Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer Degradation and Stability 81 (2003) 341–351
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Biodegradation of thermally-oxidized, fragmented low-density polyethylenes

Emo Chiellini[a,*], Andrea Corti[a], Graham Swift[b]

[a]Department of Chemistry and Industrial Chemistry, University of Pisa, via Risorgimento 35, 56126 Pisa, Italy
[b]G.S. Polymer Consultants, 10378 Eastchurch, Chapel Hill, NC 27517, USA

Received 30 September 2002; received in revised form 24 December 2002; accepted 3 January 2003

Abstract

Thermally degradable low-density polyethylene samples containing TDPA™ pro-oxidant additives from EPI Inc. were submitted to an investigation aimed at evaluating their ultimate biodegradation (e.g. mineralization) in soil and mature compost incubation media. Respirometric tests aimed at simulating soil burial and composting (mature compost) conditions, were used for testing the potential biodegradability of polyolefins in the environment. An LDPE-TDPA film sample provided by EPI Inc. was also submitted to a thermal oxidative degradation treatment in order to mimic the thermophilic phase of a full scale composting process. Retrieved degradation specimens, their solvent extracts and residues were also tested in soil burial respirometric tests in order to evaluate their potential biodegradability. Original and test samples submitted to biotic environments were characterized by means of spectroscopic analysis. LDPE-TDPA sample replicates undergo biodegradation as mediated by soil microorganisms in respirometric experiments. High mineralization levels were observed, above 60%, comparable to those occurring in the case of several natural polymers in natural environments; the time for biodegradation, though, is relatively longer. However, it is clear from the positive biodegradation profile that biodegradation continues. The degradation process is accompanied by a dramatic change in the structural characteristics of the test samples. To the best of our knowledge, this is the first study clearly indicating the biodegradation and assimilation of a synthetic polyolefin at a substantial level, even though reached at fairly long incubation time.
© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Thermally degradable polyethylene; Biodegradable polyethylene; Alkane biodegradation; Soil burial tests

1. Introduction

Attempts to produce environmentally degradable, low cost, plastic materials from polyolefins date back to the second half of the 20th century. Their potential degradability and ultimate biodegradability started to be considered in the early 1970s [1,2] as specific attributes for applications in packaging and agricultural market segments.

The resistance of polyethylene to biological attack is related to its hydrophobicity, water repellency and high molecular weight and its lack of functional groups recognizable by microbial enzymatic systems. All of these properties limit applications in which biodegradation is a desirable attribute. Major strategies to facilitate polyethylene disintegration and subsequent biodegradation, were focused on the direct incorporation of carbonyl groups within the backbone or on their in situ generation by pro-oxidants. Prodegradants included additives such as polyunsaturated compounds, transition metal ions and metal complexes, such as dithiocarbamates, which rendered polyethylene, and polyolefins in general, susceptible to hydroperoxidation. These functional groups act as initiators of thermal and photo-oxidation of the hydrocarbon polymer chains. These abiotic degradation processes result in functional macromolecules, which thermally and/or photochemically cleave repeatedly to low molecular weight fragments, especially in the presence of transition metal ions. These low molecular weight oxygenated products include aliphatic carboxylic acids, alcohols, aldehydes and ketones [3–6].

The direct incorporation of natural biodegradable polymers, such as starch, to enhance the potential

* Corresponding author. Tel.: +39-050-918299; fax: +39-050-28438.
E-mail address: chlmeo@dcci.unipi.it (E. Chiellini).

0141-3910/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0141-3910(03)00105-8

biodegradability of polyethylene has also been evaluated [7–9]. The major degradation effect promoted by the microbial assimilation of the natural polymers in the blends was the increase of the surface area of the synthetic bulk material rendering it more susceptible to abiotic oxidation. Hence, this is only an example of indirect oxidative degradation of polyethylene afforded by the biodegradation processes of natural polymers [10]. Nevertheless, significant variation of both molecular weight and mechanical properties have been recorded for starch filled polyethylene when submitted to the action of biotic environments such as composting windrows or pure microbial strains [11,12]. Accordingly, the degradation process of polyethylene in its blends with natural polymers is generally considered to be the result of complex interaction of abiotic and biotic mediated oxidative processes [13,14].

It has been repeatedly demonstrated and reported that thermal and/or photolytic pre-abiotic treatment constitutes a major route for promoting the eventual biodegradation of both low-density polyethylene (LDPE) and LDPE containing pro-oxidant additives. This is exemplified by monitoring the initial variation of molecular weight and other structural parameters (tensile strength, degree of crystallinity, spectroscopic characteristics). Biodegradation is then observed when the degraded polymers are exposed to biotic environments [15–17].

Additionally, the required degree of macromolecular breakdown for the biodegradation and microbial assimilation of polyethylene to occur is available from observing the biodegradation of lower molecular weight hydrocarbon molecules. Linear paraffin chains below 500 molecular weight [18] or *n*-alkanes up to tetratetracontane ($C_{44}H_{90}$) [19] can be significantly used as a carbon source by microorganisms. More recently, the biodegradation of higher molecular weight untreated high-density polyethylene with molecular weights up to 28,000 by a *Penicillium simplicissimum* isolate was reported [20].

There are many other previous studies aimed at evaluating the biodegradation of LDPE samples containing pro-oxidant and natural fillers that show only limited and slow conversion to carbon dioxide. The mineralization rate from long-term biodegradation experiments of both UV-irradiated samples [21], non-pretreated, and additive-free LDPE samples, in natural soils indicates more than 100 years for the ultimate mineralization of polyethylene [22].

In the present contribution, we report on an investigation aimed at evaluating the ultimate biodegradation in soil and mature compost incubation media of thermally treated LDPE samples containing TDPA™ pro-oxidant additives from EPI Environmental Products Inc., Canada.

Respirometric tests aimed at simulating the soil burial, as well as composting (mature compost) conditions, were used for testing the potential biodegradability of LDPE-TDPA™ thermally-oxidized, fragmented samples.

Biodegradation of synthetic polymers in soil may be monitored in respirometric tests normally by using whole soil as incubation substrate [23,24]. Under these conditions the accuracy of such tests may be affected by the large amount of carbon dioxide produced in the blanks, particularly when moderate sample degradation takes place. More reliable results can be obtained by using fairly large amounts of the samples under investigation. However, in some cases the large local concentration of the sample, as well as its degradation products, can negatively interfere with the optimal microbial growth conditions, and consequently compromise the reliability of the test. An alternative approach using radiolabelled samples in respirometric tests, which gives very reliable results in the presence of slowly biodegrading materials, requires the use of ^{14}C-labeled polymer samples. Expertise in the handling of radiochemicals and laboratory facilities are not widely available, however.

