



Designing safe recycled high-density polyethylene (HDPE) for child toys

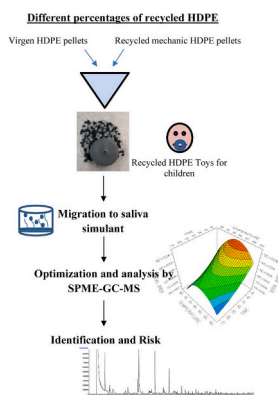
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HIGHLIGHTS

- Study of different percentage of recycled potentially used for children's toys.
- Static and dynamic migrations to saliva simulant analyzed by SPME-GC-MS.
- 69 migrant compounds including additives and NIAS as degradation and contaminants.
- Residues from cleaning products pose a potential risk.
- It is necessary to improve recycling by incorporating advanced cleaning techniques.

GRAPHICAL ABSTRACT



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ABSTRACT

New high-density polyethylene (HDPE) manufactured from different percentage of post-consumer recycled HDPE milk bottles was studied through two static and dynamic migration tests using saliva simulant to assess the potential hazard to children. Sixty-nine compounds were identified, including several additives used in PE synthesis such as alkanes, alkenes, antioxidants and plasticizers as well as non-intentionally added substances (NIAS) like degradation products such as 2,6-di-tert-butyl-1,4-benzoquinone, 2,4-di-tert-butylphenol, phenol, 2,5-bis(1,1-dimethylethyl)-, 3,5-di-tert-butyl-4-hydroxybenzaldehyde, and 3,5-di-tert-butyl-4-hydroxyacetophenone, or various residues from flavoring agents, cleaning products and essential oils. Some of these compounds as the isomers *p* and *o* *t*-butylcyclohexyl acetate, 3-Octanol, 3,7-dimethyl- and thujanol acetate (3-) pose a potential risk to children, as their concentrations exceed the recommended Cramer values for high percentages of recycling. This suggests improving recycling processes by incorporating advanced cleaning to remove residual products and contaminants.

1. Introduction

High density polyethylene (HDPE) is a type of thermoplastic polymer widely used in the manufacture of various products, including children's

toys. Its desirable properties, such as its lightweight, flexibility, durability and resistance to wear and impact, making it an ideal material for toys that can be roughly impacted and easily handled and carried by children.

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The European Union agreed that a circular economy is the primary solution to address the significant issue of accumulation of plastics in our environment [1]. Recycling is identified as the first option for plastic that has been used, discarded, collected, cleaned, reprocessed, and transformed into new products, known as post-consumer plastic. For this reason, recycled polyethylene for toys can become a good option due to the increasing environmental interest and demand for more sustainable products. Additionally, companies are responding to this demand by introducing products that incorporate recycled materials in their manufacturing. The significant advantage of this recycled polyethylene is that it retains many of the properties of virgin polyethylene, such as its lightweight, flexibility and wear resistance [2].

Children, especially the youngest ones, tend to put toys in their mouths. For this reason, it is crucial to ensure that toys are safe and manufactured with materials that meet safety standards, addressing the migration of compounds from toys to saliva and protecting children's health during play. Some of the compounds that often cause concern include certain heavy metals, phthalates, and other chemical additives that may be present in toy materials [3–6].

Without a thorough recycling process, which involves chemical decontamination, recycled post-consumer plastics present a notable challenge due to the potential migration of new compounds compared to virgin materials. This could make them unsuitable for specific applications, for example in the case of high-density polyethylene (HDPE) that has not been successfully recycled yet for food contact materials. This limitation stems from the high chemical sorption capacity, rapid diffusion of organic compounds through its matrix, high migration potential, and the absence of technology specifically designed for this kind of materials [7–11].

To prevent the use of inappropriate toy materials and, consequently to protect the children from possible health hazards, the Council of the European Union have enacted Directive 2009/48/EC [12] concerning toy safety. Specifically, harmonized standards include EN 71–9 [13], which addresses safety aspects of toys containing specific organic compounds, EN 71–10 [14] detailing sample preparation and extraction, and EN 71–11 [15] specifying methods of analysis. However, they are insufficient because there are a wide variety of additives in the market used in polymer manufacturing. Therefore, due to the absence of specific regulatory requirements, it is reasonable to rely on the labeling requirements for plastics used in food packaging [9] (specific migration limits for substances in contact with food: EU Regulation 10/2011 [16]) and EC Regulation 282/2008 for recycled plastics [17]. It is particularly valid since many materials used in toys share similar properties with formulations for food contact plastics. However, in the absence of these specific migration limits for new compounds which do not appear in these legislations, the resulting systemic exposure from the migration of recycled plastic used in toys should be below the threshold of toxicological concern (TTC) [18,19].

To the best of our knowledge, no studies have been conducted on the migration of recycled polyolefins for use in toys, and non-target migration studies have not been carried out to determine the NIAS (non intentionally added substances) [20] that may arise and pose a risk to children. Therefore, the objective of this study is: **To Investigate the Migration of Recycled Polyolefins:** To examine the migration of compounds from recycled polyolefins used in toys, addressing a gap in current research. **The Base Study on Pioneering Research:** To build on previous pioneering research on the migration of recycled HDPE material from a closed-loop recycling process [21], specifically focusing on the recycling of HDPE milk bottles. **Design Safer Materials for Toy Manufacturing:** To design a safer material for toy manufacturing by incorporating various proportions of post-consumer recycled material into virgin HDPE to determine the optimal ratios for creating a safe and sustainable material. **Simulate Realistic Conditions:** To conduct simulations of static and dynamic diffusion/migration for different percentages of recycled materials in a saliva simulant, replicating realistic conditions in the oral environment of babies (biting and sucking) and

the toy's use over time. **Identify Migrating Compounds:** To identify potential migrating compounds using gas chromatography-mass spectrometry (GC-MS), with an optimized method of solid-phase micro-extraction (SPME) for extracting these compounds from the saliva simulant. **Assess Associated Risks:** To evaluate the risks associated with the migration of compounds from recycled HDPE material.

2. Materials and methods

2.1. Reagents

For the saliva simulant: potassium chloride (CAS 7447–40-7), potassium carbonate (CAS 584–08-7), dipotassium phosphate (CAS 7758–11-4), sodium chloride (CAS 7647–14-5), calcium chloride (CAS 10043–52-4), magnesium chloride hexahydrate (CAS 7791–18-6), hydrochloric acid (CAS 7647–01-0).

