



# Selective decomposition of hexabromocyclododecane in polystyrene with a photo and thermal hybrid treatment system



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## ABSTRACT

Selective hexabromocyclododecane (HBCD) decomposition was performed with a polystyrene (PS)/HBCD flour sample by a photo and thermal hybrid treatment system. The complete HBCD decomposition required the multistep treatment to control PS crosslink reaction. The HBCD decomposition was initially performed by a TiO<sub>2</sub>/polyethylene oxide (PEO) photocatalyst and then was thoroughly done with breaking a dormant species (nitroxyl compound) by thermal treatment. The decomposition ratio reached 94% by the hybrid treatment. The <sup>1</sup>H-NMR spectrum of decomposition residue showed that HBCD fragmentation occurred and that PS part was modified. The recycled PS contained a polymer chain grafting HBCD moiety. The graft caused PS stiffness enhancement although the ratio was a very low value.

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## 1. Introduction

PS has been universally used as polymeric materials, and its commercial market had been developed for a long time. Extruded PS (XPS) is a kind of PS materials and has been employed for insulation and building materials [1]. XPS certainly contains flame retardant. In particular, HBCD had been universally employed as flame retardant for XPS [1–6]. Water solubility and vapor pressure of HBCD are very low, resulting that it is persistent in the environment [6]. Since HBCD has potential to be toxicity, it has been listed as persistent organic pollutants (POPs) in the Stockholm Convention at its sixth meeting [7,8]. A development of HBCD decomposition method has given rise to an intensive interest in an environmentally friendly XPS disposal. The HBCD decomposition has been vigorously studied with photo- and thermal-degradations, respectively [8–10]. However, it has been carried out with pure HBCD. The investigators have hardly studied about direct HBCD decomposition by using XPS. If only HBCD part is removed from XPS, PS recycling can be performed at the same time. The selective HBCD decomposition would economically become an advantageous recycling process.

In our previous work [11–13], development of a paint-type TiO<sub>2</sub>/

PEO/methyl linoleate (ML) photodegradation catalyst system has been achieved. The PEO was photo-catalytically degraded by the TiO<sub>2</sub>, and then H<sub>2</sub>O, OH radical species (initiator), acid and aldehyde (accelerator) compounds to facilitate photodegradation were produced. The ML produced radical species to block crosslinking and accelerated photodegradation rate [13]. It is an effective crosslink inhibitor. However, a large amount of ML was required to be consumed by forming C–C bond. We think that HALS has a potential ability to be the excellent crosslink inhibitor instead of ML having such weak point. Nitroxyl radical (TEMPO) (III) is formed from (I) during oxidative photodegradation of polymer containing HALS. The TEMPO traps alkyl radical species (R•) and produces dormant species (IV), leading to retardant of polymer photodegradation [14]. The R• is reproduced from (IV) by a heat treatment, and oxidative thermal degradation occurs, resulting that HBCD is redecomposed. The R• amount is able to be controlled by adjusting elevated temperature and retention time. It seems that HALS loading brings about crosslinking control and R• adjustment to selectively decompose HBCD.

In this study, the selective decomposition of HBCD in PS matrix was performed with a TiO<sub>2</sub>/PEO/HALS hybrid photo- and thermal-degradation catalyst system. The HBCD and PS decomposition behavior was studied with a gel permeation chromatography (GPC), NMR, FT-IR and HBCD selective extraction. In addition, the recycled PS properties were studied with dynamic mechanical analysis (DMA).

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## 2. Experimental

### 2.1. Materials

PS was purchased from Sigma-Aldrich Co. LLC. The weight-average molecular weight ( $M_w$ ) and molecular weight distribution ( $M_w/M_n$ ) were  $3.5 \times 10^5$  and 2.1, respectively. 1, 2, 5, 6, 9, 10-hexabromocyclododecane (HBCD) was purchased from Tokyo Chemical Industry Co., Ltd. HALS [LA-77: Bis(2, 2, 6, 6-tetramethyl-4-piperidyl) sebacate] was supplied by ADEKA Co.  $\text{TiO}_2$  (anatase-type, nano particle size < 25 nm) and copper phthalocyanine (CuPc) were purchased from Sigma-Aldrich Co. LLC, respectively. PEO (average molecular weight =  $3.1 \times 10^4$ ) was supplied by Sanyo Chemical Industries, Ltd. Methanol, ethanol, tetrahydrofuran (THF) and acetone were purchased from Wako Pure Chemical Industries, Ltd., respectively.

### 2.2. Procedure of loading and flouring

Per hundred resin (phr) unit was employed. The PS (100 phr) and HBCD (10 phr) mixture in ca. 5 wt % THF solution was vigorously stirred with a magnetic stirrer for 2 h and then was poured into a large amount of methanol. The precipitate was separated by vacuum filtration and was dried under reduced pressure at 60 °C in one day. The sample was passed through a sieve with 1 mm diameter and was employed as flour sample. HALS was dissolved by methanol. The solution was sprayed on the flour sample with a Pasteur pipette and was dried at r.t. The HALS loading amount was 0.1 phr.

