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Solid-phase extraction and gas chromatographic–mass spectrometric identification of degradation products from enhanced environmentally degradable polyethylene

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Abstract

A solid-phase extraction (SPE) method using unbonded silica (Si) and silica bonded with octadecyl (C_{18}) or aminopropyl (NH_2) groups was developed to separate into five fractions the highly complex mixture of low-molecular-mass degradation products formed from degradable polymers. Application of the method to polyethylene modified with starch and/or a pro-oxidant system, degraded for 30 weeks in water at 95°C, enabled the identification by GC–MS of over three times as many products as when the sample was prepared by liquid–liquid extraction. Over 60 degradation products were identified in each sample; mainly dicarboxylic acids, monocarboxylic acids and *n*-alkanes. In addition, several lactones, aldehydes and alcohols were detected.

1. Introduction

Environmental concerns have promoted the development of degradable plastics. To understand fully the environmental impact of such polymers, their degradation products need to be established. Environmental degradation involves not only biotic factors but also abiotic factors such as sunlight, heat, moisture and oxygen which give rise to products varying in composition, molecular mass and volatility.

The degradability of relatively inert synthetic polymers such as polyethylene (PE) can be significantly improved by incorporating additives that possess a sensitivity towards environmental degradation factors. We have studied PE containing native granular corn starch and a pro-oxidant formulation consisting of a styrene–butadiene copolymer and manganese stearate [1,2]. The first degradation step in such materials is an oxidation which can be triggered by heat, UV radiation, water etc. This oxidation may be enhanced by biodegradation of the starch granules, which produces voids leading to a greater surface/volume ratio and a greater oxygen permeability. In a secondary process, microorganisms may utilize the abiotic degradation products and low-molecular-mass polymer in anabolic and catabolic cycles [3]. The determination of the abiotic degradation products is thus an important first step towards establishing the products resulting from environmental degradation.

Degradation products from PE have been the focus of several studies but attention has mostly been directed towards determining the volatile

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products formed during short-term thermo-oxidation or pyrolysis [4–7]. Products resulting from thermo-oxidation at lower temperatures, i.e. in the solid state, have also been reported [8–12].In summary, PE yields a complex mixture of products such as water, CO, CO_2, hydrocarbons, carboxylic acids, ketones, aldehydes and cyclic ethers. If other components such as starch and pro-oxidants are incorporated into the formulation, their intermediate breakdown products and possible interactions further increase the complexity.

We have previously attempted to identify the degradation products of PE–starch–pro-oxidant materials resulting from aging at 95°C in aqueous environments [13].The aqueous phase was liquid–liquid extracted and subsequently subjected to GC–MS analysis. Highly complex chromatograms were obtained where many small peaks were obscured by larger ones which consequently limited the number of identifiable compounds. It was thus clear that it is desirable to develop some means of separating the degradation products prior to analysis by GC–MS.

Solid-phase extraction (SPE) has in recent years gained in popularity as a sample preparation technique due to its ability to selectively extract and isolate compounds of interest from various samples. The technique has found particular use in the selective extraction of steroids, lipids, peptides, drugs and pharmaceuticals from matrices such as plasma, blood, urine and culture media [14]. Bonded phase sorbents of silica gel with a wide variety of chemical functionalities are commercially available. They exhibit unusual dimensional stability, i.e. they do not swell or shrink, in virtually all organic solvents and may be used for extractions over a pH range of 1 to 14 [15]. These features make them attractive for the purpose of pre-separating complex mixtures of degradation products in aqueous matrices such as water or basal salt media.

In the present work, an SPE scheme employing bonded phase silica columns of octadecyl, aminopropyl and unbonded silica was developed for the class fractionation of degradation products formed during prolonged (30 weeks) thermal ageing in water at 95°C. The samples were PE containing pro-oxidants and/or corn starch. The extracted products were further separated and identified by GC and/or GC–MS. Products still remaining in the samples were monitored by Fourier transform infrared spectroscopy (FT-IR) at intervals throughout the degradation period. Changes in molecular mass were followed by high temperature size-exclusion chromatography (HTSEC).

