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Effect of polypropylene on the pyrolysis of flame retarded high impact polystyrene

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ABSTRACT

Pyrolysis of high impact polystyrene (HIPS), containing decabromodiphenyl oxide as brominated flame retardant (BFR) with Sb_2O_3 as a synergist (Br–Sb–HIPS), often leads to high concentrations of toxic brominated organic compounds in the pyrolysis oils which would detrimentally impact the reuse of these pyrolysis oils. In this work, the pyrolysis of Br–Sb–HIPS in the presence of polypropylene (PP) at different blending mass ratios using a fixed bed reactor at 410 °C was performed to investigate what the effect of PP has on the pyrolysis of Br–Sb–HIPS. The thermal decomposition characterization of Br–Sb–HIPS and PP was investigated using thermogravimetry analysis (TGA). The pyrolysis oils were analyzed using Fourier transform infrared spectroscopy (FTIR) and gas chromatography–mass spectrometry (GC–MS). TGA revealed that there was a synergistic interaction between Br–Sb–HIPS and PP during co-pyrolysis process. More wax/oil and less gas were produced and the yields of toluene, ethylbenzene, styrene and many other compounds in the pyrolysis oil reversely increased in the presence of PP. Moreover, PP was found to be effective to reduce bromine in the pyrolysis oil. When 30 wt.% PP was blended into Br–Sb–HIPS, it could reduce the amount of bromine in pyrolysis oil to 38% of the original value.

1. Introduction

The global generation of waste electrical and electronic equipment (WEEE) is about 20 million tons each year, and China accounting for 2.3 million has become the second largest WEEE generator next only to USA [1]. This growing waste stream has been an important environmental issue, because of hazardous heavy metals such as mercury and cadmium and the toxic organic compounds, brominated flame retardants (BFRs), contained in these waste which can lead to formation of dioxins and/or benzofurans [2]. According to the WEEE Directive [3], WEEE has been required to be recycled and reused, including the plastic fraction. For the WEEE plastics that comprise 30% of all WEEE [4], more studies [5–7] have been taken to find an environment-friendly method for recycling them into useful products. However, WEEE plastics often contain toxic brominated flame retardants such as polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), tetrabromobisphenol A (TBBPA) or polybrominated epoxy resins in combination with Sb_2O_3 synergist, which are considered toxic to both humans and the environment [8]. Therefore, WEEE plastics containing BFRs are thought as hazardous wastes which need careful processing to remove the toxic additives. It makes the processing of WEEE plastics particularly problematic to recycle. Thus far, feedstock recycling is seen as one of the most valuable options in the treatment of WEEE plastics [9]. Pyrolysis, as an important feedstock recycling method, which is a process whereby an organic material is heated in inertia atmosphere to decompose the material into gas, oil and char, has been recognized as a promising method for recycling WEEE plastics [10,11]. Through pyrolysis, WEEE plastics could be transformed into fuel or valuable chemical feedstock.

High impact polystyrene (HIPS), which approximately accounts for 30% of all WEEE plastics [12], is a main subject for pyrolysis studies in this field [13–16]. Jakab et al. [17] studied the decomposition of HIPS by thermogravimetry/mass spectrometry (TG/MS) and revealed that the synergist Sb_2O_3 could reduce the thermal stability of flame retardants and polystyrene (PS). Bhaskar et al. [18] studied the two-stage pyrolysis of high impact polystyrene containing decabromodiphenyl ethane (DDE) mixed with polyethylene/polypropylene/polystyrene in a fixed bed reactor. They reported that the controlled pyrolysis of PE/PP/PS/HIPS–Br significantly affected the decomposition behavior of HIPS–Br and subsequently the formation of products. Furthermore, Jung et al. [19] investigated the effects of the reaction temperature and three additives (CaO, $Ca(OH)_2$, oyster shells) on the removal of bromine during the decomposition of HIPS containing brominated flame retardants and Sb_2O_3 in a fluidized bed reactor. They found that Ca-based additives had some influence on the removal of bromine in the oils and the pyrolysis oil would still require further upgrading for the commercial purpose. Hall and Williams [20] studied the effect of zeolite catalysts of ZSM-5 and Y-Zeolite for debromination in the pyrolysis of

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Table 1
Ultimate analysis of samples.

Sample	Ultimate analysis (wt.%)				
	C	H	O[a]	Br	Sb
Br–Sb–HIPS	80.9	6.8	1	7.1	4.2
PP	86.5	14.2	–	–	–

[a] By difference.

HIPS and acrylonitrile–butadiene–styrene (ABS). This work demonstrated that both ZSM-5 and Y-Zeolite could be used to remove brominated compounds from the volatile pyrolysis products of brominated HIPS. But the catalyst also drastically reduced the oil yield and significantly changed the composition of the pyrolysis products. Another work of Hall et al. [21] investigated the co-pyrolysis behavior of HIPS–Br and polyolefins and focused on the effect of antimony trioxide on the pyrolysis of the mixture polymers, revealing that the presence of Sb_2O_3 influences the pyrolysis mass balance and the presence of polyolefins would lead to an increase in the concentration of alkyl and vinyl mono-substituted benzene rings in the pyrolysis oil/wax. However, there is still some uncertainty about the interactions between the HIPS with brominated additives and polyolefins. On the other hand, the unique characteristic of thermal decomposition of polyolefins could bring about some change in the migration and transformation behaviors of organic bromine existing in the pyrolysis oil.

