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Exploring the link between polymeric surface composition and emerging bisphenol release in toys and childcare products: insights from the Swiss market†

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This study investigates the release of 14 bisphenols (BPs) from various toys and childcare plastic products available in the Swiss market, using artificial saliva as a simulant. A total of 162 samples were analyzed, revealing substantial differences in BP release across polymer types. Polyethylene (PE) and polypropylene (PP) exhibited the highest release rates, while polyethylene terephthalate (PET) and polyurethane (PUR) showed lower BP release. Statistically significant differences among polymers emphasize the impact of polymer composition on leaching potential. These results enhance the understanding of BP exposure risks from polymeric materials in children's products, underscoring the need for targeted regulatory standards. By identifying high-risk polymers, this study provides valuable guidance for selecting safer materials to reduce BP exposure in products for children.

1. Introduction

Bisphenols (BPs), especially bisphenol A (BPA), have long been recognized as essential components in the production of polymeric materials, such as polycarbonates and epoxy resins, widely used in consumer products like food containers, toys, and childcare items.[1–5] Despite their functionality, increasing scientific evidence has highlighted the potential risks associated with BP release from these materials thus increasing human exposure to potentially hazardous compounds. BPA is of particular concern due to its action as an endocrine disruptor. It mimics oestrogen and interferes with various hormone receptors, including oestrogen receptors (ERα and ERβ), androgen receptors (AR), and thyroid hormone receptors (TRα and TRβ).[2,6–10] These interactions disrupt normal hormonal functions, leading to a cascade of negative health outcomes such as reproductive dysfunction, developmental abnormalities, metabolic disorders, and an increased risk of cancer.[11–14]

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The vulnerability of children to endocrine-disrupting chemicals is a growing concern due to their developmental stage and higher relative intake of BPs compared to adults. Children's metabolic systems are not fully matured, making them less efficient at detoxifying and eliminating harmful substances.[15,16] Their high hand-to-mouth behaviour and frequent contact with toys and other childcare products also raise their exposure risk. Studies have shown that BPs, including BPA and its analogues, are frequently detected in children's urine, indicating substantial exposure through ingestion, inhalation, and dermal absorption.[17–19] These findings underscore the importance of understanding how the presence of BPs in polymeric products originates and how polymer composition and usage contribute to BP release from everyday products.[20] Regulatory actions in the European Union, Canada, and the United States have imposed restrictions on BPA use in specific products, such as baby bottles, due to its recognized health risks.[2,18,19] These regulations have driven manufacturers to seek alternative compounds like bisphenol S (BPS) and bisphenol F (BPF), believed to offer similar benefits without the same level of toxicity. However, emerging research suggests that many of these analogues possess comparable or even greater endocrine-disrupting potential.[7,17,21,22] In particular, BPS, commonly found in thermal papers and plastic goods, has been shown to disrupt thyroid hormone signalling and pose risks similar to BPA, raising concerns about its widespread use and substitution trends.[23–26] Switzerland has taken significant steps to regulate BPA due to its health risks, and in 2020, it became the first European country to ban both BPA and BPS in thermal paper. Given the extensive use of BPs in plastic
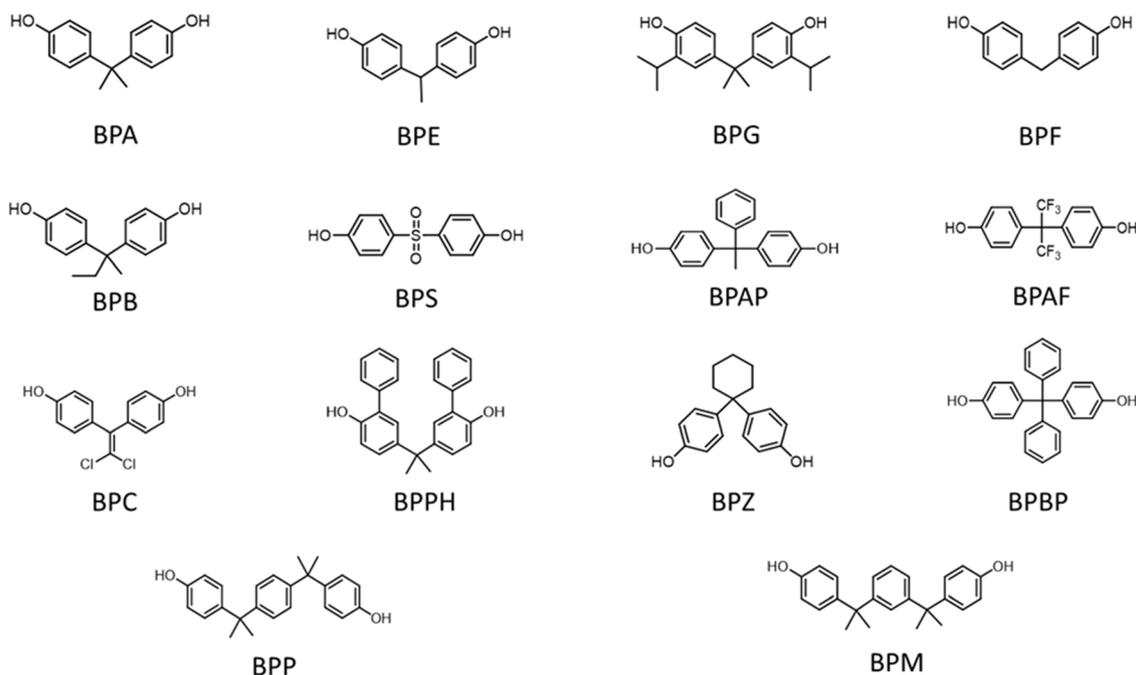
Fig. 1 Bisphenols analysed in this study.