2. Experimental

2.1. Materials and degradation procedure

Low-density polyethylene (LDPE) films (30 μm) were made by a conventional blown film process using a Betol extruder with a 25 mm screw of length/diameter ratio 20:1, a blow-up ratio of about 2.5:1 and a die temperature of 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. Pro-degradant additives were incorporated into the LDPE matrix in the form of a master batch in the amount of 20% consisting mostly of corn starch, styrene–butadiene copolymer (SBS), manganese stearate and linear low-density polyethylene (LLDPE) [16,17]. In some samples, the starch was omitted. The samples were all prepared in collaboration with Epron Industries. The degradation 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 condensors and immersed in a temperature-controlled hot water bath.

2.2. SPE procedure

After the chosen degradation time 25 ml water phase were withdrawn from each flask and extracted by an SPE scheme in portions of 5×5 ml. The sorbents used for extraction were three different chemically functionalized silica gels: silica bonded to octadecyl chains (C_{18}), silica bonded to aminopropyl chains (NH_2) and unbonded silica (Si), each packed in portions of

100 mg in disposable syringe carts. The C_{18} and Si columns were of the Isolute type from International Sorbent Technology (IST) while the NH_2 columns were of the Bond Elut type from Varian. The SPE method was developed using relevant standard compounds that had been chosen on the basis of earlier degradation studies on the same materials [13]. The standards used were fatty acids (C_4, C_6, C_9, C_{12} and C_{18}), benzoic acid, *n*-alkanes (C_9, C_{14}, C_{19} and C_{30}), 1-alcohols (C_6, C_8 and C_{14}), aldehydes (C_7, C_9 and C_{14}), 3-heptanone, 5-methyl-3-heptanone, 2-nonanone, 2-heptadecanone and γ-butyrolactone. Fig. 1 presents the SPE scheme for separation of these products. The procedure was as follows. The pH of the sample was adjusted to about 2. The C_{18} column was activated with methanol (2 ml) followed by water (2 ml, pH 2). The sample was then allowed to penetrate the reversed-phase bed merely by gravitation to ensure a sufficiently low flow-rate to allow interactions by the analyte and the sorbent to be established (this was also done with all the subsequent solvent passages through the sorbent). After very light drying by vacuum analytes were displaced by passing hexane (2 ml) through the column followed by methanol (2 ml). The hexane fraction was then passed through an NH_2 column that had been activated by hexane (2 ml). The column was washed with additional hexane (1 ml), then chloroform (1 ml) followed by final elution with 2% acetic acid in diethyl ether (3 ml), the last step according to Kaluzny et al. [18]. The combined hexane fractions (hexane fraction 2 + hexane wash) were passed through an Si column activated with hexane (2 ml). The column was washed with an additional ml of hexane and analytes eluted with dichloromethane (2 ml). The fractions of chloroform, diethyl ether, hexane 3 and dichloromethane were concentrated to 80 μl and the methanol fraction to 0.4 ml. The fractions were then subjected to GC–MS analysis.

