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A novel reutilization method for waste printed circuit boards as flame retardant and smoke suppressant for poly (vinyl chloride)

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HIGHLIGHTS

- We report a novel electronic waste-based flame retardant for PVC.
- The SCWO-treated PCBs significantly improves the flame retardancy of PVC.
- The flame retardant mechanism of SCWO-treated PCBs was studied.
- Appropriate amount flame retardant does not degrade the mechanical property of PVC.

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ABSTRACT

In this study, a novel reutilization method for waste printed circuit boards (PCBs) as flame retardant and smoke suppressant for poly (vinyl chloride) (PVC) was successfully testified. A supercritical water oxidation (SCWO) process was applied to treat waste PCBs before they could be used as flame retardants of PVC. The results indicated that SCWO conditions had a significant effect on the flame retarding and smoke suppressing properties of waste PCBs for PVC. Cu_2O, CuO, and SnO_2 were the main active ingredients in waste PCBs-derived flame retardants. A conversion of Cu elements ($Cu^0 \rightarrow Cu^+ \rightarrow Cu^{2+}$) during SCWO process with the increase of reaction temperature was found to be the key influence factor for the flame retarding properties of SCWO-treated PCBs. The experiment results also showed that there was a synergistic effect of flame retardancy between Cu^+ and Cu^{2+}. After the optimized SCWO treatment, SCWO-treated PCBs significantly improved the flame retardancy and smoke suppression of PVC. Limiting oxygen index (LOI) and char yield (CY) increased with increasing SCWO-treated PCBs content in PVC, while smoke density rating (SDR) and maximum smoke density (MSD) decreased markedly. The mechanical properties of PVC samples were influenced in different degree by adding different content SCWO-treated PCBs.

1. Introduction

In recent years, the treatment and recycling of amounts of waste electric and electronic equipment (WEEE) have attracted the most attention of the researchers around the world and the public [1]. As the fundamental part in most WEEE, waste printed circuit boards (PCBs) consisted of metals and nonmetal portions such as copper, tin, lead, gold, silver, and brominated resin [2–5]. In general, waste PCBs can be regarded as resources from the economic perspectives. Currently, many technologies, such as pyrometallurgy [6], hydrometallurgy [7], bio-technology [8], and mechanical methods [9,10], have been proposed for the treatment of waste PCBs. Mechanical method can be used as an effective pre-treatment method for the separation of metals and nonmetal portions. Pyrolysis of waste PCBs was studied intensively for decomposition of resin materials and recovery of organic products [11,12], however, the formation of secondary pollution such as dioxins and furans is difficult to be disposed of [13]. Hydrometallurgical process is an effective route to recover metals from waste PCBs. However, hydrometallurgical process generally includes multistep leaching, separation, and purification, which lead to the generation of a large amount of hazardous waste water and sludge containing heavy metals [14]. Hence, the study of novel reutilization method for waste PCBs becomes increasingly important.

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Recently, researchers proposed a few novel "direct reutilization" strategies for the treatment of waste PCBs [14–17], which provided a new perspective for the study and application of WEEE. An effective adsorbent for heavy metals was directly developed by using the nonmetal portions of waste PCBs [15–17]. Li et al. reported the direct application of metals portions in waste PCBs as a catalyst to degrade pyridine in Fenton-like reaction [14]. Hence, by directly taking full advantage of the physicochemical property of effective constituent contained in waste PCBs, the "direct reutilization" strategy is supposed to be a promising solution for waste PCBs treatment.

It is well known that copper, iron, and solder (tin and lead) are the primary metals in waste PCBs. These metals, especially copper, tin, and iron, have been reported to have the potential as flame retardants for polymer materials when they exist as oxides [18–20]. For instance, transition metal oxides can catalyze HCl-elimination reaction of PVC, which can play a role of flame retardant in gas phase [19]. These metals provide a possibility for the waste PCBs to be regarded as flame retardants applying in polymer materials. In addition, waste PCBs may have good flame retardant performance because of the poly-metallic complex system may induce synergistic effect in flame retardant behavior. Flame retardants with poly-metallic, such as artificial synthesized compounded flame retardants with metallic oxide or metal chloride [21,22], or natural materials of kaolinite, montmorillonite, and talc [23–25] could usually enhance the flame retardancy of polymer materials. However, these metals especially the copper contained in waste PCBs exist mainly as zero-valent metal, which has no any flame retardant performance. The oxidation of metals contained in waste PCBs can be realized by a variety of methods, among which the simplest one is the combustion heat treatment [26]. However, a large amount of toxic air pollutants were generated during the combustion process. Recent researches indicated that supercritical water oxidation (SCWO) treatment could solve this problem for the reason that the toxic organic matters in waste PCBs could be degraded safely in SCWO process and the formation of toxic air pollutants could be eliminated at the same time [27–29]. It's worth noting that the metals contained in waste PCBs can also be oxidized during SCWO process due to the reaction of oxidation atmosphere. As far as we know, to date, no report is on applying directly waste PCBs as a flame retardants for polymer materials. The research in this aspect could provide a novel perspective for the "direct reutilization" strategy of waste PCBs.

