Loss and Transformation Products of the Aromatic Antioxidants in MDPE Film under Long-Term Exposure to Biotic and Abiotic Conditions

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ABSTRACT: The loss of a primary phenolic antioxidant Irganox 1010 and of a secondary phosphite antioxidant Irgafos 168 from a medium density polyethylene film (MDPE) was investigated after exposure of the film for 4 years to different environments such as aqueous media at pH5 and 7, open air, and compost, with an exposure of exposition of 25°C. An ultrasonic extraction technique using chloroform as extraction solvent was applied to recover the residual antioxidants from the polymeric matrix, and this was followed by High-Performance Liquid Chromatography (HPLC) with acetonitrile as mobile phase and a quantitative analysis at a wavelength of 280 nm of the extracted antioxidants. The amount of antioxidant lost varied remarkably depending on the testing medium. The fastest loss of antioxidant was found on exposure to open air and sunlight while the slowest loss was observed in compost. Thermo-analytical measurements were made to characterize the residual thermo-oxidative stability of MDPE film in terms of oxidation temperature and oxidation induction time, to provide a greater insight into the underlying mechanisms of ageing in the different environments. Analysis by Gas chromatography–Mass Spectrometry (GC-MS) revealed that degradation of the polymeric matrix resulted in the formation of hydrocarbons and oxygen-containing compounds such as alcohols, carboxylic acids, aldehydes, and esters. The transformation products of the antioxidants formed as result of processing or exposure to the tested media were also identified. The transformation of the phenoxy radical of the Irganox 1010 produced the ester, acid, dealkylated cinnamate, and quinone products, whereas Irgafos 168 yielded oxidation products and the phenolic hydrolysis byproduct 2,4-di-*tert*-butylphenol. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 974–988, 2002

Key words: polyethylene; degradation; additives; chromatography

INTRODUCTION

A large amount of polyethylene is used in the packaging industry, mostly as film. During the processing of the polymer, chemical reactions take place under the influence of heat, shear, and oxygen, and these change the structure of the chains and the properties of the processed material. To avoid these changes and to retain the inherent properties of the materials, stabilizers are added before processing, and this initiates new reactions resulting in the consumption of the stabilizers.[1]

Polymers in the environment undergo a gradual decomposition due to the effects of different factors, for example, light (photodegradation); moisture, air, temperature (chemical degrada-

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tion); wind (mechanical degradation) and macro- and/or microorganisms (biodegradation).[2] Degradation of polyolefins under the influence of UV-radiation, for example, can lead to failure of articles in outdoor applications. Stabilizers scavenge or neutralize the effect of deteriogens and thus prolong the lifetime of the plastic. Main classes of stabilizers include: chain-breaking antioxidants such as hindered phenols, hydroperoxide-decomposing antioxidants such as phosphites and others.

Hindered phenolic antioxidants are commonly used to stabilize synthetic thermoplastic polymers against oxidation. Oxygen, an efficient radical scavenger, generates peroxides that are quickly transformed into stable oxygenated products. Antioxidants act by the formation of peroxy radicals, mainly at the early stage of oxidative degradation. The ability of phenolic antioxidants to delay the oxidative degradation of polyolefins depends on their ability to interchange phenol and quinone structures.[3] The antioxidants undergo many chemical transformations and yield numerous transformation products as a consequence of their interceding to protect the polymers against the chemical effects of oxygen, heat, and light.[4,5]

Process stabilization is usually achieved with combinations of high molecular mass phenolic antioxidants and phosphites or phosphonites.[6–8] Organic phosphites are applicable to a wide range of polymers as synergistic costabilizers with phenolic additives, in addition to this ability to inhibit discoloration by decomposing hydroperoxides and by reacting with quinoidal conversion products of the hindered phenols.[9,10]

Low molecular additives introduced into a polymer can pass from the polymer into the environment, thus changing the polymer properties, reducing its service life, and polluting the environment and materials in contact with the polymer.[11] The solubility of stabilizers decreases dramatically during cooling and an oversaturated metastable state is created at room temperature. A diffusion-controlled equilibrium state is slowly formed, and is accompanied by stabilizer blooming to the surface.[12] Thus, a physical loss of the stabilizer can occur by diffusion towards the polymer surface during exposure and its subsequent removal from the surface by evaporation, washing out, or diffusion into the material in contact with the polymer.[11,13,14] A loss a stabilizer can also occur by photochemical reactions and degradation to smaller fragments.[8,12,15] Evaporation and

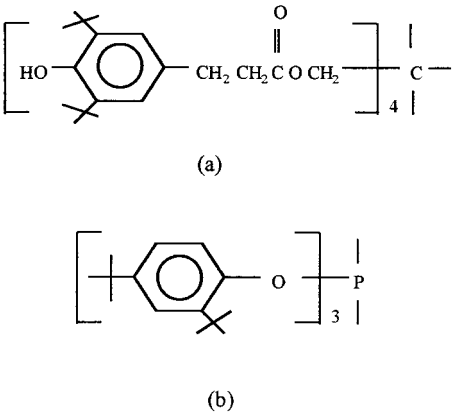


Figure 1 Structural formula of the antioxidants (a) Irganox 1010 (pentaerythrityl tetrakis [3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propionate)], and (b) Irgafos 168 [Tris(2,4-di-*tert*-butylphenyl)phosphite).

washing out are the main causes of this undesirable loss when the polymer is functioning in the open air and in contact with liquids.[11]

The physical loss of stabilizers depends upon numerous factors, in particular the solubility of the compounds, the nature of the additives, the environment, and the nature and geometry of the polymer samples. The most serious physical losses were observed from articles with a high surface-to-volume ratio, i.e., fibers, thin films, coatings, etc.[11,12] The physical loss of stabilizers accelerates the aging of polymers more than thermal oxidation or photo-oxidation.[16]

The aim of this work was to evaluate the effect of different environments on the loss of the hindered phenolic antioxidant Irganox 1010 and the aromatic phosphite antioxidant Irgafos 168 from a medium density polyethylene (MDPE) film, to identify possible transformation products of the additives and to investigate the susceptibility of the polymeric matrix to abiotic (chemical hydrolysis and photo-oxidation) and biotic (composting) degradation.

The structures of the antioxidants used in the MDPE film are shown in Figure 1.

EXPERIMENTAL

Materials

A medium density polyethylene (MDPE) film, 25 μm thick, containing two antioxidants, Irganox 1010 (220 ppm) and Irgafos 168 (1580 ppm), and two lubricants, Ca-stearate (750 ppm) and Zn-

stearate (750 ppm), was generously supplied by Borealis AS, Stathelle, Norway. The film is a medium density, strong, and relatively stiff polyethylene grade, suitable for a wide range of products such as sacks, pouches, carrier bags, refuse sacks, and liners.

