

Pyrolysis characteristics of integrated circuit boards at various particle sizes and temperatures

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Abstract

A pyrolysis method was employed to recycle the metals and brominated compounds blended into printed circuit boards. This research investigated the effect of particle size and process temperature on the element composition of IC boards and pyrolytic residues, liquid products, and water-soluble ionic species in the exhaust, with the overall goal being to identify the pyrolysis conditions that will have the least impact on the environment. Integrated circuit (IC) boards were crushed into 5–40 mesh (0.71–4.4 mm), and the crushed particles were pyrolyzed at temperatures ranging from 200 to 500 °C. The thermal decomposition kinetics were measured by a thermogravimetric (TG) analyzer. The composition of pyrolytic residues was analyzed by Energy Dispersive X-ray Spectrometer (EDS), Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). In addition, the element compositions of liquid products were analyzed by ICP-AES and ICP-MS. Pyrolytic exhaust was collected by a water-absorption system in an ice-bath cooler, and IC analysis showed that the absorbed solution comprised 11 ionic species. Based on the pyrolytic kinetic parameters of TG analysis and pyrolytic residues at various temperatures for 30 min, the effect of particle size was insignificant in this study, and temperature was the key factor for the IC board pyrolysis. Two stages of decomposition were found for IC board pyrolysis under nitrogen atmosphere. The activation energy was 38–47 kcal/mol for the first-stage reaction and 5.2–9.4 kcal/mol for the second-stage reaction. Metal content was low in the liquid by-product of the IC board pyrolysis process, which is an advantage in that the liquid product could be used as a fuel. Brominate and ammonium were the main water-soluble ionic species of the pyrolytic exhaust. A plan for their safe and effective disposal must be developed if the pyrolytic recycling process is to be applied to IC boards.

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1. Introduction

The Taiwan EPA established its *Scrap Home Appliances and Computers Recycling Regulation*, which is based on the Waste Disposal Act, to require manufacturers and importers to take back their electronic appliances [1]. Computer items to be recycled include notebooks, monitors, hard disks, power supplies, printed circuit boards and mainframe shells [2].

The integrated circuit (IC) board (i.e., a printed circuit board mounted with various integrated circuits and other electronic parts) is an important computer part. It is made of a copper-

clad laminate that consists mainly of 15% epoxy resin, 30% glass cloth filament, 22% copper coils, metals (Sn, Pb, Fe, Ni, etc.) and Br [3,4]. In general, liquefied epoxy resin is blended with brominated compounds (i.e., tetrabromo-bisphenol A or diglycidyl ether of bisphenol A solution) to enhance the fire-retardance and insulating properties of the IC board.

Fire-retardant IC boards are a major part of the waste from electrical and electronic equipment (WEEE); utilization, recycling, and final disposal of these products have become important issues. The average lifespan of a PC decreased from 4.5 to 2 years from 1992 to 2005 in the United States [5]. Based on many studies, conservative estimates show that more than 10⁵ t per year of electronic boards require disposal, with the amount increasing at the rate of 5–10% per year [6–9].

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Several potential methods, including physical and magnetic separation (crushed, ground, separated by magnetic and eddy current), smelting and scraping methods, are used to recycle IC boards [10]. These methods all have the same limitation: the brominated epoxy resin requires further treatment and disposal. In addition, electronic scrap has a high copper content (5–40%); blast furnace treatment produces black copper (70–85%) by a reduction reaction [11]. In addition, the lead in the solder and the bromine (the bromine content could be up to 15–20%) in the resin must be properly disposed of during the IC board metal recovery process [4].

The pyrolytic process is an opportunity to recycle IC boards instead of sending them to landfills, incineration and disposal by other methods. The volume of exhaust gas would be reduced as well when compared to incineration. Pyrolysis has been employed to recycle brominated printed circuit boards, and studies have addressed the compositions of IC boards [12–14], pyrolytic kinetics [9,12,13,15,16] and brominated compound formation and fate [9,14–17]. However, few studies have focused on IC board particle size effects, ideal pyrolytic temperatures, the metal contents in pyrolytic by-products, or the exhaust gas expelled during the recycling and pollution control procedures. Continued study of the pyrolytic characteristics of IC boards is necessary [16]. This study analyzed the element composition of IC boards and pyrolytic residues, liquid products and water-soluble ionic species in the exhaust. In addition, the pyrolytic kinetics of IC boards were analyzed by a thermogravimetric (TG) analyzer that could be used to design the pyrolytic equipment and operation parameters (i.e., temperature and time). The particle size effect on the metal content in liquid products of the process and the brominate content in pyrolytic exhaust has received little attention in the literature. These data could be used in recycling process design and energy recovery of IC board reuse by a pyrolytic process.

2. Experimental methods

2.1. Material

Integrated circuit boards were obtained from a recycling plant in southern Taiwan. IC boards were ground and sieved into various particle mesh sizes: #5 (4.0–4.8 mm), #10 (2.0–4.0 mm), #18 (1.0–2.0 mm) and #40 (0.42–1.0 mm) in the laboratory. The IC board samples were stored at 25 °C and 45% relative humidity until analyzed.

