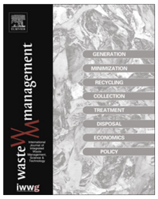
ARTICLE IN PRESS

Waste Management xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman



Recycling of plastic waste: Screening for brominated flame retardants (BFRs)

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ARTICLE INFO

Article history:
Received 16 May 2017
Revised 27 July 2017
Accepted 21 August 2017
Available online xxxx

Keywords:
Tetrabromobisphenol A (TBBPA)
Hexabromocyclododecane (HBCD)
Bromophenol
POPs
Additives

ABSTRACT

Flame retardants are chemicals vital for reducing risks of fire and preventing human casualties and property losses. Due to the abundance, low cost and high performance of bromine, brominated flame retardants (BFRs) have had a significant share of the market for years. Physical stability on the other hand, has resulted in dispersion and accumulation of selected BFRs in the environment and receiving biota. A wide range of plastic products may contain BFRs. This affects the quality of waste plastics as secondary resource: material recycling may potentially reintroduce the BFRs into new plastic product cycles and lead to increased exposure levels, e.g. through use of plastic packaging materials. To provide quantitative and qualitative data on presence of BFRs in plastics, we analysed bromophenols (tetrabromobisphenol A (TBBPA), dibromophenols (2,4- and 2,6-DBP) and 2,4,6-tribromophenol (2,4,6-TBP)), hexabromocyclododecane stereoisomers (α-, β-, and γ-HBCD), as well as selected polybrominated diphenyl ethers (PBDEs) in samples of household waste plastics, virgin and recycled plastics. A considerable number of samples contained BFRs, with highest concentrations associated with acrylonitrile butadiene styrene (ABS, up to 26,000,000 ng TBBPA/g) and polystyrene (PS, up to 330,000 ng $\sum$HBCD/g). Abundancy in low concentrations of some BFRs in plastic samples suggested either unintended addition in plastic products or degradation of higher molecular weight BFRs. The presence of currently restricted flame retardants (PBDEs and HBCD) identified in the plastic samples illustrates that circular material flows may be contaminated for extended periods. The screening clearly showed a need for improved documentation and monitoring of the presence of BFRs in plastic waste routed to recycling.

1. Introduction

Flame retardants are chemical substances introduced into flammable materials in order to increase resistance towards fire (WHO, 1997). There are indisputable benefits of flame retardants in relation to life saving and reducing property damages as the result of fires. Flame retardants are partially responsible for reduced fire incidents across the globe (Birnbaum and Staskal, 2004). There is a plethora of different types of flame retardants currently available on the market; these are commonly divided into four main classes: halogenated organic (bromine or chlorine containing), phosphorous-containing, nitrogen-containing, and inorganic (Birnbaum and Staskal, 2004). Among the halogenated organics, bromine-based chemicals have prevailed due to bromine's higher free radical trapping efficiency and lower decomposition temperature (Guerra et al., 2011). Furthermore, brominated flame retardants (BFRs) can be subsequently divided into five main classes: brominated bisphenols, diphenyl ethers, cyclododecanes, phenols, and phthalic acid derivatives; the first three represent the majority of the BFR market (Birnbaum and Staskal, 2004). Driven by more stringent fire safety measures in developing economies and increasing use of plastics in the construction sector, the market

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Abbreviations: ABS, acrylonitrile butadiene styrene; BFR, brominated flame retardant; DBP, dibromophenol; ePS, expanded polystyrene; EU, European Union; HBCD, hexabromocyclododecane; HDPE, high-density polyethylene; HIPS, high-impact polystyrene; LDPE, low-density polyethylene; LDPE(L), linear low-density polyethylene; LOD, limit of detection; NSP, non-specific plastic; PBDE, polybrominated diphenyl ether; PET, polyethylene terephthalate; PET(G), polyethylene terephthalate glycol-modified; PO, polyolefin; POP, persistent organic pollutant; PP, polypropylene; PS, polystyrene; RHW, residual household waste; RSD, relative standard deviation; SSHW, source-segregated household waste; TBBPA, tetrabromobisphenol A (CAS 7994-7); WEEE, waste electric and electronic equipment; α-HBCD, alpha hexabromocyclododecane (CAS 13423750-6); β-HBCD, beta hexabromocyclododecane (CAS 13423751-7); γ-HBCD, gamma hexabromocyclododecane (CAS 13423752-8); 2,4-DBP, 2,4-dibromophenol (CAS 61558-7); 2,6-DBP, 2,6-dibromophenol (CAS 60833-3); 2,4,6-TBP, 2,4,6-tribromophenol (CAS 11879-6).

