Degradation of brominated epoxy resin and metal recovery from waste printed circuit boards through batch sub/supercritical water treatments

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HIGHLIGHTS

- This work provides an efficient and green approach for waste printed circuit boards recycling.
- Debromination of brominated epoxy resins and recycling of metals was simultaneously achieved.
- Brominated epoxy resins can be completely decomposed by sub/SCW treatments.
- Glass fibers and copper foils in WPCBs were liberated and could be easily separated by crushing after sub/SCW treatment.

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ABSTRACT

Waste printed circuit boards (WPCBs) contain high amount of brominated flame retardants and heavy metals which may bring a series of environmental and health problems. In the present study, an effective and benign process using sub- and supercritical water (sub/SCW) to simultaneously degrade brominated epoxy resin and recover metals from WPCBs was developed. Experiments were performed in a batch-type reactor with temperatures ranging from 200 to 400 °C, water adding amounts from 10 to 40 ml and holding times from 30 to 240 min. The results showed that brominated epoxy resins (BERs) could be quickly and efficiently decomposed under sub/SCW condition. The debromination rate was 97.8% by controlling the temperature, water adding amount and holding time at 400 °C, 40 ml and 120 min, respectively. Most of the bromine was changed into HBr and around 97.7% was enriched in water. Meanwhile, bromine-free oil was obtained of which the main compositions were phenol (58.5%) and 4-(1-methylethyl)-phenol (21.7%). After the sub/SCW treatments, the glass fibers and copper foils in the residue can be easily liberated and recovered respectively. The copper recovery rate reached 98.11% in the purities of 96.74% (grain size >2.0 mm) and 92.74% (0.147–2.0 mm). This study provides an efficient and green approach for WPCBs recycling.

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1. Introduction

Printed circuit boards (PCBs) is an essential part of electrical and electronic equipments (EEEs). Recently, with the rapid development of electronic manufacturing technologies, the upgrade and replacement of EEEs have been increased rapidly which results in a large quantity of waste printed circuit boards (WPCBs) [1,2]. The most commonly WPCBs material is FR-4, which uses glass fibers as the reinforcing materials and brominated epoxy resins (BERs) as a binder [3]. BERs contain a large number of brominated flame retardants (5–15%, BFRs) for reducing the possibility of fire under the thermal stress [4]. Serious pollution can be generated if PCBs are not properly disposed of since the flame retardants therein may cause the formation of halogenated dioxin-like com-

pounds, such as polybrominated dibenzo-*p*-dioxins (PBDDs) or polybrominated dibenzofurans (PBDFs) [5,6]. Meanwhile, WPCBs is attracting more and more attention due to the valuable materials it contains [7,8]. Therefore, the recycling of WPCBs has a great practical significance for sustainable development of the human living environment and resources recycling.

In recent years, supercritical water (SCW, $T \geq 374$ °C, $P \geq 22.1$ MPa) is introduced as an environment-friendly method to recycle organic polymers due to its extraordinary properties, such as low viscosities, high mass transport coefficient, high diffusivity and high solubility for organics [9–11]. In our previous works [12], supercritical fluids were employed for debromination and recovery of oil from waste plastic containing brominated flame retardant in computer housing, where the retardant was in additive type [13]. This type of brominated flame retardant could be quickly extracted by supercritical organic fluids. However, it was found that the foregoing process was less effective for extraction

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Table 1
Composition of the WPCBs employed in this study.

	Metal							Organics	Glass fiber
	Cu	Pb	Sn	Al	Zn	Ag	Pd		
Wt (%)	19.60	0.30	0.17	2.34	0.01	0.0034	0.0016	31.25	46.32

of brominated flame retardant in WPCBs, since most of the TBBPA in WPCBs mainly used as a reactive type which is covalently bound to the polymer and is difficult to remove the TBBPA by organic solvent unless it was decomposed by thermal decomposition. Water in sub/SCW conditions can act not only as a solvent but also as a reactant, catalyst or product due to the different properties which are mainly dependent on temperature and pressure [14]. Accordingly, in the present work, sub/SCW was tested for extraction and decomposition of TBBPA in WPCBs.

