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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 ($\lambda = 1.5418$ 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

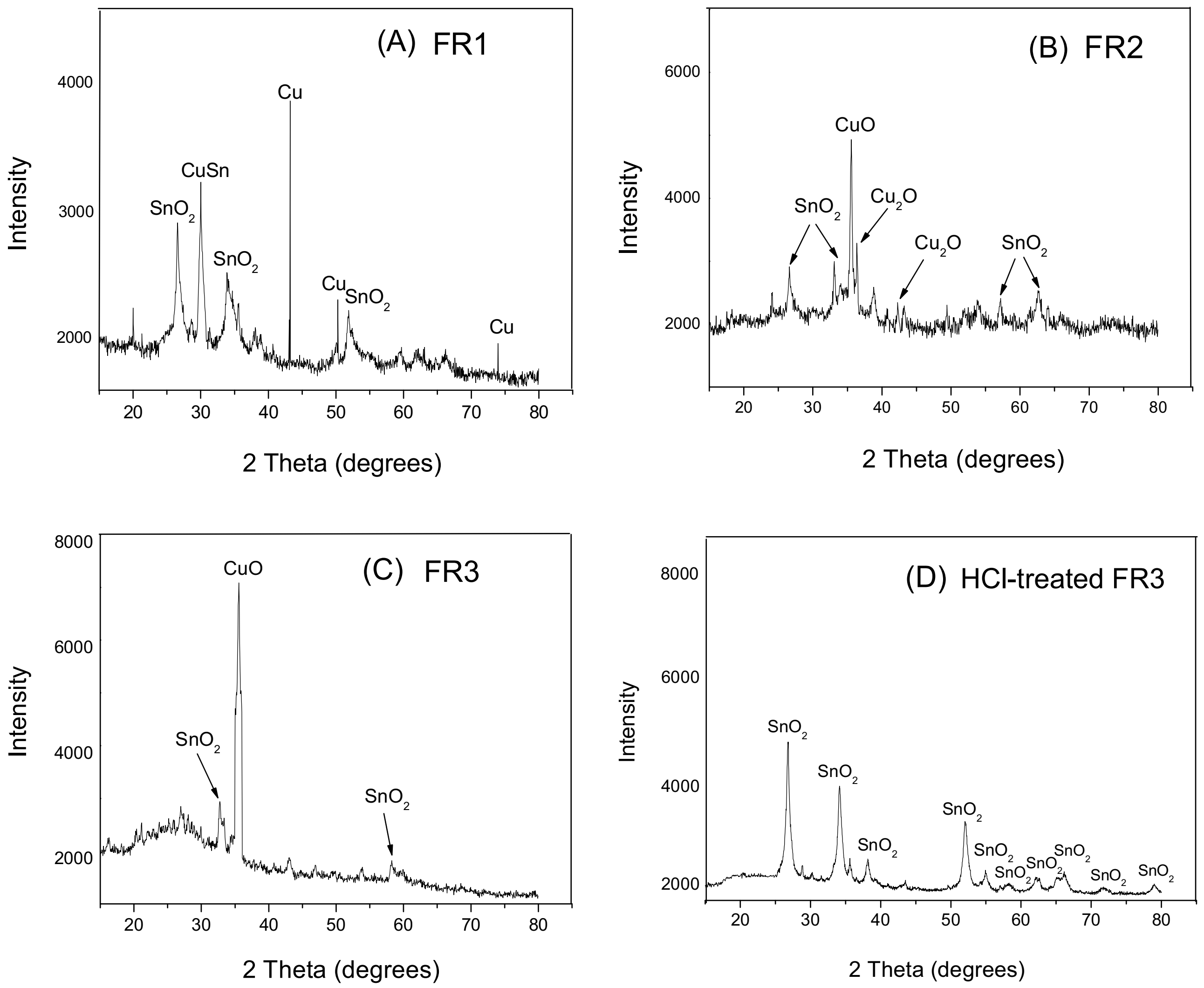

Fig. 1. XRD results of the flame retardant developed from waste PCBs after (A) SubCWO treatment at 300 °C, 10 MPa, and 30 min, (B) SCWO treatment at 420 °C, 22 MPa, and 60 min, (C) SCWO treatment at 460 °C, 30 MPa, and 60 min, and (D) SCWO + HCl treatment (SCWO: 460 °C, 30 MPa, and 60 min; HCl concentration: 1 M).

effective method for the study of flame retardancy of plastic materials. It is a technique for measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics. The LOI value is the minimum amount of oxygen in an oxygen–nitrogen mixture required to support combustion over 3 min or until the testing sample is consumed for more than 5 cm from the top. LOI values were determined in accordance with ASTM 2863-2006 on a M605 LOI instrument (Qingdao, China). A higher LOI value indicates a greater efficiency for the flame retardant. The CY was calculated as follows:

$$3\text{CY} = M_1/M_2 \qquad (1)$$

where M_1 is the remaining weight of PVC sample after the treatment under nitrogen atmosphere at 400 °C for 40 min, M_2 the weight of original PVC sample. A higher CY value indicates a greater efficiency for the flame retardant. The SDR and MSD of PVC samples were determined in accordance with ASTM D2843-1993 using a JCY-2 instrument (Nanjing, ShineRay, China). A lower SDR or MSD value indicates a greater efficiency for the smoke suppression.

