

# Biodegradation Studies of LDPE Filled with Biodegradable Additives: Morphological Changes. I

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**ABSTRACT:** Low-density polyethylene (LDPE) samples filled with three commercial biodegradable additives (Mater-Bi, Cornplast, and Bioeffect) have been subjected to an accelerated soil burial test in a culture oven for 1 year. By means of Differential Scanning Calorimetry (DSC), the effect of the degradation in soil in the samples morphology has been analyzed, in terms of their melting temperature, their crystalline content, and their lamellar thickness distribution. These morphological parameters evolve in different stages, depending on the additive used. It has been found that the LDPE–Mater-Bi samples are the ones exhibiting faster changes in their crystalline content. However, the LDPE blends with Cornplast and Bioeffect display more significant changes in their lamellar thickness distribution. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1683–1691, 2002

**Key words:** polyethylene (PE); degradation; differential scanning calorimetry (DSC)

## INTRODUCTION

Biodegradability of polymers is determined by their chemical structure and their morphology. In the case of polyethylene, its hydrophobicity and its large molecular size make this synthetic polymer quite resistant to biodegradation.

However, polyethylene with enhanced biodegradability can be obtained by simply incorporating during processing, additives containing readily degradable natural polymers. Nowadays, several biodegradable additives containing starch either in its granular or in its gelatinized form are commercialized for this purpose.<sup>1–8</sup>

A thorough characterization and knowledge of the degradation process of these polyethylenes are necessary before suggesting viable applications for such materials. These must be designed

both to behave as expected during the service life of the product and, after its use, to degrade through the action of micro-organisms for a reasonable period of time without polluting the environment.

The degradation mechanism of the biodegradable polyethylenes is complex, because their environmental degradation results from the interaction of different oxidative processes, both biotic and abiotic.<sup>9–16</sup> The analysis of the morphological changes can bring information on the microstructural changes underwent by the polymeric matrix. In this sense, Differential Scanning Calorimetry (DSC) can be considered a very useful technique, because it allows studying in detail polymer morphology. By means of this technique, changes in crystallinity and the lamellar thickness distribution of polymeric samples during their degradation process can be analyzed.

The objective of this work is to analyze by Differential Scanning Calorimetry the changes in the morphology of LDPE samples filled with dif-

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ferent biodegradable additives when subjected to an accelerated soil burial test.

## EXPERIMENTAL

### Materials

Low-density polyethylene (LDPE) 710 from Dow Chemical (Spain), previously characterized by Infrared Spectroscopy and Size-Exclusion Chromatography,<sup>17,18</sup> was blended with three types of commercial biodegradable additives.

The additives used are marketed under the Mater-Bi, Cornplast, and Bioefect trademarks.

Mater-Bi AF05H was supplied by Novamont North America (USA). It is a starch-based additive that contains thermoplastic starch heavily complexed with ethylene-vinyl alcohol (EVOH) copolymers.<sup>2</sup>

Cornplast is made up of polyethylene and a product containing starch. It is produced by the National Corn Grower Association (NCGA, USA).

Bioefect 72000, from Proquimaq Color, S.L. (Spain), combines starch and other additives. Calorimetric results reported in a previous work reveal the presence of polyethylene in this additive.<sup>19</sup>

### Samples

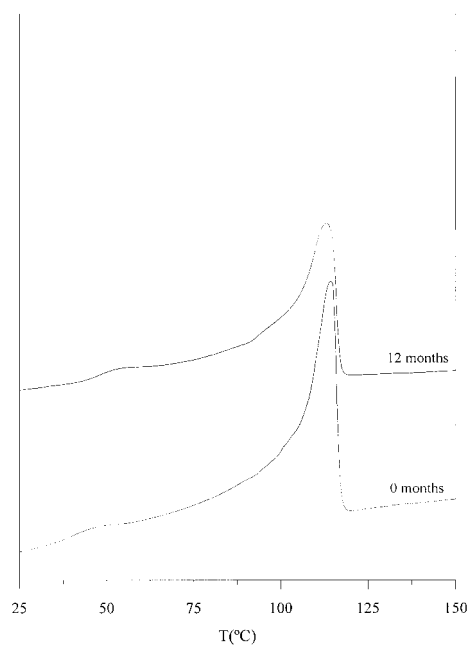
Homogeneous mixtures with 50/50% by weight of LDPE with each of these biodegradable additives were initially prepared from the melt in a Brabender Plasti-Corder PL 2100 rheometer. These mixtures were afterwards cut as nut coal and reprocessed as rectangular bars (68 × 12 × 1.8 mm) by compression molding using a model M Carver press. Samples of pure LDPE have also been prepared to be used as control materials.

