Identification and quantification of odours from oxobiodegradable polyethylene oxidised under a free radical flow by headspace solid-phase microextraction followed by gas chromatography-olfactometry-mass spectrometry

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Abstract

Recently oxobiodegradable polyethylene gained popularity as food packaging material due to its potential to reduce polymer waste. However, this type of material can release after its oxidation off-odour compounds that affect the organoleptic properties of packaged food. Odour compounds released from both polyethylene and oxobiodegradable polyethylene before and after oxidation under a free radicals flow were investigated after 1 day, 2 days and 3 days of oxidation. The samples were analysed using headspace solid phase microextraction followed by gas chromatography-mass spectrometry and headspace solid phase microextraction coupled to gas chromatography-olfactometry-mass spectrometry. Sixty-two different odorous compounds were identified. 4- methylthio-2-butanone (fruit), nonanal (fat) and 3,6-nonadienal (fat) were present in different materials before oxidation. Multiple headspace-solid phase microextraction has been used to quantify all analytes. The most abundant compound was (Z)-3-hexenyl hexanoate with a concentration range between 1.5791 ± 0.1387 µg/g and 4.8181 ± 0.3123 µg/g. Compounds such as 2-dodecenal, 2-octenal, 2-pentanol, 3-nonenal, 3,6-nonadienal, ethyl 3-methylbutanoate, ethyl octenoate, hexanone, isopropyl hexanoate, octanal were below their LOD evaluated using MS detector; however, they were detected by gas chromatography-olfactometry. The minimum LOD and LOQ were 0.011 µg/g and 0.036 µg/g, respectively.

Keywords: oxobiodegradable, low-density polyethylene, oxidation, hydroxyl free radicals, SPME, olfactometry

Introduction

Latest scientific literature dealing with environmental topics stands out oxobiodegradable plastics as a potential solution to reduce polymer waste and environmental plastic pollution problems, which are the most ubiquitous and long lasting challenges nowadays [1,2]. Biodegradable polymers used in the production of plastic packaging are petroleum-derived polymers with synthetic additives accelerating their degradation. These additives are in the form of salts or transition metal complexes, known as pro-oxidants. They catalyse the oxidation of the polymer, leading to a reduction in molecular weight and also form the hydrophilic groups on the surface of material that makes it susceptible to assimilation by microorganisms [3–7]. The oxidative degradation of polyethylene (PE) and oxo-biodegradable PE under accelerated conditions such as photo- and thermooxidation [8–15], and also examination of the synergistic effects on the oxidation and biodegradation of those materials [16,17], were widely described in the scientific literature. However, little has been done to study the degradation of oxo-biodegradable polymers using free radicals. Hydroxyl (HO·) free radicals are highly reactive oxygen species, that are capable of attacking any molecule in their vicinity in order to balance their unpaired electron configuration [18]. The production of an atmosphere enriched in free radicals has been efficiently developed and used before to evaluate the antioxidant capacity of packaging materials [19,20]. The same system can be applied to investigate the oxidation performance of biodegradable polymers, by exposing them to the free radicals stream. The free radicals are generated in situ and the material exposed to the generated stream is further analysed. One of the drawbacks of oxidised biodegradable materials is the offodour, usually produced by some volatile compounds released from the material. Odour can consist of either a single compound or a complex mixture of volatile organic compounds (VOCs) [21]. Analysis of compounds such as VOCs is important from the chemical point of view to understand the polymer degradation [22], but not all the volatile compounds can give an odour. Odour perception is often much more sensitive than the chemical sensitivity of the analytical detectors. This means that biodegradable materials can be progressively oxidized by the free radicals existing in the environment and the very low concentration of oxidised compounds can produce an off-odour in the packaged food. Odour active compounds resulting from thermal oxidation of polyolefins have been described in literature [23–26]. Nevertheless, less attention has been paid to off-flavour and off-odour compounds from oxo-biodegradable packaging origin that could affect the stored food and change its organoleptic properties [27]. A common technique used for identification of odour-active compounds in a complex matrix such as plastics is headspace-solid phase microextraction-gas chromatography-olfactometry-mass spectrometry (HS-SPME-GC-O/MS) [23]. The main objective of the present work was the identification and quantification of odour compounds released from both conventional polyethylene and oxobiodegradable polyethylene before and after oxidation under a free radicals flow. The applied materials are currently used in the food market and are also potential matrices for new active packaging.

Materials and methods

Reagents

Standard solutions such as 1-hexanol (CAS 111-27-3), 1-octen-3-ol (98%, CAS 3391-86-4), 2-ethyltoluene (99%, CAS 611-14-3), 2-pentanol (98%, CAS 6032-29-7), 3,6-nonadienal (85%, CAS 21944-83-2), acetic acid (99%, 64-19-7), caryophyllene oxide (CAS 1139-30-6), estragole (CAS 140-67-0), ethyl 3-methylbutanoate (98%, CAS 108-64-5), ethyl hexanoate (99%, CAS 123-66-0), furfural (99%, CAS 98-01-1), hexanal (98%, CAS 66-25-1), linalool (97%, CAS 78-70-6), methyl benzoate (99%, CAS 93-58-3), nonanal (Fluka, 95%, CAS 124-19-6), octanal (99%, CAS 124-13-0), octanone (99%, CAS 106-68-3), phenol (99%, CAS 108-95-2), tetradecane (CAS 629-59-4), trans-2-octenal (94%, CAS 2548-87-0) were from Sigma Aldrich. Standard of n-alkanes (C_7 to C_{40}) was supplied as 1000 g/ml hexane solution (Code No.: 49452-U) by Supelco (Bellofonte, USA) and it was used as stock solution; solution for further studies were prepared by diluting the stock solution with hexane. Hydrogen peroxide (30%; CAS 7722-84-1) was also from Sigma Aldrich. Methanol (GC ultra-trace analysis grade) and hexane (analytical grade) were from Scharlau (Barcelona, Spain). Ultrapure water was obtained from a Milli-Q system (Millipore. Billerica, MA, USA). Compressed air was supplied by a Cecatto Bluair compressor (Brendola, Italy).