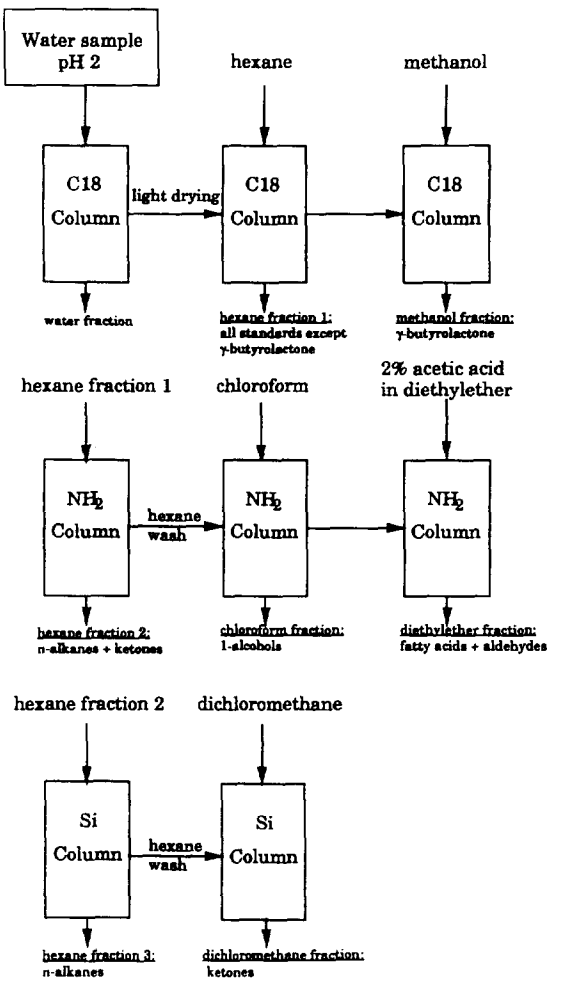

Fig. 1. Solid-phase extraction scheme for the extraction and fractionation of degradation products in aqueous matrices. Standard compounds used for the development of the scheme were fatty acids (C_4, C_6, C_9, C_{12} and C_{18}), benzoic acid, *n*-alkanes (C_9, C_{14}, C_{19} and C_{30}), 1-alcohols (C_6, C_8 and C_{14}), aldehydes (C_7, C_9 and C_{14}), 3-hepatanone, 5-methyl-3-heptanone, 2-nonanone, 2-heptadecanone and γ-butyrolactone.

2.3. GC–MS

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 μm, coupled to a Model VG-70-250SE mass spectrometer. The oven temperature was held at 50°C for 1 min, raised by 5°C/min to 310°C and held there 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 an electron

energy of 70 eV and an ion source temperature of 200°C. The resolution and scan rate were 1000 and 0.5 s/scan respectively. Compounds were identified by comparison with the national institute of standards and technology (NIST) data base.

2.4. GC

Chromatograms of degradation products and standard compounds were measured with a Varian 3400 gas chromatograph equipped with a J & W 30 m × 0.32 mm DB-5 column, film thickness 0.25 μm, and with a flame ionization detector. The oven temperature was held at 50°C for 1 min, raised by 5°C/min to 310°C and then held there for 10 min. Nitrogen was used as carrier gas. Identifications of compounds were made, complimentary to those by MS, by comparison of retention indices (relative diisooctyl phthalate or eicosane) with those of standard compounds that were analyzed by the same temperature program as the samples. For compounds identified solely by GC, relevant standard compounds were chosen on the basis of information obtained from the mass spectra.

2.5. Size-exclusion chromatography (SEC)

A Waters 150C HTSEC apparatus equipped with two PLgel 10 μm mixed-B columns was used to measure changes in molecular masses and distributions. The mobile phase was 1,2,4-trichlorobenzene (TBC) at 135°C and the flow-rate was 1 ml/min. Calibration was performed according to polystyrene standards.

2.6. FT-IR

FT-IR analyses were performed on a Perkin-Elmer 1725x. In the IR spectra special 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}.

3. Results and discussion

Both the samples, with and without starch, demonstrated a considerable loss of molecular mass during degradation as measured by SEC (Fig. 2). The samples without starch showed a slightly larger degradation. The reductions in molecular mass were accompanied by the formation of low-molecular-mass degradation products, some of diffused from the samples to the surrounding aqueous environment. These were separated by means of SPE and further characterized by GC–MS.

The aim of the SPE procedure was to achieve a class fractionation of the different products in order to facilitate the identification of the individual compounds. The five different fractions obtained by the SPE are those soluble in diethyl ether, hexane, methanol, chloroform and dichloromethane. Since the dominating products had previously been found to be fatty acids and hydrocarbons, emphasis was put on separately isolating these and they were found in the diethyl ether fraction and hexane fractions, respectively. Other products such as ketones and aldehydes were not as neatly class separated due to the

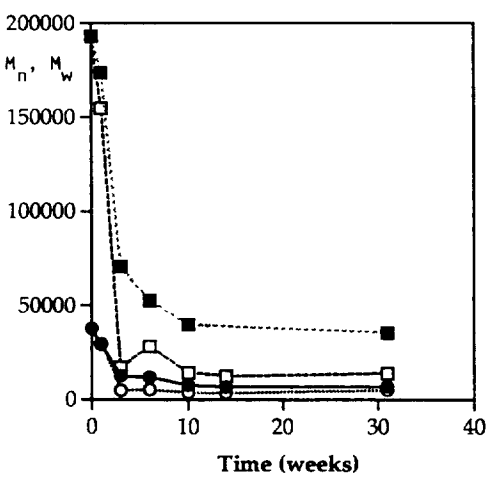

Fig. 2. Molecular mass (number average, M_n and weight average, M_w) as a function of time of degradation in water at 95°C. ● = LDPE + pro-oxidant + starch, M_n; ○ = LDPE + pro-oxidant, M_n; ■ = LDPE + pro-oxidant + starch, M_w; □ = LDPE + pro-oxidant, M_w.