### Soil Burial Test

All the samples have been subjected to an accelerated soil burial test, according to the DIN 53739 International Norm.<sup>20</sup>

Samples have been buried in biologically active soil contained in rectangular plastic boxes, which are kept opened to ensure a fresh oxygen supply. A 20-mesh stainless wire cloth has been placed all along the box perimeter to ensure good ventilation of the soil.<sup>21</sup>

The soil used in these tests is a 50/50% (by weight) mixture of a soil extract picked up from a culture field in Alginet (Valencia, Spain), and a



**Figure 1** DSC thermograms of pure LDPE as a function of the exposure time in soil.

soil typically used in tree-nurseries for pines growth.<sup>22</sup>

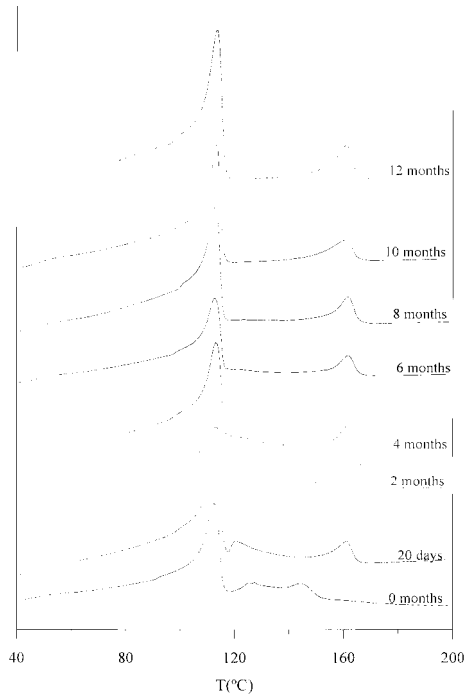
The biodegradation test was carried out in a HERAEUS B12 culture oven at a constant temperature of  $28 \pm 0.5^\circ\text{C}$ , periodically controlling the pH and the water content of the soil. Samples were removed after 20 days, 2 months, and every 2 months up to 1 year of exposure. The controls were only removed at the end of the test.

### Differential Scanning Calorimetry (DSC)

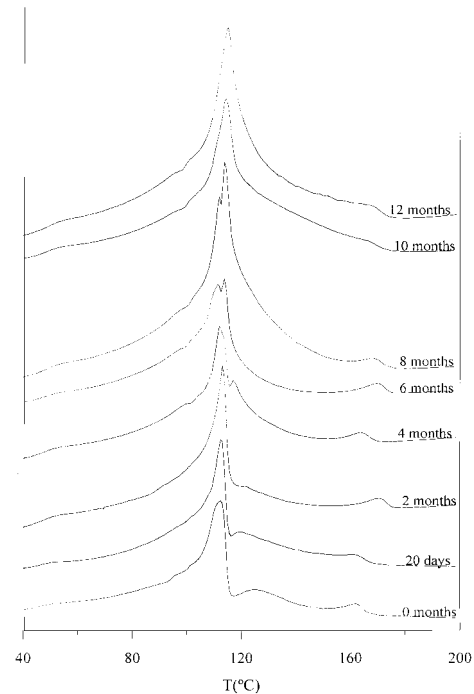
The DSC measurements were carried out with a Perkin-Elmer DSC-4 calorimeter, previously calibrated with indium. A total of 5–6 mg of samples was weighed out in standard aluminium pans. The sealed pans were scanned at a heating rate of  $10^\circ\text{C}/\text{min}$  from 0 to  $200^\circ\text{C}$  under nitrogen atmosphere. Measurements were repeated until errors of less than  $\pm 0.01^\circ\text{C}$  for melting temperatures and  $\pm 0.05$  for crystalline contents were assured.

## RESULTS AND DISCUSSION

Calorimetric analysis has been used to study the changes in the samples morphology due to degradation in soil, in terms of their melting temperature, their crystalline content, and their lamellar thickness distribution. The DSC thermograms of all the samples have been initially determined as



