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Degradation product pattern and morphology changes as means to differentiate abiotically and biotically aged degradable polyethylene

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Degradation product patterns and morphology changes are demonstrated to be means by which to differentiate between physical/chemical (abiotic) and biological (biotic) ageing of degradable polymers. Comparison is made between low-density polyethylene (LDPE), LDPE + 7.7% starch and LDPE + 20% (starch + pro-oxidant). Pro-oxidized samples were subjected to aqueous sterile and aqueous biotic (*Arthrobacter paraffineus*) environments at ambient temperatures for 15 months, and thermo-oxidation at 95°C in water. Carboxylic acids were identified in the abiotically degraded samples in contrast to the biotic environment, where assimilation of lower molecular weight products, especially carboxylic acids, had taken place as determined by gas chromatography and gas chromatography–mass spectrometry. Several hydrocarbons (C–C) were also present in these samples. This is in agreement with the proposed biodegradation mechanism of LDPE. The morphology changes, as monitored by X-ray diffraction (XRD) and scanning electron microscopy, were different in the two environments. A decrease in lamellar thickness (l) was demonstrated for biotically degraded LDPE + 20% (starch + pro-oxidant), while the corresponding abiotically aged samples showed a constant or increased value of l. The crystallinity (XRD-w_c) for samples aged at ambient temperature showed that prolonged exposure to *A. paraffineus* resulted in decreasing value of w_c. In the accelerated environment, however, a constant increase in XRD-w_c was monitored. The principal difference between abiotic and biotic degradation of polymers is that micro-organisms use polymers to gain energy. This is manifested as different degradation product patterns (reflecting degradation mechanisms) and a decreasing value of crystallinity and lamellar thickness with time. The abiotic degradation breaks bonds and releases degradation products, leaving the remaining polymer rearranged with a higher degree of order.

(Keywords: degradation; polyethylene; morphology changes)

INTRODUCTION

Many synthetic polymers have long been labelled as recalcitrant, i.e. completely resistant to microbial and/or enzymatic degradation. Synthetic polymers such as polyethylene and polystyrene are, however, not completely inert towards micro-organisms, but have demonstrated a certain, though limited, long-term biodegradability[1–4].

The idea of introducing additives to improve the degradability of synthetic polymers was exploited in the 1970s. Biopolymers such as starch were incorporated as a natural biodegradable filler according to different technologies[5,6]. To improve the overall degradability, the starch could be accompanied by other additives which promote abiotic oxidation, so-called pro-oxidants, or the pro-oxidants could be used only[6–8]. Photodegradable materials based on the additive principle were also developed. Some important examples are the Scott–Gilead patent[9] with metal dithiocarbamates, and the Guillet Ecolyte[10] polymer, where carbonyl groups are copolymerized into the material in question.

The initial step for biodegradation of many inert polymers is photo-oxidation, where hydroperoxides are incorporated through Norrish type I and II mechanisms. The next step is the attack of micro-organisms on the carboxylic parts of the polymer, releasing two carbon chain fragments which can be further used in either the anabolic or the catabolic cycle[11]. Starch-containing material can further enhance the degradation if biodegradation of this component takes place, since this increases the surface area as well as giving increased oxygen permeability. During abiotic and biotic degradation, series of low molecular weight compounds are released into the surrounding environment. In addition, the remaining polymer will be changed in regard to its crystallinity, lamellar thickness and overall morphology.

In 1990 we published a brief paper about the degradation products formed in thermo-oxidized pure low-density polyethylene (LDPE)[12]. By gas chromatography we identified 2-butanol, propionic acid,

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1-pentanol, butyric acid, valeric acid and caproic acid, in addition to several other unidentified peaks, after 17 weeks of degradation. During this abiotic degradation, a subsequent increase in the carbonyl content accompanied by an increase in the crystallinity was observed[12,13]. The rate of formation of carbonyl groups is also increased by photo-oxidation, increased stress and the presence of pollutants[14]. Thermo-oxidation results in the release of low molecular weight compounds from primarily the amorphous part of the polymer, leaving the remaining polymer more prone to reorganization, explaining the increased crystallinity. In another series of papers we analysed the volatile products formed in LDPE + starch and LDPE + starch + pro-oxidant after thermal ageing at 100°C in air and in aqueous abiotic and biotic environments, and identified over 50 different degradation products[15–17].

The objective of this paper is to find new ways for understanding the different degradation mechanisms in abiotic and biotic degradation of LDPE, LDPE + 7.7% starch and LDPE + 20% (starch + pro-oxidant).

