

## Analysis of polybrominated bipheyl ether in silicone and EPDM rubber

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### Introduction

Polybrominated diphenyl ethers (PBDEs) are used as flame-retardants in a variety of polymers. Silicone rubber is one of the most widely used polymer in electronic appliances with numerous end uses like cables, corona-resistant insulation, keyboards, contact mats, and conductive profiled seals (1,3). Ethylene propylene diene monomer (EPDM) rubber is also very frequently used in many industries. These therefore may represent a significant reservoir of BFRs. It is known that leakage of the brominated flame retardants into the environment might occur by evaporation from heated materials, as discharge from industry or from waste handling and deposition because PBDEs are additives mixed into polymers and are not chemically bound to the plastics (4). In addition, both of these two polymers are resistive to many chemicals including acids and solvents giving some difficulties to analysis of the compounds in the polymer. In this study, liquid-liquid extraction combined with soxhlet extraction was adopted to measure the content of PBDEs in these two polymers and the efficiency of the extraction measured was compared with that of soxhlet only. The results showed that the extraction with soxhlet only was not effective to measure the content of PBDEs in the polymer samples such as rubber. We could identify that there are four BDEs in silicone rubber and thirteen BDEs in EPDM rubber. In addition, we could observe the existence of the additional BDEs in both of the samples.

### Materials and Methods

**Sample preparation:** The rubber samples were obtained from a wasted refrigerator of a recycling company, Soo-Woon city, Korea. In order to prevent photodegradation processes, samples in the solid state were stored in the dark after washing with DI water to remove the dust of the surface and transferred to laboratory. The samples were grinded to a size of 1.0 mm by the combination of cutting and mills under cooling with liquid nitrogen. The samples grinded (1.0g each) were dissolved in 10 ml toluene after addition of 25  $\mu$ l of <sup>13</sup>C<sub>12</sub>-labeled polybrominated diphenyl ethers (PBDEs) mixture as internal standard. The suspensions were stirred for 3 hours and were filtrated through quartz wool. The filtrated solution was transferred to separation funnel and the glass wool containing solid parts was extracted with soxhlet. After soxhlet extraction for 24 h with toluene, the extracted samples were combined with filtrated solution and washed with H<sub>2</sub>SO<sub>4</sub> until colorless and

then with hexane-rinsed water to make them neutral. Sample cleanup was done in two stages; (a) silica gel column (with layers of neutral and acidic silica); (b) activated acidic alumina column capped with anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated with  $\text{N}_2$  gas. The final volume of the samples was adjusted to 100  $\mu\text{l}$  with toluene. All solvents and acids employed in this experiment were purchased from Merck (Darmstadt, Germany).

**Analysis:** The PBDEs analytical standard (BDE-MXE) was purchased from Wellington Laboratories, Inc. (Ontario, Canada). BDE-MXE contained the following PBDE congeners: mono-BDEs 3; di-BDEs 7 and 15; tri-BDEs 17 and 28; tetra-BDEs 47, 49, 66, 71, and 77; penta-BDEs 85, 99, 100, 119, and 126; hexa-BDEs 138, 153, 154, and 166; and hepta-BDEs 183, 184, and 191; octa-BDEs 196 and 197; nona-BDEs; 206 and 207; and deca BDE; 209. In this study, the following  $^{13}\text{C}_{12}$ -labeled congener mixture (MBDE-MXE) containing BDE-3,15,28,47,99,153,154,183,197,207, and 209 was also used as internal standard. The BDE-MXE standard was used to check the retention time of congeners and fragmentation pattern. Gas chromatography was performed on a HP-6890 gas chromatograph equipped with a DB-5 HT capillary column (30m X 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness; J&W Scientific, Folsom, CA). Helium was used as carrier gas and makeup gas. Injections were made in the splitless mode. The injection volume was 5  $\mu\text{l}$ . The column oven temperature was programmed as follows: 110  $^{\circ}\text{C}$  (5 min), 40  $^{\circ}\text{C}/\text{min}$  up to 200  $^{\circ}\text{C}$  (4.5 min), 10  $^{\circ}\text{C}/\text{min}$  to 325 (15 min). The injector temperature was held at 250  $^{\circ}\text{C}$  (2). Mass spectrometry (GC/MS) analyses were performed on a HP MSD instrument connected to the followed GC. The ion source and transfer line temperatures were 290  $^{\circ}\text{C}$ . Direct monitoring the molecular ion was not possible above octa-substituted PBDEs due to the limitations of the instrument (maximum of  $m/z$  800). The masses monitored can be seen from Table 1. Retention times of the PBDE isomers mentioned above were determined by injection of native standards of these compounds. For identification of the PBDE isomers in the samples, fragmentation pattern relative to native standard and reference provided by supplier of the standard were applied.