wide range of differing polarities and some compounds were distributed in two fractions rather than one. The main part, however, was in one of the fractions as shown in Fig. 1. Fig. 3 shows typical gas chromatograms of a liquid–liquid extracted sample and of the five different fractions from the SPE of the same sample. This separation of the products enables each individual fraction to be adequately concentrated and reveals compounds which in the total product mixture are obscured by other compounds. A knowledge of the kinds of products to expect (in terms of polarity) also simplified the identification process. Earlier [13], when employing liquid–liquid extraction (LLE), we were typically able to identify about 20 degradation products in each sample, regardless of the actual number and amounts of products present. In fact, we have found that increasing the degradation time and thereby the amount of products forme often leads to a decrease in the number of identifiable compounds due to the additional complexity. The SPE method allowed us to identify about three times as many products in each sample as was possible in our earlier work employing LLE as the isolation step. The number of identifiable compounds in the LLE fraction was in this study very low. The chromatogram was similar to that of the methanol fraction from the SPE method, but only a few shorter fatty acids and dicarboxylic acids, benzoic acid and a series of furanones were identified. The SPE method thus proved to be a powerful separation method.

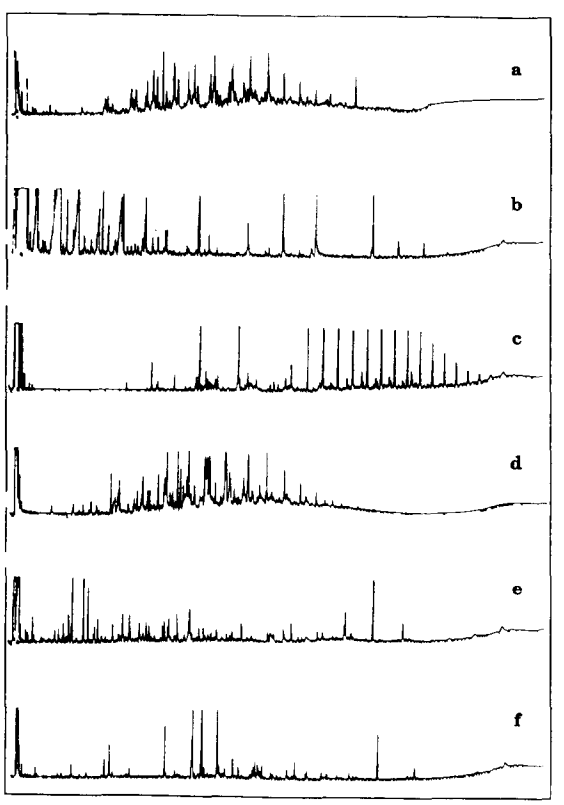

Fig. 3. Examples of GC chromatograms after liquid–liquid extraction (LLE) or solid-phase extraction (SPE), according to the scheme in Fig. 1, of degradation products present in water. The sample was LDPE + pro-oxidant degraded for 30 weeks in water at 95°C. (a) LLE with dichloromethane. (b) SPE, diethyl ether fraction. (c) SPE, hexane fraction. (d) SPE, methanol fraction. (e) SPE, chloroform fraction. (f) SPE, dichloromethane fraction.