An electrical furnace quartz tube (ID of 30 mm and length of 70 cm) was purged with pure nitrogen (99.995%) for 10 min before the pyrolysis process to reduce the oxygen content in the tube. Five grams of IC board were placed in the center of the electrical furnace under nitrogen atmosphere. Pyrolysis was carried out for 30 min at temperatures ranging from 200 to 500 °C. Pyrolytic liquid and exhaust gas were collected, maintained at 120 °C and then allowed to flow into a series of four glass bottles in an ice-bath cooler (less than 4 °C). The first two bottles were used to collect the liquid product and the other two con-

tained water to collect water-soluble compounds in the exhaust gas.

2.2. Composition analysis

2.2.1. Elemental analyzer

Elemental composition, namely of carbon, nitrogen, hydrogen and oxygen, was analyzed with a rapid element analyzer (Heraeus CHNO, USA). A total of five samples were analyzed in duplicate for quality assurance and quality control. Acetanilide was used as the standard. Sulfur and chlorine were analyzed with a Tacussel Coulomax 78 (USA) using sulfanilic acid and 1-chloro-2,4-dinitrobenzene standards.

2.2.2. EDS analysis

The surface composition of the pyrolytic residue samples was analyzed with an SEM (JXA-840, JEOL, Japan) equipped with an Energy Dispersive X-ray Spectrometer (EDS; AN10000/85S, Links, England). The analyzed elements included C, N, O, Mg, Si, Cl, K, Cu and Br.

2.2.3. INAA analysis

The analysis of the Br content in the untreated IC board (raw material) was carried out at the Nuclear Technology Center at the National Tsing-Hua University, Taiwan. The Br content was determined by Instrumental Neutron Activation Analysis (INAA) following the method of Allian and Sansoni [18]. In order to correct errors caused by the variation in neutron flux and “rabbit” placement, a 20-mg Ni flux monitor was used during each short radiation experiment. Gamma rays coming from the samples were counted with high-purity Ge detectors that were connected to a Canberra Series 35 plus multi-channel analyzer and computer system.

2.2.4. ICP-AES and MS analysis

An IC board sample was mixed with a 20-ml acid mixture ($\text{HNO}_3:\text{HClO}_4:\text{HF} = 5:3:2$, v/v) in a Teflon-lined closed vessel and placed in a high-pressure digestion oven at 170 °C for 5 h. The digested acid mixture was analyzed to determine the trace elements. A Perkin-Elmer OPTIMA 3000 ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer) was used to determine the Al, Ca, Fe, K, Mg, Na, S and Zn concentrations. Additionally, a SCIEX Elan Model 5000 ICP-MS (Inductively Coupled Plasma Mass Spectrometer) manufactured by Perkin-Elmer was employed to determine As, Ba, Cd, Cr, Cu, Mn, Co, Ni, Pb, Sb and V fractions.

To validate the digestion method, NIST Standard Reference Material SRM 1648 was used to simulate the particles. About 0.1 mg of SRM 1648, which approximates the composition of road dust particulate, was used to examine the accuracy and reliability of the digestion method. Al, As, Ba, Co, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Sb, Se, V and Zn were recovered in the acceptable range (recovery: 84–107%); only Cr was recovered at a level below that range (67%). A major error in Cr determination was due to the Cr loss incurred through volatilization during sample digestion (e.g., CrO_2Cl_2 [b.p. 117 °C]) and

Table 1
Element composition (wt.%) of IC boards by elemental analyzer ($n=8^a$) and INAA ($n=4^a$)

	C	O	H	Br	N	S
This study	48.4 ± 2.73	29.6 ± 0.64	5.77 ± 0.33	5.68 ± 0.37 ^b	3.23 ± 0.22	0.09 ± 0.05
Chien et al. [14]	52.21	Balanced	6.11	8.53	2.56	Trace
Chen et al. [12,13]	54.38	19.64	5.11	19.21	1.67	NA ^c
Barontini et al. [9]	22–27	–	2.0–2.4	6.0–6.9	0.6–1.7	–

^a n : sample number of duplicated analysis.

^b Bromine is analyzed by INAA.

^c NA: not available.

interference problems due to argon gas, filter media and/or acid-derived background ions, which inhibit detection of the $^{52}\text{Cr}^+$ isotope [19].

2.2.5. IC analysis

Ion chromatography (IC; Dionex, 120) was used to analyze the concentration of anions (Br^- , F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}). The separation of anions was accomplished using an IonPac AS 12A (4 mm × 200 mm) analytical column, AG 14 guard column, with a 10-ml sample loop and an anion self-regenerating suppressor-ultra. A solution of 2.7 mM $\text{Na}_2\text{CO}_3/0.3$ mM NaHCO_3 was used as an effluent at a flow rate of 1.5 ml/min. The separation of cations was accomplished using an IonPac CS 12A (4 mm × 250 mm) analytical column, and a CG 14 guard column, with a 50-ml sample loop, and a cation self-regenerating suppressor-ultra. The method detection limit (MDL) of ionic species was from 0.005 $\mu\text{g}/\text{m}^3$ (Mg^{2+}) to 0.10 $\mu\text{g}/\text{m}^3$ (NO_2^-), and the spike recovery was 81% (Na^+) to 115% (NH_4^+). The MDL and recovery of bromine were 0.04 $\mu\text{g}/\text{m}^3$ and 97%, respectively.

