

Effects of Hydrotalcite on the Recovery of Metals by Pyrolysis of Epoxy Resin Glass-Coated Substrates

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Abstract—Approximately 22.18 million units of electrical and electronic equipment have been shipped in Japan, whereas only 11.7 million home appliances were collected under the Home Appliance Recycling Law. Although precious metals can be recovered from such devices, this recovery is rarely practiced in the case of small home appliances. This situation is problematic because the disposal of printed circuit boards in landfills can result in the leaching of heavy metals and bromine-based flame retardant chemicals into groundwater. Unfortunately, the thermoset resins employed in these units are not readily recycled and may require special pre-treatment. The work reported herein added a synthetic hydrotalcite to epoxy resin glass-coated substrates prior to pyrolysis to allow the safe recovery of useful metals and the capture of toxic bromine compounds. This hydrotalcite was found to promote substrate decomposition through a catalytic effect together with hydrolysis. Bromine-based byproducts were also captured by the hydrotalcite.

Keywords—epoxy glass-coated substrate, pyrolysis, hydrotalcite, metal recovery, urban mining, flame retardant, recycling

I. INTRODUCTION

While approximately 22.18 million units of electrical and electronic equipment have been shipped in Japan, only approximately 11.7 million of these devices were collected under the Home Appliance Recycling Law. This is unfortunate because used electronics may contain precious metals (such as gold and palladium) that can be recycled. In addition, it has been reported that the degree of resource recovery from many small home appliances is currently inadequate. Printed circuit boards also typically contain heavy metals (such as lead and copper) together with elements such as bromine and antimony that are added to improve flame retardance, leading to concerns regarding safe disposal at landfill sites and possible groundwater contamination. For these reasons, the used electronics that are disposed of in Japan represent a source of rare metals and can be considered as so-called “urban mines” [1]. It would be advantageous to develop techniques to safely and efficiently separate and recover resources such as rare metals from these devices. Even so, the widespread use of thermosets such as epoxy and phenolic resins in printed circuit boards complicates the recycling process.

The European Union strictly regulates the disposal of electrical and electronic equipment and pyrolysis has attracted attention in that region as a means of recycling these devices. However, epoxy resin substrates must be pre-treated prior to pyrolysis because these materials tend to contain bromine compounds acting as flame retardants. The present study investigated the use of specific additives during the

pyrolysis as an approach to the safe recovery of useful metals. This process represents a new technology allowing the efficient separation and recovery of rare metals contained in electrical appliances and electronic components [2].

Sodium hydroxide (NaOH) is often added prior to pyrolysis as an alkaline catalyst. However, in the work reported herein, the synthetic hydrotalcite $Mg_1-XAlX(OH)_2(CO_3)_X/2-mH_2O$ was employed. This substance exhibits anion adsorption and exchange characteristics and has recently attracted attention as a catalyst. As an example, this material has been examined as a means of recovering bromine gas released during thermal decomposition processes. Based on the use of this additive, we attempted to reduce the pyrolysis temperature to 450 °C from the more typical range of 600 to 800 °C while recovering useful metals and trapping bromine compounds.

II. LITERATURE REVIEW

The authors previously reported that the addition of the present synthetic hydrotalcite during the pyrolysis of tantalum-based capacitors promoted resin degradation and allowed the recovery of brominated flame retardants [3]. Both combustion [4] and solubilization [5] have been previously proposed as means of treating the resins contained in computer circuit boards and capacitors. However, these techniques have several drawbacks, including the need for elevated temperatures and pressures and the generation of harmful halogen-based compounds [6]. Many investigations have therefore examined pyrolysis and chemical recycling of waste plastics [7–15]. Such studies have demonstrated that the pyrolysis of halogenated plastics can be performed in conjunction with a calcium carbonate/carbon composite [16]. The authors also previously reported that the addition of a synthetic hydrotalcite during the pyrolysis of brominated plastics reduces the concentration of bromine-based compounds in the oil that is produced [17].

A prior study assessing the recovery of useful metals via the pyrolysis of substrates coated with epoxy glass established that pyrolysis in hydrogen-donating solvents or in tetralin reduced the concentration of bromine-based compounds in the product [18]. Other work showed that pyrolysis in solvated tar reduced the amount of bromine compounds contained in the resin, although both these prior studies noted challenges related to cost and the necessity of pre-treatment [19]. To the best of our knowledge, no research to date has examined solubilization of the resin, destruction of the substrate by thermal decomposition or recovery of the halogenated gases resulting from this process.