Irganox 1010, i.e., pentaerythrityl-tetrakis(3-(3′,5′-di-*tert*-butyl-4′ hydroxyphenyl)-propionate and Irgafos 168, i.e., Tris-(2,4-di-*tert*-butylphenyl) phosphite were supplied by Ciba Specialty Chemicals Sweden AB, V. Frölunda, and used as received.

The processing of the polymer to incorporate the Irgafos 168 oxidized about 46% of the phosphite to the corresponding phosphate. A mixture of Irgafos 168 and its phosphate is, therefore, being studied.

The chloroform (p.a.) and acetonitrile (p.a.) solvents were bought from E. Merck, Darmstadt, Germany.

Exposure Conditions

UV-Irradiation and Air

The samples of MDPE film were exposed to air and direct sunlight for a period of 4 years at room temperature.

Composting

The simulated household compost used for exposure was prepared in a 270 l turnable composting facility insulated with 5 cm polyethylene foam and with no external heating. The starting mixture consisted of 48 % (v/v) dehydrated cow manure, 16 % (v/v) sawdust, 35 % (v/v) water, and 1 % (v/v) dried bacterial starter (Bio Composter™). Vegetables were also added (carrots, potatoes, and cabbage) on two occasions (at an interval of 3 weeks) to obtain suitable activity in the compost mixture. The composting time was 49 days. During the composting time, the temperature inside the compost varied between 3 and 34°C, and the pH varied between 6.3 and 6.5. The moisture content was 75 wt %.

The test samples and compost were placed in dark vessels with a solid-to-solid ratio of approximately 1 : 10, and were kept at room temperature for the whole exposure period of 4 years.

Chemical Hydrolysis

The hydrolysis was performed in a solution which simulates domestic waste leachate, consisting of 5000 ppm of acetic acid, buffered to pH 5 with sodium hydroxide,[17] and in distilled water at pH7 as a model of rainfall on waste disposited in bulk. The solid-to-liquid ratio was approximately 1 : 10, and both solutions were kept at room temperature for the whole exposure period of 4 years.

Extraction Procedure

The ultrasonic bath used for the extractions was a Branson 2210 MTH (47 kHz, 125 W), manufactured by Branson Ultrasonics BV, Soest, The Netherlands. The MDPE strips were placed in vessels with 15 mL chloroform to extract the antioxidants remaining in the polymeric matrix. In acccordance with the extraction procedure described previously,[18] these vessels were afterwards closed and placed in an ultrasonic bath at 60°C for 45 min. The chloroform phase was filtered through a Teflon filter with a pore size of 0.45 μm (Sorbent AB, V. Frölunda, Sweden) and analyzed by HPLC.

High-Performance Liquid Chromatography (HPLC)

Analysis of the antioxidants by HPLC was accomplished using a Perkin-Elmer Binary LC pump 250 fitted with a APEX I octadecyl, 3 μm 4.6 $\times$ 150 mm, column connected to a Perkin-Elmer diode array detector 235. The mobile phase was acetonitrile and the injection volume was 10 μL, with an analysis time of 30 min and a flow rate of 1 mL/min. The peak areas for the antioxidants were measured at 280 nm, and the retention times obtained were for Irganox 1010 and Irgafos 168 7.255 $\pm$ 0.3 and 26.050 $\pm$ 0.5 min, respectively.

Differential Scanning Calorimetry (DSC)

The thermo-oxidative properties of MDPE samples were studied in a Mettler-Toledo 820 DSC at a heating rate of 10°C/min in both nitrogen (crystallinity and melting temperature) and oxygen (oxidation temperature) atmospheres.

Values of the degree of crystallinity (α) were calculated based on the relationship $\alpha = \Delta H_s/\Delta H_c$ with a heat of fusion, ΔH_s, representing the experimental melting peak area and assuming a value of ΔH_c for 100% crystalline PE of 293 J/g. Tox was defined as the temperature at the intersection of the extended baseline with the extrapolated slope of the exotherm.

The oxidation induction time (OIT) was measured by first heating the polymer samples to

180°C in a nitrogen atmosphere at a heating rate of 10°C/min. Three minutes after the establishment of constant temperature, the atmosphere was switched to oxygen and the time (OIT) to the start of an exothermic (oxidation) process was measured under isothermal conditions. The OIT value was obtained by intersecting the extended baseline with the extrapolated slope of the exotherm signal.

All the results presented are based on the analysis of five replicate samples.

Gel Permeation Chromatography with Viscosity Detection (GPC-Viscosity)

GPC-Viscosity was carried out by RAPRA Technology Ltd., UK. The molecular weights were determined using a Waters 150CV instrument, with RI (concentration) and differential pressure (viscosity) detectors. The instrument was equipped with two PLgel 10 μm mixed-B (7.5 $\times$ 300 mm) columns. The solvent used for the analysis was 1,2-dichlorobenzene, the flow rate was 1.0 mL/min, and the temperature for the analysis was 140°C. The GPC-viscosity system was calibrated with polystyrene standards.

Gas Chromatography–Mass-Spectrometry (GC-MS)

The low molecular weight products were identified by a Finnigan GCQ Gas Chromatograph-Mass Spectrometer. The GC was equipped with a CP-Sil 8 CB column. The following conditions were set in the instrument: oven, 320°C; transfer line, 275°C, and scan mode, 35–650 amu. The column was first held at 40°C for 3 min, then programmed to 250°C at 10°C/min, and finally held at 250°C for 40 min. A split/splitless injector was used in the splitless mode and maintained at 250°C. Helium was used as carrier gas. The degradation products were identified by comparison of their mass spectra with the NIST MS database.

RESULTS AND DISCUSSION

The high-performance liquid chromatography results shown in Figure 2 reveal the change in antioxidant concentration in the MDPE film exposed to the various biotic and abiotic environments considered, expressed as percentages referred to the initial content. The amount of antioxidant lost varies remarkably, depending on the testing medium. For example, 61.51% of the Irganox 1010 and 63.19% of Irgafos 168 are consumed in the matrix on exposure to air and sunlight, compared with 23.65% of Irganox 1010 and 37.62% of Irgafos 168 in compost and 58.94% (55.62% at pH 7) of Irganox 1010 and 60.34% (58.43% at pH 7) of Irgafos 168 in water at pH 5.

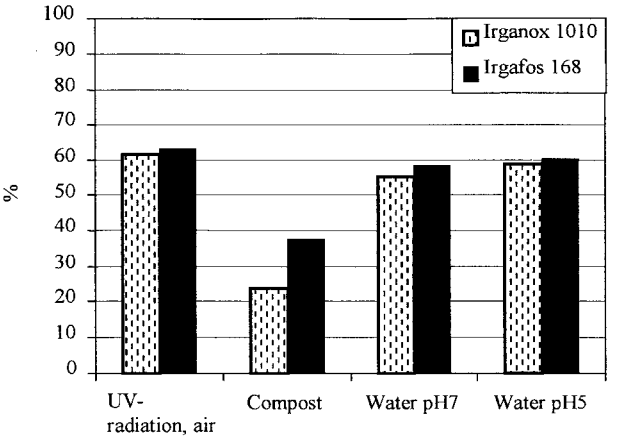


Figure 2 Loss of the antioxidants from the MDPE film exposed to the various environments.