Therefore, the procedure based on the use of the "biometer flask" previously suggested [25] was modified by using the incubation conditions of a respirometric test previously set up for testing polymeric materials with low or moderate propensity to biodegradation [26]. An analogous experimental set-up was used for the evaluation of the ultimate biodegradation of LDPE-TDPA samples in the presence of microorganisms associated with mature compost.

An LDPE-TDPA film sample provided by EPI was submitted to a thermal-oxidative degradative treatment in order to mimic the thermophilic phase of a full scale composting process.

Oxidatively degraded samples LDPE-TDPA undergo biodegradation as mediated by soil microorganisms reaching a mineralization level as high as 60%, albeit, over a relatively long time frame. Interestingly, even at this extent of biodegradation a positive degradation profile was still apparent as carbon dioxide evolution continues. The degradation was accompanied by a dramatic change in the structural characteristics of the test samples. To the best of our knowledge this is the first study clearly indicating the bioassimilation of a synthetic polyolefin at an extent comparable to that recorded for biopolymers in similar natural environments.

2. Materials and methods

2.1. Test materials

Un-degraded and thermally fragmented (Mw 6.72 kD) (designed Q-LDPE sample) low-density polyethylene (LDPE) film samples containing totally degradable plastic additives (TDPA™) pro-oxidants were supplied

by EPI Inc. (Vancouver, Canada). The following low molar mass aliphatic hydrocarbons, were also used as reference materials in the biodegradation experiments: docosane [$C_{22}H_{46}$ (DOC)-Merck, Germany], 2,6,10,15,19,23-Hexamethyltetracosane [$C_{30}H_{62}$, Squalane, (SQUA)-BDH, UK] and α,ω-docosandioic acid [$C_{22}H_{42}O_4$, (DAD) prepared at the Department of Chemistry, University of Pisa]. Cellulose (Sigma Cell 100) and filter paper (Whatman 50) were also used as positive controls in the respirometric biodegradation experiments (Table 1).

2.2. Respirometric biodegradation tests

Biodegradation tests were carried out in cylindrical glass vessels (Biometer Flask) (500 or 1000 ml capacity) containing a multilayer substrate in which defined amounts of forest sandy soil (10–15 g) or mature compost (5 g) were placed. Samples sieved at 0.6 mm, mixed with 20–25 g perlite and supplemented with 25 ml of 0.1% $(NH_4)_2HPO_4$ solution, were sandwiched between two layers of 10 g perlite wetted with 30 ml distilled water (Fig. 1). The role of perlite, a chemically inert, heat expanded naturally occurring aluminum silicate, is to reduce the amount of soil and hence the carbon dioxide production from the blanks. Perlite is widely used in horticultural applications as a component of soil-less growing mixes, where it provides aeration and optimum moisture conditions for plant growth. Accordingly perlite was used to ensure satisfactory incubation conditions, whereas soil or compost samples were used mainly as microbial inoculum. This arrangement guarantees more favorable and reliable signal-to-noise ratio resulting in improved test accuracy, particularly when limited carbon dioxide emissions are expected from the test samples.

Polymer samples, reference aliphatic hydrocarbons, and positive controls, to be tested were placed in the middle layer at 35–70 mg/g soil and 70 mg/g mature compost concentrations. The vessels were kept in the dark and incubated at room temperature in the case of soil burial tests, and at 55 °C when mature compost was used as incubation medium.

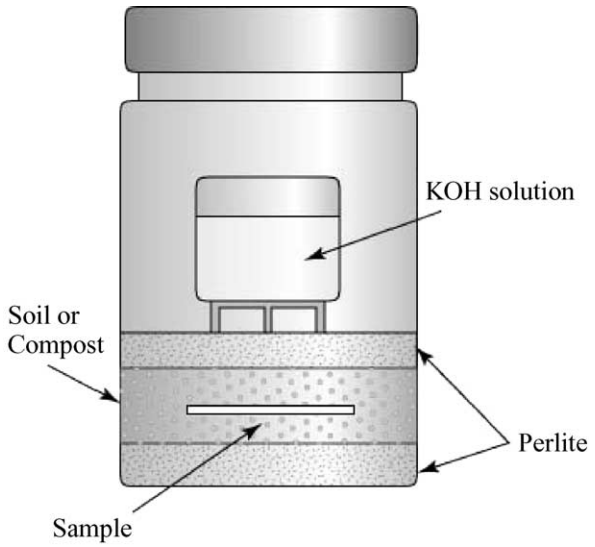

Fig. 1. Biometer flask for simulated soil burial and mature compost biodegradation tests.

For trapping the CO_2 evolved from samples and blanks, each test vessel was equipped with a beaker containing 40–50 ml of 0.05 N KOH solution which was substituted every 3-14 days and back titrated with 0.1 N HCl.

The biodegradation extent of each test material was calculated as a percentage (corrected for the inoculum endogenous emissions—blank flasks) of the overall theoretical CO_2 production calculated on the basis of the determined carbon content of the samples. The results were reproducible within a confidence of ±2% according to the tests carried out in triplicate.

2.3. Thermal degradation test

The un-degraded LDPE-TDPA blown film provided by EPI was submitted to a thermal-oxidative degradative treatment in an oven at temperature comparable to those occurring in a full scale composting process. A series of 25 specimens (18×10 cm) was cut from the original film. The specimens were kept at 55±1 °C in air and retrieved at time intervals. Weight variation of each

Table 1
EPI-TDPA polyethylene samples, low molecular weight hydrocarbons, and reference materials used in respirometric biodegradation tests

Test sample (origin)	Treatment	Sample code
EPI-TDPA LDPE	None	LDPE
EPI-TDPA LDPE	Thermally fragmented	Q-LDPE
EPI-TDPA LDPE	Q-LDPE Extractable boiling acetone fraction	QAC
EPI-TDPA LDPE	Q-LDPE Residue resistant to boiling acetone extraction	QRE
Docosane ($C_{22}H_{46}$)	None	DOC
α,ω-Docosandioic acid ($C_{22}H_{42}O_4$)	None	DAD
Squalane ($C_{30}H_{62}$)	None	SQUA
Filter paper (Whatman 50)	None	–
Cellulose (Sigma Cell 100)	None	–

specimen was evaluated, as well as the mechanical strength by using an Instron 5565 instrument. Mechanical analysis was carried out according to the ASTM D 882 method [27]. Results of gravimetric analysis and mechanical strength evaluation were averaged over 5 replicate specimen.

The organic solvent extractable fractions from original and degraded specimen were also evaluated by two sequential extractions with boiling acetone and dichloromethane, respectively.

2.4. Analytical characterization

2.4.1. Elemental analysis

Carbon content of each test sample was determined by elemental analysis by using a Carlo Erba model 1106 elemental analyzer.

