the Mater-Bi. The annealing improves the rearrangement of the crystallites, but it apparently hinders the degradation process during the first 120 days in soil.

DMTA results

The complete relaxation spectra of all the samples have been acquired in order to characterize the degradation process by means of the mechanical behavior.

Figure 7 displays the loss tangent (tan δ) at a 1-Hz frequency for pure LDPE samples as a function of temperature. Similar spectra have been obtained for 0.3-, 3-, 10-, and 30-Hz frequencies.

Two relaxation zones, labeled α and β in order of decreasing temperature, have been analyzed in this work. The α relaxation zone is composed of two overlapped relaxations named α$_I$ and α$_{II}$ in order of de-
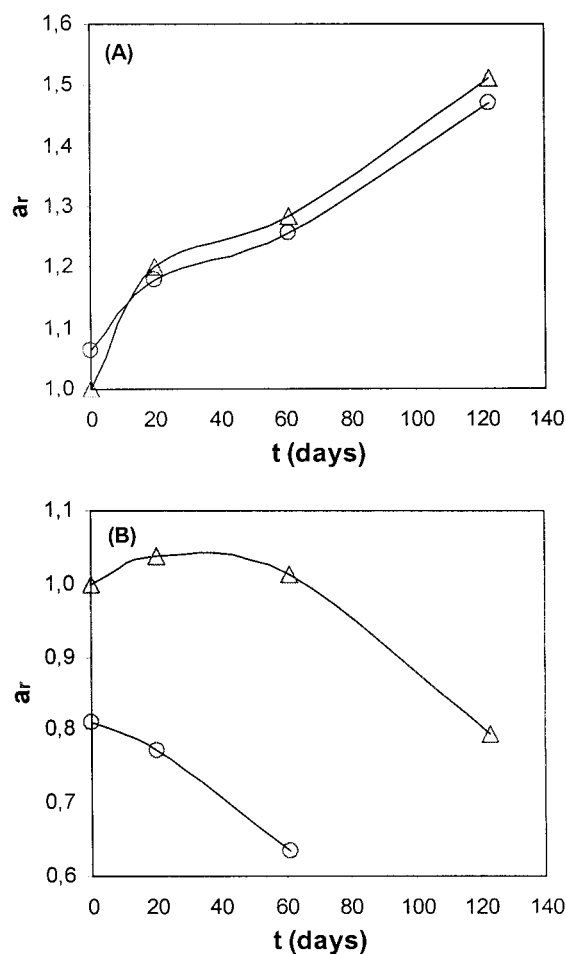