materials, a critical factor influencing BP release is the presence of BPs in different polymeric components. BPs can originate from different sources within polymeric materials, including: (i) direct use as monomers in the synthesis of polymers such as polycarbonates and epoxy resins; (ii) presence as residual precursors in polymeric additives, such as flame retardants, stabilizers, and plasticizers; and (iii) degradation of these additives over time due to environmental factors.[14,15,27,28] While BPs are not intentionally used in many widely available plastics, such as polyethylene (PE), polypropylene (PP) and acrylonitrile butadiene styrene (ABS), their presence in finished products can result from cross-contamination during manufacturing, surface treatments, or the degradation of coatings and additives over time.[25,29–31] The release potential of BPs depends not only on polymer density, crystallinity, permeability, and the presence of additives but also on their residual content within the material.[30,32,33]

Recent studies have indicated that release from materials like polycarbonate (PC), polymethyl methacrylate (PMMA), and PE varies significantly depending on polymer properties and the surrounding environmental factors, such as temperature, humidity, pH and exposure to light. These insights highlight how specific conditions and polymer characteristics contribute to BP exposure.[34,35] This study evaluates the release of 14 BPs (i.e., bisphenol A (BPA), bisphenol AF (BPAF), bisphenol AP (BPAP), bisphenol B (BPB), bisphenol BP (BPBP), bisphenol C (BPC), bisphenol E (BPE), bisphenol F (BPF), bisphenol G (BPG), bisphenol M (BPM), bisphenol P (BPP), bisphenol PH (BPPH), bisphenol S (BPS) and bisphenol Z (BPZ)) (Fig. 1) from 162 different toys and childcare products randomly selected from the Swiss market, correlating their polymeric surface composition with BP release. The selection of these 14 compounds was based on their widespread industrial use, endocrine-disrupting potential,

and regulatory significance. BPA, BPS, and BPF are among the most commonly detected bisphenols in plastics,[32,36] while others, such as BPB and BPAP, have demonstrated comparable or higher hormonal activity.[23,37] Their structural similarity facilitates robust GC-MS quantification, ensuring reliable detection across different polymeric matrices.[18,38,39] By considering both polymer classification and BP release behaviour, this study aims to identify which materials are the most relevant sources of exposure and to propose strategies for risk reduction. Artificial saliva is used as a simulant to mimic the conditions under which children interact with these products, providing a realistic assessment of potential BP release and exposure pathways.[18] Given the increasing substitution of BPA with structurally similar analogues, it is essential to assess not only the total BP content in these products but also the individual BP release potential, as this directly relates to what is bioavailable and poses a risk to human health.[16,20] The aim of this paper is to explore the relationship between polymeric surface composition and BP release from toys and childcare products in artificial saliva, highlighting the importance of polymer choice in determining exposure risks. By correlating the identified polymers, such as ABS, PP, PE, and polyvinyl chloride (PVC), with their BP release tendencies, this research offers new perspectives on material safety, especially for products intended for vulnerable populations like children. In addition, this work contributes to ongoing efforts to improve regulatory guidelines and ensure the safety of polymeric materials in consumer products.[18,28,35]

2. Materials and methods

2.1 Materials and reagents

Standard compounds bisphenol A (BPA) (≥99%), bisphenol A-d16 (BPA-d16) (≥98%), bisphenol AF (BPAF) (≥99%),

bisphenol AP (BPAP) (≥99%), bisphenol B (BPB) (≥98%), bisphenol BP (BPBP) (≥98%), bisphenol C (BPC) (≥98%), bisphenol E (BPE) (≥98%), bisphenol F (BPF) (≥98%), bisphenol G (BPG) (≥98%), bisphenol M (BPM) (≥99%), bisphenol P (BPP) (≥99%), bisphenol PH (BPPH) (≥99%), bisphenol S (BPS) (≥98%) and bisphenol Z (BPZ) (≥99%) were obtained from Neochem (EGT Chemie). Stock standard solutions (100 mg L^{-1}) were individually prepared by dissolving standard compounds in acetonitrile. A stock standard mixture containing all the individual standards (100 mg L^{-1}) was also prepared and stored at −20 °C.

Bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% of trimethylchlorosilane (TMCS) solution was used for BP derivatization and was purchased from Sigma-Aldrich. Magnesium sulfate anhydrous (≥99.5%), sodium chloride, dichloromethane (≥99.8%), acetonitrile (≥99.9%), and methanol (≥99.9%) were acquired from Sigma-Aldrich. Reagents employed for the preparation of artificial saliva, namely sodium hydrogen carbonate (≥99%), sodium chloride (≥99%), potassium carbonate (≥99%) and sodium nitrite (≥99%) were obtained from Sigma Aldrich. Nanopure water was provided by an ultrapure water system (ariumPro, Sartorius, Germany). In order to accurately simulate the real matrix, Evian water was utilized for preparing the artificial saliva and the calibration curve. Sartorius Arium® water purification systems was used for ultrapure water. Evian® water was obtained from a local supermarket.

2.2 Childcare products and toy sample collection and preparation

Childcare items and toys were randomly selected from major supermarket chains and online shops in Switzerland, focusing on products designed for infants (0–12 months) and older children (12+ months). A total of 162 products were collected. The samples were prepared by flash-freezing each item in liquid nitrogen for 15 seconds, followed by mechanical fragmentation to ensure uniform pieces. All results are reported per kg of sample. Samples were categorized according to their surface polymeric composition, determined by Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy.

2.3 Surface analysis using ATR-FTIR

The surface characteristics of the samples were examined using ATR-FTIR spectroscopy. A Nicolet IS5 FTIR Spectrometer (Thermo Scientific), equipped with a Miracle Diamond ATR module (Pike), was used to register surface spectra. Each sample was scanned 21 times, and the resulting spectra were analysed using both the Aldrich Polymers FT-IR Spectral Library and the Polymer Additives and Plasticizers Spectral Library (Thermo Scientific). Only matches with a confidence level above 80% were considered reliable.[40]

2.4 Release into artificial saliva

To evaluate BP release, artificial saliva was prepared following the guidelines of EN12868 (European Committee for Standardization, 1999). The solution was made by dissolving 4.2 g sodium hydrogen carbonate, 0.5 g sodium chloride, 0.2 g potassium carbonate, and 30 mg sodium nitrite in 1 liter of Evian® water.[41] The pH was adjusted to 6.5 using acetic acid.[42] For the release experiments, 1.0 g of each individual sample was incubated in 10 mL of artificial saliva in 40 mL sealed glass vials. The vials were placed in an orbital shaker set to 140 rpm and 37 °C for 30 minutes to mimic the mouthing behaviour of children. The BP release was quantified in both µg mL^{-1} of artificial saliva and µg kg^{-1} of the sample, based on the precise mass used in the assay.

2.5 Chemical analysis of BPs

Following release testing, 10 mL of artificial saliva from each sample was diluted with 90 mL of Evian® water (final volume of 100 mL) and subjected to Solid Phase Extraction (SPE) using Chromabond HLB cartridges (Macherey-Nagel, 3 mL, 200 mg). The SPE cartridges were preconditioned with 6 mL of an acetonitrile/methanol mixture (50 : 50, v/v), followed by 6 mL of methanol and 6 mL of nanopure water.[18] After elution of the target compounds with 6 mL of the acetonitrile/methanol mixture, the collected eluates were dried. BPs were derivatized using BSTFA with 1% TMCS at 60 °C for 45 minutes before being analysed via gas chromatography-mass spectrometry (GC-MS, Shimadzu GCMS-QP2010 Ultra) using an OPTIMA-5 MS column (30 m, 0.25 mm ID, 0.25 µm). The initial helium flow rate was set to 5 mL min^{-1}, and the injector temperature was maintained at 280 °C in splitless mode. The temperature program started at 45 °C, increased to 300 °C at 10°C min^{-1}, and was held for 5 minutes. The ion source temperature was 250 °C. Quantification was performed using selected ion monitoring (SIM), as described previously (more details are available in Table S1 of the ESI†).[18,38]

2.6 Quality assurance and quality control

A calibration curve was prepared by spiking 50 mL of artificial saliva with a standard mixture of BPs at concentrations of 0.10, 0.50, 1.00, 5.00, 10.0, and 50.00 µg L^{-1}, following the same sample preparation steps. Limits of detection (LOD) and quantification (LOQ) of 0.03 µg L^{-1} and 0.10 µg L^{-1}, respectively for all 14 BPs were determined using the signal-to-noise ratio (S/N) method, with LOD defined as S/N ≥ 3 and LOQ defined as S/N ≥ 10. This corresponds to an LOQ of 1.0 µg kg^{-1} of samples and an LOD of 0.3 µg kg^{-1}. The blank samples were subjected to extraction and analysis protocols identical to those of the analysed samples, confirming the absence of detectable levels of the target analytes. The internal standard bisphenol A-d16 was added to each sample. Duplicate and spiked samples were analyzed with every set of five samples to ensure recovery values remained between 70% and 115%. Samples with concentrations above the calibration curve were diluted and re-analysed.

2.7 Statistical analysis

Data normality was assessed using the Shapiro–Wilk test. A one-way ANOVA was applied to compare two normally distributed datasets, while a two-way ANOVA was used to analyse

differences across multiple groups within datasets. Polymer frequency distributions were analysed using a Chi-Square Test, and Kendall's tau correlation was applied to examine the linear relationships between polymers and BP release. All tests were conducted at a significance level of $\alpha = 0.05$.