Samples

Samples of blank low-density polyethylene (LDPE) film of 0.03 mm thickness and oxo-biodegradable low-density polyethylene (OB-LDPE) film of 0.02 mm thickness were supplied by Grupo WPO (Seville, Spain). Blank polyethylene film was used as a base for preparation of oxo-biodegradable low-density polyethylene film in the company. All samples were stored at room temperature in a dark and dry place.

Samples oxidation

Oxidation of all samples was carried out using the method developed by Pezo et al. [28]. Firstly Bio-Rad peristaltic pump (Hercules, CA, USA) was set at 0.8 mL/min. and total air flow was set at 3.76 L/ min. The photoreactor used to generate OH• radicals from 1.66% hydrogen peroxide solution (v:v) consisted of a 300 mm×30 mm cylindrical quartz tube with opposite inlet and outlet. UV radiation was supplied by eight 250 mm×15 mm Philips fluorescent UV lamps TL 8W/08 F8T5/BLB Hg (Eindhoven, The Netherlands) that were placed axially around the quartz tube. 1 dm2 of each material was placed in polyethylene plastic bag with internal dimensions of 150 mm×150 mm (internal volume was 420 ± 6 mL). Bags were prepared according to the instructions described by Pezo et al. [20]. Impulse sealer PFS-200 Zhejiang Dongfeng Packing Machine Co. (Wenzhou, Zhejiang, China) was used for thermo-sealing. Bags were placed in a holder with separators that contained up to eight bags at the same time. Then all bags were connected to the generator of gas-phase OH• radicals. 50 mL of Milli-Q water were placed in 100 mL Drechsler-type gas-washing bottles. Three different times of oxidation were applied: 1, 2 and 3 days. Eight replicates of each sample were prepared and they were analysed immediately.

Chromatographic analysis

HS-SPME-GC/MS analysis

A CTC Analytics system from Agilent Technologies (Madrid, Spain) was used as autosampler. The analysis of volatile compounds was conducted with the Agilent 6890 Series GC system coupled to 5973 series mass selective detector. HS-SPME-GC-MS analyses were carried out with a DVB/CAR/PDMS fibre previously selected (Table S1 presented in Supplementary material 1). Injection was performed in splitless mode and extraction conditions were as follows: 100 °C extraction temperature, 15 min extraction time and 2 min desorption time at 250 °C. Acquisition was performed in SCAN mode (50–350 m/z).

To analyse samples of LDPE and OB-LDPE, 1 dm2 of each material was placed in 20 mL glass vial. Then, the vial was incubated during 2 min at 100 °C while shaking. The sorption was carried out during 15 min also at 100 °C. The thermal desorption of analytes in the injection port lasted 2 min at 250 °C. Three replicates of each sample were injected into GC/MS for identification of the volatile compounds and six replicates of each sample were injected into gas chromatography- olfactometry-mass spectrometry (GC-O/MS) for the identification of the single odour compounds. Three blank analyses were performed using empty 20 mL glass vial.

Six trained panelists were sniffing the samples during SPME-GC-O/MS analysis. Moreover, C7–C40 alkane standard solution at 50 µg/g in hexane was used to calculate the Kovats' retention indexes (KI). During olfactometric analysis, the retention time (tR) for each odour compound was evaluated, as well as the type of aroma and also its intensity. The odour strength scale: 1–3 (1 was very weak, hardly recognizable note and 3 was very strong, intense note) was assigned to each smelled compound. Fractional values were also allowed. After this, the modified frequency (MF(%)) was calculated [29] as it permits to select the most important odour compounds from plastic samples. Compounds with MF(%) higher than 50% can be considered as the base of the aroma of analysed samples. Optimisation of the analytical method was presented in Supplementary material 1.

SPME-GC-O/MS analysis

SPME-GC-O/MS analysis was carried out using the CP-3800 Varian gas chromatograph (GC) system connected to a Saturn 2000 series with an ion trap mass detector and ODO I sniffing port supplied by SGE (Ringwood, Australia). Chromatographic separation was performed on a BP-20 column (30 m×0.25 mm×0.25 µm) supplied by SGE analytical science (Madrid, Spain). Applied oven temperature program was as follows: The initial temperature was set up to 40 °C (5 min), then raised from 40 to 220 °C at 10 °C/min, and the final temperature was maintained for 10 min. Helium was used as carrier gas at 1 mL/min flow. The ionisation was performed by electronic impact, the ion trap temperature was 220 °C; and the electron multiplier voltage was 1600 V. Temperature of injector was 250 °C. Acquisition was carried out in SCAN mode (45–350 m/z). Injection was carried out using SPME manual injector where DVB/CAR/PDMS fibre was used.

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Odorous compounds were identified by comparison of their Kovats' retention indexes determined by SPME-GC-O/MS with those reported by HS-SPME-GC/MS. Compounds were identified by matching their mass spectra vs. US National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA) commercial library (purity criterion > 85%). Moreover, identification was confirmed by characterisation of aroma of each compound using Flavornet database that is a compilation of aroma compounds found in human odour space. Also some of the compounds were confirmed by injection of standards. Whereas, quantitative analysis of plastic samples was based on the multiple headspace extraction applied by E. Canellas at al. was used [30]. The extraction was performed four consecutive times. Stock solutions at concentration 1000 μg/g containing all the standards were prepared in methanol. The solutions of different concentrations of the identified compounds were prepared also in methanol for the calibration curves. All the solutions were gravimetrically controlled. 10 μl of each standard solution was directly injected into the vial and analysed following the same procedure as that described for the samples. The procedure of sample analysis, capillary column and the chromatographic conditions described above were unchanged

Statistical analysis

All data are presented as the mean ± standard deviation for three independent measurements (n=3) in case of HS-SPME-GC/MS analysis and for six independent measurements (n=6) in case of SPME-GCO/MS analysis.

Results and discussion

Identification of odorous compounds

Sixty-two different odour compounds were found in polyethylene and oxobiodegradable polyethylene before and after oxidation under a free radicals flow. Some examples of the obtained chromatograms are shown in Fig. 1.