2.3. Pyrolysis kinetics

The IC board pyrolysis was carried out in a thermogravimetric (TG) system (thermobalance) and controlled by a computer system that recorded the temperature measured by a thermocouple system and weight (Cahn VersaTherm TGA). Heating rates of 2 and 15 K/min with sample sizes of about 5.0 mg were applied. Pure nitrogen (99.995%) was regarded as the purge gas. The sample weight variation by temperature data were used to measure the pyrolysis kinetic parameters.

The following equations of kinetics expression in Arrhenius form were derived for the IC board conversion rate [20,21]:

$$\frac{dx}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (1-x)^n \quad (1)$$

The natural logarithm of Eq. (1) is taken to obtain

$$\ln\left(\frac{dx}{dt}\right) = \ln[A(1-x)^n] - \frac{E_a}{RT} \quad (2a)$$

Hence, the plot of $\ln(dx/dt)$ versus $1/T$ can be correlated by the least-square method to measure a straight line. $-E_a/R$ is the slope and $\ln[A(1-x)^n]$ is the intercept. Furthermore, Eq. (2a)

can be expressed as follows:

$$\ln\left(\frac{dx}{dt}\right) + \frac{E_a}{RT} = \ln(A) + n \ln(1-x) \quad (2b)$$

The linear plot of $\ln(dx/dt) + E_a/RT$ versus $\ln(1-x)$ and the least-square method are used to measure the $\ln(A)$ (intercept of straight line) and n (slope of straight line), where x = transformation rate ($x = w_0 - w/w_0 - w_f$), w_0 = weight of IC board at $t=0$, w = residual weight of IC board after pyrolysis at t , w_f = weight of IC board residual at $t = \infty$, t = pyrolysis time, A = frequency factor, E_a = activation energy, R = gas constant, T = absolute temperature and n = apparent reaction order.

3. Results and discussion

3.1. Raw material composition

The representative composition of the analyzed print circuit board is shown in Table 1. Carbon and oxygen are the main elements; both bromine and hydrogen are about 6%. The carbon content is similar to data reported in Chen et al. [12,13] and Chien et al. [14], but the bromine content is lower than that in other studies [12,14]. This may be caused by the different types of IC boards and analytical methods.

In addition, the moisture, ash and combustible content (Table 2) of the IC board were 3.9–4.2, 4.7–10 and 85–91%, respectively, for the various particle sizes. The increase in moisture and ash content correlated with the decrease in particle size. The increase in the particle size corresponded to the decrease of the IC board combustible content. This could have been caused by the physical composition and shredding process; small filament particles are easier to form with glass fiber.

The unprocessed IC board was also analyzed by X-ray EDS (Table 3); carbon and oxygen were the main components. Analysis of carbon by EDS yielded a lower content than by elemental

Table 2
Moisture, ash and combustible content (wt.%) of IC Boards ($n=3^a$)

Particle size (mesh)	Moisture	Ash	Combustible
5	3.93 ± 0.17	4.66 ± 0.22	91.42 ± 0.39
10	4.08 ± 0.10	6.22 ± 0.31	89.70 ± 0.40
18	4.16 ± 0.58	9.74 ± 0.36	86.10 ± 0.23
40	4.21 ± 0.19	10.38 ± 0.46	85.41 ± 0.42

^a n : sample number of duplicated analysis.

Table 3
Elemental compositions (%) of IC board as analyzed by EDS ($n = 5^a$)