For the calibration curves: decanal (CAS 112–31-2), Diphenyl ether (CAS 101–84-8), 1-tetradecanoe (CAS 629–59-4), 2-ethylhexyl salicylate (CAS 118–60-5), benzophenone (CAS 119–61-9), butylated hydroxytoluene (BHT) (CAS 128–37-0), limonene (CAS 5989–27-5), 1-nonanol (CAS 143–08-8), 2,6-di-tert-butyl-1,4-benzoquinone (CAS 719–22-2), 3,5-di-tert-butyl-4-hydroxybenzaldehyde (CAS 1620–98-8), diethyl phthalate (CAS 84–66-2), isoborneol (CAS 124–76-5), 1-hexadecanol (CAS 36653–82-4), 2,4-di-tert-butylphenol (CAS 96–76-4), 7,9-di-tert-butyl-1-oxaspiro (CAS 82304–66-3), 1-methyl naphthalene (CAS 90–12-0), cyclohexanol (CAS 108–93-0), 3,5-bis(1,1-dimethylethyl)–4-hydroxybenzoic acid, methyl ester (CAS 6386–38-5), tetradecene (CAS 1120–36-1), toluene (CAS 108–88-3). All reagents were supplied by Sigma-Aldrich Química S.A. with a purity > 99%.

Ethanol of 99% purity supplied by Scharlau Chemie S.A and ultra-pure water were used.

The saliva simulant solution was prepared by adding 745.5 mg of potassium chloride (KCl), 525.5 mg of potassium carbonate (K₂CO₃), 753.1 mg of dipotassium phosphate (K₂HPO₄), 327.3 mg of sodium chloride (NaCl), 147.0 mg of calcium chloride (CaCl₂), and 166.7 mg of magnesium chloride hexahydrate (MgCl₂·6H₂O) to 1 liter of Milli-Q water, adjusting the pH to 6.8 with hydrochloric acid (HCl).

2.2. Samples

The analyzed samples comprised one virgin HDPE and four types of plastic containers made from different post-consumer recycled HDPE milk bottles. These flakes were supplied by a European plastic recycling company where HDPE milk bottles were collected from curbsides and separated from other plastics at its sorting facilities. Subsequently, they were shredded, washed with water and detergent, and dried to obtain recycled flake samples. Finally, they underwent additional decontamination through heating and vacuuming; further details of these processes are unavailable due to confidentiality reasons.

The supplied flakes were pelletized using a Collin ZK-50 twin-screw extruder [10]. Prior to manufacturing the final recycled containers under study, virgin pellets were blended with recycled pellets in various proportions (25%,50%,75%) or only recycled pellets (100%), and through re-extrusion, circular portions of approximately 2 g each, 2.6 cm in diameter, 10.6 cm² surface area (corresponding to the surface area of child's open mouth [22]) were manufactured (Fig. 1). The virgin containers were also manufactured in the same manner but starting with virgin pellets without mixing with recycled pellets. Fig. 1 depicts a virgin plastic circular container and virgin pellets on the left, while a 50% recycled container with mixed pellets is shown on the right.

2.3. Instrumental methods

2.3.1. GC-MS

The method used for sample analysis was solid-phase micro-extraction (SPME) coupled to gas chromatography and mass

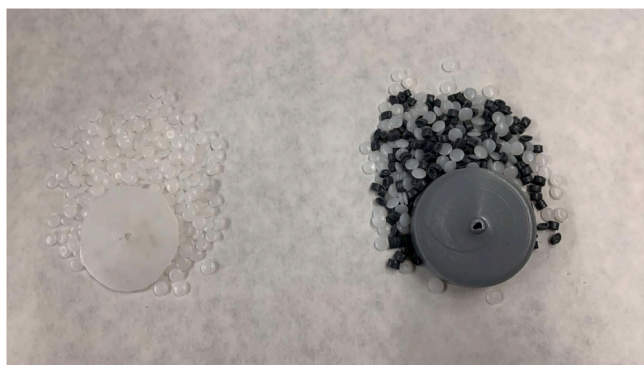


Fig. 1. Virgin plastic circular container and pellets (left) and 50% recycled container and pellets (right).

spectrometry (GC-MS). The equipment was a system gas chromatograph (7820 A) coupled to a mass detector (5977B MSN) from Agilent Technologies (Madrid, Spain). The capillary column was HP-5MS (30 m \times 0.25 μ m \times 250 μ m) from Agilent Technologies (Madrid, Spain). The injection type was splitless at 250°C of temperature and the helium flow was 1.0 mL/min. The GC-MS conditions were as follows: oven temperature ramp of 50°C (5 min), 10°C/min up to 300°C (5 min). Acquisition was carried out in SCAN mode (50–450 *m/z*).

The test conditions for SPME extraction optimized were as follows: SPME fiber (CAR/DVD/PDMS) was used by immersion in the undiluted saliva simulant during an extraction time of 45 min at 63 °C of temperature.

2.3.2. Optimization of test conditions for the SPME technique

The parameters influencing SPME extraction for the saliva simulant were optimized prior to assessing the migration from recycled material into this simulant. 100% recycled HDPE samples underwent an accelerated migration test with saliva simulant for 4 h at 70°C. The SPME optimization included evaluating extraction methods (Headspace or Immersion), sample dilutions (matrix effect), fiber exposure time, and extraction time and temperature.

2.3.3. Optimization of extraction method (headspace or immersion), dilution and fiber type

Thirty-two 100% recycled HDPE circular portions simulating of the surface area of child's open mouth [22] were placed in a 100 mL glass flask with 50 mL saliva simulant and heated at 70°C for 2 h. The saliva simulant was then replaced with a fresh portion of 50 mL, and the process was repeated.

Next, 32 vials (20 mL each) were prepared with the migrated solutions. Half were analyzed using the Headspace (HS) method, and the other half with the Direct Immersion (DI) method. For HS analysis, vials contained 5 mL of solution: two with undiluted saliva, and the others with 1/10, 1/5, and 1/2 dilutions with Milli-Q water. For DI analysis, vials contained 18 mL of solution with the same dilution scheme. Blanks were prepared for each assay.

All assays were performed in duplicate with two fibers: (PDMS 100 μ m) fiber and (DVD/CAR/PDMS 50/30 μ m) fiber. Automatic identification was also performed using the MSDIAL software (detailed in Appendix 1), which uses a library of spectra and Kovats indexes for peak determination. The migrating compounds were compared across extraction methods, dilutions, and fibers to determine the optimal conditions for extracting most of the compounds with the highest sensitivity.

2.3.4. Optimization of extraction temperature and time

Following the optimization of these variables, temperature and extraction time were studied using MODDE v6.0 software (Umetrics AB). A series of experiments were designed with a Response Surface

Methodology (RSM) model, specifically the Central Composite Face-Centered (CCF) design. In our study, 11 experiments were designed where the accelerated migration samples were analyzed by DI-SPME-GC-MS with the conditions of extraction temperature, ranging from 50 to 80 °C, and extraction time, ranging from 15 to 45 min (Appendix 2).