Thermogravimetric analysis (TG) was carried out on a TGA-101 analyzer (Nanjing Dazhan, China) under air atmosphere at a heating rate of 20 °C/min and an air flow rate of 50 mL/min. The amount of PVC samples used for thermal analysis was 4–5 mg. The temperature range was from room temperature to 750 °C.

Tensile strength of PVC samples was determined on a tensile strength tester (HY-0230, Shanghai, China) at an extension speed of 10 mm/min. The elongation at break was calculated by the specific value of displacement to original length. Impact strength measurement of PVC samples was carried out on a ZY6148 impact strength tester (Guangdong, China) at impact speed of 2.9 m/s.

3. Results and discussion

3.1. Effect of SCWO conditions on the speciation of metals contained in waste PCBs

Mass percent of metals in original waste PCBs, FR1, FR2, and FR3 are presented in Table 1. The metals contents in the aqueous phase after SCWO treatment of waste PCBs were also determined and the results indicated that the major metals such as Cu, Pb, Sn, Ni, Fe, and Zn were not leached during SCWO process. According to previous studies [27–29], the resin material contained in waste PCBs could be effectively decomposed and removed by SCWO treatment, so the dominant ingredients in solid phase product after SCWO process were metals and glass fiber (e.g., SiO_2).

To further find out the relevant information about the effect of SCWO conditions on the speciation of metals contained in waste PCBs, X-ray powder diffraction examinations of waste PCBs after

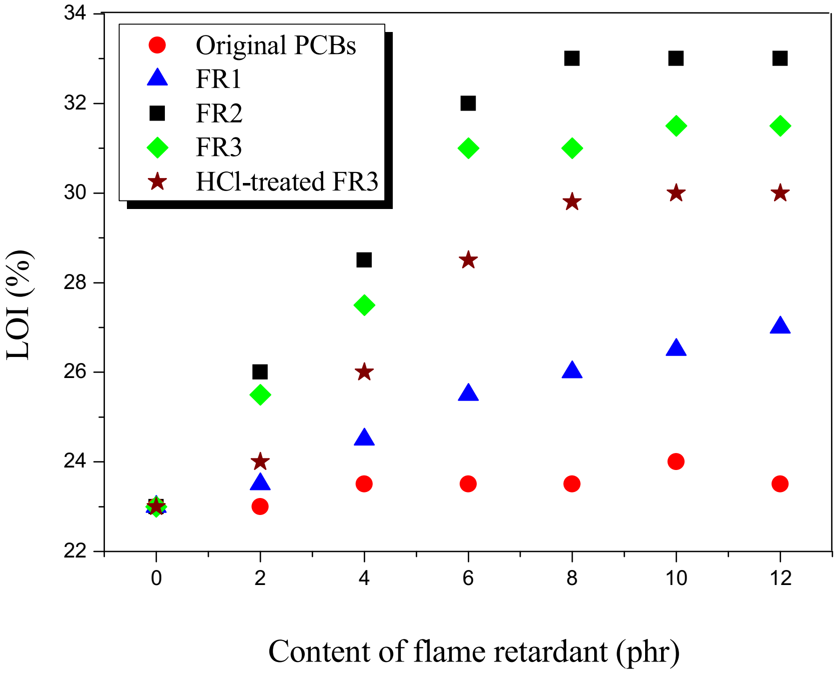

Fig. 2. Effect of flame retardant on the LOI of PVC sample (Flame retardant obtained from original waste PCBs, FR1, FR2, FR3, and HCl-treated FR3).

SCWO treatments with different conditions were performed. The XRD analytical results of FR1, FR2, and FR3 are showed in Fig. 1A–C, respectively. The main crystalline phases in FR1 were Cu, SnO_2, and CuSn alloy. The reaction condition of FR1 was subcritical water oxidation, under which Sn could be oxidized to SnO_2 to a great extent, while Cu still existed as zero valent copper or formed alloy phase with Sn according to XRD result (Fig. 1A). However, when the SCWO temperature was increased to 420 °C (FR2) and 460 °C (FR3), which were under supercritical water conditions, Cu began to be oxidized to its oxides (Fig. 1B and C). Cu could be oxidized from Cu^0 to the mixture of Cu^+ (Cu_2O) and Cu^{2+} (CuO) when SCWO temperature was controlled at 420 °C. In comparison, Cu^0 could be oxidized completely to Cu^{2+} (CuO) when SCWO temperature was increased to 460 °C. Hence, a conversion of Cu elements ($Cu^0 \rightarrow Cu^+ \rightarrow Cu^{2+}$) took place during SCWO process with the increase of reaction temperature.

