Ultrasonication and Microwave Assisted Extraction of Degradation Products from Degradable Polyolefin Blends Aged in Soil

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ABSTRACT: Two nonconventional extraction techniques, microwave assisted extraction (MAE) and ultrasonication, were used to extract degradation products from polyolefins with enhanced degradability. High-density polyethylene/polypropylene blends with two different biodegradable additives (a granular starch/iron oxide mixture and Mater-Bi AF05H) were subjected to outdoor soil burial tests and removed at different periods of time between 0 and 21 months. The extracted products were analyzed by gas chromatography mass spectrometry (GC-MS). Ultrasonication was found to be a more suitable technique than MAE because of better reproducibility. In addition, higher amounts of certain products (e.g., carboxylic acids) were extracted by ultrasonication than by MAE. The degradation products extracted from the two blends were basically a homologous series of alkanes, alkenes, carboxylic acids, and alcohols. The amount of hydrocarbons (saturated and unsaturated) and alcohols remained basically the same as the degradation times increased. However, carboxylic acids tended to decrease slightly with the exposure time. Their concentration remained practically unchanged until 12 months of soil burial when a more significant decrease was noted. The quantitative analysis of the degradation products revealed for both samples a decrease in the amount of carboxylic acids with the exposure time, although the trend was different according to the additive used in each sample. For blends with Mater-Bi the amount of carboxylic acids was at a minimum after 12-month exposure in soil, which coincided with a minimum in the molecular weight distribution. After blends with granular starch/iron oxide were exposed to 3 months in soil, tetradecanoic acid was no longer detectable and the amount of hexadecanoic and octadecanoic acids decreased significantly. Solid-phase microextraction, a solvent-free extraction technique, was used to extract the degradation products that could have migrated to the soil from blends with Mater-Bi. Small amounts of tetradecanoic acid and dodecanol were identified by GC-MS in the soil surrounding the sample. The degradation patterns observed here correlate with our previous results from mechanical and morphological characterization of these samples.
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Key words: ultrasonication; microwave assisted extraction; degradation products; polyolefin blends; soil aging

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INTRODUCTION

Interest in degradable plastics has resulted from the uncontrolled increasing volume of solid waste. Up to half of plastic production ends up as waste within 2 years because it is not used for long-term applications. The development of degradable polymers therefore offers a promising alternative for products that have a short life cycle or are impractical to recycle such as household waste, agricultural waste, and other disposables.

A way to obtain plastics with enhanced degradability is by simply incorporating into common synthetic plastics, such as polyolefins, different additives that accelerate their oxidative degradation and induce mechanical behavior and their morphological changes.[8,9] However, the degradation of such polyolefins is governed by a wide variety of factors; in addition to the morphological and mechanical characterization of the polymers, a study of the changes in their chemical structure is also needed to closely define their degradation process. In this sense, identification of the degradation products helps to elucidate the degradation mechanism of biodegradable polyolefins and to evaluate the environmental impact of such materials.[10] Degradation products remain in the sample or, depending on their volatility, also migrate to the surroundings as a potential toxicity hazard.

The objective of this work was to evaluate two nonconventional extraction techniques, microwave assisted extraction (MAE) and ultrasonication, when identifying and comparing degradation products formed in blends of 40/60 wt % high-density polyethylene/polypropylene (HDPE/PP) filled with either 10 wt % of a granular starch/iron oxide mixture (92/8 wt %) or Mater-Bi AF05H after exposure to outdoor soil environments. Both extraction techniques are generally quicker and less time consuming than the traditional extraction methods currently used (e.g., Soxhlet extraction). Solid-phase microextraction (SPME), a solvent-free extraction technique, was used to analyze the soil in which the degradation took place to find evidence of migration of the degradation products into the soil.[11] Identification of the degradation products was performed by gas chromatography mass spectrometry (GC-MS), and molecular weight changes were measured by high temperature size exclusion chromatography (HT-SEC).

Table I Sample Composition

Sample	Polymeric Matrix	Additive (10 wt %)
A	HDPE/PP 40/60 wt %	Granular starch/iron oxide 92/8 wt %
C	HDPE/PP 40/60 wt %	Mater-Bi AF05H

EXPERIMENTAL

Sample Preparation

The PP (PP 1148-TC) was supplied by BASF (Germany), and the HDPE (HDPE 5218) was supplied by British Petroleum (Spain). Two types of samples, labeled A and C, were prepared (Table I). They both had the same polymeric matrix made up of a 40/60 wt % HDPE/PP blend, but they were filled with 10 wt % of a different biodegradable additive. Sample A contained a 92/8 wt % granular starch/iron oxide mixture and sample C contained Mater-Bi AF05H obtained from Novamont North America. Both samples were processed by injection as seed boxes.

Outdoor Soil Burial Test

Samples were subjected to an outdoor soil burial test in Ayora (Valencia, Spain) and were removed after 0, 3, 6, 9, 12, 15, or 21 months. The soil had a pH (measured in water) of 6.75. After removal the samples were carefully washed with a soap solution, and they were dried with a piece of paper before being analyzed in order to stop the biodegradation process. An extract of the soil where sample C was buried for 27 months was also analyzed. The soil sample was directly picked up from the soil closely surrounding the sample. A sample of the same soil where no samples were buried was used as a blank.

MAE

The MAE of the degradation products from sample C buried in soil for different periods of time was carried out with a CEM 1000 microwave extraction system. The undegraded sample C was used as a blank. The solvent used was a 98/2 wt % chloroform/2-propanol mixture. An amount of 0.5 g of sample cut in little pieces was mixed with 10 mL of the solvent solution and extracted for 30 min at 80°C. All the measurements were repeated at least 3 times.