The aims of this study were to: (1) evaluate the feasibility of WPCBs recycling by sub/SCW treatments; (2) examine the debromination efficiency of sub/SCW treatments on WPCBs; (3) identify metal recovery efficiency from WPCBs after sub/SCW treatments; (4) optimize the operation parameters for WPCBs treatments by sub/SCW.

2. Materials and methods

2.1. Materials

The WPCBs used in this work were provided by Huaxing Environmental Protection Corporation (China). The WPCBs were mainly disassembled from discarded desktop computers which were made from glass fiber reinforced BERs. The electronic components, such as capacitors, relays were removed first. Then the WPCBs were cut into small pieces (100 mm × 15 mm) and each piece was about 10 g. After that the WPCBs were dry at 105 °C for 24 h. The major composition of WPCB were listed in Table 1. Chemical reagents used in the experiments were all analytical reagents unless otherwise mentioned.

2.2. Apparatus and procedure

The process comprised of sub/SCW treatments and mechanical treatments. Fig. 1 shows the schematic diagram. The sub/SCW treatments were carried out by using a 100-ml high-pressure reactor made of 316 alloy whose designed temperature and pressure were 500 °C and 40 MPa, respectively. About 10 g of WPCBs was used in each experiment. Then different amounts of water were added into the reactor which were 10, 20 and 40 ml. The pressure inside the reactor was monitored by a pressure gauge attached to the reactor. The system pressure was mainly depended on the reaction temperature and the filling amount of water. During the heating process, the system pressure kept on increasing with the increase of temperature. When the system temperature reached the set temperature, the system pressure stopped increasing and stabilized at a certain value. The examined temperatures were 200, 250, 300, 350 and 400 °C, respectively. Once the reactor reached the set temperature, it was held at the temperature for 30, 60, 120 and 240 min, respectively. The reaction conditions of each experiment are described in Table 2. Nos. 5, 6, 7 and 8 in the experiments reached supercritical conditions while others were subcritical. After the treatment, open the insulation cover and the reactor was cooled quickly to room temperature by an electric fan.

Fig. 1. Schematic diagram of the materials recovery process.

Table 2
Conditions of sub/SCW experiments.

Experiment	Temperature (°C)	Time (min)	Water adding amount (ml)	Pressure (MPa)
1	200	120	40	2.0
2	250	120	40	5.0
3	300	120	40	10.0
4	350	120	40	18.0
5	400	120	40	30.0
6	400	30	40	30.0
7	400	60	40	30.0
8	400	240	40	30.0
9	400	120	10	4.0
10	400	120	20	20.0
11	250	120	10	1.5
12	250	120	20	4.0

Once the autoclave cooled to room temperature, the reactor was opened and the gaseous phase was passed through methylene dichloride and NaHCO₃ solution with the purpose of capturing organic products and inorganic bromine ion, respectively. Then the solid and liquid mixture was removed from the autoclave and filtrated through a pre-weighted filter paper for separation. Afterwards, the inwall of the reactor, pipes and residue on the filter paper were all washed by the solvent and then by deionized water. The final residue with the filter paper were dried to a constant weight to obtain the mass of solid residue, and then sent to comminute in a high-speed universal crusher. At last, standard sieves were used to separate the metals from the nonmetallic materials based on their difference in size and density.

2.3. Analysis

The oxygen combustion bomb-ion chromatography (IC, Dionex ICS2000, USA) was applied for the analysis of the bromine content in the solid residue. The bromine content of raw WPCBs was 5.08%. Debromination rate was calculated according to the bromine content before and after the treatment. And the bromine distribution

was also calculated according to the bromine content in water, oil and residues. The separated metal and nonmetal materials were digested by $\text{HNO}_3\text{--HClO}_4\text{--HF}$ and examined by inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 2000). The oil was analyzed by a gas chromatograph equipped with mass selective detector (GC/MS, Agilent 7890A/5975C, USA). All the experiments were repeated three times and only the mean values were reported. The measurement errors were around $\pm 1\%$. The morphological properties of the solid residue were examined by scanning electron microscope with energy disperse X-ray analysis (SEM-EDAX, Hitachi S-3000 N, Japan).