Table 1 shows the odour compounds identified in LDPE (L0, L1, L2, L3) and OB-LDPE (B0, B1, B2, B3) samples with their KI's and their aroma perceptions described by the different panelists. Moreover, the obtained values of KI were compared with those from NIST and also Flavournet. The column BP-20 (Carbowax 20) was used for the NIST search of KI. MF (%) and KI from databases for identified

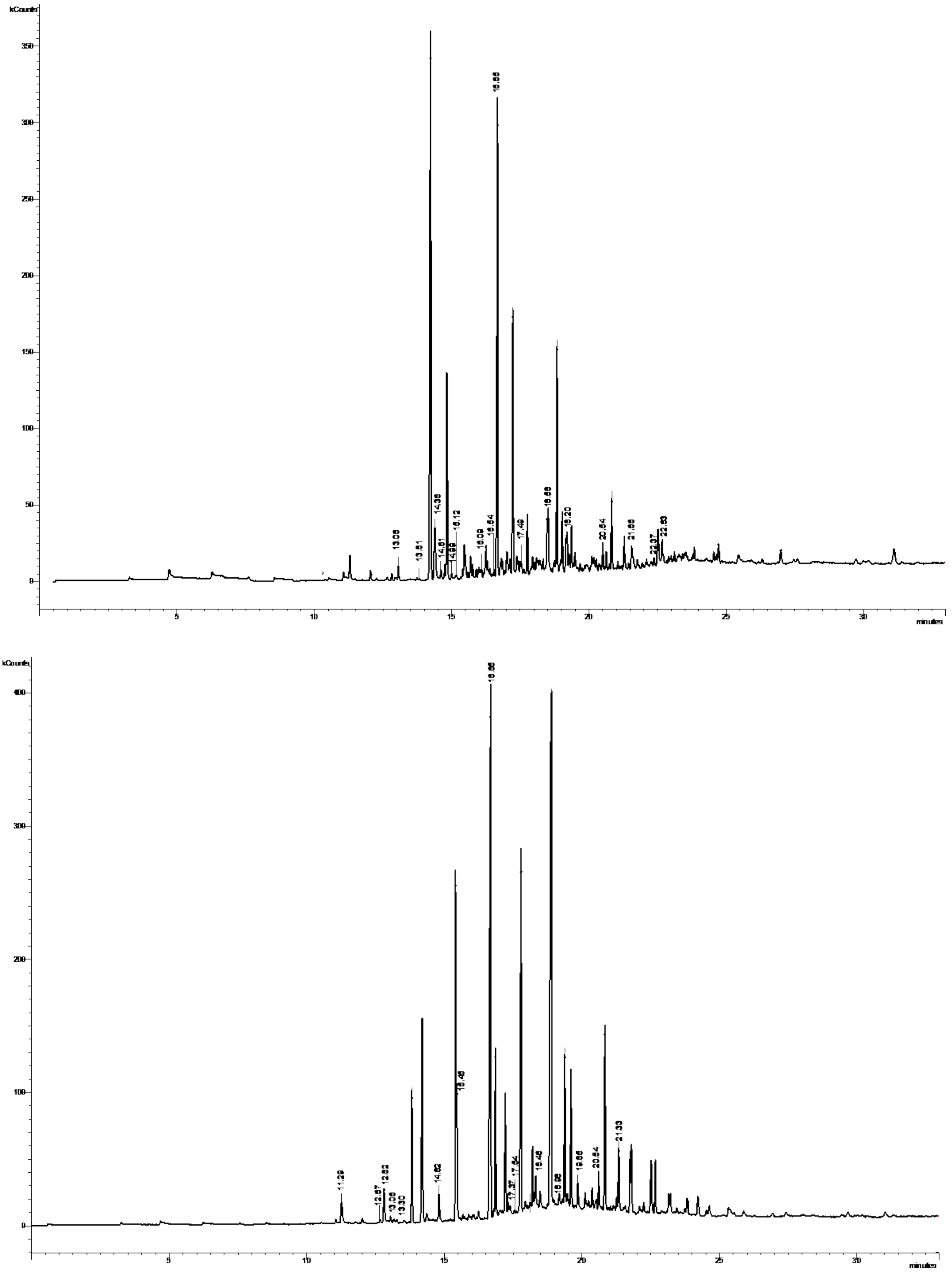
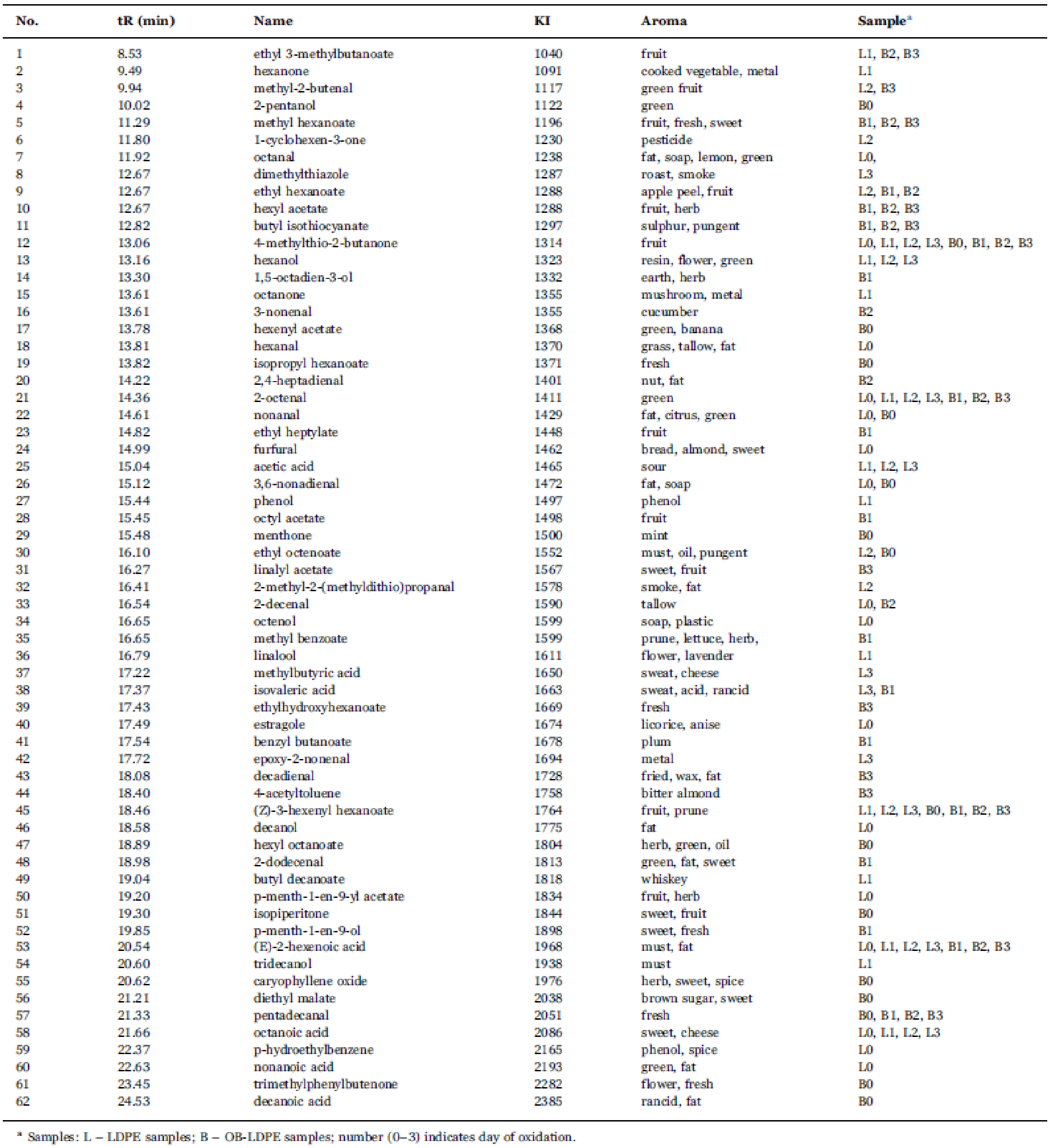