2.4.2. Polymer extraction and characterization

Thermally fragmented Q-LDPE sample powder (1.024 g), after milling in liquid nitrogen, was placed in a round-bottomed flask and treated with acetone (50 ml) at reflux with stirring for 12 h. After evaporation of the solvent at reduced pressure 110 mg (10.7%) of residue was collected and designated as QAC sample.

Extractions in Kumagawa flasks with acetone and dichloromethane were performed on unmilled LDPE specimens as retrieved from the thermal degradative treatment.

2.4.3. Scanning electron microscopy (SEM)

SEM analyses, coupled with elemental surface microanalysis, of polymer samples retrieved from degradation experiments were performed using a Jeol LSM5600LV instrument, and the collected images were compared with those recorded on the original untreated samples.

2.4.4. Spectroscopic characterization

Original and degraded polymeric materials, as well as the relevant extractable fractions were characterized by ^{1}H NMR and FT-IR, by using a Varian Gemini 200 MHz instrument and a Jasco FT-IR model 410, respectively. Carbonyl and double bond indexes were calculated on the basis of the relative intensities of the carbonyl band at 1715 cm^{-1} and the double-bond band at 1650 cm^{-1} to that of methylene scissoring band at 1465 cm^{-1}, respectively [13].

2.4.5. Size exclusion chromatographic (SEC) analysis

Molecular weight and polydispersity of the solvent extracted fraction from LDPE-TDPA degraded samples were determined by SEC with a Jasco PU-1580 HPLC pump equipped with two Plgel mixed-C columns (Polymer Laboratories, UK) connected in series, and a refractive index detector Jasco 830RI. Sample elution was carried out with THF at 1 ml^{-1} flow rate. Monodisperse poly(styrene) samples were used for relative calibration.

3. Discussion of results

3.1. Respirometric soil burial biodegradation tests

3.1.1. First experiment

In a first soil burial respirometric test the potential biodegradation of the thermally-oxidized fragmented Q-LDPE sample was assayed at two different polymer/soil ratios, corresponding to approximately 70 mg/g soil, (Q1 run) and 35 mg/g soil (Q2 run), in comparison with a filter paper sample used as positive control. The cumulative CO_2 emissions detected from the test flasks and blanks during 80 weeks incubation are reported in Fig. 2. The effectiveness of the test conditions was demonstrated by the high reproducibility of CO_2 productions from the blank runs. Incubation conditions also appeared to be satisfactory in terms of soil microorganism growth conditions, as revealed by the high level of CO_2 production from the positive control (filter paper) after 80 days of incubation. Within the same time frame significantly high CO_2 productions were recorded also for the LDPE-TDPA test samples, particularly in the case of Q1 run, which contained the largest amount of the polymer.

The mineralisation profiles of Q-LDPE sample runs and filter paper are reported in Fig. 3. As shown, the biodegradation of the synthetic polymer appeared to start without an apparent lag-phase, afterwards a plateau corresponding to about 4% mineralisation was reached after 30 days of incubation. At the 40th day each soil inoculated culture was agitated, promoting a further slight, but significant, increase in the mineralisation rate. The rate, however, still remained very slow in comparison with the rate and extent of biodegradation of the filter paper control in the same time frame.

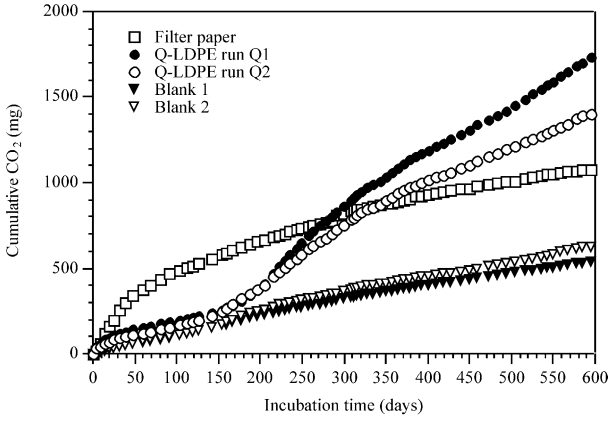

Fig. 2. Cumulative CO_2 emissions of filter paper, and thermally fragmented Q-LDPE at two different concentrations and blanks in a soil burial respirometric test.

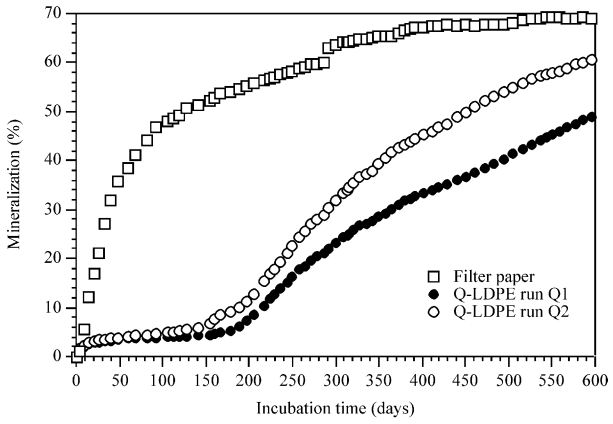

Fig. 3. Mineralisation profiles of thermally fragmented Q-LDPE samples and filter paper in soil burial test.

At this incubation time, small fragments of LDPE-TDPA sample from Q1 run were collected and characterized by SEM analysis. Microscopic characterization clearly showed microbial colonization of the film surface, attributable to filamentous microorganisms such as fungi and actinomycetes. The presence of bacterial cells was not observed (Fig. 4).

At approximately 5 months of incubation, after a prolonged stasis of the mineralisation, LDPE sample (Q1 run) and one blank (B1) replicate cultures were independently agitated again and each supplemented with further 40 ml distilled water. At the same time, the second replicate series (Q-LDPE run Q2, Blank B2) were also agitated, wetted with 40 ml distilled water and re-inoculated with 5 g of forest soil. All the cultures were then incubated again at room temperature.

The above culture treatments and modifications were performed in order to ascertain and compare the effects of the simple mixing, as well as of the addition of fresh microbial inoculum on the potential biodegradation of the test samples in the soil environment.

It was noted that a further and marked exponential increase in the biodegradation profile of the Q-LDPE samples took place after the culture treatments and reinoculation (Fig. 3). Moreover, significant differences in the overall degradation extent, as well as in the rate of mineralization can be detected depending upon the type of culture treatment and the amount of polymer sample charged into the biometer flask. In particular, the Q2 replicate, to which was added water and fresh soil inoculum, reached the highest extent of biodegradation (63.0%) after 85 weeks of incubation, whereas a lower value (49.0%) was reached by the Q1 replicate to which no further soil inoculum was added and which contained the highest initial amount of polymer. The positive slope profiles of both the biodegradation curves indicated a further increase in the biodegradation extent (Fig. 3).