Ultrasonication

The extraction of the degradation products from sample C buried in soil for different periods of time was also performed by ultrasonication with a Branson 2210 apparatus using the undegraded sample C as a blank. Again, 0.5 g of sample cut in little pieces was mixed with 10 mL of chloroform in a 22-mL vial closed with a poly(tetrafluoroethylene) (PTFE)–butyl septum. The ultrasonication extraction was carried out for 1 h in a hot water bath held at 55°C. Because more reproducible data were obtained by ultrasonication extraction than by MAE for sample C, the extraction of the degradation products from sample A was only performed by ultrasonication. Sample A subjected to different exposure times was analyzed using undegraded sample A as a blank. All the ultrasonication measurements were also repeated at least 3 times for each sample. Both the extracts obtained from the MAE and ultrasonication techniques were concentrated by total evaporation of the solvent at room temperature. Afterward 2 mL of chloroform was added, and the extract was filtered with a 0.45-μm filter before being analyzed.

SPME

The degradation products from the soil extract where sample C was buried for 27 months was carried out by SPME using a 100-μm thickness silica-based SPME fiber coated with nonpolar poly(dimethylsiloxane). A sample of the same soil where no samples were buried was used as a blank. The soil sample (0.75 g) was placed in a 22-mL vial closed with a PTFE–butyl septum. The product absorption was performed by exposing the fiber to the headspace above the soil for 30 min at 60°C. Afterward the degradation products were thermally desorbed from the fiber for 5 min in the GC injector held at 250°C. Prior to each extraction, the fiber was conditioned for 8–10 min at 250°C to remove the impurities absorbed into it. All the extractions were repeated 3 times for the soil where sample C was buried and the blank one.

GC-MS

Identification of the degradation products extracted from samples A and C, as well as from the soil, was performed by GC-MS with a Varian 3400 gas chromatograph coupled to a Finnigan SSQ 7000 (Quadropole) mass spectrometer using helium as the carrier gas. The gas chromatograph was equipped with an RTX5-MS capillary column of medium polarity. The oven temperature was programmed from 40°C for 4 min to 250°C at a heating rate of 5°C/min, and then it was held at 250°C for 20 min. Samples were introduced in the splitless injection mode at 250°C. All the degradation products were identified by comparing their mass spectrum with the one from the NST database and checking it with that of a known standard.

HT-SEC

Changes in molecular masses and distributions from both versions of sample C (undegraded and aged for different periods of time) were measured by means of a Waters l50C HT-SEC apparatus equipped with two PLgel 10-μm mixed-B columns (7.5 $\times$ 300 mm) and a refractive index detector. The mobile phase was 1,2,4-trichlorobenzene at 135°C, and the flow rate was 1 mL/min. Polystyrene standards ranging from 2000 to 1,950,000 g/mol were used for calibration. In order to obtain an appropiate average molecular weight, each sample should be analyzed at least 3 times. However, because of stabilization problems with the apparatus, only one measurement could be performed for each sample. Thus, the values obtained cannot be considered significative enough and should be checked again.

RESULTS AND DISCUSSION

Analysis of Products Obtained from Polyolefins with Enhanced Degradability

Qualitative and quantitative analyses were made based on the GC-MS results. In the first step the degradation products were identified by comparing their mass spectra with the mass spectra from the NST database and checking the retention times with those of a known standard.

The quantitative analysis was carried out in order to check whether there were any changes in the amount of products formed with the exposure time. The concentration of each product was estimated relative to that of docosane ($C_{22}H_{22}$), which was found to be the more abundant hydrocarbon in most of the samples.

Table II summarizes the products identified by GC-MS from samples A and C, regardless of the exposure time. The products were found to be basically a homologous series of hydrocarbons (both saturated and unsaturated), carboxylic ac-

Table II Identified Products from Samples A and C

Peak Number	Compounds	Sample A	Sample C
	Hydrocarbons		
	Alkanes		
1	Dodecane	×	×
2	Tridecane	×	×
3	Tetradecane	×	×
4	Hexadecane	×	×
5	Heptadecane	×	×
6	Octadecane	×	×
7	Eicosane	×	×
8	Docosane	×	×
9	Tetracosane	×	×
10	Hexacosane	×	×
11	Octacosane	×	×
12	Tricontane	×	×
—	Alkenes		
—	1-Dodecene	×	×
—	1-Tetradecene	×	×
—	1-Hexadecene	×	×
—	1-Octadecene	×	×
—	1-Eicosene	×	×
—	1-Docosene		×
—	1-Tetracosene	×	×
	Carboxylic acids		
13	Tetradecanoic	×[a]	×
14	Hexadecanoic	×	×
15	Octadecanoic	×	×
	Alcohols		
—	Dodecanol	×	×
—	Tetradecanol	×	×
—	Hexadecanol	×	×
—	Octadecanol	×	×
—	Eicosanol	×	×
	Miscellaneous		
16	Diethyl phthalate	×	

Only the mean peaks that do not need a figure magnification to be detected are numbered. (×) Present in sample.

[a] Tetradecanoic acid is only present in undegraded sample A and in sample A degraded for 3 months.

ids, and alcohols. Practically all of them were compounds with an even number of carbon atoms. We identified similar products in thermooxidized starch-based polymers[12] and thermooxidized and UV-photooxidized degradable PE.[13–15]

Tetradecanoic acid was no longer present in sample A after 3 months of exposure; otherwise, the same products were identified, regardless of the exposure time. Diethyl phthalate was identified in sample A but not C, which indicated that this product came from the additive used in sample A.