The synthetic hydrotalcite used as an additive in this study is classified as a layered double hydroxide and comprises metal complex hydroxides. The structure of this material consists of host layers of divalent Mg^{2+} and trivalent Al^{3+} ions interspersed with guest layers containing anions. The basic structure of this hydrotalcite is identical to that of magnesium hydroxide ($Mg(OH)_2$), although the present material also shows the ability to react with acids and to exchange ions over the pH range of 3.5 to 5. This material is primarily employed in industry as a heat stabilizer for poly (vinyl chloride), a film insulator for agricultural purposes and an acid-receptive agent for rubber and plastics. It may also be used as an antacid (Figs. 1 and 2).

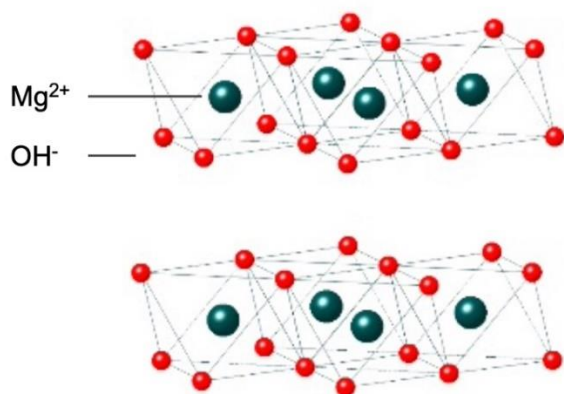


Fig. 1. The lattice structure of magnesium hydroxide.

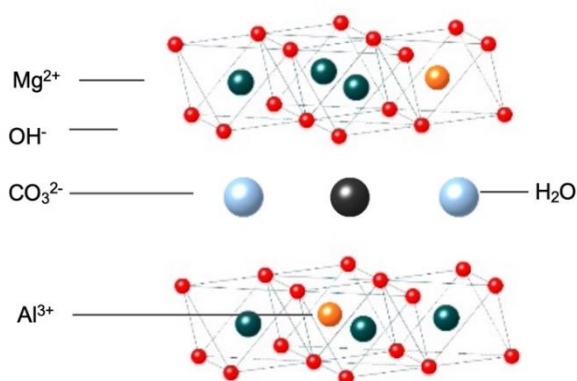


Fig. 2. The lattice structure of hydrotalcite.

Hydrotalcite has received increasing attention in recent years as a catalyst and as a gas adsorbent material or ion exchanger. The exceptional anion exchange capacity of this substance, which is comparable to that of organic ion exchange resins, is of interest and thus hydrotalcite has also been used as an adsorbent for the removal of various contaminants from aqueous solutions. Specifically, the adsorption of inorganic anions such as borate, nitrate, fluoride, phosphate, sulfate, chromate, arsenate and selenite has been investigated. The adsorption of anions on HT is believed to occur through the formation of interlayer outer sphere complexes based on anion exchange reactions. HT has also been employed as a catalyst and has been shown to increase biodiesel yields from 62% to 77% [20, 21]. Recently, it was reported that the catalytic properties of hydrotalcite can be improved by tuning the molar ratio of Mg^{2+} to Al^{3+} ions in the material [22–25]. In the present study, four synthetic hydrotalcites having varying composition ratios were used as

additives in the pyrolysis of epoxy glass-coated substrates with the aim of recovering valuable metals together with the halogens produced as by-products.

III. MATERIALS AND METHODS

Epoxy glass-coated resin substrates (Printed circuit boards; PCB, Fujitsu) were used as samples and pyrolyzed with a synthetic hydrotalcite (KW-1000, SETOLAS Holdings, Inc.) as an additive. The composition of this material is shown in Table 1 whereas the experimental conditions are summarized in Table 2. In these trials, a predetermined amount of each synthetic hydrotalcite was added to the sample. Sodium hydroxide (Wako Pure Chemicals Co.) and sea sand (Wako Pure Chemicals Co., ethanol-washed, 425–850 μm particle sizes) were also used for the purpose of comparison.

Table 1. Composition of the hydrotalcite (wt.%)

Substances	Al_2O_3	MgO
KW-1000	19.3%	35.1%

Table 2. Raw material ratios used in trials

Condition	Sample	Addition
I	PCB	-
II	PCB + KW-1000	PCB:HT = 2:1
III	PCB + KW-1000	PCB:HT = 4:1
IV	PCB + NaOH	PCB:NaOH = 2:1
V	PCB + Sea sand	PCB:Sea sand = 2:1

The experimental setup used in this study is presented in Fig. 3. In these experiments, each mixture was placed in a metal reactor, following which a 50 mL/min flow of nitrogen gas was passed through the reactor for 60 min to remove oxygen. After this, the nitrogen flow was stopped and the pyrolysis was conducted. The reactor temperature was monitored using thermocouples and the apparatus was heated to 450 $^{\circ}C$ at a rate of 5 $^{\circ}C/min$. After reaching this temperature, the sample was allowed to cool naturally. Gases generated during each pyrolysis were condensed in a cooling tube and captured in the form of an oil.