FT-IR spectra of the original Q-LDPE sample and the small fragments retrieved after 6 and 62 weeks of incubation from Q1 run in the presence of soil microorganisms are reported in Fig. 5. Typical carbonyl absorption bands can be observed in the original samples, thus indicating the oxidative functionalization of the LDPE-TDPA matrix, as a consequence of the thermo-oxidative degradation [28,29]. However a significant reduction in the IR absorption between 1710 and 1740 cm^{-1} in the soil retrieved samples was observed, most likely as a consequence of the preferential assimilation of oxidized polymer chains by soil microorganisms, as previously suggested [13,30,31]. Albertsson and co-workers [16] reported that abiotically aged pure LDPE, LDPE/starch and LDPE-additives promoting degradation were characterized by the presence of several degradation products such as mono- and dicarboxylic acids and ketoacids. These almost completely disappeared after the incubation of the polymer samples in the presence of *Arthrobacter paraffineus* as a consequence of the assimilation of the degradation products by the bacterial strain.

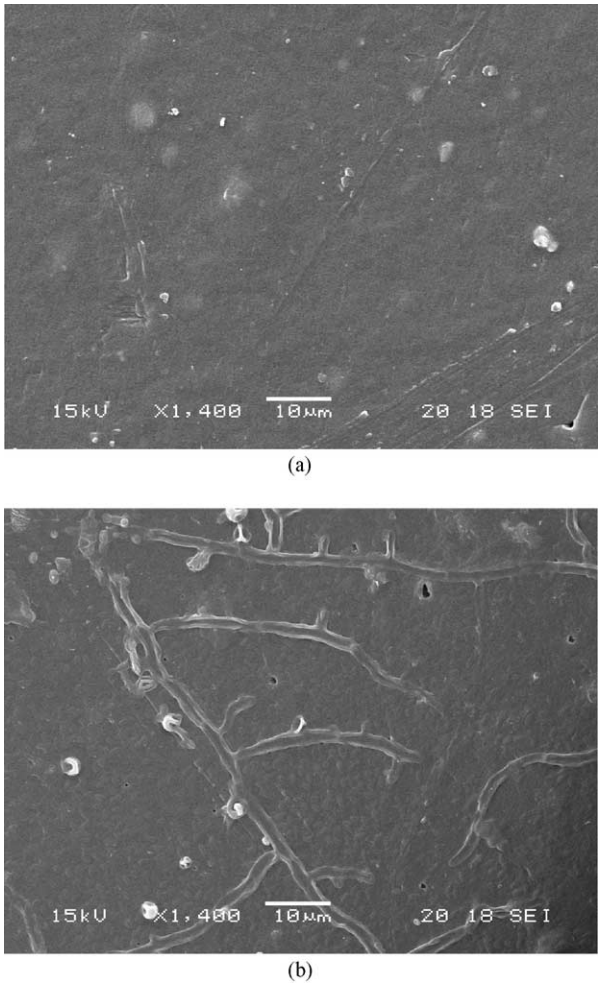

Fig. 4. SEM micrographs (magnification 1400×) of thermally fragmented Q-LDPE sample retrieved from soil burial test at 42 days of incubation: (a) original, (b) soil retrieved.

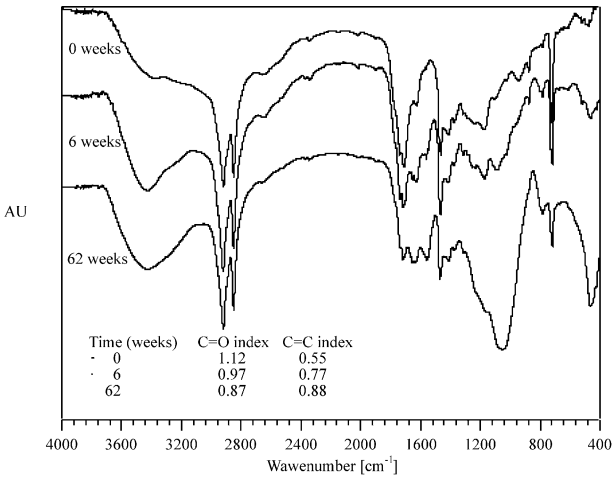

Fig. 5. FT-IR spectra of thermally fragmented Q-LDPE original sample and retrieved from soil burial test at 42 and 490 days of incubation.

An opposite trend was observed for the amount of double bonds. Also in this work, small but significant reduction in the oxygen amount in the Q-LDPE sample surface from 20.6 in the original to 16.9 wt.% in the case of soil incubated sample, was recorded by SEM microanalysis. By contrast, a substantial increase in the carbon-carbon unsaturation, as revealed by the increase of the double bond index from 0.55, in the spectra of the original sample, to 0.88, in that recorded after 62 weeks of incubation was recorded. This can be attributed to biotic dehydrogenation [13,22]. Hence it is likely that the macromolecular cleavage of thermo-oxidized LDPE-TDPA is mediated by both abiotic oxidation and biotic, enzymatic scission. Furthermore a dramatic change in the fingerprint region of the IR spectrum between 1300 and 950 cm^{-1} was observed with increasing incubation time probably attributable to lower molecular weight fragments.

After 70 weeks incubation the Q-LDPE sample completely disappeared and no significant fragments of the original sample could be detected and mechanically recovered from the soil matrix.

3.1.2. Second experiment

A second soil burial respirometric experiment was designed in order to compare the biodegradation profiles of LDPE-TDPA degraded samples with those occurring in low molar mass aliphatic hydrocarbons used as models, in the presence of soil microorganisms. Linear (Docosane, C22) and branched (hexamethyltetracosane, C30) alkanes, as well as oxidized (α,ω docosandioic acid, C22) were chosen as reference materials representative of the intermediates produced by the thermal degradation of EPI-LDPE samples.

The acetone extractable fraction (QAC) from thermally fragmented Q-LDPE sample, and the residue of the solvent extraction (QRE) were also tested in this soil burial respirometric experiment. The cumulative CO_2 emissions from the test flasks and blanks during 520 days of incubation are reported in Fig. 6. An appreciable microbial assimilation of Q-LDPE sample, as revealed by the differences in the CO_2 emissions from the experimental and the blank, appeared to start without an apparent lag phase in this soil burial experiment. The same behaviour was observed in the case of the acetone fraction (QAC) extracted from Q-LDPE powder sample. Appreciable microbial assimilation was also observed for *n*-alkane (C22) Docosane (DOC) and cellulose samples, whereas a prolonged delay in the mineralization was recorded in the case of terminally dicarboxylated docosane (DAD) and branched squalane (C30) (SQUA) samples. The mineralization of thermally fragmented Q-LDPE sample reached a first plateau corresponding to approximately 6% biodegradation after 80 days of incubation. The acetone fraction (QAC) extracted from Q-LDPE powder sample was readily biodegraded, as revealed by the fairly high rate and extent of mineralization (50%) occurring in 120 days of incubation, with a plateau at about 70% mineralization after 400 days. In contrast, the residue to the double extraction with organic solvents (sample QRE) underwent extremely low mineralization during the same incubation time (Fig. 7).