Products Extracted from HDPE/PP with Materi-Bi AF05H (Sample C) by MAE

Figures 1 and 2 show the chromatograms of products extracted by MAE from undegraded sample C and sample C buried in soil for 21 months. The major peaks of the chromatograms correspond to saturated hydrocarbons and carboxylic acids. All the identified hydrocarbons, both saturated and unsaturated, had 12–30 carbon atoms. Alkenes were present in much lower concentrations than alkanes. In general we observed that for the alkanes with an even number of carbons their concentration increased as the molecular weight increased, and a maximum was obtained for the docosane. For higher molecular weight alkanes, their amount decreased as the number of carbons in the molecule increased. Only two alkanes with an uneven number of carbons were identified, and they were only present in much lower concentrations.

For the three identified carboxylic acids, we found that their concentration increased as their molecular weights became higher. The carboxylic acids present in the undegraded sample were probably formed during its processing.

A homologous series of alcohols with 12–20 carbon atoms was also identified but in low concentrations. The lower alcohols showed very low concentrations, but these alcohols have high volatility and can be easily lost during the extract concentration by evaporation.

Table III shows the relative amount of the products obtained from sample C. It was often not possible to calculate a mean value of the amount of products because of a too big dispersion in the data, especially for the lower molecular weight alkenes and alcohols. In general, quite dispersive values were also obtained for the carboxylic acids. As the molecular weight increased, the dispersity in the results increased for the carboxylic acids. Thus, although the tetradecanoic acid showed quite reproducible data, the octadecanoic acid exhibited a much higher dispersity that sometimes did not allow a good mean value to be calculated.

Products Extracted from HDPE/PP with Materi-Bi AF05H (Sample C) by Ultrasonication

The chromatograms of the products extracted by ultrasonication of sample C were quite similar to the ones obtained after MAE.

Table IV shows the relative amount of the products obtained from sample C after ultrasonication. For sample C more reproducible data were obtained by ultrasonication extraction than by MAE. The relative amounts of the extracted prod-

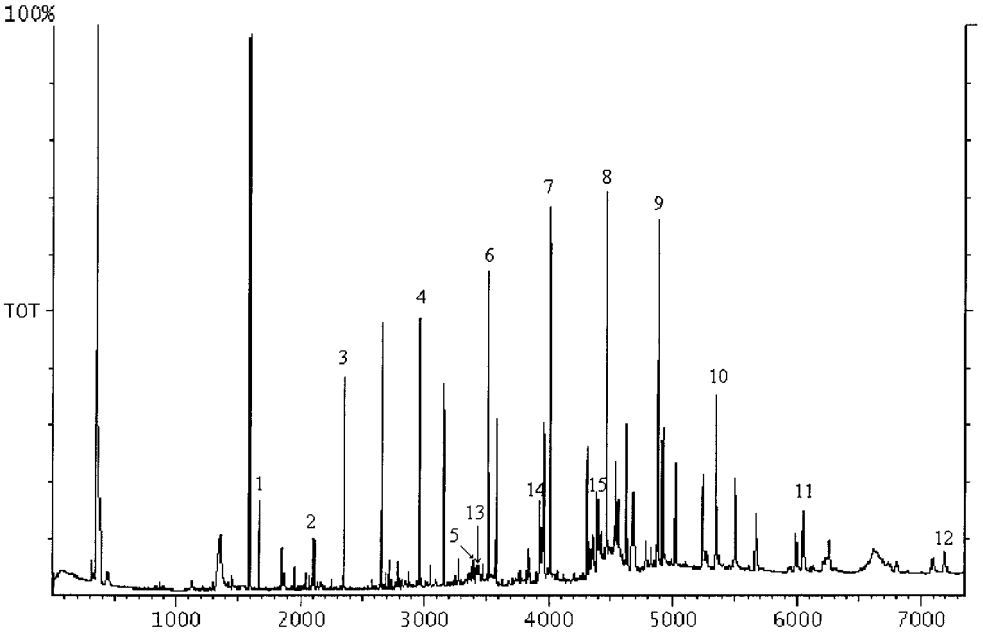

Figure 1 GC-MS chromatogram of the products extracted by MAE from the undegraded sample C.

ucts were similar in both cases; however, the estimated amount of carboxylic acids extracted was larger by ultrasonication.

In general, as the exposure time in soil increased, only slight changes in the concentrations were observed. The amount of hydrocarbons (saturated and unsaturated) and alcohols remained basically the same as the degradation times increased. Carboxylic acids, however, tended to decrease slightly with the exposure time. Their concentration remained practically unchanged until 12 months of soil burial when a more significant decrease was noted. This is in good agreement with previous results on the mechanical and mor-