3.2. Effect of SCWO conditions on the flame retardant properties of SCWO-treated waste PCBs

The waste PCBs used in this study contains resin which is treated by brominated flame retardant. If the brominated flame retardants are still in the solid phase of waste PCBs after SCWO treatment, it will play a role in the PVC as flame retardant. In order to rule out this point, the bromine content in the FR1, FR2, and FR3 was measured by an oxygen combustion bomb-ion chromatography. The bromine content in the FR1 was 0.2%, and the bromine contents in FR2 and FR3 were unable to detect. Hence, the bromine contained in FR1 might play a role in the PVC as flame retardant, but the role was very weak due to the very low bromine content (0.2%). No bromine could be detected in FR2 and FR3, indicating that proper SCWO reaction conditions could completely remove the bromine in waste PCBs.

To investigate the effect of SCWO conditions on the flame retardant properties of SCWO-treated PCBs, FR1, FR2, and FR3 were used to test. For comparison, the original waste PCBs was also used as flame retardant for PVC sample in this study. LOI and CY values of PVC samples were used to indicate the flame retardancy. From Figs. 2 and 3, it can be seen that there is almost no flame retardant effect for the original PCBs due to the unaltered LOI and CY values. Inversely, the separate addition of FR1, FR2, and FR3 could significantly increased the LOI and CY values, indicating that the near critical water oxidation treatment for waste PCBs was conducive to produce effective active ingredients and improve the flame retardant properties. FR1 was obtained by subcritical water oxidation (300 °C, 10 MPa, 30 min) of waste PCBs, in which SnO_2 was formed and copper existed as Cu^0 or CuSn alloy according to XRD analysis result (Fig. 1A). The flame retardant property of FR1 might originate from SnO_2 contained in FR1. Many studies [20,21] have found that tin compounds can be used as flame retardants in polymer materials, and the role of tin compounds occurred mainly in condensed phase. SnO_2 could effectively catalyze the removal reaction of HCl from PVC [32]. The rapid release of HCl could dilute the oxygen around to a certain degree, and have some flame-retardation effects in gas phase.

With the increase of reaction temperature, FR2 and FR3 were obtained after SCWO treatment of waste PCBs. From Figs. 2 and 3, it can be seen that SCWO conditions have a remarkable influence on the flame retardant properties of the obtained product. The LOI and CY values of PVC samples adding FR2 and FR3 were all much higher than that of PVC samples adding FR1. Judging from the composition, the crystalline phase of CuSn alloy disappeared from the XRD pattern in Fig. 1B and C, indicating the increase of active ingredients content due to the further oxidation of Sn in CuSn alloy to SnO_2. However, the Sn content only increased from 4.8% in FR1 to 6.1% in FR2 and 7.2% in FR3, respectively. Such a small amount of SnO_2 is hard to be used to explain such a significant increase of LOI and CY values of PVC samples contained FR2 or FR3. Therefore, there must be other reasons. The most important reason for the enhancement of flame retardant and smoke suppression property of FR2 and FR3 seems to be the transformation of copper contained in waste PCBs. Copper was oxidized from Cu^0 to the mixture of Cu_2O and CuO at 420 °C (Fig. 1B), and was completely oxidized to CuO at 460 °C (Fig. 1C). Oxides of copper could react with HCl and promote the removal reaction of HCl from PVC. The reactions can be expressed as follows:

$$CuO + 2HCl \rightarrow CuCl_2 + H_2O \qquad (2)$$

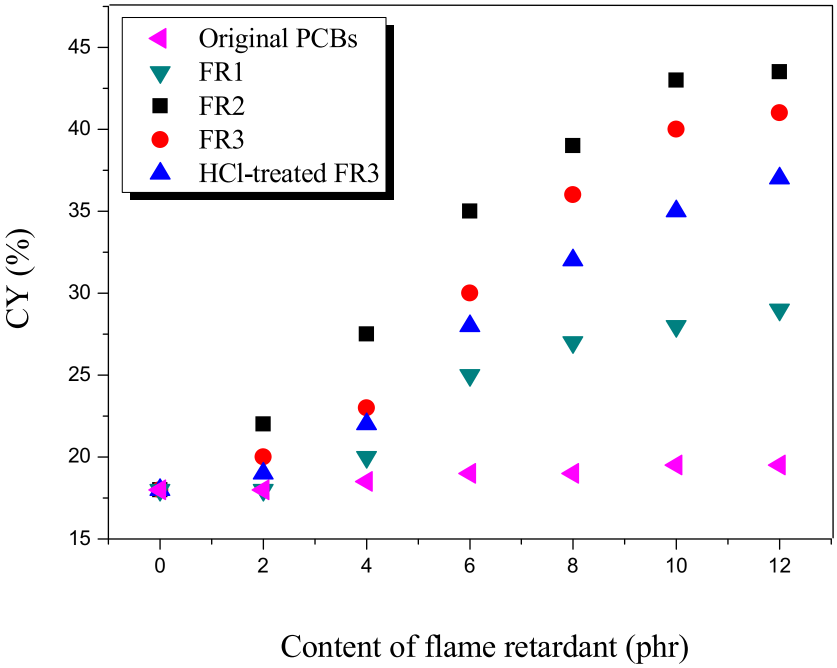

Fig. 3. Effect of flame retardant on the CY of PVC sample (Flame retardant obtained from original waste PCBs, FR1, FR2, FR3, and HCl-treated FR3).

$$Cu_2O + 2HCl \rightarrow 2CuCl + H_2O \quad (3)$$

The released HCl from PVC and the produced H_2O could dilute the oxygen around and have flame-retardation effects in gas phase. The content of copper existed as oxides in FR2 or FR3 reached up to 32.7%, which could be regarded as a key factor for the great flame retardant property of PVC samples adding FR2 or FR3.