3. Results and discussion

3.1. Effects of various parameters on debromination efficiency

Fig. 2a shows the effect of temperature on debromination efficiency. It can be seen that the debromination efficiency increased quickly with the increase of temperature. When the temperature was $<200^\circ\text{C}$, energy provided by the system was not enough to break chemical bond of BERs resulted in the degradation was restricted to a minimum level and the main products consisted of water and CO_2 . Debromination rate increased rapidly with the increase of temperature below 350°C , e.g., increased from 40.7% at 250°C to 93.0% at 350°C . When the temperature was $>350^\circ\text{C}$, the growth of debromination rate slowed down and reached its maximum value of 97.8% at 400°C . The results showed that high temperature could provide enough energy to break chemical bond of BER which was decomposed effectively in SCW condition [15]. It has been reported that temperature was the most important factor on debromination efficiency for two reasons: (1) the dielectric constant decrease with the increase of temperature lead to the hydrogen bonding in water becomes weaker and less persistent: a low dielectric constant causes water to behave more like a organic solvent.

Once the BERs was decomposed into oil and it will be quickly dissolved in SCW to enhance the debromination efficiency [16]; (2) Free radicals reaction was the main polymer decomposition mechanism in supercritical fluids. When the temperature was high enough, the reaction system can provide enough energy to broke the bond of the polymer that cause the formation of free radicals [15].

Water adding amount also plays an important role in the debromination efficiency. The injection volume of water into the reactor is directly related to the reaction pressure. The system pressure increased with the increase of water volume. When the pressure reached the critical point, the nature of the supercritical water changed significantly: the density and viscosity of the supercritical water decreased rapidly while the diffusivity and mass transport co-efficient increased. As a result, BERs can be quickly decomposed into low molecular weight organic compounds and dissolved in the SCW [17]. The change of debromination rate with water adding amount was investigated at 250°C and 400°C for 120 min and was shown in Fig. 2b. It indicated that debromination rate kept on increasing with the increase of water adding amount. At 250°C , the debromination rate increased from 6.45% at 10 ml to 40.70% at 40 ml. Moreover, the debromination rate under higher temperature (400°C) was growing much faster than at lower temperature, increased from 31.25% at 10 ml to 97.82% at 40 ml. Less water was consumed at high reaction temperature compared to low temperature to obtain the same debromination rate. In addition, under high temperature conditions, the pressure increased quickly with the increase of water adding amounts. The pressure was 30 MPa when the temperature and water adding amount were 400°C and 40 ml. If more water was added into the reactor, the pressure may easily exceed the highest safety pressure (40 MPa) and brought security risks. Therefore, water adding amount was limited at 40 ml in this study.

Fig. 2c shows the effects of holding time on debromination efficiencies. The results indicated that debromination rate increased

Fig. 2. Effects of various parameters on debromination efficiency. (a) temperature (water adding amount = 40 ml, holding time = 120 min), (b) water adding amount (holding time = 120 min) and (c) holding time (temperature = 400°C , water adding amount = 40 ml).

with the increase of residence time. Debromination rate increased rapidly in the first 30 min (97.49%) confirming that BERs could be quickly decomposed under SCW condition. When the holding time was more than 30 min, debromination rate increased slowly and reached a maximum at 240 min (98.5%). Additional, considering the debromination rate and energy consume, it is recommended that 30 min – 120 min is the optimum holding time range with temperature and water adding amount fixed at 400 °C and 40 ml.