Fig. 1. Chromatograms of LDPE sample after 1 day of oxidation compared to no oxidised sample (A) and OB-LDPE sample after 1 day of oxidation compared to no oxidised sample (B). All samples were acquired by SPME-GC-O/MS.

Table 1: Results of identification of odorous compounds in LDPE and OB-LDPE samples.



No.	tR (min)	Name	KI	Aroma	Sample*
1	8.53	ethyl 3-methylbutanoate	1040	fruit	L1, B2, B3
2	9.49	hexanone	1091	cooked vegetable, metal	L1
3	9.94	methyl-2-butenal	1117	green fruit	L2, B3
4	10.02	2-pentanol	1122	green	B0
5	11.29	methyl hexanoate	1196	fruit, fresh, sweet	B1, B2, B3
6	11.80	1-cyclohexen-3-one	1230	pesticide	L2
7	11.92	octanal	1238	fat, soap, lemon, green	L0,
8	12.67	dimethylthiazole	1287	roast, smoke	L3
9	12.67	ethyl hexanoate	1288	apple peel, fruit	L2, B1, B2
10	12.67	hexyl acetate	1288	fruit, herb	B1, B2, B3
11	12.82	butyl isothiocyanate	1297	sulphur, pungent	B1, B2, B3
12	13.06	4-methylthio-2-butanone	1314	fruit	L0, L1, L2, L3, B0, B1, B2, B3
13	13.16	hexanol	1323	resin, flower, green	L1, L2, L3
14	13.30	1,5-octadien-3-ol	1332	earth, herb	B1
15	13.61	octanone	1355	mushroom, metal	L1
16	13.61	3-nonenal	1355	cucumber	B2
17	13.78	hexenyl acetate	1368	green, banana	B0
18	13.81	hexanal	1370	grass, tallow, fat	L0
19	13.82	isopropyl hexanoate	1371	fresh	B0
20	14.22	2,4-heptadienal	1401	nut, fat	B2
21	14.36	2-octenal	1411	green	L0, L1, L2, L3, B1, B2, B3
22	14.61	nonanal	1429	fat, citrus, green	L0, B0
23	14.82	ethyl heptylate	1448	fruit	B1
24	14.99	furfural	1462	bread, almond, sweet	L0
25	15.04	acetic acid	1465	sour	L1, L2, L3
26	15.12	3,6-nonadienal	1472	fat, soap	L0, B0
27	15.44	phenol	1497	phenol	L1
28	15.45	octyl acetate	1498	fruit	B1
29	15.48	menthone	1500	mint	B0
30	16.10	ethyl octenoate	1552	must, oil, pungent	L2, B0
31	16.27	linalyl acetate	1567	sweet, fruit	B3
32	16.41	2-methyl-2-(methyldithio)propanal	1578	smoke, fat	L2
33	16.54	2-decenal	1590	tallow	L0, B2
34	16.65	octenol	1599	soap, plastic	L0
35	16.65	methyl benzoate	1599	prune, lettuce, herb,	B1
36	16.79	linalool	1611	flower, lavender	L1
37	17.22	methylbutyric acid	1650	sweat, cheese	L3
38	17.37	isovaleric acid	1663	sweat, acid, rancid	L3, B1
39	17.43	ethylhydroxyhexanoate	1669	fresh	B3
40	17.49	estragole	1674	licorice, anise	L0
41	17.54	benzyl butanoate	1678	plum	B1
42	17.72	epoxy-2-nonenal	1694	metal	L3
43	18.08	decadienal	1728	fried, wax, fat	B3
44	18.40	4-acetyltoluene	1758	bitter almond	B3
45	18.46	(Z)-3-hexenyl hexanoate	1764	fruit, prune	L1, L2, L3, B0, B1, B2, B3
46	18.58	decanol	1775	fat	L0
47	18.89	hexyl octanoate	1804	herb, green, oil	B0
48	18.98	2-dodecenal	1813	green, fat, sweet	B1
49	19.04	butyl decanoate	1818	whiskey	L1
50	19.20	p-menth-1-en-9-yl acetate	1834	fruit, herb	L0
51	19.30	isopiperitone	1844	sweet, fruit	B0
52	19.85	p-menth-1-en-9-ol	1898	sweet, fresh	B1
53	20.54	(E)-2-hexenoic acid	1968	must, fat	L0, L1, L2, L3, B1, B2, B3
54	20.60	tridecanol	1938	must	L1
55	20.62	caryophyllene oxide	1976	herb, sweet, spice	B0
56	21.21	diethyl malate	2038	brown sugar, sweet	B0
57	21.33	pentadecanal	2051	fresh	B0, B1, B2, B3
58	21.66	octanoic acid	2086	sweet, cheese	L0, L1, L2, L3
59	22.37	p-hydroethylbenzene	2165	phenol, spice	L0
60	22.63	nonanoic acid	2193	green, fat	L0
61	23.45	trimethylphenylbutenone	2282	flower, fresh	B0
62	24.53	decanoic acid	2385	rancid, fat	B0

* Samples: L – LDPE samples; B – OB-LDPE samples; number (0–3) indicates day of oxidation.

