

EMISSIONS OF PBDD/Fs, PCDD/Fs AND PBDEs FROM A TV BACK COVER UNDER THERMAL STRESS

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Introduction

There is growing concern about the potential for human exposure to brominated flame retardants (BFRs), which are present in commonly used articles such as electronic equipment, household furnishings, building materials, and car interiors¹. Some BFRs, such as polybrominated diphenyl ethers (PBDEs), are additives that are not chemically bound to the plastic and therefore may be released more readily into the environment².

Another concern is that PBDEs have the potential to form polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) in combustion processes and under thermal stress like extrusion, molding or shredding³, which may occur in production or recycling processes. The toxicity of these compounds is estimated to be similar to that of chlorinated dioxins⁴. The total amount of PBDD/Fs formed during thermal processes depends largely on the presence of precursor compounds and the specific conditions of the thermal treatment. Precursors that can form PBDD/Fs by a simple elimination step (e.g. PBDE) are thus most prone to form PBDD/Fs, while for other BFRs (e.g. TBBP-A and derivatives, aliphatic BFRs), no significant PBDD/Fs formation potential is reported³. In fact, when PBDEs are used as flame retardants, reactions via condensation or recombination of fragments are one of the main reasons for the occurrence of PBDD/Fs in thermally treated plastics.⁵

A study of the degradation of flame retarded high impact polystyrene (HIPS) at low temperatures has been performed in the present study. PBDEs, PBDD/Fs and mono- through octachlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have been analyzed, assessing the emissions of those pollutants under increasing treatment temperatures, from 50 to 250 °C.

Materials and methods

Samples

Pieces of flame retarded HIPS from a TV back cover were used as experimental samples.

Some characteristics of the material studied are presented in Table 1. An ultimate analysis of the sample was obtained with a CHNS analyzer (FlashEA 1112 Series, ThermoFinnigan), whereas semi-quantitative analysis of the remaining elements was performed by X-ray fluorescence with an automatic sequential spectrometer (model TW 1480, PHILIPS MAGIX PRO, Philips Co, Ltd.).

The bromine content (9.2 wt %) corresponds to the presence of brominated flame retardants in the sample, whereas the presence of antimony (4.1 wt %) is most probably due to the use of Sb₂O₃ as a synergist.

Table 1. Analysis of the TV casing.

Element	wt. %
Elemental analysis:	
C	79
H	6.9
N	nd
S	nd
O and ash (by difference)	14
X-Ray Fluorescence analysis:	
Br	9.2
Sb	4.1
Pb	0.03
Si	0.03
Na	0.02
Ca	0.02
Cl	0.02
K	0.01
Pb	0.01

nd: not detected

Experiments

The degradation experiments were carried out in a vertical stainless steel reactor (diameter 75 mm, length 750 mm), schematically shown in Figure 1. For each run, once the desired temperature had been reached (50, 100, 150, 200 and 250 °C, respectively), a crucible with the sample (TV casing square samples of about 10 g) supported by quartz glass wool, was placed in the middle of the reactor. Air was introduced at constant downflow (1.35 L/min) and these conditions were maintained during 30 min. Measurements of the temperature in the gas phase during the experiments showed that the desired temperature was maintained within ± 5 °C.

The gas phase was continuously sampled using the cooled probe polyurethane foam (PUF) plug technique according to EN 1948:1-3 standards⁶, where flue gases are sucked and cooled and then condensed and drawn through flasks containing water and ethylene glycol, while aerosol particles are collected in a PUF and a filter.

Analysis

All samples, including samples of the original TV casing and the emissions samples, were analyzed with respect to PBDEs, PBDD/Fs and PCDD/Fs. Gas samples were Soxhlet-Dean-Stark extracted with toluene for 24 hours. Untreated TV casing samples were dissolved in tetrahydrofuran, treated in an ultrasonic bath for 60 min to ensure dissolution and extracted overnight at room temperature; the resin was precipitated again by n-hexane addition and the solid content was removed by filtration. The filtered solution was concentrated and treated as the flue gas samples.

The extracts were purified and fractionated on two different gravity fed chromatographic columns; a multilayered silica column and a Florisil[®] column, of which the latter one allows separation of PBDEs from PBDD/F and PCDD/Fs. The purified extracts were concentrated in tetradecane and analyzed for the target compounds by three separate HRGC/HRMS runs using a Waters AutoSpec ULTIMA NT 2000D high resolution mass spectrometer equipped with a DB5-MS column (60 m x 0.25 mm x 0.25 μ m for PCDD/Fs and 15 m x 0.25 mm x 0.1 μ m for PBDD/Fs and PBDEs). All compounds were quantified by isotope dilution methodology. Recoveries of the spiked internal standards for PCDD/Fs and PBDD/Fs were well within the limits of EN 1948:1-3 (30 – 150 % for tetra- to hexa-substituted congeners and 20 – 150 % for hepta- to octa-substituted congeners), except for monoCDF, that presented recoveries between 12 – 16 %. For PBDEs, recoveries met the criteria specified in US-EPA method 1614 (25 – 150 % for tri- to nonaBDE and 20 – 200 % for decaBDE).

