FORMATION OF POLYBROMINATED DIBENZOFURANS (PBDF's) AND -DIOXINS (PBDD's) DURING EXTRUSION PRODUCTION OF A POLYBUTYLENETEREPHTHALATE (PBTP)/GLASSFIBRE RESIN BLENDED WITH DECABROMODIPHENYLETHER (DBDPE)/Sb_2O_3; PRODUCT AND WORKPLACE ANALYSIS

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Abstract

The formation of PBDF's and PBDD's was measured during pilot plant tests and during the production of PBTP/glassfibre/DBDPE/Sb_2O_3-plastic resin blends. The sampling technique necessary was developed and validated. PBDF's are formed at extruder temperatures around 250-300 °C in amounts of 1 to 560 ppb (ng/g) in the plastic resin. In the workplace area PBDF's were measured in amounts of 34 ng/m^3 (Σ of Tetra BDF's), 143 ng/m^3 (Σ of Penta-BDF's), 554 ng/m^3 (Σ of Hexa-BDF's) and about 200 ng/m^3 (Σ of Hepta-BDF's). PBDD's were found in the air in concentrations of 2 ng/m^3, 8.7 ng/m^3 and 17 ng/m^3 (Tetra-, Penta- and Hexa-BDD's respectively). The measured values, together with the risk calculations made by the governmental bodies, led BASF to the conclusion to stop the production of PBTP/Decabromodiphenylether resin blends and the use of polybrominated diphenylethers (PBDPE's) in general.

Introduction

Polybrominated diphenylethers (PBDPE's) can form PBDF's and, to a lower degree, PBDD's under thermal stress. The most interesting temperature ranges are between 200° and 300 °C and between 500° and 800 °C, for industrial extruder production and injection moulding and for pyrolysis, smoldering and real fire conditions respectively.

Because of results from the literature [1] and our own findings [2] with neat PBDPE's, gained under different experimental and temperature conditions, BASF AG performed pilot plant extruder tests and measurements during PBTP-production with an extruder. The target interest was the formation and concentration of PBDF's and PBDD's in the PBTP-blend and their concentration in the workplace air and in the exhaust gases as well, in order to obtain a rough total balance of the formation and the pathways of these compounds.

Sampling Techniques

The concentrations of PBDF's and D's expected in the workplace atmosphere and their volatility made the use of high-vol-sampling trains in combination with adsorption/absorption techniques obligatory. We therefore used the high-vol version of our polyurethane foam plug (PUFP)/impinger-sampling train [3, 4], consisting of the inlet probe, an impinger cooler, a PU-adsorber (2 PU-plugs, 100 mm length, 100 mm diameter, with a 2 cm PU-disk, impregnated with toluene/methoxyethanol, in front), 2 high-vol-impingers and a second PU-adsorber (for schematic see Fig. 1 in [8]).

Design of Sampling Plans

In order to get a rather statistial picture of the workplace situation, the sampling points (measurement points, MP's, Fig. 2 in [8]) for the sampling trains (ST's) were selected as follows: atmosphere in the building, where the production takes place, MP1, Zone 7, about 8,5 m distance from the extruder; workplace area with the most probable stay of the operator, MP2, Zone 6. Both zones, with the most probable coverage by the sampling are marked in Fig. 2. The workplace near the storage of the granulated resin and the station for refilling 50 kg sacks was monitored with ST3.

In order to obtain data for a rough balance of the total development of PCDF's and D's in the off-gases we also monitored the exhaust line of the extruder head exhaust (MP4), which is covered by a movable steel case above the hot plastic strings, running to the cooling water bath. By this measurement no workplace data are obtained, the data serve only to recalculate the necessary exhaust current and to assess an eventual risk of contamination of the working atmosphere during faults or break downs of the extruder. There were also taken samples statistically of the DBDPE resin blend during production and of the DBDPE used. The sampling time was between 24 and 30 hrs. continuously (day/night shift) and the air volumes taken were betweeen 150 m^3 and 30 m^3 (ST1-3 and ST4).

The conditions during the pilot plant test were similar, all the experiences made there, led to the above described final sampling plan design, used in the production plant.