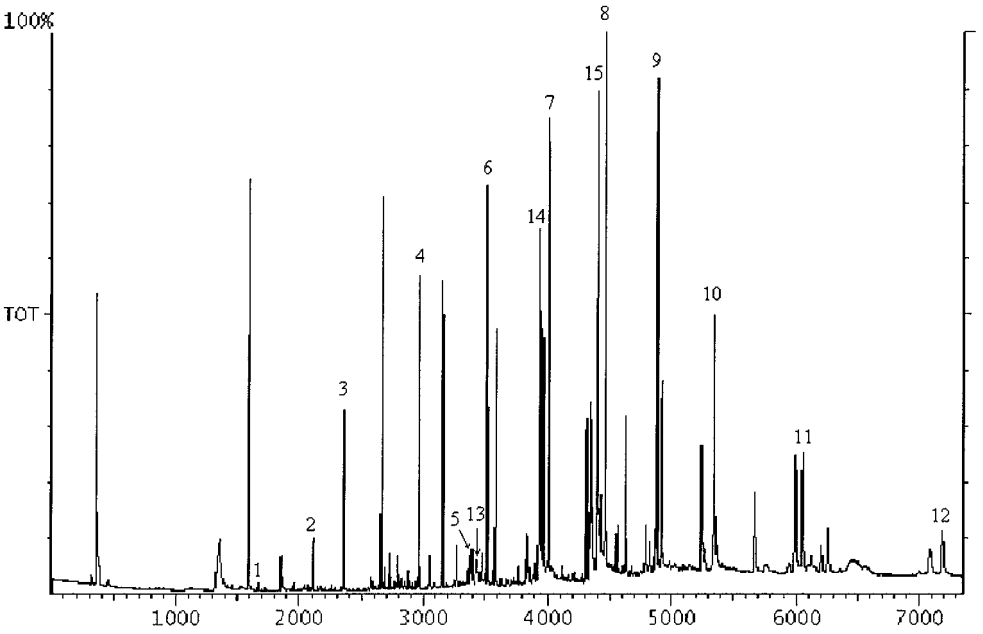

Figure 2 GC-MS chromatogram of the products extracted by MAE from sample C buried in soil for 21 months.

Table III Relative Amount of Products Obtained from Sample C by MAE

	Exposure Time (months)						
Compounds	0	3	6	9	12	15	21
Alkanes							
Dodecane	0.18	0.12	0.22	0.17	0.13	0.23	0.23
Tridecane	0.05	0.04	0.07	0.04	0.03	0.06	0.06
Tetradecane	0.45	0.47	0.55	0.40	0.41	0.55	0.52
Hexadecane	0.60	0.68	0.76	0.61	0.65	0.83	0.71
Heptadecane	0.06	0.09	0.11	0.08	0.07	0.10	0.10
Octadecane	0.77	0.88	0.99	0.82	0.93	1.02	0.86
Eicosane	0.85	0.98	1.02	0.91	0.97	1.07	0.92
Docosane	1	1	1	1	1	1	1
Tetracosane	0.90	0.78	0.71	0.86	0.82	0.70	0.88
Hexacosane	0.61	0.42	0.44	0.51	0.51	0.34	0.60
Octacosane	0.32	0.24	0.15	0.26	0.23	×	0.37
Tricontane	0.12	0.09	0.10	0.13	0.12	—	0.14
1-Alkenes							
Dodecene	—	×	×	×	×	×	—
Tetradecene	0.006	0.007	0.007	0.006	0.006	0.010	0.008
Hexadecene	0.009	0.011	0.012	0.008	0.012	0.011	0.009
Octadecene	0.010	0.024	0.026	0.013	0.016	0.011	0.013
Eicosene	0.010	0.011	0.013	0.010	0.013	0.014	0.010
Docosene	0.012	0.021	0.019	0.016	0.014	0.014	0.012
Tetracosene	0.024	0.022	0.026	0.021	0.024	0.021	0.024
Carboxylic acids							
Tetradecanoic	0.07	0.12	0.10	0.09	0.09	0.07	0.07
Hexadecanoic	0.82	1.19	0.93	1.01	1.00	0.73	0.85
Octadecanoic	1.23	1.56	1.18	1.53	×	×	1.17
1-Alcohols							
Dodecanol	—	0.08	×	×	×	×	×
Tetradecanol	—	0.05	×	×	×	×	×
Hexadecanol	0.002	0.004	—	0.001	x	—	—
Octadecanol	0.013	0.02	0.012	0.012	0.013	0.010	0.013
Eicosanol	—	×	0.02	0.015	0.026	0.017	0.018
Miscellaneous							
Diethyl phthalate	—	—	—	—	—	—	—

(×) not enough or too dispersive data to calculate a mean value; (—) not present or not possible to estimate the peak area.

phological characterization of these samples, which showed a two-stage degradation process.[8,9] The results also showed that the polymeric matrices underwent biodegradation in soil and that the formed carboxylic acids were assimilated by microorganisms.[16] In an earlier study we showed that carboxylic acids were formed in the low-density PE (LDPE) matrix of blends with a cornstarch and prooxidant formulation and that these were assimilated in biotic environments but not in abiotic ones.[17]

Products Extracted from HDPE/PP with Granular Starch/Iron Oxide (Sample A) by Ultrasonication

Figures 3 and 4 show the chromatograms of products extracted by ultrasonication from undegraded sample A and sample A buried in soil for 21 months. The main differences between these two chromatograms are in the carboxylic acids formed. The peak of the tetradecanoic acid was not present in the chromatogram of sample A aged for 21 months. In fact, it was found that the peak corresponding to the tetradecanoic acid decomposed into two peaks in the chromatogram of the samples buried in soil for more than 3 months. One of the peaks had the characteristic mass spectrum of an alkane and the other that of an alkene of the same molecular weight as tetradecanoic acid.