All experiments were carried out avoiding direct light exposure of the samples in order to prevent photodegradation of brominated compounds.

Results and discussion

A summary of the most important results is shown in Table 2. The TV casing was found to be flame retarded with decaBDE (680 mg/kg), representing 61 % of total PBDEs. NonaBDE and octaBDE were also present (280 and 160 mg/kg, respectively), accounting for 25 % and 14 % of the total PBDE amount. Regarding the less brominated diphenyl ethers homologues, only minor quantities (< 4 mg/kg) were detected.

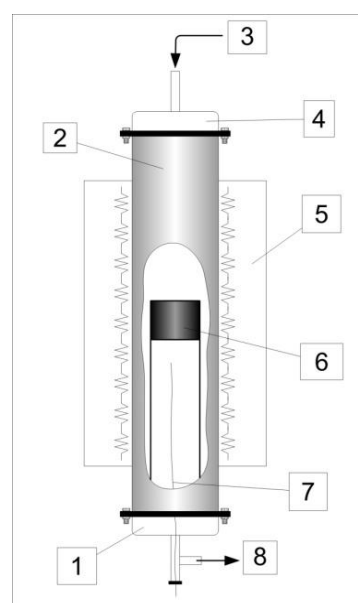


Figure 1. Schematic diagram of the experimental set-up.

- 1) Glass bottom, 2) Stainless steel tube, 3) Gas inlet,
- 4) Glass top, 5) Heating jacket, 6) Crucible,
- 7) Thermocouple, 8) Gas outlet to sampling equipment.

Table 2. Concentration (ng/g) of PBDEs, PBDD/Fs and PCDD/Fs in the flue gas samples (normalized against the amount of plastics that have been heated), as well as in the original TV casing samples.

	50 °C	100 °C	150 °C	200 °C	250 °C	untreated
Σ PBDEs	7.4	33	5 100	37 000	330 000	1100 000
Σ PBDFs	0.35	0.53	51	41 000	289 000	7 400
Σ PBDDs	<0.1	<0.1	5.5	100	3 200	100
Σ PBDD/Fs	0.35	0.53	57	41 100	292 200	7 500
Σ PCDFs	1.4	2.0	2.5	3.8	56	120
Σ PCDDs	<0.01	<0.01	<0.03	<0.01	<0.01	<0.3
Σ PCDD/Fs	1.4	2.0	2.5	3.8	56	120

The homologue profiles for total PBDEs analyzed in the flue gas samples were different from the PBDE profile found in the original TV back cover (see Figure 2). At lower temperatures, the emissions of PBDEs were dominated by decaBDE, indicating a release of unchanged PBDEs from the plastics. However, the emissions of PBDEs at these lower temperatures, i.e. 50 and 100 °C, were lower than 35 ng/g, whereas at 150 °C they increased to 5 100 ng/g. At higher temperatures, a shift was observed in the homologue profile towards less brominated PBDEs, showing that debromination occurred. At 200 °C, 37 000 ng/g of PBDEs were emitted, octaBDE being the most abundant (42 %), followed by hepta- and nonaBDEs. At the highest temperature, ten times more PBDEs were emitted (330 000 ng/g) and the profile was dominated by even less brominated PBDEs (35 % of triBDE).

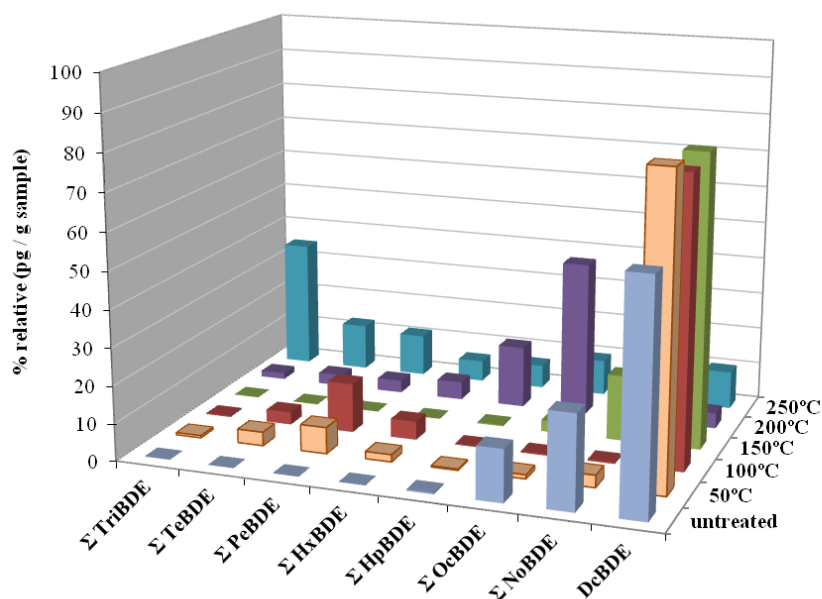


Figure 2. Homologue patterns of PBDEs in the samples (% relative).