Temperatures (°C)	Elements	5 mesh	10 mesh	18 mesh	40 mesh
Raw material	C	27.45 ± 0.33	29.45 ± 0.48	28.93 ± 0.37	29.11 ± 0.73
	N	3.54 ± 0.10	3.41 ± 0.08	3.77 ± 0.16	3.71 ± 0.13
	O	25.78 ± 0.11	27.66 ± 0.16	26.20 ± 0.55	28.42 ± 0.17
	Mg	1.94 ± 0.01	1.10 ± 0.06	1.28 ± 0.04	1.06 ± 0.08
	Si	5.17 ± 0.11	4.36 ± 0.14	5.13 ± 0.21	3.23 ± 0.24
	Cu	2.69 ± 0.06	1.24 ± 0.24	1.81 ± 0.06	1.70 ± 0.03
	Br	2.72 ± 0.47	3.66 ± 0.25	2.37 ± 0.28	2.85 ± 0.25
200	C	27.47 ± 0.06	27.53 ± 0.11	29.21 ± 0.06	29.84 ± 0.66
	N	3.49 ± 0.08	3.17 ± 0.02	3.50 ± 0.04	3.87 ± 0.18
	O	27.70 ± 0.01	28.65 ± 1.83	25.26 ± 1.06	26.82 ± 1.02
	Mg	1.34 ± 0.01	1.39 ± 0.18	1.30 ± 0.27	1.18 ± 0.15
	Si	5.14 ± 0.59	4.98 ± 0.01	3.32 ± 1.02	3.71 ± 0.76
	Cu	4.86 ± 6.33	3.78 ± 1.41	3.49 ± 0.50	2.96 ± 0.16
	Br	2.15 ± 0.75	2.01 ± 0.52	3.64 ± 1.00	2.75 ± 1.60
300	C	26.94 ± 0.25	27.76 ± 0.04	28.26 ± 0.99	30.54 ± 0.53
	N	3.43 ± 0.07	3.73 ± 0.09	3.12 ± 0.33	3.78 ± 0.18
	O	23.72 ± 1.32	22.88 ± 0.19	22.79 ± 1.92	23.80 ± 1.03
	Mg	1.37 ± 0.27	1.39 ± 0.06	1.29 ± 0.01	1.60 ± 0.11
	Si	4.03 ± 0.67	6.49 ± 0.06	5.27 ± 0.47	4.92 ± 2.29
	Cu	5.07 ± 2.52	4.30 ± 0.38	4.58 ± 2.27	4.20 ± 0.21
	Br	3.61 ± 0.64	4.05 ± 0.49	3.56 ± 0.56	3.96 ± 1.39
400	C	36.71 ± 0.99	33.26 ± 0.16	36.22 ± 0.18	36.60 ± 0.19
	N	2.76 ± 0.03	2.56 ± 0.07	2.92 ± 0.03	3.05 ± 0.10
	O	19.09 ± 0.98	19.61 ± 0.30	19.74 ± 0.40	20.67 ± 0.02
	Mg	1.14 ± 0.15	0.93 ± 0.10	1.16 ± 0.05	1.04 ± 0.02
	Si	5.31 ± 0.59	4.27 ± 0.34	4.24 ± 0.01	4.31 ± 0.01
	Cu	4.14 ± 0.33	4.56 ± 0.21	4.83 ± 0.16	4.55 ± 0.39
	Br	2.93 ± 1.27	4.23 ± 0.90	3.82 ± 0.37	3.93 ± 0.30
500	C	36.54 ± 0.65	33.50 ± 2.71	34.85 ± 0.52	36.96 ± 1.27
	N	1.96 ± 0.03	1.63 ± 0.35	1.24 ± 0.13	1.35 ± 0.03
	O	19.39 ± 2.81	17.23 ± 0.14	18.35 ± 0.04	18.44 ± 0.09
	Mg	1.59 ± 0.55	2.22 ± 0.16	1.79 ± 0.02	1.68 ± 0.09
	Si	4.40 ± 2.77	4.62 ± 0.38	4.46 ± 0.04	4.16 ± 0.04
	Cu	5.02 ± 3.37	4.25 ± 1.97	4.29 ± 0.06	4.43 ± 0.04
	Br	3.66 ± 0.02	3.73 ± 0.45	3.47 ± 0.65	3.51 ± 0.30

K and Cl are only trace values.

^a n : sample number of duplicated analysis.

analyzer. The difference may be due to the fact that the EDS analyzes the material surface by X-ray scattering, and the elemental analyzer analyzes the entire carbon content of the material by thermal volatilization. In addition, bromine content analyzed by EDS was lower than that analyzed by INAA; the different principles underlying the two methods may cause the variation.

The elemental composition of the IC board was analyzed by ICP-AES and ICP-MS (Table 4). Results indicated that copper and magnesium were the main metals with concentrations of 8–46 and 0.23–1.1 mg/g, respectively. Analysis of the other elements showed only trace amounts.

3.1.1. Pyrolysis kinetics

Figs. 1 and 2 (heating rates: 2 and 15 °C/min and DTG) show the pyrolytic kinetics curves. Two degradation stages were found during the IC board pyrolysis process. One was a narrow range at 560–580 K with a weight loss of about 60%. The other peak was wider, and the temperature ranged from 630 to 780 K. There was a 90% weight loss after 800 K. The main thermal degradation

temperature in this study was a little high when compared to the work of Chen et al. [12], which could be caused by the different compositions (low bromine content in Table 1). In general, brominated epoxy resins are thermally less stable than non-brominated ones [15]. This may cause the thermal degradation temperature shift to a lower temperature. For a similar IC board with bromine content of 6–7% (Table 1), the thermal degradation temperature was in the same range (550–620 K) as in this study [9]. However, higher pyrolytic residues were formed at 800 °C, which could be caused by the low carbon content (20–27%) [9].

According to the literature concerning the thermal decomposition of brominated epoxy resins, the initial reaction is related to the presence of an amine group (good attacking nucleophiles) and bromine atoms (good leaving group) [16,22,23]. The first-stage reaction forms C–N bonds and blocks aromatic amines from escaping to the gas phase. Therefore, the aromatic amines and tar are volatilized during second-stage pyrolysis.

Table 5 shows the IC board pyrolysis kinetic parameters, including reaction order, activation energy and frequency

Table 4
Elemental Compositions (mg/g) of IC Boards as Analyzed by ICP-AES and ICP-MS