Figure 5 The relative partial areas (a_r) of (A) PE and (B) Mater-Bi for (△) nonannealed/aged blended samples and (○) annealed/aged blended samples.
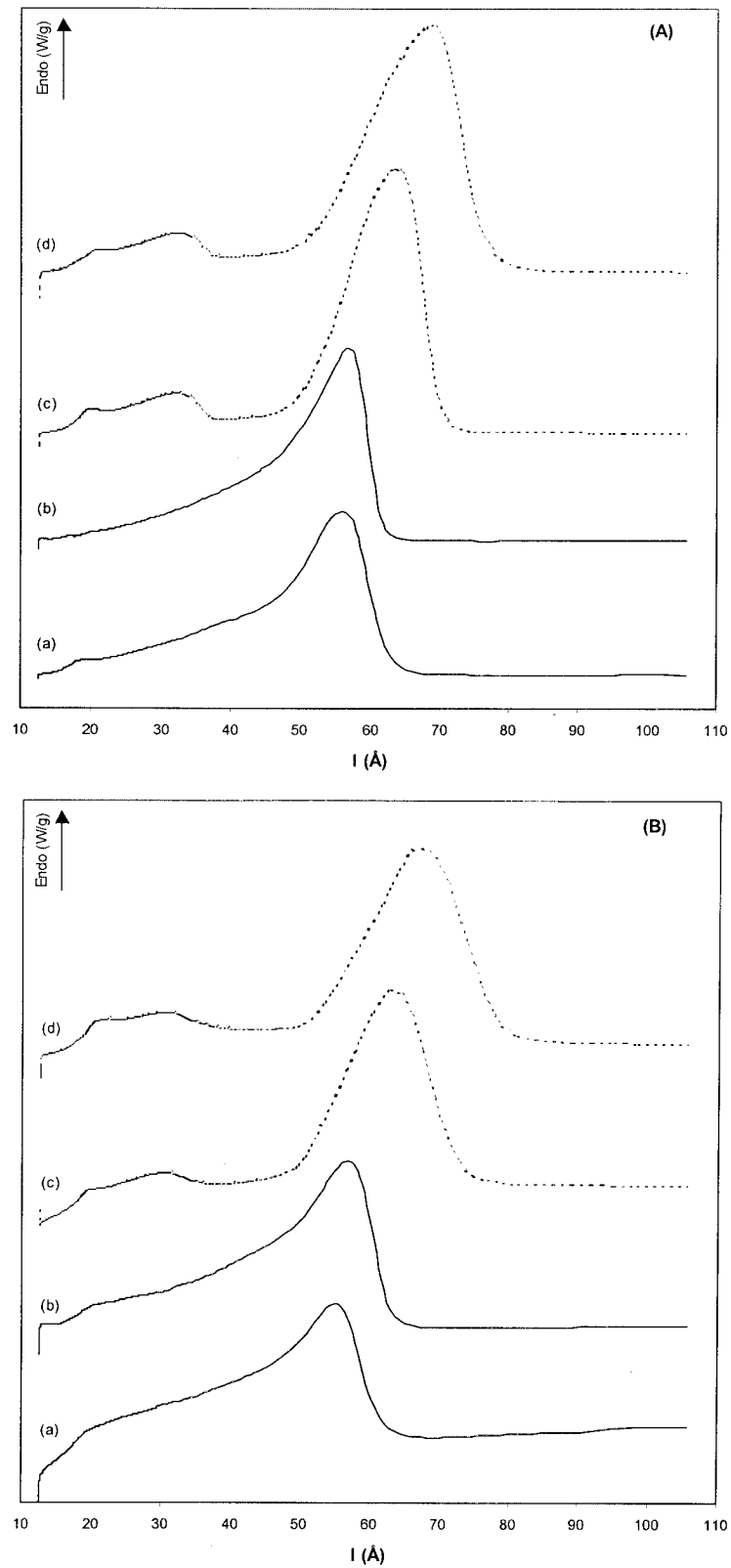
Figure 6 The lamellar thickness distribution for (A) pure LDPE samples: untreated (curve a), nonannealed/aged in soil for 255 days (curve b), annealed (curve c), and annealed/aged in soil for 123 days (curve d); and (B) blended samples: untreated (curve a), nonannealed/aged in soil for 255 days (curve b), annealed (curve c), and annealed/aged in soil for 123 days (curve d).
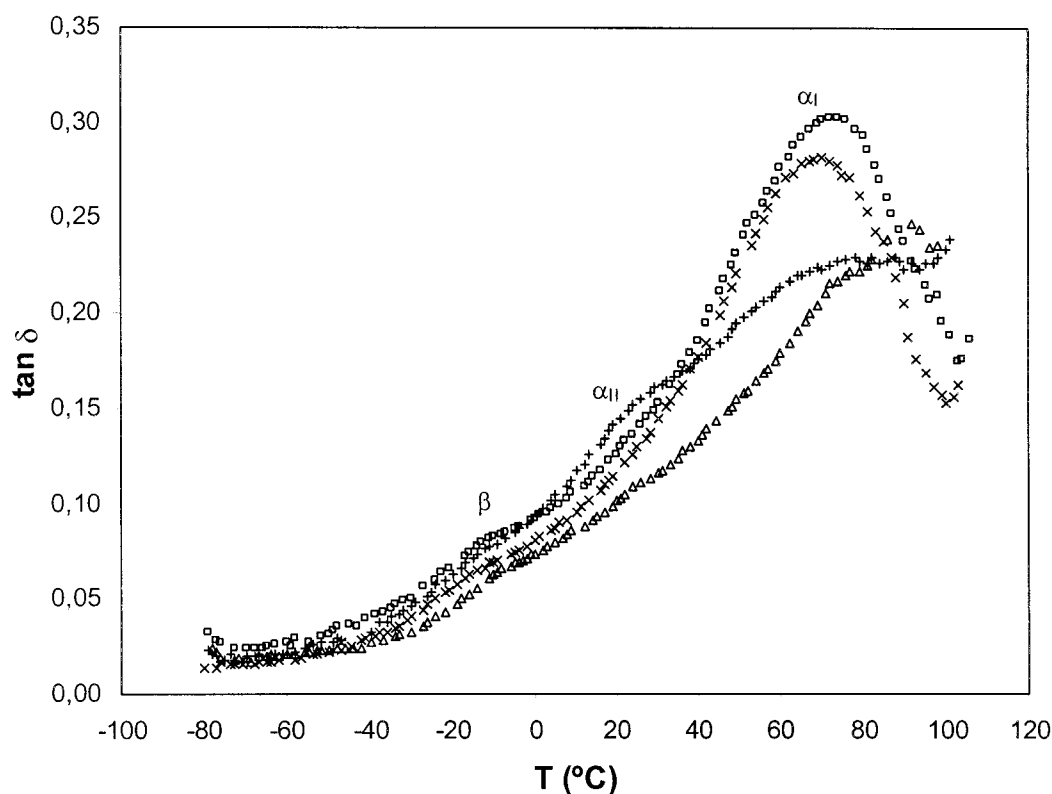
Figure 7 The loss tangent (tan δ) as a function of temperature for (□) untreated pure LDPE, (×) nonannealed/aged in soil for 255 days pure LDPE, (△) annealed pure LDPE, and (+) untreated blended samples.

creasing temperature. The α_I appears in untreated pure LDPE samples as a narrow high peak at temperatures near fusion, and the α_{II} peak results in an overlapped shoulder between the α_I and β relaxations with the maximum at approximately 30°C. The β relaxation is observed as a small wide shoulder at approximately −10°C. The thermal treatment shifts the spectra to higher temperatures. No significant variations are achieved when both nonannealed and annealed pure samples are aged in soil.

