

Formation of PBDD/F from flame-retarded plastic materials under thermal stress

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Abstract

Thermal treatment of plastics flame retarded with brominated compounds often lead to the formation of PBDD/F, especially if polybrominated diphenyl ethers are used. By the presence of antimony(III) oxide, water and some other metals, the amounts of PBDD/F increase. Even during the production and recycling processes of plastics, PBDD/F can be found in considerable amounts. By the use of flame retardants, which are not direct precursors of PBDD/F, the amounts can significantly be decreased.

An incomplete and uncontrolled incineration, occurring in fire accidents in private residences, can form high amounts of PBDD/F, which can endanger the environment and persons in contact with fire residues. Complete and controlled incineration of bromine-containing compounds as usually conducted in municipal waste incinerators, however, show no raised risk.

An overview about the formation of PBDD/F primarily during combustion and also during production and recycling processes of flame-retarded plastic materials is given in this paper.

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1. Employment of brominated flame retardants

Many plastic compounds in technical products are flame retarded in order to minimize the risk of catching fire. Brominated flame retardants are one of the most commonly used groups of substances for this employment. Brominated flame retardants are applied in plastic materials up to 20% (w/w). The consumption in Europe in 1995 amounted to about 64,000 t (Naumann, 1996), in 2001 up to 42,000 t and worldwide up to 239,000 t (www.cefic-efra.org). Some of the most common brominated flame retardants are given below (Jenkner, 1979):

- Tetrabromobisphenol A (TBBP-A) (e.g., in epoxy resins and for polycarbonates)
- Polybrominated biphenyls (PBB) (e.g., for polystyrene and acrylonitrile–butadiene–styrene copolymers—ABS; not used in Europe any longer)

- Polybrominated diphenyl ethers (PBDE) (e.g., for polystyrene and ABS)
- Hexabromo cyclododecane (HBCD) (e.g., for polystyrene foams)
- Brominated phenyl ethers and Bisphenol-A ethers (e.g., for poly- α -olefins)

Under thermal stress, brominated flame retardants release HBr. HBr inhibits the spreading of fire by substituting the more reactive H \cdot and HO \cdot radicals in the radical chain reaction for less reactive Br \cdot radicals (Troitzsch, 1982). With antimony(III) oxide as a synergist, the effect of fire inhibition is increased. A physical mechanism is discussed as a second route to inhibit fire. Due to the formation of HBr as an inflammable gas, the concentration of flammable compounds in the flame is reduced and an inflammable protective layer is formed above the plastic surface.

During this radical reaction, the formation of PBDD/F by de novo synthesis (Lahaniatis et al., 1981) is one possible mechanism. The second and, in the case of PBDE and PBB, the more likely important route via condensation or recombination of fragments without de novo synthesis is shown in Fig. 1, with decabromo diphenyl ether as an example (Bahadir, 1989).