Temperatures (°C)	Elements	5 mesh	10 mesh	18 mesh	40 mesh
Raw material	Mg	0.297	0.237	0.686	1.085
	Na	0.090	0.043	0.004	0.012
	S	ND	0.004	ND	ND
	Ba	ND	0.001	0.003	0.005
	Cu	7.92	11.33	41.4	45.8
	Mn	0.001	0.003	0.004	0.002
	Ni	0.001	0.009	0.032	0.01
	Pb	0.001	0.001	0.007	0.002
	Sb	ND	0.012	0.019	0.017
	Zn	0.004	ND	ND	0.046
200	Mg	0.215	0.218	0.408	0.524
	Na	0.097	0.087	0.045	0.091
	S	0.085	0.085	ND	ND
	Ba	0.001	0.001	0.001	0.005
	Cu	12.0	14.1	38.1	40.9
	Mn	0.001	0.003	0.001	0.001
	Ni	0.002	0.006	0.003	ND
	Pb	0.001	0.009	0.002	ND
	Sb	0.001	0.057	0.001	0.020
	Zn	0.004	0.010	ND	0.016
300	Mg	1.342	1.666	1.592	1.370
	Na	0.125	0.099	0.129	0.039
	S	0.025	ND	ND	ND
	Ba	0.004	ND	0.010	0.002
	Cu	15.7	20.5	57.6	66.5
	Mn	0.004	0.003	0.004	0.012
	Ni	0.001	0.008	0.017	0.098
	Pb	ND	ND	0.002	0.001
	Sb	0.093	0.020	0.014	0.011
	Zn	0.008	0.204	0.011	0.013
400	Mg	1.414	1.362	1.259	1.951
	Na	0.143	0.185	0.169	0.202
	As	ND	0.001	ND	0.006
	Ba	0.004	0.009	0.010	0.004
	Cu	20.0	24.2	74.0	86.4
	Mn	0.006	0.031	0.018	0.004
	Ni	0.001	0.229	0.212	0.009
	Pb	0.002	0.082	0.022	0.008
	Sb	0.052	0.081	0.026	0.022
	Se	ND	0.005	ND	ND
500	Zn	0.001	0.165	0.034	0.066
	Mg	2.027	2.861	2.381	2.701
	Na	0.187	0.104	0.138	0.170
	Ba	0.008	0.011	0.006	0.012
	Cu	30.4	35.9	98.3	113
	Mn	0.003	0.003	0.010	0.009
	Ni	0.012	0.011	0.071	0.044
	Pb	0.002	0.003	0.040	0.015
	Sb	0.011	0.026	0.035	0.057
	Zn	0.022	0.026	0.094	0.161

Al, Ca, K, Fe, As, Cd, Co, Cr, S, Se, Sr and V are trace values or lower than detection limit.

factor. The first-stage reaction is the main reaction. The activation energy was 46–47 kcal/mol (192–197 kJ/mol) and 38–40 kcal/mol (160–169 kJ/mol) for heating rates of 2 and 15 °C/min, respectively. Results indicated an insignificant difference in activation energy for different particle sizes. In addition, the reaction order and frequency factor were the same for dif-

ferent particle sizes. The second-stage reaction may come from the reaction (volatilization) of the first-stage pyrolytic residues or products. The activation energy was 5.2–9.4 kcal/mol, and the reaction energy and frequency factor during the second-stage reaction were lower than during the first-stage reaction. In general, the IC board was pyrolyzed under nitrogen atmosphere with a one-stage reaction [12,13]. The low activation energy during the second stage may be due to the volatile and cracking process of residues (volatilization and cracking of the melt-liquidized products at the first stage). Based on the heat of vaporization, low-molecular-weight organic compounds (i.e., *n*-octane, acetone, benzene, methyl-ethyl-ketone, etc.) could fit the energy of the second stage [24]. According to the literature, there was HBr, CO and CO₂ formation in the vicinity of 700 K during the pyrolysis of tetrabromobisphenol A (one of the raw materials of the IC board), which may be regarded as reference data for this study [25]. However, more data is necessary to prove the activation energy of the second stage in future work, i.e., investigation of the gas composition during the pyrolytic process.

According to the TG and Derivative TG (DTG) curves, smaller particle sizes generated little reaction delay, which was insignificant for the overall reaction. DTG curves show that the

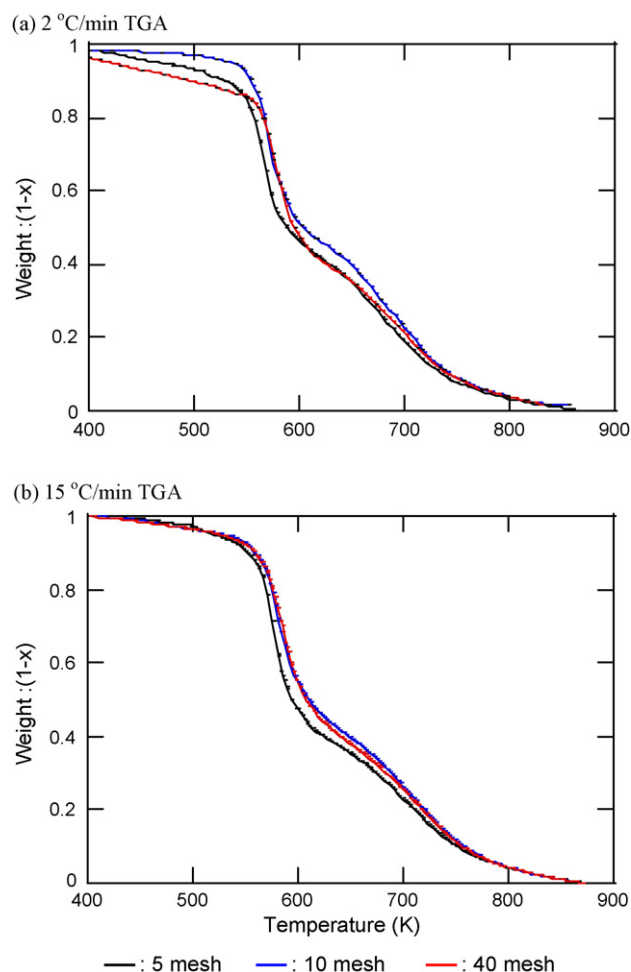


Fig. 1. Typical thermogravimetry curves at heating rates of 2 and 15 °C/min.

