

Degradation Studies of LDPE–Mater-Bi Blends Annealed and Aged in Soil

A. Vallés-Lluch, L. Contat-Rodrigo, A. Ribes-Greus

Department of Applied Thermodynamics, Escuela Técnica Superior de Ingenieros Industriales de Valencia, Apdo: 22012, 46071 Valencia, Spain

Received 31 May 2001; accepted 3 January 2002

ABSTRACT: Blends of low-density polyethylene (LDPE) and a commercial biodegradable material commonly used as an additive, Mater-Bi AF05H, were subjected to thermal treatment followed by an accelerated soil burial test in a culture oven. The effect of the degradation process on the structural and morphological properties of the samples was studied by differential scanning calorimetry and dynamic mechanical thermal analysis. The morphological properties studied in this work were the melting temperature, the crystalline content, and the lamellar thickness distribution. The α_1 relaxation zone of the mechanical spectra was characterized in terms of $\tan \delta$ and the α_{II} and β relaxations were

characterized in terms of E'' according to the Fuoss–Kirkwood equation and using a deconvolution method. It was found that the thermal treatment rearranges the crystallites in the crystalline phase and promotes a segregation of the crystallite sizes. However, the annealing seems rather to hinder than to improve the degradation of the samples. Moreover, the degradation process in the blends apparently starts in the Mater-Bi. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 405–413, 2002

Key words: polyethylene (PE); annealing; aging; differential scanning calorimetry (DSC); mechanical properties

INTRODUCTION

Polyolefins are considered as one of the most important classes of plastics both in usage and volume of production. They are commonly used in short-term applications and disposed afterward. Therefore, these materials contribute to the increasing volume of solid municipal waste. In the last years, different strategies have been suggested to develop polymers with a predetermined service life, as was reviewed by Albertsson and Karlsson.^{1,2} One of them would be to use synthetic and bulk polymers, such as polyethylene, with the addition of biodegradable components.

In this work, blends of low-density polyethylene filled with a degradable additive were used. The additive chosen was Mater-Bi AF05H, which is a starch-based material commercialized by Novamont that contains thermoplastic starch heavily complexed with ethylene–vinyl alcohol (EVOH) copolymers. The blends show similar properties to those of pure polyethylene but they contain parts differently attacked by microorganisms.³ Such blends have been exposed to a soil burial test so as to study their degradation process.

The crystalline morphology is one of the factors that must be taken into account when studying the degradation process.^{4–6} The thermal treatment alters the crystalline structure. It is believed to promote a molecular segregation of a low molecular weight fraction, which corresponds to the thinnest lamellae. Thus, the annealing could modify the degradation process. To study the influence of this parameter on degradation, samples were annealed prior to the biodegradation test.

The objective of this work was to study the change of morphological and mechanical properties in annealed and nonannealed samples by thermal analysis. As thermal techniques, differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used.

EXPERIMENTAL

Material Preparation

Low-density polyethylene (LDPE-565; $M_n = 17 \times 10^3$, $M_w = 80 \times 10^3$, $\rho = 0.9227 \text{ g/cm}^3$) supplied by Dow Chemical Iberica, S.A. (Tarragona, Spain) was blended with Mater-Bi AF05H supplied by Novamont North America (California, USA). A homogeneous mixture with 50/50% by weight of LDPE–Mater-Bi AF05H was initially prepared from the melt in a Brabender Plasticorder PL 2100 rheometer. Afterward, the blend was cut as nut coal and compression-molded into rectangular bars ($68 \times 12 \times 1.8 \text{ mm}$) using an M Carver

Correspondence to: A. Ribes Greus (aribes@ter.upv.es).

Contract grant sponsor: Ministerio de Ciencia y Tecnología of Spain; contract grant number: PPQ2001-2764-C03-01.

press. This methodology was followed in a previous work.^{7,8}

Samples of pure LDPE were also compression-molded from pellets to be used as control materials. Both pure and blended samples were taken apart so as to compare them with the samples after annealing.

Annealing and Soil Burial Test

Thermal treatment consisted of keeping the samples in a Hereaus UT6060 oven at $100 \pm 1^\circ\text{C}$ in an air atmosphere for 336 h. After this treatment, the samples were immediately immersed in a water-ice bath at $0 \pm 0.5^\circ\text{C}$. Again, samples of each type were taken apart to compare them with nontreated samples and with buried samples.

The soil burial test was carried out according to the DIN 53739 International Norm.⁹ Samples were buried in a biologically active soil contained in rectangular plastic boxes, which were kept opened 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.¹⁰ The soil used in these tests was a 50/50% by weight mixture of a soil extract picked up from a culture field and a soil typically used in tree nurseries for the pine growth. The boxes were kept in a Hereaus B12 culture oven at a constant temperature of $28 \pm 0.5^\circ\text{C}$, periodically controlling the pH and the water content of the soil. It was maintained at approximately $\text{pH } 7.3 \pm 0.1$ (measured in water) and $65.0 \pm 0.5\%$ humidity.