**Figure 2** DSC thermograms of the LDPE–Mater Bi samples as a function of the exposure time in soil.



**Figure 3** DSC thermograms of the LDPE–Cornplast samples as a function of the exposure time in soil.

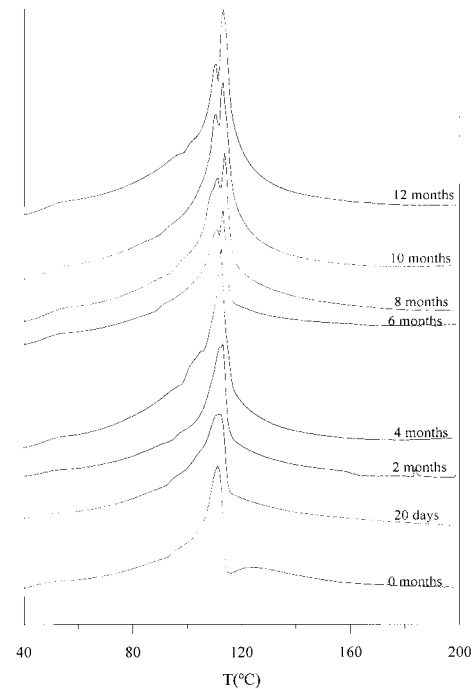
a function of the exposure time in soil. The pure LDPE control sample displays the typical DSC thermogram of low-density polyethylene, which consists in a single endotherm with maximum around 113°C (Fig.1). This remains practically unaltered after degrading in soil for 1 year.

All the thermograms of LDPE filled with Mater-Bi, Cornplast, and Bioeffect show one main endothermic peak (Figs. 2, 3, and 4). For the LDPE–Mater Bi samples, this endotherm can be due to LDPE exclusively, because the additive Mater-Bi does not include polyethylene in its formulation. In contrast, in the case of the samples with Cornplast and Bioeffect, this main peak can be originated by the carbonated chains of both the LDPE and the polyethylene contained in these additives.

The samples of LDPE–Mater Bi and LDPE–Cornplast also clearly display two small peaks at higher temperatures than that of polyethylene (Figs. 2 and 3). Comparing with the DSC thermograms of the pure additives previously determined in another work,<sup>22</sup> these small endotherms can be assigned to the corresponding additive.

The thermogram of the undegraded sample of LDPE–Bioeffect exhibits, near to the polyethylene endotherm, a wide peak around 125°C that can be attributed to the additive (Fig. 4), because such is the typical range of pure Bioeffect contributions as

shown in a previous work.<sup>19</sup> However, the degraded samples of LDPE–Bioeffect present one single endotherm in which the contributions of the two compo-



**Figure 4** DSC thermograms of the LDPE–Bioeffect samples as a function of the exposure time in soil.

**Table I Melting Temperature of the Main Endotherm,  $T_f$ , for Each of the Undegraded Samples**

Sample	$T_f$ (°C)
LDPE	113.55
LDPE-Mater Bi	112.63
LDPE-Cornplast	112.38
LDPE-Bioeffect	111.26

nents of the blend must be summed. Thus, the contributions of the polyethylene and the additive cannot be distinguished in the samples with Bioeffect. This could indicate that the blends prepared with Bioeffect are more homogeneous than the blends prepared with Mater-Bi and Cornplast, despite having used the same mixing and preparation procedures in all cases.

On the other hand, from Figures 2, 3, and 4 it is observed that changes during degradation are different, depending on the additive used. In the LDPE–Mater Bi blends, the modifications affect the additive rather than the main endotherm, which shape and location are barely modified (Fig. 2). However, in the LDPE–Cornplast and LDPE–Bioeffect blends, a gradual broadening of the main endotherm occurs, together with a segregation in different crystallite sizes (Figs. 3 and 4).

### Melting Temperature

The melting temperature of the main endotherm in all the samples has been directly determined from the thermograms. The values obtained for the undegraded samples are listed in Table I.

In general, a slight decrease in the melting temperature of the main endotherm in the undegraded blends compared to that of pure LDPE has been found. The biggest decrease in the melting temperature is exhibited by the LDPE–Bioeffect blend. This result could contribute to confirm the above-proposed hypothesis of a greater homogeneity of the blends with the additive Bioeffect.

On the other hand, the melting temperature has been plotted against the exposure time for each blend (Fig. 5). It is noted that although this parameter scarcely changes during the soil burial test, results are accurate enough to appreciate significant tendencies.

From Figure 5 it is observed that the evolution of the melting temperature in the blends takes place generally in different stages. Nevertheless, the tendency is different for each additive, sug-

gesting that LDPE is quite affected by the nature of the additive used. It has been found that, in general, such evolution can be fitted to polynomial equations. Similar results have been obtained by Hamid et al. for the evolution of the elongation at break with the exposure time of LDPE films subjected to weathering.<sup>24,25</sup>

