Debromination of Decabromodiphenyl Ether in Polystyrene Resin by Mechanochemical Treatment

Masaaki Hosomi[1*], Masayuki Shintani[1], Yugo Nomura[2], Sheng Zhou[1], Akihiko Terada[1]
[1]Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan (*corresponding author: hosomi@cc.tuat.ac.jp)
[2]Japan Quality Assurance Organization, Chiyoda 100-8308, Japan

Introduction

Mechanochemical (MC) treatment is of engineering promise in that solid-phase reaction combined with pulverization is employed as a degradation technology of contaminants. Since this treatment does not produce gases to be emitted, persistent organic chemicals (POPs) are expectedly decomposed with a small footprint. Previous researches on MC treatment have reported decomposition of dichloro diphenyl trichloroethane (DDT) (Hall *et al.*, 1996), polychlorinated biphenyl (PCB) (Birke *et al*, 2004; Nomura *et al.*, 2002) and dioxins (Nomura *et al.*, 2005), categorized as POPs.

Our previous investigation has applied MC treatment for decomposition of powdery decabrominated diphenyl ether (DBDE), recognized as brominated flame retardants (BFRs) (Shintani *et al.*, 2007). As a result, 200 mg of DBDE together with 4 g of calcium oxide (CaO) was decomposed by more than 99% within an hour, producing bromide ion from water extracts after the MC treatment. The mass balance has revealed that all bromine in DBDE was converted into bromide ion. Although the final product was considered as calcium bromide ($CaBr_2$), it is not detected by X-ray diffraction. In addition, no toxic byproducts were produced via DBDE removal pathways.

Given these previous reports, the objective of this study is to confirm whether polybromodiphenyl ethers (PBDEs) in polystyrene resin are degraded by MC treatment. Polystyrene was chosen as a model resin since DBDEs are generally added in the resin.

Materials and Methods

The MC reactor consisted of a planetary ball mill (Pulverizette-7, Fritsch, Germany) and a pair of stainless steel pots (45 cm^3, SUS304) where seven steel balls (15 mm-diameter) were respectively mounted. One gram of polystyrene resin containing DBDE beads (termed PS-DBDE hereafter) with 0.2-0.5 mm-diameter was added in the two pots together with 3 g of CaO as a reaction agent and, subsequently, the pots were sealed at an ambient pressure. A mill rotation speed was set at 700 rpm and a ratio of rotation/revolution was 1. Time of MC treatment was set at 1, 2 and 4 hour, respectively. The residues of the treatment were collected from the pots and divided into two. One sample was analyzed for PBDEs quantification by high-resolution gas chromatography-mass spectrometry (HRGC/MS) and identification of organic bromine compounds by gas chromatography-time of flight-mass (GC/TOFMS) whereas the other was analyzed for measurement of bromide ion by an ion chromatography.

(1) HRGC/MS analysis

a) Pretreatment of HRGC/MS analysis

Hundred milliliter of toluene was added to a sample, followed by ultrasonication for 1 hour. The supernatant was transferred to a bottle whereas the residue was applied for ultrasonication again for 30 minutes. The extracts (0.2 mL) after the first and second ultrasonication were diluted to 20 mL and the

0.5 mL of diluted sample was used for further analysis. For internal standards, 1-7 diphenyl ether (DE) (2.5 ng), 8-9 DE (2.5 ng) and 10DE (5 ng) as 13C-PBDE were added.

For purification, 44% of silica sulfate was added to a sample, followed by heating at 60°C for 30 minutes. Then, the supernatant was taken and filtered through a Pasteur pipette filled with silica gel, followed by dissolution of the filtrate into hexane.

b) Identification and quantification of PBDEs and PBBs

HRGC/MS was applied after the protocol as previously reported (Shintani *et al.* 2007).

(2) GC/TOFMS analysis

For quantitative analysis, GC/TOFMS was used. According to electron impact and negative-ion chemical-ionization methods, characteristic ions of bromine compounds were screened and identification of the compounds was carried out.

Results and Discussion

1) Decomposition of PS-DBDE

Before and after MC treatment, appearances of PS-DBDE are shown in **Figure 1**. The MC treatment with CaO pulverized the PS-DBDE, resulting in mixed powder of PS-DBDE and CaO. However, 9-15 wt% of PS-DBBE was captured between the pot and lid with the appearance unchanged.

