

## Tetrabromobisphenol A as a brominating agent for heavy metal oxides

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### Introduction

Due to the complex nature of waste electrical and electronic equipment (E-waste), recycling is a technological challenge. The main component of WEEE is plastics, which often include either halogenated or non-halogenated flame retardants to increase fire safety of the electric and electronic products (Vilplana & Karlsson, 2008). Tetrabromobisphenol A (TBBPA) is the most widely applied brominated flame retardant (BFR) with the major applications in printed circuit board laminates, electric and electronic equipment housing and in transportation applications such as plastic car parts (Tohka & Zevenhoven, 2001). Together with BFRs, E-wastes contain a significant number of various metals. The precious metals (e.g. silver, gold, platinum), copper and zinc are of the highest value in the electronic scraps while aluminum, lead and iron are of lesser value (Vehlo et al., 2002; Cui & Zhang, 2008). From the point of E-wastes composition, the selection of a proper recycling method is an important task and two aspects should be taken into consideration: 1) the economical, concerning the highest recovery of valuable metals; and 2) the environment, concerning eco-efficient recycling of the plastic fraction.

Prior to developing of a new thermal process for the simultaneous treatment of plastics waste containing brominated flame retardants and recycling of metal oxides (printed circuit board, automotive shredder residue, plating sludge, metallurgical dusts) mechanisms of the bromination reactions between the flame retardant and heavy metal oxides must be well recognized.

Aim of this study was to investigate reactivity of ZnO, PbO, and Fe<sub>2</sub>O<sub>3</sub> (components of electric arc furnace dust) with HBr originating from the thermal decomposition of TBBPA. All experiments were conducted with thermogravimetric (TGA) and differential scanning calorimetry (DSC) methods under inert atmosphere. The solid residues remaining after heating were analyzed by X-ray diffractometry.

### Materials and Methods

*Materials:* TBBPA (97.0 %) was obtained from Aldrich Co. ZnBr<sub>2</sub>, ZnO, PbO, and Fe<sub>2</sub>O<sub>3</sub> with purities of 99.9 % were purchased from Wako Pure Chemical Industries, Ltd. PbBr<sub>2</sub> (99.99 %) was supplied by Alfa Aesar Company, while FeBr<sub>2</sub> (98 %) and FeBr<sub>3</sub> (99 %) were purchased from Stream Chemicals.

Mixtures of TBBPA with individual metal oxides (TBBPA:M<sub>x</sub>O<sub>y</sub>) were prepared according to the stoichiometric mass ratio (Table 1), assuming that all bromine present in TBBPA releases and reacts with the individual metal to form the bromide metal of interest.

*Methods: Differential Scanning Calorimetry (DSC)* analyses of the mixtures of interest and the pure compounds were performed on a heat-flux calorimeter 2920 DSC (Thermal Analysis Instruments, Inc.). Samples of about 10 mg were hermetically sealed in alodined aluminum pans (comprising materials nonreactive to our samples and capable of resisting internal pressures up to 3 atmospheres),

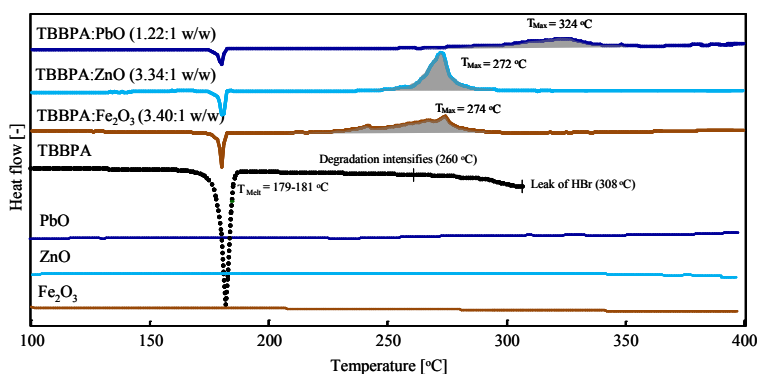
and thermally scanned in the range of 50-400 °C, at a heating rate of 1 °C/min and an argon flow rate of 50 mL/min. An empty pan served as a reference. The obtained DSC curves were analyzed to determine the reaction temperature. Solid products were collected at a temperature corresponding to the maximum of the exothermic peak on the DSC curve (related to the reaction in the TBBPA:M<sub>x</sub>O<sub>y</sub> mixture) and characterized using X-ray diffractometry (XRD, Rigaku, Rint 220).

