

Thermal and Viscoelastic Properties of Some Commercial Starch Products

L. Contat-Rodrigo, A. Ribes-Greus

Department of Applied Thermodynamics, ETSIV, Universidad Politécnica de Valencia, Apartado 22012, 46071 Valencia, Spain

Received 14 January 2002; accepted 3 May 2002

Published online 19 February 2003 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/app.11794

ABSTRACT: Three commercial starch products for polyolefins, marketed under the Mater-Bi, Cornplast, and Biofect trademarks, were subjected to an accelerated soil burial test. Their thermal and viscoelastic behaviors were studied by differential scanning calorimetry (DSC) and dynamic mechanical spectroscopy. Degradation in soil leads to more significant changes both in the DSC thermogram and the mechanical relaxation spectrum of Mater-Bi. The relaxation spectra of Cornplast and Biofect,

two products containing polyethylene, basically coincide with that of pure low density polyethylene. The α -relaxation zone of these starch products is the most affected by the degradation process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1242–1251, 2003

Key words: biodegradable; differential scanning calorimetry (DSC); viscoelastic properties; polyolefins

INTRODUCTION

A solution to the significant increase of plastic waste is the valuation of waste, which seeks to find industrial applications of recycled plastic and thus to allow its expansion in the market. When the products have a short service life, or when they cannot be recycled, the development of degradable polymers constitutes a new alternative.

Polyolefins with enhanced biodegradability can be obtained through the incorporation of products containing readily degradable natural polymers.

Already in the 1970s, Griffin¹ introduced the idea of using natural granular starch as a filler to induce biodegradability in polyethylene. Its later formulations also contain a prooxidant, consisting of a transition metal salt and an unsaturated polymer that enhances the oxidation of the polymeric matrix.^{2–7}

Later, Otey et al.^{8,9} blended gelatinized starch with polyethylene. These products also include other components that act as compatibilizers between starch and polyethylene, such as ethylene/acrylic acid (EAA) copolymers. These formulations allow starch contents of 40% to be reached.

More recently, starch-based materials have also been developed.^{10–14} These products have starch contents greater than 50%. These consist of thermoplastic

starch mixed with other polymers. Tomka and Wittwer¹⁵ described a process to obtain thermoplastic starch. Although its sensitivity to humidity makes thermoplastic starch unsuitable for most applications, thermoplastic starch composites with other synthetic polymers can satisfy a broad spectrum of market needs.

Nowadays, several products containing starch, either in its granular or in its gelatinized form, are commercialized as master batches. Polyolefins with enhanced biodegradability are obtained by simply incorporating these products into the polymeric matrix during processing. Before studying the properties of such polyolefins, a thorough characterization of these starch products and their biodegradation process is necessary.

The objective of this work was to analyze, by differential scanning calorimetry and dynamic mechanical spectroscopy, the thermal and viscoelastic behaviors of three commercial starch products for polyolefins, when subjected to an accelerated soil burial test.

EXPERIMENTAL

Samples

Three types of commercial starch products, marketed under the Mater-Bi, Cornplast, and Biofect trademarks, were studied.

Mater-Bi AF05H was supplied by Novamont North America (CA). It contains thermoplastic starch heavily complexed with ethylene-vinyl alcohol (EVOH) copolymers.¹⁰ Cornplast is produced by the National Corn Growers Association (NCGA, Washington DC). Ac-

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.

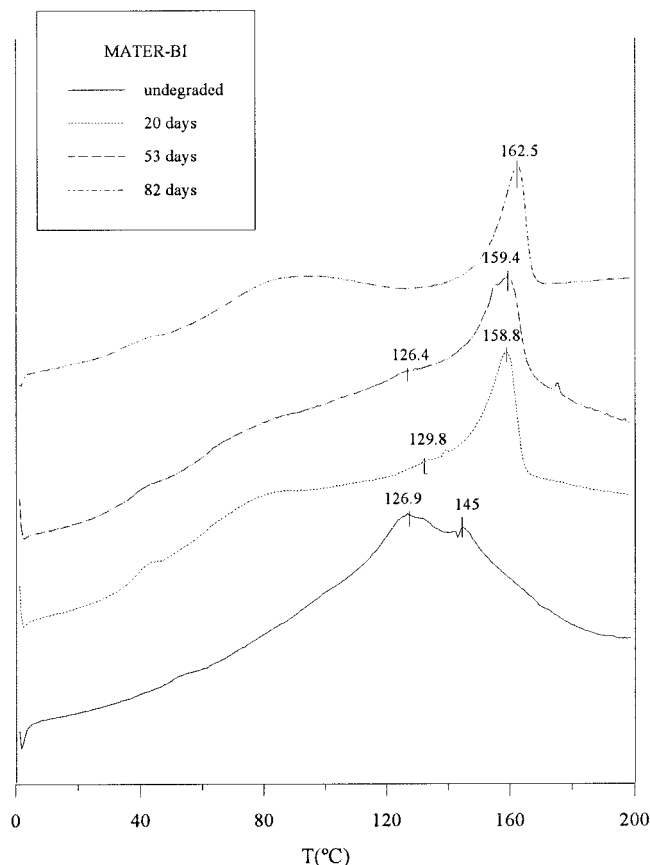


Figure 1 DSC thermograms of Mater-Bi AF05H as a function of the exposure time in soil.

According to the manufacturer’s specifications, it is made up of 20% polyethylene and 80% of a product containing starch. Bioeffect 72000 (Proquimaq Color, S.L., Spain) combines 75% low density polyethylene (LDPE), 20% starch, and 5% prooxidants containing fatty acids.

Rectangular samples (68 × 12 × 1.8 mm) of each of these starch products were prepared by compression molding using a Carver M press (WI).