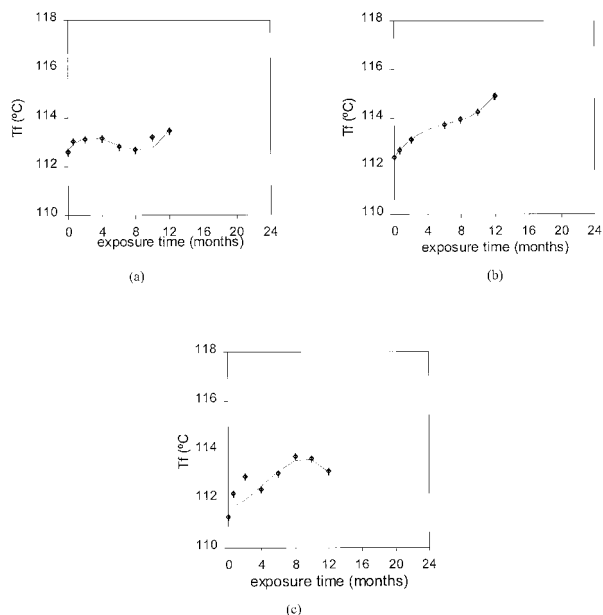
On the other hand, these results are in good agreement with the idea proposed by Albertsson et al.<sup>23</sup> that degradation is a complex process consisting of various stages that evolve differently in time depending on the additive.

### Crystalline Content

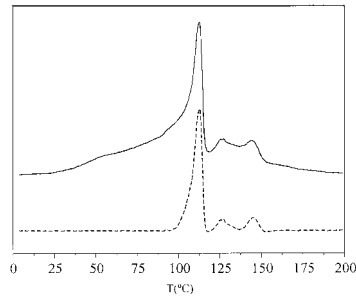
The total crystalline content of the pure LDPE controls has been calculated according to the following equation:

$$X = \frac{(H_a - H_c)}{H_m} \quad (1)$$

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 thermo-



**Figure 5** Variation with the exposure time of the melting temperature of the main endotherm for (a) the LDPE–Mater Bi samples, (b) the LDPE–Cornplast samples, and (c) the LDPE–Bioeffect samples. Polynomial fit: (a)  $y = 0.0059.x^3 - 0.0999.x^2 + 0.4198.x + 112.69$  ( $r^2 = 0.9560$ ); (b)  $y = 0.0033.x^3 - 0.0619.x^2 + 0.4764.x + 112.37$  ( $r^2 = 0.99998$ ); (c)  $y = -0.0043.x^3 - 0.0554.x^2 + 0.0751.x + 111.63$  ( $r^2 = 0.9042$ ).



**Figure 6** Peaks separation for the DSC thermogram of the undergraded LDPE-Mater Bi sample, for the application of the method of calculation of partial areas. — DSC thermogram, - - - DSC thermogram after the peaks separation.

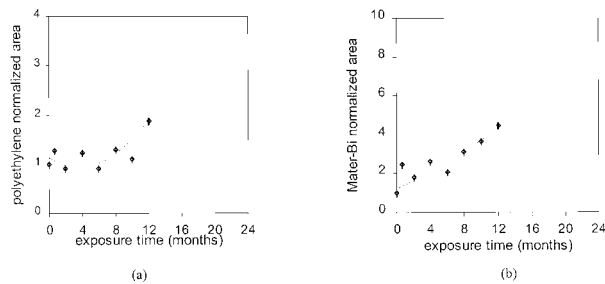
gram.  $H_m$  is the change in the melting enthalpy of a perfect crystal of infinite size. For polyethylene,  $H_m = 70 \text{ cal/g}$ .<sup>26</sup>

It has been found a crystallinity of 48% for pure LDPE, both before and after the soil burial test.

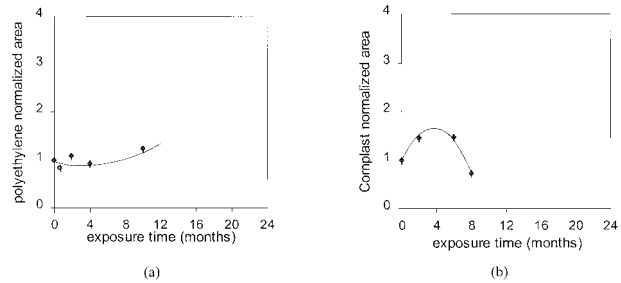
#### Method of Partial Areas

To study the evolution of the crystalline content of the carbonated chains of polyethylene and the additive separately during the degradation process, a method of calculation of partial areas has been applied.

Such a method is based on the determination of the main peak of the thermogram including the melt of crystals from all the polyethylenes, and the different characteristic peaks of the additives, and the later subtraction of all the other contributions (Fig. 6). The contributions due to the melt of the less perfect crystals of polyethylene and those made up of thinner lamellae are then not considered in the area assigned to polyethylene.



**Figure 7** LDPE-Mater Bi samples. Normalized partial areas of (a) polyethylene and (b) Mater Bi as a function of the degradation time in soil. Polynomial fit: (a)  $y = 0.0139.x^2 - 0.1028.x + 1.1329$  ( $r^2 = 0.8689$ ); (b)  $y = 0.0059.x^2 - 0.1907.x + 1.2295$  ( $r^2 = 0.9191$ ).