^1H NMR spectra of QAC sample, revealed the presence of signals attributable to protons on carbons in the α-position to and directly bound to a carboxylic group (Fig. 8). Conversely, no significant signals attributable to oxygen bound protons could be observed in the case of the QRE sample, whose ^1H NMR spectrum appears closely related to that of a typical linear polyethylene (Fig. 9). This latter observation could explain the very limited, if any, biodegradation of QRE recorded during 39 weeks of incubation in soil matrix.

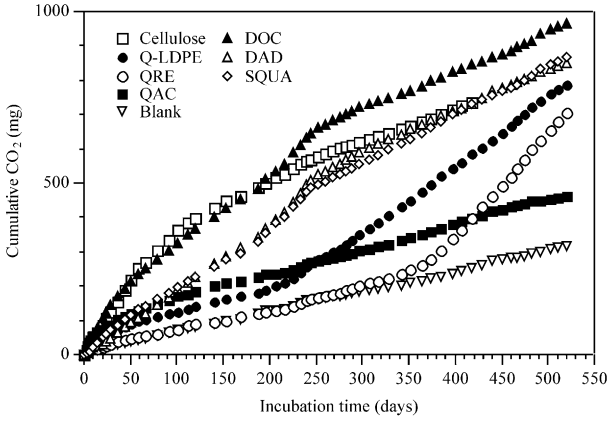

Fig. 6. Cumulative CO_2 emissions of Q-LDPE, residue to solvent extraction (QRE), acetone extract (QAC) of Q-LDPE sample, and reference aliphatic hydrocarbons (Docosane DOC, α,ω-docosandioc acid DAD, and squalane SQUA) in soil burial test.

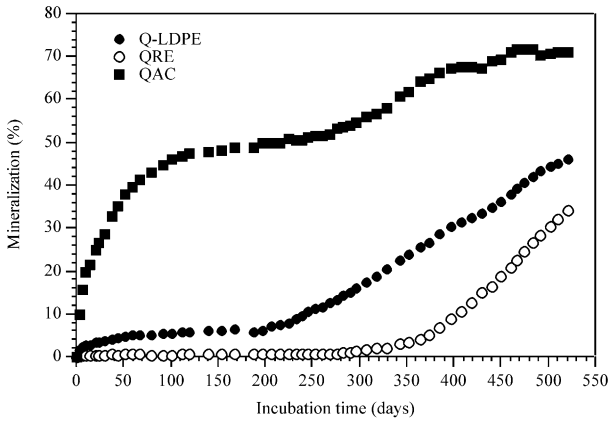

Fig. 7. Mineralization profiles of Q-LDPE, residue to solvent extraction (QRE), and acetone extract (QAC) of Q-LDPE sample in soil burial test.

As in the case of first soil burial test experiment, after 5 months of incubation each culture was agitated and wetted. The response was, as before, a new exponential phase in the mineralization of the thermally treated Q-LDPE sample. It reached 46.2% mineralization after 74 weeks of incubation and still maintained a positive trend (Fig. 7). Surprisingly, similar treatment of sample QRE, produced a similar exponential phase in the mineralization even after a prolonged stasis during which no appreciable biodegradation occurred. QRE reached a mineralization extent of approximately 34%, continuing to show a fairly positive slope of the biodegradation curve after 74 weeks of incubation (Fig. 7).

High extents of mineralization were, as anticipated, reached in the case of low molar mass hydrocarbons (56–70%) and cellulose (85%), thus validating the efficiency of the incubation conditions used in the test procedure. In particular a major propensity to the assimilation by soil microorganisms was recorded in the case of *n*-alkane (C22) docosane, whereas slightly lower mineralization extents, 57.7 and 56.1%, were reached by terminally dicarboxylated docosane (DAD) and branched squalane (C30) samples, respectively.

The reported results, compared with those obtained in the soil burial tests carried out on Q-LDPE sample not subjected to solvent extraction, indicate that the prooxidant additives in TDPA, modulate the microbial attack of the conventional LDPE.

3.2. Respirometric aerobic test in mature compost incubation medium

The biodegradation behaviour of thermally treated Q-LDPE sample was also determined in a respirometric test in the presence of mature compost as incubation medium. The cultures were maintained at 55 °C for a week in order to simulate full scale composting conditions. During this test, the mineralisation profile of Q-LDPE sample approached a plateau after 30 days, indicating approximately 7% biodegradation. Subsequently, it remained constant up to 180 days of incubation, thus recording a behaviour comparable to that observed previously in the soil burial tests (Fig. 10). The thermophilic conditions applied during the first period in the mature compost biodegradation test do not seem to enhance significantly the mineralisation rate of the thermally degraded Q-LDPE.

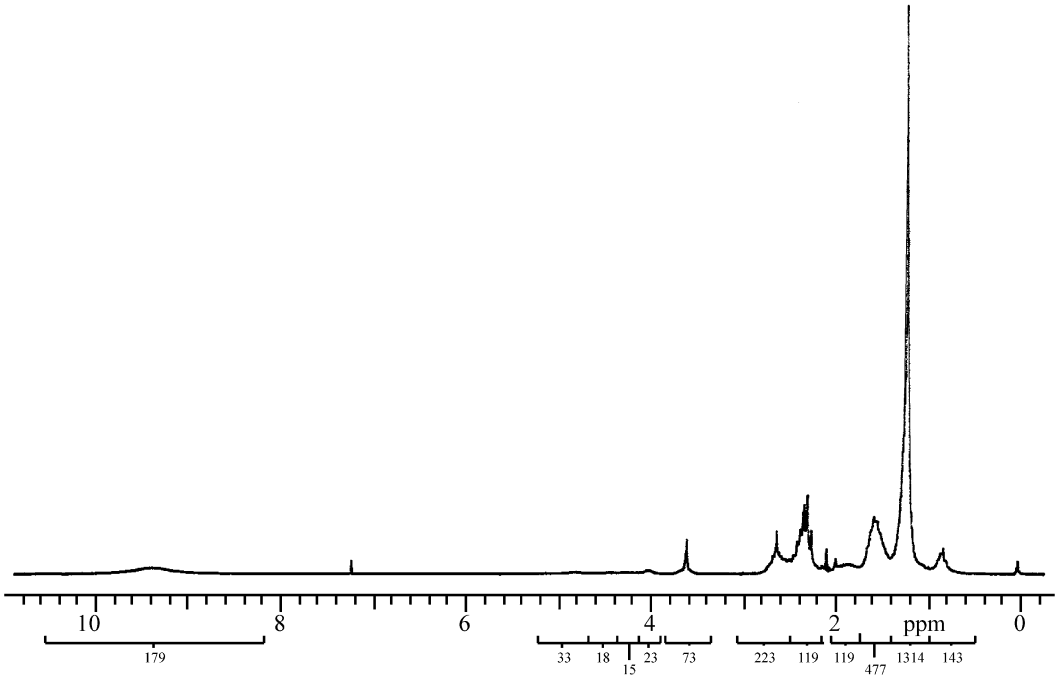

Fig. 8. ^{1}H NMR spectra of QAC extracted with acetone from thermally fragmented Q-LDPE sample.

