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Controlled pyrolysis of polyethylene/polypropylene/polystyrene mixed plastics with high impact polystyrene containing flame retardant: Effect of decabromo diphenylethane (DDE)

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Abstract

The pyrolysis of polyethylene(PE)/polypropylene(PP)/polystyrene(PS) mixed with high impact polystyrene (HIPS-Br) containing decabromo diphenylethane (DDE) as a brominated flame retardant with antimony trioxide as a synergist was performed under controlled temperature programmed pyrolysis (two steps) conditions to understand the decomposition behaviour and evolution of brominated hydrocarbons from flame-retardant additives. The liquid products were extensively analyzed by gas chromatographs equipped with FID, ECD, MSD, TCD, AED and FT-IR. The solid residue samples were analyzed by powder X-ray diffraction and combustion followed by ion-chromatography. The controlled pyrolysis of PE/PP/PS/HIPS-Br significantly affected the decomposition behaviour of HIPS-Br and subsequently the formation of decomposition products. GC/ECD analysis confirmed that the brominated hydrocarbons were concentrated in step 1 liquid products leaving less brominated hydrocarbons in the step 2 liquid products, similar to the decabromo diphenyl ether flame retardant containing mixed plastics. The yield of liquid products in step 1 from 3P/DDE-Sb(5) was 5 wt% and from 3P/DDE-Sb(0) was 2.4 wt%. The presence of antimony in the DDE containing plastics affected the yield of liquid, gas and residue products. ECD analysis showed that the presence of antimony increased the Br containing hydrocarbons and step 1 has 3–4 times higher brominated compounds than step 2 hydrocarbons in both the samples.

Keywords: HIPS-Br; Flame retardant; Pyrolysis; Decabromo diphenylethane; Thermal decomposition; Waste plastics

1. Introduction

The production of electric and electronic equipment (EEE) is increasing worldwide. Due to the presence of hazardous material contents, WEEE may cause environmental problems during the waste management process at the end of life, if it is not properly pre-treated. Recycling of WEEE is an important subject not only from the point of waste treatment but also from the aspect of recovering valuable materials such as the plastic portion of WEEE. A significant and increasing proportion of plastic waste is being used in consumer products such as television casing materials, computer equipment, etc. The conversion of waste plastics into chemical feedstock or fuel represents a sustainable way for the recovery of the organic content of the polymeric waste. Approximately 50% of waste WEEE plastics are high impact polystyrenes (HIPS), with the next largest fraction being acrylonitrile–butadiene–styrene (ABS) [1]. High impact polystyrene makes up a significant proportion of WEEE plastics and is often fire

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retarded with decabromo diphenyl ether and diantimony trioxide to decrease the flammability of the plastics. Deca-BDE is added to HIPS because the bromine radicals quench combustion reactions while diantimony trioxide is added as a synergist as it increases the rate of bromine release by forming antimony bromides and antimony oxybromides [2]. The flame retardant content of WEEE, particularly the presence of bromine and antimony, represents a major hindrance to the development of recycling technologies. Decabromo diphenyl ether (DDO) and decabromo diphenylethane (DDE) are the two most common flame retardants in the WEEE plastics.

There has been a plethora of research work on the recycling of polymers containing brominated flame retardants and the debromination of brominated hydrocarbons by using catalysts and/or sorbents [3–12]. Hall and Williams reported on the fast pyrolysis of halogenated plastics from waste computers and showed that the pyrolysis products contained a chemically heterogeneous mixture of hydrocarbons which would need to be treated before they were used in the hydrocarbon industry [3]. Analytical pyrolysis of flame retarded polymers of electronic scrap and debromination was studied by Blazso et al. [4]. It was reported that brominated epoxy resins pyrolysed with sodium hydroxide enhanced bromomethane evolution, while a depressed brominated phenol formation was observed. Due to the debromination of dibromo- and tribromophenyl groups of brominated polystyrene, co-pyrolysis with sodium hydroxide and with basic zeolites resulted in a considerably reduced yield of dibromo- and tribromo-styrenes [4].

