

Effect of Hydrotalcite on Bromine Content in Oil Produced from the Pyrolysis of Acrylonitrile-Butadiene-Styrene Plastics

N. Morita, M. Nakayasu, T. Wajima, A. T. Saito, and H. Nakagome

Abstract—In this study, a method is presented to reduce the halogen concentration in the oil produced upon pyrolysis of acrylonitrile-butadiene-styrene (ABS) resins containing brominated flame retardants. More specifically, hydrotalcite was added to a predetermined amount of ABS in a glass reactor, and subjected to pyrolysis at 400 °C in nitrogen atmosphere. The bromine content in the product oil, residue, and gas released upon pyrolysis was analyzed. The main components of the product oil following pyrolysis of ABS in the absence of hydrotalcite additive were toluene, ethylbenzene, styrene, 1-bromomethyl-4-methylbenzene, phenol, *n*-butyl benzene, 1-methoxy-1-methylethyl benzene, and bromine compounds 2-bromophenol, 4-benzyloxy bromobenzene, 2,6 dibromophenol, and 2-bromotoluene. In contrast, the content of bromine in the product oil decreased when hydrotalcite was added to ABS. Moreover, negligible amounts of bromine were detected when the amount of added hydrotalcite was greater than 8 g. The reduced content of bromine in the product oil was attributed to the efficient trapping of bromine in the hydrotalcite matrix (as determined by the content of bromine in the residue).

Index Terms—Acrylonitrile-Butadiene-Styrene (ABS), halogen, hydrotalcite, pyrolysis.

I. INTRODUCTION

Electrical and electronic equipments (EEEs) are ubiquitous in our society, and have increasingly shorter lifespans as they become outdated and are replaced by newer models. EEEs constitute not only of computers, mobile phones, hair dryers, or refrigerators, but also cathode ray tubes [1]. These EEEs are subsequently considered as waste electrical and electronic equipments (WEEEs) at the end of their lifespan. Hence, the treatment of WEEEs has gained considerable importance [2]. In the European Union, the amount of WEEE generated per capita in 2005 was 17 kg that corresponds to an estimated 8.3–9.1 million tons of waste [3]. The EU has recently introduced legislation aimed to encourage reuse of WEEE and recycling to reduce the amount of WEEE sent to landfills and incineration [4]. These products contain many materials that can be recycled, such as glass or metal. However, the

remaining components that can constitute 15 types of plastics currently make the recycling process difficult [5]. Chemical recycling of plastics by thermal decomposition of WEEE has attracted interest as a promising technology. Upon thermal decomposition, the plastic polymer is converted into oil, residual carbon, and gases, which can be used as a chemical raw material and fuel [6]. Furthermore, there is a rich literature on basic research and chemical recycling of waste plastic based on thermal decomposition in the presence of a catalyst [7]–[18]. WEEE plastics typically consist of a flame retardant containing halogen compounds, and thus require special handling. Flame retardants can reduce the flammability of plastics, however, they represent a health hazard to humans owing to their toxic polybrominated compound components. Examples of such toxic components include polybrominated dibenzo-*p*-dioxins and polybrominated dibenzofurans [19]. The main plastic components in WEEE are acrylonitrile-butadiene-styrene (ABS) and high impact polystyrene (HIPS). Additionally, antimony trioxide is typically present as a synergist for the bromine-based flame retardant compounds. Is a technology for recycling the plastic of WEEE from hazards to health of these compounds research. In particular, extensive studies on the thermal decomposition of ABS [20]–[24], the use of catalyst [25]–[30], and the use of ammonia as a reducing agent [31], [32] have been carried out. As reported in the literature, the pyrolysis of brominated flame retardants-containing ABS in tubular reactors affords the release of bromine from the middle distillate and heavy oil component [23]. Moreover, studies on the thermal degradation of ABS using semi-batch reactors showed that the brominated flame retardant components could be converted into residual carbon [21]. Another study examined the thermal decomposition of tetrabromobisphenol A, a brominated flame retardant, in the presence of a zeolite catalyst (ZSM-5 or Y-type zeolite), whereby the latter catalyst was more effective in removing the bromine compound [27]. We previously reported that it was possible to reduce the content of bromine in the oil produced upon thermal decomposition of brominated polystyrene by using hydrotalcite (HT) additive [33]. HT is a layered double hydroxide consisting of a metal complex hydroxide comprising anionic species in the divalent Mg^{2+} and trivalent Al^{3+} host layers and interlayer of the guest layer [34], [35]. HT is the catalyst [36], [37] and gas removal [38] material for the [39], as ion exchanger [34], [35], [40], [41] has received increasing attention in recent years. High anion exchange capacity comparable to HT organic ion-exchange resins has