The concentration of Irgafos 168 was found to be reduced slightly faster than that of Irganox 1010. However, Dörner et al.[19] pointed that, with the HPLC method the tetrafunctional primary antioxidant Irganox 1010 is detected only if none of the phenolic groups has reacted. In other words, if only one of the four phenolic groups has reacted, a stabilizer molecule is no longer detected by the HPLC technique used, although the remaining phenolic groups are still active. Thus, the true and effective residual Irganox 1010 concentration would be somewhat higher if those antioxidant molecules were taken into account in which one or more, but less than four phenolic groups have reacted. In the case of the secondary antioxidant Irgafos 168, on the other hand, both the original phosphite and its reaction product upon ageing, the corresponding phosphate can be determined quantitatively.

The more rapid consumption of the antioxidants under UV-radiation and air exposure is probably related to the high content of oxygen and the associated formation of hydroperoxides. Dörner et al.[19] demonstrated that while the concentration of Irgafos 168 is being reduced upon aging in air at higher temperatures (up to 105°C), the phosphate content in the material is increasing by the corresponding amount, the total concentration of both always being equivalent to the nominal original Irgafos 168 content. Thus, even at

high temperatures in air, evaporation of Irgafos 168 from MDPE is negligible, and the consumption of the antioxidant is primarily related to the oxidation of the phosphite to the corresponding phosphate.

The loss of stabilizer in water and compost environments occurs mostly by diffusion to the polymer surface followed by further extraction into the surrounding aqueous environment, due to diffusive effects. Because the content of the liquid phase in the compost is limited, the appearance of a concentration gradient responsible for the diffusion from the polymer surface into the surrounding environment will be favoured in a pure aqueous media, and this explains the faster release of the stabilizer in water than in compost. The slower consumption of the antioxidants in water and compost can be also explained by the much lower oxygen concentration. In a compost environment, the lower amount of O_2 is due partly to the high vapor pressure of water in the wet waste and partly to oxygen-consuming effects, combined with microbial phenomena.[20]

The release of both antioxidants proceeds slightly faster in water at pH 5 than at pH 7, probably due to the higher solubility of the antioxidants at the lower pH, which is related to their polar structure and which accelerates the desorption from the polymeric surface.

The migration of the stabilizer is confined to the more accessible amorphous regions of the polymer. One factor in polyethylene found to influence its susceptibility to degradation is its semicrystalline structure in which polymer chains pass through alternating thin lamellar crystalline and amorphous regions.[21]

Exposure of polyethylene films to UV-radiation in air leads to the uptake of oxygen, the formation of carbonyl, hydroxyl, and vinyl groups, the evolution of acetone, acetaldehyde, water, carbon monoxide, and carbon dioxide, an increase in brittleness, the formation of crosslinks, and the mechanical failure of the polymer samples. It has been shown that the crosslinking of polyethylene chains increases when the crystallinity decreases. The crosslinking promotes gel formation predominantly in the amorphous regions of the polymer.[22,23]

To evaluate the possibility of gel formation, the solution experiments were performed for all aged the MDPE samples in 1,2-dichlorobenzene at 140°C. The results of the solubility experiments and the DSC measurements are summarized in Table I.

Table I Results of Solubility Test in TCB and of DSC Measurements Performed on MDPE Films

Exposure Conditions	% Insoluble Polymer	α %	T_m, °C
Unaged	0	55.51	125.33
UV-light, air	40	54.27	128.22
Compost	24	61.21	126.82
Water pH7	4	61.62	127.17
Water pH5	2	61.81	127.24

Measurements of the crystalline fraction show a small apparent increase in crystallinity for compost-aged and water-aged samples, but a decrease in crystallinity for the air-aged sample. Moreover, an increase in melt temperature as well as in crosslinking was observed in all the MDPE samples aged under natural conditions. Although no insoluble components were found in unaged sample and only an insignificant amount of insoluble polymer was found in the water-aged MDPE samples, the compost-aged and air-aged samples revealed significant portions of insoluble gel material (about 24% and 40%, respectively).

The increase in crystallinity is a result of oxidative crystallisation and scission of constrained chains in the amorphous region; the chain scission allows the resulting freed segments to crystallize. This also provides evidence that oxidation during degradation is restricted to the amorphous phases during the initial stages.[24]

Thus, an increase in crystallinity in the case of the compost-aged sample is probably due to elimination by micro-organisms of the oxidized small chains located primarily in the amorphous phase.

The increase in crystallinity in the water-aged samples can, to some extent, be due to a plasticisation effect of the aqueous media, leading to an increased possibility for the small chains to migrate from the amorphous phase and crystallize.

The very small amount of insoluble material in the water-aged samples (about 2 and 4%) and the increase in crystallinity imply that only negligible crosslinking takes place in the amorphous phase of MDPE and the chain scission occurs to a much stronger extent. In the case of the compost-aged sample, the small increase in crystallinity and, at the same time, the significant amount of insoluble polymer (about 24%) demonstrate that the tendency for postcrystallization to occur balanced by crosslinking reactions. In contrast, the air-aged

sample exhibits a decrease in crystallinity, and the domination of the crosslinking reaction in the amorphous phase (amount of insoluble material is about 40%). Thus, the tendency for postcrystallization to occur is in this case clearly outweighed by crosslinking reactions. The antioxidants inhibit crosslinking due to a reaction with active macroradicals of polyethylene,[25] and the greater extent of crosslinking in the air-aged sample can be likely explained by the higher amount of lost antioxidants.

The fact that postcrystallisation takes place as a result of the ageing process is confirmed by the increase in melt temperature. In addition, the oxidation processes taking place can result in the development of polar groups on the macromolecules of MDPE, bringing about a possible amplification of the intermolecular interactions in the polymer matrix due to hydrogen bonds and dipole–dipole interactions, and thus contributing to a rise in the melting point and heat of fusion.

The GPC-viscosity measurements did not show any significant differences in the molecular weight or branching of the tested samples.

There was some correlation between the stabilizer content and the thermo-oxidative stability of the polymeric matrix. When the concentration of antioxidant was increased, the onset of oxidation was delayed and an increase in the OIT was observed. A linear relationship between the concentration of the antioxidant and the OIT has been found for combinations of phenolic and phosphite stabilizers.[26]

The effects of the residual amounts of Irganox 1010 and Irgafos 168 on the Tox and OIT of the MDPE film are shown in Figures 3 and 4, respectively.