Soil burial test

All the samples were subjected to an accelerated soil burial test, according to the DIN 53739 International Norm.¹⁶

Samples were buried in biologically active soil contained in rectangular plastic boxes. All the boxes were kept opened to ensure a fresh oxygen supply. A 20-mesh stainless wire cloth was placed along the box perimeter to ensure good ventilation of the soil.¹⁷ The soil used in these tests was a 50/50% (w/w) mixture of two kinds of soils: a soil extract from a culture field in Valencia, Spain, and a soil typically used in tree nurseries for growing pines.¹⁸

The biodegradation test was carried out in a Heraeus B12 culture oven (Hanau, Germany) at a con-

stant temperature of 28 ± 0.5°C, with period control of the pH and water content of the soil. Samples were removed after 20 days of exposure. The Mater-Bi samples were also removed after 53 and 82 days, given that they were the ones exhibiting the greatest changes during the first stages of the biodegradation test.

Differential scanning calorimetry (DSC)

The DSC measurements were carried out with a Perkin-Elmer DSC-4 calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT), previously calibrated with indium. A total of 5–6 mg of samples was weighed out in a standard aluminum pan. The sealed pans were scanned at a heating rate of 10°C/min from 0 to 200°C under nitrogen atmosphere.

Dynamic mechanical measurements

The viscoelastic properties were determined by means of a Mark II DMTA dynamic mechanical thermal analyzer (Polymer Laboratories, now Rheometrics, Poole, UK). Deformation was applied in the cantilever double-clamping flexure mode. The storage modulus (*E'*) and the loss tangent (*tan δ*) were measured from –80 to 150°C at frequencies of 0.3, 1, 3, 10, and 30 Hz with a heating rate of 1°C/min.

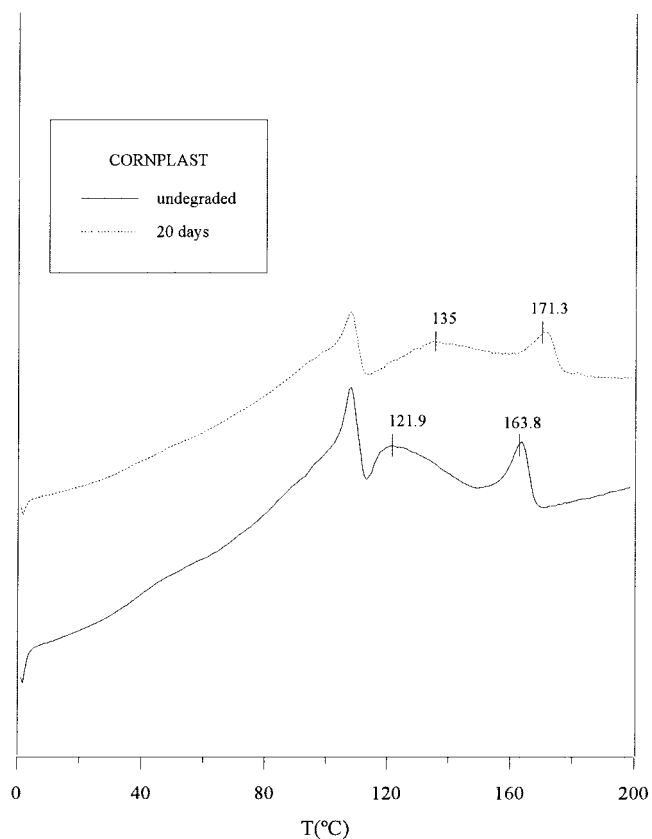


Figure 2 DSC thermograms of Cornplast as a function of the exposure time in soil.

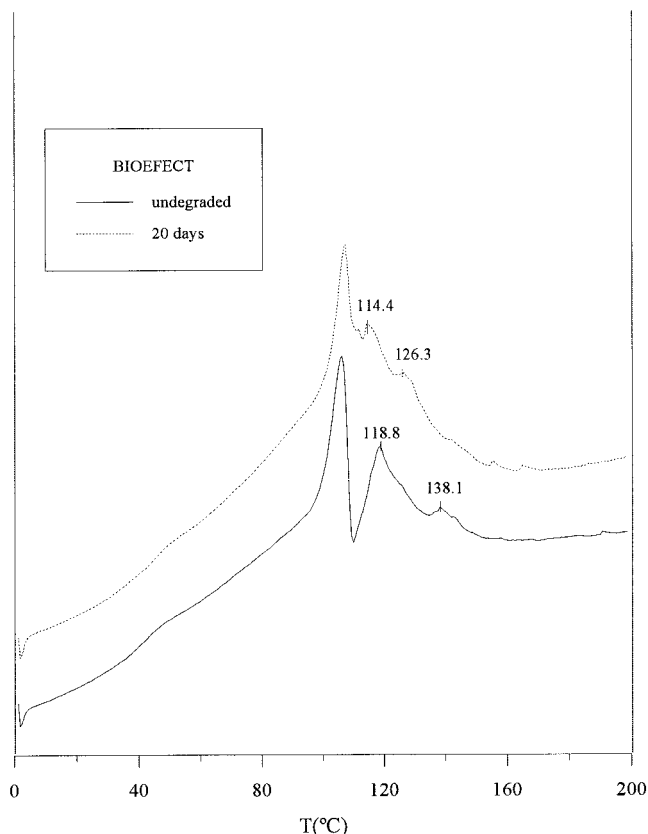


Figure 3 DSC thermograms of Bioeffect 72000 as a function of the exposure time in soil.

RESULTS AND DISCUSSION

DSC

The thermal properties of the starch products Mater-Bi AF05H, Cornplast, and Bioeffect 72000 were studied by DSC, in terms of their melting behavior. Figures 1, 2, and 3 show, respectively, the thermograms of Mater-Bi, Cornplast, and Bioeffect as a function of the exposure time in soil. All the thermograms consist of several overlapped endotherms.