## Results and Discussion

**Extraction of samples:** At the first, we tried to extract PBDEs by soxhlet after grinding. The recovery rate of the internal standard was over 90 % (Data not shown). However, the concentration of PBDEs was too much lower than expected even after 24 hrs extractions. This result indicated that extraction with soxhlet only was not effective to take out PBDEs from both of two polymers used in this study. Liquid-liquid extraction after dissolving the materials with hydrofuran or toluene was not considerable because it required too many acid washings and clean ups. Thus, in this experiment, the solvents swallowed the samples grinded. Then, solvents used for swallowing the samples and the rest of solid residues were extracted separately. With the method, the recovery rates were from 57.4% to 101.3% according to isomer with much less acid washing and column purification.

**Identified Congeners:** BDE-17, BDE-66, BDE-71, and decaBDE were identified in silicon rubber. Among the BDEs analyzed, deca BDE was found at the highest relative concentration. BDE-66 was also relatively higher than another congeners. In the case of EPDM rubber, thirteen di-to decaBDEs were identified and quantified by comparison of relative retention time and

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fragmentation pattern with the standards. In this study, relatively higher concentration of the additional BDEs was observed. However, those BDEs were could not be identified and quantified because the number of congeners in the standard was not sufficient to match all of the congeners in the sample. The analysis of EPDM rubber showed that relatively high concentration of tetra BDEs of which usage was banned. This study also showed that PBDEs are ubiquitously used in the electronic appliances even when the usage was not necessary.

**Table 1:** Analytical standard adopted in this study, ions monitored and concentration of selected known PBDEs in silicon and EPDM rubber

PBDE congeners		Ions Monitored	Concentration (ug/g)	
Isomer No.	Structure		Silicone Rubber	EPDM rubber
3	4	247.9 141.0	N/D	N/D
7	2,4	327.8 325.8 329.8	N/D	8.2
15	4,4		N/D	152.2
17	2,2,4	405.8 403.8 407.8	68.0	60.6
28	2,4,4		N/D	342.1
47	2,2,4,4		N/D	80.6
49	2,2,4,5		N/D	N/D
66	2,3,4,4	485.7 483.7 487.7	31.1	3887.0
71	2,3,4,6		21.7	209.0
77	3,3,4,4		N/D	1416.6
85	2,2,3,4,4		N/D	N/D
99	2,2,4,4,5		N/D	966.2
100	2,2,4,4,6	563.6 561.6 565.6	N/D	128.0
119	2,3,4,4,6		N/D	N/D
126	3,3,4,4,5		N/D	N/D
138	2,2,3,4,4,5		N/D	110.9
153	2,2,4,4,5,5	643.5 641.5 645.5	N/D	N/D
154	2,2,4,4,5,6		N/D	250.8
156	2,3,3,4,4,5		N/D	N/D
183	2,2,3,4,4,5,6		N/D	N/D
184	2,2,3,4,4,6,6	721.4 719.4 723.4	N/D	N/D
191	2,3,3,4,4,5,6		N/D	N/D
196	2,2,3,3,4,4,5,6	799.3 , 642.0 321.0	N/D	N/D
197	2,2,3,3,4,4,6,6		N/D	N/D
206	2,2,3,3,4,4,5,5,6	721.0 360.0	N/D	N/D
207	2,2,3,3,4,4,5,5,6,6		N/D	N/D
209	Deca	799.0 400	249.3	457.1

**Table 2:** Relative retention, structures and concentration of selected known and unknown PBDEs in silicon and EPDM rubber.

RT (min)	Cognerner	Structures	Concentration (ug/g)	
			Silicone rubber	EPDM rubber
12.23-12.33	di-BDE	Unknown Strcture		12.4
12.49-12.58		BDE-7		8.2
12.78-12.90		BDE-15		152.2
14.94-14.99	Tri-BDE	Unknown Strcture		5.3
15.10-15.19		Unknown Strcture		6.9
15.35-15.56		Unknown Strcture		134.3
15.76-15.98		BDE-17	68.0	60.6
16.06-16.11		BDE-28		342.1
16.16-16.21		Unknown Strcture		1134.53
16.32-16.38		Unknown Strcture		57.17
17.52-17.61	Tetra-BDE	Unknown Strcture	1.2	86.8
17.77-17.86		BDE-49		32.3
17.91-18.04		BDE-71		1416.7
18.04-18.10		BDE-47		80.6
18.32-18.61		BDE-66	211.6	3887.0
18.68-18.83		BDE-77	14.9	209.12
19.19-19.24		Unknown Strcture		1069.4
19.45-19.50	Penta-BDE	BDE-100		37.8
20.06-20.12		BDE-119	3.2	128.0
20.12-20.32		BDE-99		966.2
20.55-20.74		BDE-85		80.1
21.32-21.38		BDE-126		3.2
21.54-21.59	Hexa-BDE	BDE-154		250.0
21.82-21.92		BDE-138		110.9
22.02-22.07		BDE-156	45.48	
22.16-22.21		Unknown Strcture		1.1
23.90-23.95	Hepta-BDE	BDE-184		1.2
24.15-24.22		BDE-183		10.4
32.40-32.60	Deca-BDE	BDE-209	249.3	457.1
SUM			593.6	10740.5

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