Through the co-pyrolysis of Br–Sb–HIPS and polypropylene (PP) at different mass ratios (9:1, 8:2 and 7:3), this paper further investigated the effect of PP on the pyrolysis of HIPS brominated with decabromodiphenyl oxide (DDO). The pyrolysis experiments were performed using a fixed bed reactor at a final pyrolysis temperature of 410 °C. The liquid pyrolysis products were analyzed by Fourier transform infrared spectroscopy (FTIR) and gas chromatography–mass spectrometry (GC–MS).

2. Experimental

2.1. Materials

In this work, commercially available high impact polystyrene and polypropylene were used. HIPS was obtained from Qimei Co., Zhenjiang; PP was from Aladdin Industrial Inc., (Shanghai). HIPS containing flame retardant DDO and synergist Sb_2O_3 (Br–Sb–HIPS) was prepared by melt blending in an internal mixer working at 190 °C for 15 min. Both samples were pulverized into particles of 0.6 mm with a pulverizer that was refrigerated with liquid nitrogen. The elemental composition of Br–Sb–HIPS and PP samples is presented in Table 1.

2.2. Thermogravimetry

Thermogravimetry (TG)/differential thermogravimetry (DTG) experiments were carried out on a thermobalance (NETZSCH STA 449F3). Samples of 10 (±0.5) mg were heated in a ceramic crucible from the ambient temperature up to the final temperature of 800 °C at a heating rate of 10 °C/min, while the furnace was flushed with nitrogen flow rate of 100 ml/min in advance.

2.3. Experiment procedures

The pyrolysis of samples was performed at 410 °C in a fixed bed reactor (Fig. 1). The reactor measured 35 mm in internal diameter and was heated by an electrical furnace equipped with a programmable temperature controller. A 10 g aliquot of the plastic sample was placed in a crucible, which was then placed in the bottom of the reactor. Before the pyrolysis process, the reactor was purged with N_2 (100 ml/min) for at least 60 min to remove any oxygen. Then, N_2 flow was adjusted down to 30 ml/min and the temperature was increased to the required temperature with a heating rate of 10 °C/min. The temperature was maintained till the pyrolysis was complete.

The volatile pyrolysis products exited from the reactor were cooled by a water and ice condenser to trap the liquid products. The condenser was followed by a fiber filter to prevent any organic materials from entering into the subsequent alkali solution (Na_2CO_3/$NaHCO_3$) flask which was used to trap HBr or Br_2. The remaining gas was not collected for analysis.

Pyrolysis products were classified as char, wax, oil and gas. The char residue mass was determined by measuring the mass of the crucible before and after each experiment. Mass of wax and oil was determined by measuring the mass of quartz reactor and each component of the condenser train before and after each experiment. Then oil was separated from the mixture by filtering. Gas mass was obtained by the method of difference.

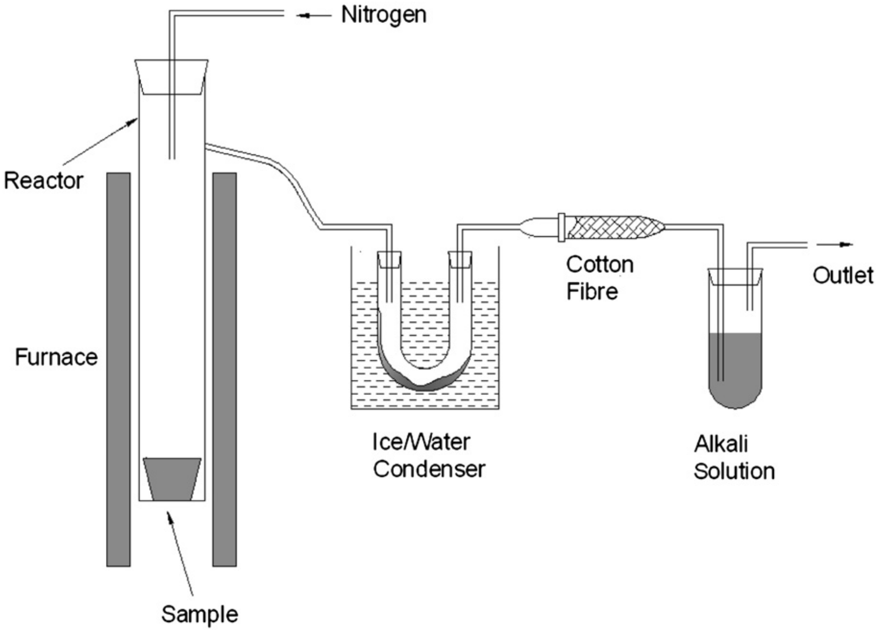

Fig. 1. Schematic of the fixed bed reactor.