The spectrum of the untreated blended sample is also plotted in Figure 7. It displays a more pronounced α_{II} peak and a lower α_I peak compared to the spectrum of the untreated pure sample.

Figure 8(A) shows the spectra for nonannealed blended samples. With the exposure time in soil, a decrease in the β and α_{II} peaks and a later decrease in the α_I peak are observed. The spectra for annealed blended samples are plotted in Figure 8(B). The thermal treatment promotes a shift of the spectrum of the untreated blended samples to higher temperatures, an attenuation of the β and α_{II} peaks, and a strong increase of the α_I peak. With the exposure time in soil, a decrease of the α_I relaxation can again be observed.

As can be observed in Figure 9, when the loss modulus (E'') is represented as a function of the temperature, the β relaxation becomes prominent over the α relaxation. The α_{II} relaxation appears as a small shoul-

der of the β relaxation and the α_I relaxation is observed as an abrupt decrease in intensity. Because the relaxations appear to be overlapped, it has been supposed that the experimental data are the addition of these relaxations, as proposed by Charlesworth.[17] This fact is well reflected in Figure 9.

For this reason, the analysis of the mechanical behavior was carried out in terms of E'' for the β and α_{II} relaxations but in terms of tan δ for the α_I relaxation. Thus, the temperature of the maximum (T_{max}) of tan δ for each frequency (f) was taken for each sample.

In addition, the β and α_{II} relaxation zones have been characterized by means of E'' by fitting the experimental data to the Fuoss–Kirkwood equation:

$$E'' = \frac{E''_{max}}{\cosh\left[m\dfrac{E_a}{R}\left(\dfrac{1}{T} - \dfrac{1}{T_{max}}\right)\right]} \tag{2}$$

from which the maximum of the loss modulus (E''_{max}), the temperature of the maximum of the loss modulus (T_{max}), and the term mE_a/R have been obtained for each frequency (f) in each sample.