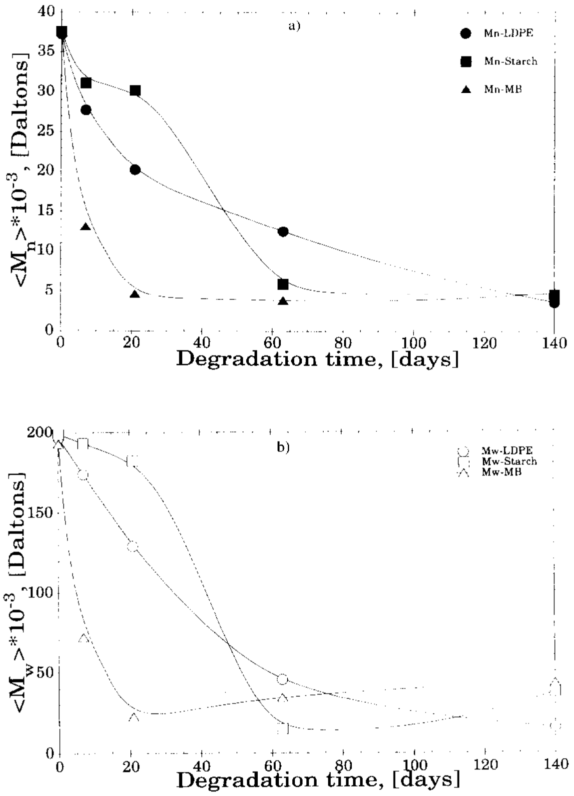


Figure 1 Changes in number-average molecular weight (a) and weight-average molecular weight (b) as a function of thermo-oxidation time (95°C). ○, ●, LDPE; □, ■, LDPE + 7.7% starch; △, ▲, LDPE + 20%MB

EXPERIMENTAL

Materials and degradation procedure

LDPE films (80 mm) were made by a conventional blown-film process using a Betol extruder with a 25 mm screw of *L* : *D* 20 : 1, a blow-up ratio of about 2.5 : 1 and die temperature 185°C. The polymer was a conventional LDPE grade of MFI 2 acquired from ATO (France), which incorporated a conventional thermal stabilizer of undisclosed composition. Prodegradant additives were incorporated into the LDPE matrix in the form of a masterbatch (MB) in the amount of 20%, mostly consisting of corn starch (7.7%), styrene–butadiene copolymer (SBS), manganese stearate and linear LDPE. Degradation took place according to the following procedure. The films were pre-oxidized by heating in air at 100°C for 6 days in order to surpass the induction period and ensure that oxidation of the LDPE matrix had commenced, whereafter the samples were subjected to abiotic and biotic aqueous environments. The aqueous environment consisted of an autoclaved basal salt medium, pH 7.0, which contained (per litre of distilled water) 1.0 g $(NH_4)_2C_4H_4O_6$, 0.2 g KH_2PO_4, 0.205 g $MgSO_4 \cdot 7H_2O$, 0.166 ml of a 1% solution of $FeCl_3 \cdot 6H_2O$, and 1.6 ml of a 1% solution of $ZnSO_4 \cdot 7H_2O$. The samples, which constituted the sole carbon source, were inoculated with the bacterium *Arthrobacter paraffineus* (biotic environment) or kept sterile by the addition of 0.2% NaN_3 (abiotic environment). Three replicates of each sample type were made. Incubation took place at ambient temperature for periods up to 3 years.

Another series of degradation experiments took place in water at 95°C for a period of 30 weeks. Samples (2 g) were placed in glass flasks filled with 100 ml distilled water, pH 7.0, equipped with condensers and immersed in a temperature-controlled hot water bath.

Gas chromatography–mass spectrometry (g.c.–m.s.)

Degradation products were separated and identified by means of a Hewlett-Packard 5890 gas chromatograph equipped with a 60 m × 0.32 mm DB-5 column, film thickness 0.25 mm, coupled to a mass spectrometer, model VG-70-250SE. The oven temperature was held for 1 min at 50°C, then increased at 5°C min^{-1} to 310°C and held for 10 min. The carrier gas was helium. The injector temperature was 250°C and the interface was maintained at 300°C. Electron impact spectra were obtained with electron energy, ion source temperature, resolution and scan rate of 70 eV, 200°C, 1000 and 2 scan s^{-1}, respectively. Compounds were identified by comparison with the NBS database.

Gas chromatography (g.c.)

Chromatograms of degradation products and standard compounds were recorded on a Varian 3400 gas chromatograph equipped with a J&W 30 m × 0.32 mm DB-5 column, film thickness 0.25 mm, and with a flame ionization detector. The oven temperature was held for 1 min at 50°C, then increased at 5°C min^{-1} to 310°C and held for 10 min. Nitrogen was used as carrier gas. Identifications were made by comparison of retention indices with those obtained by g.c.–m.s. and/or by comparison with retention indices from standard compounds. For compounds identified solely by g.c., relevant standard compounds were chosen by virtue of information obtained from the mass spectra.

Size exclusion chromatography (s.e.c.)

A Waters 150C high-temperature size exclusion chromatograph equipped with two PLgel 10 mm mixed-B columns was used to measure changes in molecular weights and distributions. The mobile phase was 1,2,4-trichlorobenzene (TBC) at 135°C and 1 ml min^{-1} flow rate. Calibration was performed according to polystyrene standards.