2.4. Migration assays

2.4.1. Dynamic study

This study replicated children biting on toys at specific moments. For this purpose, the circular containers of virgin HDPE and 25%, 50%, 75%, and 100% recycled HDPE were placed in a 100 mL glass flask with 50 mL saliva simulant and 4 g of glass balls (to simulate biting). These flasks were agitated on an orbital and reciprocating shaker (Rotaterm, JP SELECTA) at 60 rpm and 37 °C. A fresh 50 mL portion of saliva simulant was then added and the process was repeated for 15 min, 30 min, and 1, 3, 6 h, and 1 day. The two portions of saliva were combined and analyzed using DI-SPME-GC-MS. Each sample was tested in triplicate.

2.4.2. Static study

Unlike the static study, this investigation replicated the long-term interaction between children's saliva and toys, simulating children playing with and sucking on toys over several days. Virgin and recycled HDPE samples were exposed to 50 mL of a saliva simulant and incubated at 37 °C (simulating body temperature) for 5 days. After this period, the simulant was replaced, and the test was repeated for another 5 days period. The two portions of simulant were then combined and analyzed using DI-SPME-GC-MS. Each sample was tested in triplicate, along with one blank.

2.5. Identification of migrant compounds from saliva simulant

After both dynamic and static migration analyses, compounds present in all kind of migration were identified. Recycled samples showed considerable complexity with many migrants detected in each sample, making manual analysis of GC-MS profiles laborious. Therefore, MSDIAL [11,23] was used to expedite data interpretation through automated processes such as peak detection, alignment, blank subtraction, and identification (Appendix 2).

2.6. Migration quantification and risk assessment

After identifying all migrant compounds, their quantifications were carried out for both dynamic and static migration assays. For this purpose, the calibration curves of each available standard were analyzed using the same DI-SPME-GC-MS method, spanning concentrations from 0.1 ppb to approximately 200 ppb in simulated saliva. To quantify the migration of the compounds, we relied on MSDIAL, which allowed for the automatic extraction of the corresponding area for each compound. For compounds no commercially available, they were quantified using other standards that share similar structures. The limits of detection (LOD) and quantification (LOQ) were determined by considering the minimum amount of the analyte of interest that produces a chromatographic peak with a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively, in the presence of background signal noise.

The risk assessment highlights that migration studies span various timeframes and contact conditions to simulate the transfer of compounds from plastics used in toy manufacturing to a simulated saliva medium. However, accurately determining a child's exposure to these migrating substances is complex. Therefore, the specific migration limits provided should be seen as indicative, offering guidance on potential exposure impacts.

Regarding current legislation, the Directive 2009/48/EC [12] concerning toy safety, is now insufficient and outdated due to new additives and the use of new or recycled materials in toy manufacturing. The

Commission Regulation 10/2011/EC (2011) [16] addressed the limits for substances migration from plastic materials in contact with food and has been used as a preliminarily guiding principle due to the lack of specific regulations for the toys.

The risk assessment also applies the Threshold of Toxicological Concern (TTC), a concept estimating safe exposure levels for chemicals with no toxicity data. TTC values are based on potential hazards and molecular structural, categorized by Cramer into three levels: class I, II, and III (low, intermediate, and high toxicity, respectively), with estimated maximum values of human exposure at 1800, 540, and 90 $\mu\text{g}/\text{kg}$, respectively. It is crucial to recognize that TTC is a theoretical approach and cautious tool, and additional safety assessments may be needed if more information becomes available or if exposure levels approach the TTC value [18].

3. Results and discussion

3.1. Optimization of SPME conditions

The total immersion technique was employed to attain ideal conditions, eliminating the need for saliva dilution. This method entailed the use of a CAR/PDMS/DVB fiber (30/50 μm), resulting in enhanced detection of migrating compounds, most of which exhibited larger surface areas. Fig. 2a shows a response surface depicting the total migration area, representing the sum of areas for all detected compounds, as a function of temperature and time. As depicted in this figure, the majority of compounds achieved their peak areas within a temperature range of 60 to 65 $^{\circ}\text{C}$, with the extraction process lasting for 45 min, as highlighted by the red area on the figure.

In contrast, for other compounds such as isoborneol (Fig. 2b), alpha terpineol, and cyclohexanol, 2 (1,1-dimethyl) acetate, distinctive yet analogous trends emerged, with the most favorable extraction yields occurring at 50 $^{\circ}\text{C}$ for a duration of 30 min.

Other compounds, including eucalyptol, 1-menthone, cyclohexanol, 4-(1,1-dimethylethyl)-, cis-, 4,7-Methano-1 H-indenol, hexahydro-, 2-buten-1-one, 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-, (E)-, 3-buten-2-one, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-, diethyl Phthalate, benzophenone, and cyclohexyl salicylate, demonstrated a more pronounced response surface (Fig. 2c), with the optimal response conditions identified at 50 $^{\circ}\text{C}$ for 45 min.

In the majority of instances, extending the extraction time to 45 min led to improved extraction efficiency. Nevertheless, the temperature response varied depending on the type of compound. The selection of 63 $^{\circ}\text{C}$ as the optimal extraction temperature was based on two factors: firstly, it was the temperature at which the maximum response, as indicated by the cumulative area of all compounds, was observed (Fig. 2a). Secondly, individual analysis of each compound revealed that a temperature range of 55 to 70 $^{\circ}\text{C}$ generally resulted in better extraction for most of them.

It should be noted that in all cases, the response surfaces generated by MODDE v6.0 software, showed very good model fits in terms of validity, prediction, and reproducibility, with values ranging from 0.9 to 1.

3.2. Identification of migrant compounds

A total of sixty-nine different compounds, shown in Table 1, were identified (68 compounds detected for static and 23 compounds for dynamic migration). As expected, the number of compounds that migrated in dynamic migration assay was much smaller, since the contact time were lower. Among all these compounds found, two groups could be differentiated: intentionally added substances (IAS) and non-intentionally added substances (NIAS). Some IAS found were very common compounds used in the manufacturing of PE: 1-tetradecene (used in PE synthesis), butylated hydroxytoluene, diethyl phthalate (plasticizer), benzophenone (UV absorber), methanone, (4-