After calculating these parameters, the apparent activation energy (E_a) was calculated for each sample by fitting the dependence of the mean relaxation times at the temperature to the Arrhenius equation:
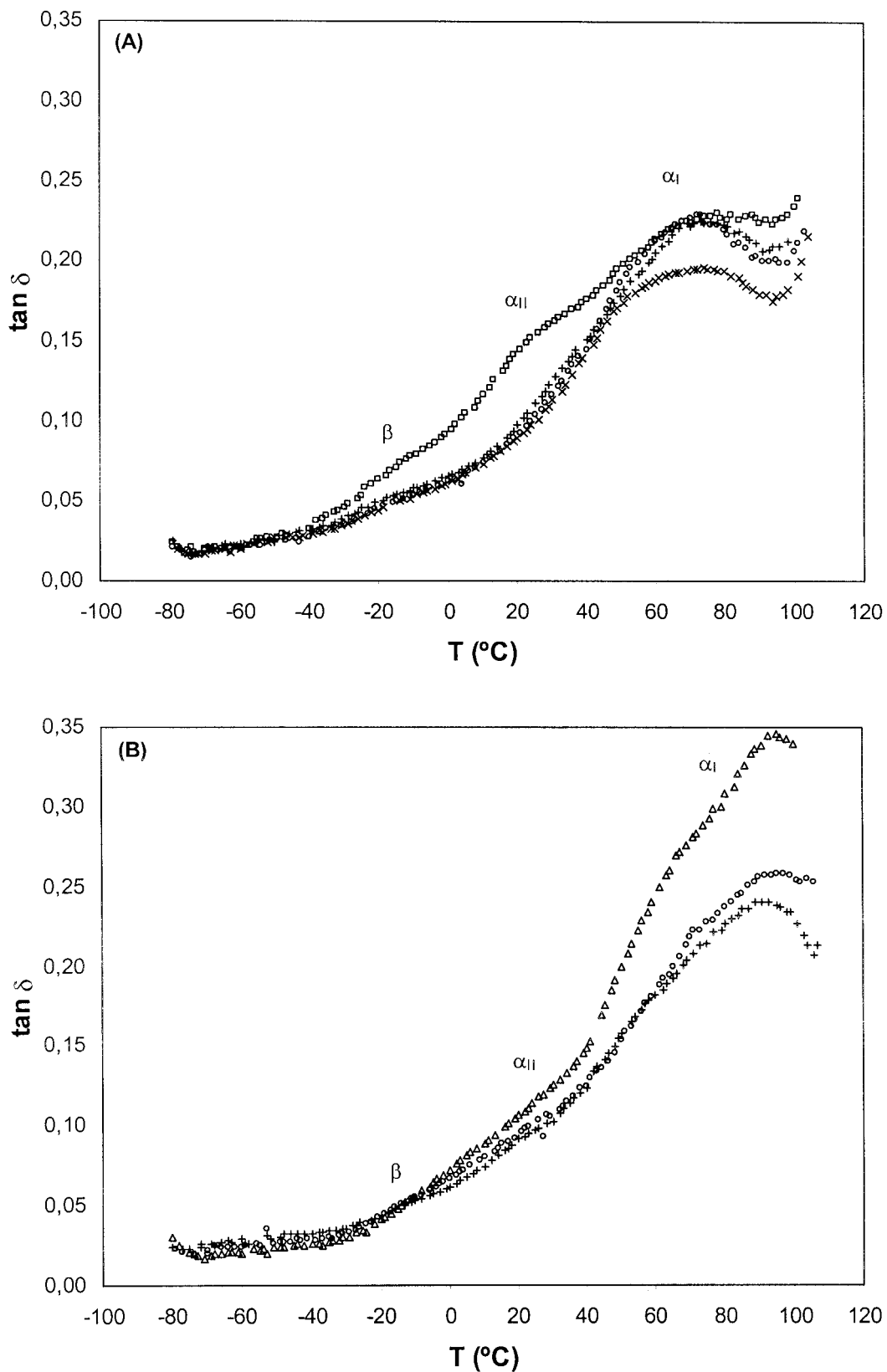
Figure 8 The loss tangent (tan δ) as a function of temperature for blended samples: (A) nonannealed/aged in soil for (□) 0 (untreated), (○) 20, (+) 123, and (×) 255 days and (B) annealed/aged in soil for (△) 0, (○) 20, and (+) 123 days.
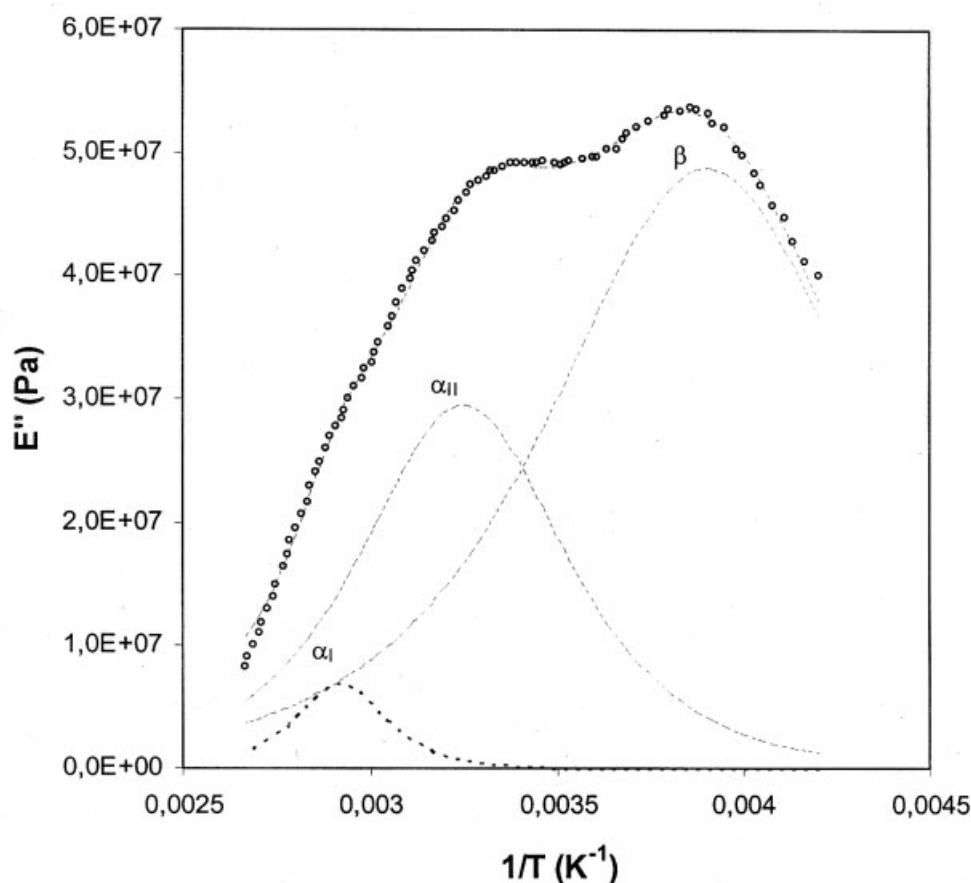
Figure 9 Deconvolution in terms of the loss modulus (E″) of the relaxations at 3-Hz frequency for the nonannealed/aged in soil for 123 days blended sample.

$$f = f_0 \exp\left(\frac{-E_a}{RT_{\max}}\right) \qquad (3)$$

The E_a values and the temperatures of the maximum of tan δ or E″ ($T_{\max}$) are listed in Table II. In some cases it was not possible to separate the different relaxations.