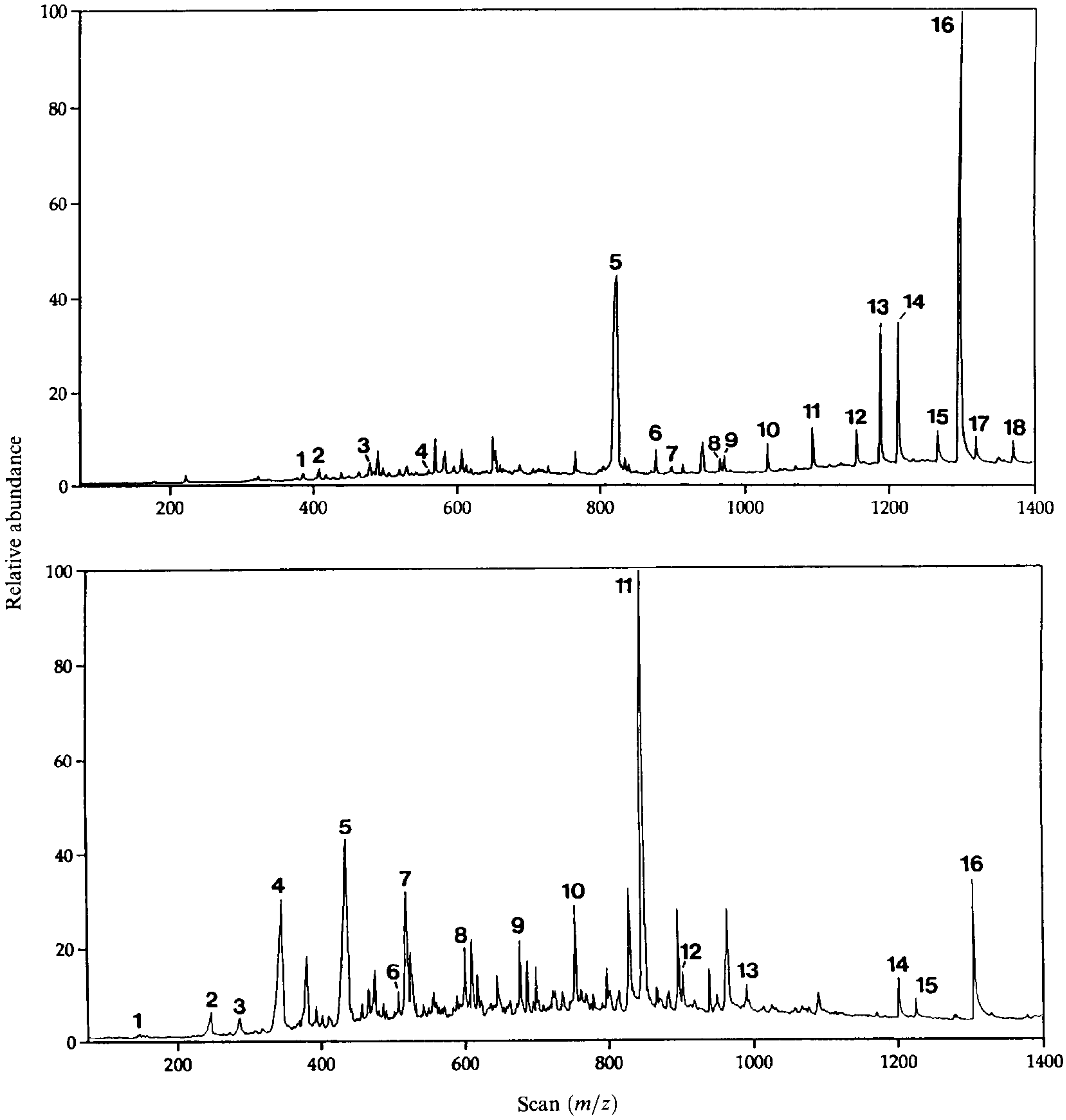


Figure 2 Ion chromatograms obtained by g.c.–m.s. of products formed after 15 months exposure of pre-oxidized samples (LDPE + 20%MB) to (a) *A. paraffineus* (biotic) and (b) sterile (abiotic) aqueous environments at ambient temperatures

*Fourier transform infra-red spectroscopy (*FT *i.r.)*

FT i.r. analyses were performed on a Perkin-Elmer 1725X. In the i.r. spectra, interest was focused on the carbonyl region. Carbonyl absorbance at 1718 cm^{-1} was measured relative to the CH_2 scissoring peak at 1463 cm^{-1}.

U.v.-vis. spectroscopy

U.v.-vis. absorbance spectra on the solid films were recorded by a Hewlett Packard 8451A diode array spectrophotometer in the range 190–500 nm.

Differential scanning calorimetry (d.s.c.)

Measurements of melting endotherms were made on a Perkin-Elmer DSC-7 calorimeter with sample weights of 5 ± 2 mg and a heating rate of 20°C min^{-1}. Calibration was made with indium ($T_m = 429.8$ K, $\Delta H_f = 28.46$ J g^{-1}). The first heating is used and the given values of the crystallinities from d.s.c. (d.s.c.-w_c) are the averages of three measurements, if not otherwise indicated. The degree of crystallinity is evaluated according to the base-line method proposed by Gray[18]:

$$w'_c = \frac{\Delta H_f}{\left[\Delta H^0_{T^0_m} - \int_{T_l}^{T^0_m} (c_{pa} - c_{pc})\,dT\right]} \qquad (1)$$

where ΔH_f is the value of the measured heat of fusion, c_{pa} and c_{pc} are the specific heats of amorphous and 100% crystalline phases of polyethylene, respectively, T^0_m is the equilibrium melting temperature and T_l is an arbitrary temperature below the melting range. Values of T^0_m(= 414.6 K), $\Delta H^0_{T^0_m}$(= 291.3 J g^{-1}), c_{pa} and c_{pc} for polyethylene were obtained from ref. 19. The value of $(c_{pa} - c_{pc})$ over the temperature interval in equation (1) is approximated with a nine-degree polynomial.