3. Results and discussion

This study assesses the release of BPs from 162 items by analysing their release into artificial saliva, used as a simulant. The use of simulants in toxicological studies is crucial, as they mimic real-life scenarios, offering insights into how plastic components may leach into food or biological systems.[4,5,33] Release into simulants is more relevant than the total content within the plastic itself, as it reflects actual human exposure and the associated risks, highlighting what is bioavailable for safety evaluations.[43,44] Artificial saliva simulates key physicochemical properties of natural saliva, including pH and ionic composition, ensuring consistency in release assessments.[42,45–48] The release results were categorized based on the type of polymer present on the object surface.

3.1 Polymeric surface composition

The rate and extent of BP release from polymers into the surrounding environment and biological systems are key factors that shape exposure levels and potential health risks.[2,23,49] Certain polymers may facilitate higher BP release due to their structural and chemical properties, affecting the overall safety and regulatory compliance of consumer products.[4,30,50] Studies have demonstrated that polymers such as PE, PP, and PMMA exhibit higher BP release rates, which is consistent with their chemical structure and leaching potential, as reported in previous research.[33,36,51,52] Conversely, PET, ABS, and PUR show lower BP release, likely due to their higher stability, reduced permeability, and resistance to hydrolytic degradation.[50,52–54] In this study, the polymeric surface composition was assessed using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, a rapid and straightforward technique commonly employed in the polymer industry, including quality control departments.[55] ATR-FTIR offers several advantages that make it particularly suitable for large-scale screening applications due to its speed, cost-effectiveness, and ease of use.[40,55–57] This technique requires minimal sample preparation, does not involve the destruction of the sample, and allows for direct analysis of solid materials without the need for extensive extraction steps. Its ability to provide real-time data with high reproducibility makes it an efficient tool for rapid polymer identification in manufacturing control, regulatory inspections, and compliance verification processes.[56,58,59] ATR-FTIR analysis of objects allowed their classification into 13 categories based on the surface polymer identified: acrylonitrile butadiene styrene (ABS), ethylene vinyl acetate (EVA), polyethylene (PE), polymethyl methacrylate (PMMA), polypropylene (PP), polyethylene terephthalate (PET), polyurethane (PUR), polyvinyl chloride (PVC), silicone, polycarbonate (PC), cellophane, polyamide (PA), and cellulose (Table 1). Furthermore, ATR-FTIR has been increasingly integrated into automated industrial workflows, facilitating high-throughput

Table 1 Surface polymeric composition of analysed samples categorized by polymer type. Mix: samples with single composition not identifiable *via* ATR-FTIR

Polymer	Abbreviation	No. of samples
Acrylonitrile butadiene styrene	ABS	7
Ethylene vinyl acetate	EVA	8
Mix	MIX	56
Polyethylene	PE	19
Polymethyl methacrylate	PMMA	7
Polypropylene	PP	32
Polyethylene terephthalate	PET	11
Polyurethane	PUR	5
Polyvinyl chloride	PVC	6
Silicone	—	3
Polycarbonate	PC	3
Cellophane	—	2
Polyamide	PA	2
Cellulose	—	1
Total samples		162

analysis of polymer batches for quality assurance and regulatory compliance, particularly in sectors such as toy manufacturing, food packaging, and consumer goods.[60,61] Samples composed of silicone, polycarbonate, cellophane, polyamide, and cellulose were excluded from further analysis due to their underrepresentation (1–3 items per polymer type). Additionally, single reliable identification for ATR-FTIR could not be obtained for 56 samples, which were categorized as "Mixture composition" (MIX), likely due to the presence of mixtures of polymers and additives on their surface.[55,57,62] Rather than representing a limitation of the analytical technique, the high number of MIX samples (~33% of the total dataset) highlights a significant issue in the use of complex and composite polymeric materials in consumer products.[63] The difficulty in pinpointing a single polymer suggests that many of these items are composed of multilayer structures, polymer blends, or coated surfaces, which complicate both material characterization and risk assessment.[63,64] This finding is particularly relevant from a toxicological perspective, as the interaction between different polymeric components, additives, and surface coatings may influence the release behaviour of BPs.[29,30,51,65,66] Complex polymeric structures can lead to unpredictable migration patterns due to differential degradation rates, additive diffusion, and surface modifications. Additionally, the presence of coatings or polymer blends might facilitate the retention or delayed release of BPs, prolonging human exposure over time.[31,53,67] Bisphenol release is influenced by various chemical and environmental factors, including polymer hydrolysis, oxidation, and ionic interactions.[65,68]

Hydrolysis of ester and carbonate bonds in polycarbonates enhances bisphenol release,[68] while ionic components in saliva alter polymer surface, potentially affecting BP leaching kinetics.[69]

3.2 Variety and amount of migrating BPs according to the type of polymer

Factors such as polymer density, crystallinity, permeability, and presence of additives can influence the release of BPs.[4,31,32,49]

Table 2 Total average, minimum and maximum concentration and % of positive samples of BPs migrated per type of polymer. Results are expressed in µg kg⁻¹ of sample. The % of positive samples: samples that release at least one type of BP