The results for each relaxation zone were analyzed separately.

α_I relaxation

The annealing produces a shift of the α_I peak to higher temperatures but no significant changes in E_a are observed. The aging in soil does not modify the position of this relaxation but promotes an increase in E_a in both nonannealed and annealed blended samples.

α_{II} relaxation

Neither the annealing nor the aging in soil seem to significantly modify the position of the α_{II} peak. In the cases wherer the E_a value could be calculated, it was

found to slightly decrease with the exposure time in soil.

β relaxation

Because of the annealing, the temperature of the β peak shifts toward higher temperatures in both pure and blended samples. During the soil burial test, a slight but continuous decrease in E_a is observed. The activation energies decrease to lower values in the annealed blended samples in comparison with those of nonannealed blended samples.

In general, the β relaxation has been found to be the most sensitive to the degradation process. The α_{II} and β relaxation zones observed for the blends include the α_{II} and β relaxations of PE overlapped with the β wide relaxation of Mater-Bi.[5] The results obtained for these relaxations would therefore be related to motions of the molecular chains containing the —OH groups in both the starch and the vinyl alcohol in Mater-Bi, as well as the carbonated chains in PE.

The decrease of the E_a in the β relaxation seems to be strongly influenced by the presence of Mater-Bi. This

TABLE II
Characterization of α_I, α_{II}, and β Relaxations: Apparent Activation Energy (E_a) and Maximum Temperature (T_{max}) for Annealed and Nonannealed Pure and Blended Samples

Sample	Soil Exposure Time (days)	α_I (tan δ)		α_{II} (E'')		β (E'')	
		E_a (kJ/mol)	T_{max} (K)	E_a (kJ/mol)	T_{max} (K)	E_a (kJ/mol)	T_{max} (K)
Nonannealed							
Pure LDPE	—	132	347	123	303	256	255
	255	131	343	116	297	250	255
LDPE/Mater-Bi blend	—	130	349	—	291	213	254
	20	137	347	102	298	208	255
	61	141	342	88	295	197	253
	123	—	—	—	302	—	255
	179	158	338	103	291	174	252
	255	150	347	—	289	164	253
Annealed							
Pure LDPE	—	137	355	—	307	278	262
	123	—	—	—	309	255	271
LDPE/Mater-Bi blend	—	—	366	—	292	—	—
	20	140	368	—	286	147	257
	61	—	366	—	287	126	257
	123	159	364	—	290	137	258

agrees with the idea suggested above and in a previous work[9] that degradation starts in the Mater-Bi and not in the PE. As Mater-Bi degrades, PE chains remain less restricted, thereby decreasing the activation energy.

However, in view of the evolution of the apparent activation energies with the time of burial in soil, it can be suggested that the first stage of degradation is a complex process in which two different competitive processes are present. On the one hand, deriving from the fact that the apparent activation energies in the β zone decrease more strongly for the annealed blended samples than for the nonannealed ones, it could be thought that the annealing possibly facilitates the degradation of Mater-Bi. On the other hand, the annealing improves the crystalline structure, which is reflected in the increase of the apparent activation energies in the α_I zone, therefore making the carbonated chains more resistant to degradation in the first stage.

TGA study

Finally, samples were characterized by TGA in order to study their thermal stability and obtain the kinetic parameters characterizing the decomposition process, because these parameters reveal the possible ruptures of the molecular chains as a result of degradation.

Figure 10(A,B) shows the mass loss as a function of temperature (TG curves) for nonannealed and annealed samples. Derivative thermogravimetry plots were obtained after the tests by numerical differentiation and smoothing of the TG data. The traces are shown in Figure 11(A,B) for the nonannealed and annealed samples.

In order to determine the activation energies, the kinetics of each degradation process has been studied by the Broido integral method.[18] Each degradation process can be characterized by fitting the experimental data to the Broido equation:

$$\ln \ln\left(\frac{1}{x}\right) \equiv -\frac{E}{RT} + \text{const} \qquad (4)$$

where R is the gas constant, T is the absolute temperature, and x is the residual fraction defined as

$$x = \frac{\omega - \omega_\infty}{\omega_0 - \omega_\infty} \qquad (5)$$

where ω_0, ω, and ω_∞ are the sample weight initially, at time t, and at infinite time, respectively.

The plot of $\ln(\ln(1/x))$ against the reciprocal of the temperature should give a straight line for each thermochemical process, from which the slope of the E_a can be calculated. Figure 12 shows as an example the curve for the nonannealed/aged in soil for 61 days blended sample. Similar figures have been obtained in the same way for all samples. The calculated activation energies are summarized in Table III for all samples.