The products identified in the different fractions are presented in Table 1. In the diethyl ether fraction mostly fatty acids ranging from C_6 to C_{22} were detected. Emulsions were often formed when using LLE, which is ascribed to the presence of fatty acids or other partly water-soluble compounds, and this reduced the extractability. Fatty acids were found in about the same yields from samples with starch and/or pro-oxidant. These compounds are one of the main types of degradation products formed, as established by earlier studies. A few branched acids were also identified. The formation of carboxylic acid is proposed as the result of various reactions involving alkoxy or peroxy radicals as precursors [8–11,16]. These radicals are formed in the initial autoxidation steps of the material. A possible route of carboxylic acid formation is a radical decomposition of hydroperoxide groups via aldehyde groups (Fig. 4) [9]. This is supported by the fact that only trace amounts of octanal and nonanal were found since the aldehydes serve only as intermediate products and are quickly further oxidized. Benzoic acid and benzaldehyde were identified from both sample types. These are known thermal degradation products from polystyrene [17,18], hence, we

Table 1
Compounds formed and identified after degradation of LDPE with starch and/or pro-oxidant in water at 95°C for 30 weeks

Compound	LDPE + pro-oxidant + starch	LDPE + pro-oxidant
Diethyl ether fraction		
2,2-Dimethylpropanoic acid[a]	–	+
Hexanoic acid[a,b]	+	+
Heptanoic acid[a,b]	+	+
2-Ethylhexanoic acid[a]	+	+
Benzoic acid[a,b]	+	+
Octanoic acid[a,b]	+	+
Nonanoic acid[a,b]	+	+
Decanoic acid[a,b]	+	+
Undecanoic acid[a,b]	+	–
Dodecanoic acid[a,b]	+	+
Tetradecanoic acid[a,b]	+	+
Pentadecanoic acid[a,b]	–	+
Hexadecanoic acid[a,b]	+	+
Octadecanoic acid[a,b]	+	+
Eicosanoic acid[a,b]	+	–
Docosanoic acid[a,b]	+	
Phthalic acid[a,b]		+
Benzaldehyde[a,b]	–	+
Octanal[a,b]	–	+
Nonanal[a,b]	+	+
2,6-Di-*tert.*-butyl-4-methylphenol[a,b]	+	+
Butyl-8-methylnonyl phthalate[a]	+	
Hexane fraction		
Dodecane[a,b]	–	+
Tridecane[a,b]	–	+
Tetradecane[a,b]	–	+
2-Methyltetradecane[a]	+	
Pentadecane[a,b]	+	+
Hexadecane[a,b]	+	+
3-Methylhexadecane[a]	+	–
Heptadecane[a,b]	+	+
Octadecane[a,b]	+	+
Nonadecane[a,b]	+	+
Eicosane[a,b]	+	+
Heneicosane[b]	+	+
Docosane[a,b]	+	+
Tricosane[a,b]	+	+
Tetracosane[a,b]	+	+
Pentacosane[b]	+	+
Hexacosane[a,b]	–	+
Heptacosane[a,b]	+	+
Octacosane[a,b]	+	+
Nonacosane[b]	–	+
Triacontane[b]		+
Hentriacontane[b]		-
Dotriacontane[b]		-
Tritriacontane	–	+
2,6-Di-*tert.*-butyl-4-methylphenol[a,b]	+	+
Butyl-8-methylnonyl phthalate[a]	-	–
Diisooctyl phthalate[a,b]	+	–