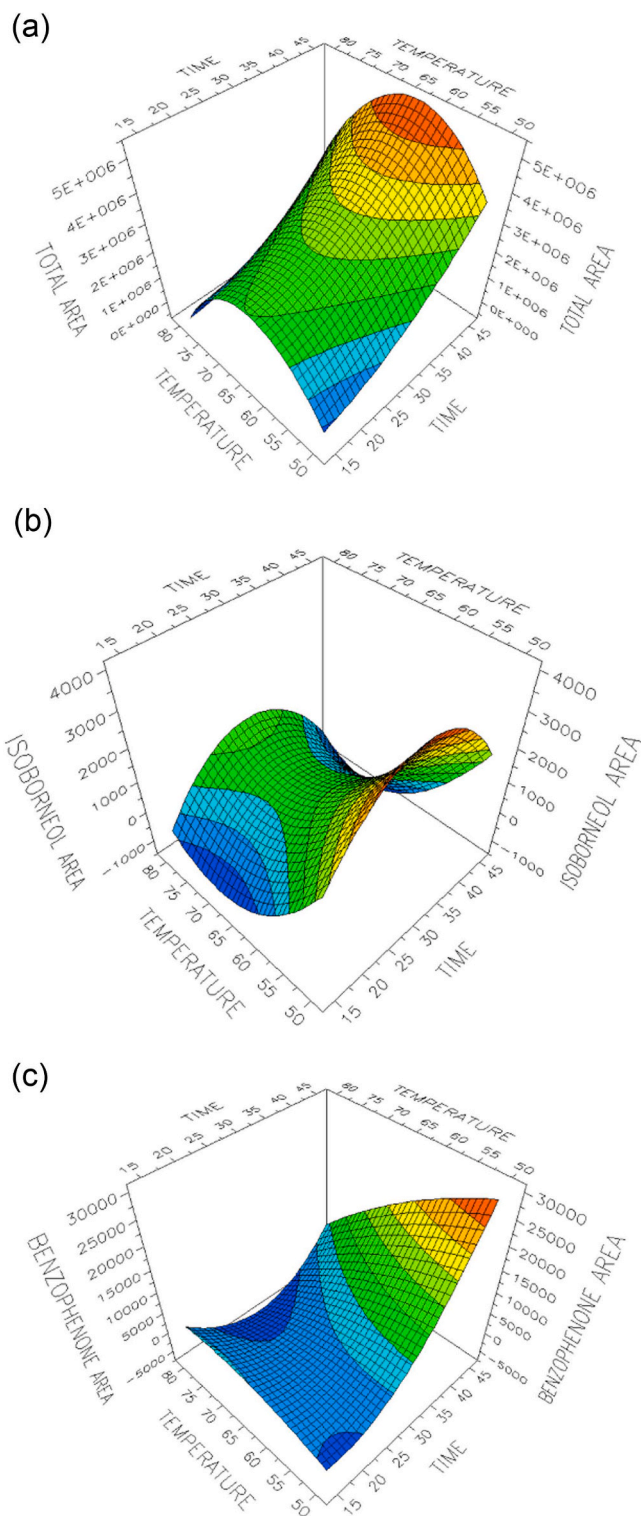


Fig. 2. a: Response Surface Plot of the sum of all compounds expressed in area concerning extraction time and temperature. 2b: Response Surface Plot of the isoborneol expressed in area concerning extraction time and temperature. 2c: Response Surface Plot of the benzophenone expressed in area concerning extraction time and temperature.

methylphenyl) phenyl- (stabilizing agent) and 1-(4-tert-butylphenyl) propan-2-one phenyl as antioxidant [8,11,24–26]. On the other hand, several NIAS were also found related to degradation products, impurities or residual products resulting from contaminations prior to the recycling process, or during storage in collection curbsides, or new

Table 1

List of compounds identified in the dynamic and static migration study with their retention times (RT), CAS numbers and kovat indexes (IK). Standard used for their quantifications and their SML or Cramer classes classifications.