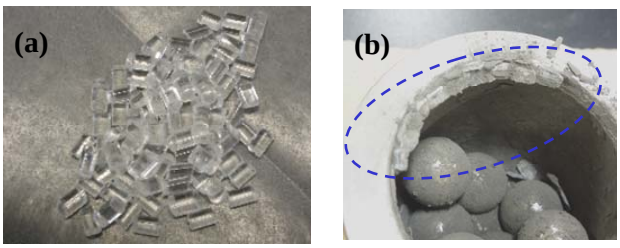

Figure 1 Pictures of PS-DBDE resin: (a) prior to MC treatment; (b) after the treatment. The area surrounded by dashed line-circle represents the resin captured between a MC pot and lid.

PBDE homologues concentrations are shown in **Table 1**. The concentrations were calculated by the following equation:

$$\text{Concentration [µg/total]} = \text{Measured conc. [µg/total]} \times \frac{\text{Total amount of collected sample [g]}}{\text{Analyzed sample [g]}}$$

Table 1 Concentrations of PBDEs homologues. N. D. represents "not detected".

MC treated time	0 h	1 h	2 h	4 h
Unit	µg/Total	µg/Total	µg/Total	µg/Total
MoBDEs	N.D.	N.D.	N.D.	N.D.
DiBDEs	N.D.	N.D.	N.D.	N.D.
TrBDEs	N.D.	N.D.	N.D.	N.D.
TeBDEs	N.D.	N.D.	41	N.D.
PeBDEs	N.D.	21	103	N.D.
HxBDEs	N.D.	164	454	N.D.
HpBDEs	N.D.	637	452	N.D.
OBDEs	N.D.	3080	413	N.D.
NBDEs	4167	7803	846	764
DBDE	111111	32856	26813	24114
Total PBDEs	115079	45178	28875	24114

While most of PBDFs were DBDEs, PBDEs with small bromine numbers, *e.g.* TeBDE and PeBDE were also detected. These concentrations were higher than the result on powdery DBDE (Shintani *et al.*, 2007), indicating that hydrogen in PS displaced bromine due to substitution reaction. However, PBDEs with less than 3 bromines were never detected; breakdown of diphenyl ether was likely to occur before displacement of bromine as also suggested in powdery DBDE in our previous work (Shintani *et al.*, 2007).

A molar percentage of PBDE over the sum of the initial PBDE (from **Table 1**) is shown in **Figure 2**. After MC treatment for 1 and 4 hour, 60% and 80% of DBDE in PS-DBDE was decomposed, respectively. The decomposition ratio of PS-DBDE was lower than the powdered DBDE probably due to the effect of non-decomposed PS-DBDE captured between a pot and lid during MC treatment. No PBDEs other than DBDE and NBDE, which was contained in the initial PS-DBDE, was detected in the 4 hour MC treatment, exhibiting that the reaction was completed in 4 hour.

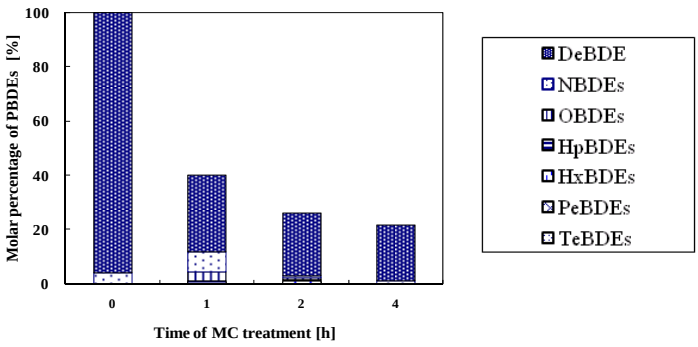

Figure 2 The effect of MC treatment time on molar percentage of PCDEs

2) Qualitative analysis by GC/TOFMS

Organic bromine compounds produced by MC treatment are listed in **Table 2**. Mo-DeBDEs were detected in the sample after 1 and 2 hour MC treatment and so were polybrominated benzene group (PBBzs) and polybrominated dibenzofurans (PBDFs), *a.k.a.* brominated dioxins. The sample after 2 hour MC treatment had higher peak intensity than that after 1 hour MC treatment, indicating a higher production than 1 hour MC treatment. No brominated compounds were detected. Hence, MC treatment putatively produces intermediates, *e.g.* debrominated PBDEs (Mo-NBDE), PBBzs due to breakage of ether linkage, and PBDFs, resulting in mineralization.