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received much attention and has been used as an adsorbent for the removal of various contaminants in aqueous solutions. The adsorption properties of inorganic anions such as sulfates, chromates, arsenates, selenate, borates, nitrates, fluorides, and phosphates have been studied [42]. The adsorption of anions onto HT is known to proceed via the formation of inter-layer outer sphere complexes upon an anion exchange reaction [43]. Additionally, HT has been generating interest as a catalyst in bio-diesel fuel production, whereby a noted increased yield from 62% to 77% has been observed in the presence of HT catalyst [44], [45]. The catalytic activity of HT has been further demonstrated in the aerobic oxidation of benzyl alcohol [46].

In this study, a method is presented to reduce the content of bromide in oil generated upon thermal decomposition of ABS at 400 °C, whereby HT was employed as an additive during the pyrolysis process.

II. EXPERIMENTAL

A. Materials

ABS was obtained from Asahi Kasei Chemicals Corporation. A synthetic HT was used as an additive (DHT-4A; Kyowa Chemical Industry Co., Ltd.).

B. Experimental Apparatus and Procedures

The experimental apparatus used in this study is shown in Fig. 1. A mixture of HT and ABS (20 g) were introduced into a glass reactor. To remove oxygen from the reactor, the latter was flushed with nitrogen gas at 50 mL/min for 1 h. Pyrolysis was then initiated. The temperature of the glass reactor where the sample resided was monitored using a thermocouple. The temperature of the reactor was increased to 400 °C at a heating rate of 5 °C/min, after which it was allowed to cool naturally. The gases generated during pyrolysis were recovered in a recovery container as the product oil passed through the cooling condensation pipe. Non-condensable gases were collected in a gas pack via bubbling of an alkaline aqueous solution, a bromine alkaline generated gas bromide ions in the solution.

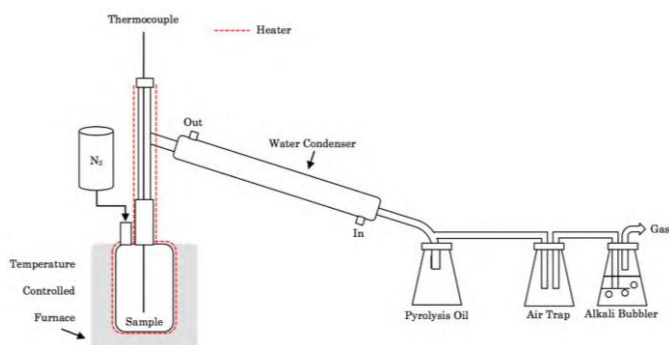


Fig. 1. Experimental apparatus.

C. Analysis

The product oil was diluted 100 times with hexane (Guaranteed Reagent grade, Wako Pure Chemical Industries), and analyzed by comparing the peaks obtained by gas chromatography–mass spectrometry (GC–MS) on a Shimadzu GCMS-QP2010 Ultra. The compounds were

identified using a GC–MS spectral library. Pure helium was used as a carrier gas and a Rtx-1 column (inner diameter of 0.25 mm and film thickness of 0.25 μm) was used. For analysis, the temperature was maintained at 40 °C for 30 min, and then increased to 230 °C at a heating rate of 5 °C/min.