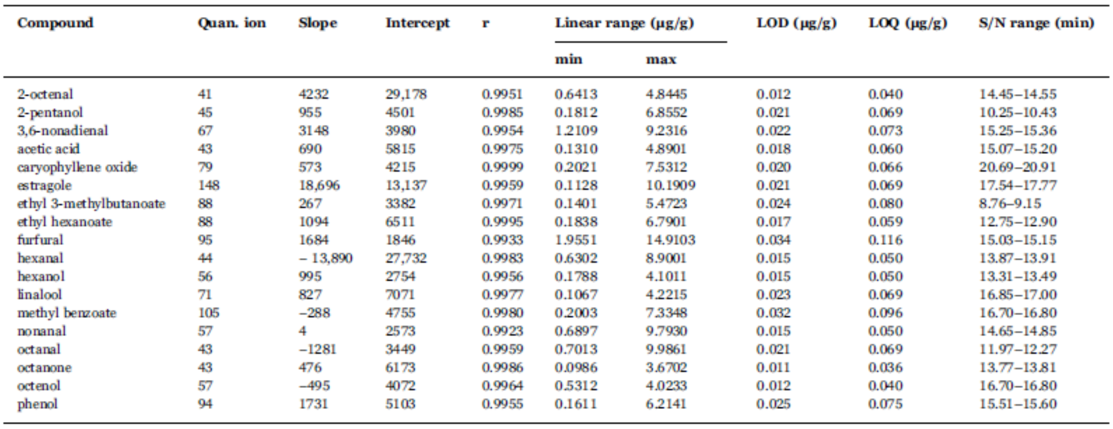
compounds were presented in Table S2 (Supplementary material 2). The compounds determined in blank polyethylene are coherent with those described in the literature [21,24]. Compounds such as octanal, 4-methylthio-2-butanone, hexanal, 2-octenal, nonanal, 3,6- nonadienal, 2-decenal, octenol, estragole, decanol, p-menth-1-en-9-yl acetate, (E)-2-hexenoic acid, nonanoic acid were determined as basic odorous compounds for blank LDPE samples, as they have a MF(%) higher than 50%. While compounds such as hexenyl acetate, 3,6- nonadienal, isopiperitone and diethyl malate were determined as basicodorous compounds for blank OB-LDPE samples.In case of 1 day oxidised LDPE samples basic odorous compoundswere ethyl 3-methylbutanoate, hexanone, 4-methylthio-2-butanone,hexanol, octanone, acetic acid, phenol, (Z)-3-hexenyl hexanoate, (E)-2-hexenoic acid and butyl decanoate. While in case of OB-LDPE oxidised during 1 day under the hydroxyl radical flow no compounds were detected with MF(%) higher than 50%. However, (Z)-3-hexenyl hexanoate with MF(%) equal to 49% could be considered as potential basic odorous compound. Besides, compounds such as 1-cyclohexen-3-one, 4-methylthio-2-butanone and hexanol were identified as basic odorous compounds for 2 days oxidised LDPE samples. While compounds such as hexyl acetate, 2,4-heptadienal and 2-decenal were identified as basic odorous compounds for 2 days oxidised OB-LDPE samples. Moreover, compounds such as 4-methylthio-2-butanone and acetic acid were identified as basic odorous compounds for 3 days oxidised LDPE samples. While hexyl acetate and methyl-2-butenal were identified as basic odorous compounds for 3 days oxidised OB-LDPE samples. To sum up, blank LDPE samples released much more odorous compounds, which can be part of the main plastic odour compared to OB-LDPE. After the first day of oxidation no compounds with high value of modified frequency were detected in case of oxobiodegradable polyethylene. An explanation may be the presence of protecting antioxidants in composition of OB-LDPE. As a result longer time is necessary to start oxidation of oxobiodegradable plastics. On the other hand, 1 day oxidised LDPE released a lot of odorous compounds. Analysis data from second day of oxidation, it can be observed decrease in appearance of odorous compounds in case of both samples. However, after the third day of oxidation more odorous compounds were released from OB-LDPE samples. Moreover, the change of type of aroma was also investigated during the oxidation process. After studying the data from Table 1 it can be clearly seen that odorous compounds, especially the basic ones released from blank materials, had pleasant scent. Oxidised samples of LDPE can be characterised by compounds responsible for unpleasant odours. After the first day of oxidation of LDPE samples unpleasant aromas such as metal, phenol and must were detected. Then, after the second day of oxidation of LDPE samples unpleasant aromas such as pesticide, must, oil and pungent were also detected. Finally, after the third day of oxidation of LDPE samples unpleasant aromas such as sweat, acid, rancid, metal, must, fat, roast and smoke were detected. The change of modified frequency of the same compounds occurring in samples with different stage of oxidation was studied. Fig. 2 shows the results of this study. The same seven compounds were detected in all samples of LDPE. A progressive decrease of value of MF(%) was observed in the case of (E)-2-hexenoic acid, 2-octenal, 4-methylthio-2-butanone and octanoic acid during the oxidation process, whereas compounds such as (Z)-3- hexenyl hexanoate, acetic acid, hexanol were not present in the blank sample of LDPE. However, they appeared during oxidation process. The behaviour of the listed three compounds was different. MF(%) of (Z)-3-hexenyl hexanoate decreased during the oxidation, while MF(%) of acetic acid increased during the oxidation. In contrast, MF(%) of hexanol remained at a constant level. The same eight compounds were detected in all samples of OBLDPE. Successive decrease of MF(%) was observed for pentadecanal. The modified frequency of 4-methylthio-2-butanone was constant while MF(%) of (Z)-3-hexenyl hexanoate increased and it was maintained since 1 day of oxidation. In addition, compounds such as (E)-2-hexenoic acid, 2-octenal, butyl isothiocyanate, hexyl acetate and methyl hexanoate were not present in the blank sample of OB-LDPE. They appeared during the oxidation process. An increase of MF(%) was observed for butyl isothiocyanate and hexyl acetate and a decrease of MF(%) was observed for methyl hexanoate.