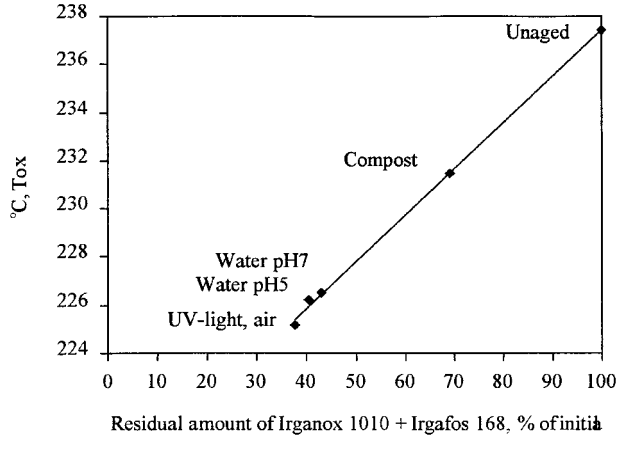


Figure 3 Effect of the residual amount of the antioxidants on Tox of the MDPE film.

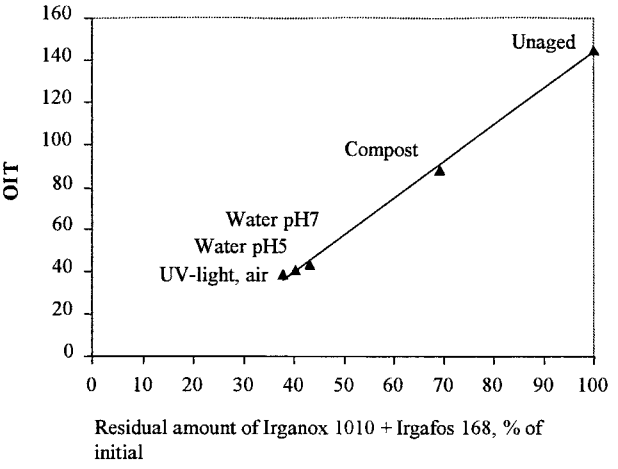


Figure 4 Effect of the residual amount of the antioxidants on OIT of the MDPE film.

The oxidation temperature, Tox, and oxidation induction time, OIT, decrease in all cases as a result of exposure to the various environments, indicating the occurrence of a material aging process (Figs. 3 and 4). The greatest decrease in the Tox and OIT takes place during exposure to UV-radiation and air, when Tox decreases from 237.42°C for unaged sample to 225.17°C and OIT decreases from 145.03 to 38.47 min. Samples exposed to a compost environment exhibit the smallest decrease of Tox to 231.50°C and OIT to 88.56 min. The differences in the oxidation behavior of the polymeric matrix exhibit a linear dependence on the amount of consumed/migrated antioxidants and, in this sense, the changes in oxidation temperature and OIT as measured by DSC were found to be in good agreement with the changes in the amount of antioxidant remaining in the polymeric matrix measured by HPLC.

Photo-oxidation plays a major role in the degradation of polyethylene exposed to UV-radiation. The physical and chemical changes occurring involve the increase in concentration of a variety of oxygen-containing groups in addition to the promotion of crosslinking and chain scission. The oxygen-containing groups include hydroperoxide, peroxide, and various carbonyl-containing moieties, in particular, the ketonic carbonyl. These initiate further photo-oxidation in the polymer by undergoing reactions of the Norrish I and II types typically observed during the oxidation of hydrocarbons.[27,28]

Figures 5 and 6 show the GC-MS chromatograms of the degradation products formed in the

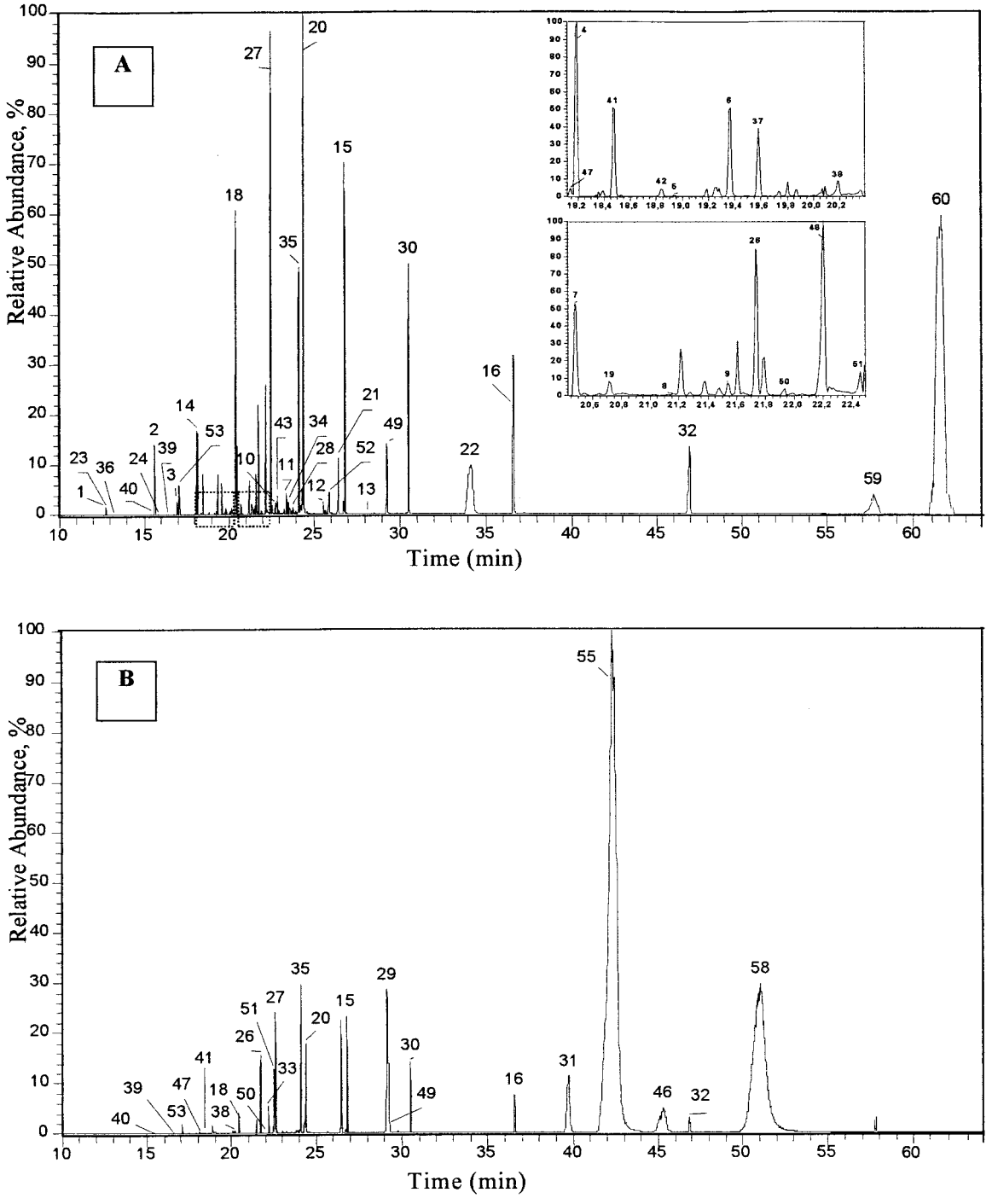


Figure 5 GC-MS chromatogram of the degradation products formed in the MDPE exposed to (A) air and (B) compost.