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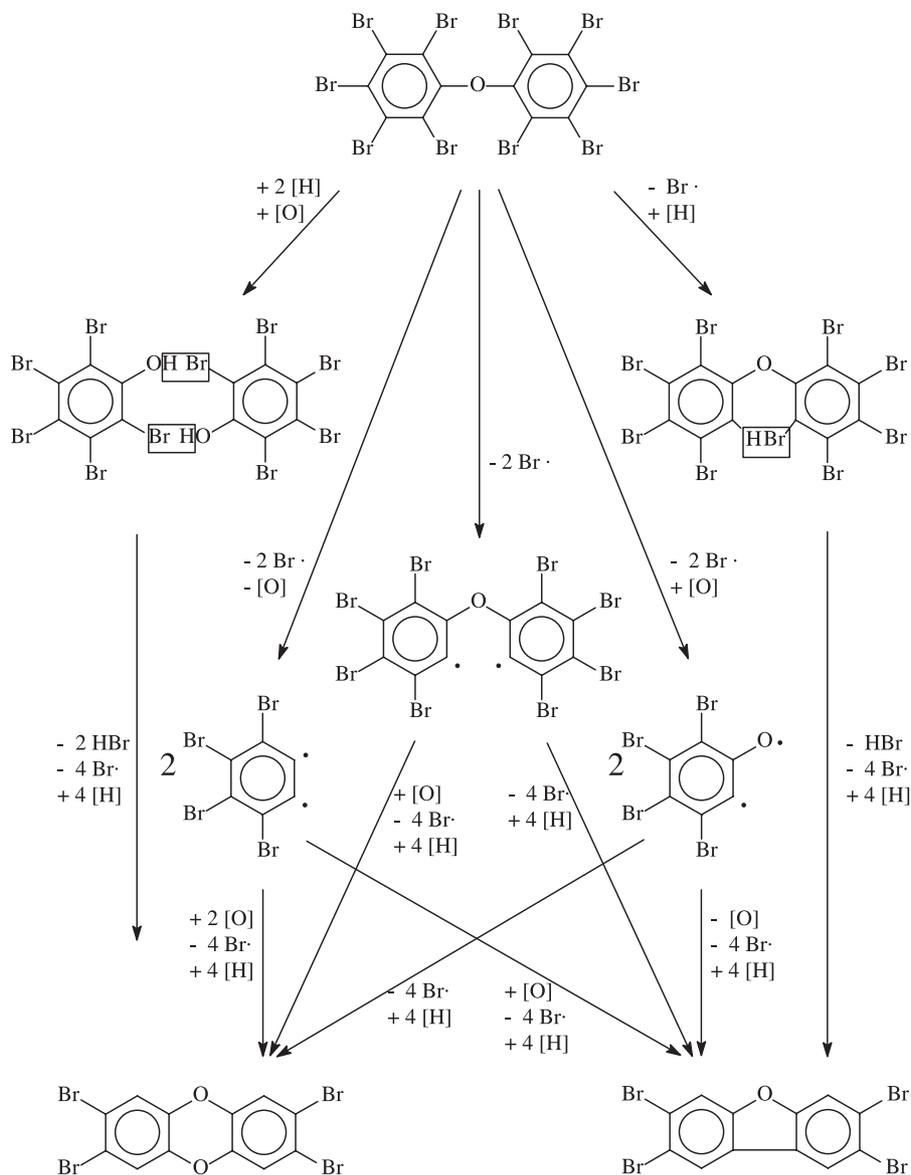


Fig. 1. Pathways for the formation of PBDD/F from decabromodiphenyl ether.

These reactions are the main reasons for the occurrence of PBDD/F in thermally treated plastics above all, when polybrominated diphenyl ethers, biphenyls and phenols are used as flame retardants. Due to the high toxicity of PBDD/F comparable with their chlorinated analogues, combustion residues of plastics containing these flame retardants are of environmental concern and, hence, they should be dealt with care.

2. PBDD/F formation during the production of plastics and further processes at a temperature range below 300 °C

The PBDD/F-forming reactions described above can also occur during the synthesis of some flame-retardant prepa-

rations. PBDD/F have been found in total concentrations of up to 0.4 mg/kg in different polybrominated diphenyl ethers (Ranken et al., 1994; Donnelly et al., 1989; Holderman and Cramer, 1995; Remmers et al., 1993), TBBPA (Thies et al., 1990; Thoma et al., 1986), 1,2-bis-(tribromophenoxy)ethane (Holderman and Cramer, 1995) and hexabromo cyclododecane (Brenner, 1993). In this paper, the sum of Te to OBDD/F are always used, and not toxic equivalents (TE). However, the input of PBDD/F from these compounds into the raw material of plastics is mostly insignificant.

As the temperatures may increase during the production up to 270 °C in some cases, the formation of PBDD/F was also determined. The maximum described values of PBDD/F formed during the production processes are shown in Table 1. Only the detected values are shown, but there are further results cited in the literature reporting on PBDD/F

Table 1
Formation of PBDD/F during production of plastic materials

Flame retardant	Plastic	Maximum temperature	Total amount of PBDD/F in mg/kg (ppm) (maximum value)
Decabromo diphenyl ether (DeBDE)	PBT/AT	254 °C	713 (Donnelly et al., 1989)
	PBT/AT	255 °C	62 (McAllister et al., 1990)
	PS	270 °C	34 (McAllister et al., 1990)
	PS	250–300 °C	1 (Brenner and Knies, 1990)
	PS	275 °C	54 (Luijk et al., 1992)
	PS/AT	275 °C, oven	1310 (Luijk et al., 1990, 1991a)
Octabromo diphenyl ether (OBDE)	PS/AT	271 °C	6 (Donnelly et al., 1989)
	ABS/AT	245 °C	136 (McAllister et al., 1990)
	ABS/AT	246 °C	45 (Donnelly et al., 1989)
Mixture of PBDE TBBP-A	ABS	no specification described	85 (Bonilla et al., 1990)
	ABS	no specification described	0.04 (Meyer et al., 1993)
	ABS	no specification described	0.006 (Bonilla et al., 1990)
TBBP-A oligo carbonate	PBT/AT	240 °C, oven	0.17 (Thies et al., 1990)
	PBT/AT	no specification described	0.004 (Brenner and Knies, 1994)
	PBT/AT	250 °C	0.007 (Brenner and Knies, 1993a)
	PBT/AT	no specification described	0.007 (Brenner and Knies, 1993b)
TBBPA/Bisphenol A copolycarbonate	PC	240 °C, oven	0.14 (Thies et al., 1990)
Hexabromo cyclododecane	PS	no specification described	0.003 (Brenner, 1993)
1,2-Bis-(tribromophenoxy)ethane	ABS	no specification described	0.028 (Bonilla et al., 1990)
Brominated styrene	ABS	no specification described	0.084 (Bonilla et al., 1990)