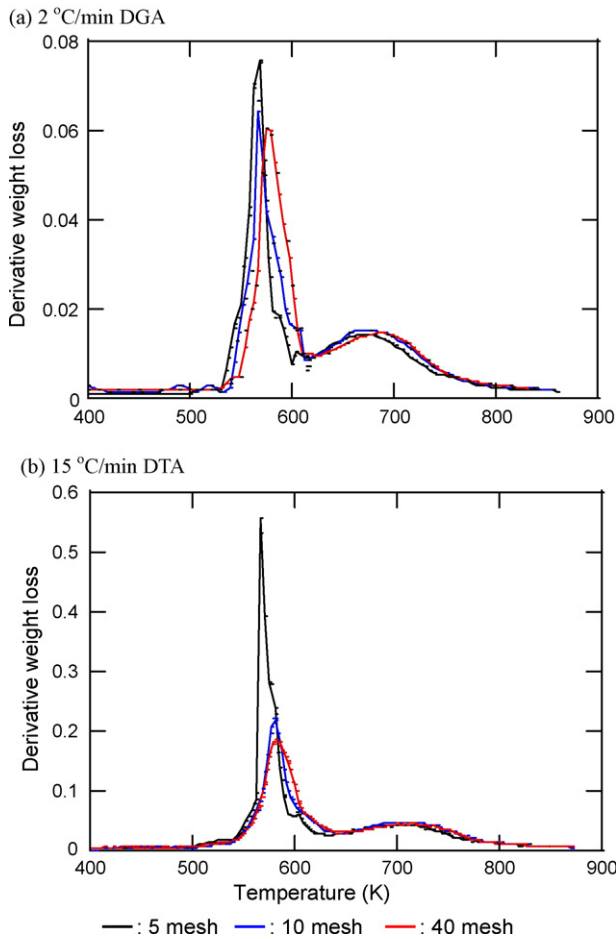


Fig. 2. Typical derivative thermogravimetry curves at heating rates of 2 and 15 °C/min.

initial thermal reaction could have occurred earlier for large particles.

3.2. Pyrolytic residues

Five grams of IC board samples were put into the center of a quartz glass tube in a horizontal electrical furnace. The samples were pyrolyzed for 30 min at various degradation temperatures between 200 and 500 °C. Fig. 3 shows the percent of pyrolytic residue at different particle sizes by thermal degradation. Results indicated that the pyrolytic residues decreased from 96 to 39%,

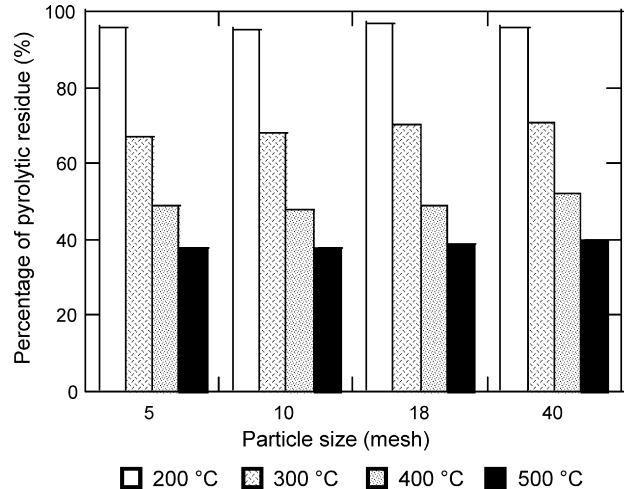


Fig. 3. Percentage of pyrolytic residues of different particle sizes and pyrolytic temperatures.

corresponding to degradation temperatures from 200 to 500 °C. The effect of particle size (5–40 mesh) on the percentage of pyrolytic residues under the same 30-min thermal degradation temperature tests was insignificant. In this study, the pyrolytic temperature was the more important factor, and the percentage of residue depended on the pyrolytic temperature.

Table 3 shows the elemental composition of the pyrolyzed IC board at varying particle sizes as analyzed by EDS. Potassium and chlorine were found in trace amounts in the IC board and pyrolytic residues. Results indicate that the carbon and oxygen content were 27–37% and 18–29%, respectively. The oxygen content was not significantly different with different particle sizes at the same pyrolytic temperature, but it decreased with the increase of pyrolytic temperature. Carbon content increased with the increase of temperature (<400 °C); the carbon soot formation on the surface of pyrolytic residues may be one of the reasons (EDS analyzes the surface of samples). Copper and magnesium were the dominant metals in the pyrolytic residues. Bromine concentration was 2–4%; it came from the flame-retardant additives. Silicon was 3–5%, and it came from the epoxy resin glass fiber. The EDS analysis results could be used as reference data, because they represented the element’s content on the sample surface and reflected a relative concentration of elements.

