RECOVERY OF ORGANIC CHEMICALS AND INORGANIC MATERIALS BY THE TREATMENT OF LASTIC-INORGANIC COMPOSITES IN HIGH-TEMPERATURE WATER

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Abstract: It is not easy to recover organic and inorganic compounds from waste IC devices because inorganic valuable materials of them were covered and protected by thermosetting resin such as epoxy resin. Incineration treatment was believed as the possible recycling process of inorganic valuable materials. However, organic compounds were no recovered. We have already indicated that molding materials of thermosetting resin such as phenol resin and epoxy resin could be decomposed easily into their monomers in sub- and supercritical water. In this study recovery of organic chemicals and inorganic materials was attained by the treatment of various plastic – inorganic composites in high-temperature water. We have confirmed the effects of pretreatment and reaction conditions such as temperature, reaction time and additives on the yields of products.

1. Introduction

It is well known plastic is an important material to modern times. Plastic is the general common term for a wide range of synthetic or semisynthetic organic amorphous solid matericals suitable for the manufacture of industrial products. However, along with plastic manufacture's development, we are facing a lot of questions which are more and more severe, such as resources, environment and recycling.

In recent years, supercritical water has been received more and more attention as a medium for chemical reaction[1-3], because that supercritical water behaves similar to organic solvents having high thermal stability.[4,5] We have already reported decomposition reactions of plastics including thermosetting resin into their monomeric compounds in supercritical water.[6,7] The addition of basic compounds such as Na_2CO_3 was effective on

the decomposition reaction. Furthermore, chemical participation of water on the reaction was suggested.

In this study, to obtain information on the decomposition reaction of plastics-inorganic composites in high-temperature, various IC waste devices and then model compounds were treated in high-temperature by using a 10 ml tubing bomb reactor.

2. Experimental

2.1 General

The organic products after decomposition were identified qualitatively by gas chromatography-mass spectrometry (GC-MS, Shimadzu, QP-5000, Column CBJ-M30-025, T=50^{o}C, T_{max}=270^{o}C, T_{rated}=10^{o}C/min) and were analyzed quantitatively by gas chromatography (GC-9A, Shimadzu, FID, Column SE-30(OV-1), T=130^{o}C, T_{max}=250^{o}C, T_{rated}=10 ^{o}C/min). Morphology of the samples was investigated using a scanning electron microscope (JEOLJSM-6330F, SEM) equipped with EDS (JEOL, Super Mini-cup, EDS). The images were analyzed with a computer (JEOL JED-2140) with EDS-ZAF correction software.

2.2 Materials

Various IC waste devices were provided by Tendokankyo Co.Ltd. Dry acetone, Diphenyl (TCI) N,N-Diethylformamide (Wako) Diethylether, phenol, Na_2CO_3 (KANTO) were used for the phenol resin decomposition reactions.

2.3 Decomposition reaction (Typical Procedure)

Decomposition reactions in high-temperature water or/and Na_2CO_3(3wt% or 10wt%) mixture were carried out by 10 ml tubing bomb reactor. Typically, 0.1 g of IC waste device was introduced in the tubing bomb reactor. The reaction was carried out at 430^{o}C with assigning reaction time. After decomposition reaction, solid residuum was dried, analyzed by SEM, and the liquid product was extracted with organic solvents and identified by GC/MS and quantified by GC with a flame ionization detector (FID).

3. Results and discussion

The effect of various conditions on the decomposition reaction using IC sample 1 was examined, such as additive, temperature and reaction time (Fig. 1). The reactions with high-temperature water in the absence of additive for 1h, 3h, 5h, 7h, respectively, were carried out (A). The result that as treatment time increases, the effect of decomposition reaction has been changed for the better, nevertheless, the presence of unreacted plastic on the surface of the metal was observed. Then Na_2CO_3 (3wt%) was added in the high-temperature water which applied to the reactions (B). The decomposition reaction proceeded smoothly than reaction A, whereas which did not completely decompose. In order to increase decomposition of IC waste device at high reaction temperature, the step-method

C with Na_2CO_3 (3wt%) was then investigated. This work was the best effective way to decompose organic and inorganic IC waste devices. In this treatment, the decomposition of IC waste device, probably its reaction time, additive, and physical deterioration effects was also an important factor for the decomposition process.

Tab. 1 shows the GC/MS analysis of residual component obtained using the method B and C. The yields of monomers in the recovery solution obtained with step-method C at 400^{o}C (runs a″-d″) were identical to those for the reaction without step-method B (runs a′-d′). It was confirmed that only decomposition reaction of IC waste device at the surface was accelerated by using step-method in Na_2CO_3 aqueous solution. In the case of d″, the yield of phenol reached 1.68%, 2-methylphenol reached 2.92%, and 2,4-dimethylphenol reached 1.66%. It is considered that phenol and its derivatives can be reused as raw materials of plastics such as phenol resin.