ABS: acrylonitrile–butadiene–styrene copolymer, PBT: polybutylene terephthalate, PC: polycarbonate, AT: antimony trioxide, PS: polystyrene.

concentrations below detection limits. Not all values shown in the table are directly comparable to each other because some authors determined the sum of all PBDD/F congeners and other gave just the sum of the 2, 3, 7, 8-substituted congeners according to German Chemical Prohibition Decree (Chemikalienverbotsverordnung, ChemVerbotsVO) (shown in Table 2) or American Toxic Substances Control Act.

The highest concentrations up to 1310 mg/kg are found in plastics equipped with DeBDE, as expected, where sometimes threshold values given by law are exceeded. In plastics with other flame retardants, the threshold values are normally remained under.

Table 2
Threshold values of PBDD/F according to German chemical prohibition decree

	Congeners	Threshold values
Group 1	2,3,7,8-TeBDD 1,2,3,7,8-PeBDD 2,3,7,8-TeBDF 2,3,4,7,8-PeBDF	Sum \leq 1 μ g/kg
Group 2	1,2,3,4,7,8-HxBDD 1,2,3,7,8,9-HxBDD 1,2,3,6,7,8-HxBDD 1,2,3,7,8-PeBDF	Sum \leq 5 μ g/kg

In some cases, PBDD/F formation increases with the number of extrusion cycles (Luijk et al., 1992). PBDD/F can also be found in the air of workplace area (Donnelly et al., 1989; Thies et al., 1990; Brenner, 1993; Lorenz and Bahadir, 1993; Luijk et al., 1992; Brenner and Knies, 1993a,b, 1994), in commercially available plastic products (Fluthwedel and Pohle, 1996; Hamm et al., 1992; Sedlak et al., 1996) and in ambient air (Fluthwedel and Pohle, 1996; Ball et al., 1992).

Table 3
Formation of PBDD/F during recycling

Flame retardant	Plastic	Recycling step or conditions	Total amount of PBDD/F in μ g/kg (ppb) (maximum value)
Mixture of PBDE	ABS	Recompounding	60 (Meyer et al., 1993)
	ABS	210 °C	140 (Riess et al., 2000)
	PS	different recycling processes	5 (Riess et al., 1998)
	PS	no specification described	5 (Riess et al., 2000)
TBBP-A	ABS	Recompounding	4 (Meyer et al., 1993)
	ABS	210 °C	0.3 (Riess et al., 2000)
Different	Electronic scrap	Hammer mill	0.7 (Lorenz and Bahadir, 1993)
		Impact grinder	0.7 (Lorenz and Bahadir, 1993)
		300 °C	5 (Lorenz and Bahadir, 1993)
		no specification described	18 (Dumler-Gradi et al., 1995)
		different recycling processes	30 (Meyer et al., 1993)
Poly(pentabromo-benzylacrylate)	PBT	275 °C (six times recycling)	0.4 (Scheinert et al., 2000)
Polybrominated biphenylenes	PS	210 °C	1.3 (Riess et al., 2000)
1,2-Bis(tribromophenoxy)ethane	ABS	210 °C	12 (Riess et al., 2000)

ABS: acrylonitrile–butadiene–styrene copolymer, PBT: polybutylene terephthalate, PC: polycarbonate, AT: antimony trioxide, PS: polystyrene.