Samples were removed after different time periods: 20, 60, and 120 days. Pure samples were only removed at the end of the test. After removal, all the samples were carefully washed up with a soap solution to stop the degradation process and then blotted before analysis.

DSC Measurements

DSC measurements were performed on a DSC 4 Perkin-Elmer calorimeter, under a nitrogen atmosphere and previously calibrated with an indium standard. About 6 mg of the sample 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 $10^\circ\text{C}/\text{min}$. Measurements were repeated to assure errors of $\pm 0.01^\circ\text{C}$ for melting temperatures and $\pm 0.05^\circ\text{C}$ for crystalline contents.

DMTA

The viscoelastic properties were determined using a Mark II dynamic mechanical thermal analyzer from Polymer Laboratories (now Rheometrics). Deformation was applied in the cantilever double-clamping bending mode. Samples were scanned from -80 to

120°C at a heating rate of $1^\circ\text{C}/\text{min}$, at five different frequencies: 0.3, 1, 3, 10, and 30 Hz.

RESULTS AND DISCUSSION

DSC Measurements

Calorimetric analysis was used to study the melting temperature, crystalline content, and lamellar thickness distribution during the degradation process. Figure 1 shows the DSC thermograms of pure LDPE samples, before and after the thermal treatment. The melting temperature (T_m) in all the samples was determined directly from the thermograms as the maximum of the main endotherm. Pure LDPE shows the typical DSC thermogram of LDPE, which consists of a main endotherm with a maximum around 112°C (ref. 11) and a small shoulder at lower temperatures.

As can be observed in Figure 1, the thermal treatment promotes a shift of the main peak to higher temperatures, whereas the small shoulder at lower temperatures transforms into two major peaks, at 50 and 80°C approximately. After 120 days of exposure time in soil, no significant changes are observed. All the obtained values of the melting temperatures (T_m) are listed in Table I.

Figure 2 displays the DSC thermogram of LDPE-Mater-Bi blends. Before annealing, the thermogram displays one main endothermic peak at approximately 110°C assigned to polyethylene which may be overlapped with Mater-Bi and a small not well-resolved endotherm at approximately 140°C , which is consistent with the broad peak observed for undegraded Mater-Bi at around 127 and 145°C .¹² The thermal treatment leads to a shift of the main peak to higher temperatures for the pure LDPE samples. The peak assigned to Mater-Bi broadens and shifts to higher temperatures, at approximately 160°C . The thermograms of the blends subjected to the soil burial test show slight modifications. All the results are listed in Table I. In general, the annealing seems to improve the crystalline structure of polyethylene.

To study the evolution of the crystalline content of polyethylene and Mater-Bi separately during the degradation process, a method of calculation of partial areas was applied. This method was employed in previous works^{7,12} and is based on the determination of the peaks corresponding to polyethylene and Mater-Bi in each thermogram and the subtraction of all the other contributions. After the peak separation, the area of each peak was calculated. It was assumed that this area is directly proportional to the heat flow necessary for the phase change of this crystalline fraction. The area of each peak is then divided by the area of the peak for the annealed sample, to obtain the relative partial areas.

Table II shows the obtained results for the partial areas and relative partial areas of polyethylene and

