Simultaneous Recovery of Organic and Inorganic Materials by the Thermal Decomposition of Plastic-Metal Composites

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Abstract

In this investigation, we examined the possibility of the simultaneous recovery of oil and metal from metal containing plastic composites. X-ray film, video tape, and prepaid cards based on poly(ethylene terephthalate) (PET) were hydrolyzed at 450 °C in steam atmosphere, resulting in volatile terephthalic acid (TPA). Metals were recovered together with carbonaceous residue at an average yield of more than 90% of the initial content. In a second step, TPA was decarboxylized in the presence of calcium oxide (CaO) at 700 °C, producing benzene with an average yield of 34%. Also, paper laminated printed-circuit boards (PCB) based on phenol and epoxy resin were decomposed in the presence and absence of calcium hydroxide ($Ca(OH)_2$) in a tube reactor, recovering both organic and inorganic products. As a result, oil with an average yield of 7 wt%, consisting of phenol and phenol derivatives, was obtained.

Keywords: *PET, printed circuit board, pyrolysis, hydrolysis, calcium oxide*

1. Introduction

Plastic-metal composites are widely used in our daily life. Poly(ethylene terephthalate) (PET), phenol resin, and epoxy resin are often used in electric and electronic equipment. Metals incorporated in the organic matrix are silver, iron, indium, chrome, tin, copper, gold, antimony, etc. These metals are often of economic interest. However, for the sake of the environment, the organic matrix should be considered as a resource, as well.

One of the recycling methods for plastic-metal composite is pyrolysis, which can convert plastics into organic feedstock and simultaneously remove metals.

We reported earlier [1] that PET could be thermally decomposed in the presence of calcium oxide (CaO), resulting in oil with a high benzene content. In this work, the reported benzene production process was applied to PET based X-ray film, video tape, and prepaid cards. Additionally, paper laminated printed circuit boards (PCB) based on phenol and epoxy resin was pyrolyzed. The possibility of the simultaneous recovery of organic materials and metals from plastic-metal composites was investigated

2. Materials and Methods

2.1 Materials

Cut PET bottles, X-ray film, video tape, and prepaid cards (2.8 mm × 2.8 mm), and crushed paper laminated PCB based on phenol and epoxy resin (0.3~1.0 mm) were used (Table 1). CaO and calcium hydroxide ($Ca(OH)_2$) were used as catalyst.

2.2 Experiments and Analytical Methods

PET materials were decomposed in the presence and absence of CaO using a two-step tube reactor with two separated zones, one for the hydrolysis of PET and the other for the decarboxylation of terephthalic acid (TPA) [1]. In order to recover metals after degradation, samples were filled into a perforated quarts holder. Samples were hydrolyzed at 450 °C in steam atmosphere. The resulting TPA was decarboxylated by CaO at 700 °C.

PCB was pyrolyzed in the presence and absence of $Ca(OH)_2$ in a horizontal tube reactor at 700 °C.

Liquids and gaseous products were analyzed by GC-MS, FID, and TCD. Metals were investigated by XRD and ICP-AES. The Br content was quantified by IC and GC-ECD. Organic products were normalized on the basis of the initial polymer weight (100 wt%).

3. Results and Discussion

3.1 PET Materials Degradation

The PET materials were hydrolyzed in the presence and absence of CaO (Fig. 1). Sublimating substances were visibly deposited at the reactor wall in the absence of CaO. In addition, oxygen containing compounds such as acetophenone derived from the thermal decomposition of PET [2] were observed. Benzene production was comparable small.

Table 1. Elemental composition of the samples.

	Bottle	Film	Tape	Card	PCB (Phenol)	PCB (Epoxy)
C	61.9	61.5	50.1	49.2	51.5	55.9
H	4.3	4.4	3.7	3.6	5.7	6.4
N	-	0.4	0.4	0.4	1.5	4.0
Br	-	0.5	-		3.8	7.7
P	-	-	-		0.4	0.5
Ag	-	0.4	-		-	-
Fe	-	-	13.1	7.9	-	-
Ti	-	-	-	7.3	-	-
Al	-	-	-	0.4	-	-
Cu	-	-	-		1.8	2.0
Sb	-	-	-		-	0.6

In contrast, benzene yields increased drastically in the presence of CaO, resulting in an average yield of 34%. However, less benzene was obtained than reported earlier (benzene yield: 74%, purity: 96%) [1] because of the inefficient hydrolysis of PET in the sample holder. TPA and other oxygen containing compounds were not observed. Hence, these compounds were decomposed in the presence of CaO.