It was interesting that the SCWO reaction temperature of FR3 (460 °C) was higher than that of FR2 (420 °C), but contrary to what one might suppose, the flame retardant property of FR3 was obviously lower than that of FR2 (Figs. 2 and 3). It seemed that the flame retardant property of the mixture of Cu_2O and CuO were superior to that of single CuO. We speculated that there might be a synergistic effect of flame retardancy between Cu_2O and CuO. It can be found from Table 1 that main metals (especially Cu and Sn) contents in FR2 and FR3 were consistent, indicating that the amounts of Cu and Sn in FR2 and FR3 were unchanged, and the only thing that changed was the valence state of Cu according to XRD analysis results (Fig. 1B and C). It is well known that Cu^+ is unstable and the disproportion reaction of Cu^+ can produce Cu^0 and Cu^{2+}. The fresh Cu^0 produced from the disproportion reaction of CuCl generated by reaction (3) was also unstable and easily oxidized to Cu_2O or CuO by oxygen, $CuCl_2$ or other oxidizing species in the system such as Fe^{3+} and Pb^{4+}. Fe and Pb contained in waste PCBs could be oxidized to high valence state species such as Fe_2O_3 and PbO_2 during SCWO process [33,34], and the formed Fe_2O_3 and PbO_2 could react with HCl, which was derived from the dehydrochlorination of PVC, to produce oxidizing species (Fe^{3+} and Pb^{4+}). The relevant reactions can be expressed as follows:

$$2Cu^+ \rightarrow Cu^0 + Cu^{2+} \quad (4)$$

$$2Cu^0 + O_2 + 2Cu^{2+}(CuCl_2) \rightarrow 2Cu_2O \quad (5)$$

$$3Cu^0 + O_2(Fe^{3+}, Pb^{4+}) \rightarrow Cu_2O + CuO \quad (6)$$

The regenerated Cu_2O or CuO could continue to conduct the Reaction (2) and (3). Therefore, the superior flame retardant property of FR2 might be attributed to the coexisting of Cu_2O and CuO and their synergistic effect.

However, it is not clear whether there is a synergistic effect between oxides of copper and SnO_2 in FR2 or FR3. Although the flame retardant property of FR3 was inferior to that of FR2, the property of FR3 was much better than that of FR1 (Figs. 2 and 3), indicating that the coexisting of SnO_2 and CuO, which was derived from the complete oxidation of copper, still showed higher flame retardant activity. To further confirm the positive effect of CuO, a sample from which the CuO contained in FR3 was removed was prepared to evaluate the effect of CuO. This sample was prepared by leaching out CuO from FR3 using 1 M hydrochloric acid solution for 2 h. This sample is termed “HCl-treated FR3”. The XRD analysis result of HCl-treated FR3 is showed in Fig. 1D. The main crystalline phase was SnO_2, and the weak CuO diffraction peak indicated that vast majority of CuO was removed by hydrochloric acid. The metals contents in HCl-treated FR3 were determined and the results were presented in Table 1. Sn (15.1%) tops the list of metals contents, followed by Cu (0.2%). With the removal of CuO, the flame retardant property of HCl-treated FR3 decreased significantly when compared to FR3 (Figs. 2 and 3). It is concluded that the CuO in FR3 play an important role with SnO_2 in the flame retardant property of FR3.

3.3. *Effect of the dosage of SCWO-treated waste PCBs on the flame retardancy and smoke suppression of PVC samples*

From Fig. 2, it can be seen that the LOI values of PVC increase with increasing the dosage of SCWO-treated PCBs. In comparison with PVC with FR2, FR3, and HCl-treated FR3, the effect of dosage on the LOI value of PVC with FR1 was much smaller, the LOI value just increased from 23% (no FR1 added) to 27% (12 phr FR1 added). The possible reason is the lower content active ingredients and the higher content organics residual contained in FR1. Although the content of copper in FR1 (27.7%) was much higher than that in HCl-treated FR3 (0.2%), the copper in FR1 existed as Cu^0 and CuSn alloy which almost had no flame retardant abilities. In addition, the content of organics residual in FR1, FR2, FR3, and HCl-treated FR3 was determined, and the result was 12.1, 0.2, 0.1, and 0.1%, respectively. Obviously, the preparation condition of FR1 (300 °C, 10 MPa, 30 min) could not completely remove the resin materials, and such