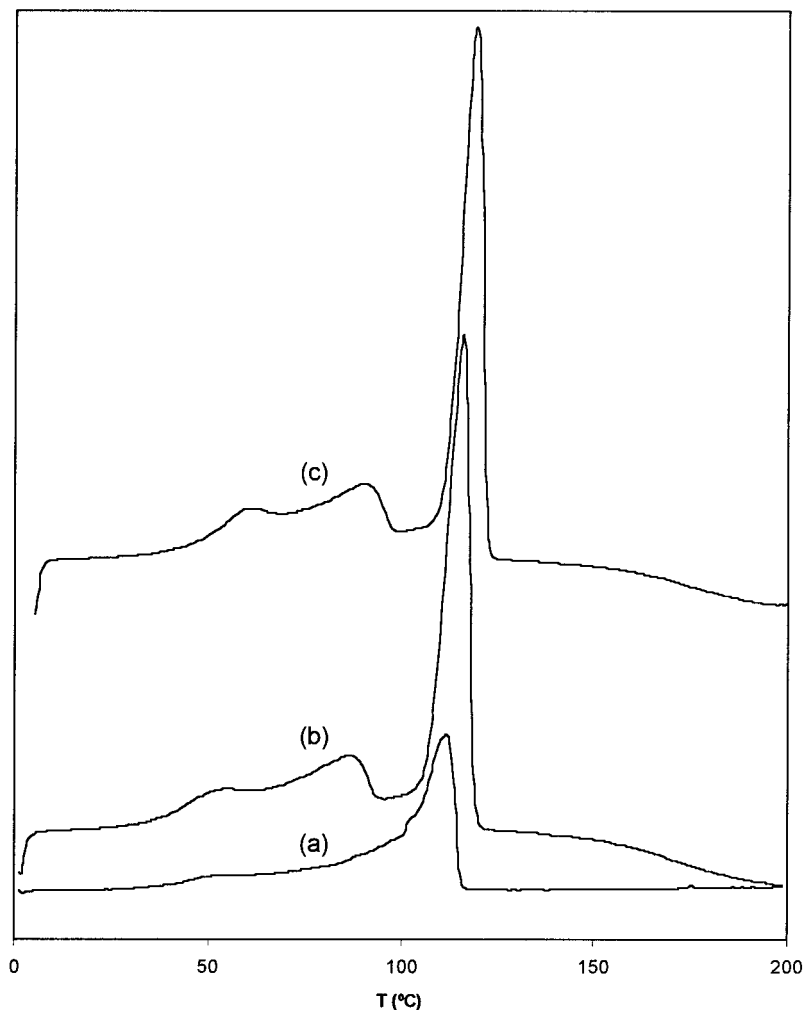


Figure 1 DSC thermograms for pure LDPE samples: (a) without treatment; (b) thermal treatment; (c) thermal treatment plus 120 days of exposure time in soil.

Mater-Bi in pure and blended samples. A considerable increase (more pronounced in the pure samples) of the partial area of polyethylene after the thermal treatment was found in comparison to the untreated samples. This is in agreement with the results found previously by the authors,¹² indicating a considerable increase in the crystallinity of polyethylene caused by annealing. Besides, the thermal treatment causes a

strong decrease in the partial area of Mater-Bi in the blended samples.

After the soil burial test, no variation of the relative partial area of polyethylene in the pure samples was obtained, in comparison with the annealed samples. In blended samples, the relative partial area of Mater-Bi strongly increases, whereas that of polyethylene very scarcely changes with the exposure time in the soil.

TABLE I
Morphological Parameters Determined by DSC: Melting Temperature (T_m) and Melting Enthalpy (ΔH) of Polyethylene for Pure and Blended Samples

Sample	Treatment	T_m (°C)	ΔH (J/g)
Pure LDPE	Untreated	111.77	130.88
	Annealed	116.03	150.58
	Annealed + 120 days of exposure time in soil	—	150.28
LDPE-Mater-Bi	Untreated	110.37	121.63
	Annealed	115.64	163.26
	Annealed + 20 days of exposure time in soil	115.40	158.39
	Annealed + 60 days of exposure time in soil	115.22	166.29
	Annealed + 120 days of exposure time in soil	114.80	153.44

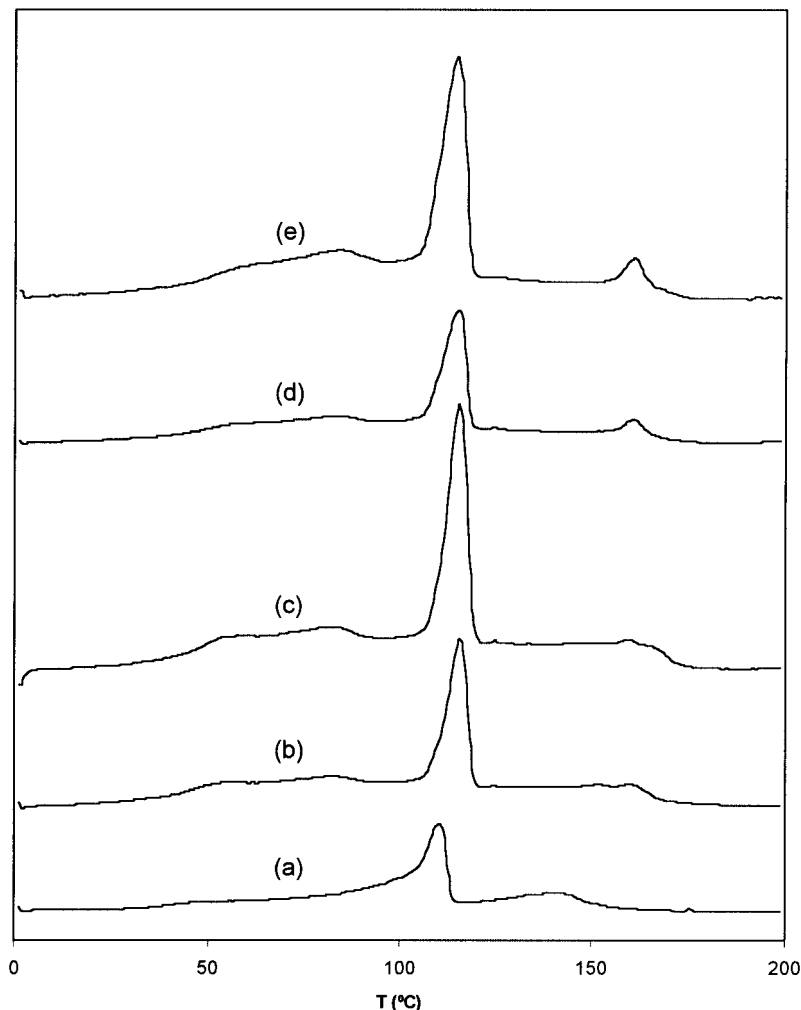


Figure 2 DSC thermograms for LDPE-Mater-Bi samples: (a) without treatment; (b) thermal treatment; (c) thermal treatment plus 20 days of exposure time in soil; (d) thermal treatment plus 60 days of exposure time in soil; (e) thermal treatment plus 120 days of exposure time in soil.