Table 1. *(continued)*

Compound	LDPE + pro-oxidant + starch	LDPE + pro-oxidant
Methanol fraction		
5-Methyldihydro-2(3H)-furanone[a]	+	–
5-Ethyldihydro-2(3H)-furanone[a]	+	+
5-Pentyldihydro-2(3H)-furanone[a]	–	+
5-Hexyldihydro-2(3H)-furanone[a]	–	+
4-Oxopentanoic acid[a]	–	+
Butanedioic acid[a,b]	+	+
Pentanedioic acid[a,b]	+	–
Benzoic acid[a,b]	+	+
2-Oxopentanedioic acid[a]	+	–
Hexanedioic acid[a,b]	+	–
7-Oxooctanoic acid[a]	+	+
Heptanedioic acid[a,b]	+	–
Octanedioic acid[a,b]	+	–
9-Oxodecanoic acid[a]	+	–
Nonanedioic acid[a,b]	+	–
Decanedioic acid[a,b]	+	–
Undecanedioic acid[a,b]	–	–
Dodecanedioic acid[a,b]	–	–
Chloroform fraction		
Hexadecanol[a,b]	+	–
Octadecanol[a,b]	+	–
2,4-Dimethyltetrahydrofuran[a]	–	+
2,5-Dipropyltetrahydrofuran[a]	–	+
5-Ethyldihydro-2(3H)-furanone[a]	–	+
5-Ethyldihydro-5-methyl-2(3H)-furanone[a]		+
5-Pentyldihydro2(3H)-furanone[a]	–	+
1,1-Diethoxyheptane[a]	–	+
Acetic acid, 1-methylethyl ester[a]	–	+
2,6-Di-*tert.*-butyl-4-methylphenol[a,b]	+	+
Benzyl butyl phthalate[a]	+	–
4-Nonylphenol[a]	+	–
Butyl-8-methyinonyl phthalate[a]	–	+
Diisooctyl phthalate[a,b]	–	+
Diisononyl phthalate[a,b]	+	+
Dichloromethane fraction		
1-Hexadecene[a,b]	–	+
1-Octadecene[a,b]	+	–
1-Eicosene[a,b]	+	–
2,6-Di-*tert.*-butyl-4-methylphenol[a,b]	+	+
Butyl-8-methylnonyl phthalate[a,b]	–	+
Diisooctyl phthalate[a,b]	+	–
Benzyl butyl phthalate[a]	+	–
Diisononyl phthalate[a]	+	–

Prior to analysis by GC and/or GC–MS the degradation products in the aqueous phase were extracted and fractionated by the SPE scheme shown in Fig. 1.

[a] Identification by MS by comparison with the National Institute of Standards and Technology (NIST).

[b] Identification by GC by comparison with standard retention indices.

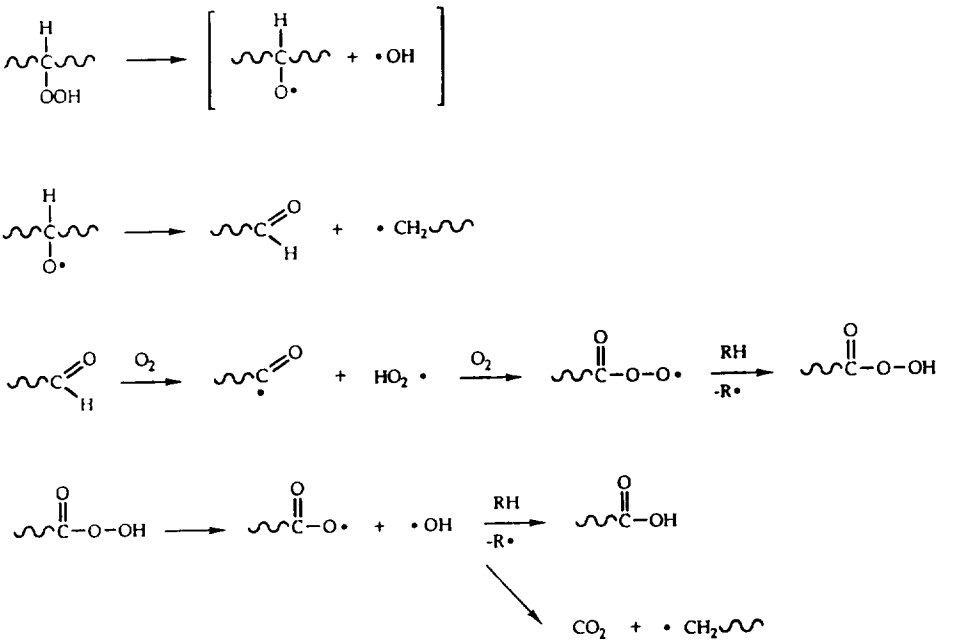

Fig. 4. Examples of carboxylic acid formation during degradation of LDPE.

attribute them to the breakdown of the styrene part of the SBS pro-oxidant.

Aliphatic hydrocarbons constitute another major class of breakdown products formed upon chain scission. A homologous series of *n*-alkanes, C_{12}–C_{33} as well as a few branched alkanes were the main components identified in the hexane fraction. Unsaturated hydrocarbons may be further oxidized and consequently only a few unsaturated hydrocarbons were found in any of the fractions. Only 1-hexadecene, 1-octadecene and 1-eicosene were detected in the dichloromethane fraction.

