Behavior of Additive Brominated Flame Retardants in Textile Products

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Introduction

We are exposed to brominated flame retardants (BFRs) in daily life through multiple media including food products, air, and dusts; direct exposure to BFRs from treated goods is also of considerable importance. However, very little is known about behavior of BFRs in the consumer products. Since textile products such as curtains, carpet, and seat covers have high specific surface areas among household articles, BFRs added to textiles may be emitted to the indoor environment and thus contribute as sources of indoor air and dust pollution. As curtains are normally used under sunlight-exposed condition, photodegradation and isomerization potentials of BFRs in the products are of interest as well.

Hexabromocyclododecanes (HBCDs) are the most frequently added BFR for textiles in Japan, followed by decabromodiphenyl ether (DecaBDE) and decabromodiphenyl ethane. Recently, wide ranges of HBCD concentrations were found in house dust samples (Stapleton et al., 2004; Abdallah et al., 2008a; Takigami et al., 2009), and apparently higher HBCD levels were observed in indoor air than in outdoor air (Abdallah et al., 2008b), indicating that significant sources of HBCDs very possibly are present indoors. We demonstrated recently an increase of HBCD concentration of indoor air when flame-retarded curtain was hanged over the wall of a room (Kose et al., 2008). However, detail behaviors of BFR emission from textile products remain poorly understood because diastereomer-specific analysis of HBCDs was not conducted in the previous study.

This study was designed to examine the behavior of BFRs including HBCDs and polybrominated diphenyl ethers (PBDEs) added to textile products, and to expand the existing knowledge base related to the contribution of these products/materials to contamination of the indoor environment. The aims of this study were: (a) to determine the emission rates of HBCD diastereomers from flame-retarded curtains; and (b) to elucidate the potential of HBCD photolysis when exposed the curtains to natural sunlight, in comparison to PBDEs.

Materials and Methods

Samples

Three different kinds of flame-retarded upholstery textiles for manufacturing curtains, labeled A, B, and C, were used in this study. They were confirmed to be treated with either HBCD or PBDE technical mixtures in our previous study (Kajiwara et al., 2009). Textile A and B contain approximately 4 wt% of HBCDs, whereas textile C was treated with DecaBDE and contains approximately 11 wt% of BDE 209. Information of samples is given in Table 1.

Table 1. Concentrations (mg/kg) of bromine, HBCD diastereomers, and PBDEs in the flame-retarded curtains used in this study

ID	Color	Material	Bromine	α-HBCD	β-HBCD	γ-HBCD	ΣHBCDs	ΣPBDEs
Textile A	light blue	polyester	35,000	18,000	7,500	17,000	43,000	1.0
Textile B	black	95–99% polyester	35,000	19,000	6,300	18,000	42,000	11
Textile C	beige	100% polyester	88,000	0.32	0.050	2.1	2.5	120,000

Emission Test

Small stainless steel containers (7 cm i.d. x 5.5 cm high, ca. 210 cm^3) equipped with polyurethane foam (PUF) to which BFRs absorb were used for emission measurements (Fig. 1). PUF for high volume air sampler (9 cm diameter x 5 cm long, SIBATA, Japan) cut into four round slices was put into the upper side of the container. The sample material (5 cm x 5 cm) was placed on the other side of the container with careful attention to ensure no direct contact with PUF. After sealing with Teflon tape, the containers were placed in a constant-temperature oven set to 40°C, 60°C, or 80°C for 120 h to investigate emission behavior of BFRs from the curtain surface. The emission of BFRs was also tested at room temperature (20°C). At the end of each experiment batch conducted in triplicate, PUF were removed for subsequent chemical analysis. BFRs sorbed on PUF were extracted in a Soxhlet apparatus with acetone for 16 h after adding ^{13}C-PBDE and ^{13}C-HBCD mixtures as internal standards. The extract was concentrated and cleaned up by a multilayer silicagel column, which consisted of silica gel, 22% sulfuric acid−impregnated silica gel, and 44% sulfuric acid−impregnated silica gel. Quantification was performed by using a HRGC-HRMS and a LC-MS-MS for PBDE congeners and HBCD diastereomers, respectively. The emission rates ($\mu g/m^2/h$) were calculated using the amount of BFRs extracted from the PUF (μg), the sample area (0.0025 m^2), and sampling time (120 h).

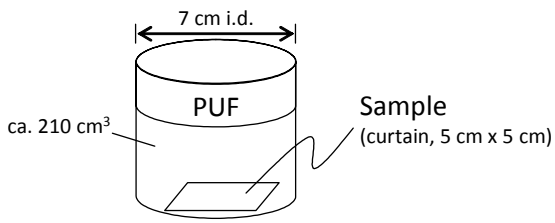

Fig. 1. The emission test device

Sunlight Exposure Test

The experiment was performed for almost a year from November 2007 to November 2008 at the NIES campus in Tsukuba, Japan (36˚02'N, 140˚07'E). To keep out the rain, the experiment was conducted in a temperature-controlled glass room (22˚C). Each textile sample, 120 cm long and 20 cm wide, was hanged over a window to achieve uniform sunlight exposure. Samples were collected at a four-week interval after initiation of the irradiation, at approximately the same time of day. At each sampling time, approximately 5-centimeter-long textile samples were cut from the bottom edge, wrapped in aluminum foil, and stored at room temperature in the laboratory until chemical analysis. According to a previously described method (Kajiwara et al., 2009), HBCD diastereomers in textile A and B were quantified by using a LC-MS-MS. As for textile C, along with PBDEs, polybrominated dibenzo-*p*-dioxins (PBDDs) and furans (PBDFs) were analyzed by a HRGC-HRMS as described previously (Kajiwara et al., 2008).

