Polymers in Waste Electric and Electronic Equipment (WEEE) contain PBDD/F in the ppb-Range

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Introduction

Waste electric and electronic equipment (WEEE) consists of metals (60%), polymers (20%) and residual materials as wood or glass (20%). Whereas state-of the art-technologies are able to recover most of the metals present, recovery rates for polymers and residuals are negligible low. Primarily, this is due to low disposal costs, which refers to landfill or incineration depending on geographic circumstances.

The European WEEE directive, which assesses material recovery rates above 70%, and changes in the German disposal regulation, which will prohibit the landfill of organic materials starting 2005, currently alter the legislative conditions. This leads to an increased interest in polymer recovery strategies [1]. Approaches discussed include polymer recycling and pyrolysis-based material recovery, both characterised by temperatures below 240°C or 600°C, respectively.

Polybrominated biphenyls (PBB) and/or diphenyl ethers (PBDE) in these waste streams complicate waste treatment techniques, since they are known to form brominated dioxins and furans (PBDD/F) under thermal stress, either in polymer recyclates or in pyrolysis products [2]. Additionally, polymer recycling is affected by European directive 2003/11/EC, restricting the distribution of products containing more than 0.1 % of octa- or pentabrominated diphenyl ethers, respectively [3].

Aim of this study was to determine concentration levels of polybrominated compounds including PBDD/F and brominated flame retardants in polymers from WEEE. Both, mixed polymer waste and pre-sorted polymer fractions consisting mainly of monitors, TV-sets or telecommunication housings, were examined. Furthermore, the dependency of PBDD/F concentrations on waste source, pre-treatment and flame retardant system was investigated, implication on waste treatment alternatives are discussed.

Methods and Materials

<u>Samples and samples extraction</u>

Five pre-sorted polymer mixtures from housing materials of electronic devices only and four mixed WEEE polymer fractions were analysed in this study. Sample denotations and descriptions are listed in table 1.

Table 1: Samples investigated in this study

Sample name	Pre-sorted housing polymers	Sample name	Mixed WEEE polymer shredder
H 1	Coarse-grained monitor shredder	M 1	Coarse-grained WEEE shredder (rotor shredder)
H 2	Fine-grained monitor shredder	M 2	Fine-grained WEEE shredder (rotor impact mill)
H 3	Shredded housings (Monitors and TV-sets)	M 3	Polymer dust 1 (hammer mill)
H 4	Shredded housings (telecommunication)	M 4	Polymer dust 2 (hammer mill)
H 5	Hand-sorted Monitors containing brominated flame retardants		

PBDD/F analysis

About 5 g of the samples were dissolved in dichloromethane, spiked with ^{13}C-PBDD/F standards and mixed with silica. Evaporating dichloromethane at moderate temperatures led to polymer covered particles which were extracted with toluene by accelerated solvent extraction (ASE, Dionex) applying the following extraction conditions: 120°C, 100 bar, 4x45 minutes static extraction duration. Extracts were treated with a four column clean-up using acid/basic silica, alumina oxide and florisil. A second florisil column was applied to eliminate residual flame retardants, which might disturb the analysis of polybrominated furans. After clean-up the samples were analysed by GC-HRMS (HP 5980 equipped with a 60m DB5-MS, coupled to a MAT 90, ThermoFinnigan) and quantified with an isotope dilution method.

Sum 4 and sum 5, sum parameters of 2,3,7,8-substituted PBDD/F, which are defined in the German Chemikalienverbotsverordnung (ChemVV [4], see table 2), were calculated for all samples.