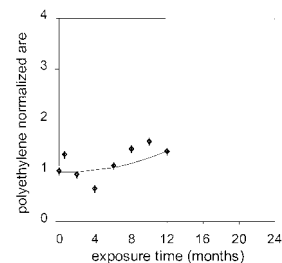
**Figure 8** LDPE-Cornplast samples. Normalized partial areas of (a) polyethylene and (b) Cornplast as a function of the degradation time in soil. Polynomial fit: (a)  $y = 0.0061.x^2 - 0.0391.x + 0.9381$  ( $r^2 = 0.8700$ ); (b)  $y = -0.0499.x^2 + 0.3715.x + 0.9697$  ( $r^2 = 0.9768$ ).

After the peaks separation, the area of each peak is calculated. This area is directly proportional to the heat flow necessary for the melt of this crystalline fraction. It can also be assumed that this heat flow is, in turn, directly proportional to the crystalline content,  $X$ .

Figures 7, 8, and 9 show the variation with the exposure time of the normalized partial areas (with respect to that of the corresponding undergraded blend) of polyethylene and the additive for each sample.

Concerning the areas of polyethylene, a common tendency to increase with the degradation time in soil is observed for all the blends, regardless of the additive used [Figs. 7(a), 8(a), and 9].

All the samples display an initial stage in which the crystallinity of polyethylene is kept basically constant. In semicrystalline polymers, degradation starts in the amorphous phase and in the interfacial regions, in which oxygen is soluble.<sup>27,28</sup> Thus, this period could be assigned to the first stages of the degradation process, when the amorphous chains start to degrade and the crystalline phase still remains unaltered.



**Figure 9** LDPE-Bioefect samples. Normalized partial areas of polyethylene as a function of the degradation time in soil. Polynomial fit:  $y = 0.0031.x^2 - 0.0019.x + 0.9718$  ( $r^2 = 0.9665$ ).

However, when degradation of the amorphous chains is significant enough, an increase of the crystalline content is produced, as it is observed in this case. These results agree with those reported by other authors.<sup>13,29–31</sup>

On the other hand, Hawkins suggests that the crystalline content of a semicrystalline polymer is conditioned by the amorphous phase that restricts the crystallization process.<sup>32</sup> A scission of the molecules of the amorphous regions, caused for example by oxidation, allows the crystallization to proceed to a higher extent. Such an increase in crystallinity could be then considered as a degradation sign.

In this case, crystallinity increases faster for the LDPE–Mater Bi samples than for the blends with Cornplast. The LDPE–Bioeffect blends are the ones for which crystallinity increases at a slowest rate. These results indicate that degradation proceeds faster for the LDPE–Mater Bi samples.

On the other hand, it has been found that the evolution with the degradation time of the main crystalline content of polyethylene can also be adequately represented by parabolic equations.

The analysis of the peaks of the additives has only been carried out for Mater-Bi and Cornplast, whose contributions in the blends are more clearly separated from that of the main endotherm.

For these two additives it has only been studied the evolution with the exposure time of the areas corresponding to their peaks at higher temperatures than the main endotherm, because they are the ones persisting during all the degradation test [Figs. 7(b) and 8(b)]. As it can be observed from the DSC thermograms, the peaks of Mater-Bi and Cornplast at lower temperatures are reduced progressively, until disappearing (Figs. 2 and 3). For that reason, the areas of these peaks have not been analyzed.

Both Mater-Bi and Cornplast display different evolutions of their normalized partial areas during degradation in soil. Although for Mater-Bi a continuous increase is observed, Cornplast exhibits an initial increase followed by a later decrease. This reduction could be partly due to the progressive overlapping with the main endotherm, assigned to polyethylene (Fig. 3).

### Lamellar Thickness Distribution

The lamellar thickness distribution of polyethylene in each sample has been determined according to the procedure proposed by Eder.<sup>33</sup>

**Table II** Values of the Parameters  $T_m^0$ ,<sup>34</sup>  $\sigma_e$  and  $\Delta h_m$ ,<sup>33</sup> of the Thomson Equation for Polyethylene

Parameter	Polyethylene
$T_m^0$ (K)	414.6
$\sigma_e$ ( $\text{J} \cdot \text{m}^{-2}$ )	$60.9 \times 10^{-3}$
$\Delta h_m$ ( $\text{J} \cdot \text{m}^{-3}$ )	$2.88 \times 10^8$

Eder considers that the flow rate of the heat of fusion at a given temperature, determined by the deflection of the DSC trace from the baseline, is directly proportional to the fraction of lamellae with this melting point.