The bubbling alkaline aqueous solution was diluted to 100-fold with ultrapure water and subjected to ion chromatography on a Shimadzu ion chromatograph to determine the bromine concentration. A Shim-pack column (150 L × 4.6) and CDD-10Asp detector were used.

The structure of the residue (following pyrolysis) was examined by X-ray diffraction (XRD; D2 PHASER, Bruker xxx). The composition of the residue was examined by scanning electron microscopy (TM3030, Hitachi) coupled with energy-dispersive X-ray spectroscopy (BURUKER QUANTAX). Elemental distribution mapping of the surface of the sample residue following thermal decomposition was conducted. Energy-dispersive X-ray spectroscopy images were collected from five different samples areas, and provided quantitative determination of the bromine contents in these areas. The obtained values were averaged accordingly to determine the representative content of bromine.

Furthermore, assuming that the landfill .The residue obtained after pyrolysis was subjected to a bromine dissolution test. The residue was mixed with distilled water at a ratio of 3: 100 of 200 times / min, and the mixture was shaken for 2 h. The supernatant liquid following centrifugation was subjected to ion chromatography to determine the content of bromine leached from the residue.

III. RESULTS AND DISCUSSION

A. Product Oil

The yield of the product oil obtained upon pyrolysis of ABS is shown in Fig. 2. As the results show, the yield of the product oil varied in the range of 35–45% regardless of the amount of added HT (0–20 g).

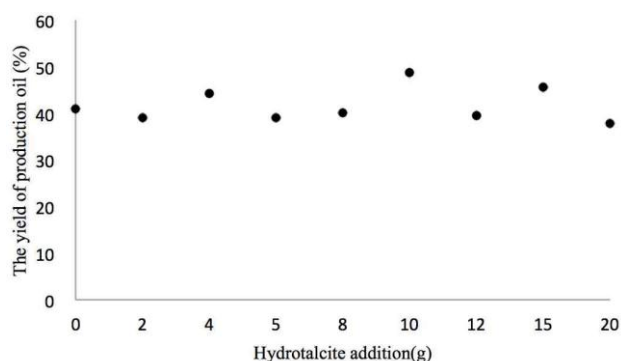


Fig. 2. Yield of product oil following pyrolysis of ABS in the presence of varying amounts of HT additive.

B. Residue

Table I lists the chemical components in the oil generated upon thermal decomposition of ABS in the presence of varying amounts of HT. Toluene, ethylbenzene, styrene, phenol, *n*-butyl benzene, and 1-methoxy-1-methylethylbenzene were detected along with

bromine compounds 1-bromomethyl-4-methylbenzene, 2-bromophenol, 4-benzyloxy bromobenzene, 2,6-dibromophenol, and 2-bromotoluene upon thermal decomposition of ABS in the absence of HT additive. In contrast, the bromine compounds were not detected when the HT additive amount was greater than 8 g.

TABLE I: COMPONENTS OF PRODUCT OIL OBTAINED USING VARYING AMOUNTS OF HT ADDITIVE

Compound	Formula	Amount of hydrotalcite additive (g)								
		0	2	4	5	8	10	12	15	20
Toluene	C ₇ H ₈	o	o	o	o	o	o	o	o	o
Ethylbenzene	C ₈ H ₁₀	o	o	o	o	o	o	o	o	o
Styrene	C ₈ H ₈	o	o	o	o	o	o	o	o	o
1-Bromomethyl-4-methylbenzene	C ₈ H ₉ Br	o	o	o	o	nd	nd	nd	nd	nd
Phenol	C ₆ H ₅ OH	o	o	o	o	nd	nd	nd	nd	nd
<i>n</i> -Butyl benzene	C ₁₀ H ₁₄	o	o	o	o	nd	nd	nd	nd	nd
1-Methoxy-1-methylethylbenzene	C ₁₀ H ₁₄ O	o	o	o	o	nd	nd	nd	nd	nd
2-Bromophenol	C ₆ H ₅ BrO	o	o	o	o	nd	nd	nd	nd	nd
4-Benzyloxy bromobenzene	C ₁₃ H ₁₁ BrO	o	o	o	o	nd	nd	nd	nd	nd
2,6-Dibromophenol	C ₆ H ₄ Br ₂ O	o	o	o	o	nd	nd	nd	nd	nd
2-Bromotoluene	C ₇ H ₇ Br	o	o	o	o	nd	nd	nd	nd	nd