Table 4
Formation of PBDD/F after thermal degradation above 300 °C

Flame retardant	Temperatures examined	Maximum formation at	PBDD/F in mg/kg (ppm)
Decabromodiphenyl ether	400–800 °C	600 °C	3 ^a (EL) (Lahaniatis et al., 1991)
	700–900 °C	800 °C	67,800 (PS) (Thoma et al., 1985)
	800 °C	800 °C	1630 (PS) (Hutzinger et al., 1989; Dumler et al., 1987)
	600–800 °C	600 °C	150,000 (PS/AT) (Dumler et al., 1989a)
	360–860 °C	780 °C (N ₂)	1440 (PS/AT) (Luijk et al., 1990, 1991a)
	500–800 °C	n.s.	1630 (PS/AT) (Pinkerton et al., 1989)
	n.s.	n.s.	n.q. (PS/AT) (Luijk et al., 1991b)
	700–900 °C	700 °C	165,600 (PE) (Thoma et al., 1985)
	400–800 °C	600 °C	13 ^a (PL-Cu) (Lahaniatis et al., 1991)
	400–800 °C	400 °C	392,000 (PP/AT) (Dumler et al., 1990b)
	400–800 °C	400 °C	255,000 (PP/AT) (Lenoir and Kampke-Thiel, 1995)
	600–800 °C	600 °C	100,000 (PP/AT) (Dumler et al., 1989a)
	300–800 °C	500 °C	160,000 (PBT/AT) (Dumler et al., 1990a)
	300–800 °C	500 °C	160,000 (PBT/AT) (Lenoir and Kampke-Thiel, 1995)
	300–800 °C	500 °C	160,000 (PBT/AT) (Dumler et al., 1989b)
	300–800 °C	500 °C	158,000 (PBT/AT) (Dumler et al., 1989c)
	500 °C	–	105,000 (PBT/AT) (Lenoir et al., 1994)
	400–1000 °C	400 °C	13,700 (PBT/AT) (Zier et al., 1990)
	400–800 °C	400 °C	13,100 (PBT/AT) (Clausen et al., 1987)
	400–800 °C	400 °C	13,100 (PBT/AT) (Bieniek et al., 1989)
	400–800 °C	400 °C	13,100 (PBT/AT) (Lahaniatis et al., 1989)
	400 °C	400 °C	2810 (PBT/AT) (Donnelly et al., 1989)
	400–800 °C	400 °C	52 ^a (PBT/AT) (Lahaniatis et al., 1991)
	500 °C	–	23,600 (PBT) (Lenoir et al., 1994)
	400–800 °C	400 °C	4 ^a (PBT) (Lahaniatis et al., 1991)
	400–600 °C	n.s.	n.q. (PBT) (Sovocool et al., 1990)
Octabromo diphenyl ether	600–800 °C	600 °C	200,000 (ABS/AT) (Dumler et al., 1989a)
	800 °C	800 °C	9050 (ABS/AT) (Neupert et al., 1989)
Pentabromo diphenyl ether	700–900 °C	800 °C	199 (ABS) (Hutzinger et al., 1989; Dumler et al., 1987)
	700–900 °C	800 °C	420,000 (PS) (Thoma et al., 1985)
	700–900 °C	800 °C	213,000 (PE) (Thoma et al., 1985)
	600–800 °C	600 °C	50,000 (PU) (Dumler et al., 1989a)
Tetrabromo bisphenol A (TBBP-A)	800 °C	800 °C	2000 (PU) (Hutzinger et al., 1989; Dumler et al., 1987)
	400–700 °C	700 °C	3 (ABS) (Luijk and Govers, 1992)
	600 °C	–	3 (ABS/AT) (Thies et al., 1990)
	600–800 °C	800 °C	50 (EL) (Dumler et al., 1989a)
	800 °C	800 °C	39 (EL) (Hutzinger et al., 1989; Dumler et al., 1987)
	600–800 °C	800 °C	80 (EL-Cu) (Dumler et al., 1989a)
	400–800 °C	800 °C	6 ^a (EL-Cu) (Lahaniatis et al., 1991)
	600–800 °C	n.c.	80 (PBTP) (Dumler et al., 1989a)
	600–800 °C	n.c.	10 (PC) (Dumler et al., 1989a)
	600 °C	–	0.1 (PBT/AT) (Thies et al., 1990)
TBBP-A oligo carbonate	600 °C	–	0.4 (ABS) (Thies et al., 1990)
TBBP-A/Bis-phenol A-copolycarbonate	600 °C	–	80 (PP/AT) (Dumler et al., 1989a)
TBBP-A bis(2,3-dibromopropyl-ether)	400–700 °C	600 °C	400 (PBT) (Luijk and Govers, 1992)
Decabromobiphenyl	700–900 °C	800 °C	8900 (PS) (Thoma et al., 1985)
Hexabromo biphenyl	700–900 °C	700 °C	42,900 (PE) (Thoma et al., 1985)
Tetrabromo phthalic acid anhydrous	600–800 °C	n.c.	80 (PU) (Dumler et al., 1989a)
1,2-Bis-(tribromo-phenoxy)ethane	600–800 °C	800 °C	1000 (ABS/AT) (Dumler et al., 1989a)
Polybrominated polystyrene	600–800 °C	n.c.	50 (PE) (Dumler et al., 1989a)
1,2-Bis-(tetra-bromophthalimido)-ethane	600–800 °C	800 °C	100 (ABS/AT) (Dumler et al., 1989a)
Hexabromocyclododecan	800 °C	–	5 (PS) (Dumler et al., 1989a)
	700 °C	700 °C	0.4 (PS) (Brenner, 1993)
	800 °C	800 °C	0.16 (PS) (Hutzinger et al., 1989; Dumler et al., 1987)
Dibromopropyldian	600–800 °C	800 °C	100 (PP/AT) (Dumler et al., 1989a)
Various electronic scrap	1100 °C	N ₂ /H ₂ ; 1100 °C	13 (Dumler-Gradi et al., 1995)