The DSC thermogram of the undegraded sample of Mater-Bi displays a single broad peak, located from about 80 to 170°C (Fig. 1). This peak resulted from the overlapping of two main contributions, one with a maximum at 127°C and the other with a maximum at about 145°C. Degradation in soil leads to significant changes in the shape of the DSC trace of this starch product. The contribution develops at about 145°C, originating a sharp endotherm at about 159°C. On the other hand, the peak at 127°C is reduced to a small shoulder overlapped to this new endothermic peak. As the exposure time increases, this small shoulder tends to decrease until it finally disappears after 82 days of degradation in soil. Simultaneously, the main endotherm shifts toward higher temperatures.

The undegraded sample of Cornplast shows an endotherm at about 164°C, overlapped to a broader one

located at about 122°C (Fig. 2). The DSC thermogram of Cornplast also exhibits another peak with a maximum at about 108°C, which was attributed to the polyethylene present in the composition of this product. Furthermore, the melting temperature range of this peak indicates that this is a low density polyethylene. The thermogram of Cornplast degraded in soil for 20 days does not display any change in the position of the peak associated with polyethylene (108°C). However, it is observed that the other two contributions shift to higher temperatures, and are then located at 170 and 135°C, respectively.

The DSC thermogram of the undegraded sample of Bioeffect shows a peak at about 119°C, overlapped to a smaller one with a maximum at about 138°C (Fig. 3). This product also exhibits an endotherm at about 106°C, corresponding to the LDPE in the formulation of Bioeffect. After 20 days of exposure, the position of the peak attributed to polyethylene (106°C) remains unaltered, whereas the other two endotherms shift to lower temperatures. Their maxima are then located at around 114 and 126°C, respectively.

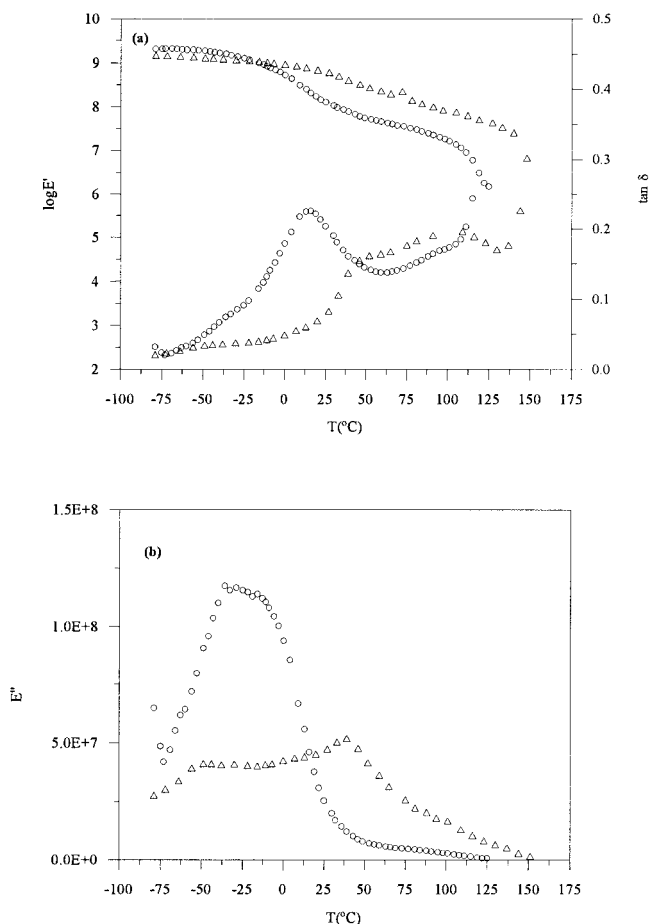


Figure 4 Mechanical relaxation spectra of Mater-Bi AF05H as a function of the exposure time in soil: \circ , undegraded; \triangle , after 82 days. Plots of (a) $\tan \delta$ and $\log E'$ and (b) E'' versus temperature at 1 Hz of frequency.