X-ray diffraction (XRD)

Measurements were carried out under vacuum using a Philips generator PW 1830 with nickel-filtered CuK_α radiation ($l = 1.542$ Å), a Warhus camera, and an Image Analysis System consisting of a Northern Light model

Table 1 Compounds formed and identified by g.c. after 15 months of exposure of pre-oxidized samples (LDPE + 20%MB) to sterile (abiotic) or *A. paraffineus* (biotic) aqueous environments at ambient temperatures

Figure no./peak no.	Compound	Abiotic environment	Biotic environment
2a/1	Hexanoic acid[a,b]	+	–
2a/2	Heptanoic acid[a,b]	+	–
2a/3	2-Ethylhexanoic acid[a]	+	–
2a/4	Octanoic acid[a,b]	+	–
2a/5 and 2b/1	Nonanoic acid	+	+
2a/7 and 2b/3	Decanoic acid[a,b]	+	+
2a/8 and 2b/4	Undecanoic acid[a,b]	+	+
2a/9	Dodecanoic acid[a,b]	+	–
2a/13 and 2b/8	Eicosane[a,b]	+	+
2b/10	Heneicosane[b]	–	+
2b/11	Docosane[a,b]	–	+
2b/12	Tricosane[b]	–	+
2b/15	Tetracosane[b]	–	+
2b/17	Pentacosane[b]	–	+
2b/18	Hexacosane[b]	–	+
2a/6	Dihydro-5-pentyl-2(3H)-furanone[a]	+	–
2a/10	11-Dodecene-2-one[a]	+	–
2b/2	3-Methyl-3-octanol[a]	–	+
2b/7	1-Hexadecanol[a,b]	–	+
2b/9	1-Hexadecanol, acetate[a]	–	+
2a/15 and 2b/14	Hexanedioic acid, dioctyl ester[a]	+	+
2a/11 and 2b/5	Benzenesulfonamide[a]	+	+
2a/12 and 2b/6	Butyl-8-methylnonyl phthalate[a]	+	+
2a/14 and 2b/13	Benzyl butyl phthalate[a]	+	+
2a/16 and 2b/16	Diisooctyl phthalate[a,b]	+	+

[a] Identification by mass spectroscopy by comparison with the NBS data base
[b] Identification by gas chromatography by comparison with standard retention indices

B90 light table, Dage MTI 70 series camera, DTK 486-33 MHz PC, Optimas software by Bioscan Inc., and a UN-Scorpion Framegrabber. The diffractogram were converted from light to intensity and analysed, assuming a linear Lorenz–Gaussian relation[20], using the Kaleidagraph 3.0 software with a Macintosh computer. The determination of intensities from film was made according to the procedure proposed by Baltá-Calléja and Vonk[21]. Corrections were made according to the procedure proposed by Kakudo and Kasai[22]. As a measure of the degree of crystallinity of the samples, we used[23]:

$$w_c = \frac{I_c^{110} + I_c^{200}}{I_a + I_c^{110} + I_c^{200}} \qquad (2)$$

where I_a and I_c^{hkl} are the areas under the amorphous halo and the *hkl* reflections, respectively. Additionally, the virgin linear LDPE was investigated by a counting method using a focusing Guinier-Hägg camera with transmission geometry, at the University of Stockholm. The values of crystallinity obtained by the film method were similar to those evaluated through the counting method, as has been reported earlier[24]. From the XRD reflections obtained, the dimensions of the lamellar thickness were determined according to the Scherrer equation[25]:

$$l_{hkl} = \frac{0.9\lambda}{b\cos\theta_{110}} \qquad (3)$$

where $2\theta_{110}$ is the Bragg angle and b is the corrected half-width of the respective reflection.

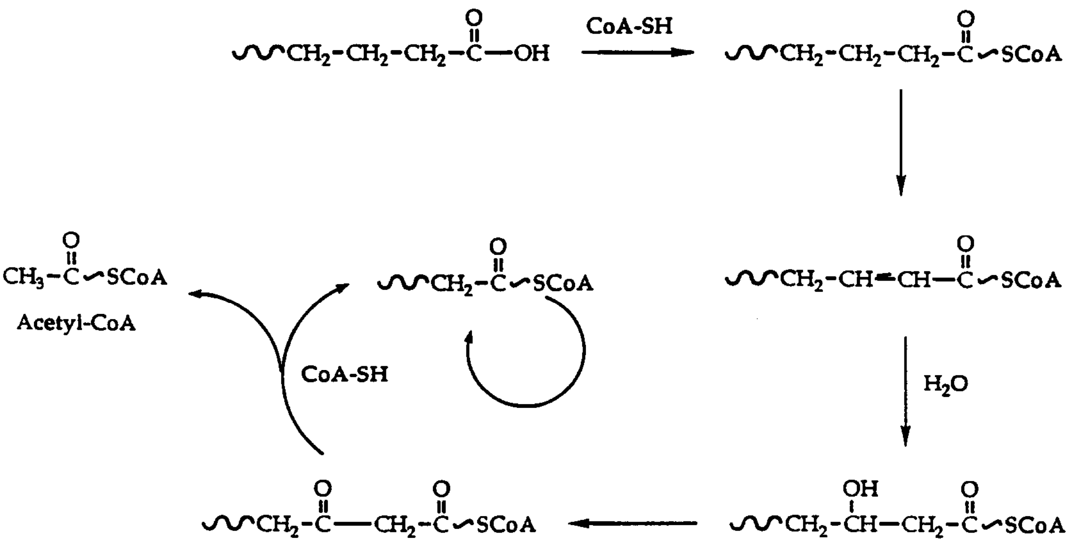
Scanning electron microscopy (SEM)

Specimen preparation was performed in liquid nitrogen (LN_2) and the sputtering material was applied from an Au/Pd cathode to a thickness of approximately 10 nm. Microscopy was performed on a Jeol SEM-5400 with an acceleration voltage of 20 kV and a working distance of 20 ± 5 mm.