ABS: acrylonitrile–butadiene–styrene copolymer, EL: epoxy laminate, n.c.: not comparable experiments, n.q.: not quantified, PC: polycarbonate, PL-Cu: copper-traced phenyllamine, PS: polystyrene, AT: antimony trioxide, EL-Cu: copper-traced epoxy laminate, n.s.: not specified, PBT: polybutylene terephthalate, PE: polyethylene, PP: polypropylene, PU: polyurethane.

^a Only 2,3,7,8-substituted congeners.

3. PBDD/F formation in plastics during recycling processes

During recycling processes, elevated temperatures and high pressures can occur due to lights or beats of hammers and knives. Therefore, the preconditions for possible PBDD/F formation are given. Table 3 shows the highest observed concentrations of PBDD/F in the material after recycling processes. All concentrations are only the sums of 2, 3, 7, 8-tetra to hexabrominated dibenzo-*p*-dioxins and dibenzofurans according to German law. Especially in the case of polybrominated diphenyl ether, threshold values are exceeded as well, as in production.

4. PBDD/F formation in plastics after thermal degradation in laboratory experiments at temperatures above 300 °C

Table 4 shows concentrations of PBDD/F formed by combustion at temperatures above 300 °C. Not all values are comparable because some author calculated their results on the amount of flame retardant in the starting material and others on the amount of plastic used for the combustion.

Extremely high concentrations are found when polybrominated diphenyl ethers were used. Here, the structure of PBDF is prebuilt in the molecule and the reaction to form PBDD/F is only a ring closure under cleavage of Br₂ or HBr. This is the reason for the prohibition of producing PBDE in Germany and in Europe. Nevertheless, PBDE can still be found in imported products.

The amount of PBDD/F formed increases by the presence of antimony(III) oxide, water and iron(III) oxide (Lahaniatis et al., 1991; Zier et al., 1990; Clausen et al., 1987; Lenoir et al., 1994; Dumler et al., 1990a). The distribution pattern often changes to higher PBDD and lower PBDF concentrations compared with the combusted plastic residues without metals and metal oxides.

5. PBDD/F formation in MSW incinerators and during fire accidents

Due to increased use of brominated compounds in plastics PBDD/F are found in MSW incinerator ashes and flue gases, although in small amounts, even by routine analysis (Riggs et al., 1990). A chlorine/bromine exchange is observed leading to the predominate formation of PBCDD/F and PCDD/F (Thoma et al., 1987). The processes occurring in MSW incinerators and mechanisms of PBDD/F formation are thereby dealt with in more details in another chapter of this volume by Roland Weber and Bertram Kuch.

It was repeatedly reported that PBDD/F are formed during fire accidents. Typical concentrations in fire residues of private residences are 1–50 µg/kg in average (Wichmann

et al., 1992; Fabarius et al., 1990; Zelinski et al., 1993, 1994; Lorenz, 1997). An incinerated TV housing showed concentrations up to 150 mg/kg. Residues of other electrical equipment amounted up to 8700 mg/kg (Fluthwedel and Pohle, 1996; Schacht et al., 1995; Soederstroem and Marklund, 1999). Even clothing of firemen is contaminated up to 2 µg/kg (Fabarius et al., 1990).

These high values compared with the municipal waste incineration are based on the incomplete incineration under uncontrolled conditions often with a reduced oxygen supply. Here, both reactions occur: the de novo synthesis and the formation of PBDD/F by condensation directly from precursors.

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