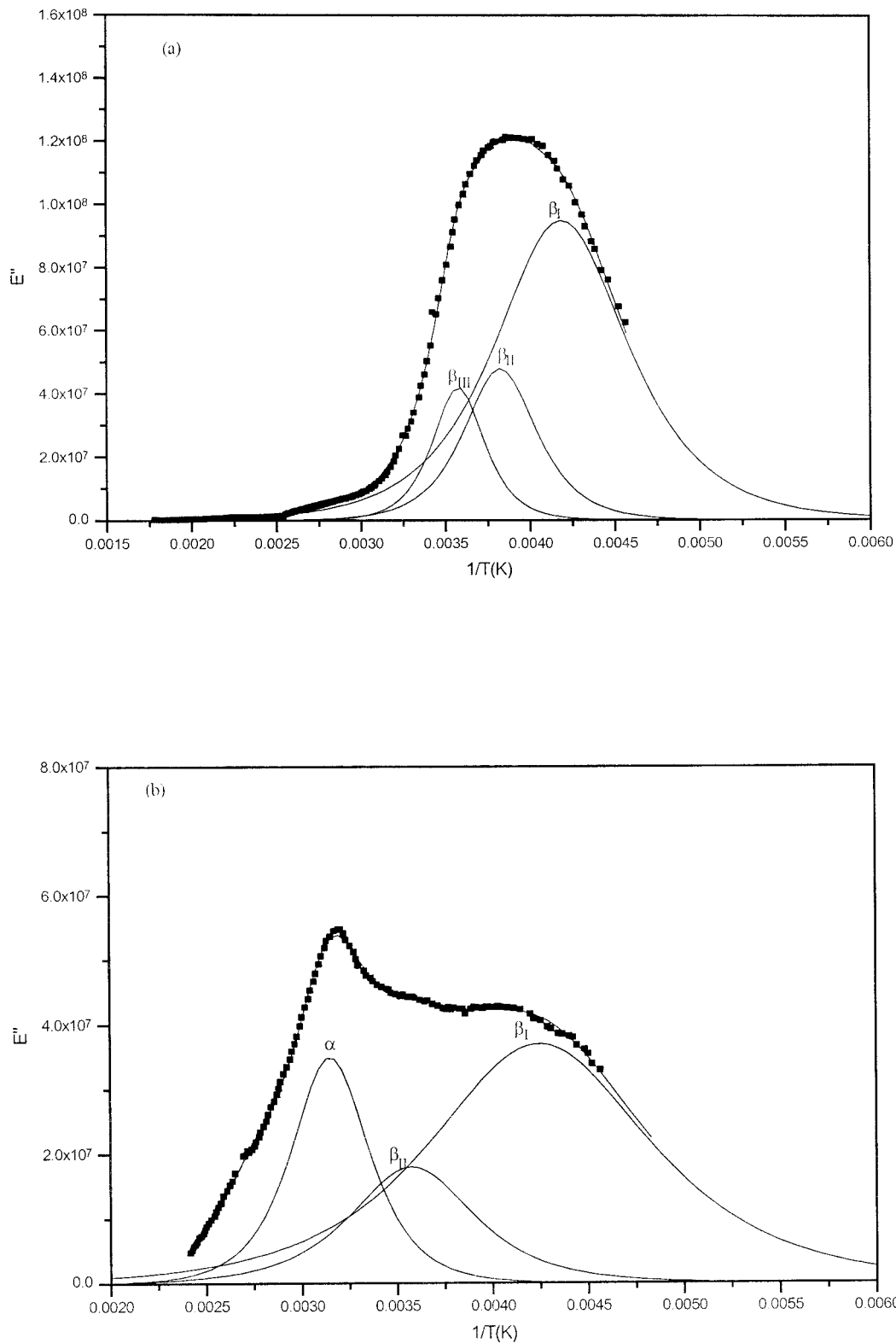


Figure 5 Deconvolution in terms of E' at 10 Hz of frequency of the relaxations of Mater-Bi AF05H (a) undegraded and (b) after 82 days of soil burial.

These results indicate the similar melting behaviors of Cornplast and Biofect, two starch products containing polyethylene. Besides the endotherm attrib-

uted to polyethylene, these products display other overlapped peaks at higher temperatures. Degradation in soil during a short period of time affects only

these latter endothermic peaks. Their melting temperature and their higher susceptibility to biodegradation suggest that these endotherms can be associated with the starch and other degradable components present in these products.

Dynamic mechanical measurements

The viscoelastic properties of these three starch products were analyzed by the determination and characterization of their mechanical relaxation spectra.

Figure 4 shows the relaxation spectrum of Mater-Bi as a function of the degradation time in soil. The mechanical relaxation spectrum of the undegraded sample consists of a single complex peak in the β -zone. Because of the complex nature of this peak, its characterization was carried out using the deconvolution method proposed by Charlesworth,¹⁹ together with the Fuoss–Kirkwood equation. Charlesworth considered the experimental data of the loss modulus E'' as the sum of each of the contributions:

$$E'' = \sum_{i=1}^n E''_i \quad (1)$$

On the other hand, the Fuoss–Kirkwood equation gives the following relationship between E'' and the temperature at a given frequency:

$$E'' = \frac{E''_{\max}}{\cosh m \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right)} \quad (2)$$

where E''_{\max} is the maximum of the loss modulus, T_m is the temperature of the maximum of the loss modulus, and m is the Fuoss–Kirkwood parameter.

Thus, by applying this equation together with the deconvolution method proposed by Charlesworth, it was possible to decompose the β -complex peak of the undegraded Mater-Bi into three subrelaxations called β_I , β_{II} , and β_{III} in order of increasing temperature [Fig. 5(a)]. Table I gives as an example the characteristic parameters of each of these relaxations for the frequency of 10 Hz.

The characterization of each of these relaxations was completed with the calculation of their apparent activation energy, according to the Arrhenius equation:

$$\ln f_m = \ln f_0 + \exp(E_a/RT) \quad (3)$$

where T_m and f_m are the temperature and the frequency of the maximum of the loss modulus, respectively.

The values of the activation energies of Mater-Bi, for those cases for which their calculation was possible,

TABLE I
Characterization of the Relaxations of Mater-Bi AF05H as a Function of the Exposure Time in Soil: Apparent Activation Energy (E_a), Values of the Temperature of the Maximum of the Loss Modulus (T_m), and the Fuoss–Kirkwood Parameter (m) at 10 Hz of Frequency

Relaxation	T_{\max} (°K)	m	E_a (kcal/mol)
Undegraded			
β_I	238.8	0.087	30.3
β_{II}	261.5	—	—
β_{III}	279.6	0.22	65.1
After 82 days			
β_I	235.4	0.18	21.1
β_{III}	279.6	—	—
α	317.5	—	—

are also listed in Table I. The results obtained for the undegraded Mater-Bi sample show that the main contribution is the β_I relaxation, which is located between -50 and -30°C , depending on the frequency, and whose activation energy is about 30 kcal/mol. The β_{II} relaxation is located in the characteristic temperature range of the β -relaxation of polyethylene. For the β_{III} relaxation, an activation energy of 65 kcal/mol was obtained.

According to the manufacturer's specifications, the Mater-Bi AF05H used in this study consisted of starch heavily complexed with ethylene-vinyl alcohol (EVOH). The molecular origin of this β -complex relaxation of Mater-Bi may then be related to motions of the molecular chains containing the $-\text{OH}$ groups, both in the starch and in the vinyl alcohol, as well as to the motions of the carbonated chains in the copolymer.

From its position in the temperature axis, the β_{II} relaxation could correspond to those movements of the carbonated chains in the copolymer. On the other hand, taking into account the calculated values of the activation energies, the β_I and β_{III} relaxations could result from motions of the molecular chains in which the $-\text{OH}$ groups are located, both in the starch and in the vinyl alcohol.