Category	Average (µg kg⁻¹)	Min–max (µg kg⁻¹)	% of positive samples
ABS	170.75	<LOQ–644.77	71
EVA	230.01	<LOQ–1099.38	88
MIX	473.22	<LOQ–1802.78	88
PE	1212.52	<LOQ–9112.83	89
PMMA	482.13	77.10–1402.38	100
PP	249.14	<LOQ–469.26	72
PET	109.66	<LOQ–370.53	82
PUR	290.52	<LOQ–833.87	80
PVC	706.74	<LOQ–2023.86	83

Therefore, BP release was examined both quantitatively and statistically with respect to the polymeric composition. Samples identified as PE released the highest amount of BPs with an average concentration of 1212.52 µg kg⁻¹, followed by PVC and PMMA objects, which averaged 706.74 and 482.13 µg kg⁻¹, respectively (Table 2). PET samples exhibited the lowest BP release, consistent with findings from other studies (Table 2).[51,70,71] All PMMA samples released BPs above the limit of quantification (LOQ), making it the only category of polymer

without any negative results, and it also showed the greatest variety, with one sample releasing up to 11 different BP types. This variety in BPs released is important as it provides insight into the complexity of BP exposure profiles, which may vary in toxicological impact depending on the types of BPs present.[11,66] This highlights the necessity for ongoing regulatory efforts to limit the use of high-risk polymers in consumer products, particularly those intended for children. BPs are not typically used in the production of PMMA objects, and no evidence suggests BP release, such as BPA, from these items.[72] Thus, the presence of BPs in PMMA samples could result from their addition in melt blends, or in coatings on the surface to improve product characteristics or even as external contaminants absorbed on the surface.[2,3,29,32,73–76] PE, MIX, PUR and EVA also showed high percentages of detection frequency (80–89%), while ABS and PP had lower frequencies (71% and 72%, respectively), suggesting less frequent BP release in these materials.[36,77]

Individual bisphenols exhibited significant variations in their release profiles depending on polymer composition, as detailed in Tables 3 and 4. PP showed the highest BPA release at 9070.00 µg kg⁻¹, along with high levels of BPB (403.13 µg kg⁻¹) and BPZ (439.59 µg kg⁻¹). ABS exhibited moderate BPA levels, ranging from 35.42 to 93.13 µg kg⁻¹, BPB up to 114.33 µg kg⁻¹ and BPAP in the range of 55.56 to 133.33 µg kg⁻¹. EVA displayed a wide range of BP concentrations, with BPA up to 159.80 µg

Table 3 Migrating BPAF, BPF, BPE, BPA, BPB, BPG and BPC according to the polymeric composition. Average and min–max in µg kg⁻¹; "—" meaning < LOQ or no detection frequency. ABS: acrylonitrile butadiene styrene; EVA: ethylene vinyl acetate; MIX: mix; PE: polyethylene; PMMA: polymethyl methacrylate; PP: polypropylene; PET: polyethylene terephthalate; PUR: polyurethane; PVC: polyvinyl chloride

Polymer	Parameter	BPAF	BPF	BPE	BPA	BPB	BPG	BPC
ABS	Average	—	—	—	56.54	73.36	—	—
	Min–max	—	—	—	35.42–93.13	45.56–114.33	—	—
	Frequency	—	—	—	57.1%	57.1%	—	—
EVA	Average	95.76	16.81	25.55	73.26	84.85	256.06	193.33
	Min–max	44.13–147.39	ND[a]	ND[a]	22.29–159.80	54.87–138.20	ND[a]	ND[a]
	Frequency	25.0%	12.5%	12.5%	75.0%	62.5%	12.5%	12.5%
MIX	Average	21.41	15.25	28.06	31.40	76.48	48.05	12.31
	Min–max	11.41–31.41	6.16–34.00	2.00–240.00	6.00–254.40	0.51–1156.75	4.56–137.30	2.33–41.29
	Frequency	3.6%	27.3%	32.7%	40.0%	61.8%	9.1%	14.5%
PE	Average	40.69	55.97	45.13	154.30	77.89	5.91	1.63
	Min–max	19.90–61.47	5.78–167.71	19.50–83.60	2.38–1150.00	1.87–224.28	1.27–10.56	ND[a]
	Frequency	8.3%	12.5%	16.7%	37.5%	37.5%	8.3%	4.2%
PMMA	Average	—	90.00	66.00	55.69	64.39	—	—
	Min–max	—	ND[a]	ND[a]	16.49–99.50	20.95–117.00	—	—
	Frequency	—	14.3%	14.3%	85.7%	85.7%	—	—
PP	Average	2157.88	89.63	18.84	965.83	69.59	17.43	113.63
	Min–max	ND[a]	11.56–182.81	1.29–65.13	2.28–9070.00	3.05–403.13	11.09–23.77	ND[a]
	Frequency	3.0%	24.2%	30.3%	30.3%	48.5%	6.1%	3.0%
PET	Average	—	31.01	22.37	35.16	30.08	6.22	46.63
	Min–max	—	5.05–43.74	5.57–31.45	6.05–59.39	5.60–77.61	ND[a]	ND[a]
	Frequency	—	36.4%	36.4%	72.7%	81.8%	9.1%	9.1%
PUR	Average	40.27	31.62	—	27.90	35.90	141.40	108.63
	Min–max	ND[a]	2.50–60.73	—	14.65–45.87	18.20–59.60	ND[a]	ND[a]
	Frequency	20.0%	40.0%	—	60.0%	60.0%	20.0%	20.0%
PVC	Average	—	14.89	—	—	39.72	3.37	3.25
	Min–max	—	ND[a]	—	—	17.50–61.94	ND[a]	ND[a]
	Frequency	—	16.7%	—	—	33.3%	16.7%	16.7%

[a] ND: not determined, based on a single positive result; min–max range not shown.