Pure LDPE samples display similar thermograms. despite the annealing or the soil burial test. There is a single mass loss zone centered at about 485°C.

By contrast, blended samples clearly display different weight loss zones with different activation energies. The first very small weight loss zone, which is in the temperature range of 90–130°C, is attributed to the loss of water absorbed by starch.
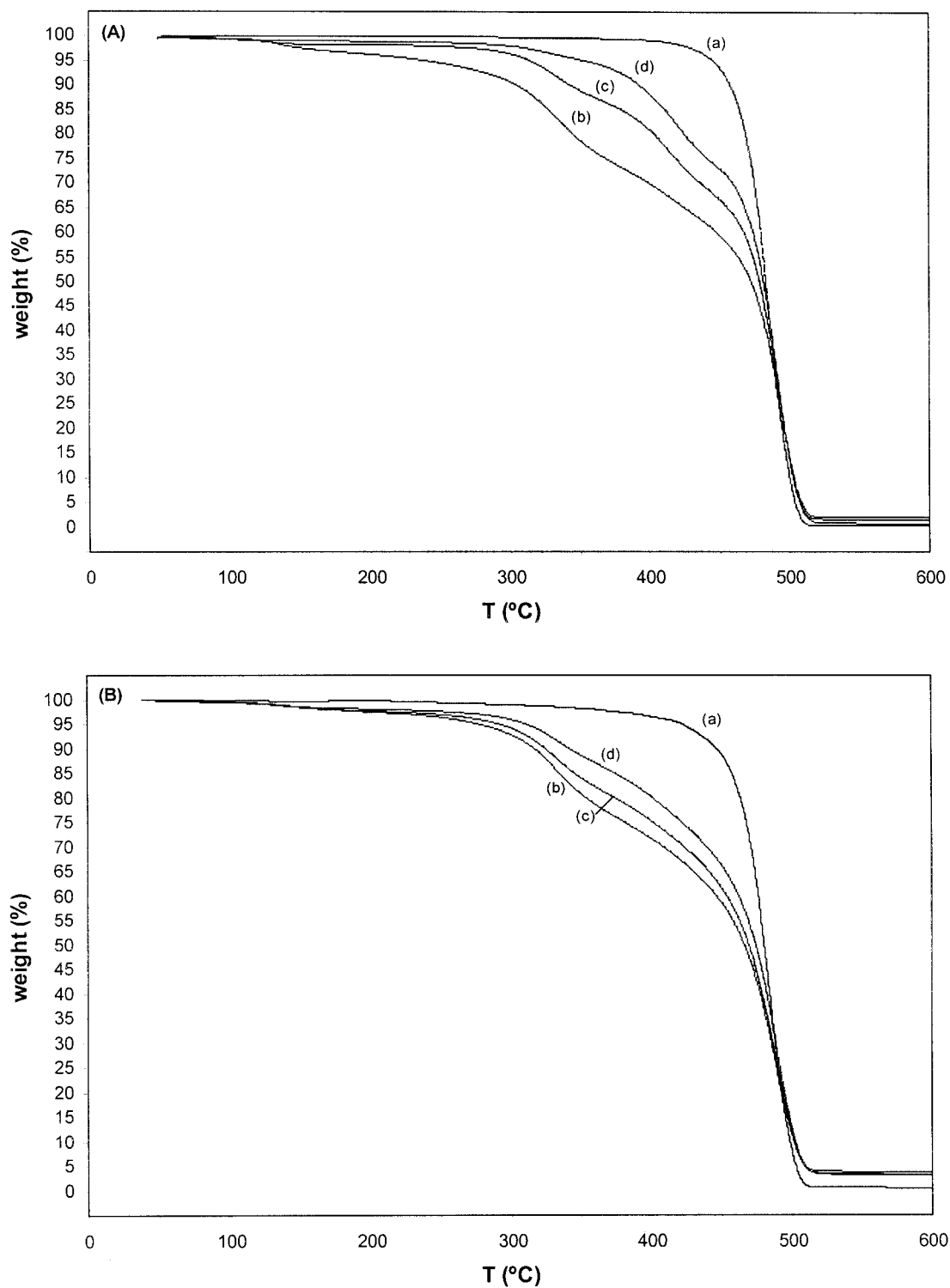
Figure 10 TG curves for (A) nonannealed pure (curve a), blended (curve b), blended/aged in soil for 2 months (curve c), and blended/aged in soil for 9 months (curve d) samples and (B) annealed pure/aged in soil for 4 months (curve a), blended (curve b), blended/aged in soil for 20 days (curve c), and blended/aged in soil for 4 months (curve d) samples.

