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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.

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 compounds, 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, $T \geqslant 374$ °C, $P \geqslant 22.1$ 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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