MDPE exposed to the various environments and extracted by chloroform. A variety of degradation products have been identified in the different MDPE samples, including hydrocarbons and oxygen-containing compounds.

Table II presents the low molecular weight degradation products identified by GC-MS.

The main components found were linear and branched alkanes, alkenes, alcohols, carboxylic acids, aldehydes, and esters. Among the degrada-

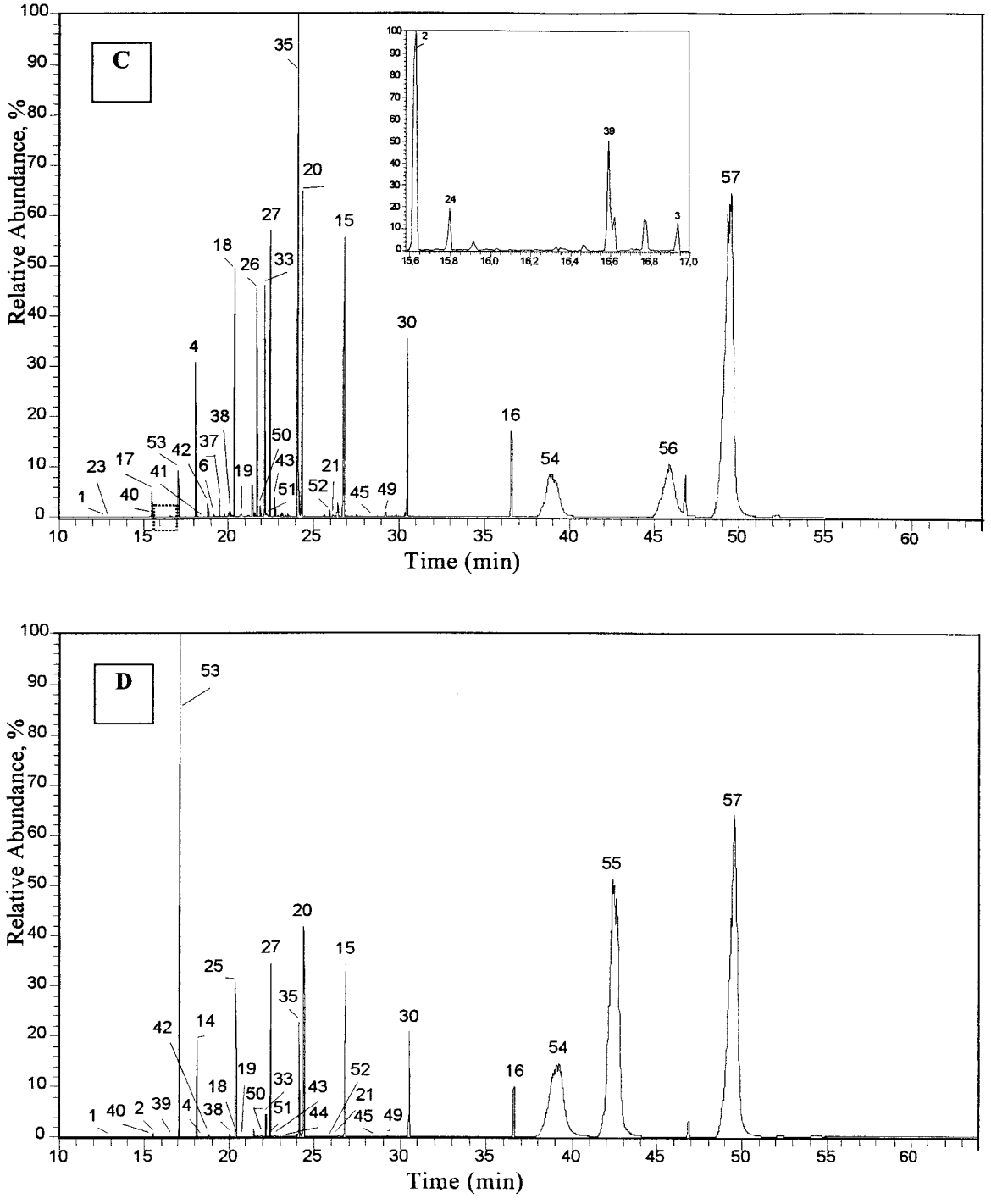


Figure 6 GC-MS chromatogram of the degradation products formed in the MDPE exposed to (C) water at pH 5 and (D) water at pH 7.

tion products, alkanes, alkenes, and alcohols were found in homologous series. Alcohols are formed principally by reactions of peroxy and hydroperoxy radicals.

Most degradation products were formed in the samples exposed to UV-radiation and air, indicating a greater extent of degradation in this media. The predominant compounds observed in the samples aged in the open air under direct sunlight were oxygen-containing compounds such as alcohols, carboxylic acids, aldehydes, and esters. A range of alkanes and alkenes were also formed.

Table II Degradation Products Identified in the MDPE Exposed to the Abiotic and Biotic Environments