In this study, the SCWO-treated waste PCBs were tested for the first time as a flame retardant and smoke suppressant for polymer materials with the aim of recycling these waste resources in a new "direct reutilization" strategy. Poly (vinyl chloride) (PVC) was selected as a model polymer material. The objectives of the present work are (1) to evaluate the effect of SCWO conditions on the speciation of metals contained in waste PCBs and the flame retardant mechanism of SCWO-treated waste PCBs, and (2) to investigate the influence of waste PCBs-derived flame retardant on the flame retardancy and smoke suppression of PVC such as limiting oxygen index (LOI), char yield (CY), smoke density rating (SDR), and maximum smoke density (MSD). In addition, the mechanical properties of PVC samples with SCWO-treated PCBs were also evaluated.

2. Materials and methods

2.1. SCWO treatment of waste PCBs

Waste PCBs used in this work were collected from discarded personal computer in Fujian University of Technology, China. Firstly, the components (relays, capacitors, etc.) were manually disassembled, then the waste PCBs were sent to comminute in a cutting mill until the fractions reached particle size smaller than 4 mm. Metal content in the original PCBs powder was determined by ICP-OES (OPTIMA 2000, PerkinElmer) after digestion according to a literature [30]. The analysis results are given in Table 1.

Table 1
Mass percent of metals in original waste PCBs and solid product obtained after SCWO process (wt.%).

Metal element	C_0	C_1	C_2	C_3	C_4
Cu	21.8	27.7	32.7	32.7	0.2
Pb	1.1	1.4	1.7	1.7	0.1
Sn	4.8	6.1	7.2	7.2	15.1
Fe	2.3	2.9	3.4	3.4	0.01
Zn	3.5	4.4	5.2	5.2	0.01

C_0: mass percent of metals in original waste PCBs.
C_1: mass percent of metals in FR1.
C_2: mass percent of metals in FR2.
C_3: mass percent of metals in FR3.
C_4: mass percent of metals in HCl-treated FR3.

The SCWO treatment was conducted in a batch-type reactor made of 316 alloy, having an inner volume of 200 mL. In a typical treatment, 5 g of PCBs sample, 50 mL of distilled water, and 40 mL of H_2O_2 solution (30 wt.%) were introduced into the reactor. Three groups of experiments with different SCWO treatment conditions were performed: (1) 300 °C, 10 MPa, 30 min; (2) 420 °C, 22 MPa, 60 min; (3) 460 °C, 30 MPa, 60 min. The reaction condition of group (1) is subcritical water oxidation, while group (2) and (3) are supercritical water oxidation. The reactions were terminated by quenching the reactor in a cold water bath, then the obtained product was collected and centrifugated. After that, solid phase product was washed and dried in a vacuum desiccator for 24 h. The obtained solid phase product from group (1)–(3) was marked as FR1, FR2, and FR3, respectively. Metal content in SCWO-treated PCBs was determined by ICP-OES (OPTIMA 2000, PerkinElmer) after digestion [30]. The bromine content in the FR1, FR2, and FR3 was measured by an oxygen combustion bomb-ion chromatography (IC, DionexICS2000, USA) according to a literature [31]. The structure of SCWO-treated PCBs were characterized by X-ray diffraction spectroscopy (XRD) at 50 kV and 100 mA using Cu Kα radiation (λ = 1.5418 Å).

2.2. Preparation of flame retarded PVC samples

After SCWO treatment of waste PCBs, the obtained solid phase product was used as flame retardant in the preparation of PVC samples. Samples of PVC were prepared by mixing PVC with Dioctyl Phthalate (DOP), heat stabilizer, lubricant, coupling agent, and the flame retardant prepared from waste PCBs after SCWO treatment. The basic composition for all of the samples was as follows: PVC 100 phr (parts per hundred resins), DOP 40 phr, stabilizer 3 phr, lubricant 1 phr, and some flame retardant prepared from waste PCBs. The dosage of flame retardant was controlled at 0, 2, 4, 6, 8, 10, and 12 phr, respectively. PVC samples were blended in a two-roll mill at 170 °C for 10 min, and then the samples were introduced into a flat vulcanizing machine to be compressed at 180 °C. The sheets with dimensions of 90 mm × 6 m × 3 mm were formed after compression. Testing samples were cut from the molded PVC sheets.

2.3. Flame retardancy, smoke suppression, and mechanical properties testing of PVC samples with SCWO-treated PCBs

The flame retardancy and smoke suppression of PVC samples in this study was determined by Limiting Oxygen Index (LOI), char yield (CY), smoke density rating (SDR), and maximum smoke density (MSD). The LOI method is a simple, convenient, fast, and