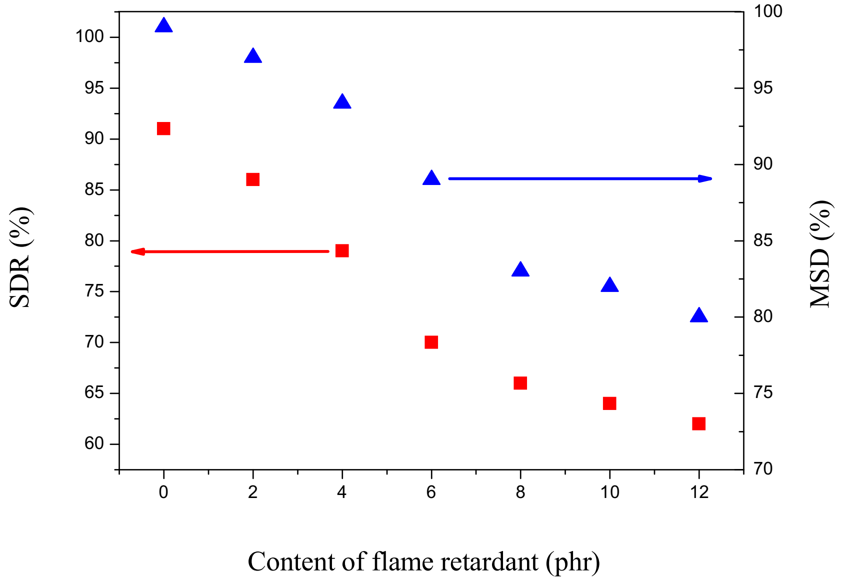

Fig. 4. Effect of FR2 on the SDR and MSD of PVC sample.

high levels of organics residual in FR1 had inevitably a negative influence on the flame retardant property of FR1.

The effect of the dosage of SCWO-treated waste PCBs on the CY of PVC is showed in Fig. 3. The CY of PVC with FR2 significantly increased with increasing the dosage of FR2. The CY increased from 18% (PVC with no flame retardant) to 43.5% (10 phr FR2 added). However, for the PVC with FR1, FR3, and HCl-treated FR3, when the content of flame retardant <6 phr, the CY of PVC sample changed a little. For instance, the CY of PVC with FR1 only increased from 18% (PVC with no flame retardant) to 20% (4 phr FR1 added). This may be due to the higher content organics residual contained in FR1 (12.1%). The CY can be used as an important indicator for the function of char forming. The higher CY value means higher function of char forming during the combustion of PVC. From Fig. 3, it can be found that the increase of flame retardant content in PVC can lead to the increase of char yield and the higher function of char forming, which is highly favorable for improving the LOI value of PVC and enhancing the flame retardant property (Fig. 2).

To investigate the effect of the dosage of SCWO-treated PCBs on the smoke suppression performance of PVC, the SDR and MSD were measured. FR2 was used here due to its highest flame retardant efficiency among our prepared flame retardants. The results are presented in Fig. 4. The SDR and MSD of PVC with FR2 significantly decreased with increasing FR2 content. The SDR of PVC decreased to 70% when 6 phr FR2 was added. The smoke suppression standard of flame retardant for building materials in China is SDR $\leq$ 75%. This may be due to the great enhancing of char forming function when the FR2 content added exceeds 6 phr, the CY of PVC with FR2 could reach up to 35% (Fig. 3). The enhancing of char forming function could significantly suppress the generation of smoke. The MSD value of PVC in Fig. 4 could also show the above changes. On the other hand, Cu_2O contained in FR2 could be transformed into CuCl during the combustion of PVC according to the above discussions. CuCl could efficiently absorb poisonous gas such as CO and generate $Cu_2Cl_2(CO)_2$. Thus, the Cu_2O contained in FR2 might also be an important reason for the great smoke suppression performance.

Thermogravimetric analysis can reveal the thermal properties and the degradation process of polymer, and provide the information of flame-retardant mechanism [21]. The TG curve of PVC with no flame retardant is shown in Fig. 5A. The thermal degradation weightlessness of PVC can be divided into three stages. The first stage of the degradation weightlessness occurred in the temperature interval of 200–350 °C. At this stage, the main reaction occurred were the removal of HCl from PVC and the decomposition of DOP. The weight loss was very obvious at the first stage and the percentage of weight loss exceeded 65%. Compared with the PVC with no flame retardant added, PVC with 6 phr waste PCBs-derived flame retardant, especially FR2, had the much steeper slope for the weightlessness curve (Fig. 5B–D), indicating the faster weightlessness reaction speed. In addition, the temperature range of weight loss for the PVC with no flame retardant added was 200–350 °C. However, when 6 phr FR2 was added, the temperature range of weight loss for PVC was narrowed down, and the thermal degradation weightlessness was completed when the temperature was increased to 320 °C. All of the above results indicated that waste PCBs-derived flame retardant, especially FR2 had a significant catalytic and facilitative role for the removal of HCl from PVC at the first stage of degradation weightlessness. The rapid removal of HCl in PVC could facilitate the early cross-linking and char-forming in the first stage, and increase the LOI and CY value (Figs. 2 and 3).