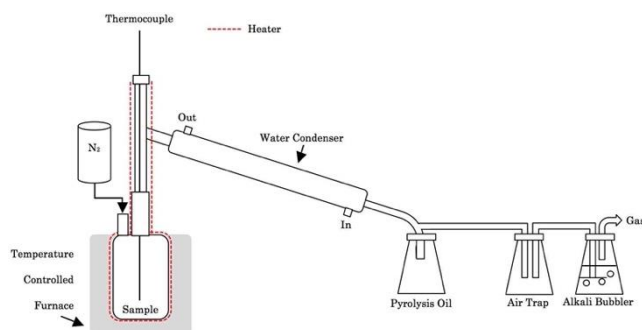


Fig. 3. The experimental apparatus.

IV. RESULT AND DISCUSSION

A. PCB Destruction

Table 3 presents photographic images of the PCBs before and after pyrolysis while the percentages of metal recovered

from each specimen are provided in Fig. 4. Observations of stacked cross-sections of the PCBs immediately after pyrolysis were performed using a digital microscope

(EVIDENT Japan, DSX1000) at 105× magnification and are shown in Table 4.

Table 3. Photographic images of PCB specimens before and after pyrolysis

















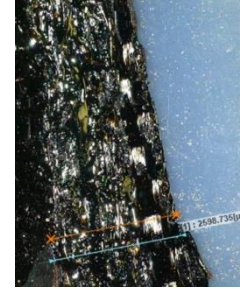

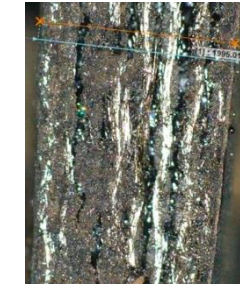
	I	II	III	IV	V
Before					
After					
Destruction	Indestructible				

Table 4. Images showing stacked cross-sections of PCB specimens after pyrolysis

I	II	III	IV	V
				

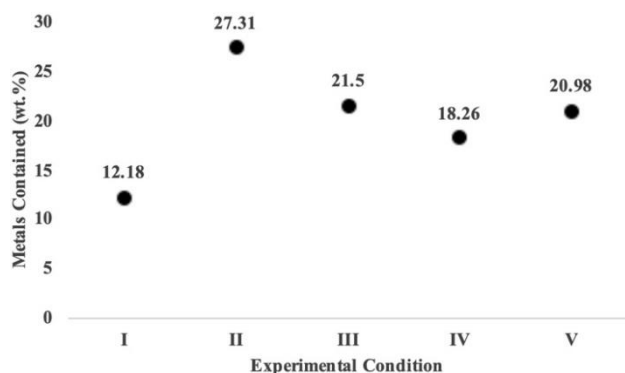


Fig. 4. Percent metal recoveries from PCB specimens after pyrolysis using various conditions.

In the absence of the synthetic hydrotalcite, metals could not be easily recovered from the PCB. Following the addition of either sodium hydroxide or sea sand, metals could be recovered but not as readily as with the addition of the hydrotalcite. Condition II resulted in the highest yield of metals. Interestingly, digital microscopy observations indicated a spreading of the lamination area during this trial, to which the greater recovery can likely be attributed. The hydrotalcite used in this work contained interlayer water and so it appears that the catalytic effect of the hydrotalcite combined with hydrolysis reactions degraded the PCB. The results obtained from conditions II and III suggest that there is an optimal amount of hydrotalcite when using this

technique.

B. Qualitative Analysis of Product Gases

Non-condensable gases were collected by bubbling the reaction effluent through an alkaline water trap and then analyzed using a gas chromatograph (GC-2014). It should be noted that less than 1 L of gas was produced from each trial. Although H₂, CO₂ and other gases were identified, it appears that the major products were condensable, carbon-based compounds.

C. Ion Chromatographic Analysis of Alkaline Aqueous Solutions

A 0.1 mol/L NaOH solution in water was diluted 50-fold and qualitatively analyzed using an ion chromatograph (IC-20, Shimadzu). Although epoxy resin glass-coated substrates tend to contain brominated and chlorinated flame retardants, neither bromide nor chloride ions were detected.

Table 5. Results from IC analysis of the alkaline aqueous solutions

	I	II	III	IV	V
Cl	nd	nd	Nd	nd	nd
Br	nd	nd	nd	nd	nd

nd: not detected

D. Residues

The hydrotalcite residues were recovered after pyrolysis and assessed for heat-induced structural changes by acquiring

X-Ray Diffraction (XRD) patterns (D2 PHASER, Bruker). Representative data are shown in Fig. 5.