Table 5
Pyrolysis kinetic parameters of IC boards

Kinetic parameters	Heating rate											
	2 °C/min						15 °C/min					
	First stage			Second stage			First stage			Second stage		
	<i>n</i>	<i>E_a</i> (kcal/mol)	<i>A</i> (min ⁻¹)	<i>n</i>	<i>E_a</i> (kcal/mol)	<i>A</i> (min ⁻¹)	<i>n</i>	<i>E_a</i> (kcal/mol)	<i>A</i> (min ⁻¹)	<i>n</i>	<i>E_a</i> (kcal/mol)	<i>A</i> (min ⁻¹)
Particle size												
5	1.32	47.13	1.73 × 10 ¹⁷	1.01	8.5	11.78	1.23	38.75	2.56 × 10 ¹⁴	1.03	7.26	33.43
10	1.47	46.14	4.28 × 10 ¹⁶	0.62	8.2	6.26	1.58	40.44	9.05 × 10 ¹⁴	1.07	9.42	156.6
40	1.24	45.87	2.11 × 10 ¹⁶	1.23	5.15	1.35	1.54	38.16	1.05 × 10 ¹⁴	0.98	6.3	16.87

Table 6
Elemental compositions (mg/g) of pyrolytic liquid from IC Boards as analyzed by ICP-AES and ICP-MS

Temperatures (°C)	Compositions	5 mesh	10 mesh	18 mesh	40 mesh
300	Ca	0.8403	0.2038	0.9738	0.4735
	Fe	ND	0.1792	1.1396	0.4756
	K	0.0186	0.0031	0.0119	0.1356
	Mg	0.0137	0.0002	ND	0.0018
	Na	0.1085	0.0971	0.1477	0.1290
	S	0.0379	ND	ND	ND
	As	0.0014	0.0013	0.0056	ND
	Ba	0.0023	0.0007	0.0017	0.0015
	Co	ND	0.0005	0.0092	0.0009
	Cr	ND	0.0469	0.2568	0.2052
	Cu	0.0010	0.0001	0.0017	0.0007
	Mn	ND	0.0032	0.0117	0.0064
	Ni	ND	0.0300	0.0748	0.0492
	Pb	0.0003	0.0032	0.0057	ND
	Sb	0.0030	0.0006	ND	0.0002
	Se	0.0050	0.0035	0.0150	ND
	400	Sr	0.0091	0.0018	0.0054
V		0.0816	0.0029	0.0321	ND
Zn		0.0148	0.0014	0.0567	0.0097
Ca		0.0923	0.7050	0.0920	0.1096
Fe		0.0372	0.0063	0.0033	0.0063
K		0.0014	0.0264	0.0118	0.0000
Mg		0.0055	0.0056	ND	0.0049
Na		0.0592	0.0866	0.0360	0.0530
S		0.2112	0.1463	0.2832	0.2348
As		0.0002	0.0022	0.0008	0.0016
Ba		0.0065	0.0039	0.0031	0.0016
Cr		0.0032	0.0002	ND	ND
Cu		0.0053	0.0040	0.0102	0.0034
Pb		ND	0.0032	0.0005	ND
Sb		0.0167	0.0224	0.0128	0.0113
Se		0.0008	0.0078	0.0026	0.0048
500		Sr	0.0007	0.0014	0.0007
	V	0.0006	0.0079	0.0020	0.0051
	Zn	ND	0.1505	0.0011	0.0001
	Ca	0.1037	0.1629	0.1623	0.1409
	Fe	0.0054	ND	ND	0.0232
	K	ND	ND	0.0114	0.0487
	Mg	0.0004	0.0033	ND	0.0021
	Na	0.0406	0.0425	0.0855	0.0501
	S	0.2579	0.1743	0.1539	0.3612
	As	0.0026	0.0021	0.0020	0.0015
	Ba	0.0044	0.0034	0.0038	0.0058
	Co	0.0004	0.0005	ND	ND
	Cr	0.0013	ND	ND	0.0097
	Cu	0.0592	0.0250	0.0310	0.0220
	Mn	ND	ND	ND	0.0001
	Ni	ND	0.0078	ND	0.0037
	Pb	0.0050	ND	0.0008	0.0001
Sb	0.0227	0.0255	0.0266	0.0110	
Se	0.0091	0.0077	0.0067	0.0043	
Sr	0.0012	0.0009	0.0011	0.0010	
V	0.0091	0.0089	0.0092	0.0066	
Zn	0.0017	ND	0.0009	0.0002	

Al and Cd are lower than detection limit.