RESULTS AND DISCUSSION

Degradation product pattern

The degradation of polymers is manifested in various ways. Chemical, physical and mechanical changes occur and may be followed by various techniques. Analyses of molecular weight changes and molecular weight distributions give the degradation rate and make it possible to distinguish between chain scission and the unzipping mode of degradation. *Figures 1a* and *b* show the number-average molecular weights (M_n) and weight-average molecular weights (M_w) for the thermo-oxidized LDPE, LDPE + 7.7% starch and LDPE + 20% MB. The pure LDPE reveals a monotonic decrease while both sample types with starch first decrease in molecular weight then increase, although with different initiation times. In the LDPE + 7.7% starch samples, the increase in average molecular weight is initiated at approximately 70 days of degradation and in the LDPE + 20% MB at approximately 30 days. This feature is due to cross-linking within the LDPE matrix and the difference



Scheme 1 Biotic conversion of carboxylic acids (β-oxidation)

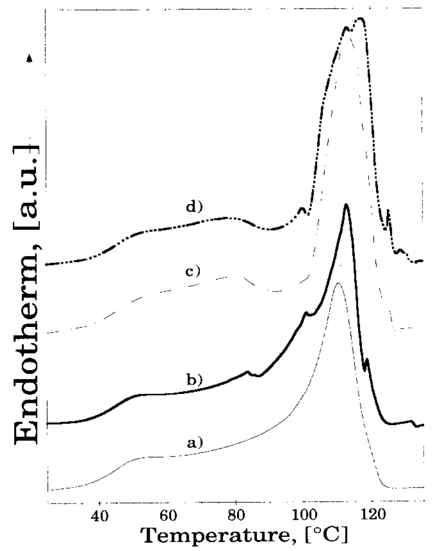


Figure 3 D.s.c. thermograms for aqueous abiotic and biotic LDPE + 20%MB aged at ambient temperature. (a) Sterile (abiotic; 3 years incubation); (b) *A. paraffineus* (biotic; 3 years incubation); (c) sterile (abiotic; 6 days pro-oxidation + 10 months incubation); (d) *A. paraffineus* (biotic; 6 days pro-oxidation + 10 months incubation)

Table 2 Crystallinities d.s.c.-w_c and XRD-w_c and l for LDPE + 20%MB exposed to sterile (abiotic) and *A. paraffineus* (biotic) aqueous environments. (For a new undegraded LDPE + 20%MB, d.s.c.-w_c = 38, XRD-w_c = 42 and l_{110} = 144)

Environment	Time	d.c.s.-w_c (%)	XRD-w_c (%)	l_{110} (Å)
Sterile	10 months[a]	38	50	149
A. paraffineus		37	48	143
Sterile	3 years	37	49	144
A. paraffineus		37	46	140

[a] Pre-incubated at 100°C for 6 days in order to shorten the induction time

between the systems is explained by the enhanced triggering features from the double bonds of SBS phase and the presence of transition metal (Mg) within the masterbatch of the starch + pro-oxidant additive.

The degradation mechanism governs, in principle, the type of degradation products obtained; in the case of biodegradation, micro-organisms can assimilate abiotic degradation products, thus complicating the resolving of the degradation product pattern of environmentally degraded polymers. *Figures 2a* and *b* display the g.c.–m.s. chromatograms of the products formed during abiotic and biotic degradation of LDPE + 20%MB. The amount of products in the lower molecular weight region was clearly lower in the biotic environment as a result of assimilation of these products by the bacteria. The nature of these products is revealed in *Table 1*, where the identified products are summarized. Carboxylic acid was previously established[12,16,17,26] as a major product category formed during the abiotic oxidation processes. In the biotic environment we observed the complete disappearance of the shortest chain acids as well as dodecanoic acid, while traces remained of nonanoic, decanoic and undecanoic acids.

The degradation mechanism of carboxylic acid *in vivo* takes place according to the β-oxidation of fatty acids removing two carbon fragments (*Scheme 1*). The process requires activation by adenosine triphosphate (ATP) and coenzyme A (CoA), and involves several enzymes. It takes place by dehydration, water rearrangement and a new dehydration step whereupon an acetyl–CoA fragment is formed, leaving behind a still activated acid. The activated acid repeatedly participates in the same process until the whole chain is split into two carbon fragments. The acetyl–CoA enters the citric acid cycle and is cycled and used in either the catabolic or the anabolic cycle. In the case of odd-chain fatty acids, the process is the same but yields propionyl–CoA. Branching can interfere with the degradation. Methyl groups in the α-position present no obstacles, the β-oxidation yields acetyl–CoA and propionyl–CoA. 2-Ethylhexanoic acid, with an ethyl group in the α-position, seemed to have been utilized, but perhaps according to a different mechanism.