Peak No.	Compounds	RT, min	Air	Compost	Water, pH5	Water, pH7
	Alkanes					
1	Dodecane	12.78	+		+	+
2	Tetradecane	15.68	+		+	+
3	Pentadecane	16.99	+		+	
4	Hexadecane	18.22	+		+	+
5	4,9-Di-*n*-propyldodecane	18.89	+			
6	Heptadecane	19.40	+		+	
7	Octadecane	20.49	+			
8	3-Methyloctadecane	21.17	+			
9	Eicosane	21.55	+			
10	Tetracosane	22.64	+			
11	Pentacosane	23.24	+			
12	Nonacosane	25.26	+			
13	Dotriacontane	28.12	+			
	Cycloalkanes					
14	Cyclotetradecane	18.10	+			+
15	Cyclotetracosane	26.81	+	+	+	+
16	Cyclooctacosane	36.57	+	+	+	+
	Alkenes					
17	Tetradecene	15.56			+	
18	1-Octadecene	20.44	+	+	+	+
19	1-Nonadecene	20.77	+		+	+
20	1-Eicosene	24.41	+	+	+	+
21	1-Docosene	26.18	+		+	+
22	13-Methyl-Z-14-nonacosene	34.15	+			
	Alcohols					
23	*cis*-7-Dodecen-1-ol	12.88	+		+	
24	(Z)6-Pentadecen-1-ol	15.81	+		+	
25	1-Heptadecanol	20.40				+
26	5-Nonadecen-1-ol	21.79	+	+	+	
27	1-Eicosanol	22.50	+	+	+	+
28	2-*cis,cis*-9,12-Octadecadienyloxyethanol	23.78	+			
29	1-Pentacosanol	29.16		+		
30	1-Hexacosanol	30.50	+	+	+	+
31	1-Triacontanol	39.73		+		
32	Tetratriacontanol	46.93	+	+		
	Carboxylic acids					
33	*n*-Hexadecanoic acid	22.16		+	+	+
34	(E)-9-Octadecenoic acid	23.41	+			
35	Octadecanoic acid	24.14	+	+	+	+
	Aldehydes					
36	2,5-Dimethyl-benzaldehyde	13.18	+			
37	(Z)-9,17-Octadecadienal	19.58	+		+	
38	3,5-di-*tert*-Butyl-4-hydroxybenzaldehyde	20.21	+	+	+	+
	Ketones					
39	*p*-Benzoquinone, 2,6-di-*tert*-butyl-	16.64	+	+	+	+
	Esters					
40	Benzoic acid, butyl ester	15.45	+	+	+	+
41	Dodecanoic acid, 1-methylethyl ester	18.47	+	+	+	
42	Decanoic acid, cyclohexyl ester	18.88	+		+	+
43	Hexadecanoic acid, 1-methylethyl ester	22.81	+		+	+

Table II *Continued*

Peak No.	Compounds	RT, min	Air	Compost	Water, pH5	Water, pH7
44	1-Docosanol, formate	23.34				+
45	2-Tetracosanol, acetate	28.37			+	+
46	(Z,Z)-9-Hexadecenoic acid, 9-octadecenyl ester	45.37		+		
	Phthalates					
47	Diethyl Phthalate	18.17	+	+		
48	Dibutyl phthalate	22.25	+			
49	Bis(2-ethylhexyl) phthalate	29.33	+	+	+	+
	Degradation products from Irganox 1010					
50	Methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate	21.91	+	+	+	+
51	3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid	22.45	+	+	+	+
52	2-Propenoic acid,3-(4-methoxyphenyl)-,2-ethylhexyl ester	25.96	+		+	+
	Degradation products from Irgafos 168					
53	2,4-di-*tert*-Butyl-phenol	17.09	+	+	+	+
54	Derivated phosphate	39.23			+	+
55	Derivated phosphite	42.41		+		+
56	Derivated phosphate	45.80			+	
57	Drivated phosphite	49.55			+	+
58	Derivated phosphate	51.06		+		
59	Derivated phosphate	57.70	+			
60	Derivated phosphite	61.43	+			

In the case of the samples aged in water, the unoxidized hydrocarbons, such as alkanes and alkenes, are represented to almost the same extent as oxidation products such as alcohols, ketones, and esters. Because more degradation products were formed in the samples exposed to chemical hydrolysis at pH 5 than at pH 7, these is a greater degradation of the MDPE matrix in this case and this contributes to explain the faster release of the antioxidants at pH 5 than at pH 7.

In case of samples aged in compost, the predominant products observed were oxygen-containing compounds.

The solvent-extractable transformation products were produced from Irganox 1010 after exposure to the tested environments by cleavage of the molecules from the parent compound and oxidative transformation of the hindered phenol units. The mass spectra and structures of the three main products are presented in Figure 7.

The mass spectra of methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate [Fig. 7(A)] and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid [Fig. 7(B)] exhibit the molecular ions $M^{+\cdot}$ at *m/z* 292 ($C_{18}H_{28}O_3$) and at *m/z* 278 ($C_{17}H_{26}O_3$), respectively. In both cases the most intense fragment ions, *m/z* 277 and *m/z* 263 in the corresponding spectra, are assigned to the molecular ion minus a methyl group. Further fragmentation yields similar ion peaks for both compounds due to their similar structures. The presence of the *m/z* 91 ion peak is attributable to the tropylium ion and the peak at *m/z* 57 is due to a *tert*-butyl fragment.

The mass spectrum of 2-ethylhexyl *p*-methoxycinnamate [Fig. 7(C)] exhibits the molecular ion $M^{+\cdot}$ at *m/z* 290 ($C_{18}H_{26}O_3$). The fragment ion *m/z* 178 is suggested to be generated by the loss of the ethylhexylic group from the molecular ion. The fragment ion at *m/z* 77 is attributable to the benzenium ion. In contrast to the other two cases, no ion peak appears at *m/z* 57 because of the absence of the *tert*-butylic group.

The abundance of the transformation products of Irganox 1010 formed in the various environments is shown in Figure 8.

As shown in this figure, methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate was formed as result of processing and was found in the unaged sample. The amount of this compound decreased after exposure to all of the tested media, but the greater consumption was detected in the compost environment. The formation of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid was observed in all cases, and was greater in water at pH 5. Oxidative transformation of hindered phenol