The same compounds released from different plastics behaved in different way. Four odorous compounds were found in all samples of both plastics. Therefore, decreasing values of MF(%) for LDPE samples and constant values of MF(%) for OB-LDPE samples were observed in case of 4-methylthio-2-butanone, (Z)-3-hexenyl hexanoate and (E)-2-hexenoic acid. On the other hand, decreasing values of MF(%) for LDPE samples and increasing values of MF(%) for OB-LDPE samples were observed for 2-octenal.

Quantification of odorous compounds

Quantification of odorous compounds was carried out using SPMEGC- O/MS. The entire analytical procedure was validated in terms of linear range (µg/g) of the external solvent calibration, regression coefficient (r), limit of detection and limit of quantification for all standards. LOD and LOQ were determined using signal-to-noise method. Value noise-to-signal was established using the chromatogram of low concentrations of analytes. The characteristic peak of each analyte was used. Moreover, time range applied for the calculation of S/N was presented in Table 2.

Table 2: Analytical parameters of SPME-GC-O/MS method.



Compound	Quan. ion	Slope	Intercept	r	Linear range (μg/g)		LOD (μg/g)	LOQ (μg/g)	S/N range (min)
					min	max			
2-octenal	41	4232	29,178	0.9951	0.6413	4.8445	0.012	0.040	14.45–14.55
2-pentanol	45	955	4501	0.9985	0.1812	6.8552	0.021	0.069	10.25–10.43
3,6-nonadienal	67	3148	3980	0.9954	1.2109	9.2316	0.022	0.073	15.25–15.36
acetic acid	43	690	5815	0.9975	0.1310	4.8901	0.018	0.060	15.07–15.20
caryophyllene oxide	79	573	4215	0.9999	0.2021	7.5312	0.020	0.066	20.69–20.91
estragole	148	18,696	13,137	0.9959	0.1128	10.1909	0.021	0.069	17.54–17.77
ethyl 3-methylbutanoate	88	267	3382	0.9971	0.1401	5.4723	0.024	0.080	8.76–9.15
ethyl hexanoate	88	1094	6511	0.9995	0.1838	6.7901	0.017	0.059	12.75–12.90
furfural	95	1684	1846	0.9933	1.9551	14.9103	0.034	0.116	15.03–15.15
hexanal	44	– 13,890	27,732	0.9983	0.6302	8.9001	0.015	0.050	13.87–13.91
hexanol	56	995	2754	0.9956	0.1788	4.1011	0.015	0.050	13.31–13.49
linalool	71	827	7071	0.9977	0.1067	4.2215	0.023	0.069	16.85–17.00
methyl benzoate	105	–288	4755	0.9980	0.2003	7.3348	0.032	0.096	16.70–16.80
nonanal	57	4	2573	0.9923	0.6897	9.7930	0.015	0.050	14.65–14.85
octanal	43	–1281	3449	0.9959	0.7013	9.9861	0.021	0.069	11.97–12.27
octanone	43	476	6173	0.9986	0.0986	3.6702	0.011	0.036	13.77–13.81
octenol	57	–495	4072	0.9964	0.5312	4.0233	0.012	0.040	16.70–16.80
phenol	94	1731	5103	0.9955	0.1611	6.2141	0.025	0.075	15.51–15.60

The accuracy of the method was not determined. It would be assessed by analysing a polymer sample before and after spiking by known mass of analyte. However, added analyte does not behave in the same way as the analyte naturally present in the test material. This is a drawback of liberation of odorous compounds from solid sample. In this case it was impossible to spike the samples neither in stage of formation of material, nor during the oxidation process. Analytical parameters of the quantification method are shown in Table 2.

Linear ranges from 0.0986 to 14.9103 µg/g with the regression coefficient between 0.9923 and 0.9999 were obtained. In terms of sensitivity of the method, the minimum LOD and LOQ were 0.011 µg/g and 0.036 µg/g, respectively. The obtained values are of relevance for the expected use.

The quantitative results are presented in Table 3. Due to the lack of some standards some compounds were quantified using estragole as standard.

Table 3: Results of quantification analysis by SPME-GC-O/MS.

