Removal of brominated flame retardant from electrical and electronic waste plastic by solvothermal technique

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ABSTRACT

Brominated flame retardants (BFRs) in electrical and electronic (E&E) waste plastic are toxic, bioaccumulative and recalcitrant. In the present study, tetrabromobisphenol A (TBBPA) contained in this type of plastic was tentatively subjected to solvothermal treatment so as to obtain bromine-free plastic. Methanol, ethanol and isopropanol were examined as solvents for solvothermal treatment and it was found that methanol was the optimal solvent for TBBPA removal. The optimum temperature, time and liquid to solid ratio for solvothermal treatment to remove TBBPA were 90 °C, 2 h and 15:1, respectively. After the treatment with various alcohol solvents, it was found that TBBPA was finally transferred into the solvents and bromine in the extract was debrominated catalyzed by metallic copper. Bisphenol A and cuprous bromide were the main products after debromination. The morphology and FTIR properties of the plastic were generally unchanged after the solvothermal treatment indicating that the structure of the plastic maintained after the process. This work provides a clean and applicable process for BFRs-containing plastic disposal.

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1. Introduction

With the market expansion of electrical and electronic (E&E) equipment during the last two decades, around 20–50 million tons of waste electrical and electronic equipment (WEEE) are generated worldwide every year [1]. Generally, WEEE contains 18% styrenic polymers such as acrylonitrile–butadiene–styrene (ABS), high impact polystyrene (HIPS) and polystyrene (PS) [2]. In view of the growing interest in the sustainable use of resources, recycle use of E&E waste plastic is becoming more and more important, especially since European commission published the directive on WEEE, which has set high recycling targets for E&E waste plastic [3,4]. Moreover, it should be noted that high concentration of brominated flame retardants (BFRs), mainly polybrominated diphenyl ether (PBDE) and tetrabromobisphenol A (TBBPA) [5,6], were added to plastic matrices during the manufacture of E&E equipment to increase the fire resistance of the product. Owing to the lipophilic and bioaccumulative nature of these BFRs [7], the recovery of E&E waste plastic has further become a challenging task for decades.

Various technologies, including landfills [8], incineration [9], pyrolysis [10] and mechanical recycling [11] have been developed for disposal of E&E waste plastic. However, among these techniques, contamination by harmful bromine-containing compounds is inevitable [8–11]. Elimination of BFRs before recycling E&E waste plastic and following destruction of BFRs is imperative to reduce such negative environmental effects.

A promising way of removing BFRs from E&E plastic is supercritical carbon dioxide (Sc-CO$_2$) extraction, in which harmless plastic as well as high-priced BFRs were recycled [12]. Further studies [13] indicated that the removal efficiency of BFRs by solvent extraction was better than that of Sc-CO$_2$ modified with solvents. Recently, we have revealed that solvothermal process was a powerful method to remove organic pollutants from soil matrix [14]. As a consequence, we applied this technique to the removal of BFRs from E&E waste plastic. As for dehalogenation of aromatic halides, a few methods using metals (Fe, Ni, Zn, etc.) were developed thus far [15–20]. Among these studies, it was discovered that metallic calcium in ethanol was highly effective at ambient temperature [15,16]. Moreover, copper has been extensively studied due to possible Ullmann reactions (i.e. coupling of aryl halides with copper) [17–20]. Meanwhile, zinc dust/sodium hydroxide/ammonium formate system is highly effective for the debromination of TBBPA to bisphenol A [21]. Therefore, we also combined these methods to conduct the debromination of BFRs. To our knowledge, there is no report regarding application of solvothermal procedure for the removal and debromination of BFRs from E&E waste plastic.

The primary objective of this study was to evaluate the effectiveness of solvothermal procedure for the removal of BFRs from E&E waste plastic. Effects of various conditions on BFRs removal efficiency were evaluated, and a suitable procedure for debromination of BFRs in organic solvent was also established.

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2. Experimental

2.1. Materials

Waste computer housing plastic was supplied by HuaXing Environment Protection Co. Ltd. The plastic, which was ABS resin with TBBPA as additive flame retardant, was cut into small pieces and ground to 14–20 mesh by a grinder under cooling with liquid nitrogen. HPLC grade acetone, methanol, ethanol and isopropanol were purchased from J&K Chemical Ltd., USA. Standard stock solution of bromine ion (1000 mg/L) was purchased from the National Research Center for Certified Reference Materials of China and TBBPA (≥97% purity) was supplied by ACROS Ltd., USA. Anhydrous sodium sulfate (Na_2SO_4) and copper powder (200 mesh) were analytical reagents from domestic manufacturers.

2.2. Experimental procedures

A series of reactors consisted of 100 mL Teflon interiors and stainless exteriors were employed for the solvothermal experiments. In a typical run, a certain amount of organic solvent and weighed plastic were introduced into a reactor and the reactor was sealed. The reactor was then placed into an oven, raised to the desired temperature and held for a specified time. On the termination of the reaction, the mixture was separated by centrifugation (10,000 g, 10 min, TG16-WS, China). The solid phase was allowed to air-dry overnight, followed by oxygen bomb combustion and ion chromatography (IC) analysis to determine the bromine content in the solid phase. The solvent phase was first evaporated on the vacuum rotary evaporator for solvent substitution with acetone and then dehydrated by anhydrous sodium sulfate. After concentrated, the solvent phase was transferred to Kuderna–Danish (K–D) concentrator and evaporated to 1 mL under a stream of nitrogen flow for gas chromatography–mass (GC/MS) analysis of TBBPA.