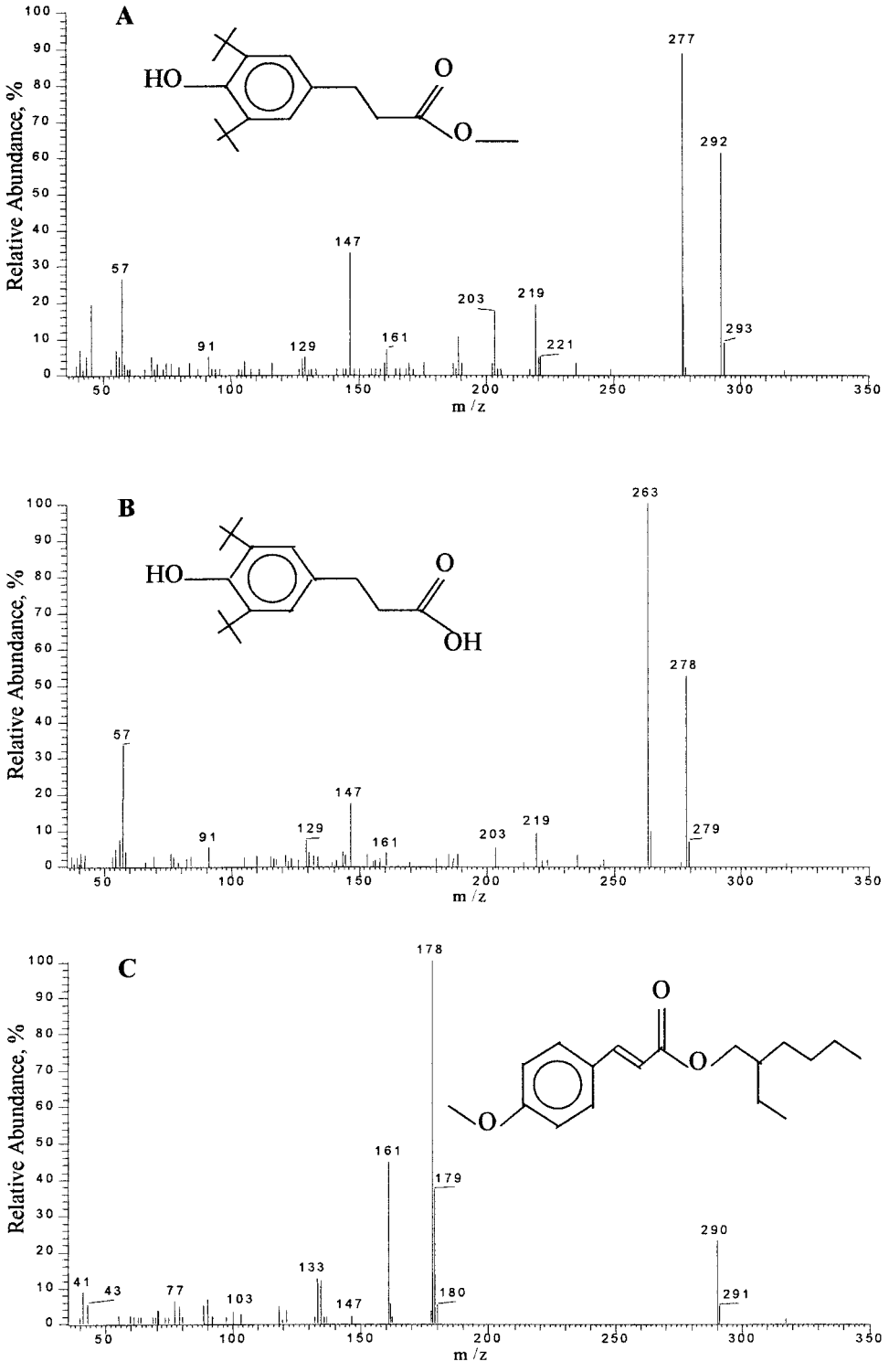


Figure 7 The structures and mass spectra of the degradation products of Irganox 1010: (A) methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate; (B) 3-(3-di-*tert*-butyl-4-hydroxyphenyl) propionic acid; (C) 2-ethylhexyl *p*-methoxycinnamate.

units led to the formation of the debutylated cinnamate ester: 2-ethylhexyl *p*-methoxycinnamate [Fig. 7(C)], which was found in air and water environments, but not in compost. According to Allen et al.,[29] such dealkylations probably arise as a result of the generation of acidic conditions in

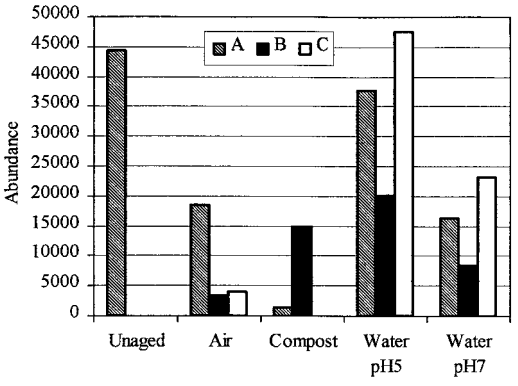


Figure 8 Abundance of the degradation products of Irganox 1010 before and after exposure to the various environments: (A) methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate; (B) 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionic acid; (C) 2-ethylhexyl *p*-methoxycinnamate.

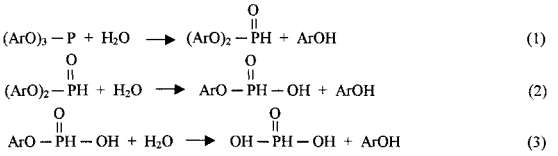
the polymer, which is confirmed by the fact that the largest amount of the ester was formed during exposure to water at pH 5.

If the transformation compounds still retain hindered phenol functionality, such as methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid, they will continue to be effective as stabilizers and may undergo further progressive transformation. The 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde found in all the polymer extracts is a result of such a transformation. Another oxidative transformation product, 2,6-di-*tert*-butylbenzoquinone, was also detected in all the polymer extracts. This product caused a certain light yellowing of all the aged MDPE films, and is a common product of the oxidation of such hindered phenols.[26,29,30]

The stabilizing function of the organic phosphites is based on the presence of the phosphite moiety. The two basic conversion products of Irgafos 168 are the phosphate that forms as a result of oxidation and the phosphonate that forms as a result of hydrolysis. Both the phosphate and the phosphonate are pentavalent, and this valence renders them ineffective as processing stabilizers because the lone pair of electrons on the phosphorus is involved in the stabilization process.[31]

About 46% of the phosphate degradation product of Irgafos 168 was already formed in the unaged sample of MDPE film as a result of the polymer processing.

Phosphites are sensitive to hydrolysis, resulting in depletion of the antioxidative active species.[32] The hydrolysis of Irgafos 168 is shown in Scheme I.[10]



The hydrolysis follows a reaction sequence in which bis(2,4-di-*tert*-butyl-phenyl)phosphonate is formed initially (reaction 1 in Scheme I) together with the free-phenol byproduct 2,4-di-*tert*-butylphenol (2,4-DTBP). The phosphonate formed in reaction 1: reacts further with water to produce the hydrophosphate (reaction 2). On completion of the hydrolysis reaction (reaction 3), phosphorous acid is formed. In each reaction, 2,4-DTBP is formed as the byproduct. The slight antioxidant behavior of degraded Irgafos 168 at low temperature was attributed to the presence of the 2,4-DTBP byproduct.[10]

The 2,4-DTBP product was found in all the MDPE extracts (see Table II), implying that hydrolysis took place to some extent in each of the tested environments. Its concentration was especially high in the sample exposed to hydrolysis at pH 7.

Figure 9 shows the mass spectra of 2,4-DTBP, Irgafos 168, and its phosphate degradation product. The Irgafos 168 and its phosphate were first identified in the unexposed sample, and showed retention times of 25.93 and 34.82 min.

The mass spectrum of 2,4-DTBP [Fig. 9(A)] exhibits the molecular ion $M^{+\cdot}$ ($C_{14}H_{22}O$) *m/z* 206. The intense fragment ion at *m/z* 191 is generated from the molecular ion by the loss of the methyl group. In the phosphite mass spectrum [Fig. 9(B)] the molecular ion $M^{+\cdot}$ is present at *m/z* 646, and the most intense peak at *m/z* 441 is assumed to be formed by loss of 2,4-di-*tert*-butylphenoxyl group from the molecular ion. In turn, an intense peak at *m/z* 647 in the spectrum of phosphate [Fig. 9(C)] is assigned to the fragment ion formed by the loss of a methyl group from the molecular ion $M^{+\cdot}$ at *m/z* 662. The abundant ion peak at *m/z* 316 in the mass spectrum of the phosphate is totally absent in the spectrum of the phosphite. The 2,4-di-*tert*-butylphenol species are present at *m/z* 206 in both the phosphite and phosphate spectra. The fragment ion *m/z* 91 attributable to the tropylium ion and the fragment ion *m/z* 57 assigned to a *tert*-butyl fragment are present in the all spectra.

