A novel process for detoxification of BERs in waste PCBs

Mingfei Xing*, Fushen Zhang

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China

Abstract

Waste printed circuit boards (WPCBs) contain high amount of brominated flame retardants that may bring a series of environmental and health problems. In the present study, an effective and environmental-friendly process using sub- and supercritical water (sub/SCW) to simultaneously degrade brominated epoxy resin and recover metals from WPCBs was developed. The results showed that brominated epoxy resins (BERs) can be quickly decomposed under SCW condition. Most of the bromine was changed into HBr and enriched in water. Meanwhile, bromine-free oil was obtained of which the main compositions were phenol and 4-(1-methylethyl)-phenol. This study provides an efficient and green approach for WPCBs recycling.

1. Introduction

The most commonly WPCBs material is FR-4 which using glass fibers as the reinforcing materials and brominated epoxy resins (BERs) as a binder [1]. BERs containing a large number of brominated flame retardants (5%-15%, BFRs) which are widely used in the PCBs to reduce the possibility of fire under the thermal stress [2]. Serious pollution may be generated if WPCBs are not properly disposed of since the flame retardants therein may cause the formation of halogenated dioxin-like compounds, such as polybrominated dibenzo-p-dioxins (PBDDs) or polybrominated dibenzofurans (PBDFs) [3]. Meanwhile, WPCBs is attracting more and more attention due to the valuable materials it contains [4]. 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≥374 °C, P≥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 [5, 6]. In the study, we tentatively separated metals and glass fibers by mechanical methods from WPCBs after sub/SCW...
treatments. It was found that the process had an excellent debromination effect to obtain bromine-free oil and high metal recovery efficiency.

The aims of this study were to: (1) evaluate the feasibility of WPCBs recycling by SCW treatments; (2) examine the debromination efficiency and bromine distribution after sub/SCW treatments on WPCBs.

2. Materials and methods

The WPCBs used in this work were mainly disassembled from discarded desktop computers which were made from glass fiber reinforced BERs. 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 hours. The major compositions of WPCB were metal (22.34%), organics (31.25%) and glass fiber (46.32%).

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%. The oil was analyzed by a gas chromatograph equipped with mass selective detector (GC/MS, Agilent 7890A/5975C, USA).

3. Results and discussion

3.1. Effects of various parameters on debromination efficiency

Table 1 shows the effect of temperature on debromination efficiency. It could be seen that the debromination efficiency increased quickly with the increase of temperature. Temperature was the most important factor on debromination efficiency for two reasons: (1) Once the BERs was decomposed into oil and it will be quickly dissolved in SCW to enhance the debromination efficiency [7]; (2) higher temperature could increase the probability of collision among molecules to enhance the debromination efficiency [8].

Table 1 Effect of temperature on debromination efficiency (holding time = 120 min).

| Temperature (°C) | Debromination Efficiency |
|------------------|--------------------------|
| 200              | 0                        |
| 250              | 40.70                    |
| 300              | 78.16                    |
| 350              | 93.04                    |
| 400              | 97.82                    |

Table 2 shows the effects of holding time on debromination efficiencies. The results indicated that debromination rate increased with the increase of residence time. Debromination rate increased fast 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%).

Table 2 Effect of holding time on debromination efficiency (temperature = 400 °C).

| Holding Time | Debromination Efficiency |
|--------------|--------------------------|
| 30 min       | 97.42                    |
| 60 min       | 97.54                    |
| 120 min      | 97.83                    |
| 240 min      | 98.50                    |

3.2. Analysis of BERs decomposition products
Table 3 shows the bromine distribution among residues, aqueous and oil after sub/SCW treatments under different temperatures. Under lower temperature, the bromine in BERs could not be completely decomposed into HBr and some bromine still existed in the oil in the form of organic compounds. Under higher temperature, most of the bromine was transferred into the aqueous in the form of hydrogen bromide.

| Temperature ºC | Residue % | Aqueous % | Oil %    |
|---------------|-----------|-----------|----------|
| 200           | 100       | 0         | 0        |
| 250           | 59.29674  | 35.00829  | 5.694967 |
| 300           | 21.83779  | 78.04467  | 0.11754  |
| 350           | 6.63825   | 93.36175  | 0        |
| 400           | 2.26173   | 97.73827  | 0        |

The main decomposition products of BERs were oil which were initially colorless and gradually turned from yellow to brown with the increase of temperature. The compositions of oil products changed obviously with reaction temperature. At 250 ºC, the major compounds of the oil were phenol, 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%. Under the temperatures of 400 ºC, 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%.

4. Conclusions

The results of this study demonstrated that sub/SCW treatments were efficient approach for simultaneously recovering valuable metals and glass fibers from WPCBs. During the process, BERs can be quickly and efficiently decomposed. The optimum temperature, and holding time for the process were 400 ºC, and 30-120 min, respectively, and the maximum debromination rate was 97.8%. Most of the bromine was changed into HBr and enriched in water. Meanwhile, bromine-free oil was obtained and the main components of which were phenol (58.5%) and 4-(1-methylethyl)-phenol (21.7%). The glass fibers and copper foils in the residue could be easily liberated and recovered respectively.

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