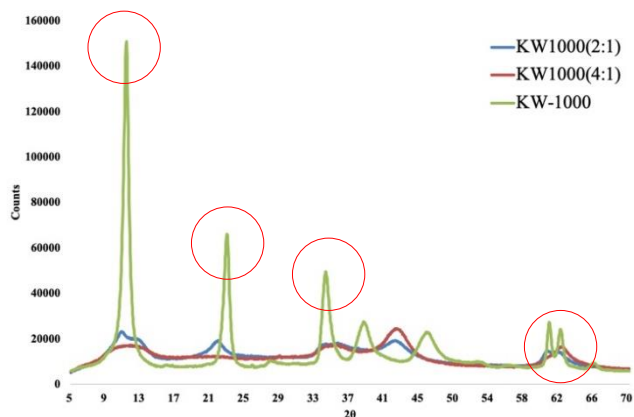


Fig. 5. XRD patterns of KW-1000 samples before and after pyrolysis.

Fig. 5 demonstrates that the same hydrotalcite peaks were obtained following pyrolysis but were much less intense. From these data, it appears that the layered structure of the hydrotalcite was not disrupted but there was an effect associated with the loss of interlayer water. The residue obtained after pyrolysis was also analyzed using energy dispersive X-ray spectroscopy (EDS), employing a Bruker QUANTAX instrument attached to a HITACHI TM3030 electron microscope. Images acquired at $\times 250$ are presented in Figs. 6 and 7.

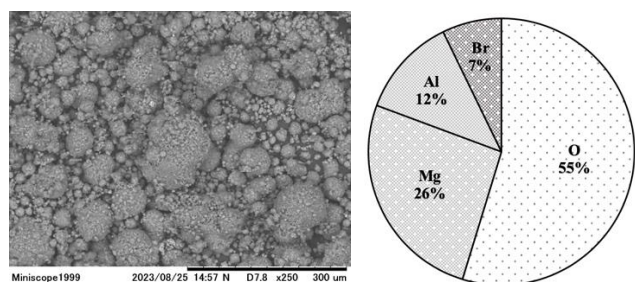


Fig. 6. An electron microscopy image and EDS results for the residue from the Condition II trial.

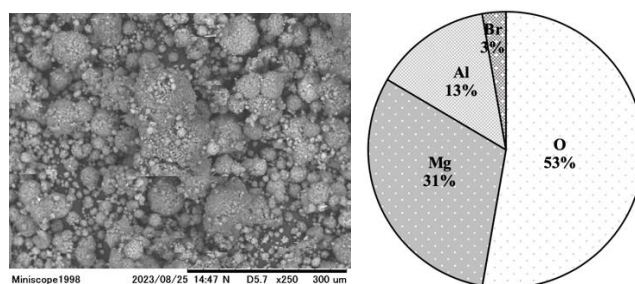


Fig. 7. An electron microscopy image and EDS results for the residue from the Condition III trial.

Figs. 6 and 7 show that bromine was detected in the hydrotalcite after pyrolysis. Although hydrotalcite exhibits a capacity for anion exchange, the fact that bromine was observed on the surface of the hydrotalcite does not indicate that ion exchange occurred. Rather, an acid/base neutralization reaction is thought to have occurred between the basic hydrotalcite and acidic bromine gas generated during pyrolysis.

V. CONCLUSION

In this study, a synthetic hydrotalcite was added to PCBs prior to pyrolysis at 450 °C to assist in destruction of the resin and recovery of metals. The amount of hydrotalcite that was added evidently determined the effectiveness of the process. The incorporation of this material promoted decomposition of the PCBs, presumably based on a catalytic effect resulting from magnesium and aluminum hydroxides. Water in the hydrotalcite interlayers may also have led to hydrolysis. Following pyrolysis of the PCBs in the presence of the hydrotalcite, the resin was found to have been degraded without the need for any special pre-treatment. A hydrotalcite-to-PCB mass ratio in the range of 0.25 to 0.5 was found to be optimal.

Halogen-based gaseous products are thought to have been generated during the pyrolysis. These were captured by the hydrotalcite as a consequence of neutralization reactions rather than anion exchange. If anions had been captured by the hydrotalcite via exchange, the captured bromine would likely have been retained between the hydrotalcite layers. Because bromine was instead observed on the residue surfaces, neutralization reactions were likely responsible. An XRD analysis of the hydrotalcite following use demonstrated that the layered structure was retained but modified by the release of interlayer water after pyrolysis at 450 °C. The material remained capable of degrading PCBs and capturing bromine gas. These data demonstrate that the addition of hydrotalcite to PCBs at a mass ratio of 0.25 to 0.5 can allow metals to be easily recovered while trapping bromine gas produced as a by-product.

CONFLICT OF INTEREST

All authors declare that: (i) no support, financial or otherwise, has been received from any organization that may have an interest in the submitted work and (ii) there are no other relationships or activities that could appear to have influenced the submitted work.

AUTHOR CONTRIBUTIONS

C. Inaba, M. Arai, K. Masuda and S. Momiyama performed the experimental work and data analysis. The wording of the final paper was agreed upon by all authors.

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