Compound	Concentration (μg/g)							
	LDPE				OB-LDPE			
	0	1	2	3	0	1	2	3
(E)-2-hexenoic acid[a]	3.3512 ± 1.0221	1.3431 ± 0.1178	0.2641 ± 0.1011	0.2815 ± 0.0431	nd	0.3603 ± 0.2408	0.3912 ± 0.1652	0.3446 ± 0.0822
(Z)-3-hexenyl hexanoate[a]	nd	4.2607 ± 0.7511	2.0825 ± 0.0973	1.5818 ± 1.0328	1.5791 ± 0.1387	4.6362 ± 0.1958	4.7032 ± 0.3011	4.8181 ± 0.3123
1-cyclohexen-3-one[a]	nd	nd	1.6211 ± 0.2754	nd	nd	nd	nd	nd
1,5-octadien-3-ol[a]	nd	nd	nd	nd	nd	0.4512 ± 0.3101	nd	nd
2-decenal[a]	4.4201 ± 1.0223	nd	nd	nd	nd	nd	2.9904 ± 1.6211	nd
2-dodecenal[a]	nd	nd	nd	nd	nd	< LOD	nd	nd
2-methyl-2-(methyldithio) propanal[a]	nd	nd	0.3711 ± 0.2503	nd	nd	nd	nd	nd
2-octenal	3.846 ± 0.9322	2.1610 ± 0.0691	2.1521 ± 0.0943	2.0001 ± 0.3432	nd	< LOD	1.9423 ± 0.4113	2.1712 ± 0.1743
2-pentanol	nd	nd	nd	nd	< LOD	nd	nd	nd
2,4-heptadienal[a]	nd	nd	nd	nd	nd	nd	5.4101 ± 0.1508	nd
3-nonenal[a]	nd	nd	nd	nd	nd	nd	< LOD	nd
3,6-nonadienal	1.6601 ± 0.0649	nd	nd	nd	< LOD	nd	nd	nd
4-acetyltoluene[a]	nd	nd	nd	nd	nd	nd	nd	2.0009 ± 0.3642
4-methylthio-2-butanone[a]	0.9526 ± 0.2010	0.8309 ± 0.0837	0.8520 ± 0.0633	0.8544 ± 0.0214	0.6503 ± 0.1222	0.7393 ± 0.0711	0.6874 ± 0.1850	0.7036 ± 0.2367
acetic acid	nd	1.7012 ± 0.9425	2.5311 ± 0.3509	6.9101 ± 1.0310	nd	nd	nd	nd
benzyl butanoate[a]	nd	nd	nd	nd	nd	0.9435 ± 0.6377	nd	nd
butyl decanoate[a]	nd	1.4704 ± 0.2566	nd	nd	nd	nd	nd	nd
butyl isothiocyanate[a]	nd	nd	nd	nd	nd	1.7297 ± 0.1583	1.2063 ± 0.2243	1.1382 ± 0.1787
caryophyllene oxide	nd	nd	nd	nd	2.0456 ± 0.2696	nd	nd	nd
decadienal[a]	nd	nd	nd	nd	nd	nd	nd	6.6829 ± 0.6412
decanoic acid[a]	nd	nd	nd	nd	0.4554 ± 0.2066	nd	nd	nd
decanol[a]	0.4572 ± 0.0938	nd	nd	nd	nd	nd	nd	nd
diethyl malate[a]	nd	nd	nd	nd	1.4608 ± 0.3421	nd	nd	nd
dimethylthiazole[a]	nd	nd	nd	0.6469 ± 0.0945	nd	nd	nd	nd
epoxy-2-nonenal[a]	nd	nd	nd	2.7607 ± 0.5024	nd	nd	nd	nd
estragole	1.8101 ± 0.2204	nd	nd	nd	nd	nd	nd	nd
ethyl 3-methylbutanoate	nd	0.4005 ± 0.2769	nd	nd	nd	nd	< LOD	0.4003 ± 0.2848
ethyl heptylate[a]	nd	nd	nd	nd	nd	3.3201 ± 0.3029	nd	nd
ethyl hexanoate	nd	nd	1.8809 ± 0.2518	nd	nd	nd	nd	nd
ethyl octenoate[a]	nd	nd	1.5503 ± 0.1027	nd	< LOD	nd	nd	nd
ethylhydroxyhexanoate[a]	nd	nd	nd	nd	nd	nd	nd	0.5020 ± 0.2209
furfural	5.7577 ± 0.4612	nd	nd	nd	nd	nd	nd	nd
hexanal	1.0401 ± 0.0233	nd	nd	nd	nd	nd	nd	nd
hexanol	nd	1.8194 ± 0.9011	2.4049 ± 0.1855	2.4617 ± 0.2209	nd	nd	nd	nd
hexanone[a]	nd	< LOD	nd	nd	nd	nd	nd	nd
hexyl acetate[a]	nd	nd	nd	nd	< LOD	0.4633 ± 0.2325	< LOD	< LOD
hexyl octanoate[a]	nd	nd	nd	nd	0.3002 ± 0.1623	nd	nd	nd
isopiperitone[a]	nd	nd	nd	nd	2.2014 ± 0.4107	nd	nd	nd
isopropyl hexanoate[a]	nd	nd	nd	nd	< LOD	nd	nd	nd
isovaleric acid[a]	nd	nd	nd	2.6611 ± 0.1623	nd	1.5711 ± 0.0391	nd	nd
linalool	nd	3.7221 ± 0.7614	nd	nd	nd	nd	nd	nd
linalyl acetate[a]	nd	nd	nd	nd	nd	nd	nd	6.0585 ± 0.1070
menthone[a]	nd	nd	nd	nd	3.2201 ± 0.5692	nd	nd	nd
methyl benzoate	nd	nd	nd	nd	nd	2.6426 ± 0.0511	nd	nd
methyl hexanoate[a]	nd	nd	nd	nd	nd	3.3008 ± 0.2615	2.1377 ± 0.0312	1.2912 ± 0.0337
methyl-2-butenal[a]	nd	nd	< LOD	nd	nd	nd	nd	< LOD
methylbutyric acid[a]	nd	nd	nd	1.0511 ± 0.4674	nd	nd	nd	nd
nonanal	7.8337 ± 0.4851	nd	nd	nd	6.3921 ± 1.9009	nd	nd	nd
nonanoic acid[a]	1.7511 ± 0.3109	nd	nd	nd	nd	nd	nd	nd
octanal	< LOD	nd	nd	nd	nd	nd	nd	nd
octanoic acid[a]	2.0627 ± 1.0001	1.5559 ± 0.1663	0.9930 ± 0.1036	0.6182 ± 0.0901	nd	nd	nd	nd
octanone	nd	1.3748 ± 0.1012	nd	nd	nd	nd	nd	nd
octenol	4.3102 ± 0.1911	nd	nd	nd	nd	nd	nd	nd
octyl acetate[a]	nd	nd	nd	nd	nd	0.5024 ± 0.6680	nd	nd
p-hydroethylbenzene[a]	1.9405 ± 0.4525	nd	nd	nd	nd	nd	nd	nd
p-menth-1-en-9-ol[a]	nd	nd	nd	nd	nd	2.6101 ± 0.1217	nd	nd
p-menth-1-en-9-yl acetate[a]	4.9417 ± 0.5232	nd	nd	nd	nd	nd	nd	nd
pentadecanal[a]	nd	nd	nd	nd	3.5547 ± 0.1511	1.3127 ± 0.1312	1.3046 ± 0.2707	1.1001 ± 0.2002
phenol	nd	4.9939 ± 1.4475	nd	nd	nd	nd	nd	nd
tridecanol[a]	nd	1.6151 ± 0.1219	nd	nd	nd	nd	nd	nd
trimethylphenylbutenone[a]	nd	nd	nd	nd	0.9230 ± 0.3268	nd	nd	nd

nd – compound not detected in the sample.