Results and Discussion

Emission of BFRs from Curtain Samples

HBCD diastereomers were detected in all the PUF samples collected after the emission tests for textile A and B. In other words, the emission of HBCDs from the curtains was demonstrated even at room temperature (Fig. 2). The emission rate at the test temperature of 80˚C showed a sharp increase by approximately 20 times compared to that at the temperature of 60˚C, indicating that HBCD emission from curtains accelerated with increasing temperature. Although HBCD diastereomer profiles detected in PUF at the test temperature of 20˚C and 40˚C were closely similar to those found in the original curtain sample investigated, those at higher temperature showed higher proportion of α-HBCD contributing up to 70% of the total HBCD emission (Fig. 3). Since we found no significant differences in concentration and profile of HBCD diastereomers in the sample materials between before and after

the emission tests, it is unlikely that γ-HBCD was isomerized to α-diastereomer during the heating at 60°C and 80°C for 120 h. These results might be explained by the differences in vapor pressures among HBCD diastereomers, which are reported to decrease in the following order of α>β>γ, and those of α-HBCD is one order of magnitude higher than γ-diastereomer (Kuramochi et al., 2009).

From the chemical analysis of PUF samples after the emission test of textile C, we confirmed that PBDEs including BDE 209 were also emitted from the flame-retarded curtain even at room temperature. As in the case with HBCDs, the maximum emission rate of PBDEs was observed at the test temperature of 80°C. Although mono- to tri-BDE concentrations in textile C were lower than detection limits, we also observed their emission from textile C. This result may suggest that lower brominated congeners with higher vapor pressure will be emitted from articles even when their contents are very low. There is also a possibility that the lower brominated congeners detected in PUF were the debrominated products originated in the higher brominated congeners that are abundant in textile C, as this product was treated with the DecaBDE technical mixture which mainly contains octa- to deca-BDE (La Guardia et al., 2006).

The emission rates of HBCDs from the curtains obtained in the present study were two orders of magnitude higher than those of PBDEs, indicating relatively more volatility of HBCDs from textile products to the indoor environment. These emissions may affect indoor air quality and could be a source of indoor pollution.

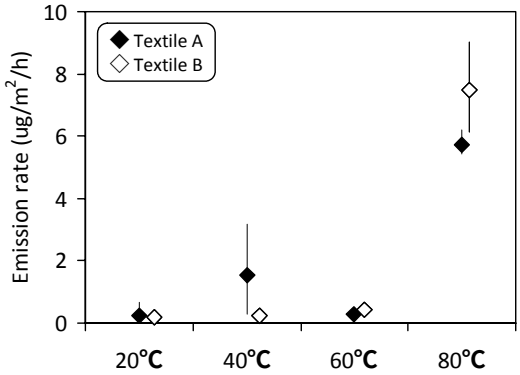

Fig. 2. Emission rates of total HBCDs in textile A and B

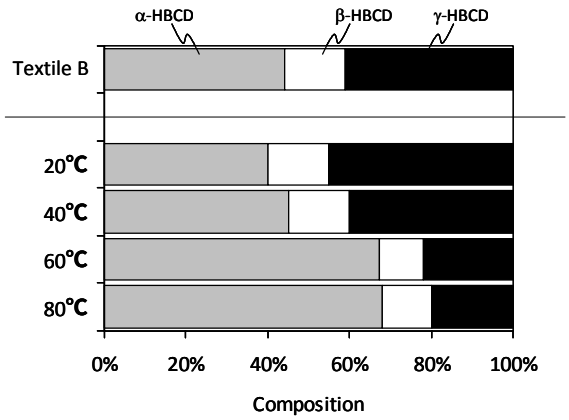

Fig. 3. Diastereomer compositions of HBCDs originally contained in textile B and those absorbed in PUF after each experiment batch.

Photolysis of BFRs in Curtain Samples

No marked loss of HBCD diastereomers in both textile A and B were observed during sunlight exposure for 371 days. Although there is a study reporting debromination and isomerization of HBCD diastereomers in indoor dust and standard solutions by exposure to light (Harrad et al 2009), we did not clearly observe this trend in this study.

In contrast, formation of PBDFs as photodecomposition products was apparent in the textile C which is flame-retarded by DecaBDE. Although the textile C samples showed no clear disappearance of BDE 209 and formation of less-brominated BDE congeners throughout the 371 days of sunlight irradiation,

the concentrations of mono- to penta-BDF congeners showed a continuous increase during the experimental period. Total PBDF concentrations in the curtain samples after the one-year exposure reached 17,000 ng/g which were approximately 7 times the initial levels (2,400 ng/g), suggesting that flame-retarded products under daily usage have the potential to be major sources of PBDF contamination in indoor air and dust. Among the congeners analyzed, octa-BDF was the predominant congener throughout the exposure, constituting 50% to 80% of the total PBDFs. These results suggest that BDE 209 added to the curtain material indeed photodegraded and contributed to the synthesis of PBDFs, as the same trend found in the television casing we reported previously (Kajiwara et al., 2008).

From all the results of the present study, we conclude that HBCDs have more resistance than BDE 209 to sunlight exposure; however, HBCDs are easier to be emitted to the indoor environment from the textile samples investigated than PBDEs. Further studies are required to estimate their contribution to air and dust pollution.

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