Analysis of Sampling Trains and Products

The sampling trains were, in part, analyzed in stages, i.e. each compartment, as there is probe, PU-plugs, impingers, were analysed separately, in order to get a validation of the sampling efficiency of the ST's.

The analytical procedures, including the preparation of the samples prior to the clean up, will be given in a separate paper [5]. In all cases the inverse clean up on active carbon/glassfibre was necessary after the normal clean up, in order to get rid of the interfering PBDPE's.

The methods for the PBDF and PBDD-analysis of the DBDPE and the PBTP-blend will be published later.

Results

Validation of Sampling Trains

The sampling trains equipped with two types of high vol impingers [6] were validated by separate analysis of 4 compartments (probe/cooler impinger, P/CI), PU-adsorber 1/2, impinger 1/2, PU adsorber 3/4) e.g. of sampling train ST2. The percent recoveries corresponding to these 4 compartments are given in Fig. 3, together with the absolute values in ng/m^3 x compartment. It can be clearly seen that almost 100 % of the total amount of the PBDF's are recovered from the PU-adsorber 1 (PU 1/2, ≈39 %) and from the impingers (≈60 %). The PU-adsorber captures preferently the lower brominated, the impingers (absorption) the higher brominated PBDF's. Because of the low concentrations of PBDD's no separate analysis was meaningful.

Analytical Results

The results from the pilot plant test showed the formation of mainly PBDF's during PBTP-blending with DBDPE. The exhaust gases had rather high concentration of PBDF's, the PBDD's were markedly lower in concentration. The sampling trains showed a tendency to overload, which led to the development of new high-vol- impingers, in order to combine high-vol-PU-adsorption with high-vol- absorption. One of the results was that the major part of the PBDF's formed stays in the PBTP/DBDPE/ glassfibre blend (about 98,5 %), only 1,5 % go into the atmosphere, especially at high temperatures (>200 °C) and in presence of water (vapour steam transport). Because of the experimental state of this test no values are given in this paper. The analytical results of the extruder production test are summarized in the bar diagram in Fig. 4. The values for the room sample (ST1, RS) are, in the limits of precision for sampling plus analysis, almost identical with the values of the workplace (ST2, WP), which indicated the general distribution in the building at low concentrations.

The storage and refilling station for the granulate sacks (ST3, SR) showed much lower, but still measurable concentrations of PBDF's. The high PBDF-values in the concentrated exhaust stream from the extruder head (ST4, EH) are reported here only to show the general tendency of PBDF-formation and to indicate the need for a rigorous exhaust stream around the extruder head.

In the schematic in Fig. 5 the data are summarized in relation to the ST-positions. The tentatively determined 2,3,7,8-isomeric PBDF's are also included in the figure. The PBDD-values found in the ST2, WP are summarized in the following table, they are two orders of magnitude lower than the PBDF-values. Surprisingly we found, although still tentatively determined selective, 1,3 ng/m^3 1,2,3,7,8-Penta-, 1 ng/m^3 1,2,3,6,7,8-Hexa- and 1,6 ng/m^3 1,2,3,7,8,9-Hexa-bromdibenzodioxins.

PBDD's found in ST2, WP, workplace area

2,3,7,8 TBDD ng/m^3	1,2,3,7,8 PBDD ng/m^3	1,2,3,6,7,8 Hexa_BDD ng/m^3	1,2,3,7,8,9 Hexa_BDD ng/m^3
<0.5	1.3	1	1.6

Σ Di- ng/m^3	Tri ng/m^3	Tetra ng/m^3	Penta ng/m^3	Hexa ng/m^3	Hepta ng/m^3	Octa- ng/m^3	Dibenzodioxins
<0.05	0.35	2.04	8.73	17	n.d.	n.d.	

n.d. = not detected

The DBDPE used and the PBTP/DBDPE/Glassfibre-resin blend were analysed with recently developed methods [7], the analytical results obtained are summarized below:

Σ of	Di	Tri	PBDF's Tetra	Penta	Hexa	Hepta	Octabromo Dibenzo-furans (ppb = μg/kg)
DBDPE batch*	0.04	<0.9	0.15	<0.01	<0.2	1842	195
PBTP/DBDPE-glassfibre blend**	1.0	4.9	6.2	26.8	151	≈560	≈280

* PBDD's were determined as 0.05 ppb tetra- and 0.35 ppb penta-bromo-dibenzodioxins respectively.