N°	RT (min)	Compound	Quantification Standard	CAS	IK	Dinamic	Static	SML (ng/kg) /Cramer Class
1	2.63	Toluene	Toluene	108 –88 –3	773	X		Class I
2	2.70	Cyclohexanol	Cyclohexanol	108 –93 –0	912		X	Class II
3	3.51	Heptanal	Decanal	111 –71 –7	950		X	Class I
4	4.07	Camphene	Isoborneol	79 –92 –5	977		X	Class I
5	4.59	Octanal	Decanal	124 –13 –0	1001		X	Class I
6	5.01	D-Limonene	D-Limonene	5989 –27 –5	1031		X	Class I
7	5.05	Eucalyptol	Isoborneol	470 –82 –6	1034	X	X	Class III
8	5.55	7-Octen–2-ol, 2,6-dimethyl-	1-Nonanol	18479 –58 –8	1068	X	X	Class III
9	5.97	3-Octanol, 3,7-dimethyl-	1-Nonanol	78 –69 –3	1097	X	X	Class III
10	6.06	Nonanal	Decanal	124 –19 –6	1103	X	X	Class I
11	6.83	2-tert-Butylcyclohexanone	3,5-di-tert-Butyl–4-hydroxybenzaldehyde	1728 –46 –7	1144		X	Class II
12	7.05	1-Menthone	3,5-di-tert-Butyl–4-hydroxybenzaldehyde	14073 –97 –3	1155		X	Class II
13	7.14	Isoborneol	Isoborneol	124 –76 –5	1160		X	Class I
14	7.28	1-Nonanol	1-Nonanol	143 –08 –8	1168		X	Class I
15	7.40	Cyclohexanol, 2-(1,1-dimethylethyl)-, cis-	Cyclohexanol	7214 –18 –8	1174	X	X	Class I
16	7.42	Cyclohexanol, 5-methyl–2-(1-methylethyl)-	Cyclohexanol	1490 –04 –6	1174	X	X	Class I
17	7.64	Cyclohexanol, 3,3,5-trimethyl-, acetate, cis-	Cyclohexanol	24691 –16 –5	1187		X	Class I
18	7.77	.alpha.-Terpineol	Cyclohexanol	8000 –41 –7	1194		X	Class III
19	7.88	Dodecane	Tetradecane	112 –40 –3	1200		X	Class I
20	7.98	Decanal	Decanal	112 –31 –2	1204		X	Class I
21	8.15	1-Heptanol, 2-propyl-	1-Nonanol	10042 –59 –8	1211		X	Class I
22	8.19	Cyclohexanol, 4-(1,1-dimethylethyl)-, trans-	Cyclohexanol	21862 –63 –5	1214		X	Class I
23	9.05	p-Menth–8-en–3-ol, acetate	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)–4-hydroxy-, methyl ester	89 –49 –6	1251	X	X	Class II
24	9.48	1-Decanol	1-Nonanol	112 –30 –1	1269		X	Class I
25	9.68	4,7-Methano–1 H-indenol, hexahydro-	Isoborneol	37275 –49 –3	1278		X	Class III
26	9.95	Thujanol acetate (3-)	Isoborneol		1290	X	X	Class II
27	10.08	o-t-Butylcyclohexyl acetate (cis)	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)–4-hydroxy-, methyl ester		1296	X	X	Class II
28	10.34	Undecanal	Decanal	112 –44 –7	1306		X	Class I
29	10.46	4-(t-Butyl)benzaldehyde	2,4-Di-tert-butylphenol	939 –97 –9	1311		X	Class I
30	10.58	Cyclohexanol, 2-(1,1-dimethylethyl)-, acetate, cis-	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)–4-hydroxy-, methyl ester	20298 –69 –5	1316	X	X	Class II
31	10.68	Benzeneethanol,.alpha.,.alpha.-dimethyl-, acetate	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)–4-hydroxy-, methyl ester	151 –05 –3	1319	X	X	Class I
32	11.04	4-tert-Butylcyclohexyl acetate	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)–4-hydroxy-, methyl ester	32210 –23 –4	1334	X	X	Class II
33	11.44	.alpha.-Terpinyl acetate	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)–4-hydroxy-, methyl ester	80 –26 –2	1349	X	X	Class I
34	11.96	p-t-Butylcyclohexyl acetate (cis)	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)–4-hydroxy-, methyl ester		1370	X	X	Class II
35	12.11	2-Buten–1-one, 1-(2,6,6-trimethyl–2-cyclohexen–1-yl)-, (E)-	2,4-Di-tert-butylphenol	43052 –87 –5	1376		X	Class I
36	12.52	1-Tetradecene	1-Tetradecene	1120 –36 –1	1391		X	50
37	12.74	Tetradecane	Tetradecane	629 –59 –4	1400	X	X	Class I
38	12.81	Diphenyl ether	Diphenyl ether	101 –84 –8	1403		X	Class III
39	13.85	5-Methyl–5-phenyl–3-hexanone	2,4-Di-tert-butylphenol	4927 –36 –0	1441		X	Class I
40	14.03	1-(4-tert-Butylphenyl)propan–2-one	2,4-Di-tert-butylphenol	81561 –77 –5	1448	X	X	Class I
41	14.15	Naphthalene, 2-methoxy-	1-methyl- naphthalene	93 –04 –9	1452		X	Class III
42	14.37	3-(4-Isopropylphenyl)–2-methylpropionaldehyde	2,4-Di-tert-butylphenol	103 –95 –7	1461		X	Class I
43	14.56	2,6-di-tert-butyl–1,4-benzoquinone	2,6-di-tert-butyl–1,4-benzoquinone	719 –22 –2	1468	X	X	Class II
44	14.67	Butylated Hydroxytoluene	Butylated Hydroxytoluene	128 –37 –0	1471		X	3000
45	14.70	1-Dodecanol	1-Hexadecanol	112 –53 –8	1473		X	Class I
46	14.92	alpha. Isomethyl ionone	2,4-Di-tert-butylphenol	127 –51 –5	1481	X	X	Class I
47	15.08	3-Buten–2-one, 4-(2,6,6-trimethyl–1-cyclohexen–1-yl)-	2,4-Di-tert-butylphenol	14901 –07 –6	1487		X	Class I
48	15.19	Butanoic acid, 1,1-dimethyl–2-phenylethyl ester	2-Ethylhexyl salicylate	10094 –34 –5	1491	X	X	Class I
49	15.48	Phenol, 2,5-bis(1,1-dimethylethyl)-	2,4-Di-tert-butylphenol	5875 –45 –6	1501		X	Class I
50	15.75	2,4-Di-tert-butylphenol	2,4-Di-tert-butylphenol	96 –76 –4	1511	X	X	Class I
51	15.99	1-Penten–3-one, 1-(2,6,6-trimethyl–2-cyclohexen–1-yl)-	2,4-Di-tert-butylphenol	7779 –30 –8	1520		X	Class I
52	16.16	Lilial	2,4-Di-tert-butylphenol	39390 –70 –0	1526		X	Class I
53	17.94	1-Hexadecene	1-Tetradecene		1592		X	Class I
54	17.97	Diethyl Phthalate	Diethyl Phthalate	84 –66 –2	1593		X	Class I
55	18.14	Hexadecane	Tetradecane	544 –76 –3	1600		X	Class I
56	18.88	Benzophenone	Benzophenone	119 –61 –9	1627	X	X	600
57	19.90	(7a-Isopropenyl–4,5-dimethyloctahydroinden–4-yl)methanol	7,9-Di-tert-butyl–1-oxaspiro(4,5)deca–6,9-diene–2,8-dione		1665		X	Class I

(continued on next page)

Table 1 (continued)

N°	RT (min)	Compound	Quantification Standard	CAS	IK	Dinamic	Static	SML (ng/kg) /Cramer Class
58	20.22	n-Hexyl salicylate	2-Ethylhexyl salicylate	6259-76-3	1678		X	Class I
59	20.70	(7a-Isopropenyl-4,5-dimethyloctahydroinden-4-yl)methanol	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione		1695		X	Class I
60	21.70	Cyclohexyl salicylate	2-Ethylhexyl salicylate	25485-88-5	1734		X	Class I
61	22.03	Octanal, 2-(phenylmethylene)-	2-Ethylhexyl salicylate	101-86-0	1746	X	X	Class I
62	22.25	Methanone, (4-methylphenyl)phenyl-	Benzophenone	134-84-9	1755		X	Class III
63	22.45	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	1763	X	X	Class II
64	23.40	Octadecane	Tetradecane	593-45-3	1800		X	Class I
65	23.80	3,5-di-tert-Butyl-4-hydroxyacetophenone	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	14035-33-7	1816		X	Class II
66	24.70	Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	1222-05-5	1853		X	Class III
67	24.72	7-Acetyl-6-ethyl-1,1,4,4-tetramethyltetralin	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	88-29-9	1853		X	Class I
68	25.36	1-Hexadecanol	1-Hexadecanol	36653-82-4	1879		X	Class I

additives introduced during the recycling process such as during washing or re-extrusion to manufacture new pellets. For example, compounds as 2,6-di-tert-butyl-1,4-benzoquinone, 2,4-di-tert-butylphenol, phenol, 2,5-bis(1,1-dimethylethyl)-, 3,5-di-tert-butyl-4-hydroxybenzaldehyde, and 3,5-di-tert-butyl-4-hydroxyacetophenone could be degradation products of higher molecular weight plasticizer additives like Irganox 1076 and Irganox 1010. These compounds might have been generated in previous recycling stages such as heating and re-extrusion to manufacture the pellets under study. Some of them could be expected since they were found in previous bibliography related to recycling steps [27–31]. Other newly identified intermediate compounds could be associated with insufficient or ineffective cleaning processes in earlier stages or the addition of these additives during the mechanical recycling process, such as toluene compound, detected only in the dynamic migration, which is used as solvent that acts as a recycling agent [32] or diphenyl ether and 1-decanol used in the manufacture of high-temperature lubricants and surfactants, or 2-propyl-1-heptanol as a starting material for plasticizer production or 4-(t-Butyl) benzaldehyde as intermediate substance for manufacturing of other substances [33].