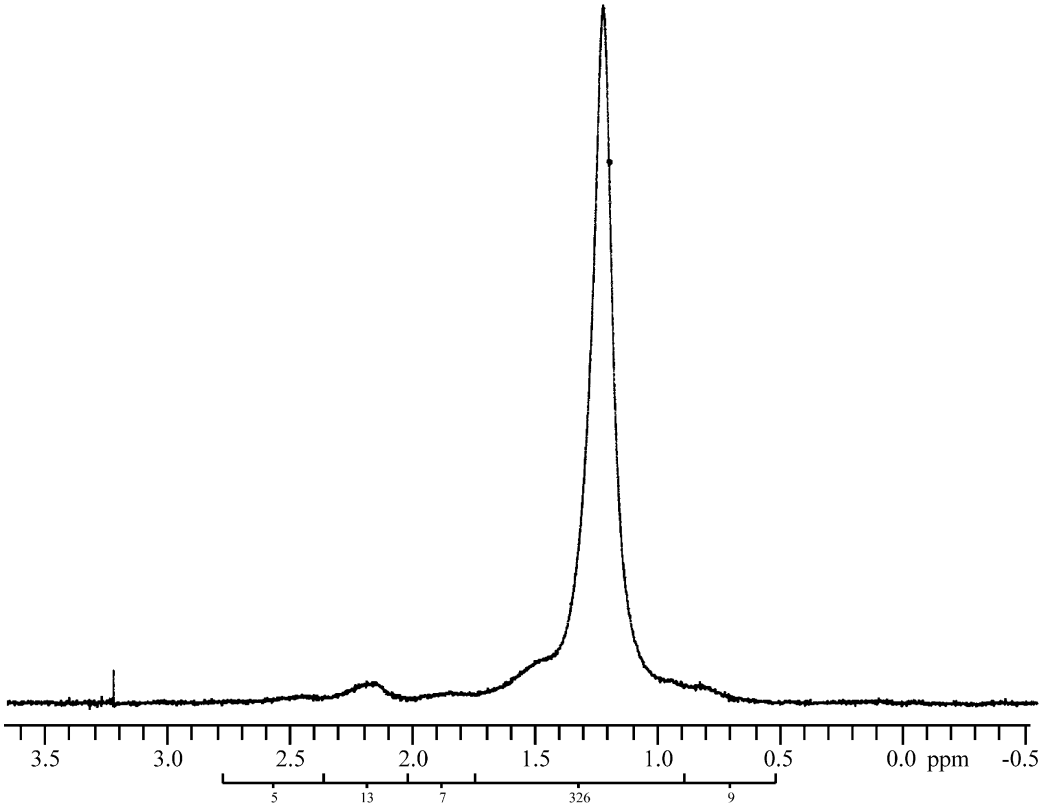

Fig. 9. ^{1}H NMR spectra of residue to solvent extraction (QRE sample) of thermally fragmented Q-LDPE sample.

Analogously to that occurring in the soil burial respirometric tests, a second, more pronounced, exponential phase in the biodegradation process of the polymer sample took place after the culture reinoculation with mature compost mixed with fresh forest soil carried out after 169 days of incubation. Hence, the mineralisation degree was shown to reach 27.8% after 426 days of incubation with a noteworthy positive slope of the biodegradation curve (Fig. 10).

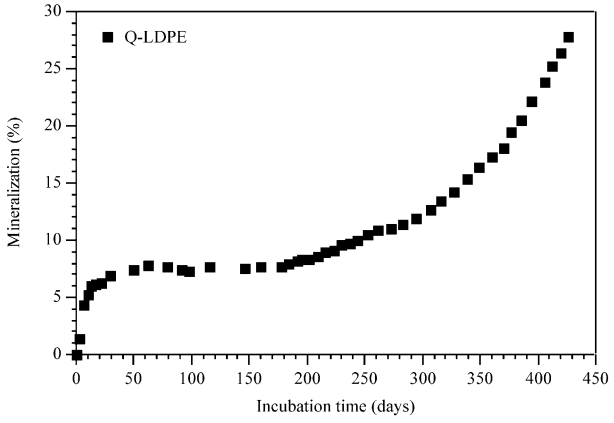

Fig. 10. Mineralization profiles of thermally fragmented Q-LDPE sample in mature compost incubation medium.

3.3. Thermal degradation test

An unexposed LDPE-TDPA blown film provided by EPI was thermally degraded in air in an oven at 55 °C for 44 days. Weight variation, as well as the organic solvent extractable fraction and the mechanical properties of LDPE specimens were assayed throughout the test.

Weight variations of LDPE film sample recorded during treatment at 55° C are reported in Fig. 11. A significant increase of the original weight of test sample was recorded after 11 days, most likely due to the oxygen uptake by the polymer matrix induced by the pro-oxidant additives (Fig. 11). The solvent extractable fraction was also shown to increase after a few days of thermal treatment, reaching fairly high value (26%) after 20 days incubation (Fig. 11), indicating oxidative molecular weight degradation consistent polymer chain cleavage.

In the case of mechanical analysis, an initial increase of strength was recorded, followed by a fast decrease of the film integrity after 11 days of incubation as a result of the fragmentation of the polymer chain (Fig. 12). The initial increase of the strength at break was accompanied by an analogous behaviour in the strain property (data not shown). This behaviour could be tentatively attributed to a sort of plasticisation effect exerted by low molecular weight fraction produced in the first stage of the thermal oxidative degradation of the polymer matrix,