The second weight loss, ranging between 250 and 450°C, can be associated basically with the thermal degradation of the Mater-Bi. It appears at higher temperatures than those found in the literature,[3] probably

due to the higher heating rate (20°C/min). This zone can be divided into two small weight losses. The first one, in the temperature range of 290–340°C, may be attributed to starch. During the aging in soil, in either
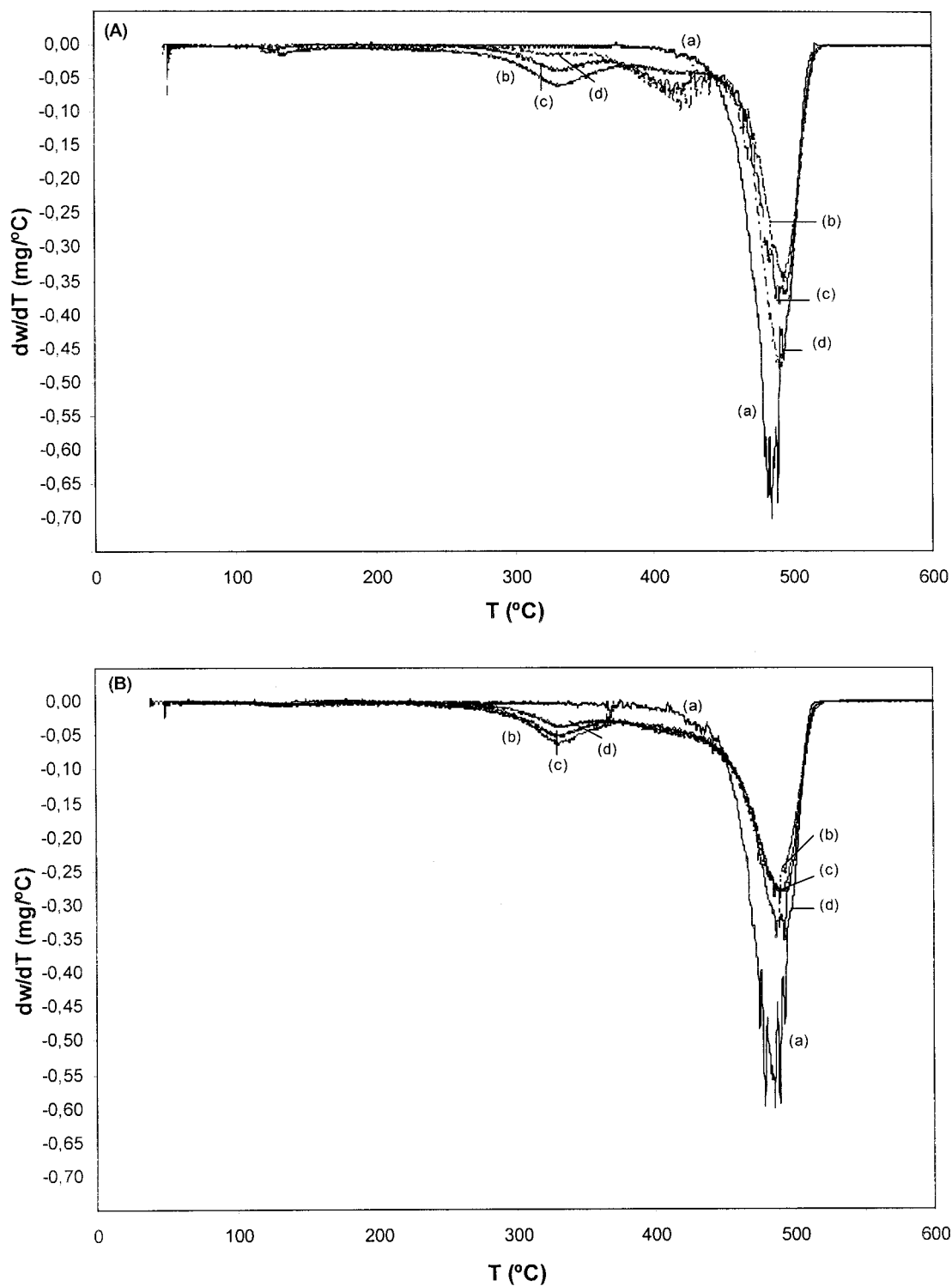
Figure 11 Derivative TG curves for (A) nonannealed pure (curve a), blended (curve b), aged in soil for 2 months blended (curve c), and aged in soil for 9 months blended (curve d) samples and (B) annealed pure/aged in soil for 4 months (curve a), blended (curve b), blended/aged in soil for 20 days (curve c), and blended/aged in soil for 4 months (curve d) samples.