o, detected; nd, not detected

Fig. 3 illustrates the amount of bromine in the product oil upon thermal decomposition of ABS in the presence of varying amounts of HT additive. As the results show, in the absence of HT additive, the amount of bromine determined was 100%, which decreased upon addition of HT. Further increases to >8 g resulted in negligible detectable amounts of bromine. Hence, the results reveal that the amount of bromine in the product oil can be considerably reduced to zero upon addition of HT (>8 g).

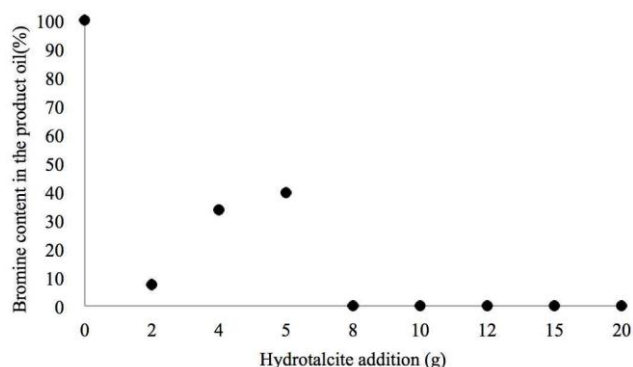


Fig. 3. Bromine content in the product oil following pyrolysis of ABS in the presence of varying amounts of HT additive.

The observation results of the residue by SEM are shown in Fig. 4. When the added amount of HT increased, the large particles and the small particles could be observed on the surface. The former can be interred to be Mg-Al oxides. And bromine can be interred to have been absorbed on the surface of the later.

The amount of bromine in the residue following pyrolysis is shown in Fig. 5. As the results show, the amount of bromine was 8.9% when HT was not added, and increased to 16% as the additive amount of HT increased (2–5 g). The amount of bromine was 23% when more than 8 g of HT was used. Thus, the results further confirmed that bromine was trapped within the residue upon addition of HT.

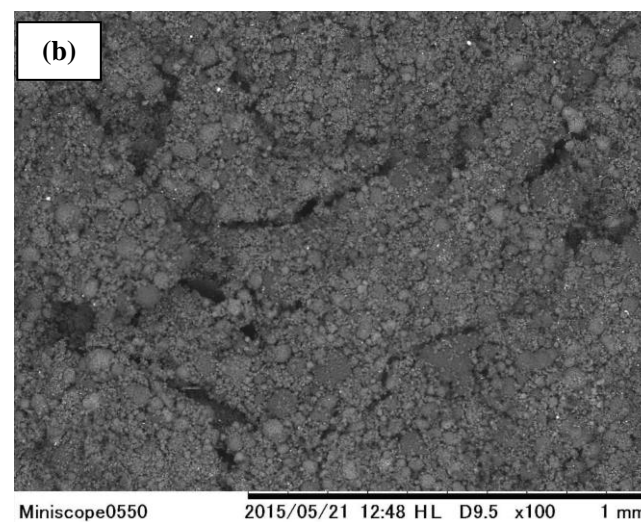
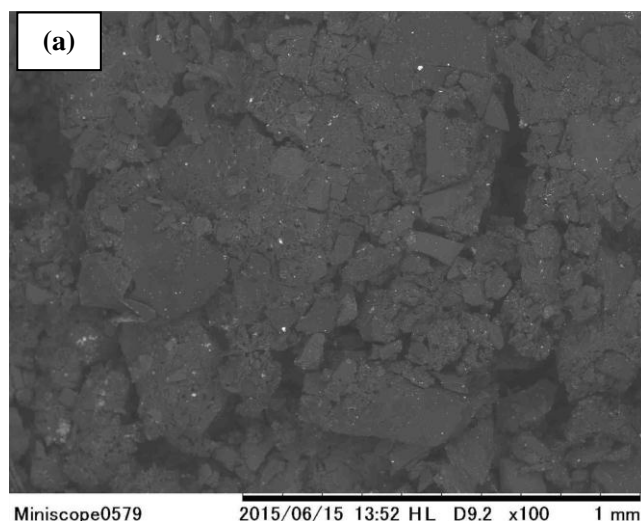