In addition, the peak shape and height of the hexadecanoic and octadecanoic acids changed with the exposure time as shown in Figure 5. For

Table IV Relative Amount of Products Obtained from Sample C by Ultrasonication

	Exposure Time (months)						
Compounds	0	3	6	9	12	15	21
Alkanes							
Dodecane	0.18	0.18	0.20	0.23	0.22	0.22	0.17
Tridecane	0.05	0.06	0.06	0.06	0.05	0.08	0.06
Tetradecane	0.47	0.52	0.48	0.56	0.43	0.53	0.41
Hexadecane	0.67	0.71	0.64	0.74	0.61	0.78	0.60
Heptadecane	0.09	0.10	0.10	0.08	0.07	0.07	0.09
Octadecane	0.87	0.93	0.85	0.91	0.82	0.92	0.86
Eicosane	0.96	1.01	0.95	0.98	0.91	0.99	0.94
Docosane	1	1	1	1	1	1	1
Tetracosane	0.75	0.72	0.78	0.76	0.81	0.76	0.79
Hexacosane	0.40	0.40	0.41	0.39	0.47	0.38	0.46
Octacosane	0.20	0.21	0.29	0.21	0.26	0.23	0.20
Tricontane	0.14	0.10	0.13	0.12	0.12	0.09	0.19
1-Alkenes							
Dodecene	0.003	0.003	0.002	0.003	0.002	0.003	0.003
Tetradecene	0.007	0.006	0.006	0.008	0.006	0.009	0.01
Hexadecene	0.012	0.013	0.012	0.011	0.011	0.012	0.012
Octadecene	0.013	0.016	0.015	0.013	0.013	0.011	0.012
Eicosene	0.013	0.015	0.013	0.012	0.012	0.012	0.011
Docosene	0.016	0.017	0.017	0.016	0.017	0.016	0.018
Tetracosene	0.018	0.021	0.026	0.020	0.020	0.022	0.023
Carboxylic acids							
Tetradecanoic	0.16	0.13	0.13	0.13	0.13	0.10	0.12
Hexadecanoic	1.52	1.42	1.50	1.31	1.46	0.98	1.30
Octadecanoic	2.15	2.09	2.17	1.94	2.11	1.48	1.74
1-Alcohols							
Dodecanol	0.07	0.08	0.07	0.07	0.06	0.07	0.07
Tetradecanol	0.03	0.02	0.02	0.02	0.02	0.03	0.03
Hexadecanol	0.004	0.003	×	0.002	0.002	×	0.001
Octadecanol	0.02	0.02	0.02	0.01	0.02	0.01	0.01
Eicosanol	—	0.01	0.008	0.009	0.01	—	0.009
Miscellanous							
Diethyl phthalate	—	—	—	—	—	—	—

(×) not enough or too dispersive data to calculate a mean value; (—) not present or not possible to estimate the peak area.

samples degraded more than 3 months, the peak height of the hexadecanoic and octadecanoic acids decreased significantly. Moreover, a new peak overlapping the one of the hexadecanoic acid appeared with increasing height with the degradation time. This peak could be assigned to dibutyl phthalate according to the NST database.

Table V summarizes the changes in the estimated relative amounts of the carboxylic acids formed in sample A. Tetradecanoic acid was present in the undegraded sample but in low concentration, and after 3 months of exposure to soil it vanished. The hexadecanoic and octadecanoic acids already showed a significant decrease in their concentrations after 3 months of soil burial. After 3 months they continued to decrease but much more slowly. These results also agree with the conclusions obtained from the analysis of the mechanical and morphological behavior of the samples.[8,9]

In general, hydrocarbons do not show a regular formation and their relative amounts remained basically the same. However, it was observed that the alkanes formed in sample A had slightly higher concentrations than the ones formed in sample C and the alkenes demonstrated lower concentrations. Alcohols were only present in low concentrations, similar to sample C.

Diethyl phthalate was present in all the samples, even in the undegraded ones. The concentration

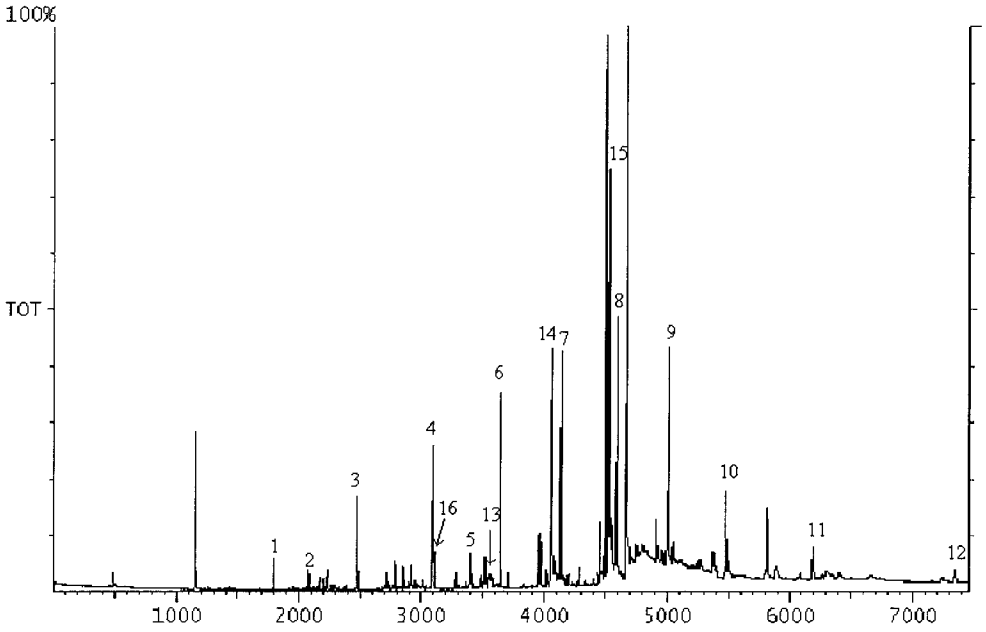

Figure 3 GC-MS chromatogram of the products extracted by ultrasonication from the undegraded sample A.

was relatively significant, but it exhibited no regular changes with the exposure time. Phthalates are normally associated with polymer additives or external contaminants.[14] In this case, because diethyl phthalate was identified in sample A but not in sample C and both samples had the same polymeric matrix, this product must come from the additive used in sample A. This was previously shown by other authors in samples of LDPE containing a biodegradable master batch.