After degradation in soil, this β -complex peak was reduced to a small shoulder overlapped with a peak located in the α -zone (Fig. 4). Following the deconvolution method explained above, it was possible to separate the relaxations of the β - and α -relaxation zones for the Mater-Bi sample degraded in soil. It was found that the β -relaxation may result from the overlapping of two contributions, β_I and β_{III} in order of increasing temperature [Fig. 5(b)], which were related to β_I and β_{III} from the undegraded sample because of their position in the temperature axis.

The characteristic parameters of these relaxation processes are also shown in Table I. It is observed that the reduction of the β -relaxation took place together

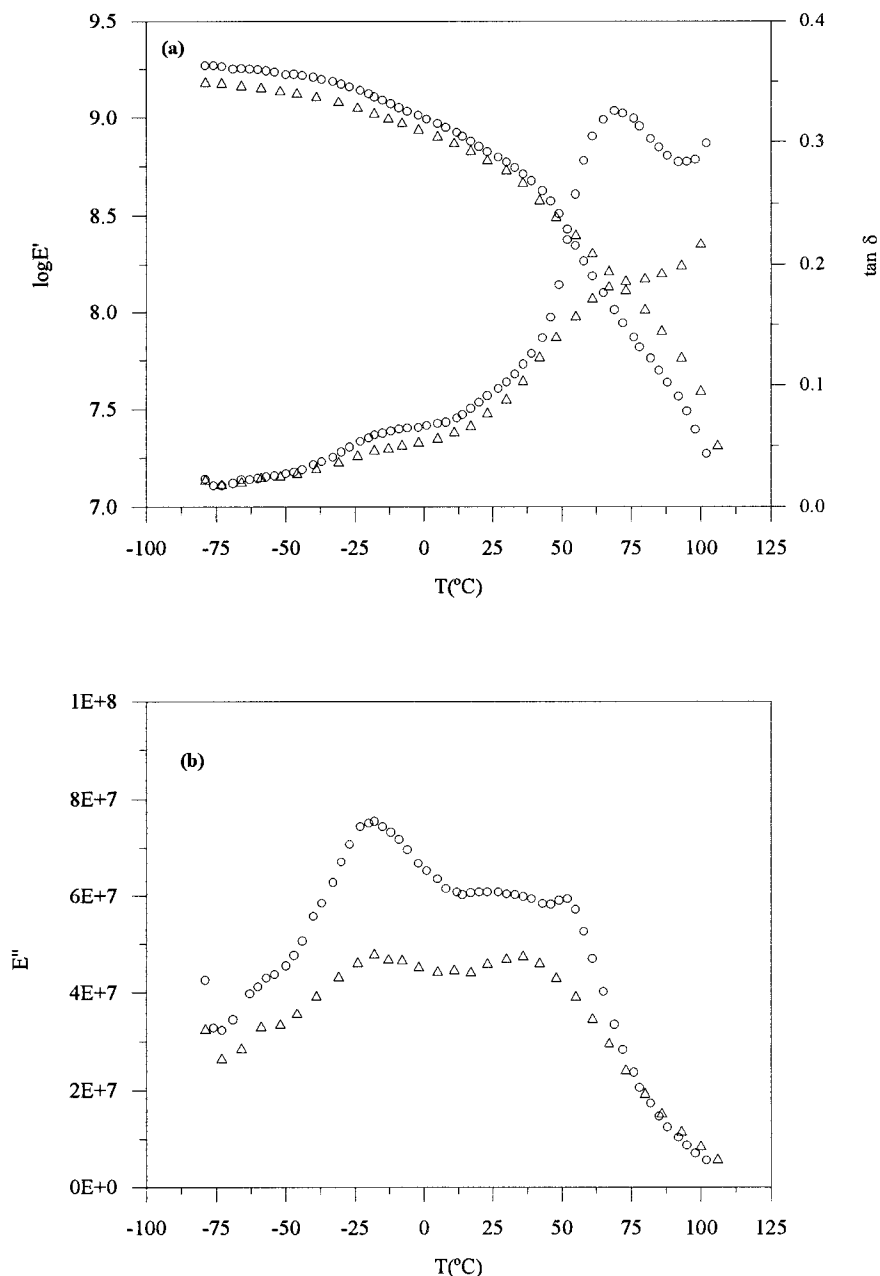


Figure 6 Mechanical relaxation spectra of Cornplast as a function of the exposure time in soil: \circ , undegraded; \triangle , after 20 days. Plots of (a) $\tan \delta$ and $\log E'$ and (b) E'' versus temperature at 1 Hz of frequency.

with a decrease in the activation energy of the β_1 contribution. This fact could indicate the degradation of Mater-Bi.

Cornplast includes in its formulation polyethylene and a product containing starch that accelerates biodegradation. The mechanical relaxation spectrum of the undegraded Cornplast basically coincides with that of pure LDPE (Fig. 6). Thus, it was also possible to characterize the α - and β -relaxations.

The peak observed in the β -zone of polyethylene is very similar to that of pure LDPE.^{20,21} This proves that the β -relaxation zone of the polyethylene in Cornplast is only slightly modified by the presence of starch and

other components of the product. However, in the zone associated with the α -relaxation processes in polyethylene, only a peak at high temperatures similar to the α_{II} relaxation of the LDPE was observed, although shifted to lower temperatures.^{20,21}

It was established that the α -relaxation of polyethylene is associated with molecular motions occurring in the crystalline phase.^{22,23} On the other hand, the β -relaxation of polyethylene may result from movements of the molecular chains that form the crystalline-amorphous interface. Considering these assumptions, the analysis of the relaxation spectrum of the undegraded Cornplast suggested that the crystalline