These results could indicate that thermal treatment does not improve the degradability of polyethylene in soil.

On the other hand, the lamellar thickness distribution of polyethylene was determined for each sample. It followed the method proposed by Wlochowicz and Eder,¹³ which assumes that the rate of heat consump-

tion at a given temperature is directly proportional to the fraction of melting lamellae whose thickness is given by the Thomson equation:

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

TABLE II
Partial Areas of Polyethylene (*a*) and Mater-Bi (*b*) and Relative Partial Areas of Polyethylene (*a_r*) and Mater-Bi (*b_r*) for Pure and Blended Samples

Sample	Treatment	<i>a</i>	<i>a_r</i>	<i>b</i>	<i>b_r</i>
Pure LDPE	Untreated	5.4	—	—	—
	Annealed	6.2	1.0	—	—
	Annealed + 120 days of exposure time in soil	6.2	1.0	—	—
LDPE-Mater-Bi	Untreated	3.4	—	1.1	—
	Annealed	3.4	1.0	0.1	1.0
	Annealed + 20 days of exposure time in soil	3.7	1.1	0.3	1.9
	Annealed + 60 days of exposure time in soil	3.8	1.1	0.5	3.2
	Annealed + 120 days of exposure time in soil	3.8	1.1	0.5	3.7

where T_m is the observed melting point of lamellae of thickness L ; T_m^0 , the equilibrium melting point of an infinite crystal; σ_e , the surface free energy of the basal plane; and ΔH , the enthalpy of melting per unit volume. Considering the values of these parameters for polyethylene as $T_m^0 = 414.6$ K,¹⁴ $\sigma_e = 60.9 \times 10^{-3}$ J/m²,¹³ and $\Delta H = 2.88 \times 10^8$ J/m³,¹³ the lamella thickness corresponding to each melting temperature can be calculated. This method yields the distribution curves of lamellae thickness for the pure and blended samples displayed in Figures 3 and 4, respectively.

In the case of the undegraded pure LDPE samples (Fig. 3), the distribution extends from approximately 15 to 70 Å, with the maximum at approximately 60 Å. For undegraded LDPE-Mater-Bi samples, the shape of the distribution is similar but the peak appears at a slightly lower thickness (54 Å), suggesting that the carbonated chains of the vinyl alcohol and the other components of which are composed the Mater-Bi hinder the perfect growth of the crystallites.

The thermal treatment promotes a shift of the distribution of pure LDPE samples to higher thickness and the development of the distribution into two distinguished zones: the main peak from 45 to 90 Å and a small shoulder from 15 to 35 Å. These results are in agreement with those found by other authors^{15,16} and suggest that the thermal treatment produces a segregation of the crystallite sizes that affects mostly the

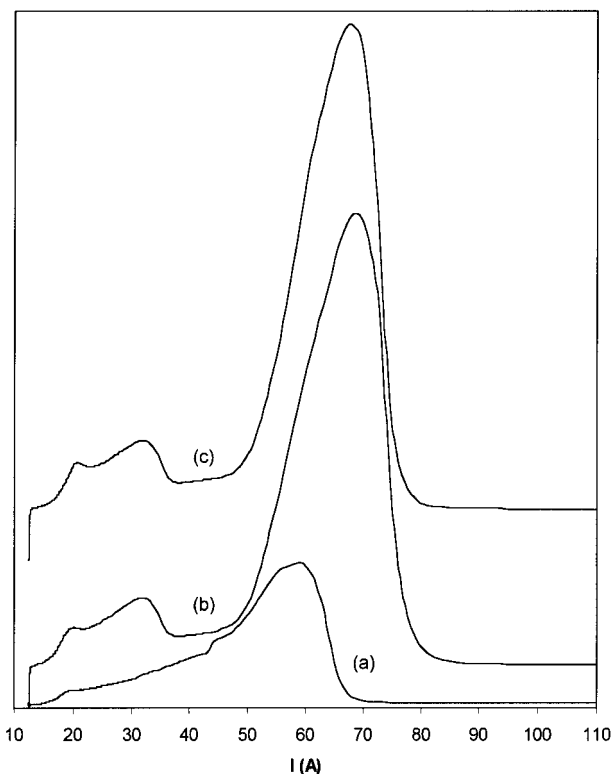


Figure 3 Distribution of lamellae thicknesses for pure LDPE samples: (a) without treatment; (b) thermal treatment; (c) thermal treatment plus 120 days of exposure time in soil.

