THERMAL BEHAVIOR OF BROMINATED FLAME RETARDANTS AND PBDDs/DFs

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Introduction

Recently, environmental pollution caused by organic brominated flame retardants, mainly PBDEs, has been reported [1-3] and their effects on the environment and human health has been a cause of concern. In addition, there is the problem of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDDs/DFs) formation as by-products during the thermal processes of products containing organic brominated flame retardants.[4] This research investigated organic brominated compounds in flame retardant plastic materials and examined the behavior of organic brominated flame retardants and PBDDs/DFs during incineration. High-temperature melting in more than 1300•leading to destruction of these compounds was also discussed.

Materials and Method

Laboratory-scale incineration experiments were performed with a feed capacity of 1.0kg/h.[5] Experimental samples were burned in the first combustion chamber of a rotary kiln furnace, and then the first combustion gas including incompletely burned combustibles was introduced into the secondary combustion chamber. Flue gas was passed through cooling duct, acid scrubber and activated carbon adsorption tower. Polybrominated diphenyl ethers (PBDEs), Tetrabromobisphenol-A (TBBP-A) and waste TV casing and waste printed circuit board were used as experimental samples. To observe thermal behaviors of PBDDs/DFs and mixed-Br/Cl-PXDDs/DFs, various experimental parameters were investigated such as chlorine bromine contents in waste, addition of heavy metals and temperature of the flue gas cooling process.

Melting experiments of a mixture of incineration residue (bottom ash and fly ash) and plastic resins were performed at a surface melting furnace, a test plant with a capacity of approximately 2.5ton/day.[6] Incinerated residues of municipal solid waste (MSW), 93.8% (bottom ash: fly ash=6:4), PBDEs/ABS resin 2.4%, PVC resin 3.8% were mixed as experimental samples. These samples were melted at a temperature of 1350°. Inorganic materials were converted to melting slag and discharged into water to be cooled. The flue gas was passed through the secondary combustion chamber, post combustion chamber, and gas cooling tower, followed by bag filter to remove particulates, then the flue gas was emitted. The flue gas sampling points were set at the outlet of post combustion chamber, the inlet and outlet of bag filter. The experiment was conducted under two conditions in the melting furnace. The oxidizing condition was set to supply all of the combustion air into the primary chamber of the melting furnace. The reducing conditions was set to supply the primary combustion air with 80% of stoichiometric air into melting furnace and 20% into post combustion chamber.

Results and Discussion

Concentrations of PBDEs and PBDDs/DFs in Flame Retardant Products

The concentrations of PBDEs and TBBP-A contained in the samples are shown in Table1. Concentrations of bromine tended to be higher than those of chlorine. Waste TV products had 2,100~11,000ug/g of PBDEs and 2.4~1,300ug/g of TBBP-A were present. The PBDEs homologue distribution profiles showed that the ratio of high brominated compounds (N_9 ~D_{10} BDE) in TV casing materials and the ratio of low brominated compounds (T_4~P_5BDEs) in printed circuit boards were high. PBDDs/DFs concentrations in the experimental samples of PBDEs/PE, waste TV casing materials and printed circuit boards ranged between 3,000 and 130,000ng/g. These values are very high, even compared to other investigations.[4] Former studies showed the following potential cases for the formation of PBDDs/DFs in the product; 1) formation during the brominated flame retardant manufacturing process, 2) formation during the processing of flame retardants with polymer resin. More samples are necessary to measure PBDEs and PBDDs/DFs concentrations in flame retarded plastics and further investigations are under way.

Behavior of Flame Retardant Compounds

Table 1: Concentration of PBDEs and PBDDs/DFs in Flame retardant Products

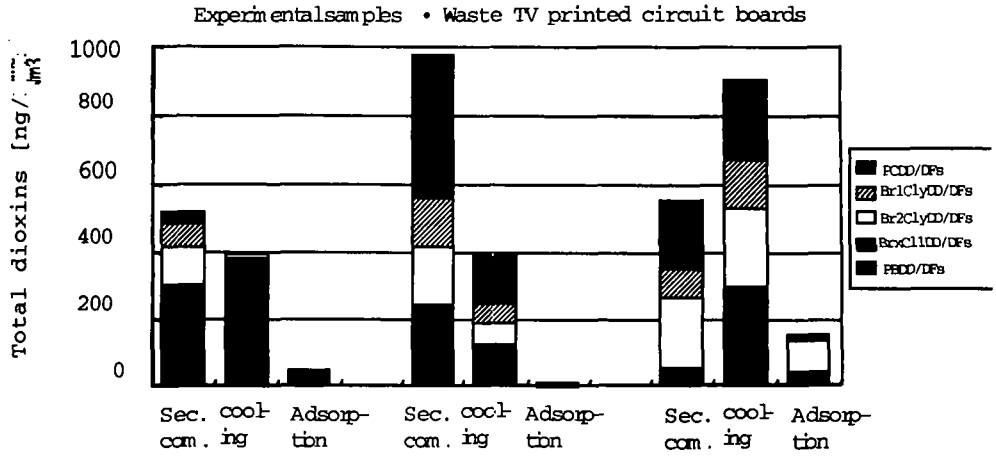
	PBDEs/PE resin	TBBP-A/ABS resin	Waste TV casing (n=2)	Waste TV printed circuit (n=2)
Cl [%]	<0.025	2.0	<0.01 - 0.021	1.1 - 1.
Br [%]	8.8	8.8	2.7 - 3.	7 1.4 - 2.
PBDEs [ƒÊg/g]	20,000	-	2,100 -6,300	4,100 -11,000
TBBP-A [ƒÊg/g]	-	420	2.4 -1,300	500 -520
PBDDs/DFs [ng/g]	3,100	0.62	3,000 - 66,000	38,000 - 130,00