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Tab. 1 The GC/MS analysis of residual component in the recovery solution

method	run	Phenol yield (wt%)	2-methylphenol yield (wt%)	2,4-dimethylphenol yield (wt%)
B	a′	1.48	2.81	1.29
B	b′	1.49	2.82	1.33
B	c′	1.49	2.83	1.35
B	d′	1.50	2.83	1.38
C	a″	1.48	2.82	1.51
C	b″	1.53	2.86	1.62
C	c″	1.62	2.88	1.64
C	d″	1.68	2.92	1.66

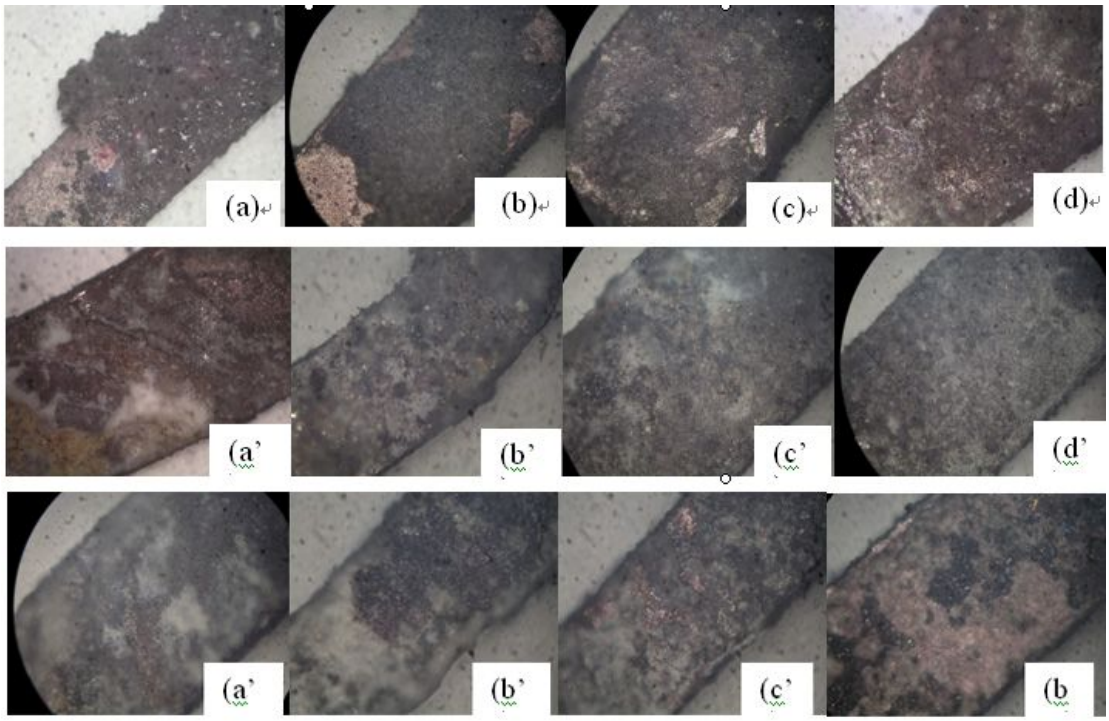

Fig. 1 The image of the IC sample 1 after decomposition reaction (A) only 1.0ml high-temperature water (a) reaction time: 1h, (b) 3h, (c) 5h (d) 7h; (B) a mixture of 3wt% $NaCO_3$ and 1.0ml high-temperature water (a′) 1h, (b′) 3h (c′) 5h (d′) 7h (C) The step reaction with natural cooling or forced cooling (a″) heating 2h→natural cooling 1h→heating 2h (b″) heating 2h→forced

Thermal decomposition of IC sample 2 was carried out at 430°C for 2h (Fig.2). In this case, the addition of Na_2CO_3 was shown to have a marked effect on the decomposition reaction. The reaction with high-temperature water in the absence of additive for 2h resulted in a poor yield of monomers, although body part of IC sample 2 was completely decomposed (b). In contrast, the decomposition reaction in the presence of additive was given a good yield of monomers, and the organic resin of connecting part which accepted thermal reaction was also decomposed, but not completely (c). With the increase of the amount of additive, Na_2CO_3 (10wt%) was shown have a significant effect and yield. Whether it was the body or connecting part has been completely decomposed (d).

(a) (b) (c) (d)

Fig. 2 The image of the IC sample 2 after decomposition reaction at 430°C for 2h (a) IC sample 2 before decomposition reaction (b) in the 1ml high-temperature water (c) Na_2CO_3(3wt%) aqueous solution (d) Na_2CO_3(10wt%) aqueous solution

4. Conclusions

Effective decomposition reactions of various IC waste devices were carried out in high-temperature water or in Na_2CO_3 aqueous solution. Although due to different materials for the decomposition reaction, the results did not achieve a unified. However, the results suggested that water is excellent solvent for the decomposition reaction of IC waste devices to separate organic and inorganic parts, and reaction time and additive are important factor for effective decomposition reaction. These conditions can be applied to chemical recycling process for manufacture's waste devices in high-temperature water.

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