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Table 4 Migrating BPZ, BPS, BPAP, BPM, BPP, BPBP and BPPH according to the polymeric composition. Average and Min–Max in µg kg^{-1}; "—" meaning <LOQ or no detection frequency. ABS: acrylonitrile butadiene styrene; EVA: ethylene vinyl acetate; MIX: mix; PE: polyethylene; PMMA: polymethyl methacrylate; PP: polypropylene; PET: polyethylene terephthalate; PUR: polyurethane; PVC: polyvinyl chloride

Polymer	Parameter	BPZ	BPS	BPAP	BPM	BPP	BPBP	BPPH
ABS	Average	—	—	104.63	—	1.75	—	—
	Min–max	—	—	55.56–133.33	—	ND^a	—	—
	Frequency	—	—	42.9%	—	14.3%	—	—
EVA	Average	39.89	103.43	163.91	215.28	97.98	223.84	140.60
	Min–max	28.68–51.11	28.26–178.60	64.52–400.00	126.84–303.72	22.45–250.00	135.52–312.17	140.60–140.60
	Frequency	25.0%	25.0%	50.0%	25.0%	50.0%	25.0%	12.5%
MIX	Average	772.90	304.28	106.54	54.65	60.45	87.30	24.92
	Min–max	10.10–4022.25	9.24–1462.35	17.86–250.00	0.50–142.33	1.22–215.15	3.56–353.77	4.89–51.09
	Frequency	14.5%	21.8%	20.0%	16.4%	25.5%	20.0%	9.1%
PE	Average	526.76	568.40	87.24	71.56	73.53	30.74	1.65
	Min–max	7.47–1186.68	17.61–1533.43	25.97–181.82	1.69–201.43	1.84–259.43	1.98–59.50	ND^a
	Frequency	16.7%	16.7%	33.3%	29.2%	37.5%	8.3%	8.3%
PMMA	Average	33.93	115.63	139.93	77.06	121.78	115.25	101.63
	Min–max	ND^a	ND^a	29.85–250.00	76.13–78.00	97.00–146.56	ND^a	ND^a
	Frequency	14.3%	14.3%	28.6%	28.6%	28.6%	14.3%	14.3%
PP	Average	184.26	41.65	201.92	141.69	132.84	54.83	102.50
	Min–max	30.28–439.59	7.67–116.00	153.85–250.00	84.88–198.50	1.10–249.56	2.84–133.75	ND^a
	Frequency	15.2%	15.2%	6.1%	6.1%	21.2%	12.1%	3.0%
PET	Average	—	370.95	55.58	32.18	39.71	61.90	41.26
	Min–max	—	47.47–1016.10	19.80–105.26	32.16–32.21	39.05–40.37	47.21–89.86	40.42–42.11
	Frequency	—	27.3%	27.3%	18.2%	18.2%	27.3%	18.2%
PUR	Average	33.33	—	66.67	104.63	65.30	107.43	—
	Min–max	ND^a	—	ND^a	ND^a	ND^a	ND^a	—
	Frequency	20.0%	—	20.0%	20.0%	20.0%	20.0%	—
PVC	Average	—	206.00	162.04	4.88	6.38	1.38	—
	Min–max	—	ND^a	74.07–250.00	ND^a	ND^a	ND^a	—
	Frequency	—	16.7%	33.3%	16.7%	16.7%	16.7%	—

^{a} ND: not determined, based on a single positive result; min–max range not shown.

kg^{-1} and BPAP up to 400.00 µg kg^{-1}. MIX samples showed significant variability, with BPA ranging from 6.00 to 254.40 µg kg^{-1} and BPZ up to 4022.25 µg kg^{-1}. PE samples showed a wide range of BPA levels, with a minimum of 2.38 µg kg^{-1} and maximum of 1150.00 µg kg^{-1}, and notable releases of other BPs like BPZ and BPS, with values up to 1186.68 and 1533.43 µg kg^{-1}, respectively. PVC samples have moderate BP levels, with only a relatively high release of BPAP up to 250.00 µg kg^{-1}. Notably, PVC samples were the only ones in which no BPA release was detected. This finding aligns with the literature showing that PVC materials generally exhibit very low levels of BPA. PET samples exhibited a maximum BPA concentration of 59.39 µg kg^{-1} but a relatively high release of BPS (up to 1016.10 µg kg^{-1}). The identification of high BPS migration from PET further supports concerns that BPA replacements may present similar risks and require further toxicological assessment.[10,11,78] These results underscore the variability in BP release depending on the polymer type, with PP, MIX, and PE exhibiting particularly high levels. In terms of frequency, the most detected BPs were BPA, BPB, BPP, and BPAP; with BPB, BPAP, and BPP observed across all polymer categories. The polymer categories EVA, MIX, PE, and PP showed the broadest release of BPs, encompassing each type examined in this study. In contrast, ABS exhibited the lowest BP diversity, limited to BPA, BPB, BPAP, and BPP. BPAF was the least frequently detected BP, absent in all ABS, PMMA, PET, and PVC samples. Overall, these