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http://dx.doi.org/10.1016/j.wasman.2017.08.038
0956-053X/© 2017 Published by Elsevier Ltd.

Please cite this article in press as: Pivnenko, K., et al. Recycling of plastic waste: Screening for brominated flame retardants (BFRs). Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.08.038

for flame retardants is expected to grow (Freedonia, 2013; Grand View Research, 2016; ICL, 2015). Phosphorous-based substances were forecast to be the fastest-growing types (ICL, 2015), surpassing BFRs in market size in 2015 (Freedonia, 2017). While, global market shares for BFRs decreased from approximately 36% in 2004 (Mack, 2004) to 25% in 2014 (Zion, 2015), introduction of novel halogenated retardants could support partial gains (ICL, 2015).

The single BFRs with the highest global production volumes are tetrabromobisphenol A (TBBPA; 170,000 tonnes in 2004 (George and Häggblom, 2008)), polybrominated diphenyl ethers (PBDEs; approximately 70,000 tonnes in 2001 (CP/RAC, 2009)) and hexabromocyclododecanes (HBCDs; approximately 23,000 tonnes in 2011 (UNEP, 2011)). However, the demand for PBDEs has been in constant decline worldwide (Harrad et al., 2008) and current PBDEs production volumes are expected to be lower. Although HBCD can have a total of 16 isomers, α-, β-, and γ-HBCD are the ones commonly used in commercial mixtures, with γ-HBCD being the most abundant (Heeb et al., 2005). Phenol-based BFRs, such as 2,4-dibromophenol (2,4-DBP), 2,4,6-tribromophenol (2,4,6-TBP), pentabromophenol, etc. have been identified as an emerging class of flame retardants (Bergman et al., 2012; Covaci et al., 2011; EFSA, 2012; Wit et al., 2011). Among those, in particular 2,4,6-TBP is used in the highest quantities in the European Union (EU) (1000–10,000 t/a), primarily as an intermediate for production of other flame retardants such as TBBPA (Miljøstyrelsen, 2014). Dibromophenols (DBPs including 2,4 and 2,6-DBP), as well as 2,4,6-TBP may also result from thermal or UV decomposition of TBBPA as well as selected PBDEs (Barontini et al., 2004; Bendig and Vetter, 2013; de Wit, 2002; Eriksson, 1998).

The persistent nature of flame retardants in general and the brominated ones in particular, allows them to be accumulated and detected in humans and the environment in areas far away from the points of production or consumption (Covaci et al., 2006; Law et al., 2006; Meironyté et al., 1999). BFRs exert a variety of toxic effects, which differ depending on the BFR group in focus and dose it appears at (Darnerud, 2003). According to a recent publication from the International Agency for Research on Cancer (IARC), and reflecting on “sufficient evidence of carcinogenicity in experimental animals”, TBBPA has been upgraded to group 2A (probably carcinogenic to humans) (Grosse et al., 2016). The concerns related to human health and the environment resulted in a ban (EC, 2003) and restrictions on use of selected BFRs (<0.1% for Polybrominated biphenyls and PBDE (EC, 2011)) within the EU. Selected PBDEs and HBCD have also been included in the list of chemicals covered by the Stockholm Convention on Persistent Organic Pollutants (POPs), promoting their elimination in use and imposing a ban on recycling of products containing BFRs. Under the REACH regulation (EC, 2006), in 2015 HBCD has been classified as a substance of very high concern with only authorized production and use.