Table 2: Definition of sum 4 and 5 and their threshold limits according to German ChemVV [4]

	PBDD/F-congeners	Threshold limit [µg/kg]
Sum 4	2,3,7,8-tetrabromdibenzo-*p*-dioxin 1,2,3,7,8-pentabromdibenzo-*p*-dioxin 2,3,7,8-tetrabromdibenzofuran 2,3,4,7,8-pentabromdibenzofuran	1
Sum 5	2,3,7,8-tetrabromdibenzo-*p*-dioxin 1,2,3,7,8-pentabromdibenzo-*p*-dioxin 1,2,3,4,7,8-hexabromdibenzo-*p*-dioxin 1,2,3,6,7,8-hexabromdibenzo-*p*-dioxin 1,2,3,7,8,9-hexabromdibenzo-*p*-dioxin 2,3,7,8-tetrabromdibenzofuran 1,2,3,7,8-pentabromdibenzofuran 2,3,4,7,8-pentabromdibenzofuran	5

Analysis of brominated flame retardants
ASE extracts were obtained as described in the previous paragraph. They were diluted with ethanol and analysed for brominated flame retardant additives with HPLC-UV/MS as described elsewhere[5]. For quantification, the system was calibrated using flame retardant reference materials, donated by Great Lakes Chemicals Corporation.

Results and Discussion

PBDD/F concentrations determined in the samples are displayed in figure 1 and compared with threshold values of the German ChemVV. With sum values between 1 and 35 µg/kg or 1 and 14 µg/kg for housing based or mixed polymer shredder, respectively, all nine samples exceeded the threshold limits for sum 4 and/or sum 5. According to this directive, they must not be distributed as products anymore. PBDD/F levels are in accordance with data reported in previous studies [6,7,8], indicating that until now efforts to phase out flame retardants on the base of PBB and PBDE, which are known PBDD/F precursors, did not result in decreasing PBDD/F levels.

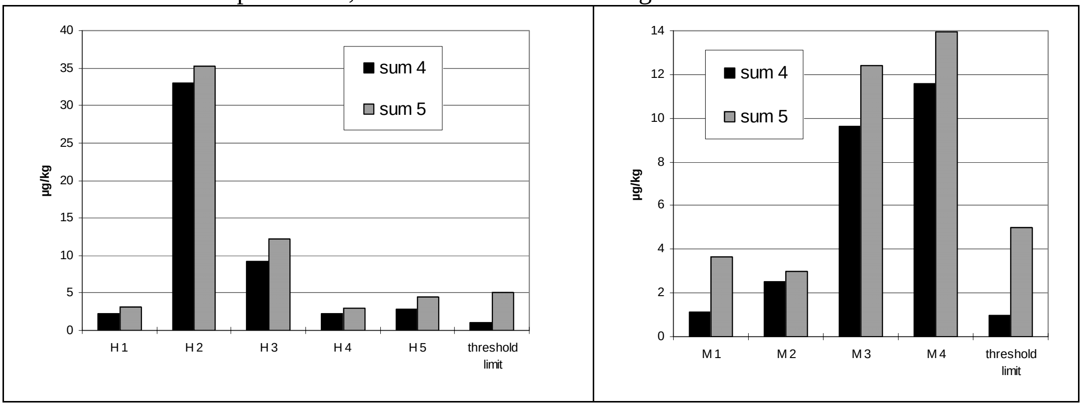

Figure 1: PBDD/F concentration according to German ChemVV, identified in housing based (H1-H5) and mixed (M1-M4) polymer fractions of waste electric and electronic equipment (WEEE).

Four brominated flame retardants, tetrabromobisphenol A (TBBPA), decabromodiphenyl ether (DecaBDE), octabromodipheyl ether (OctaBDE) and 1,2-bis-tribromophenoxyethan (TBPE) were identified and quantified in the samples. Their levels were between 0.25 and 2.5% in housing-based samples and between 0.10 and 0.70% for mixed WEEE polymers, as shown in figure 2. PBB were not identified in any mixture. Most obvious differences between housing-based and mixed polymer materials were the higher absolute levels in the housing materials and the absence of TBPE in the mixed polymer samples.

OctaBDE, which must not exceed the level of 0.1% in new products according to European directive 2003/11/EC was identified in 3 of 5 housing samples and in 2 of 4 mixed shredder samples. Whenever OctaBDE was detected, it exceeded the 0.1% level clearly.