Table 2 Brominated compounds detected by GC/TOFMS

MC treatment time [h]	PBDEs	PBBzs	PBDFs
1	Mo-DBDE	Mo-PeBDEs	Mo-HpBDFs
2	Mo-DBDE	Mo-PeBDEs	Mo-HpBDFs
4	N.D.	N.D.	N.D.

3) Debromination efficiency and bromine mass balance

Analytical debromination efficiency was obtained by the amount of produced bromide ion divided by the one contained in the initial DBDE. Based on the analytical debromination efficiency, debromination efficiency was finally calculated:

$$\text{Debromination efficiency [\%]} = \text{Analytical debromination efficency [\%]} \times \frac{\text{Total amount of collected sample [g]}}{\text{Amount of analyzed sample [g]}}$$

Time course of debromination efficiency is shown in **Figure 3**. The result clearly indicates that bromine compounds contained in the PS-DBDE resin were collected as bromide ion.

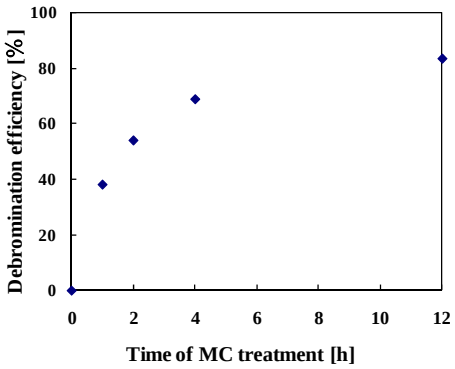

Figure 3 Time course of debromination efficiency at PS-DBDE and CaO of 1 and 3 g, respectively

The mass balance on bromine is shown in **Figure 4**. Throughout the MC treatment, the mass balance was kept at 70-90%. It is likely that the rest (10-30%) was unquantified organic bromine compound, which was detected by GC/TOFMS, e.g., PBDEs PBBzs and PBDFs.

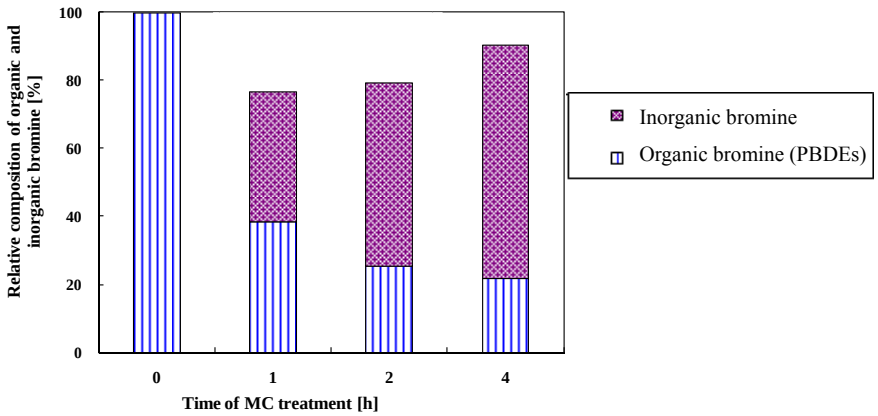

Figure 4 The effect of MC treatment time on relative composition of organic and inorganic bromine

Acknowledgement (optional)
This work was financially supported by scientific funding on promotion of establishing recycle-based society (K2001) in Ministry of the Environment in Japan.

References

Birke V, Mattik J, Runne DJ. 2004. J. Material Sci. 39: 5111
Hall AK, Harrowfield JM, Hart RJ, Maccormick PG. 1996. Environ. Sci. Technol. 30:3401
Loiselle S, Branca M, Mulas G, Cocco G. 1997. Environ. Sci. Technol. 31: 261
Nomura Y, Nakai S, Lee BD, Hosomi M. 2002. Kagaku Kougaku Ronbunshu. 28:565
Nomura Y, Nakai S, Hosomi M. 2005. Environ. Sci. Technol. 39: 3799
Shintani M, Nomura Y, Nakashimada Y, Hosomi M. 2007. Proc. Dioxin 2007 69: 2677