In both types of sample, with and without starch, the methanol fraction was about five times larger by mass than the other fractions and had an intense yellow colour. A number of species seemed to be responsible for this discoloration since no clear-cut absorption maximum was found in the visible range as observed by UV–Vis spectroscopy (data not shown). We were not able by GC–MS to identify specific compounds that could account for the yellow colour. Dicarboxylic acids dominated among the identified compounds. These can be formed according to the mechanisms for monocarboxylic acid formation involving a dual β-scission of alkoxy radicals. In previous degradation studies [13] we have not encountered these compounds, but they may be formed under the severe oxidation conditions applied in this study. Dicarboxylic acids have been reported as degradation products when polyethylene is oxidized in boiling nitric acid [19]. We detected the dicarboxylic acids as dimethyl esters since reaction had occurred with the methanol from the SPE extraction step. This derivatization reaction took place due to the prolonged contact of the analytes with the methanol and is an advantage since it facilitates the identification of the acids. The dicarboxylic acids were mainly determined from the samples containing starch, and this may be due to the fact that this material more easily allows the products formed to diffuse out to the surrounding environment. Other products in this fraction were a series of alkyl-substituted dihydro-2(3H)-furanones, some of which were also found in the chloroform fraction. In an earlier work [13] we suggested that the starch component contributed to the formation of these products. In this work,

however, these products were detected from both types of sample, with and without starch. The formation of γ-lactones can occur whenever carboxylic acid and hydroxyl groups are generated in the 1,4-positions of the polymer backbone [11]. The decomposition of 1,4-dihydroperoxides [23] according to Fig. 5, reaction 1, and/or through homolysis of a percarboxyl group, reaction 2 [19] are other possible mechanisms.

With the exception of hexadecanol and octadecanol, few alcohols were detected in the chloroform fraction and no ketones in the dichloromethane fraction. Owing to the extent of the degradation, these structures had most probably been further oxidized. We have earlier in less severe oxidation studies detected these types of compounds. Several compounds were detected in each fraction, which we assign to external contaminants introduced during the analytical handling procedure and impurities in the solvents used in the extraction. These include 2,6-di-*tert.*-butyl-4-methylphenol and several types of phthalate esters. The facts that these compounds were found in all fractions and that they are not normally additives in LDPE or the other components support this view.

With the exception of the dicarboxylic acids, we could establish no major differences in degradation behaviour between samples with and without starch by virtue of the degradation products. The SBS pro-oxidant is the primary component initiating the oxidation. As shown earlier [24], the transition metal salt, which is the other part of the pro-oxidant formulation, catalyses a decomposition of any hydroperoxides formed which is a crucial step in the onset of autoxidation [25]. If starch degradation occurs, this can promote the primary oxidative reactions due to the increased oxygen permeability and the increased surface/volume ratio. It also facilitates the release of degradation products from the samples. This can be achieved under biotic conditions when the starch granules are consumed, as by the action of hot water when the starch granules are disrupted.

Degradation products, either of the backbone type or trapped inside the films were monitored by FT-IR throughout the test period. Special interest was focused on the carbonyl region