Apart from the absence of low molecular weight carboxylic acids in the biotic environment, the lactone and ketone detected during abiotic degradation seem to

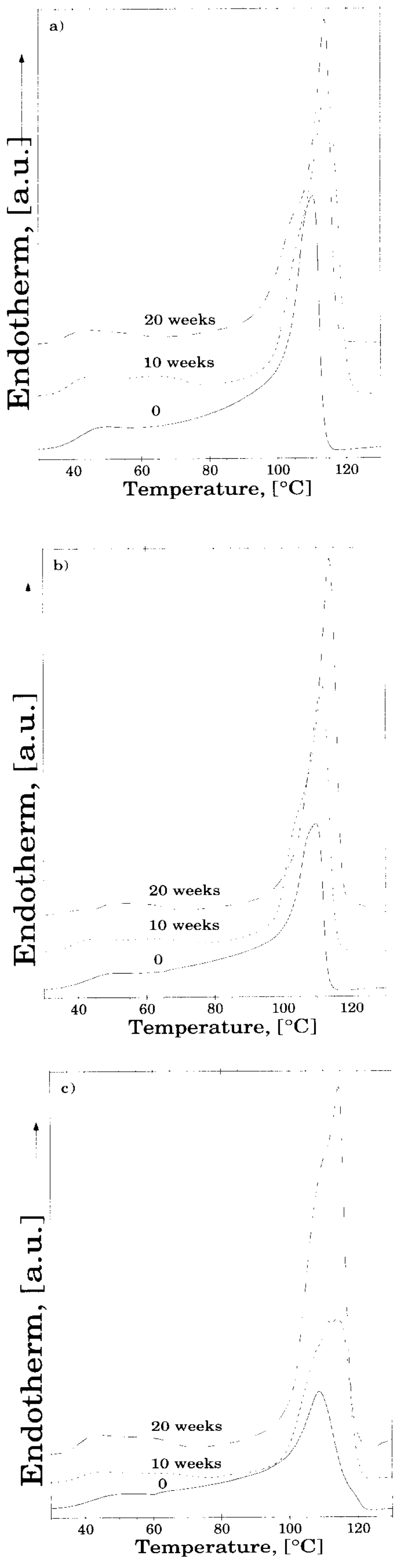


Figure 4 D.s.c. thermograms for thermo-oxidized samples. (a) LDPE; (b) LDPE + 7.7% starch; (c) LDPE + 20%MB. Degraded for 0, 10 and 20 weeks at 95°C in water

have been assimilated by the biotic environment. On the other hand, 3-methyl-3-octanol and 1-hexadecanol were detected only in the biotic environments, as were a series of n-alkanes C21–C26. Alkanes are not water soluble and therefore not inclined to be leached out easily upon their formation. The opportunities are, however, much increased if the permeability of the samples is enhanced, as in the biotic environment. The detected alkanes can be microbiologically metabolized through oxidation to carboxylic acid and then according to β-oxidation. The last four products in *Table 1* – the benzenesulfonamide and the different phthalates – are attributed to external contaminants introduced during the handling procedures.

The utilization of low molecular weight carboxylic acids as a carbon source by thermophilic fungi commonly found in composting refuse has been reported by Mills and Eggins[27]. These acids, of dicarboxylic type, had, however, been formed through partial oxidation of polyethylene by boiling with nitric acid. Similar studies, extended to include polypropylene and polystyrene, were later performed by Brown *et al.*[28].

The absence of carboxylic acids in biotically aged LDPE samples is thus a confirmation of the biodegradation mechanism proposed in 1987 where, based on *FT* i.r. analysis, we demonstrated a decrease in carbonyl index during biodegradation and from these analyses proposed the mechanism[11]. The subsequent lowering of the carbonyl index thus occurs simultaneously with the assimilation of soluble carboxylic acids in the biodegraded LDPE samples. The carboxylic acids are, however, present and easily identified in the abiotic samples.

Morphology changes

Figure 3 shows the d.s.c. thermogram of abiotically and biotically aged LDPE + 20%MB samples. The biotically aged samples exhibit multiple peaks associated with a distribution of lamellar sizes. An additional peak is observed for the samples exposed to *A. paraffineus* for 10 months, and the main peak is also considerably wider than the corresponding peak for samples exposed for 3 years. This can be explained by the gradual degradation of the imperfect crystallites leaving a more perfect material.

The XRD-w_c and lamellar thickness (l) demonstrate, for both degradation periods, large differences between the biotic and the sterile environments (*Table 2*). The sample exposed to *A. paraffineus* for 10 months has a w_c of 48% compared with 50% for the sterile one. The LDPE + 20%MB sample aged for 3 years shows a greater difference between the biotic and abiotic environments (46% compared to 49%). The lamellar thickness demonstrates the same type of behaviour; the lowest value (140 Å) was calculated for the LDPE + 20%MB sample aged biotically for 3 years. The initial value of l is 144 Å, which is also the value obtained in the sterile samples aged for 3 years.

D.s.c. thermograms in *Figure 4a* display the thermo-oxidation of pure LDPE from zero to 140 days of degradation. They all clearly exhibit wide main peaks composed of two-, three- or four-fold peaks with the main peak at around 112°C, indicating a broad distribution of lamellar sizes. As the degradation time is increased, the peaks become more pronounced and the mean peak occurs at a higher temperature, i.e. undegraded (sample LUN) 110°C, 71 days of

Table 3 Crystallinities d.s.c.-w_c and l for LDPE, LDPE + 7.7% starch and LDPE + 20%MB as a function of thermo-oxidation time (95°C for 0–20 weeks)