The Thomson equation gives the relationship between the lamella thickness,  $l$ , and the melting temperature of lamellae of thickness  $l$ :

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

where  $T_m$  is the melting temperature of lamellae of thickness  $l$ ;  $T_m^0$  is the equilibrium melting temperature of an infinite crystal;  $\sigma_e$  is the surface free energy of the basal plane;  $\Delta h_m$  is the enthalpy of fusion per unit volume; and  $l$  is the lamellae thickness.

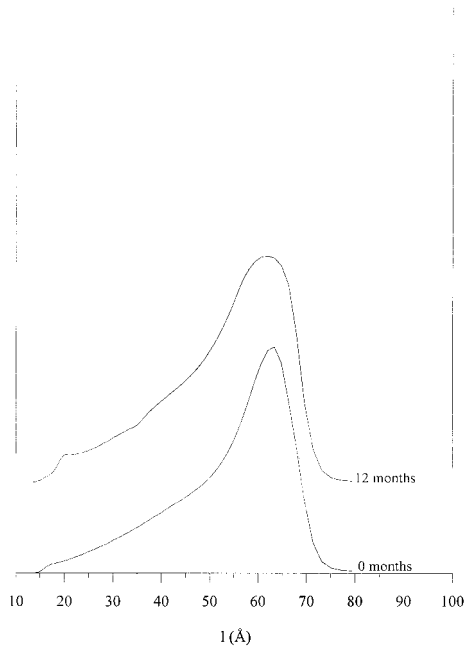
The values of these parameters for polyethylene are listed in Table II.

According to this equation, Eder assumes that at a given temperature for a sample of molten polymer, the rate of heat consumption is proportional to the fraction of lamellae whose thickness is obtained with the Thomson equation.

Thus, the plot of the normalized deflection against lamella thickness,  $l$ , corresponding to the temperature,  $T$ , as calculated from the Thomson equation, yields the distribution curve of lamellae thicknesses.

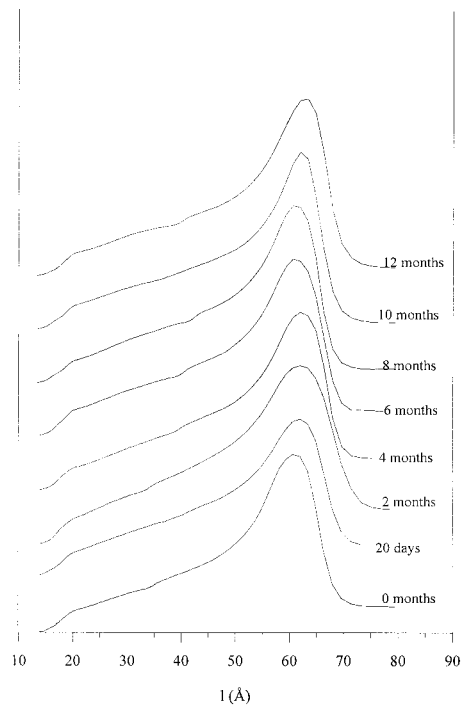
Pure LDPE shows a relatively narrow lamellar thickness distribution, ranging between 15 and 80 Å, with a maximum at about 62 Å (Fig. 10). The presence of Mater-Bi or Cornplast does not affect in general the distribution of the LDPE in the undegraded blends with these additives (Figs. 11 and 12). However, the undegraded blend with Bioeffect displays a slightly narrower distribution than that of pure LDPE (Fig. 13). This result could as well support the idea of a greater homogeneity of the blends with Bioeffect, suggested previously.

Pure LDPE does not undergo any variations in the shape or in the location of its lamellar thick-

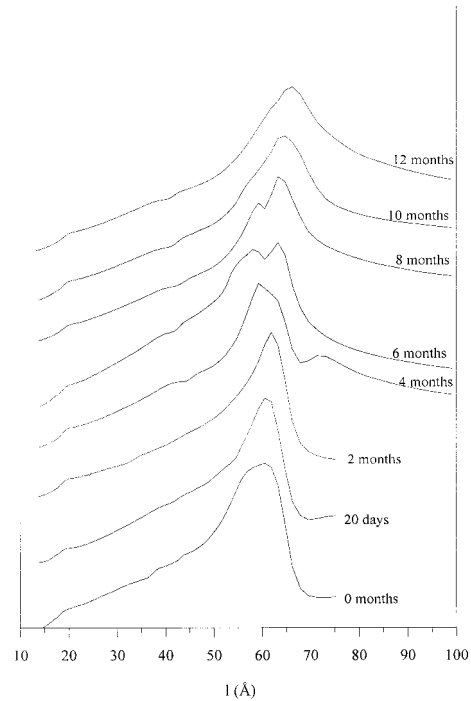


**Figure 10** Lamellar thickness distribution of pure LDPE as a function of the exposure time in soil.

ness distribution, after being buried for 14 months (Fig. 10). However, significant changes in the lamellar thickness distribution of polyethyl-



**Figure 11** Lamellar thickness distribution of polyethylene in the LDPE–Mater–Bi samples as a function of the exposure time in soil.