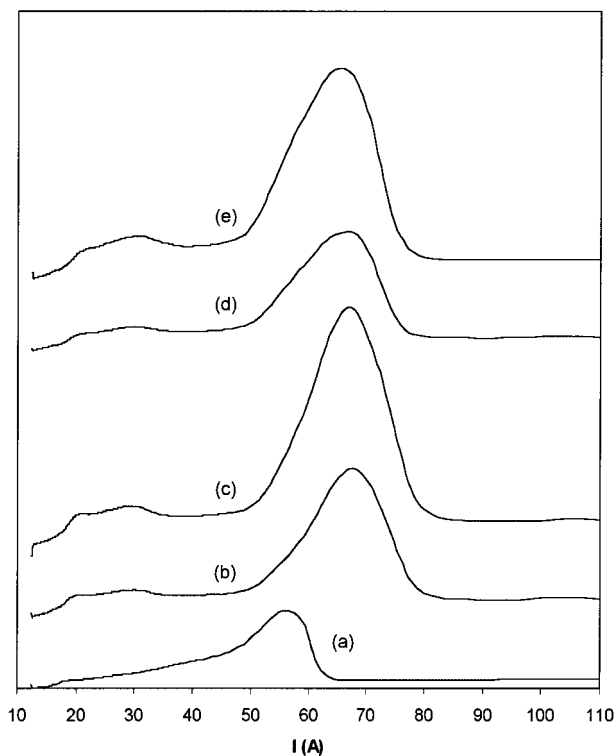


Figure 4 Distribution of lamellae thicknesses for LDPE-Mater-Bi samples: (a) without treatment; (b) thermal treatment; (c) thermal treatment plus 20 days of exposure time in soil; (d) thermal treatment plus 60 days of exposure time in soil; (e) thermal treatment plus 120 days of exposure time in soil.

smallest crystallites. The increase in the lamellar thickness could be understood as a rearrangement of the crystalline phase caused by diffusion of molecules from the interspherulitic zone to the crystalline zone. After the soil burial test, no appreciable variations in the distribution of pure LDPE samples were observed.

The lamellar thickness distribution for blended samples can be observed in Figure 4. Similar effects occurred for blended samples with the annealing treatment. It causes a shift of the distribution to a higher thickness and a development of the distribution into two distinguished zones. But, in this case, the carbonated chains in the Mater-Bi seem to obstruct the increase of the lamellae thickness, and the segregation of the crystallite sizes in the main endotherm is not so pronounced. Some changes in the distribution shape can be noted during the degradation process in soil. The peak narrows and broadens without any specific trend. These results are in agreement with the above-mentioned idea that the annealing improves the crystalline structure of polyethylene, which hinders the degradation process in soil.

DMTA Measurements

As stated previously, the degradation process can also be studied by the characterization of the mechanical

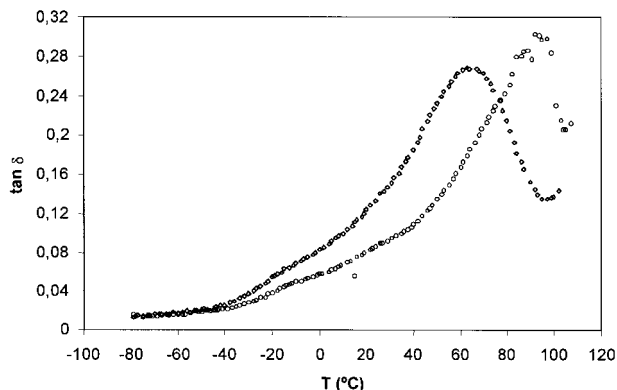


Figure 5 Loss tangent ($\tan \delta$) as a function of temperature for pure LDPE samples: (\diamond) without thermal treatment; (\circ) with thermal treatment.

behavior. For this purpose, the complete relaxation spectra of all the samples were obtained. The instrument measures the values of the tensile storage modulus (E') and the loss tangent ($\tan \delta$).

Curves showing the loss tangent ($\tan \delta$) at 1-Hz frequency as a function of temperature are displayed in Figures 5 and 6 for pure samples and in Figures 7 and 8 for blended samples. Similar spectra were obtained for 0.3, 3, 10, and 30 Hz.

Figure 5 shows the relaxation spectra for pure samples in terms of $\tan \delta$. The spectrum of polyethylene exhibits three relaxation zones, α , β , and γ , in order of decreasing temperature, as is extensively known.^{11,17-21} In this work, only the α and β relaxations were studied. The α relaxation zone is composed of two overlapped relaxations, α_I and α_{II} , in order of decreasing temperature, and the β relaxation is observed as a small wide shoulder with the main peak at approximately -10°C . The α_{II} is a slightly higher shoulder with the main peak at approximately 30°C , and the α_I relaxation zone results in a narrow still higher peak at temperatures near to fusion.