		Pure LDPE			LDPE + 7.7% starch			LDPE + 20%MB		
Sample designation	Degradation time (days)	d.s.c.-w_c (%)	XRD-w_c (%)	l_{110} (Å)	d.s.c.-w_c (%)	XRD-w_c (%)	l_{110} (Å)	d.s.c.-w_c (%)	XRD-w_c (%)	l_{110} (Å)
L/S/M-UN	0	42.7[a]	44.4	131	38.3[b]	41.1	126	37.5	42.5	144
L/S/M-1	7	42.9	45.3	130	42.0	47.1	166	39.3	51.5	171
L/S/M-2	14	41.9	48.6	166	39.7	45.7	158	38.9	60.3	160
L/S/M-3	21	40.3	47.9	154	40.0	46.3	161	38.6	56.9	165
L/S/M-4	28	39.2	47.1	156	40.1	51.1	177	37.9	63.6	172
L/S/M-5	35	38.9	45.4	152	41.8	49.3	180	40.0	56.3	164
L/S/M-6	42	40.0	44.8	163	41.5	51.9	174	41.2	59.8	170
L/S/M-8	57	42.3	53.0	147	40.1	53.2	156	41.1	61.8	161
L/S/M-10	71	42.6	53.7	154	41.1	52.9	164	41.9	61.6	165
L/S/M-20	140	42.3[c]	51.7	149	43.2[c]	56.9	173	45.3[c]	59.4	167

[a] An average of 11 measurements
[b] An average of nine measurements
[c] An average of two measurements

degradation (sample L10) 114°C, and 140 days of degradation (sample L20) 114°C. This behaviour is attributed to the increased formation of lamellar stacks with determined distributions of lamellar sizes. Similar features are revealed for the LDPE + 7.7% starch sample (*Figure 4b*), the main difference being that the processes commence at a later stage. The LDPE + 20% MB sample (*Figure 4c*) reveals evolution into several peaks, indicating more pronounced lamellar distributions. The main difference between the unaged and the aged LDPE + 20%MB samples is the constitution of the main peak, composed of two merging peaks in the range 110–114°C. As degradation proceeds, the ratio of (H_{114}/H_{110}) increases dramatically, indicating a transformation of the lamellar arrangement from one lamella thickness to a larger lamellar thickness. The increase in the ratio is attributed to the chain cleavage within the LDPE matrix, generating more linear chains which enable access to the lamellae of linear LDPE upon reorganization.

Table 3 presents the crystallinity (w_c), as obtained by d.s.c. and XRD, of samples thermo-oxidized for up to 140 days. In contrast to the w_c values of *Table 2* (biotic *versus* abiotic degradation), crystallinity increases slowly; however, the end XRD-w_c of LDPE + 20%MB is higher than both pure LDPE and LDPE + 7.7% starch. The greater crystallinity of the LDPE + 20%MB sample (60 ± 2%) as compared to pure LDPE (53 ± 2%) and LDPE + 7.7% starch (55 ± 2%) is explained by the presence of linear LDPE within the pro-oxidant. This phase and the degraded LDPE, i.e. more linear molecules, may cocrystallize as the LDPE is primarily degraded in the tertiary branch points. The lamellar dimensions given in *Table 3* demonstrate an increase in l with ageing time for all three sample types, which again is the opposite to the biodegraded samples given in *Table 2*.

Figures 5a–c show the SEM pictures of pure LDPE, LDPE + 7.7% starch and LDPE + 20%MB before (left-hand side) and after (right-hand side) 42 days of thermo-oxidation. The lateral surface of pure LDPE displays small but rough ridges which originate from the processing (*Figure 5a*). After degradation for 42 days, the ridges are still present but have become smoothened. In *Figure 5b* the lateral surface of the LDPE + starch sample is shown. The unaged sample has globules on an otherwise totally smooth surface. The globules are starch particles, entirely covered by the LDPE matrix. After degradation for 42 days (*Figure 5b* right-hand side), the surface is heavily transformed: the starch particles close to the lateral surface have disintegrated, generating collapsed areas which allow much greater access of oxygen to the LDPE matrix as the surface area to volume ratio is increased, and the lateral surface of the LDPE matrix contains cracks. These features are explained by the gelatinization of starch as water penetrates the starch granules and the starch is broken up. The LDPE + 7.7% starch sample shows more degradability than pure LDPE, mainly due to the creation of new surfaces. In *Figure 5c* the lateral surface of the LDPE + 20% MB is exposed. These images exhibit similar erosional changes to the surface upon degradation as the LDPE + 7.7% starch. In the LDPE + 20% MB, the presence of the prodegradant is severely affecting the degradation behaviour.

The morphology, as manifested by crystallinity and lamellae thickness, thus shows a clear difference between abiotic and biotic ageing. Constant or increasing values of w_c and l are observed in the abiotically exposed samples, while the corresponding biotically exposed samples show slowly decreasing values.

Agreement between degradation product pattern and morphology

Environmental degradation is a complex process in which both abiotic and biotic factors degrade polymers. We have earlier shown that *FT* i.r. analysis is a valuable tool for differentiating between abiotic and biotic degradation of LDPE[13]. In the abiotic environment, a continuous increase in the amount of carbonyl compounds with exposure time can be seen, contrary to the observed decrease in the biotically aged samples[11,13,14]. In the present paper this observation is related and compared to the differences in degradation product pattern and morphology. The principal difference between abiotic and biotic ageing is that microorganisms gain energy by degrading polymers and attack both crystalline and amorphous parts, while