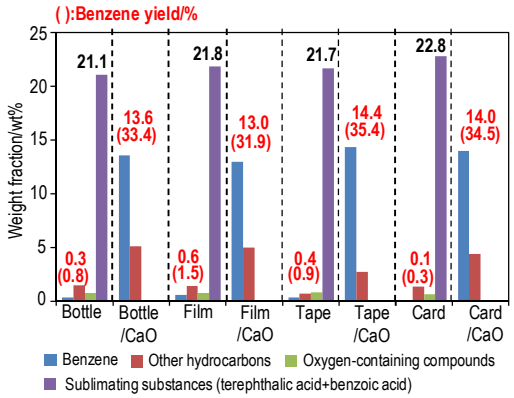

Fig. 1. Weight fraction of liquid products and sublimating substances obtained from PET hydrolysis in the presence and absence of CaO.

3.2 PCB Materials Degradation

The PCB materials were pyrolyzed in the presence and absence of $Ca(OH)_2$, resulting in an average of 7 wt% of liquid products (Fig. 2). The liquid products consisted mainly of phenol and derivatives. Brominated organic compounds and phosphor-based flame retardants were drastically decreased in the presence of $Ca(OH)_2$, since bromine and phosphorus could be fixed by $Ca(OH)_2$. Because of the degradation of brominated organic compounds and phosphor-based flame retardants, yields of phenol and phenol derivatives, especially phenol and cresol, increased in the presence of $Ca(OH)_2$. The bromine content in the oil was reduced by 95% by adding $Ca(OH)_2$.

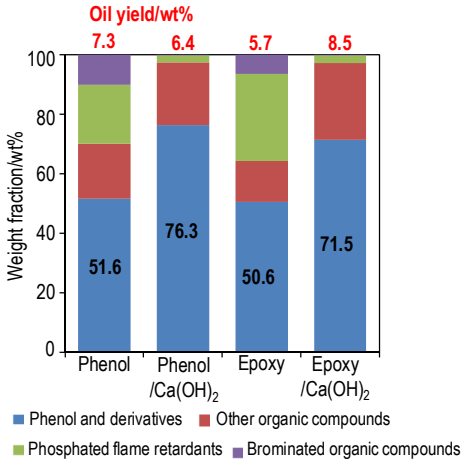

Fig. 2. Weight fraction of liquid products obtained from PCB materials in the presence and absence of $Ca(OH)_2$.

3.3 Metal Recovery

The metal containing carbonaceous residue was qualitatively analyzed by XRD (Fig. 3). According to ICP analysis, an average yield of over 90% of the initial metal content was recovered from PET samples. More than 80% of copper was recovered from PCB. The composition and crystal structure of the recovered metals did not change after the degradation. However, antimony yielded 22% and 65% in the absence and presence of $Ca(OH)_2$, respectively, because of the formation of volatile antimony bromide ($SbBr_3$, b.p. 280 °C). More antimony was recovered in the presence of $Ca(OH)_2$, since bromine was fixed by $Ca(OH)_2$, suppressing the bromination of antimony.

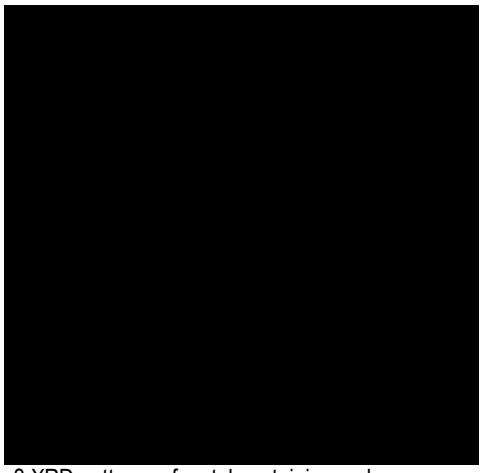

Fig.3 XRD patterns of metal containing carbonaceous residue after sample degradation.

4. Conclusion

Simultaneous recovery of benzene and metals from PET-metal composites was achieved, resulting in an average benzene yield of 34%. Calcium oxide was an efficient catalyst for the recovery of benzene. In contrast, little oil was recovered from PCB (maximum oil yield: 8.5 wt%) in the presence of $Ca(OH)_2$. Although $Ca(OH)_2$ increased the oil production only to a small extent, the bromine content in the oil decreased significantly in the presence of $Ca(OH)_2$. Furthermore, metals were recovered by more than 90% in average compared with the initial content and incorporated within the carbonaceous residue. After enhancing the oil yield, this method can be applied to plastic-metal composites which cannot be recycled effectively otherwise.

5. Acknowledgment

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6. References

[1] G. Grause, T. Handa, T. Kameda, T. Mizoguchi and T. Yoshioka. *Chem. Eng. J.*, 166 (2011), 523-528.
[2] M. E. Bednas, M. Day, K. Ho, R. Sander and D. M. Wiles. *J. Anal. Appl. Pyrol.*, 26 (19811111), 277-289.