Analysis of Degradation Products in Soil Surrounding Polymeric Blends

Degradation products that could have migrated to the soil surrounding the samples were extracted by

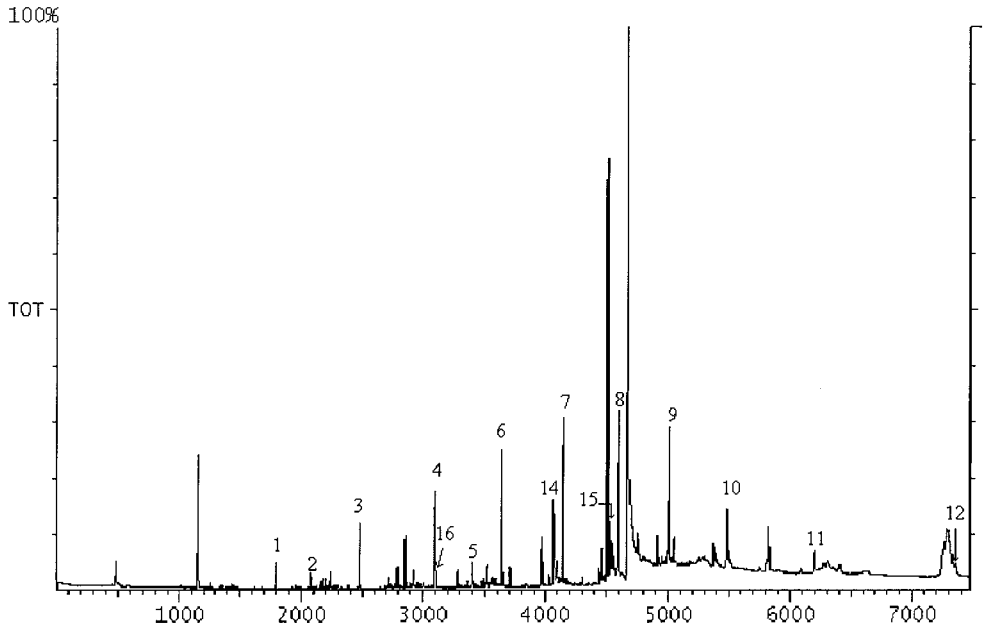

Figure 4 GC-MS chromatogram of the products extracted by ultrasonication from sample A buried in soil for 21 months.