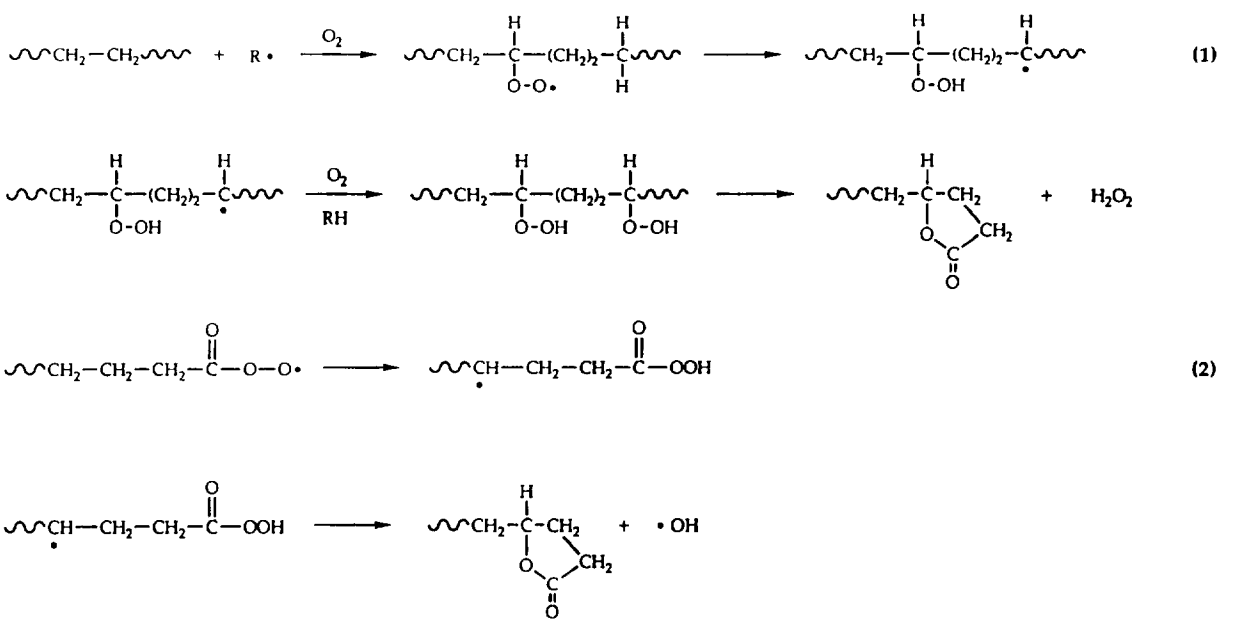

Fig. 5. Examples of γ-lactone formation during degradation of LDPE.

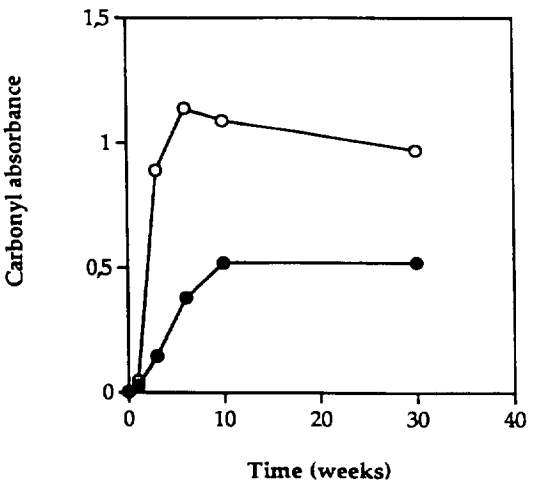

Fig. 6. Carbonyl absorbance as a function of time of degradation in water at 95°C. ● = LDPE + pro-oxidant + starch; ○ = LDPE + pro-oxidant.

which encompasses several types of compounds with a maximum absorbance at 1718 cm^{-1}. The carbonyl absorbance index is presented in Fig. 6 versus degradation time. The samples not containing starch display a sharp increase in carbonyl content, reaching a maximum after about 6 weeks, after which the absorbance decreases slightly while the samples containing starch reach a maximum which is less than half that value after about 10 weeks. Since the starch-containing samples were expected to allow more of the degradation products to diffuse out to the surrounding environment, these results are reasonable.

4. Conclusions

An SPE method based on solid sorbents of bonded silica of the octadecyl and aminopropyl type and unbonded silica type, has been developed for the separation of highly complex product mixtures. The method is applicable to the class fractionation of products obtained upon degradation of polymers. The products are separated into five different fractions which facilitates the qualitative identification by e.g. GC–MS due to the less complex chromatograms obtained, the possibility of adequately concentrating each fraction and the increased knowledge of what kind of products to expect. Application of this method to LDPE with starch and/or pro-oxidant degraded for 30 weeks in water at 95°C proved to be powerful and enabled the identification of over three times as many products as when liquid–liquid extraction was used followed by GC–MS. Over 60 degradation products were identified in each sample; mainly dicarboxylic and monocarboxylic acids, and *n*-alkanes. The rate of the oxidation processes is altered by the incorporation of additives but we have not, as yet, found that these additives alter the degradation products so as to render these materials less environmentally acceptable than in our earlier degradation studies of pure LDPE.

5. Acknowledgements

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