3.2. Analysis of BERs decomposition products

It has been reported that traditional thermal degradation process of BERs can be divided in three steps: Step one (<297 °C) caused the generation and release of H₂O and CO₂. In step two (297 °C and 400 °C), the BFRs decomposed, releasing HBr and brominated aromatics. In step three, (>400 °C), the resin decomposed and char was formed [18]. Sub/SCW is an excellent reaction medium for depolymerization or decomposition of polymers. The BERs are relatively easily depolymerized into monomers without catalysts in water which act as reactant as well as solvent [19]. In subcritical region, ion product in water is higher than in ambient conditions, meaning that it acts as an acid/base catalyst precursor. In supercritical region, water assumes particular properties making it highly reactive and miscible with organic molecules and gases due to its low dielectric constant [20]. Therefore, compared with the traditional thermal degradation process, the initial degradation temperature of BERs can be obviously reduced under the sub/SCW reaction conditions. The main decomposition products of BERs were oil which was initially colorless and gradually turned from yellow to brown with the increase of temperature. The oils were further analyzed by GC/MS so as to understand their organic compositions. Table 3 presents the list of the compounds of the oils obtained from 250 °C to 400 °C. The results showed that the compositions of oil products changed obviously with reaction temperature. At 250 °C, the major compounds of the oil were phenol and 4-(1-methylethyl)-phenol whose relative peak areas were 83.3% and 7.6% respectively. However, the liquid products still contained some bromides and mainly in the form of 2-bromo-phenol and its relative peak area was 5.2%. This indicated that BER in WPCBs began to be incompletely decomposed at 250 °C which was lower than traditional thermal degradation (297 °C). When temperature increased to 300 °C, the relative peak area of phenol decreased to 71.0% while the 4-(1-methylethyl)-phenol quickly increased from 7.6% to 21.9%. 2-bromo-phenol was decomposed into HBr and enriched in the water phase. Under the temperatures of 350 °C–400 °C, phenol and 4-(1-methylethyl)-phenol were still major compounds while the relative peak area of 4-(1-methylethyl)-phenol was around 22.0%, but the phenol decreased to about 57%. Meanwhile, more organic compounds were detected, e.g. 2-methyl-phenol, 2-methyl-benzofuran.

3.3. Bromine distribution

Fig. 3 shows the bromine distribution among the residue, water and oil after sub/SCW treatments under different temperatures.

Table 3
Main components of the oil identified by GC/MS (relative peak area %).

No.	Compound	250 °C	300 °C	350 °C	400 °C
1	Phenol	83.3	71.0	56.4	58.5
2	4-(1-methylethyl)-phenol	7.6	21.9	22.6	21.7
3	2-bromo-phenol	5.2	–	–	–
4	2-methyl-phenol	–	–	5.5	5.7
5	2-methyl-benzofuran	–	–	4.8	5.2
6	(Z)-9-octadecenamamide	0.8	4.7	2.7	1.9

– Not detected.

When each experiment was finished, nitrogen was used to drive the gas away from the reactor and NaHCO₃ solution was used to capturing the HBr in the gas phase. But the results showed that no inorganic bromine was detected in the gaseous phase in all experiments. The reason is that the brominated flame retardants were first degraded into HBr and enriched in gas phase during the sub/SCW treatments process. However, water has high solubility on HBr and most of the HBr in the gas phase were transferred into water during the cool process [12]. Therefore, the amount of HBr in aqueous phase also represented the HBr content in the gas phase.

Under lower temperature, the bromine in BERs cannot be completely decomposed into HBr and some bromine still existed in the oil in the formation of organic compounds. Under higher temperature, most of the bromine was transferred into the aqueous in the formation of hydrogen bromide. At 200 °C, the temperature was too low to decompose the BERs and all the bromine were in the residue. When the temperature increased to 250 °C, BERs began to be incompletely decomposed. The degradation product including organic bromine compounds in oil (5.7%) and inorganic bromine compounds in water (35.0%). However, about 60% of the bromine was still left in the residue. By increasing the temperature to 300 °C, bromine in the residue and oil kept on decreasing with the increase of temperature, but bromine in the aqueous phase decreased continuously. Bromine in the solid residue decreased rapidly to 21.8% while it was only 0.1% in the oil. With the temperature increased to 350 °C or higher, most of the bromine was removed from the solid phase and no organic bromine could be found in the oil. In this case, most of the bromine was enriched in the water phase (97.7%) and only 2.3% was left in the residue.