main findings are consistent with previous studies, in particular concerning the release of BPA and BPS.[4,19,20,27,29,33,43–45,51,53,79–81] This comprehensive dataset sheds light on how different polymer types contribute to BP release in everyday products and underscores the importance of selecting safer polymeric materials in product manufacturing.

The results of BP release based on the polymer identified on the sample surfaces were statistically analysed using a two-way ANOVA (Table 5). Significant differences were observed for the compounds BPA, and BPS (all comparisons p-value <0.05). BPA release is significantly higher in PE and PMMA samples than in MIX and PP, respectively. BPS release was found significantly higher in EVA and PE samples compared to MIX and PP, respectively. Overall, PE, PMMA and EVA samples showed the

Table 5 Statistically significant results of bisphenol release based on polymeric composition. Release of BPs is statically compared according to the polymeric composition using a two-way ANOVA. Group 1 is the polymeric composition with the highest values compared to group 2

BPs	Group 1	Group 2	p-value
BPA	PE	MIX	0.01
BPA	PMMA	PP	0.01
BPS	EVA	MIX	0.01
BPS	PE	PP	0.04

Table 6 Correlation between polymeric surface of samples and BP release

Polymer	BP	Correlation coefficient	p-value
EVA	BPBP	0.61	0.008
MIX	BPE	0.69	0.003
MIX	BPZ	0.71	0.003
PE	BPAF	0.67	0.004
PE	BPA	0.73	0.002
PET	BPB	0.64	0.006
PET	BPS	0.66	0.005
PUR	BPF	0.65	0.005

most significant release differences compared to other samples. These results indicate that the polymer type on the sample surface influences the amount of migrating BPs, likely due to the polymer manufacturing process and its interaction with other elements of the objects, such as packaging, labels, adhesives, and coatings as potential sources of contamination.[4,27,30–33,44,45,51,53,54,75,82] Interestingly, although BPB was found at a relatively high frequency overall, no significant differences emerged when comparing different polymeric compositions. This suggests that BPB release may not be strongly associated with any polymer type.

The analysis of BP release by polymer type revealed statistically significant differences for certain compounds, prompting an examination of potential correlations between polymer type and BP release. The statistical analysis of the dataset shows significant correlations between various BPs and specific polymers (Table 6).

For BPAF, a correlation with PE suggests that objects made from polyethylene are likely to release higher levels of this BP.

Similarly, BPF shows a significant correlation with PUR, indicating a potential risk associated with polyurethane-based materials. BPE and MIX exhibit a noteworthy correlation, highlighting the importance of monitoring mixed polymer compositions for BPE release. Furthermore, MIX correlates significantly with BPZ, emphasizing the complex potential exposure that can result from mixed polymer compositions.

BPA is significantly correlated with PE, reinforcing the observation that polyethylene objects might pose a higher risk of BPA release and confirming previous findings.[27,32,36,83] PET shows a significant correlation with BPB and BPS. EVA exhibits significant correlations with BPBP, indicating that ethylene-vinyl acetate might be a considerable source of these BPs. Studies exploring the correlation between polymer composition and BP release are relatively scarce in the literature and mostly focus on BPA. These studies typically show that certain polymers, such as PE, and manufacturing methods are positively correlated with BPA release.[4,84–86] Thus, this work confirms findings from the existing literature and provides additional insights into the relationship between different polymers and BP release.

3.3 Surface polymeric composition and object usage analysis

Although the focus of this study is mainly on polymeric materials on the surfaces of consumer products, it is crucial to
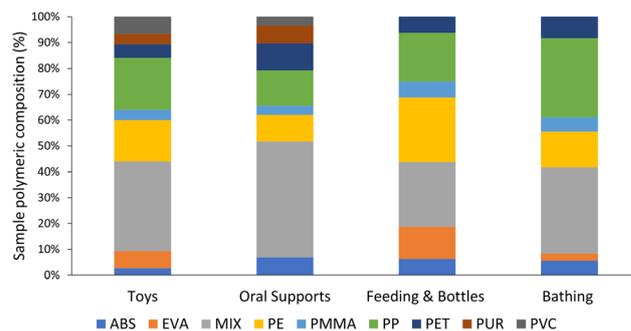
Fig. 2 Frequency of polymeric composition among sample categories. Polymer frequency is expressed by use category: toys, oral supports, feeding & bottles: feeding accessories and baby bottles; and bathing: bathing toys and bathing accessories.