Hornung et al. reported that the optimal pyrolysis conditions were 350 °C with a residence time of 10–30 min for the detoxification of brominated pyrolysis oil model compounds such as 2,6-dibromophenol and tetrabromobisphenol-A with polypropylene [5] and found that the polypropylene acts as a reductive agent for the dehalogenation of brominated organic compounds [7]. Bhaskar et al. reported the pyrolysis of HIPS-Br mixed with PP/PE/PS/PVC and debromination by carbon composite of calcium carbonate (Ca–C) [10], as well as the thermal decomposition of HIPS-Br containing various brominated flame retardants and debromination by carbon composite of iron oxide catalyst (Fe–C) [11]. Antos and Sedlar investigated the influence of flame retardant on thermal decomposition and found that brominated flame retardants may undergo thermal decomposition at temperatures lower than those of polymer combustion [6]. The optimization of catalysts/sorbents for the effective removal of halogens especially brominated hydrocarbons is an intense area of research. In our recent report, we found that the controlled pyrolysis of PVC or PVDC containing PP/PE/PS mixed plastics produced the chlorine free hydrocarbons in the absence of catalyst/sorbent [12] and also found that the decabromo diphenyl ether (DDO) containing HIPS-Br plastics pyrolysis step 1 liquid products with 2 times higher brominated hydrocarbons than step 2 liquid products [13]. In the present investigation, we report on the controlled (two step) pyrolysis of PE/PP/PS mixed with high impact polystyrene containing decabromo diphenylethane (DDE) flame retardant and an extensive analysis of the pyrolysis products. The liquid products were collected independently for the two pyrolysis steps to better understand the pyrolysis behaviour of the flame retardant and subsequently the formation of brominated compounds in the pyrolysis oils.

Table 1
Bromine and Sb_2O_3 content in brominated flame retardant containing high impact polystyrene (HIPS-Br) samples and their codes

Code	Description	Br content (wt%)	Sb_2O_3 content (wt%)
3P/DDE-Sb(5)	HIPS with decabromo diphenylethane (DDE)	10.7	5
3P/DDE-Sb(0)	HIPS with decabromo diphenylethane (DDE)	10.7	0

3P: PE (3 g) + PP (3 g) + PS (3 g).

2. Experimental

2.1. Materials

High density polyethylene (PE; 2200 J) was obtained from Mitsui Chemical Co. Ltd., Japan; polypropylene (PP; J 105G) from Ube Chemical Industries Co. Ltd., Japan; polystyrene (PS; 666) from Asahi Kasei Industries Co., Ltd., Japan; high

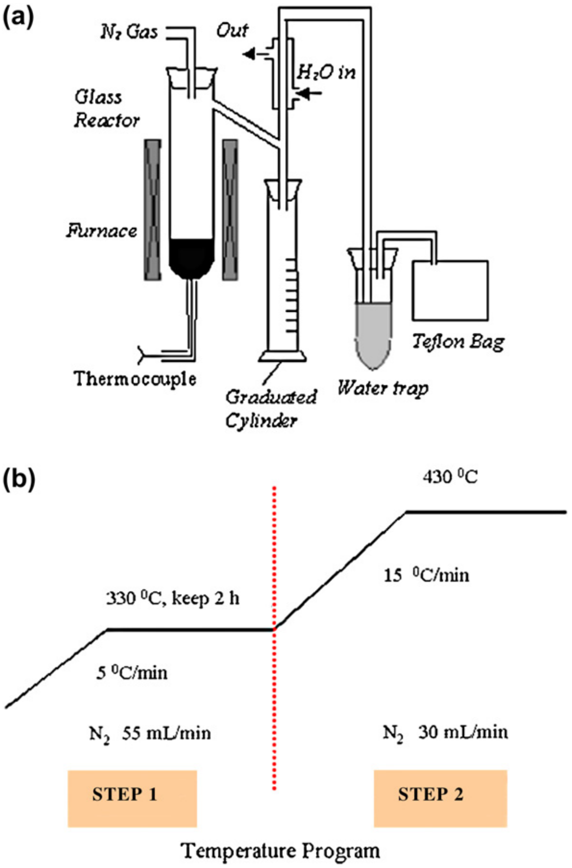

Fig. 1. (a) Schematic experimental setup for pyrolysis of 3P mixed with 3P/DDE-Sb(5) and 3P/DDE-Sb(0) samples at 430 °C; (b) temperature profile for the pyrolysis experiment.