The temperature range of weight loss for the second and third stage is around 430–650 °C. Compared to the weight loss rate and mass loss of the first stage, it is much smaller for those of the second and third stage. It can be found from Fig. 5 that after the adding of FR2, the temperature range of weight loss for the third stage (Fig. 5C) becomes wider obviously when compared to that of the PVC with no flame retardant added (Fig. 5A). The temperature range of weight loss was broadened from 520 to 600 °C for PVC with no flame retardant added to 520–640 °C for PVC with 6 phr FR2 added. The broadening of temperature range of weight loss in the third stage indicated that the thermostability of the formed char was improved significantly with the adding of FR2, thus the flame retardant and smoke suppression performance of the PVC were enhanced.

3.4. Effect of SCWO-treated PCBs on the mechanical property of PVC samples

The mechanical properties such as tensile strength and impact strength of PVC containing FR2 with different content were tested. In addition, the elongation at break was also calculated. The results are shown in Table 2. The tensile strength decreased with increasing the content of FR2. In particular, the tensile strength declined obviously when the additive amount of FR2 was higher than 6 phr.

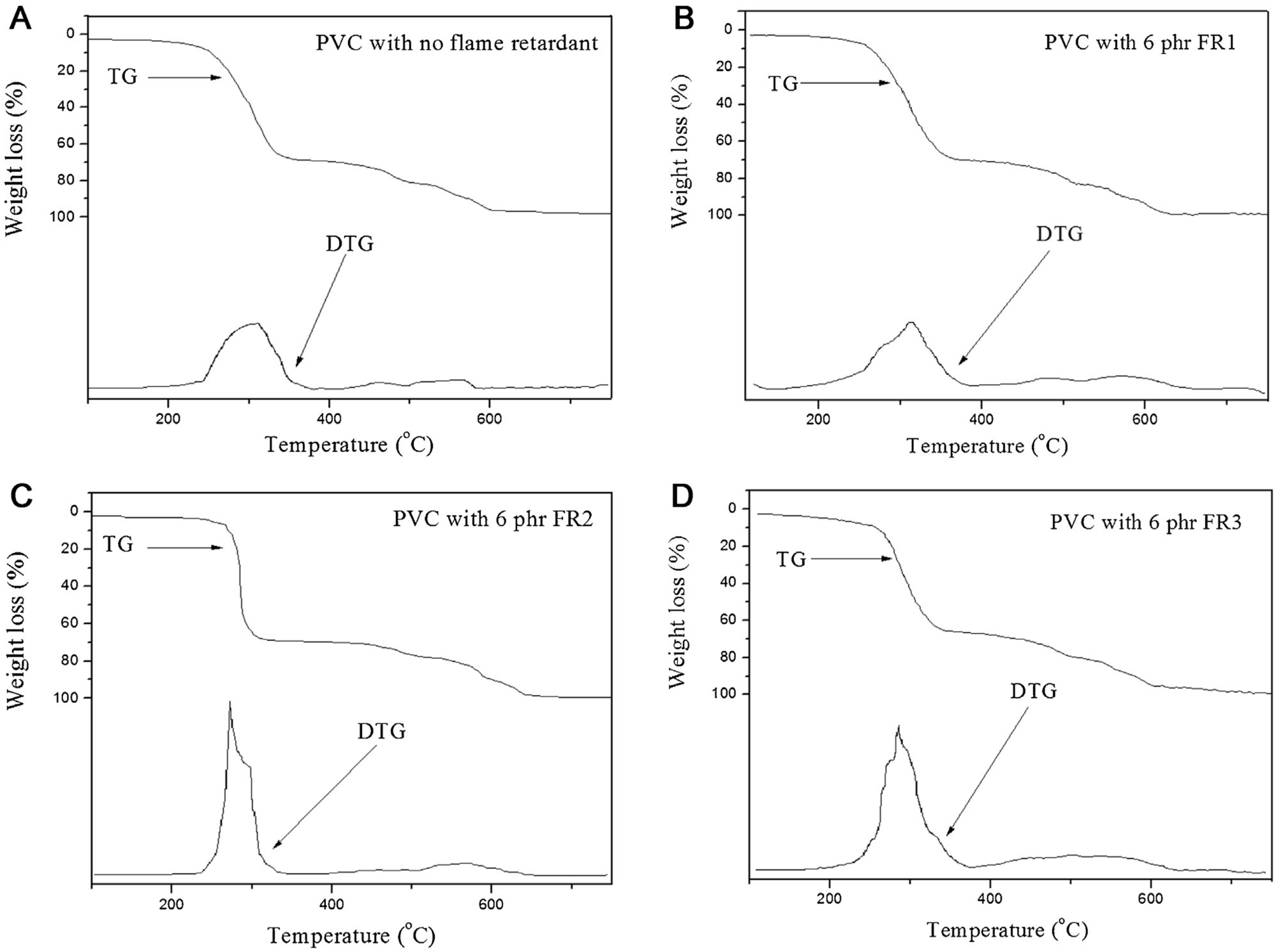

Fig. 5. TG and DTG analysis results of (A) PVC with no flame retardant and (B) PVC with 6 phr FR2.

Table 2
Effect of FR2 on the mechanical property of PVC samples (Basic recipe of PVC sample: PVC 100 phr, DOP 40 phr, stabilizer 3 phr, lubricant 1 phr).