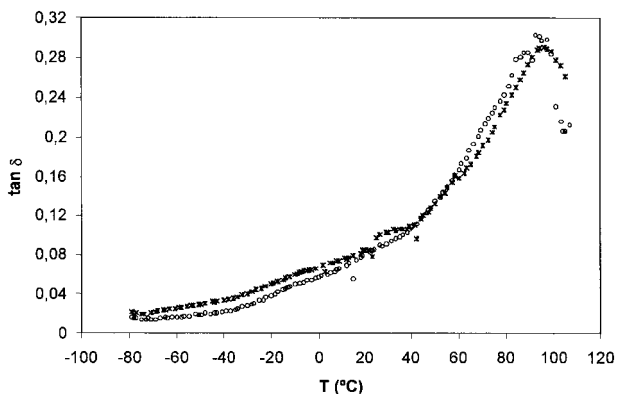


Figure 6 Loss tangent ($\tan \delta$) as a function of temperature for pure LDPE samples: (\circ) with thermal treatment; (*) with thermal treatment plus degraded in soil 120 days.

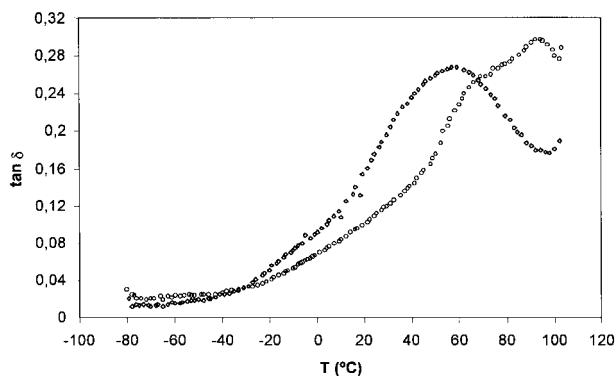


Figure 7 Loss tangent ($\tan \delta$) as a function of temperature for LDPE-Mater-Bi samples: (\diamond) without thermal treatment; (\circ) with thermal treatment.

The thermal treatment produces a shift of the spectra of pure samples to higher temperatures and an increase in $\tan \delta$ of the α_I peak, as displayed in Figure 5. In Figure 6, no significant changes in the spectra after 120 days of exposure time in soil were observed.

Figure 7 shows the three relaxation zones for the blended samples, but, in this case, the α relaxation zone is broader in comparison to those of the pure samples. Again, the thermal treatment promotes a shift of the spectra to higher temperatures, an attenuation of the α_{II} , and an increase of the α_I peak. It seems that the spectra tend to resemble the spectra of the annealed pure samples. With the exposure time in the soil, the spectra in Figure 8 do not shift in the temperature axis but show a decrease in intensity and a more homogeneous α relaxation.

If the loss modulus (E'') is represented as a function of the temperature, the β relaxation appears as the most prominent, the α_{II} relaxation appears as a small shoulder of the β relaxation, and the α_I relaxation is observed as an abrupt decrease in intensity at temperatures near fusion. This fact is well reflected in Figure 9. For that reason, the α_I relaxation zone cannot be characterized using the E'' results.

Thus, the α_I relaxation was characterized using the $\tan \delta$ results. The temperature of the maximum T_{\max} of $\tan \delta$, for each frequency f , was considered. The apparent activation energy E_a was calculated by fitting the dependence of the mean relaxation times on the temperature to the Arrhenius equation:

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

Table III displays the apparent activation energy E_a and the temperature of the maximum T_{\max} for the α_I relaxation calculated for the pure samples. It was not possible to obtain accurate values of E_a for nontreated samples as all the relaxations appear overlapped. The annealing treatment produces a shift of the α_I peak to

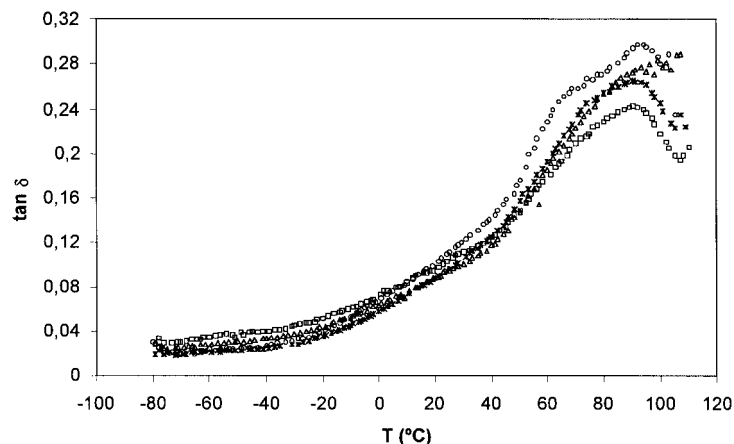


Figure 8 Loss tangent ($\tan \delta$) as a function of temperature for LDPE-Mater-Bi samples: (○) with thermal treatment; (*) with thermal treatment plus degraded in soil 20 days; (△) with thermal treatment plus degraded in soil 60 days; (□) with thermal treatment plus degraded in soil 120 days.

higher temperatures, as shown by the increase in the T_{\max} . After 120 days of exposure time in soil, no significant changes are observed either in the T_{\max} or in the apparent activation energy.