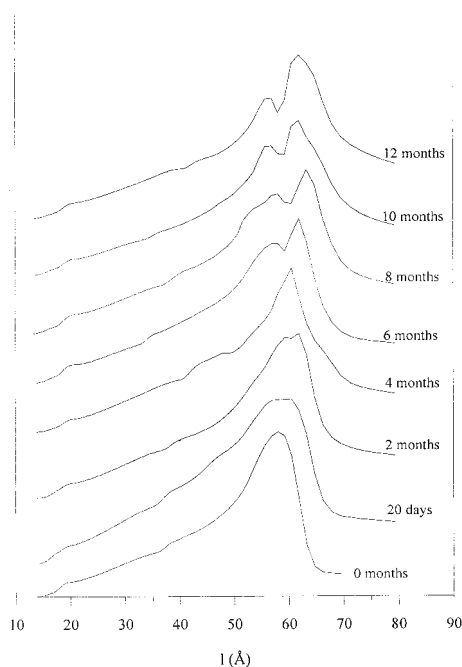


**Figure 12** Lamellar thickness distribution of polyethylene in the LDPE–Cornplast samples as a function of the exposure time in soil.

ene in the blends are observed during the soil burial test. The variation of the distributions with the degradation time depends on the type of additive used.

In the LDPE–Mater Bi samples, only small changes throughout the degradation process are noted (Fig. 11). These basically consist in successive broadenings and narrowings. During the first 6 months of exposure, a slight broadening of the distribution is observed, followed by a later tendency to become narrower.

On the other hand, the evolution underwent by the lamellar thickness distribution of the LDPE–Cornplast samples reveal a more complex behaviour of these materials during degradation (Fig. 12). In a first stage, taking place during the first 2 months of exposure, the distribution tends to become more homogeneous. As a result, the main endotherm is better defined. Between the 4 and 6 months of degradation, 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. The last stage begins at the eighth month of exposure, when the distribution tends again to homogeneity. The overall result of this evolution is a broader distribution than that of the undegraded



**Figure 13** Lamellar thickness distribution of polyethylene in the LDPE–Bioeffect samples as a function of the exposure time in soil.

blend, with maximum at slightly higher thicknesses.

Probably the homogeneity and the segregation of the crystallite sizes are competitive processes that occur simultaneously during degradation. The fact that the effects of one of these processes are more clearly manifested during a period of time indicates that this phenomenon prevails over the other in this period. This confirms that degradation is a complex process into which are involved a great variety of molecular mechanisms.

The LDPE–Bioeffect samples also display a complex evolution of their lamellar thickness distribution during degradation in soil (Fig. 13). During the first 2 months of the test, the distribution shifts to higher thicknesses. Since then, homogeneity and segregation of the crystallite sizes combine, although do not clearly display the predominance of one effect over the other, as it occurred for the LDPE–Cornplast samples.

In the LDPE–Bioeffect blends, the segregation process is more clearly manifested than in the case of the blends with Cornplast. This could be due to the better affinity of the additive Bioeffect with the LDPE. The gradual degradation of the additive could provoke a rearrangement of the crystalline phase of polyethylene that leads to the

formation of crystallites of different sizes. In the same way, the presence of Bioeffect could hinder the recrystallization process predicted by Hawkins,<sup>32</sup> which contributes to more homogeneous lamellar thicknesses.

## CONCLUSIONS

The evolution of the morphological parameters studied in this work takes place generally in different stages. In the case of the melting temperature and crystallinity, their evolution can be fitted to polynomial equations, and it occurs at different time scales depending on the additive used. This indicates that degradation is a complex process consisting of various stages that combines in time depending on the additive. These results agree with the different degradation rates observed by Albertsson et al.

On the other hand, the variation of the lamellar thickness distributions of polyethylene with the degradation time indicates a more complex behaviour of the LDPE–Cornplast and LDPE–Bioeffect samples during the degradation process. In both blends, a tendency towards homogeneity and segregation of the crystallite sizes of the matrix takes place.

It can also be concluded that among the three blends studied, the LDPE–Mater Bi samples are the ones degrading more rapidly, as shown by their faster increase of crystallinity. However, the small changes underwent by the lamellar thickness distribution of polyethylene indicates that degradation little affects the polymeric matrix.

Cornplast and Bioeffect cause bigger changes in the matrix than Mater-Bi, as proven by the more significant changes undergone by the lamellar thickness distribution of polyethylene in the LDPE–Cornplast and LDPE–Bioeffect blends.