Fig. 4. Residue after pyrolysis of ABS (a) without HT and (b) with 10g of HT.

The bromine dissolution test did not show leaching of bromine from the residue under all conditions examined.

Therefore, we can conclude that bromine is strongly encapsulated into hydrotalcite.

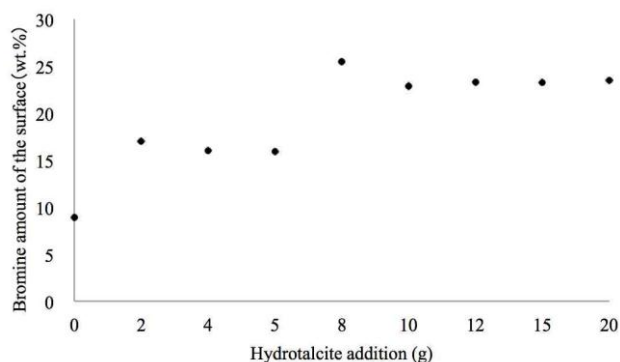


Fig. 5. Variations in the amount of bromine on the residue surface as a function of HT additive amount.

C. Content of Bromine in Gas

The gases generated upon pyrolysis of ABS were analyzed. Incidentally, the volume of gas generated by thermal decomposition was less than 1 L in all experiments conducted. The components of the water-insoluble gas include H_2 , CH_4 , and CO_2 . H_2 and CH_4 were derived from the thermal decomposition of the plastic, whereas CO_2 was derived from the combustion of hydrotalcite.

The content of bromine in the generated water-soluble gas is shown in Fig. 6. In the absence of HT additive, bromine was detected in the generated gas. In contrast, bromine was not detected when HT additive was used within the HT amounts studied. This result further confirmed that bromine was firmly trapped within the HT matrix and thus was not released in the gases produced during pyrolysis.

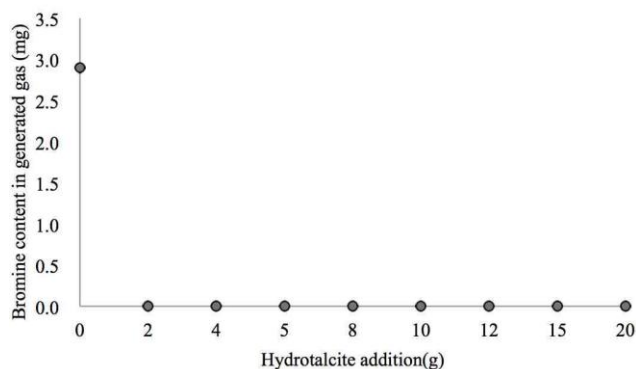


Fig. 6. Bromine content in the gas generated upon pyrolysis of ABS in the presence of HT at varying amounts.

IV. CONCLUSION

In this study, the reduction of bromine content in the product oil obtained upon thermal decomposition of bromine-based plastic ABS was examined by introducing hydrotalcite additive. The results showed that the addition of an appropriate amount of hydrotalcite (>8 g) to ABS sample (20 g) resulted in considerable reduction of the content of bromine (to zero) detected in the product oil.

The residue was added hydrotalcite is concentrated bromine, it is believed that the reason may be obtained a product oil of bromine does not contain. Furthermore, the

bromine dissolution test confirmed that bromine was efficiently encapsulated within the hydrotalcite matrix, and thus did not leach in solution.

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