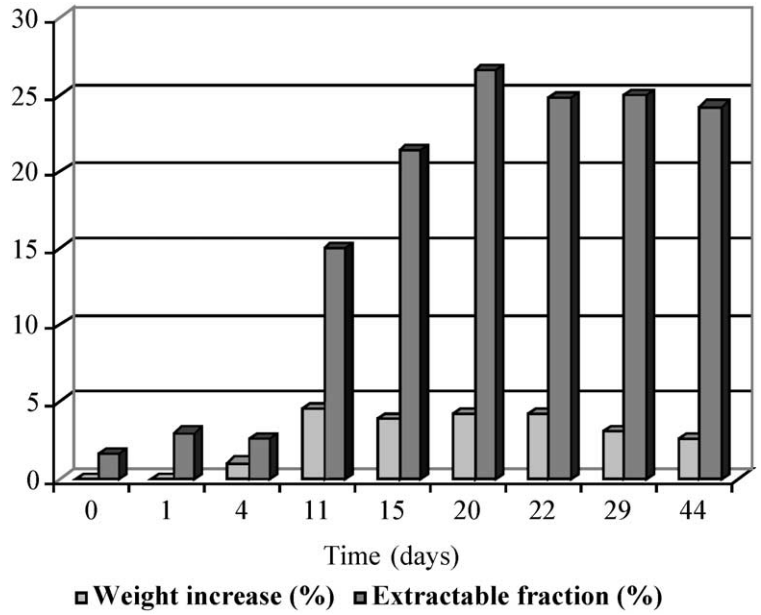

Fig. 11. Increase of dry weight and solvent extractable fraction of LDPE blown film specimens submitted to thermal degradation test.

as suggested by the initial increase of the specimen weight during the same time frame. Crosslinking may also be occurring through unstable peroxide bridges.

These results indicate that a moderate thermal treatment such as that occurring in a full scale composting process is able to induce a significant degradation in the LDPE-TDPA polymer matrix. Moreover, by taking into account the high propensity to soil biodegradation of solvent extractable fraction of Q-LDPE sample recorded in the soil burial test, it may be inferred that a significant amount (~25% or more) of LDPE-TDPA film can be readily and effectively mineralised when submitted to a composting process. This hypothesis appears also to be substantiated by the relatively low molecular weight (M_w = 1.5 kD) of the acetone fraction of LDPE film after 15 days of thermal aerobic treatment, as determined by SEC analysis.

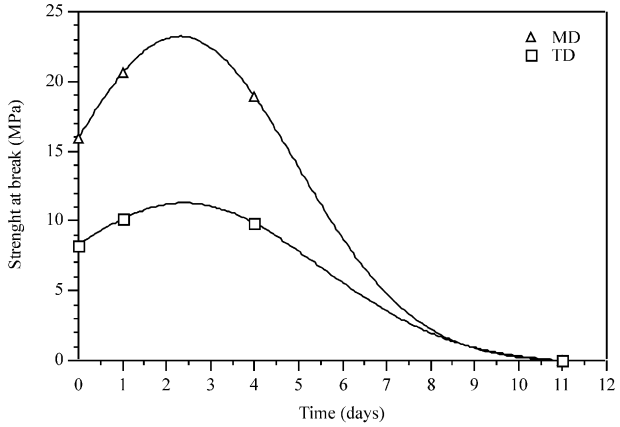

Fig. 12. Strength variation of LDPE specimens retrieved from the thermal treatment.

LDPE specimens submitted to thermal treatment at 55 °C for 0, 22, and 44 days, relevant acetone extracts and residues to extraction were also investigated for their potential biodegradation in a soil burial test carried out by using the biometer flask procedure. Preliminary results seem to confirm previous findings recorded in soil burial respirometric tests carried out on thermally fragmented Q-LDPE samples. A noteworthy difference (about 110 mg) in the cumulative CO_2 emissions from the blanks and test flask containing the acetone extract of the LDPE specimen submitted to 44 days oxidative thermal treatment (LDPE T44 AC) was recorded in a relatively short time (74 days) (Fig. 13). Significantly higher CO_2 net emissions (50–60 mg) were

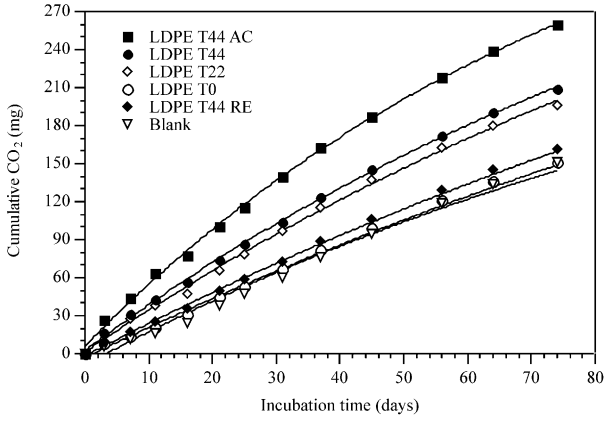

Fig. 13. Cumulative CO_2 emissions of acetone extract of the LDPE specimen submitted to 44 days oxidative thermal treatment (LDPE T44 AC), entire LDPE film specimens collected after 22 (LDPE T22) and 44 (LDPE T44) days thermal treatment, residues to extraction (LDPE T44 RE), original LDPE film (LDPE T0) and blank in a soil burial test.

monitored also in the case of the entire LDPE film specimens collected after 22 (LDPE T22) and 44 (LDPE T44) days of degradative treatment. The relevant residues (LDPE T44 RE) after extraction and the original LDPE film (LDPE T0) exhibited only minor differences in the overall carbon dioxide productions from the blank during the same time frame (Fig. 13).

4. Summary of significant results

LDPE-TDPA oxidized samples undergo significant biodegradation (50–60% by carbon dioxide evolution) over a period of 18 months as mediated by soil microorganisms in closed respirometric vessels (biometer flasks). In the case of thermally degraded Q-LDPE sample the mineralisation does not show any lag phase, but it tends to a plateau at about 4–7% mineralisation reached after about 6 weeks incubation. Interestingly, after a prolonged stasis in a dormant situation at room temperature, a substantial jump in the biodegradation activity was repeatedly detected in different soil burial and mature compost biodegradation tests, after agitating, moisturizing and reinoculating the degradation mixtures.

Extraction of original thermally treated LDPE-TDPA samples with boiling solvent (acetone) leads to an extractable fraction and to a residue resistant to extraction. The extractable fraction (QAC) is mineralised to a level of 50% in 80 days of incubation in soil burial respirometric tests, whereas the non-extractable fraction is apparently resistant to biodegradation for up to 10 months of incubation. Subsequently, an exponential increase in the mineralisation was detected. These results, along with the biodegradation profiles recorded for Q-LDPE sample not submitted to solvent extraction, strongly supports the hypothesis that the biodegradation of the thermally fragmentable polyethylene sample is promoted and modulated by the presence of the formulation additives in TDPA. Furthermore, the contribution of enzymatic attack in the continued macromolecular scission of thermally oxidized polyethylene matrix appears to be substantiated by the increase of unsaturation recorded in Q-LDPE samples submitted to the biotic environment.

The incubation temperature and environment of exposure of Q-LDPE samples appears to influence oxidation and biodegradation. This is apparent in the effectiveness of oxidations to low molecular weight at 55 °C, yet limited biodegradation is seen in mature compost as opposed to soil. This may be due to microbial population requirements for the biodegradation of oxidized fragments. Mature compost and soil differ substantially in this aspect.