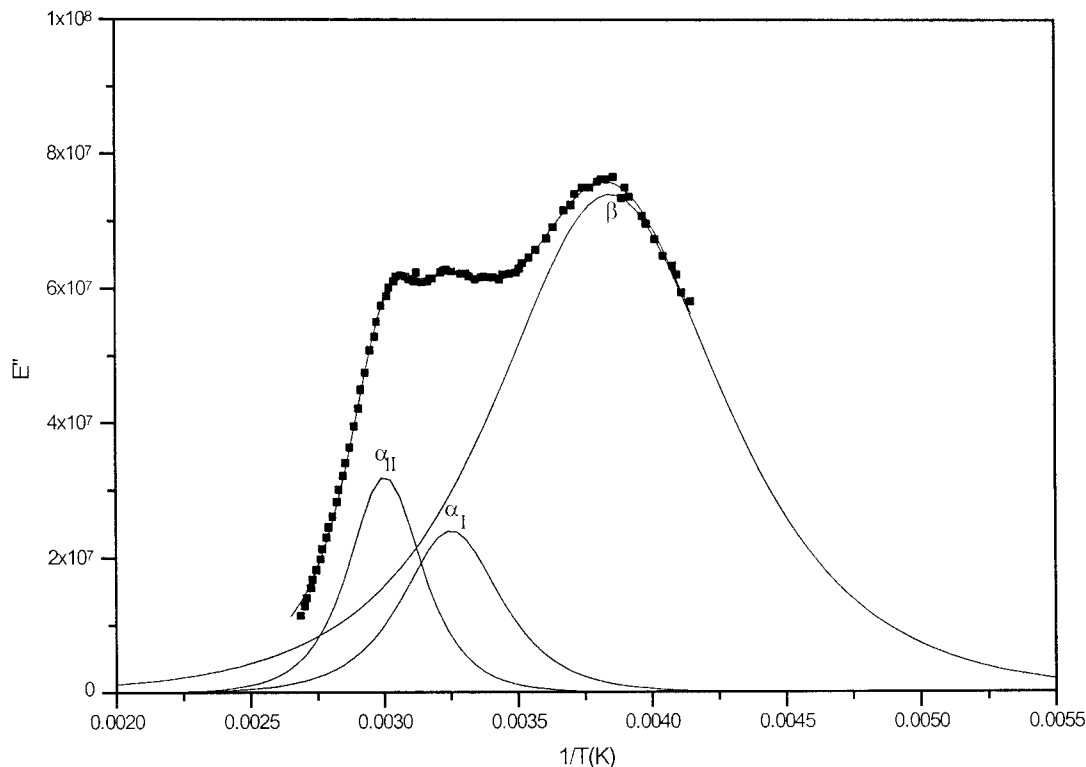


Figure 7 Deconvolution in terms of E'' of the relaxations of the undegraded Cornplast at 10 Hz of frequency.

phase of the polyethylene in Cornplast was more affected than the interfacial region by the presence of other components in this product.

The mechanical relaxation spectrum of the undegraded Cornplast was decomposed into one β -relaxation and two α -relaxations, using the deconvolution method of Charlesworth together with the Fuoss-Kirkwood equation (Fig. 7). The characteristic parameters of each relaxation are summarized in Table II. For the β -contribution of the undegraded sample of Cornplast, an activation energy very similar to that of the β -relaxation of pure LDPE was obtained,^{18,20}

TABLE II
Characterization of the Relaxations of Cornplast as a Function of the Exposure Time in Soil: Apparent Activation Energy (E_a), Values of the Temperature of the Maximum of the Loss Modulus (T_m), and the Fuoss-Kirkwood Parameter (m) at 10 Hz of Frequency

Relaxation	T_{\max} ($^{\circ}\text{K}$)	m	E_a (kcal/mol)
Undegraded			
β	259.8	0.10	49.8
α_I	307.6	0.14	89.1
α_{II}	332.9	0.19	90.2
After 20 days			
β	257.1	0.13	34.9
α_I	314.9	—	—
α_{II}	347.4	0.41	47.5

whereas the α_I and α_{II} contributions had activation energies higher than those reported for pure LDPE.^{18,20}

Degradation in soil provoked a reduction of both the β - and α -relaxations of Cornplast (Fig. 6). The shape of the α -relaxation was also altered. These modifications in the β - and α -relaxations revealed changes after the biodegradation test in the interfacial region and the crystalline phase of the polyethylene in Cornplast. Activation energies of the β - and α -relaxations were considerably reduced after the biodegradation process (Table II).

On the other hand, the relaxation spectrum of the undegraded Bioeffect displayed as well the typical form of pure LDPE (Fig. 8). Moreover, in this case the presence of starch and other components in this product mainly affected the crystalline phase of polyethylene, whereas the interfacial regions remained basically the same.

Changes observed in the α -zone were similar to those observed in Cornplast. This zone was decomposed using the deconvolution method described previously, into three relaxations called α_{IV} , α_{IV} , and α_{III} (Fig. 9). The β -contribution was predominant over the α -contributions; the main contribution of the α -zone was the α_{II} . The activation energies of all these processes in the undegraded Bioeffect were very similar to those reported for pure LDPE^{18,20} (Table III).