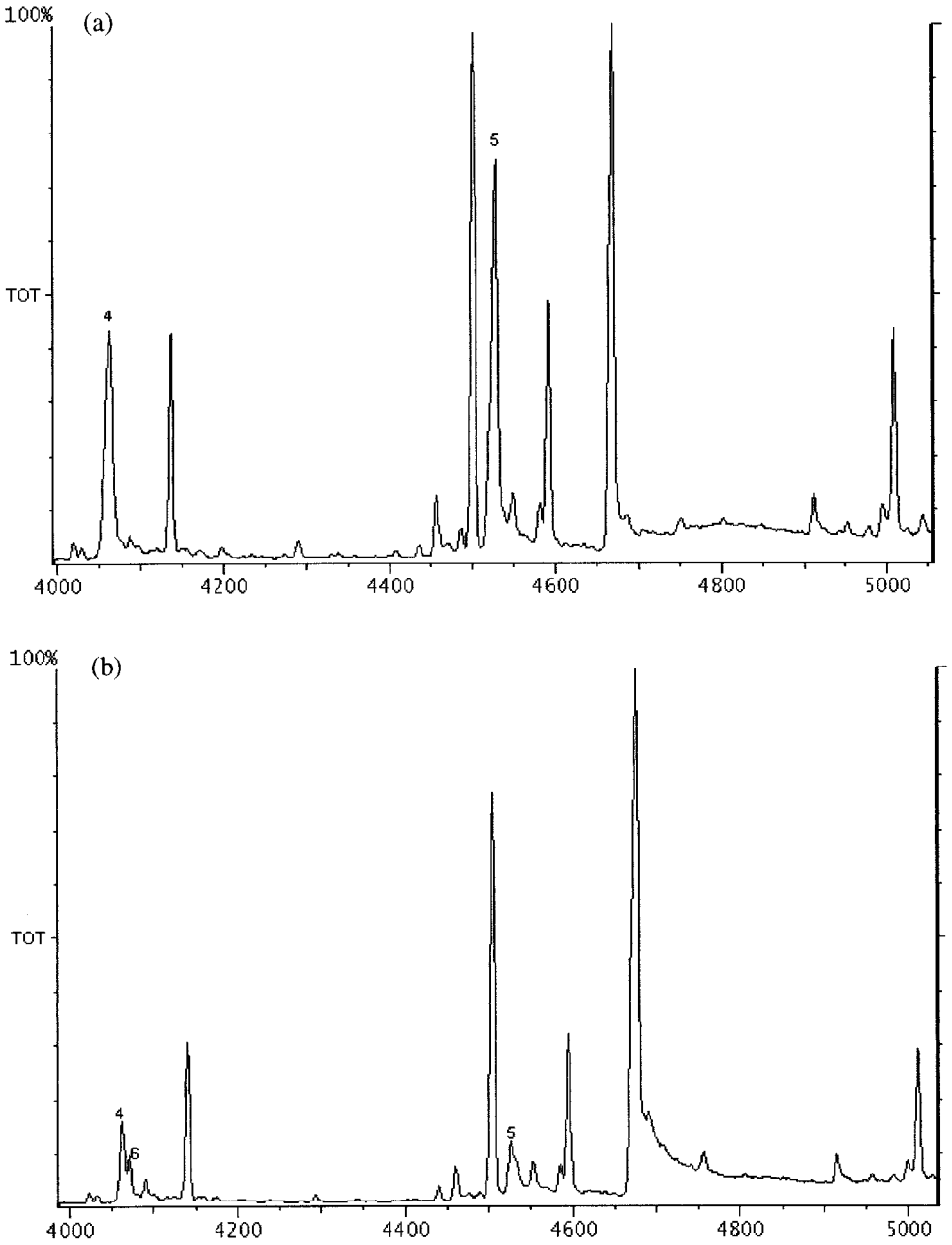

Figure 5 GC-MS chromatograms of the products extracted by ultrasonication from sample A: (a) undegraded and (b) buried in soil for 21 months. Peaks 4 and 5 corresponds respectively to the hexadecanoic and the octadecanoic acids. Peak 6 is a new peak which appears for samples degraded more than 3 months.

SPME and identified by comparing their mass spectrum with the mass spectrum from the NST database and checking it with that of a known standard.

Table VI summarizes the products identified by GC-MS from a soil extract where sample C was buried for 27 months and for the soil blank sample consisting of the same soil where no samples were buried. The products in Table VI are the only ones with significative peaks that were present in the soil where sample C was buried. In cases where they were also detected in the soil blank, they exhibited a higher peak in the chromatogram obtained from the soil with sample C.

Tetradecanoic acid was detected in both the soil blank and the soil sample. As shown Figure 6, this acid appears as a small shoulder overlapping another peak in the soil sample but exhibits a

Table V Relative Amount of Products Obtained from Sample A by Ultrasonication

Compounds	Exposure Time (months)						
	0	3	6	9	12	15	21
Alkanes							
Dodecane	0.12	0.10	0.11	0.15	0.11	0.12	0.13
Tridecane	0.07	0.04	0.04	0.05	0.04	0.08	0.08
Tetradecane	0.31	0.27	0.27	0.35	0.27	0.30	0.29
Hexadecane	0.46	0.44	0.43	0.51	0.44	0.43	0.43
Heptadecane	0.15	0.07	0.11	0.07	0.08	0.14	0.15
Octadecane	0.64	0.64	0.63	0.67	0.63	0.64	0.63
Eicosane	0.81	0.81	0.81	0.84	0.79	0.80	0.77
Docosane	1	1	1	1	1	1	1
Tetracosane	0.90	0.91	0.89	0.86	0.90	0.86	0.86
Hexacosane	0.49	0.52	0.53	0.54	0.55	0.47	0.51
Octacosane	0.29	0.31	0.32	0.33	0.34	0.26	0.35
Tricontane	0.17	0.23	0.24	0.26	0.26	0.17	0.24
1-Alkenes							
Dodecene	0.001	0.001	0.001	0.002	0.001	0.002	0.002
Tetradecene	0.004	0.003	0.004	0.004	0.003	0.004	0.004
Hexadecene	0.007	0.009	0.007	0.007	0.007	0.007	0.007
Octadecene	0.007	0.009	0.009	0.009	0.008	0.008	0.008
Eicosene	0.009	0.01	0.009	0.009	0.01	0.009	0.008
Docosene	—	—	—	—	—	—	—
Tetracosene	0.04	0.02	0.03	0.02	0.03	0.04	0.05
Carboxylic acids							
Tetradecanoic	0.08	0.06	—	—	—	—	—
Hexadecanoic	1.26	0.61	0.43	0.38	0.31	0.39	0.46
Octadecanoic	1.70	1.01	0.46	×	0.28	0.20	0.36
1-Alcohols							
Dodecanol	0.05	0.03	0.04	0.03	0.04	0.04	0.06
Tetradecanol	×	0.02	0.02	0.01	0.03	0.02	0.02
Hexadecanol	0.005	0.001	0.001	0	0.001	0	—
Octadecanol	0.01	0.01	0.008	0.009	0.01	0.01	0.01
Eicosanol	0.02	0.01	0.01	0.01	0.02	0.02	0.02
Miscellaneous							
Diethyl phthalate	0.23	0.16	0.20	0.17	0.16	0.23	0.23

(×) not enough or too dispersive data to calculate a mean value; (—) not present or not possible to estimate the peak area.

quite high peak in the soil blank. Because this compound was also identified as a degradation product from sample C, the higher concentration of this acid in the soil sample could be due to its migration from the sample to the surrounding soil. Unfortunately, this acid did not totally desorb from the SPME fiber, which resulted in the appearance of tetradecanoic acid in the fiber conditioning chromatogram also. Tetradecanoic acid was however always much higher in the soil sample than in the soil blank.

Dodecanol was the only identified product detected in the soil sample but not in the soil blank. However, it was present in quite a low concentration (small peak). This low molecular weight alcohol was identified as a degradation product from sample C, so its presence in the soil where this sample was buried for several months could be due to its migration from the sample to the surrounding soil.