annealed or nonannealed blended samples, the activation energies do not show any significant tendency. The other weight loss that composes this weight loss zone, located between 360 and 450°C, could be associated with the short carbonated chains. Concerning the activation energies, the obtained values are initially very low and have not been represented and they seem to increase with the aging time in soil in both annealed and nonannealed blended samples.
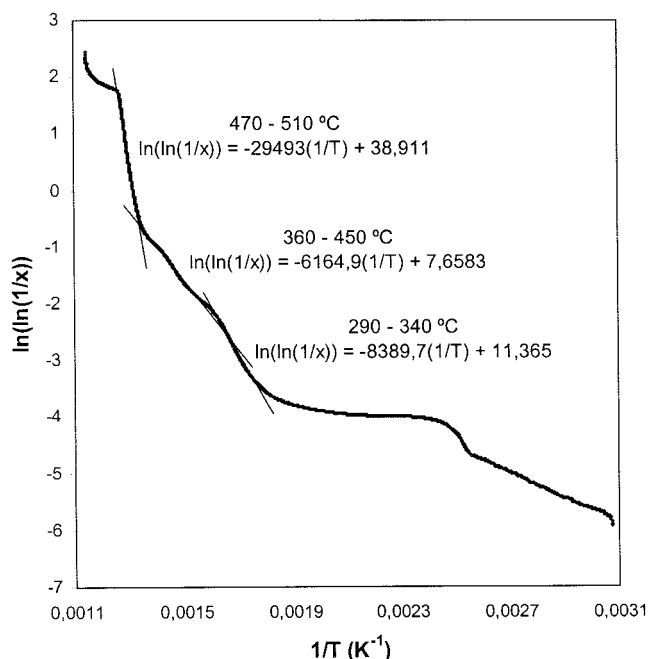
Figure 12 The fitting of the chemical processes for the nonannealed/aged in soil for 61 days blended sample, according to the Broido integral method.

Finally, the main weight loss zone, between 470 and 510°C, appears centered at temperatures slightly higher than those of pure samples. The main weight loss is attributed to the thermodegradation of the PE backbones. This zone exhibits the highest activation energies.

The activation energies in the temperature range of 470–510°C of both pure and blended samples are plotted in Figure 13 to compare them. The highest value corresponds to the nonannealed pure samples. During
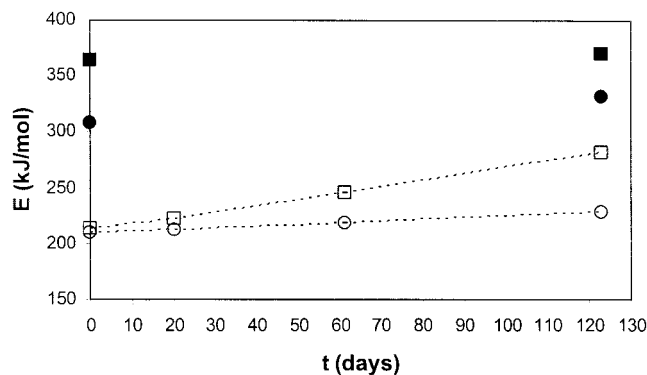

Figure 13 The activation energies (E_a) calculated with the Broido integral method in a temperature range of 470–510°C for nonannealed (■) pure and (□) blended samples and annealed (●) pure and (○) blended samples.

the aging in soil a common tendency for an increase of the activation energies has been found for both annealed and nonannealed blended samples, and it seems that the values tend to approach those of the pure samples as the exposure time in soil increases. However, the activation energies in nonannealed blended samples increase more quickly than in the annealed ones, suggesting that the annealing may have hindered the degradation process during the first 120 days.

CONCLUSIONS

Soil burial did not affect the pure samples. The main effects observed during the aging in soil of the blended samples indicate that the degradation of the blends is mainly due to the Mater-Bi. On the one hand, this is because the carbonated chains of Mater-Bi

TABLE III
Activation Energies (E_a) Calculated with Broido Integral Method

Sample	Soil Exposure Time (days)	T_{Range} (°C)	E_a (kJ/mol)	T_{Range} (°C)	E_a (kJ/mol)	T_{Range} (°C)	E_a (kJ/mol)
Nonannealed							
Pure LDPE	—	—		—		470–510	363.44
	255						370.33
LDPE/Mater-Bi blend	—	290–340	52.19	360–450	—	470–510	213.62
	20		72.42		40.50		221.95
	61		69.75		51.25		245.21
	123		49.90		96.94		282.34
	179		39.53		97.17		277.98
	255		51.00		85.28		270.72
Annealed							
Pure LDPE	—	—		—		470–510	308.14
	123						332.15
LDPE/Mater-Bi blend	—	290–340	62.79	360–450	—	470–510	209.12
	20		64.43		—		212.03
	61		57.71		53.76		218.06
	123		61.73		46.13		228.97

hinder the uniform growth of crystallites in PE and facilitate the degradation process; on the other hand, this is because of its own biodegradability.

The annealing seems to promote a rearrangement of the crystallites in the crystalline phase, resulting in segregation of the smallest crystallite sizes and growth of the most perfect crystallites. This effect is more significant in pure samples than in blended ones. However, thermal treatment does not seem to improve the scarce degradability of the PE during the first 120 days of burial in soil. Furthermore, it apparently hinders the degradation in soil for blended samples, because the development of Mater-Bi appears to be obstructed by the thermal treatment at this first stage.

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