[a] Compounds quantified with estragole as standard.

Nonanal was the most abundant odorous compound in both blank samples LDPE and OB-LDPE. Whereas, in case of 1 day oxidized samples the most abundant were phenol released from LDPE sample and Z-3-hexenyl hexanoate released from OB-LDPE sample. The most abundant odorous compound for 2 days and 3 days oxidised LDPE was acetic acid. However, the most abundant odorous compound for 2 days and 3 days oxidised OB-LDPE were 2,4-heptadienal and decadienal, respectively. There was also observed a relationship between MF% and the concentration of compounds in the case of odours detected in all samples. The same tendency was observed as in the case of MF% results

(Fig. 2). It was impossible to compare different compounds with the same MF%, as these relationships between the concentration and MF% disappeared. This fact is coherent with literature [29] and the reason is that each compound has a different odour threshold and therefore, each one was perceived by the panelists with different intensity.

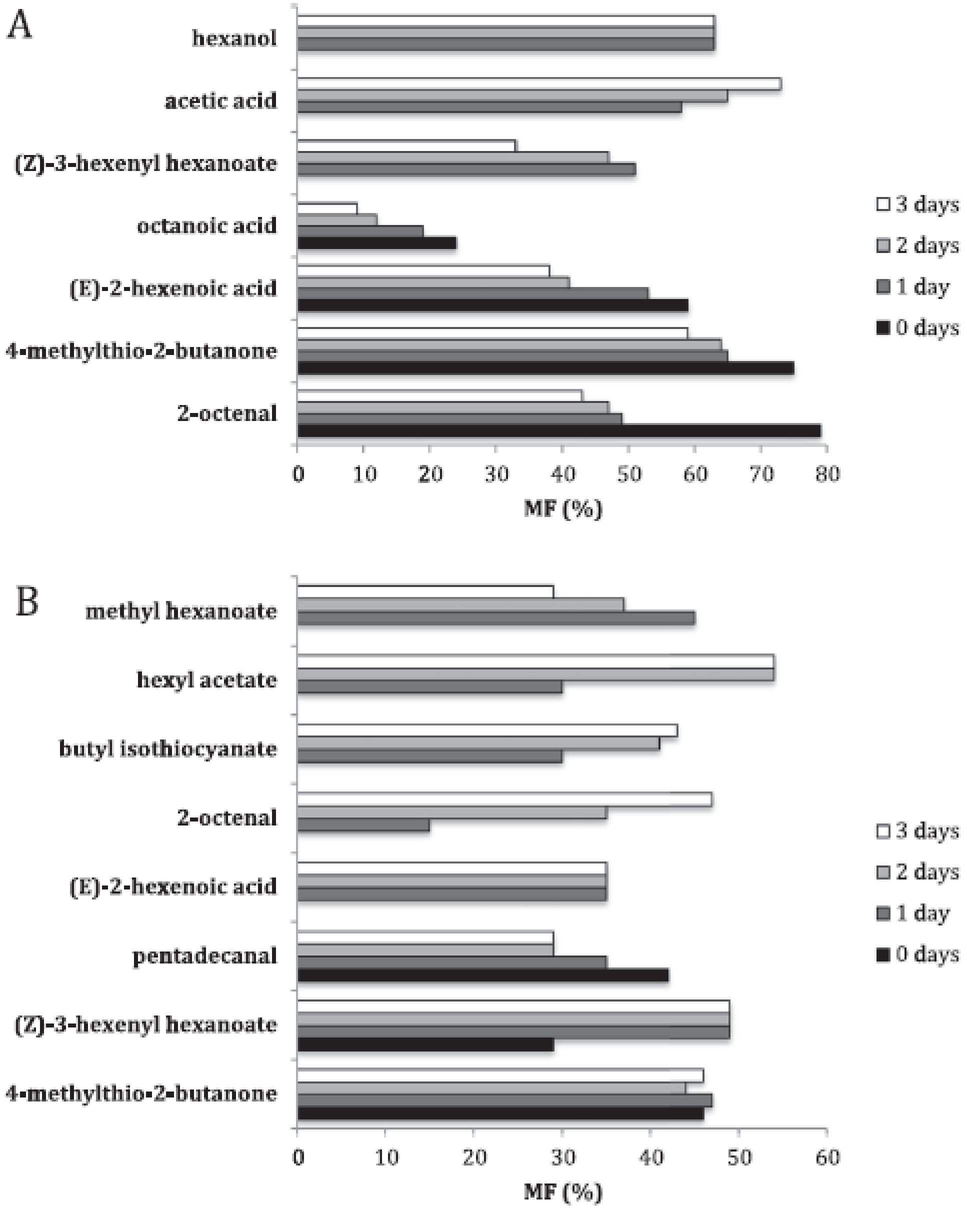


Fig. 2. Change of the value of modified frequency of odorous compounds detected in LDPE sample (A) and OB-LDPE sample (B).

Conclusions

Qualitative and quantitative analysis of sixty-two odour compounds from oxobiodegradable polyethylene immersed under hydroxyl radicals oxidation has been successfully performed. The multiple headspace solid phase microextraction method was used to quantify analytes. The most abundant compound was (Z)-3-hexenyl hexanoate with a concentration range between 1.5791 ± 0.1387 µg/g and 4.8181 ± 0.3123 µg/g with a fruit and prune aroma. Several compounds such as 2-dodecenal, 2-octenal, 2-pentanol, 3-nonenal, 3,6-nonadienal, ethyl 3-methylbutanoate, ethyl octenoate, hexanone, isopropyl hexanoate and octanal were below their LOD using MS detector; however, they were detected by the panelists by GC-O. This fact emphasizes the importance of using this second method to detect more number of odour compounds. After the oxidation, the amount of oxidised compounds decreased with an increment of oxidation time for LDPE samples. However for OB-LDPE samples, no compounds were detected with MF(%) higher than 50% after oxidation. It can concluded that this study accentuates the importance of identifying a large number of chemical compounds responsible for offflavours in the different materials. This leads the companies to a possible way forward to using determined compounds as markers of oxidation of plastic samples.

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