It is worth noting the large number of compounds found used as fragrances in decorative cosmetics, fine fragrances, shampoos, toilet soaps and other toiletries, as well as in non-cosmetic products such as cleaners and detergents. For example, the compounds 2,3,5,9,10,12,13,14,20,22,27,34,35,42,45,46,47,48,52,58,60,61,66,67 and 68 (Table 1) [8,33–36]. The presence of these compounds could be related to three aspects. One would be prior contamination that occurs when these HDPE bottles come into contact with other containers intended for non food uses for example, cleaning products. This is closely related to the high capacity of this material to absorb and diffuse these compounds within their matrices. Additionally, it would also indicate that the cleaning stages prior to the manufacture of the pellets have been insufficient. Other aspects could be related to cross-contamination, where these compounds were incorporated during some of the cleaning stages, or simply that during the sorting stage, milk bottles were not properly separated and were mixed with other type of packaging that had previously been used for other purposes, such as containers for cleaning products.

Finally, the appearance of compounds such as camphene, limonene, thujanol acetate (3-), eucalyptol and alpha-terpineol [37] used in active packaging as antioxidants or antimicrobial components, also lends weight to the idea that the cleaning stages have not been sufficient to eliminate these compounds. In this case, they could have migrated from other containers used for these purposes or these compounds may have been part of the container in its previous use.

3.3. Quantification of migration compounds to saliva as simulant

The calibration curves for each compound are shown in Table 2. Very low limits of detection (ranging between 0.12 and 10.2 µg/kg) and good linearity ($R^2 > 0.99$) were obtained. Validation tests provided good results of these tested parameters.

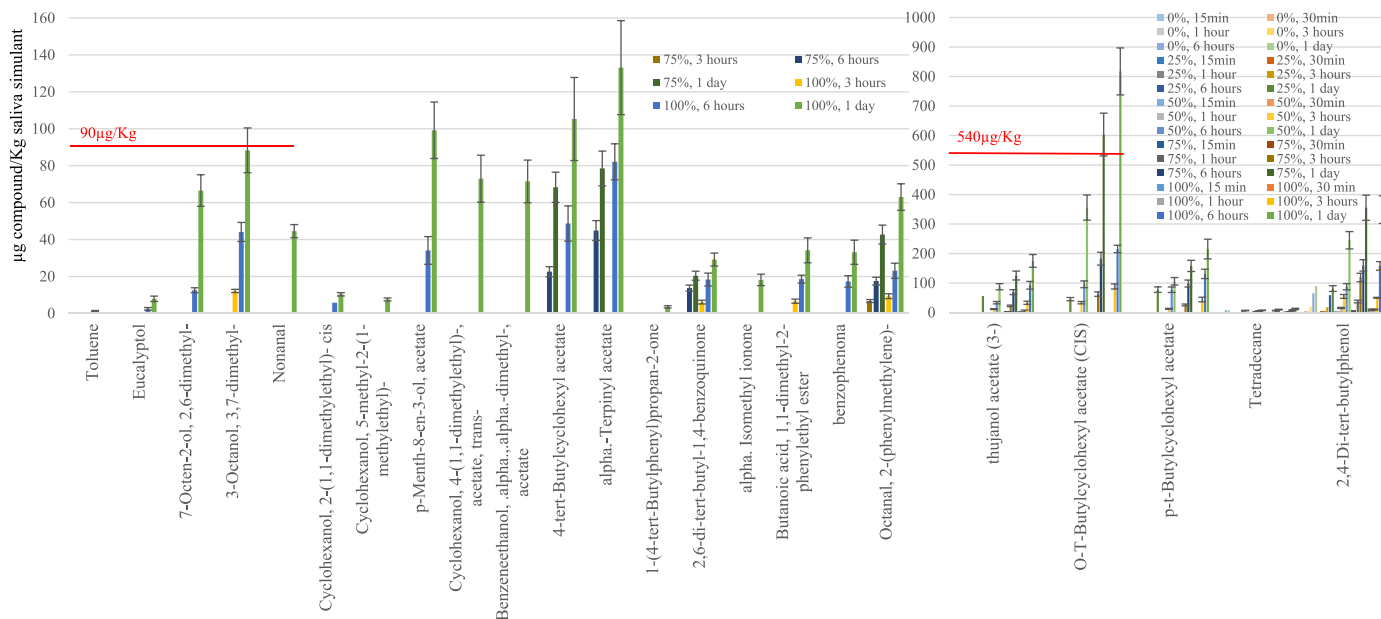
Fig. 3 shows the migration values for the dynamic assay representing the concentration of migrating compounds at the different exposure times grouped by different recycling percentages. Most of the compounds increased their concentration as the time of contact increased, as expected. However, in the case of toluene (found only in 100% of recycled materials) the concentration decreased from 3.62 ± 0.55 µg/kg (15 min) to lower than LOQ = 1.67 (3 h) or below LOD with longer migration time. Toluene is used as recycling agent to dissolve polymers as polyethylene. Its presence could be related to the possibility of being superficially present as residue at low concentrations, which allowed for its migration during the initial conditions, but subsequently undetected.

Most of the compounds were detected for the first time after three hours of exposure, progressively increasing their concentration up to one day (Fig. 3 on the left). This means that at an exposure temperature of 37 °C, it would take at least 3 h for the migrating compounds to diffuse to saliva simulant and be detected. Thirteen migrants out of these compounds (Fig. 3 on the left), were detected only at 100% recycling, and four compounds as 4-tert-butylcyclohexyl acetate, alpha-terpinyl acetate, 2,6-di-tert-butyl-1,4-benzoquinone and octanal, 2-(phenylmethylene)-. were also found at 75% recycling but at lower concentrations. The most restrictive maximum concentration for migration, recommended by Cramer, if the compounds are not regulated, should be 90 µg/Kg (corresponding to Class III). Four compounds (Fig. 3 on the left) exceeded this concentration for 100% recycling after 1 day of exposure. Out of these four, two as p-menth-8-en-3-ol, acetate and 4-tert-butylcyclohexyl acetate were Class II (Table 1) compounds with a recommended maximum concentration of 540 µg/Kg, and alpha-terpinyl acetate was Class I (1800 µg/Kg), which did not exceed these values. However, the compound 7-Octen-2-ol, 2,6-dimethyl- was Class III and exceeded the recommended value.