Table 4 shows the element compositions of the pyrolyzed and ground IC board as analyzed by ICP-AES and ICP-MS. Al, Ca, Fe, K, As, Cd, Co, Cr, Se Sr and V were not detected by ICP-AES and ICP-MS. The concentrations of Fe, Co, Cr and Se were ND-1.097, ND-0.002, ND-0.23 and ND-0.009 mg/g,

respectively. Results indicated that copper and magnesium were the main metals in the raw materials and pyrolytic residues. The result is similar to the EDS findings. The smaller particle size of the IC board corresponded to a higher copper content caused by the copper foil; A 10, 8 and 3% (w/w) recovery was shown for 5,

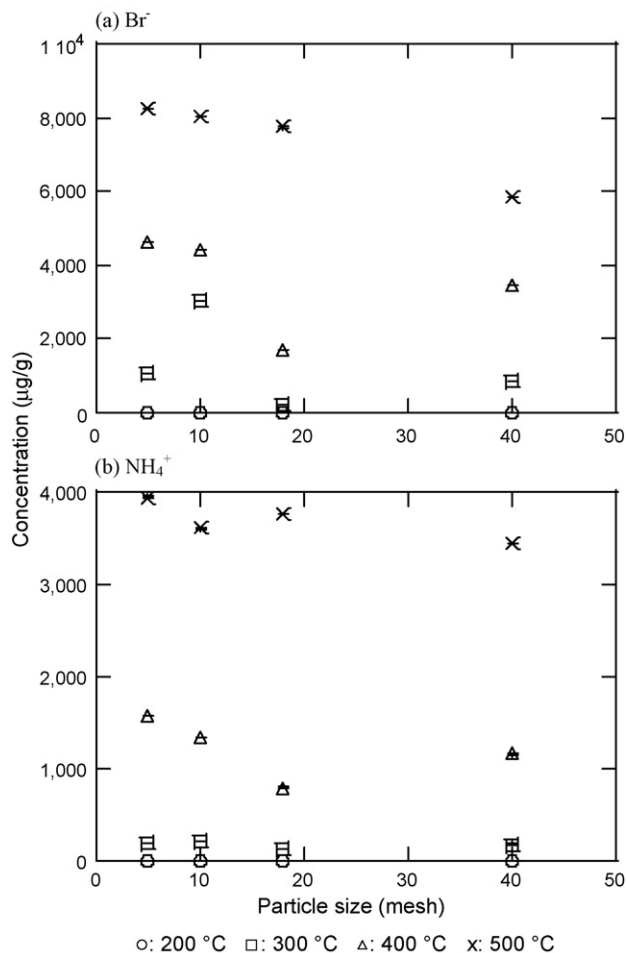


Fig. 4. Water-soluble ionic species concentrations in pyrolytic exhaust.

10 and 18 mesh, respectively, before the pyrolytic process (data not shown). The pyrolytic process could permit copper content up to 11% for 40 mesh at 500 °C.

3.3. Element compositions of liquid products

Twenty-one elements in the liquid products were analyzed by ICP-AES and ICP-MS. The amount of all analyzed elements ranged from 0.43 to 2.1 mg/g (Table 6), which indicated low heavy metal content in the liquid products. The yield of liquid product was about 30 and 40% at 400 and 500 °C, respectively. The heat value of the liquid product was 7500–9000 kcal/kg; this is about 10–20% lower than commercial diesel fuel. It has the potential to be reused as fuel, but further study of the Br content in the liquid product is necessary. In addition, WEEE used polypropylene as a reductive agent for de-halogenation to generate clean fuel oil [26].

3.4. Water-soluble ionic species of exhaust gas

Eleven water-soluble ionic species were analyzed by ionic chromatography. Brominate and ammonium were the main species (Table 6 and Fig. 4); there were trace amounts of other species (i.e., concentrations less than a tenth of the main species).

F⁻ and NO₂⁻ were not detectable. The concentration of Cl⁻ was ND-85 µg/g, NO₃⁻ was ND-0.55 µg/g, SO₄²⁻ was ND-116 µg/g, Na⁺ was 1.2–88 µg/g, K⁺ was 0.71–43 µg/g, Mg²⁺ was ND-0.52 µg/g and Ca²⁺ was ND-0.67 µg/g for different particle sizes and pyrolytic temperatures. At 200 °C, a small amount of the IC board was decomposed; therefore, a little water-soluble ionic species was found in the pyrolytic exhaust. Above 300 °C, a large fraction of the IC board was decomposed by heating, and the highest brominate and ammonium emissions were found at 500 °C.

Below 500 °C, the pyrolytic yield of water-soluble ionic species was lower at 18 mesh. That may be caused by the pile structure of the IC board and thermal conductivity efficiency (gas penetration and heat transfer) [27]. In addition, the presence of an amine-containing curing agent (i.e., dicyandiamide) in the resin [15,16] was the source of ammonium in the exhaust during the IC board thermal decomposition.

4. Conclusions

Carbon, oxygen and hydrogen were the major IC board elements, and the bromine content was over 5%. Two-stage reactions were carried out for the IC board pyrolysis; the activation energy of the first-stage reaction (38–47 kcal/mol) was 4.3–8.9 times that of the second-stage reaction (5.2–9.4 kcal/mol). Pyrolytic temperatures are a more important factor than particle size during the pyrolytic process. Copper and magnesium are the main metals in the raw material and pyrolytic residues. The metal content in the pyrolytic liquid product was less than 2 mg/g, and the heating value was 7500–9000 kcal/kg. Therefore, the liquid product (yield 30–40%, w/w) is a potential fuel after the proper treatment. Based on the metal content, heat value and yield of the liquid product, the pyrolytic technology can be a potential method to recycle IC board. However, the emission factors of brominate and ammonium were 5850–8230 and 3450–3940 µg/g, respectively, at 500 °C for 30 min. Compounds with high bromine content were emitted in the exhaust during the pyrolytic process; therefore, the proper disposal of exhaust is necessary for IC board recycling.

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