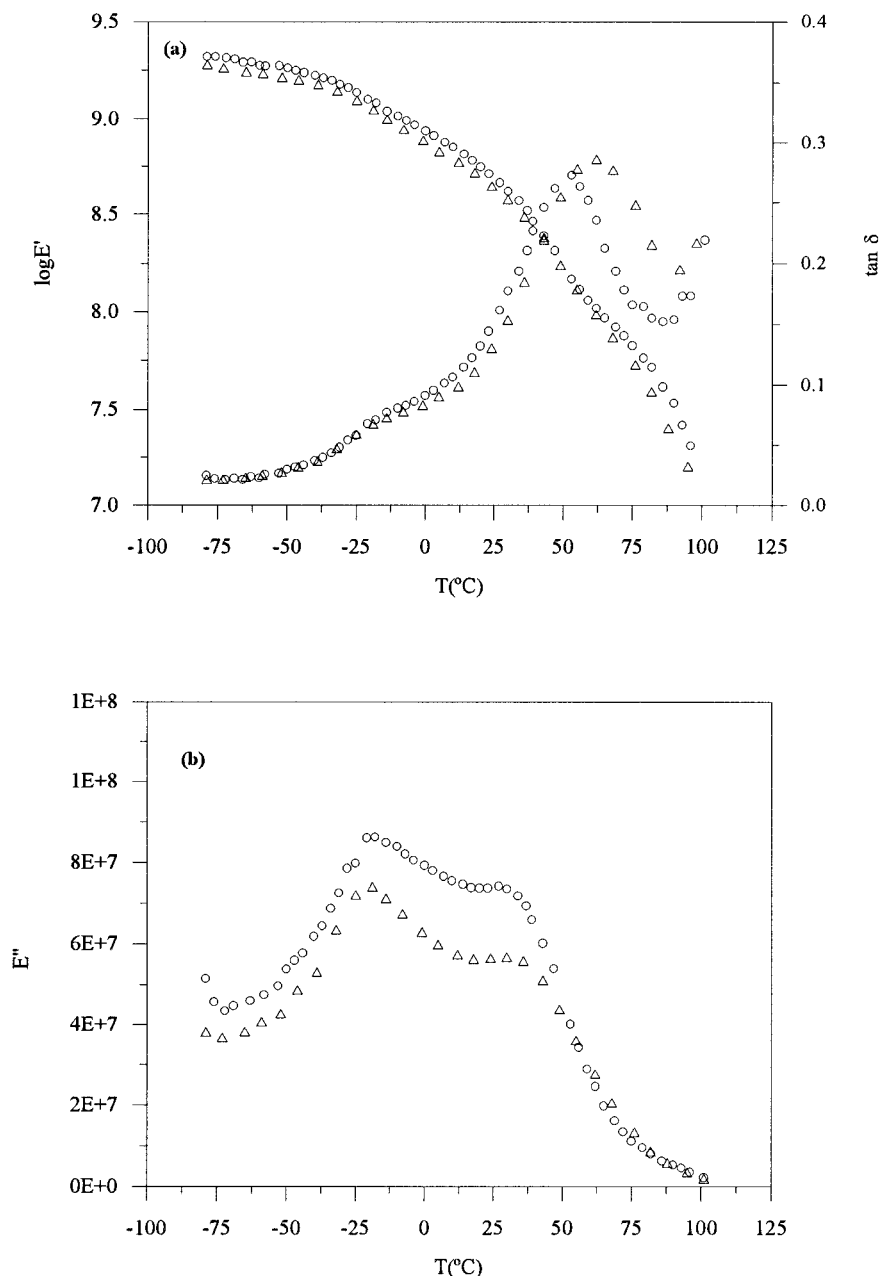


Figure 8 Mechanical relaxation spectra of Bioefect 72000 as a function of the exposure time in soil: \circ , undegraded; \triangle , after 20 days. Plots of (a) $\tan \delta$ and $\log E'$ and (b) E'' versus temperature at 1 Hz of frequency.

After degradation in soil, the β -relaxation basically preserved its width and the position of its maxima (Fig. 8). However, the α -relaxations showed some modifications. In general, a broadening and a shift of the maxima toward higher temperatures were observed. The characteristic parameters obtained for the β - and α -relaxations of Bioefect after degradation in soil confirmed these results (Table III). On the other hand, although the apparent activation energy of the β -relaxation did not change significantly during degradation, an increase of the activation energies of the α -relaxations of Bioefect was noted.

CONCLUSIONS

The DSC thermograms of the commercial starch products Mater-Bi AF05H, Cornplast, and Bioefect 72000 consist of several overlapped endotherms. In the case of Cornplast and Bioefect, two products containing LDPE, the endotherm attributed to polyethylene can be distinguished from those associated with the starch and other degradable components present in these materials. After degradation in soil, significant changes in the shapes of the thermograms of these products were noted, especially for Mater-Bi.