Flame retardants in plastics are mostly associated with the construction sector, electric and electronic equipment, textiles, and furniture where BFRs are commonly added to polymers as high-impact polystyrene (HIPS) and polystyrene (PS) foam, polyterephthalate, unsaturated polyesters, epoxy resins, etc. (Alaee et al., 2003; Birnbaum and Staskal, 2004; Koch et al., 2015). BFRs can be incorporated in different ways into the polymers, and thus commonly divided into groups such as: additive, reactive, and polymeric (Mack, 2004). While additive and polymeric BFRs are simply blended into a polymer, reactive BFRs are chemically bonded into polymer matrix. HBCD and TBBPA are common examples of additive and reactive BFRs, respectively. Studies have shown the presence of a variety of BFRs in the polymer fraction of waste electric and electronic equipment (WEEE), raising concerns about the fate of BFRs in potential waste management practices (Schlummer et al., 2007, 2005). Polymers commonly found in WEEE include PS, acrylonitrile butadiene styrene (ABS), polycarbonate blends, HIPS and polypropylene (PP) (Martinho et al., 2012). Selected BFRs have been found in food contact materials and children’s toys purchased on the European market (Ionas et al., 2014; Puype et al., 2015; Samsonek and Puype, 2013). Puype et al. (2015) as well as Samsonek and Puype (2013) suggested that presence of BFRs in food contact plastics may be the result of contamination of the polymer products with recycled plastics potentially derived from WEEE. Although BFR levels found in food samples are mostly associated with environmental contamination, potential influence from packaging cannot be excluded (Schecter et al., 2012). Finally, alternative management of waste materials containing BFRs may also create environmental issues e.g., generation of contaminated leachate from landfills (Osako et al., 2004) or formation of toxic chemicals (i.e. dioxins and furans) upon incineration (Weber and Kuch, 2003). The current knowledge of BFRs in waste materials is limited. In order to ensure safe and intelligent recycling and management of the materials, further documentation of the presence of BFRs in plastic articles and waste plastics is needed.

The overall aim of this study was to provide an improved overview of the presence of BFRs in household waste plastics, as well as virgin and recycled plastics collected from industry. This involved quantification of selected BFRs: TBBPA (CAS 79-94-7), dibromophenols (2,4-DBP and 2,6-DBP, CAS 615-58-7 and CAS 608-33-3), 2,4,6-TBP (CAS 118-79-6), α-, β-, and γ-HBCD (CAS 134237-50-6, CAS 134237-51-7, and CAS 134237-52-8), as well as screening of selected PBDEs: BDE-47, BDE-85, BDE-99, BDE-100, BDE-153 and BDE-154.

2. Materials and methods

2.1. Sample collection and pre-treatment

A schematic representation of a generic plastic product lifecycle is provided in Fig. 1. The figure also indicates the sources of plastic samples addressed in this study (e.g., virgin plastics). Samples of waste plastics were collected from residual (#1–13, Table 1) and source-segregated (#14–20, Table 1) household waste from a Danish municipality in April 2013. The waste stream derived from at least 100 households and represented waste generation and collection over two weeks for each household. Details of the sampling campaign can be found elsewhere (Edjabou et al., 2015). After being sampled, waste plastics were manually sorted into plastic packaging and other plastics, in total 14 fractions. Sorting and identification of polymer types followed the internationally accepted classification system, which includes marking plastic packaging with a code 1–7 (ASTM D7611). Plastic items not bearing the classification code were combined in a single fraction (non-specific plastics (NSPs)), which could potentially contain any plastics commonly used in households. Metal-coated and uncoated plastic foils were categorized in separate fractions; commonly made of polyethylene, PP or polyvinyl chloride plastic resins. The details of the individual plastic fractions are presented in Table 1.

After being sorted into the individual fractions, the waste plastics were coarsely shredded (ARP SC2000, Brovst, Denmark), and then finely shredded (SM2000, Retsch, Germany) after being treated with liquid nitrogen to increase the material brittleness. The particle size of the finely shredded plastics was <1 mm.

Samples of processed plastics (virgin and recycled) were collected from a variety of plastics producers and recyclers in China, Denmark, Germany, and the Netherlands. Obtained samples were not anticipated to represent plastics composition on the global

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