Table VI Identified Products from Soil Samples

Compounds	Soil Blank	Soil Sample
Carboxylic acids		
Tetradecanoic	×	×
Alcohols		
Dodecanol		×

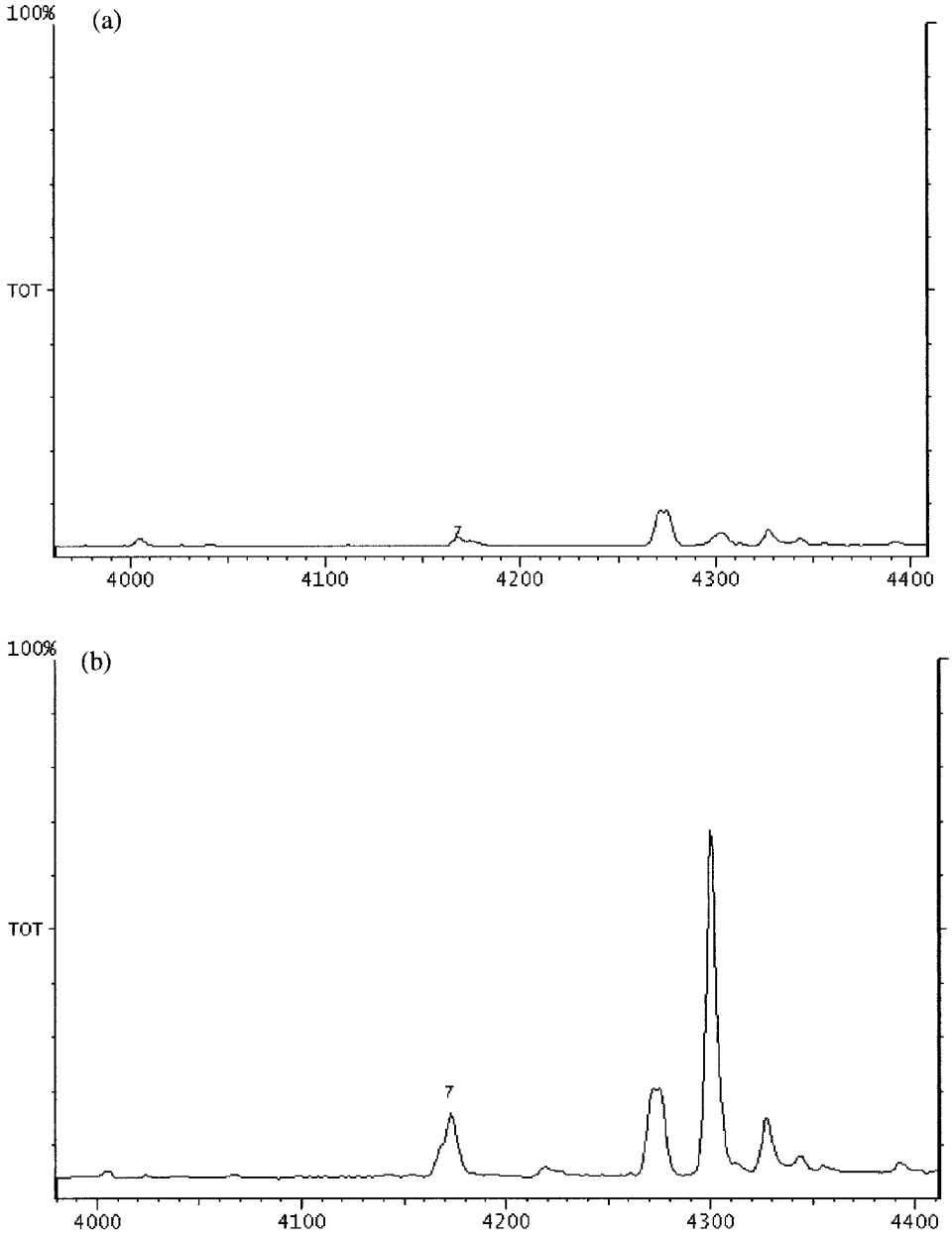

Figure 6 GC-MS chromatograms of the products extracted by SPME from: (a) soil blank and (b) soil sample. Peak 7 corresponds to tetradecanoic acid.

Molecular Weight Changes in Polyolefins with Enhanced Degradability

Table VII presents the results from the HT-SEC measurements. Table III showed that the amount of carboxylic acids extracted from sample C remained basically unchanged until 12 months of exposure, when a more significant decrease occurred. After that, the carboxylic acids concentration tended to increase again. The molecular weight distribution followed the same pattern; the results obtained by thermal analyses (DSC and dynamic mechanical thermal analyses) confirmed the development of the degradation process in two stages.[8,9] The first stage was characterized by an increase in the crystallinity and a change in the lamellar size distribution, and the second stage demonstrated a decrease in the crystallinity content and a broader distribution of the lamellar sizes representing basically a homologous series of hydrocarbons (both saturated and unsaturated), carboxylic acids, and al-

Table VII Average Molecular Weights and Molecular Weight Distribution (MWD) of Sample C Undegraded and After Different Exposure Times

Months of Soil burial	M_n	M_w	M_z	MWD
0	12,800	166,500	668,800	13.0
3	11,400	117,000	356,100	10.3
6	11,900	128,600	431,400	10.8
9	16,200	171,100	603,900	10.6
12	8,020	77,700	291,100	9.7
15	17,400	181,300	551,400	10.4
21	11,200	127,100	484,200	11.4

cohols. Practically all of them are compounds with an even number of carbon atoms.

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