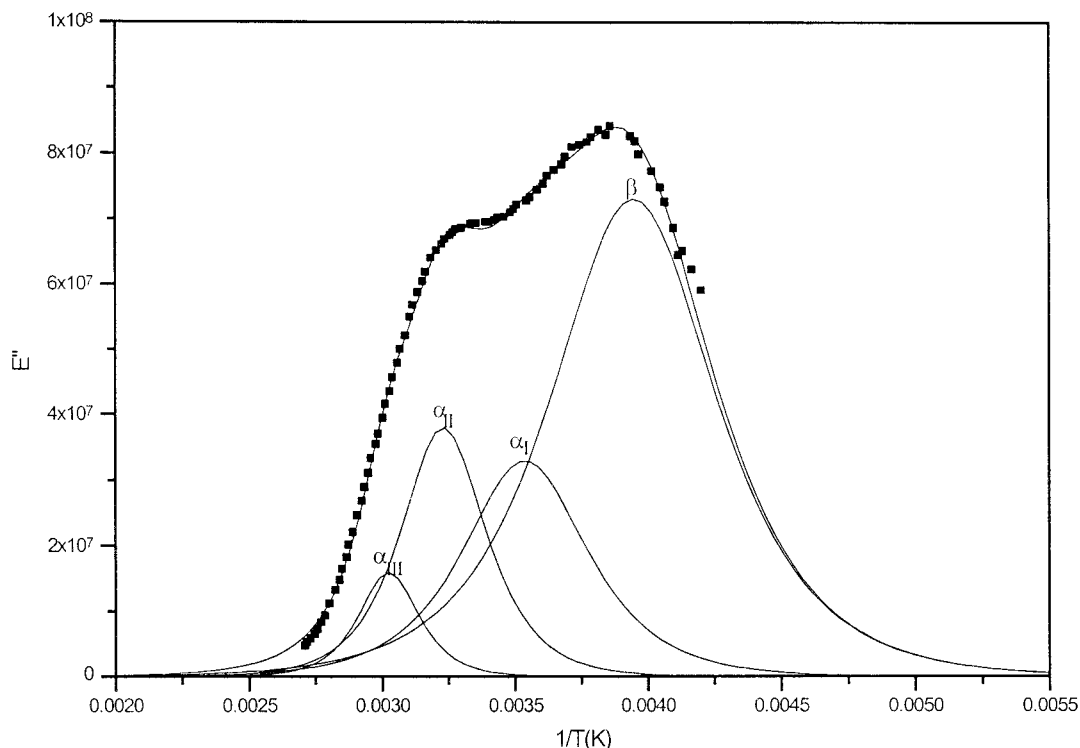


Figure 9 Deconvolution in terms of E'' of the relaxations of the undegraded Bioeffect 72000 at 10 Hz of frequency.

In the temperature zone under study, the mechanical spectrum of the undegraded Mater-Bi displayed a single complex peak in the β -zone, consisting of three subrelaxations. This relaxation was attributed to molecular movements of the chains containing the $-OH$ groups both in starch and in EVOH, as well as to the motions of the carbonated chains in the copolymer. After degradation in soil, this complex β -peak was considerably reduced, nearly disappearing, which could be considered as a sign of Mater-Bi's biodegradation.

TABLE III
Characterization of the Relaxations of Bioeffect 72000 as a Function of the Exposure Time in Soil: Apparent Activation Energy (E_a), Values of the Temperature of the Maximum of the Loss Modulus (T_m), and the Fuoss-Kirkwood Parameter (m) at 10 Hz of Frequency

Relaxation	T_{max} ($^{\circ}K$)	m	E_a (kcal/mol)
Undegraded			
β	253.3	0.13	57.8
α_I	282.6	0.20	47.4
α_{II}	309.5	0.23	60.5
α_{III}	330.6	0.47	41.7
After 20 days			
β	256.7	0.11	54.0
α_I	295.1	0.19	64.6
α_{II}	316.5	0.13	—
α_{III}	342.7	0.49	52.9

The mechanical relaxations spectra of the undegraded Cornplast and Bioeffect basically coincide with that of pure LDPE. The crystalline phase of the polyethylene in these products is the most affected by the presence of starch and other components. Degradation in soil modifies the β - and α -relaxation zones of Cornplast, as well as their activation energies. However, in Bioeffect the biodegradation process mainly affects the α -relaxation zone rather than the β -relaxation.

Thus, the calorimetric and mechanical results indicate that, for short exposure times, the effects of biodegradation in soil are more significant for Mater-Bi than for Cornplast and Bioeffect, two products containing 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

- Griffin, G. J. L., Ed.; Chemistry and Technology of Biodegradable Polymers; Blackie Academic and Professional: Glasgow, 1994.
- Chiellini, E.; Solaro, R.; Corti, A.; Picci, G.; Lepori, C.; Pera, A.; Vallini, G.; Donaggio, P. *Chim Ind* 1993, 8/9, 656.
- Albertsson, A.-C.; Barenstedt, C.; Karlsson, S. *J Appl Polym Sci* 1994, 51, 1097.
- Johnson, K. E.; Pometto, A. L., III; Nikolov, Z. L. *J Appl Environ Microbiol* 1993, 59, 1155.
- Lee, B.; Pometto, A. L., III; Fratzke, A.; Bailey, T. B. *J Appl Environ Microbiol* 1991, 57, 678.

6. Greizerstein, H. B.; Syracuse, J. A.; Kostyniak, P. J. *Polym Degrad Stab* 1993, 39, 251.
7. Albertsson, A.-C.; Karlsson, S. *Makromol Chem Macromol Symp* 1991, 48/49, 395.
8. Otey, F. H.; Westhoff, R. P.; Doane, W. M. *Ind Eng Chem Prod Res Dev* 1980, December, 592.
9. Otey, F. H.; Westhoff, R. P.; Doane, W. M. *Ind Eng Chem Prod Res Dev* 1987, August, 1659.
10. Bastioli, C. *Polym Degrad Stab* 1998, 59, 263.
11. Bastioli, C.; Degli Innocenti, F.; Guanella, I.; Romano, G. In *Degradable Polymers, Recycling and Plastic Waste Management*; Albertsson, A. C.; Huang, S. J., Eds.; Marcel Dekker: New York, 1995; p. 247.
12. Vikman, M.; Itavaara, M.; Poutanen, K. *J Macromol Sci Pure Appl Chem* 1995, A32, 863.
13. Lörcks, J. *Polym Degrad Stab* 1998, 59, 245.
14. Funke, U.; Bergthaller, W.; Lindhauer, M. G. *Polym Degrad Stab* 1998, 59, 293.
15. Wittwer, F.; Tomka, I. U.S. Pat. 4,673,438, 1987.
16. DIN 53739. *Testing of Plastics. Influence of Fungi and Bacteria. Visual Evaluation. Change in Mass and Physical Properties*, Nov. 1984.
17. Goheen, S. M.; Wool, R. P. *J Appl Polym Sci* 1991, 42, 2691.
18. Contat Rodrigo, L. Ph.D. Thesis, Universidad Politécnica de Valencia, Spain, 2000.
19. Charlesworth, J. M. *J Mater Sci* 1993, 28, 399.
20. McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover Publications: New York, 1991.
21. Riande, E.; Díaz-Calleja, R.; Prolongo, M. G.; Masegosa, R. M.; Salom, C. *Polymer Viscoelasticity: Stress and Strain in Practice*; Marcel Dekker: New York/Basel, 2000.
22. Boyd, R. H. *Polymer* 1985, 26, 323.
23. Popli, R.; Glotin, M.; Mandelkern, L. *J Polym Sci Part B: Polym Phys* 1987, 22, 407.