*Thermogravimetric analyses (TGA)* of the mixtures of interest and pure compounds were carried out on a Rigaku Thermo Plus TG 8120. 5-6 mg of a given sample was placed into an open alumina pan and heated from room temperature up to 1300 °C at a heating rate of 10 °C/min under a helium flow rate of 150 mL/min.

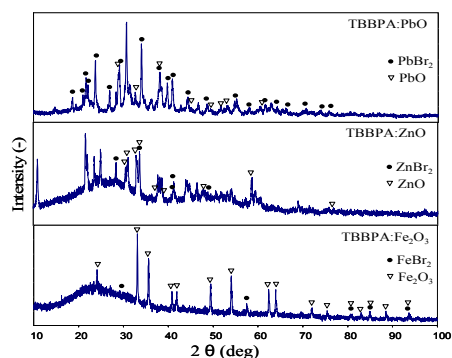
Additionally, an individual mixture of TBBPA:M<sub>x</sub>O<sub>y</sub> was thermally treated up to 320 °C (at this temperature the TBBPA almost completely decomposes), then the collected solid residue was analyzed by X-ray diffractometry.

## Results and Discussion

DSC analyses were performed to investigate the reactivities of the selected metallic oxides with HBr (decomposition product of TBBPA) during thermal treatment of individual mixtures (TBBPA:M<sub>x</sub>O<sub>y</sub>) under an inert atmosphere.



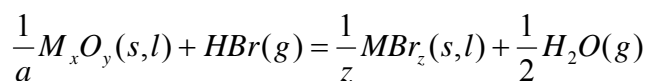
**Fig.1.** DSC curves for mixtures of TBBPA:M<sub>x</sub>O<sub>y</sub> and pure comp.



**Fig.2.** X-ray of solid residues collected at the maximum of exothermic peak.

As can be seen from the DSC thermograms (Fig. 1), the pure metal oxides are stable in the studied temperature range. Thermal scanning of TBBPA reveals two successive endothermic phenomena: melting (179-181 °C) and degradation (from 260 °C onwards). At a temperature of 308 °C, the internal pressure of gases evolved during the degradation of TBBPA exceeds the hermetic pan's resistance and causes an extensive leak of the sample. Since many studies on degradation of TBBPA report HBr to be the main gaseous product of its decomposition, its intensive formation is also supposed in this experiment.

In contrast to the pure TBBPA, during thermal scanning of the mixtures of TBBPA:M<sub>x</sub>O<sub>y</sub> heated under the same DSC conditions, an exothermic peak occurs following an enhanced evolution of HBr. The peak reaches its maximum at 324 °C for TBBPA:PbO, 272 °C for TBBPA:ZnO, and 274 °C for TBBPA:Fe<sub>2</sub>O<sub>3</sub>. This may suggest that the evolved HBr reacts with an individual metal oxide leading to the formation of the brominated metals according to the reaction:

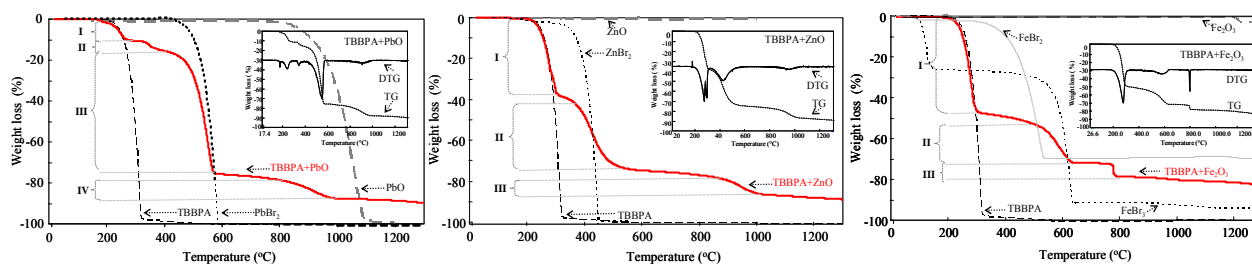


Where:  $x/a = 1/z$ ,  $y/a = 1/2$

XRD (Fig. 2) analyses of the solid residue (collected at a temperature corresponding to the maximum of the exothermic peak on the DSC curve for the individual mixture) confirm the presence of the formed brominated compounds and remained un-reacted metallic oxides.