3.4. Recovery of metals and glass fibers

Copper foil is the main metallic component in WPCBs whose ductility changes little with temperature. Under the action of impact and shearing force, the copper foil was prone to bending instead of being crushed into powders for the high ductility. But the shape of nonmetal was greatly influenced by the temperature. The shapes of nonmetals crushing products varied with different particle sizes which could be observed on SEM as shown in Fig. 4. Fig. 4a shows that the majority of glass fibers were encapsulated in thermosetting resin and the glass fiber could not be separated at 200 °C. At 250 °C, the BER became brittle and all the nonmetal was broken into long single glass fibers. The length of

Fig. 3. Relative amount of Br in different products under various temperatures (holding time = 120 min, water adding amount = 40 ml).

Fig. 4. SEM images of nonmetal materials in the crushing products (temperature (a) = 200 °C, (b) = 250 °C, (c) = 300 °C and (d) = 400 °C, holding time = 120 min, water adding amount = 40 ml).

glass fiber kept on decreasing with the increase of temperature. When the temperature reached 400 °C, the BER was completely decomposed and all the nonmetal could be broken into powders. Under this temperature, the powders nonmetals can be easily separated from the metals by screening separations and the separation pictures of the crushing products are shown in Fig. 5. It could be seen that copper was completely liberated by the high-speed universal crusher due to the lower interfacial bonds of the residues after SCW treatments.

10 mesh (2 mm) and 100 mesh (0.147 mm) were used for separation in order to study the metal distribution in different particle sizes. Three distinct fractions were observed: large metal products

(LM > 2.0 mm), small metal products (0.147 mm < SM < 2.0 mm) and nonmetal products (NM < 0.147 mm). The WPCBs used in this study have four layers of copper foil which can be divided into signaling layer (filamentous and located in the upper and lower surface of WPCBs) and conductive layer (sheet and located in the inner of WPCBs) according to their functions. During the crushing process, the signaling layer mainly concentrated in the SM fraction while the conductive layer mainly concentrated in the LM fraction. Other metals such as Pb, Sn, Zn, Ag which were used for solders were still left on the surface of signaling layer thus mainly concentrated in SM fractions. Table 4 showed the mass distribution and metal purities within different particle sizes under the optimum

Fig. 5. Pictures of the crushing products (temperature = 400 °C, 30 MPa, holding time = 120 min, water adding amount = 40 ml).

Table 4

Crushing and separating results of solid residue obtained from WPCBs.

	Mass distribution (%)	Metal purity (%)						
		Cu	Pb	Sn	Al	Zn	Ag	Pd
LM ^a	27.39	96.74	0.00	0.00	0.02	0.06	–	0.004
SM ^b	8.90	92.74	2.59	1.32	0.36	0.12	0.148	0.006
NM ^c	63.71	1.05	0.28	0.02	6.24	0.01	–	0.004

– No detected.

^a Large metal products <2 mm.^b Small metal products 0.147–2 mm.^c Nonmetal products <0.147 mm.

condition (temperature, S/L ratio and holding time were 400 °C, 1:4 g/ml and 120 min). The mass distribution of LM, SM and NM were 27.39%, 8.09% and 63.71% respectively. The copper purity of LM and SM were 96.74% and 92.74% whereas the copper purity of NM was very low that was only 1.05%. Therefore, high copper recovery rate (98.11%) was obtained. Al₂O₃ is the main composition of glass fiber, thus Al was mainly concentrated in NM fraction. However, Pd was found in the three fractions that caused by the special preparation process of copper plated through hole (PTH) [21,22].

4. Conclusions

The results of this study demonstrated that sub/SCW treatments were efficient approach for detoxification of brominated flame retardants and simultaneously recovering valuable metals and glass fibers from WPCBs. During the process, BERs can be quickly and efficiently decomposed. Temperature, S/L ratio and holding time were the major parameters controlling debromination efficiency. The optimum temperature, S/L ratio and holding time for the process were 400 °C, 1:4 g/ml and 120 min, respectively, and the maximum debromination rate was 97.8%. Most of the bromine changed into HBr and enrich in water. Meanwhile, bromine-free oil was obtained and the main components were phenol (58.5%) and 4-(1-methylethyl)-phenol (21.7%). After sub/SCW treatments, glass fiber and copper foil in the residue could be easily crushed and separated by a high-speed universal crusher. After screening separation, copper recovery rate reached 98.11% in the purities of 96.74% (grain size >2.0 mm) and 92.74% (0.147–2.0 mm).

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