PBDEs and TBBP-A concentrations in incineration residues and flue gases, as well as their decomposition rates were analyzed. PBDEs concentrations in incineration residues were between 2.9 and 180 ug/g, and PBDEs concentrations at the exits of the secondary combustion chamber ranged between ND (<0.15~<0.45) ~5.9ug/Nm^3. Destruction rates of PBDEs were more than 99.9% and those of TBBP-A were more than 95%.

Behavior of PBDDs/DFs in the System of Incineration

Total concentration of PBDDs/DFs, PXDDs/DFs, PCDDs/DFs in incineration flue gas are shown in Figure 1. The temperature of combusting at the first and secondary combustion chamber were set at 900° in the conditions of Figure 1. The ratio of PCDDs/DFs increased in flue gas and the ratio of PBDDs/DFs decreased in accordance with an increase of input chlorine content. PBDDs/DFs tended to decrease significantly at the exit of activated carbon adsorption tower. The total concentration of PBDDs/DF, PCDDs/DFs and PXDDs/DFs in flue gas at the exits of the secondary combustion chamber and in incineration residues with combusting temperature of 600° were higher than those in runs with those at 900°. PBDDs/DFs concentrations at a temperature of

300° at the cooling duct exit tended to be higher than those at 200°. Furthermore, an input material mixed with metals tends to promote formation of PBDDs/DFs. PBDDs/DFs at the exit of the secondary combustion chamber in runs with heavy metals were higher than those without heavy metals of in put.



Input chlorine conc.	0.38•	0.81•	1.66•
Input bromine coc.	3.2•	3.2•	3.2•

Figure 1 Total Dioxins Concentrations in Flue Gas

Output amounts of PBDDs/DFs were lower than their input amounts of all runs in this incineration system. The presence of PBDDs/DFs in incineration residues dominated the output profiles. Amounts of PCDDs/DFs and PXDDs/DFs released, on the other hand, were higher than those amounts of input. When PBDDs/DFs, PCDDs/DFs and PXDDs/DFs were considered as a total, the total amount released was lower than the total input amount.

Behavior of PBDDs/DFs and PCDDs/DFs in the Melting System

Table 2 shows the concentration of PBDDs/DFs and PCDDs/DFs in the melting test. PBDDs/DFs and PCDDs/DFs in the experimental samples were found to be 760 ng/g and 1600ng/g

Table 2 Behavior of PBDDs/DFs• PCDDs/DFs in the melting system [6]

		Experimental samples [ng/g] ([ng-TEQ/g])			Flue gas [ng/Nm^3] ([ng-TEQ/Nm^3])			Melting product [ng/g] ([ng-TEQ/g])	
		PBDEs/ABS resin	Incineration residues of MSW	Input samples*1	Exit of chamber	Inlet of B.F.	Outlet of B.F.	Melting slag	Melting ash fly
PBDDs/DFs	Reducing test	27000	120	762	34	32	16	024	20
	Oxidizing test		018	649	34	073	34	0014	0044
PCDDs/DFs*2	Reducing test	ND 0)	1700 (82)	1597 (77)	19 (022)	48 (12)	90 (16)	027 (00033)	28 (0031)
	Oxidizing test		802 (60)	752 (66)	27 (021)	26 (049)	67 (090)	038 (00055)	088 (00097)

*1 Each concentration in experimental samples was the calculated value. *2 Values in parentheses are 2,3,7,8-TCDD toxicity-equivalent

(7.7ngTEQ/g) in the reducing test and 650ng/g and 750ng/g (5.6ngTEQ/g) in the oxidizing test. High concentration of PBDDs/DFs were from ABC resin mixed with PBDEs and those of PCDDs/DFs were due to fly ash.

PBDDs/DFs and PCDDs/DFs in melting slag and melting fly ash were lower than those in the experimental samples. Concerning the behaviors in the flue gas path, PBDDs/DFs decreased in the bag filter for the reducing test and increased for the oxidation test. Considering the total release of PBDDs/DFs in the flue gas and output solid, melting treatment destructed PBDDs/DFs and PCDDs/DFs. The destruction efficiency of PBDDs/DFs and PCDDs/DFs was calculated as higher than 99.9%. On TEQ basis of PCDDs/DFs more than 99.8% were destructed. PBDEs contained in the experimental samples at about 19ug/g was almost completely decomposed by the melting process. In the oxidizing test, the concentration of PBDEs was lower than 0.004ug/g in the slag and in the fly ash as well. In reducing test, those were lower than the detection limits.

Conclusion

The concentrations of PBDDs/DFs contained in flame retarded products themselves were detected at ppm levels. In the future, more samples are necessary to evaluate PBDEs and PBDDs/DFs concentration in flame retarded products. PBDDs/DFs were detected in many samples of incineration residues during the combustion of flame retarded products. Melting treatment decreased more than 99.9% of PBDDs/DFs in incineration residues.

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