## REFERENCES

1. Griffin, G. J. L., Ed. *Chemistry and Technology of Biodegradable Polymers*; Blackie Academic & Professional: Glasgow, 1994.
2. Bastioli, C. *Polym Degrad Stabil* 1998, 59, 263.
3. Vikman, M.; Itaväara, M.; Poutanen, K. *J.M.S.-Pure Appl Chem* 1995, A32, 863.
4. Otey, F. H.; Westhoff, R. P.; Doane, W. M. *I&EC Prod Res Dev* 1980, December, 592.
5. Otey, F. H.; Westhoff, R. P.; Doane, W. M. *I&EC Prod Res Dev* 1987, August, 1659.



6. Gould, J. M.; Gordon, S. H.; Dexter, L. B.; Swanson, C. L. In *Agricultural and Synthetic Polymers: Biodegradability and Utilization*; ACS Symposium Series 433; Edward Glass, J.; Swift, G., Eds.; American Chemical Society, Washington, DC, 1990, p. 65.
7. Lörcks, J. *Polym Degrad Stabil* 1998, 59, 245.
8. Funke, U.; Bergthaller, W.; Lindhauer, M. G. *Polym Degrad Stabil* 1998, 59, 293.
9. Albertsson, A.-C.; Andersson, S. O.; Karlsson, S. *Polym Degrad Stabil* 1987, 18, 73.
10. Flemming, H. C. *Polym Degrad Stabil* 1998, 59, 309.
11. Albertsson, A. C.; Huang, S. J., Eds. *Degradable Polymers, Recycling and Plastic Waste Management*; Marcel Dekker: New York, 1995.
12. Hakkarainen, M.; Albertsson, A.-C.; Karlsson, S. *J Appl Polym Sci* 1997, 66, 959.
13. Lee, B.; Pometto, A. L., III; Fratzke, A.; Bailey, T. B. *Appl Environ Microbiol* 1991, March, 678.
14. Greizerstein, H. B.; Syracuse, J. A.; Kostyniak, P. J. *Polym Degrad Stabil* 1993, 39, 251.
15. Chiellini, E.; Solaro, R.; Corti, A.; Picci, G.; Leporini, C.; Pera, A.; Vallini, G.; Donnaggio, P. *Chim Indust* 1991, 8-9, 656.
16. Erlandsson, B.; Karlsson, S.; Albertsson, A.-C. *Polym Degrad Stabil* 1997, 55, 237.
17. Ribes-Greus, A.; Díaz-Calleja, R. *J Appl Polym Sci* 1987, 34, 2819.
18. Ribes-Greus, A.; Díaz-Calleja, R. *J Appl Polym Sci* 1989, 37, 2549.
19. Contat-Rodrigo, L.; Ribes-Greus, R.; Díaz-Calleja, R. *J Appl Polym Sci* 2001, 82, 2174.
20. DIN 53739; *Testing of Plastics. Influence of Fungi and Bacteria. Visual evaluation. Change in mass and physical properties*, Nov. 1984.
21. Goheen, S. M.; Wool, R. P. *J Appl Polym Sci* 1991, 42, 2691.
22. Contat-Rodrigo, L. Ph.D. Thesis, Valencia, 2000.
23. Albertsson, A.-C.; Karlsson, S. *Prog Polym Sci* 1990, 15, 177.
24. Amin, M.-B.; Hamid, S. H.; Rahman, R. *J Appl Polym Sci* 1995, 56, 279.
25. Hamid, S. H.; Amin, M. B. *J Appl Polym Sci* 1995, 55, 1385.
26. Turi, E. *Thermal Characterization of Polymeric Materials*; Academic Press: New York, 1997, vols. I and II.
27. Scott, G. *Mechanisms of Polymer Degradation and Stabilisation*; Elsevier Applied Science: London, 1990.
28. Grassie, N.; Scott, G. *Polymer Degradation and Stabilisation*; Cambridge University Press: Cambridge, MA, 1988.
29. Albertsson, A.-C.; Barenstedt, C.; Karlsson, S.; Lindberg, T. *Polymer* 1995, 36, 3075.
30. Khabbaz, F.; Albertsson, A.-C.; Karlsson, S. *Polym Degrad Stabil* 1998, 61, 239.
31. Khabbaz, F.; Albertsson, A.-C.; Karlsson, S. *Polym Degrad Stabil* 1998, 61, 127.
32. Hawkins, W. *Polymer Degradation and Stabilization*; Springer-Verlag: Berlin, 1984.
33. Wlochowicz, A.; Eder, M. *Polymer* 1984, 25, 1268.
34. Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1973, p. 388, vol. 1.