On the other hand, five compounds (Fig. 3 on the right) migrated from the first assay at 15 min, increasing their concentrations to 1 day depending on the percentage of recycled material. This fact could be due to either their higher initial concentrations in the recycled material, requiring less time to be detected with shorter contact times, or their greater affinity for the simulant rather than the polymer matrix. Among them, 1-tetradecene and 2,4-Di-tert-butylphenol were found in all virgin and different recycling percentages samples with a similar concentration and tendency, increasing their concentration respect to the time of contact from 0.40 ± 0.10 µg/kg (1 h, 100% recycled) to 12.5 ± 2.1 (1 day, 100% recycled) for 1-tetradecene and from 7.55 ± 0.35 µg/kg

Table 2Calibration curves, coefficient of correlation (R²), limits of detection (LOD), limits of quantification (LOQ) and linear range.

Compounds	Calibration curves	R ²	LOD	LOQ	Lineal Range
Toluene	y = 62352.50x - 1872	0.9877	0.50	1.67	1.67 - 25.3
Cyclohexanol	y = 1938.8x + 1061.9	0.9924	1.02	3.42	3.42 - 50.1
Decanal	y = 6421.6x - 46987.4	0.9924	4.09	13.6	13.6 - 81.3
Isoborneol	y = 4176.5x + 11850.3	0.9947	0.19	0.63	0.63 - 86.1
Limonene	y = 16019.2x - 9755.2	0.9915	0.17	0.57	0.57 - 15.7
Nonanol	y = 1671.3x - 2636.7	0.9979	1.77	5.90	5.90 - 172
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	y = 1728.7x + 374	0.9998	0.19	0.63	0.63 - 84.7
1-tetradecene	y = 5257.7x - 7879.6	0.9905	0.17	0.57	0.57 - 38.6
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester	y = 596.9x - 38385.7	0.967	10.2	33.9	33.9 - 659
2,4-di-tert-butylphenol	y = 3961.9x - 3688.3	0.9985	0.24	0.79	0.79 - 79.7
Diphenyl ether	y = 31805.8x - 58487.5	0.998	0.85	2.82	2.82 - 81.1
1-methyl naphthalene	y = 2240.8x - 12191.6	0.9902	1.66	5.53	5.53 - 80.8
2,6-di-tert-butyl-1,4-benzoquinone	y = 1852.9x - 4865.2	0.9921	0.19	0.63	0.63 - 84.3
Butylated Hydroxytoluene	y = 17372.4x - 21109.9	0.9947	0.18	0.60	0.60 - 39.3
Diethylfthalate	y = 1387.6x + 423.3	0.9949	0.91	3.03	3.03 - 83.9
2-Ethylhexyl salicylate	y = 612.4x - 966.9	0.9977	1.67	5.57	5.57 - 163
Benzophenone	y = 2894.3x - 3073.1	0.992	4.30	14.3	14.3 - 81.9
1-Hexadecanol	y = 82957.8x - 22339.3	0.9988	0.10	0.33	0.33 - 11.5
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	y = 6757.4x + 1632.8	0.9992	0.43	1.43	1.43 - 403
Tetradecane	y = 7072.7x + 2796.7	0.9982	0.12	0.40	0.40 - 40.6

**Fig. 3.** Migration concentration of compounds at different contact time and different percentage of recycled to saliva simulant in dynamic assay.

(15 min) to 355 ± 43 (1 day, 75% recycled) for 2,4-di-tert-butylphenol. But these compounds did not pose a risk, 1-tetradecene with a SML of $50 \mu\text{g}/\text{kg}$ and the other one of Class I of toxicity (Table 1) and their concentrations were below than $1800 \mu\text{g}/\text{kg}$. The other three compounds were Class II, and in the case of o-t-butylcyclohexyl acetate (CIS) exceeded this value of $540 \mu\text{g}/\text{kg}$ for 75% and 100% of recycled material after 1 day of exposure.

Fig. 4 depicts the migrant concentrations for the different recycling percentages over 10 days at 37°C in static tests. As expected, for most of the compounds, their migratory concentrations increased with higher recycling percentages due to elevated contamination levels. However, certain compounds such as alkanes (dodecane, tetradecane, hexadecane and octadecane), alkenes (1-tetradecene and 1-hexadecene), diethyl phthalate (Fig. 3 on the left) and 2,4-di-tert-butylphenol (Fig. 4 on the right) showed consistent concentrations even when recycling percentages increased. These are common components used in the synthesis of HDPE (such as alkanes and alkenes), or they are added as antioxidants and plasticizers, remaining present in the virgin plastic without increasing the concentration when recycled material is added. Among

them, only 1-tetradecene was included in the Regulation 10/2011 [16] (shown in Table 1) with SML of $50 \mu\text{g}/\text{kg}$ and its migrant concentrations remained below this threshold. The other compounds were classified as Class I for toxicity, with concentrations also below than $1800 \mu\text{g}/\text{kg}$.

The most abundant compounds were o-t-butylcyclohexyl acetate with concentration range between $619\text{--}2110 \mu\text{g}/\text{kg}$, 2,4-di-tert-butylphenol with $700\text{--}816 \mu\text{g}/\text{kg}$, thujanol acetate (3-) (Fig. 4 on the right) and thujanol acetate (3-) and p-t-butylcyclohexyl acetate (Fig. 4 on the left) with ranges of $145\text{--}503$ and $243\text{--}461 \mu\text{g}/\text{kg}$ respectively. These two isomeric compounds of butylcyclohexyl are commonly used in perfumes and fragrances for washing, cleaning, cosmetics, and personal care products above mentioned. This suggests that the sorting step of post-consumer HDPE may not have been perfect, and some HDPE containers that previously contained these products were mixed with milk bottles under study. Alternatively, these compounds could have diffused and been absorbed into the study samples due to their high absorption capacity within curbsides containers. Thujanol acetate (3-) is a constituent of essential oils for active packaging above mentioned. Therefore, its presence may result from insufficient cleaning capacity during the