FR2 (phr)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (KJ/m^2)
0	30.9	189	6.7
2	29.9	196	6.7
4	29.4	202	6.5
6	28.9	194	6.5
8	27.7	175	5.8
10	26.5	168	5.2
12	25.6	158	4.9

However, the additive amount of FR2 had little impact on the tensile strength when the additive amount is small (for example, less than 6 phr). The tensile strength only decreased from 30.9 to 28.9 Mpa when the additive amount was increased from 0 to 6 phr.

Both elongation at break and impact strength decreased obviously with the increase of FR2 when the FR2 amount was more than 6 phr, which was similar to the changing law of tensile strength. However, elongation at break and impact strength are at high values when the amount of FR2 is lower than 6 phr. By controlling appropriate adding amount, PVC samples could possess both good flame retardancy and satisfactory mechanical properties.

4. Conclusions

The adding of SCWO-treated PCBs could remarkably improve the flame retardancy and smoke suppression of PVC. Cu_2O, CuO, and SnO_2 were the main active ingredients of the waste PCBs-derived flame retardant, and the conversion of Cu elements ($Cu^0 \rightarrow Cu_2O \rightarrow CuO$) during SCWO process with the increase of reaction temperature played a positive role in improving the flame retardancy and smoke suppression of PVC. The SCWO-treated PCBs containing the mixture of $Cu_2O/CuO/SnO_2$ had the highest flame retardant and smoke suppression performance. The SCWO-treated PCBs had a significant catalysis and facilitation role for the removal of HCl from PVC at the first stage of degradation weightlessness. The rapid removal of HCl in PVC could facilitate the early cross-linking and char-forming in the first stage, and increase the LOI and CY value. The temperature range of weight loss was broadened at the third stage of degradation weightlessness of PVC when SCWO-treated PCBs was added. The broadening of temperature range of weight loss in the third stage indicated that the thermostability of the formed char was improved significantly with the adding of SCWO-treated PCBs, thus the flame retardant and smoke suppression performance of PVC were enhanced.

The mechanical properties such as tensile strength, elongation at break, and impact strength of PVC were influenced in different degree by adding different content SCWO-treated PCBs. By controlling appropriate adding amount, PVC could possess both good flame retardancy and satisfactory mechanical properties.