** PBDD's below limit of detection (0.1-6 ppb, depending on homologue group)

Conclusions & Consequences

Shortly after the first results published [1] and our own measurements BASF AG decided, as a precautionary measure, to stop the production of decabromodiphenylethe PBTP-plastic resins and the use fo PBDPE's in general, although the up-to-date toxicological risk assessments still lack full prove by toxicological experiments.

References

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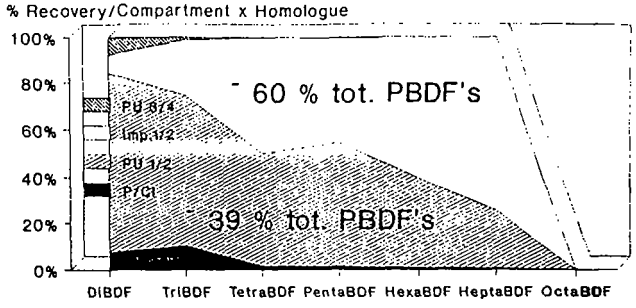
Validation for Sampling Train ST2
Compartments: Probe,PU1/2,Impg.1/2,PU3/4



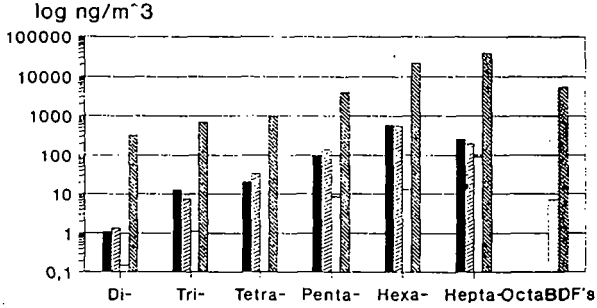
PU 3/4	0,1	0,1		0,2	0,6	
Imp.1/2	0,1	1,8	16,8	64,6	333,2	148
PU 1/2	1	4,8	16,3	75,9	214,1	50
P/Cl	0,1	0,8	0,6	2,5	6	2

Homologue PBDF's,ng/m^3 x Compartment

Stages of ST combined (PU's, Impg.'s,)

Fig.3

Extruder Test, Production, PBTP/DBDPE
PBDF's, Sampl. Train 1 - 4



ST1,RS	1,08	13	20,3	97,7	594	260	
ST2,WP	1,31	7,35	33,7	143,2	553,9	200	
ST3,SR	0,15	1,1	5,08	8,55	13,1	88	7
[ST4,EH]	321,5	704,7	980,3	3910,4	22162	39550	5275

Homologue BrDF's, ng/m^3 Air

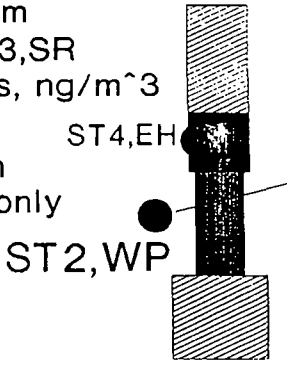
Fig. 4

Schematic of the Workplace Situations

Fig. 5

Measured Values from
ST1,RS, ST2,WP, ST3,SR
Sums of Homologues, ng/m^3

* Tentative Correlation of 2,3,7,8 -Isomers only



	Σ ng/m^3	2,3,7,8-*
D2BF's	1,3	-
T3BF's	7,4	-
T4BF's	34	-
P5BF's	143	1,3
H6BF's	554	2,6
H7BF's	~200	-
O8BF's	-	-

	Σ ng/m^3	2,3,7,8-*
D2BF's	1,1	-
T3BF's	13	-
T4BF's	20	-
P5BF's	98	-
H6BF's	594	-
H7BF's	~260	-
O8BF's	-	-

ST1,RS

	Σ ng/m^3	2,3,7,8-*
D2BF's	0,2	-
T3BF's	1,1	-
T4BF's	5,1	-
P5BF's	8,6	-
H6BF's	13	0,3
H7BF's	~88	-
O8BF's	~7	-

ST3,SR