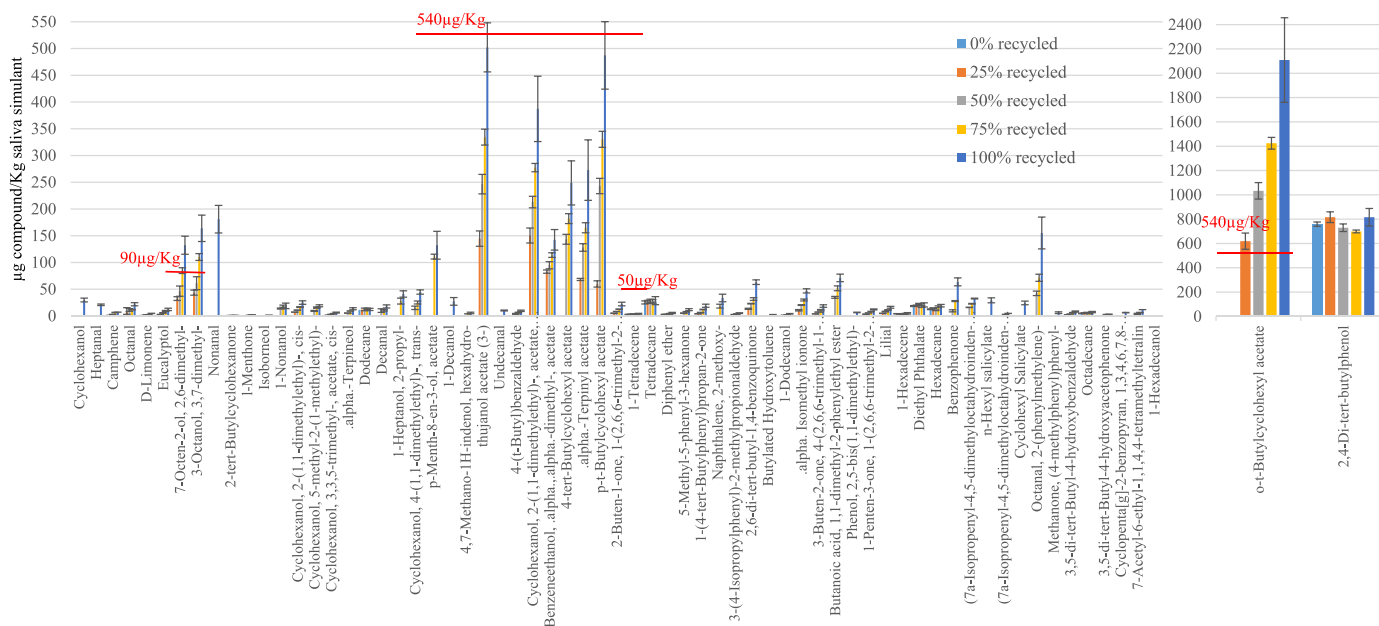


Fig. 4. Migration concentrations of compounds from different percentage of recycled of HDPE to saliva simulant in static assays.

recycling process, posing more complex safety risks. The compound *t*-butylcyclohexyl acetate of Class II did not meet the criteria for any percentage of recycling, and thujanol acetate (3-) and *p*-*t*-butylcyclohexyl acetate, also Class II, did not comply for 100% recycling, as their concentrations were above 540 µg/Kg recommended by Cramer. Furthermore, the compounds 7-Octen-2-ol, 2,6-dimethyl- and 3-Octanol, 3,7-dimethyl- both of class III, their concentrations were above 90 µg/Kg for 75% and 100% of recycled.

4. Conclusions

A fast, sensitive, reproducible, and efficient DI-SPME-GC-MS method has been developed to determine the migration to saliva simulant of different containers made of recycled post-consumer HDPE, potentially used for children's toys.

Sixty-nine compounds were found, six of which, such as the isomers *p* and *o* *t*-butylcyclohexyl acetate, thujanol acetate (3-), 7-Octen-2-ol, 2,6-dimethyl-, and 3-Octanol, 3,7-dimethyl-, did not comply with the maximum concentration recommended by Cramer, showing an increase in their migrations influenced by both contact time and percentage of recycled material increasing. Several of these NIAS were related to components of perfumes and fragrances for washing, cleaning, cosmetics, and personal care products, indicating an insufficient cleaning capacity during the recycling process. Therefore, it suggests that the recycling system should incorporate advanced cleaning and more precise sorting technologies, purification to more effectively remove residual products and contaminants, and stricter quality control systems for recycled HDPE compounds.

Environmental implication

Using recycled plastic in toy manufacturing offers significant potential for reducing plastic pollution and conserving resources, aligning with circular economy goals. These toys don't usually contain harmful substances, ensuring children's safety, but discarded toys contribute to plastic waste. Recycled plastics help minimize waste and environmental

problems, adhering to circularity principles. However, challenges like ensuring safety, maintaining quality, and managing supply chain logistics must be addressed. Innovation, collaboration, and responsible stewardship are crucial for the toy industry to harness the environmental benefits of recycled plastics while ensuring product safety, quality, and sustainability, ultimately benefiting both the environment and future generations.

CRedit authorship contribution statement

Cristina Nerín: Resources, Project administration, Funding acquisition, Conceptualization. **Elena Canellas:** Project administration, Investigation, Funding acquisition, Conceptualization. **PAULA VERA:** Writing – review & editing, Writing – original draft, Validation, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix 1. Parameters for MS-DIAL

The MS-DIAL parameters used included a minimum peak height of 2000, a sigma window of 0.5, and an EI spectra cut-off of 1 for deconvolution. Identification preceded alignment and involved comparing spectra against the NIST 14 library, with an 85% score cut-off to reduce false positives. Alignment was performed with a 0.1 min retention time tolerance and a 70% EI similarity. Features with a sample max/blank average fold change below 10 were excluded. The compiled list of compounds was then manually verified to confirm identification, using a retention index tolerance of 30 where applicable. This process also noted which samples definitively contained the identified migrants.

Appendix 2. Experiments designed by MODDE v6.0 software

MODDE v6.0 software (Umetrics AB) was used to design a series of experiments to optimize both extraction time and temperature variables for accelerated migration of 100% recycled HDPE samples analyzed by DI-SPME-GC-MS.

To carry out this optimization, a Response Surface Model (RSM) was applied using the Central Composite Design (CCD), which fits the obtained response to a quadratic mathematical model.

The number of experiments was determined by $2^f + 2f + n$, where 'f' is the number of variables to study and 'n' is the number of center points. In our case, there were 2 variables ('f') and 3 center points.

In our study, 11 experiments were designed to investigate extraction temperature, ranging from 50 to 80 °C, and extraction time, ranging from 15 to 45 min.

Experiment	Extraction time	Extraction Temperature
1	15	50
2	45	50
3	15	80
4	45	80
5	15	65
6	45	65
7	30	50
8	30	80
9	30	65
10	30	65
11	30	65

The response obtained both from the areas corresponding to the migration of each compound under the extraction conditions as well as the total area as the sum of all compound areas obtained in each experiment, were adjusted to the quadratic model.

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1x_2 + b_5x_1x_3 + b_6x_2x_3 + b_7x_1^2 + b_8x_2^2 + b_9x_3^2$$

The validity of this model was evaluated on a range of 0–1 according to these parameters:

- **R2:** Measures the model's capability to predict responses within the studied range.
- **Q2:** Measures the model's ability to predict responses within the studied range.
- **Model validity:** Indicates the fit of the data by the model and its error. Values less than 0.25 suggest lack of fit, indicating that the model's error is greater than the experimental error associated with reproducibility
- **Reproducibility:** Measures the model's reproducibility based on the response obtained at the center points.

The values of these parameters should be close to 1 to indicate high predictive power and good reproducibility of the model.

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