Table IV displays the apparent activation energy E_a and the temperature of the maximum T_{\max} for the α_1 relaxation calculated for blended samples. It was not possible to find accurate enough values for untreated samples. Again, a shift of the α_1 peak to higher temperatures was observed after annealing. Only slight changes are observed in E_a and in T_{\max} during the soil burial test.

If it is assumed, as suggested by other authors,¹⁵ that the α_1 relaxation is associated with the molecular movements of the chains in the crystalline phase, then the changes observed in the position of this relaxation can be correlated with the changes observed for the crystalline content and the lamellar thickness distribution. Thus, the annealing process alters the morphol-

ogy of the pure samples by allowing the thinner crystallites to rearrange in the crystalline phase and this produces a shift of the α_1 peak to higher temperatures. The calorimetric results suggest that the degradation in soil does not affect the crystalline zone in pure samples, and the same results can be observed in the shape and position of the α_1 relaxation.

The apparent activation energies of the α_1 relaxation for the blended samples are much lower than those of the pure samples. This fact is in agreement with the supposition that the carbonated chains of the components of Mater-Bi AF05H hinder the uniform growth of crystallites in polyethylene and produce a certain reorganization of the molecular chains that facilitate molecular motions.

The analysis of the mechanical behavior was carried out in terms of the loss modulus (E'') for α_{II} and β relaxations. Each one of the relaxation zones for each sample was characterized for this purpose. The values of E'' were calculated as $E'' = \tan \delta \times E'$. It was fitted to the experimental data to the Fuoss-Kirkwood equation, and the maximum of the loss modulus E''_{\max} , the temperature of the maximum of the loss modulus T_{\max} , and the term $m_{FK}E_a/R$ were found:

$$E'' = \frac{E''_{\max}}{\cosh \left[m_{FK} \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right]}$$

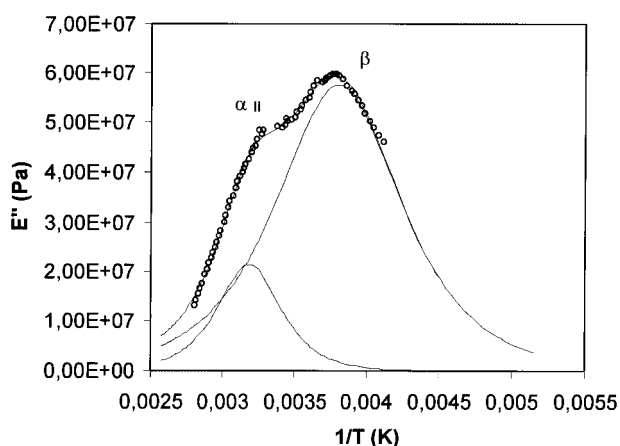


Figure 9 Deconvolution in terms of E'' of the relaxations at 3-Hz frequency for a pure LDPE sample annealed and buried in soil for 120 days.

As these relaxations appear to be overlapped, it was supposed that the experimental data are the addition of these relaxations, in order to apply a deconvolution method, which consists of considering E'' as equivalent to $E'' = E''_{\alpha_{II}} + E''_{\beta}$.²² Figure 9 shows, as an example, the deconvolution of the relaxations at 3-Hz frequency for a pure sample annealed and buried in soil for 120 days. Similar figures were obtained for all

TABLE III
Characterization of the α_I , α_{II} , and β Relaxations: Apparent Activation Energy (E_a) and Temperature of the Maximum (T_{max}) of Pure LDPE Samples

Treatment	α_I ($\tan \delta$)		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)
Untreated	—	337	125	306	339	260
Annealed	230	366	142	304	192	259
Annealed + 120 days of exposure time in soil	217	369	—	311	244	261

samples and frequencies. In these figures, the β relaxation appears as a broader peak, with higher intensity, in comparison with the α_{II} relaxation. Once the mentioned parameters were calculated, the apparent activation energy E_a was calculated by fitting the dependence of the mean relaxation times on the temperature to the Arrhenius equation.

The results obtained for pure samples are displayed in Table III. The values of the apparent activation energy E_a and the temperature of the maximum T_{max} for α_{II} and β relaxations were calculated. Neither the thermal treatment nor the burial test significantly altered the T_{max} for both relaxations. It was not possible to characterize the α_{II} relaxation after 120 days of degradation in soil, since it was completely overlapped with the β relaxation.

The results obtained for blended samples are displayed in Table IV. The values of the apparent activation energy E_a and the temperature of the maximum T_{max} for α_{II} and β relaxations were calculated. The annealing slightly shifts the T_{max} to higher temperatures and diminishes considerably the E_a . With the exposure time in soil, both the E_a and the T_{max} change in a nonuniform way for both relaxations, which could be interpreted as a complex process in different stages.