consider how the intended use of an object can influence BP release. The results obtained on polymeric composition were then related to the uses of the different objects analysed, i.e., toys, oral supports, such as pacifiers and teething rings, bath toys and accessories, and feeding utensils including baby bottles, cutlery, and plates. Indeed, investigating the polymer composition with respect to object usage provides deeper insights into potential exposure risks, as certain products may exhibit higher release rates under typical conditions of use. Children's frequent contact with these products, coupled with behaviours such as mouthing, increases their risk of exposure.[36,47,87] For example, toys and feeding accessories may be subject to more frequent handling or direct contact with liquids, factors that can enhance leaching. The frequency of polymers identified on the surfaces of the samples was compared with respect to the different use groups (Fig. 2). Statistical analyses reveal significant differences in polymer distribution among these groups. Notable differences were observed for MIX, PE, and PP polymers, with p-values of 0.023, 0.041, and 0.032, respectively (chi-square tests). MIX polymers are most frequently found in oral supports (45%), followed by toys (35%), bath toys and accessories (33%), and feeding accessories (25%). This high frequency in oral supports suggests that MIX polymers are commonly used in products designed for this application, potentially due to specific material properties or manufacturing requirements. In the case of PE, feeding accessories exhibit the highest frequency (25%), followed by toys (16%), bath toys (14%), and oral supports (10%). These differences suggest variability in the application of PE across product types. For PP, significant frequency differences were noted, with bath toys showing the highest frequency (31%), followed by toys (20%), feeding accessories (19%), and oral supports (14%). PUR and PVC were only detected in toys and oral supports. The polymer frequencies observed in this study are generally consistent with the existing literature, except for PVC, which was found at lower frequencies.[36,88,89] It is possible that some PVC objects were classified under the MIX category due to surface pigments or additives that hindered precise identification using the employed technique.[40,57] Given the variability in polymer usage across product categories and

the significant differences in BP release rates, future research should focus on refining material selection guidelines to minimize human exposure risks. Expanding regulatory oversight on high-risk polymers in children's products will be essential to ensuring safer alternatives in the marketplace.

The correlation between the composition of the polymeric surface and the category of use did not reveal any significant results (p-value > 0.05 for all comparisons). These findings suggest there is no relationship between use categories and polymers, indicating that the combination of a given use category and a specific polymer does not provide statistically useful information for predicting any significantly higher or lower BP release.

4. Conclusions

This study demonstrates significant differences in BP release depending on the polymeric composition of children products, emphasizing the key role that polymer type plays in BP release. By analysing 162 consumer products, this study provides one of the most extensive datasets on BP release from different polymeric materials, offering critical insights into human exposure risks. From a toxicological perspective, the release of BPs from these polymeric materials is concerning due to the potential for human exposure, particularly among children, who are more vulnerable to the effects of endocrine-disrupting chemicals.[15,22,36,53] Given their frequent contact with these materials and hand-to-mouth behaviours, children are at heightened risk of exposure.[27,36,47,87] Previous studies have shown that BPs, particularly BPA, BPF and BPS, can interfere with hormone regulation, leading to adverse health effects such as reproductive issues, developmental disruptions, and metabolic disorders.[10,11,78] This highlights the necessity for ongoing regulatory efforts to limit the use of high-risk polymers in consumer products, particularly those intended for children. The inclusion of a wide array of BP derivatives in this study also underlines the potential need for broader regulatory frameworks that address the diverse BPs present in consumer products. However, this study presents certain limitations. Although artificial saliva serves as a reliable and standardized release simulant, it lacks enzymatic activity and organic components such as mucins and proteins,[90] which may interact with polymer surfaces and influence the release of bisphenols.[47] While the use of artificial saliva improves reproducibility, it may underestimate the impact of enzymatic degradation and protein binding on release kinetics. Additionally, the polymeric composition of some objects was complex, with mixed materials potentially influencing release behaviour in ways that ATR-FTIR could not fully elucidate.[40,55,57] Another notable finding is that several samples contained multiple BPs, suggesting that different bisphenol compounds may originate from distinct sources within the same product.[7,36,51,79] This could indicate the use of different BP-based monomers in polymer blends, the presence of additive precursors containing BPs, or contamination from recycled materials or packaging.[32,52,63,91] While these hypotheses provide plausible explanations, further investigation is needed to fully understand the underlying causes of this phenomenon, in particular about the mechanisms driving the presence of multiple BPs in consumer products, particularly in relation to material formulation and manufacturing processes. At the same time, efforts should focus on refining release models by incorporating microbial and enzymatic activity to better approximate real exposure scenarios. Expanding the scope to include a wider range of polymer formulations and manufacturing additives will further improve risk assessment. These efforts will be essential to guide regulatory policies and ensure safer material choices for children's products. In conclusion, this study emphasizes the urgent need for stricter regulations on high-risk polymeric materials in consumer products, particularly those intended for vulnerable populations such as children. By providing robust data on BP release across different polymer types, it contributes to ongoing efforts in improving material safety standards and reducing human exposure to endocrine-disrupting chemicals.

Data availability

Data will be made available on request.

Author contributions

CR and SD performed all the experimental work. AO and LC conceived the study. FL and DS supervised the project. The manuscript was written by FL and DS. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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