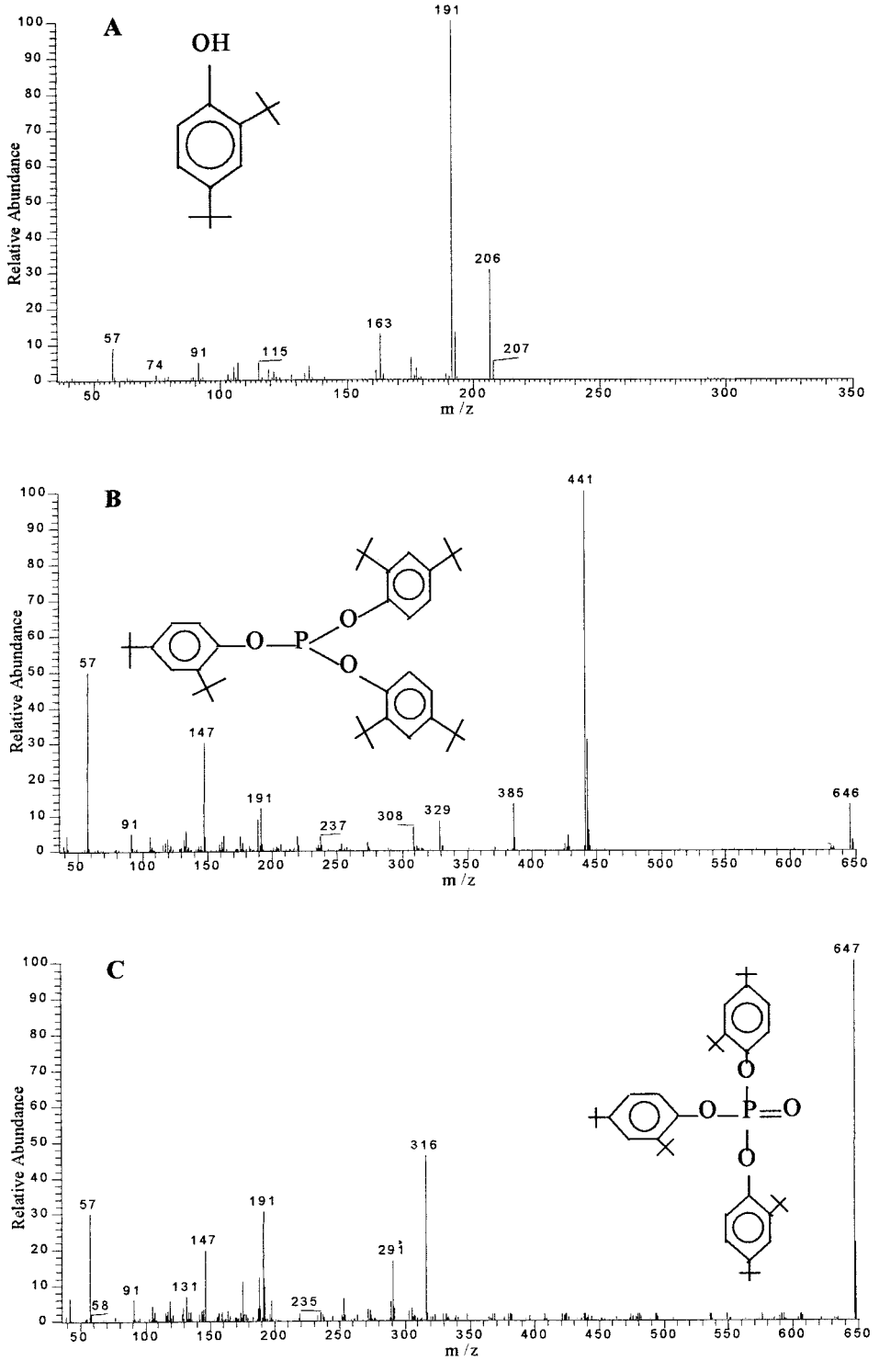


Figure 9 The structures and mass spectra of (A) 2,4-di-*tert*-butyl-phenol; (B) Irgafos 168; (C) phosphate product.

Several products formed from Irgafos 168 were identified in the samples exposed to air, compost, and water environments (see Table II) but, despite their different retention times, all of them exhibited either the phosphite or phosphate mass spectra, coinciding with either the mass spectrum

of Irgafos 168 or the mass spectrum of its phosphate oxidation product. Some oligomeric structures with much higher molecular weights, containing either the phosphite or phosphate fragments, were probably formed during the exposure. Because a 2,4-DTBP byproduct was found to a sufficiently large extent, it can imply that the hydrolysis was completed, and that the phosphorous acid was obtained as a result. Phosphorous acid is highly soluble in water, and was probably removed from the matrix because it was not identified.

The 2,5-dimethyl-benzaldehyde found in the air-exposed polymer and the butyl ester of benzoic acid found in all the polymer extracts are probably oxidative transformation products of either Irganox 1010 or Irgafos 168. Phthalates identified are either additives from the polymer or contaminants from the sample preparation.

CONCLUSIONS

The nature of the environment has a remarkably influence on both the consumption of the antioxidants in the MDPE matrix and the changes occurring in the polymeric matrix. The loss of the antioxidants was most intense under exposure to air and sunlight than during exposure to water or compost environments, and Irgafos 168 was consumed slightly more rapidly than Irganox 1010. The oxidation behavior of the polymeric matrix exhibited a linear dependence on the amount of antioxidant consumed. A variety of transformation products from the phenoxy radical of the Irganox 1010 and conversion products from the Irgafos 168 were produced as a result of processing and/or exposure to the tested environments, indicating that several chain scissions occurred in the antioxidant structure. During exposures, changes occurred in the polymeric matrix such as a change in crystallinity, an increase in melting temperature, crosslinking, and the formation of a range of polymer degradation products. The greater extent of degradation was found for the MDPE matrix exposed to air and sunlight where a variety of both unoxidized hydrocarbons and oxygen-containing compounds were formed. The degradation products formed in the MDPE matrix exposed to chemical hydrolysis and compost were mostly oxygen-containing products.

The loss of the antioxidants from the MDPE matrix is caused by photo-oxidative reactions in air and sunlight or by migration from the surface into water and compost environments, is promoted by degradation of the MDPE matrix, and is also related to the degradation of the antioxidants to smaller fragments.

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