The total level of PBDD/Fs in the TV casing was 7 500 ng/g, completely dominated by furans (98 %). OctaBDD was the only PBDD congener found in this sample, whereas furans were detected in every bromination degree (tri- to octa-), with octaBDF (56 %) and heptaBDF (16 %) as the most abundant homologues. The PBDD/Fs are probably originating from impurities in the technical PBDE-mixtures used, from various thermal processes during production of the plastic cover, as well as from transformation processes during normal usage of the TV.

The PBDD/F congener profiles are compared in Figure 3 and show that furans were dominant in all samples. In fact, in the experiments at 50 and 100 °C, no PBDD at all were detected, while PBDF levels were below the ppb range (0.35 and 0.53 ng/g, respectively). For the samples treated at 150 °C, the total amount of PBDD/F increased significantly up to 57 ng/g (90 % of PBDF and 10 % of PBDD). At 200 °C, almost 1000 times more PBDD/F were released (41 100 ng/g) and at 250 °C the total amount of PBDD/F showed more than a sevenfold increase (292 200 ng/g) in comparison to the previous treatment temperature. At the two highest temperatures, the congener profile was clearly dominated by hexaBDF (constituting 37 % and 51 % of total PBDD/Fs, respectively) followed by pentaBDF. The homologue profile for PBDD/Fs in the original TV casing was dominated by highly brominated PBDFs, whereas it shifted towards less brominated congeners for gas samples.

In comparison to PBDD/Fs, levels of the chlorinated analogues are considerably lower, both in the TV plastic and in the gas samples from the heated samples, most likely due to the low chlorine content of the material studied (0.02 wt %).

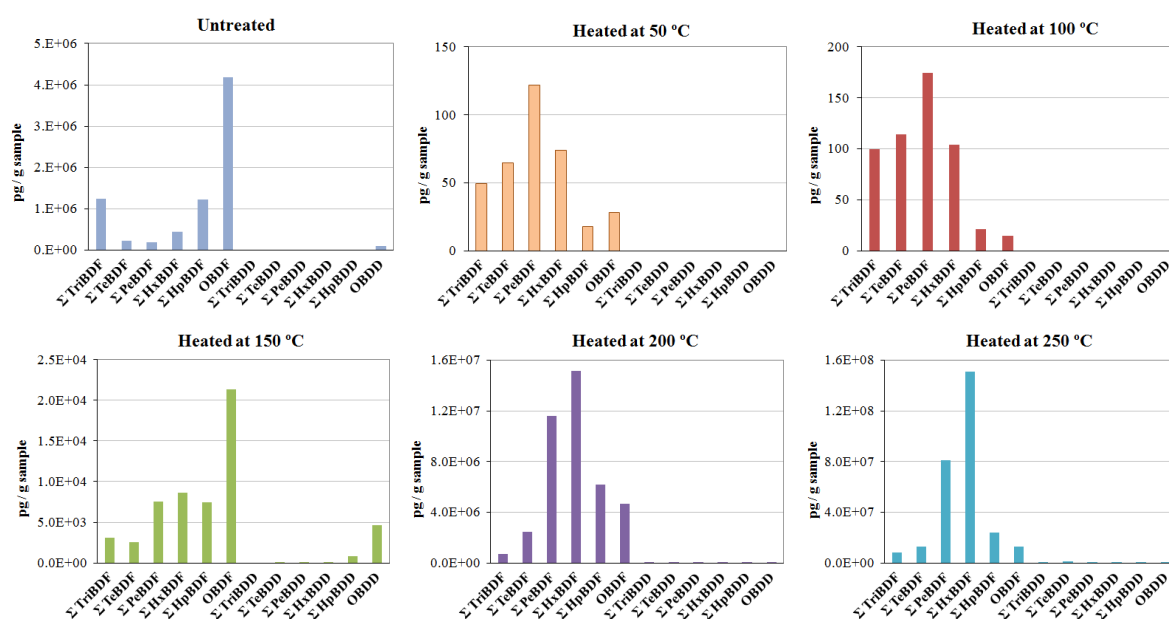


Figure 3. Homologue profiles of PBDD/Fs in the samples (pg/g).

To summarize, the homologue profile for PBDD/Fs in the TV casing was dominated by highly brominated PBDFs, further verifying that they mainly originate from PBDEs. The homologue profile from the emissions at 50 through 250 °C were shifted towards less brominated congeners for both PBDEs and PBDD/Fs. For temperatures up to 200 °C, an increasing release of the PBDEs from the plastic occurred. At higher temperatures, levels of PBDD/Fs are significantly higher and equal the emitted amounts of PBDEs, thus confirming the role of PBDEs as precursors in the formation of brominated dioxins and furans.

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