These results suggest that the influence of Mater-Bi is more significant in the evolution of the E_a in the case of the α_{II} and β relaxations than in the α_I relaxation. This effect could be understood by assuming that the observed α_{II} and β relaxation zones in the blends include the α_{II} and β relaxations of polyethylene overlapped with the β wide relaxation of Mater-Bi.¹² Thus, the observed β relaxation results from the contribution of different β relaxations, which could be related to motions of the molecular chains containing the —OH

groups, both in the starch and in the vinyl alcohol in Mater-Bi, and the carbonated chains in polyethylene.

It was assumed in a previous work¹² that the degradation in soil produced in the Mater-Bi causes a decrease of the β relaxation. The fact that the β relaxation assigned to the Mater-Bi decreases with the annealing process and the soil burial treatment diminishes considerably the contribution of Mater-Bi to the spectra of the blends. For this reason, the spectra of the treated blends tend to resemble the spectra of pure polyethylene. In this sense, it could be stated that the degradation process is started in the Mater-Bi, whereas the carbonated chains in polyethylene are less affected.

CONCLUSIONS

The annealing treatment produces a rearrangement of the crystallites in the crystalline phase and a segregation of the crystallite sizes in both pure and blended samples, but this effect is more significant for pure samples. No changes were noted for pure samples after the exposure time in soil, indicating that the morphology of polyethylene is practically not affected by the soil burial treatment. Thus, the annealing treatment does not seem to improve the scarce degradability of the polyethylene in soil.

The changes observed in the blended samples indicate that the degradation of the blends is due mainly to the presence of the Mater-Bi, whose carbonated chains seem to act in hindering the uniform growth of crystallites in polyethylene, promoting a broader distribution of crystallites in it. With the exposure time in soil, the changes observed in the β relaxation could indicate the degradation of the Mater-Bi, since the

TABLE IV
Characterization of the α_I , α_{II} , and β Relaxations: Apparent Activation Energy (E_a) and Temperature of the Maximum (T_{max}) of LDPE-Mater-Bi Samples

Treatment	α_I ($\tan \delta$)		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)
Untreated	—	330	280	297	305	262
Annealed	146	365	184	306	167	268
Annealed + 20 days of exposure time in soil	138	361	—	314	234	274
Annealed + 60 days of exposure time in soil	163	365	188	307	134	259
Annealed + 120 days of exposure time in soil	130	363	226	307	142	259

spectra for blended samples tend to resemble the spectra for pure polyethylene.

The authors are grateful for the financial support received for this work from the Ministerio de Ciencia y Tecnología of Spain (Project PPQ2001-2764-C03-01).

References

1. Albertsson, A.-C.; Karlsson, S. *Chemistry and Technology of Biodegradable Polymers*; Blackie: Glasgow, 1994.
2. Albertsson, A.-C.; Karlsson, S. *J Macromol Sci A* 1996, 33, 1565.
3. Bastioli, C. *Polym Degrad Stab* 1998, 59, 263.
4. Albertsson, A.-C.; Karlsson, S. *Polym Degrad Stab* 1988, 35, 1289.
5. Scott, G. *Mechanisms of Polymer Degradation and Stabilisation*; Elsevier Applied Science: London, New York, 1990.
6. Schnabel, W. *Polymer Degradation: Principles and Practical Applications*; Hanser: Munich, 1992.
7. Contat-Rodrigo, L.; Ribes-Greus, A., submitted for publication in *J Appl Polym Sci*.
8. Contat-Rodrigo, L.; Ribes-Greus, A.; Díaz-Calleja, R. *J Appl Polym Sci* 2001, 82, 2174.
9. DIN 53739, Nov. 1984.
10. Goheen, S. M.; Wool, R. P. *J Appl Polym Sci* 1991, 42, 2691.
11. Turi, E. A. *Thermal Characterization of Polymeric Materials*; Academic: New York, 1997.
12. Contat-Rodrigo, L. Ph.D. Thesis, Valencia, 2000.
13. Wlochowicz, A.; Eder, M. *Polymer* 1984, 25, 1268.
14. Wunderlich, B. *Macromolecular Physics*; Academic: New York, 1973; Vol. 1, p 388.
15. Rueda, D. R.; Martínez-Salazar, J. F.; Balta-Calleja, J. *J Polym Sci Polym Phys* 1984, 22, 1811.
16. Alamo, R.; Mandelkern, L. *J Polym Sci Polym Phys* 1986, 24, 2087.
17. Popli, R.; Glotin, M.; Mandelkern, L.; Benson, R. *J Appl Polym Sci* 1984, 22, 407.
18. Boyd, R. H. *Polymer* 1985, 26, 1123.
19. Boyd, R. H. *Polymer* 1985, 26, 323.
20. Popli, R.; Mandelkern, L. *J Polym Sci Polym Phys* 1987, 25, 441.
21. McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover: New York, 1991.
22. Charlesworth, J. M. *J Mater Sci* 1993, 28, 399.