The TG results for the mixtures of interest and the corresponding pure compounds are shown in Fig. 3. TG profiles all the pure compounds (TBBPA, metal oxides and metal bromides) show one step weight losses (with the exception of  $FeBr_3$  which has two stages). However, for the studied mixtures (TBBPA: $M_xO_y$ ) three distinct stages of weight loss can be distinguished (with the exception of the mixture of TBBPA:PbO which has four stages).

Generally, in the first (I) stage (up to 310 °C) the quick mass loss from the mixture (TBBPA: $M_xO_y$ ) can be associated with decomposition and evaporation of TBBPA. Only in the TBBPA:PbO mixture, decomposition of TBBPA and evaporation of the organic products is continued in the second (II) stage (the results were confirmed by simultaneous TG-MS analyses – data not shown here).



**Fig. 3.** TG profiles for mixtures of TBBPA: $M_xO_y$  and the corresponding pure compounds.

Very slow weight loss within 310-340 °C (TBBPA:ZnO), 310-540 °C (TBBPA: $Fe_2O_3$ ) and 280-340 °C (TBBPA:PbO) may suggest that the bromination reaction occurs at these temperature ranges and in the next stage the formed brominated compounds evaporate from the mixture (the solid residue collected at 320 °C characterized by XRD confirmed the presence of brominated products - data not shown here). The weight losses in the second (II) stage within 340-490 °C (TBBPA:ZnO) and 540-640 °C (TBBPA: $Fe_2O_3$ ) agree well with the TG profiles of pure  $ZnBr_2$  and  $FeBr_2$ , respectively, indicating evaporation of the formed brominated products. Evaporation of  $PbBr_2$  can be associated with stage III (450-580 °C), here the profile of the mass loss overlaps with that of pure  $PbBr_2$ .

All the mixtures show further mass loss upon thermal treatment at higher temperatures, which can be associated with evaporation of the remaining metallic oxides or decomposition and evaporation of the char. Furthermore, since carbon is the main component of the char, reduction of the remaining metallic oxides into metallic compounds may also take place. Such carbothermic reduction can be observed in TBBPA:ZnO and TBBPA:PbO mixtures where the remained ZnO and PbO are reduced into metallic Zn and Pb (confirmed by XRD analyses of solid residue- data not shown here). Evaporation of the Zn

is observed in the stage (III) at temperatures range of 890 – 1020 °C, while Pb evaporation can be associated with mass loss at stage (IV) within 810-970 °C. In case of TBBPA:Fe<sub>2</sub>O<sub>3</sub> mixture, further heating leads to the reduction of the remained Fe<sub>2</sub>O<sub>3</sub> into Fe. Characteristic of the solid residue collected at 700 and 830 °C by XRD (data not shown here) indicate the following sequence of reduction: Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> → FeO → Fe. The formed Fe, however, is very stable thermally and remains in the solid residue.

*Quantification of the formed brominated compounds:* The amount of MBr<sub>z</sub> formed during the thermal treatment of TBBPA:M<sub>x</sub>O<sub>y</sub> was estimated from the weight loss in stage II (for TBBPA:PbO that from stage (III)), which corresponds to the evaporation of the formed MBr<sub>z</sub>. Our estimation indicates that the bromination efficiency during thermal treatment of TBBPA with the selected metal oxides decreases as follows: PbO>ZnO>Fe<sub>2</sub>O<sub>3</sub> (Table 1).

Table 1. Estimated amounts of the formed brominated compounds (MBr<sub>z</sub>) from the TG profiles of individual mixtures (TBBPA:M<sub>x</sub>O<sub>y</sub>). (The weight loss (%)) is average of three to four experimental runs).

TBBPA:M <sub>x</sub> O <sub>y</sub>	Stage II		Stage III			
	MBr <sub>z</sub>		M <sub>x</sub> O <sub>y</sub>		Me	
	Temp/ °C	%	Temp/ °C	%	Temp/ °C	%
TBBPA:ZnO (3.34:1 w/w)	340-490	53±4.0	-	-	890-1020	47±8.0
TBBPA:Fe <sub>2</sub> O <sub>3</sub> (3.40:1 w/w)	540-640	22±3.8	-	-	-	-
	Stage III		Stage IV			
TBBPA:PbO (1.22:1 w/w)	450-580	78±2.4	-	-	810-970	20±3.0

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