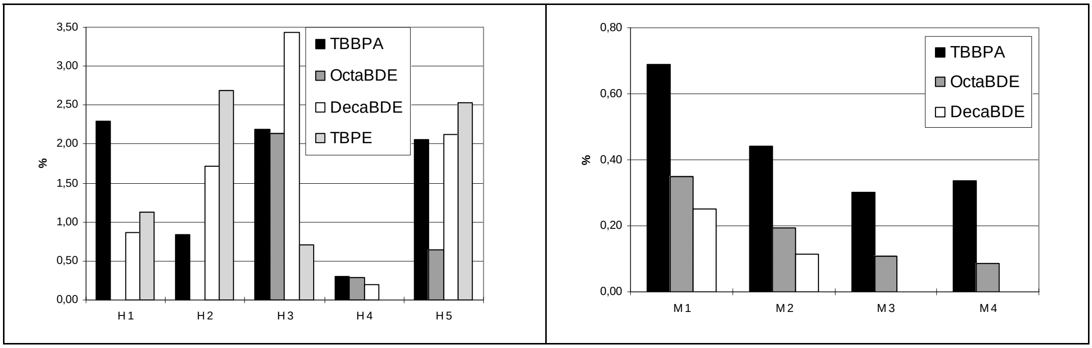

Figure 2: Concentration levels of brominated flame retardants, identified in housing based (H1-H5) and mixed (M1-M4) polymer fractions of waste electric and electronic equipment (WEEE).

As the presence of OctaBDE, DecaBDE and TBPE was related to increased PBDD/F levels in polymer samples [8], a correlation between concentrations of these flame retardants and of PBDD/F was expected. However, this could not be verified, neither for single flame retardants nor for groups of them. As depicted in figure 3 for the mixed shredder samples, even increasing PBDD/F levels were observed with decreasing OctaBDE concentrations.

However, at least for these four samples, the preceding waste treatment, i.e. the shredding technique and resulting particle size, seem to correlate with PBDD/F levels: With increasing energy amount per polymer mass (M1 < M2 < M3 = M4) and decreasing particle sizes, increasing PBDD/F levels were obtained (see fig. 3).

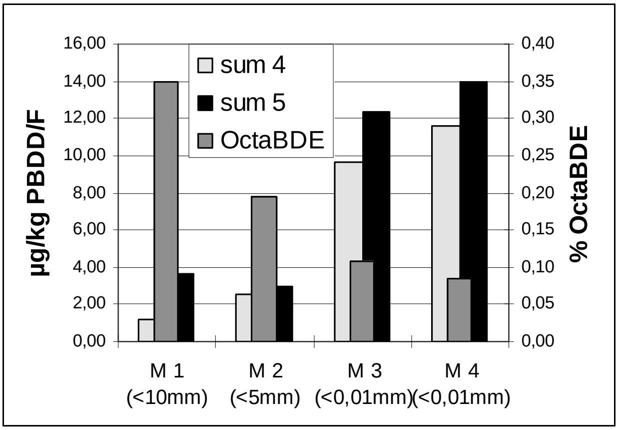

Figure 3: Increase of PBDD/F levels with decreasing particle size, despite decreasing OctaBDE levels.

The levels of polybrominated compounds determined in this study influence the waste management of polymer fractions from WEEE: Polymer recycling is restricted to waste polymers, which do not contain TBPE or PBDE [6], or to innovative polymer recycling techniques that includes an elimination step for PBDD/F and brominated flame retardants, as reported for the CreaSolv™ process [9]. However, in these cases elimination rates of more than 90% are required for PBDD/F and flame retardants in order to yield recyclates in compliance with both, directive 2003/11/EC and German ChemVV.

Otherwise, material recovery rates of the European WEEE directive can only be fulfilled by pyrolysis or gasification techniques. However, these processes have to cope with high bromine (and chlorine) loads and, additionally, their residues and products have to be tested for elevated PBDD/F levels, too.

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