### 2.3. Preparation of CuPc-modified $\text{TiO}_2$ (CuPc/ $\text{TiO}_2$ )

The CuPc- $\text{TiO}_2$  was prepared in reference to Shang et al. paper [15]. 0.2 g- $\text{TiO}_2$  was impregnated with  $2.0 \times 10^{-3}$  mol/L-CuPc ethanol solution at 60 °C for 180 min and was washed with water for several times by centrifugalization. The precipitate was dried at 80 °C. The CuPc content was ca. 7.0%.

### 2.4. Spraying of photocatalyst system on sample

251 g-ethanol, 1.4 mg-CuPc- $\text{TiO}_2$  and 2.51 g-PEO were mixed at 60 °C for 30 min. The 0.38 ml-mixture was sprayed on 0.13 g-flour samples with a Pasteur pipette, and they were dried at ca. 20 °C (r.t.) and were used to be photodegraded.

### 2.5. Hybrid treatments

The sprayed flour sample was laid on a petri dish. A light-emitting diode (LED) lamp of 25 W (Yazawa Corporation Co.,Ltd., CLED10012WH) was used as a visible light source. The distance between specimens and the lamp was ca. 40 cm, and its photo flux density was ca.  $50 \mu\text{mol}/\text{m}^2 \text{ sec}$ . The light irradiation treatment was carried out at r.t.

The irradiated sample was placed in an oven at 120 °C for 110 min to be thermally treated.

### 2.6. Extraction of HBCD in PS

The detailed procedure was shown as follows: The 0.52 g-flour sample was dissolved in a methanol (33 ml) and acetone (67 ml) mixture solvent in a stirred 300 ml glass reactor and then was vigorously stirred at 80 °C for 15 min [16]. The solution was cooled up to room temperature, and precipitate was filtered under reduce pressure. The precipitate obtained was dried under reduced pressure at 60 °C for 8 h. The filtrate was evaporated and was dried

under reduced pressure at r.t. for 6 h. On the other hand, the soluble part solvent was evaporated with a rotary evaporator, and the solidified product was thoroughly dried under reduced pressure at 60 °C for 8 h. The obtained polymer was used as “recycled PS”.

### 2.7. Preparations of films

After the treatments, the flour sample was dissolved in 3 wt% THF solution and was dried. The cast film (0.05 mm thickness) was used to perform the dynamic mechanical analysis (DMA) measurement.

### 2.8. Gel permeation chromatography (GPC) analysis

Sample in a small vial was dissolved in 5 ml of chloroform, and the obtained sample solution was directly measured by GPC. The molecular weight was determined by GPC (SHIMADZU, Prominence GPC system) at 40 °C using chloroform as a solvent.

### 2.9. Nuclear magnetic resonance (NMR) spectroscopy measurement

NMR spectrum was measured using a Varian Gemini 300 spectrometer at 20 °C in chloroform-d. Tetramethylsilane was added and used as an internal chemical shift reference.

### 2.10. Fourier transform infrared (FT-IR) analysis

The IR spectra 64 scans of the sample films were measured by an FT-IR spectrometer (Thermo Nicolet NEXUS 670 FTIR) with an ATR option at a resolution of  $4 \text{ cm}^{-1}$  over the full mid-IR range (from 600 to  $4000 \text{ cm}^{-1}$ ).

### 2.11. Thermogravimetry (TG) measurement

TG measurements were made with a Shimadzu DTG-60. The samples of about 5 mg weight were sealed in aluminum pans. The measurement of the samples was carried out at a heating rate of 10 °C/min in dried air.

### 2.12. Dynamic mechanical analysis (DMA)

The DMA measurements were made with a DMA spectrometer (Seiko Instruments Inc., DMS6100). The sample specimens were cut with dimensions  $20 \times 3 \times 0.05 \text{ mm}$  shape in which the gauge length was 5 mm. The measurements of the polyurethane films were carried out at 10 Hz and at a heating rate of 2 °C/min in the measurement range from 20 to 150 °C under a nitrogen atmosphere.

## 3. Results and discussion

Fig. 1 shows the schematically complete HBCD decomposition path by using the photo and thermal hybrid treatment system. The PEO component was photo-catalytically degraded by the  $\text{TiO}_2$ , and then  $\text{OH}\bullet$  to initiate the HBCD and PS photodegradation was produced. The  $\text{OH}\bullet$  attacks the HBCD, leading to decomposition (Step 1). On the other hand, it does the PS as well as the HBCD and transfers to the PS chains, causing the HBCD decomposition (Step 1) and PS crosslinking. The crosslink reaction occurs by collision between the  $\text{PS}\bullet$  species and causes a drastic decrease of the molecular motion, leading to disturbing recycle use of the PS. When the  $\text{TiO}_2$ /PEO catalyst provides a large amount of the  $\text{OH}\bullet$  to completely decompose the HBCD, the crosslinked PS is produced in large amounts at the same time. The complete HBCD decomposition requires a multistep approach to control PS crosslink reaction. In addition, a part of the  $\text{PS}\bullet$  attacks the HBCD at the same time (see

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