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References

[1] J. Wang, Z. Xu, Disposing and recycling waste printed circuit boards: disconnecting, resource recovery, and pollution control, Environ. Sci. Technol. 49 (2015) 721–733.
[2] B. Ghosha, M.K. Ghosh, P. Parhi, P.S. Mukherjee, B.K. Mishra, Waste printed circuit boards recycling: an extensive assessment of current status, J. Clean. Prod. 94 (2015) 5–19.
[3] C.L. Duan, Z.J. Diao, Y.M. Zhao, W. Huang, Liberation of valuable materials in waste printed circuit boards by high-voltage electrical pulses, Miner. Eng. 70 (2015) 170–177.
[4] M. Xing, F.-S. Zhang, Degradation of brominated epoxy resin and metal recovery from waste printed circuit boards through batch sub/supercritical water treatments, Chem. Eng. J. 219 (2013) 131–136.
[5] S. Fogarasi, F. Imre-Lucaci, Á. Imre-Lucaci, P. Ile, Copper recovery and gold enrichment from waste printed circuit boards by mediated electrochemical oxidation, J. Hazard. Mater. 273 (2014) 215–221.
[6] J. Moltó, S. Egea, J.A. Conesa, R. Font, Thermal decomposition of electronic wastes: mobile phone case and other parts, Waste Manag. 31 (2011) 2546–2552.
[7] A. Tuncuk, V. Stazi, A. Akcil, E.Y. Yazici, H. Deveci, Aqueous metal recovery techniques from E-scrap: hydrometallurgy in recycling, Miner. Eng. 25 (2012) 28–37.
[8] Y. Yang, S. Chen, S. Li, M. Chen, H. Chen, B. Liu, Bioleaching waste printed circuit boards by *Acidithiobacillus* ferrooxidans and its kinetics aspect, J. Biotechnol. 173 (2014) 24–30.
[9] K. Huang, J. Guo, Z. Xu, Recycling of waste printed circuit boards: a review of current technologies and treatment status in China, J. Hazard. Mater. 164 (2009) 399–408.
[10] J. Li, H.Z. Lu, J. Guo, Z.M. Xu, Y.H. Zhou, Recycle technology for recovering resources and products from waste printed circuit boards, Environ. Sci. Technol. 41 (2007) 1995–2000.
[11] Q.J. Guo, X.H. Yue, M.H. Wang, Y.Z. Liu, Pyrolysis of scrap printed circuit board plastic particles in a fluidized bed, Powder Technol. 198 (2010) 422–428.
[12] F. Barontini, V. Cozzani, Formation of hydrogen bromide and organobrominated compounds in the thermal degradation of electronic boards, J. Anal. Appl. Pyrol. 77 (2006) 41–55.
[13] H.L. Chiang, K.H. Lin, Exhaust constituent emission factors of printed circuit board pyrolysis processes and its exhaust control, J. Hazard. Mater. 264 (2014) 545–551.
[14] N. Li, X. Lu, S. Zhang, A novel reuse method for waste printed circuit boards as catalyst for wastewater bearing pyridine degradation, Chem. Eng. J. 257 (2014) 253–261.
[15] P. Hadi, P. Gao, J.P. Barford, G. McKay, Novel application of the nonmetallic fraction of the recycled printed circuit boards as a toxic heavy metal adsorbent, J. Hazard. Mater. 252–253 (2013) 166–170.
[16] M. Xu, P. Hadi, G. Chen, G. McKay, Removal of cadmium ions from wastewater using innovative electronic waste-derived material, J. Hazard. Mater. 273 (2014) 118–123.
[17] P. Hadi, J. Barford, G. McKay, Toxic heavy metal capture using a novel electronic waste-based material-mechanism, modeling and comparison, Environ. Sci. Technol. 47 (2013) 8248–8255.
[18] W.-K. Ho, J.K. Walker, S.V. Orski, T.W. Fuller, A.G. Zestos, C.L. Grinnell, R.D. Pike, J.W.H. Starnes, A new synergistic effect in the smoke suppression of plasticized poly(vinyl chloride) by mixed-metal Cu(II) oxides, J. Vinyl Add. Technol. 14 (2008) 16–20.
[19] B. Li, A study of the thermal decomposition and smoke suppression of poly (vinyl chloride) treated with metal oxides using a cone calorimeter at a high incident heat flux, Polym. Degrad. Stab. 78 (2002) 349–356.
[20] P.A. Atkinson, P.J. Haines, G.A. Skinner, Inorganic tin compounds as flame retardants and smoke suppressants for polyester thermosets, Thermochim. Acta 360 (2000) 29–40.
[21] H. Qu, W. Wu, Y. Zheng, J. Xie, J. Xu, Synergistic effects of inorganic tin compounds and Sb_2O_3 on thermal properties and flame retardancy of flexible poly (vinyl chloride), Fire Saf. J. 46 (2011) 462–467.
[22] J. Jang, J. Kim, J.-Y. Bae, Synergistic effect of ferric chloride and silicon mixtures on the thermal stabilization enhancement of ABS, Polym. Degrad. Stab. 90 (2005) 508–514.
[23] M. Batistella, B. Otazaghine, R. Sonnier, A.-S. Caro-Bretelle, C. Petter, J.-M. Lopez-Cuesta, Fire retardancy of ethylene vinyl acetate/ultrafine kaolinite composites, Polym. Degrad. Stab. 100 (2014) 54–62.
[24] F. Bertini, M. Canetti, G. Audisio, G. Costa, L. Falqui, Characterization and thermal degradation of polypropylene-montmorillonite nanocomposites, Polym. Degrad. Stab. 91 (2006) 600–605.
[25] L. Clerc, L. Ferry, E. Leroy, J.M. Lopez-Cuesta, Influence of talc physical properties on the fire retarding behaviour of (ethylene-vinyl acetate copolymer/magnesium hydroxide/talc) composites, Polym. Degrad. Stab. 88 (2005) 504–511.
[26] T. Havlik, D. Orac, M. Petranikova, A. Miskufova, F. Kukurugya, Z. Takacova, Leaching of copper and tin from used printed circuit boards after thermal treatment, J. Hazard. Mater. 183 (2010) 866–873.
[27] Y.-C. Chien, H.P. Wang, K.-S. Lin, Y.W. Yang, Oxidation of printed circuit board wastes in supercritical water, Wat. Res. 34 (17) (2000) 4279–4283.
[28] Y. Matsumoto, Y. Oshima, Au and Cu recovery from printed boards by decomposition of epoxy resin in supercritical water, J. Supercrit. Fluids 95 (2014) 462–467.
[29] F.-R. Xiu, Y. Qi, F.-S. Zhang, Leaching of Au, Ag, and Pd from waste printed circuit boards of mobile phone by iodide lixiviant after supercritical water pre-treatment, Waste Manag. 41 (2015) 134–141.
[30] J. Li, X. Xu, W. Liu, Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones, Waste Manag. 32 (2012) 1209–1212.
[31] F.-R. Xiu, Y. Qi, F.-S. Zhang, Co-treatment of waste printed circuit boards and polyvinyl chloride by subcritical water oxidation: removal of brominated flame retardants and recovery of Cu and Pb, Chem. Eng. J. 237 (2014) 242–249.
[32] E.M. Bulewicz, P.J. Padley, Mechanism of SnO_2 on flame retardant in polymer, in: In: Proceeding of the ninth symposium on combustion, New York, Academic Press, 1963, pp. 53–56.
[33] F.-R. Xiu, F.-S. Zhang, Recovery of copper and lead from waste printed circuit boards by supercritical water oxidation combined with electrokinetic process, J. Hazard. Mater. 165 (2009) 1002–1007.
[34] F.-R. Xiu, F.-S. Zhang, Electrokinetic recovery of Cd, Cr, As, Ni, Zn and Mn from waste printed circuit boards: effect of assisting agents, J. Hazard. Mater. 170 (2009) 191–196.