A preliminary test of thermal degradation at 55 °C under aerobic conditions carried out on thermally unexposed LDPE-TDPA blown film gave substantial polymer fragmentation, with loss of mechanical properties in 11 days. The extraction with boiling solvents of the degraded sample provided about a 25% by weight of a quickly biodegradable extractable fraction. This indicated low molecular weight oxidized fragments from LDPE are rapidly biodegradable.

5. Conclusion

At this stage of ongoing research activity, it is clear that LDPE-TDPA formulations are effective in promoting the oxidation and subsequent biodegradation of polyethylene in soil environments. Several questions remain to be answered including, control of rate and completeness of biodegradation, and cumulative time for oxidation and biodegradation under different environmental conditions.

Acknowledgements

This work was performed within the framework of an ongoing contract commitment with EPI Environmental Plastics Inc. (EPI). The authors wish to thank Mr. Joseph G. Gho for having inspired and promoted the research activity whose results constitute the body of the present work.

References

[1] Guillet J, editor. Polymers and ecological problems. New York: Plenum Press; 1973.
[2] Scott G, Wiles DM. Programmed-life plastics from polyolefins: a new look at sustainability. Biomacromolecules 2001;2:615–22.
[3] Scott G. In: Scott G, editor. Developments in polymer stabilisation-4. London: Applied Science Publishers; 1981 [Chapter 1].
[4] Carlsson DJ, Wiles DM. Encyclopedia of polymer science and engineering, Vol. 4. 2nd ed. New York: Wiley; 1986.
[5] Scott G. Atmospheric oxidation and antioxidants. Vol. II. Amsterdam: Elsevier; 1993 [Chapter 3].
[6] Scott G. Environmental biodegradation of hydrocarbon polymers: initiation and control. In: Doi Y, Fukuda K, editors. Biodegradable plastic and polymers. Amsterdam: Elsevier; 1994. p. 79–91.
[7] Griffin GJL. Degradable plastic films. In: Proceedings of Symposium on Degradable Plastics. Washington DC: Society of Plastic Industry; 1987. p. 44–49.
[8] Otey FH, Westhoff RP, Doane WM. I&EC Prod Res Dev 1980; December:592.
[9] Gould JM, Gordon SH, Dexter LB, Swanson CL. In: Glass E, Swift G, editors. Agricultural and synthetic polymers: biodegradability and utilization; ACS Symposium Series 433. Washington DC: American Chemical Society; 1990. p. 65.
[10] Chiellini E, Solaro R, Corti A, Picci G, Leporini C, Pera A, Vallini G, Donaggio P. Degradation of starch-filled polyethylene films in a composting environment. Chim Indust 1991;8–9:656–63.

[11] Lee B, Pometto III AL, Fratzke A, Bailey TB. Biodegradation of degradable plastic polyethylene by *Phanerochaete* and *Streptomyces* species. Appl Environ Microbiol 1991;57:678–85.
[12] Vallini G, Corti A, Pera A, Solaro R, Cioni F, Chiellini E. Effect of intensive microbial metabolism on starch-filled polyethylene films in controlled composting windrow. J Gen Appl Microbiol 1994;40:445–61.
[13] Albertsson A-C, Andersson SO, Karlsson S. The mechanism of biodegradation of polyethylene. Polym Degrad Stab 1987;18:73–87.
[14] Erlandsson B, Karlsson S, Albertsson A-C. The mode of action of corn starch and a pro-oxidant system in LDPE: influence of thermooxidation and UV-irradiation on the molecular weight changes. Polym Degrad Stab 1997;55:237–45.
[15] Volke-Sepulveda T, Saucedo-Castaneda G, Gutiérrez-Rojas M, Manzur A, Favela-Torres E. Thermally treated low density polyethylene biodegradation by *Penicillium pinophilum* and *Aspergillus niger*. J Appl Polym Sci 2002;83:305–14.
[16] Albertsson A-C, Erlandsson B, Hakkarainen M, Karlsson S. Molecular weight changes and polymeric matrix changes correlated with the formation of degradation products in biodegraded polyethylene. J Environ Polym Degrad 1998;6:187–95.
[17] Contat-Rodrigo L, Ribes Greus A. Biodegradation studies of LDPE filled with biodegradable additives: morphological changes. I. J Appl Polym Sci 2002;83:1683–91.
[18] Potts JE, Clendinning RA, Ackart WB. EPA-R2-72-046. Washington DC: US Environmental Protection Agency; 1972.
[19] Haines JR, Alexander M. Microbial degradation of high-molecular weight alkanes. Appl Microbiol 1975;28:1084–5.
[20] Yamada-Onodera K, Mukumoto H, Katsuyama Y, Saiganji A, Tani Y. Degradation of polyethylene by a fungus, *Penicillium simplicissimum* YK. Polym Degrad Stab 2001;72:323–7.
[21] Albertsson A-C, Karlsson S. The three stages in degradation of polymers-Polyethylene as a model substance. J Appl Polym Sci 1988;35:1289–302.
[22] Ohtake Y, Kobayashi T, Asabe H, Murakami N. Studies on biodegradation of LDPE-observation of LDPE films scattered in agricultural fields or in garden soil. Polym Degrad Stab 1998;60:79–84.
[23] Yabannavar A, Bartha R. Biodegradability of some food packaging materials in soil. Soil Biol Biochem 1993;25:1469–75.
[24] Yabannavar A, Bartha R. Methods for assessment of biodegradability of plastic films in soil. Appl Environ Microbiol 1994;60:3608–14.
[25] Marinucci AC, Bartha R. Apparatus for monitoring the mineralization of volatile ^{14}C-labeled compounds. Appl Environ Microbiol 1979;38:1020–2.
[26] Solaro R, Corti A, Chiellini E. A new respirometric test simulating soil burial conditions for the evaluation of polymer biodegradation. J Environ Polym Degrad 1998;6:203–8.
[27] ASTM, American Society for Testing and Materials. Annual Book of ASTM Standards, 15.06, 1993.
[28] Albertsson A-C, Barenstedt C, Karlsson S. Susceptibility of enhanced environmentally degradable polyethylene to thermal and photooxidation. Polym Degrad Stab 1992;37:163–71.
[29] Scott G. Abiotic control of polymer biodegradation. Trends Polym Sci 1997;5:361–8.
[30] Volke-Sepulveda T, Favela-Torres E, Manzur-Guzman A, Limon-Gonzalez M, Trejo-Quinter G. Microbial degradation of thermo-oxidized low-density polyethylene. J Appl Polym Sci 1999;73:1435–40.
[31] Albertsson A-C, Barenstedt C, Karlsson S, Lindberg T. Degradation product pattern and morphology changes as means to differentiate abiotically and biotically aged degradable polyethylene. Polymer 1995;36:3075–83.