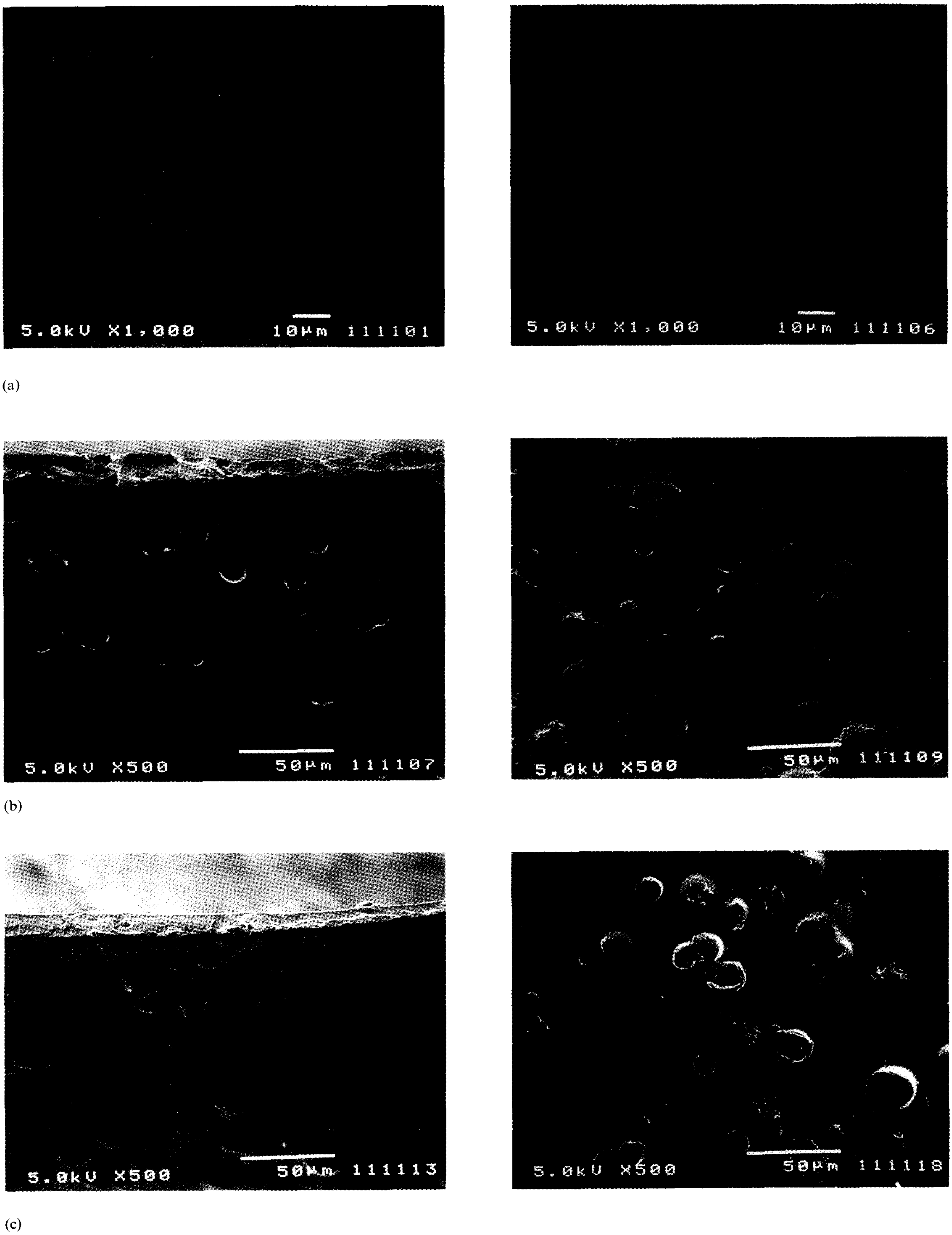


Figure 5 SEM images of (a) pure LDPE, (b) LDPE + 7.7% starch and (c) LDPE + 20%MB. Left-hand side, unaged samples; right-hand side, samples thermo-oxidized for 42 days

abiotic degradation results in the remaining polymer becoming more organized after release of the degradation products. This is observed as decreasing values of crystallinity and lamellar thickness in the biotic environment, and increasing values in the abiotic environment. We previously used the volatile organic acid pattern to differentiate two types of bacterial responsible for biodegradation of casein (a natural polymer) in concrete[29]. This concept of 'finger-printing' is well known in bacteriology (microbiology), where g.c. is used to distinguish between pathogenic bacteria. We now use the same concept of 'finger-printing' to describe the difference in degradation product pattern of a synthetic polymer (LDPE) degraded abiotically and biotically.

CONCLUSIONS

We have presented evidence showing that the degradation product pattern and morphology changes may be used to differentiate between physical/chemical (abiotic) and biotic degradation. The product patterns of biotically and abiotically aged degradable LDPE confirm that the biodegradation of LDPE takes place through the mechanisms proposed in ref. 11. By using the degradation product pattern obtained by g.c.–m.s. we now demonstrate that micro-organisms consume carboxylic acids (carbonyl compounds), which is observed both as a decrease with time of the carbonyl index and as an absence of carboxylic acids in biodegraded LDPE samples. We now compare this with the concept of 'finger-printing', previously demonstrated for volatile organic acids formed by biodegradation of a natural polymer (casein)[29], and show that the same type of 'finger-printing' is useful to differentiate between abiotic and biotic degradation of synthetic polymers. In parallel with this, the morphology is affected in a similar way: decreasing values of w_c and l in the biotic environment with time, and increasing values of w_c and l in the abiotic environment.

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