There solvents, i.e. methanol, ethanol and isopropanol were examined to compare their solvothermal removal efficiency for TBBPA. The temperature varied from 50 °C to 170 °C at constant time and liquid to solid ratio, the treating time varied from 0.5 h to 15 h at constant temperature and liquid to solid ratio, and the liquid to solid ratio varied from 5:1 to 20:1 (mL/g) at constant temperature and time were performed to optimize the parameters of solvothermal process to remove TBBPA.

Since it is hard to separate copper and plastic if they were combined and this is unfavorable for recycle use of copper and plastic, only the solvent extract and copper powder were combined for possible debromination of TBBPA. In this section, methanol extract (15 mL) and copper powder (0.50 g) were introduced to the 100 mL Teflon interior placed inside the stainless exterior. The reactor was sealed, placed into the oven, and the temperature was increased to 150 °C and maintained for 10 h. After cooling to room temperature, the mixture was separated by centrifugation (10,000 g, 10 min, TG16-WS, China). The spent copper powder was allowed to air-dry and subjected to X-ray diffraction (XRD) analysis. The liquid product was subjected to GC/MS and high performance liquid chromatography (HPLC) analysis after solvent substitution and sodium sulfate dehydration. This mixture of methanol extract (15 mL) and copper powder (0.50 g) was also stirred at room temperature for 24 h and compared with the above results.

2.3. Analytical procedures

The oxygen bomb combustion-IC was applied for the analysis of bromine content in raw plastic and solid phase after solvothermal treatment [22,23]. In a typical run, 10 mL Milli-Q water (Millipore, USA) was transferred to the bomb with moistening of its inner surface. Accurately weighed solid sample (0.2–0.5 g) was placed into a stainless steel capsule. The bomb was assembled and purged with oxygen for 1 min. The bomb was then immersed in a water bath at room temperature, ignited by an electric discharge and kept in the water bath for 30 min. After the pressure of the bomb was reduced, the sample capsule and the interior of the bomb were rinsed with Milli-Q water and collected in a 100 mL volumetric flask. The sample solution was filtered through a 0.45 μm membrane filter before IC analysis. IC analysis was performed using an ion chromatograph (ICS-2000, Dionex, USA) with an IonPac AS18 (4 mm × 250 mm) analytical column and IonPac AG18 (4 mm × 50 mm) guard column, coupled to an ASRS-300 4 mm suppressor. Hydroxide eluent gradients were generated online using EGC II KOH cartridge. A continuously regenerated anion trap column (CR-ATC) was installed at the EGC eluent outlet. The optimized hydroxide eluent gradient was: 0–7 min: 12 mM isocratic; 7–8 min: gradient from 12 to 40 mM; 8–15 min: 40 mM isocratic; 15–20 min: 12 mM isocratic.

As for the identification of bromine in the spent copper powder, spent copper powder (0.50 g) was stirred in 10 mL of 0.1 M HNO_3 for 24 h. On the termination of the reaction, the mixture was separated by centrifugation (10,000 g, 10 min, TG16-WS, China). The obtained solution was used in Mohr's titration [15] after adjusting pH to 6.5–10.5 with 1 M $NaHCO_3$.

TBBPA in solvent phase was analyzed by an Agilent 7890A gas chromatograph equipped with an Agilent 5975 C mass spectrometry detector and a HP-5 capillary column (USA). High purity He was used as carrier gas with a flow rate of 1 mL/min. The column temperature of chromatographic analysis was programmed as follows: the initial oven temperature was set at 50 °C and ramped to 150 °C at 20 °C/min, then to 180 °C at 10 °C/min, finally to 280 °C at 3 °C/min hold for 2 min. HPLC analysis was accomplished by Agilent 1200 (USA) with a C_{18} reversed-phase column (150 mm × 4.6 mm, 5 μm particles, Agilent, USA), a diode array detector and an auto sampler controlling under a Chemstation data acquisition system. The measurement was performed in a methanol/water = 85:15 (v/v) as mobile phase with a flow rate of 1 mL/min and a detection wavelength of 230 nm. The type of plastic was identified by in situ Fourier transform infrared (FTIR) spectrometer (BrukerTensor27). XRD analysis was carried out using Philips PW 1700 X-ray diffractometer.

Procedure blanks were run to determine background levels. Blank levels for the solvothermal procedure were typically ≤3% of the concentrations of TBBPA in the samples. The presented concentrations were corrected accordingly. Bromine ion was not detected in blank test for oxygen bomb combustion. Each experiment was carried out in triplicate for parallel test, and average values with standard errors were reported.

3. Results and discussion

3.1. Characterization of the solvothermal products

The chromatogram of solvent phase by solvothermal treatment reveals TBBPA was the major component of extract in all cases (Fig. 1), followed by corresponding hexadecanoic esters and octadecanoic esters. As shown in Fig. 1(a)–(c), ethyl ester, methyl ester and isopropyl ester of hexadecanoic acid and octadecanoic acid were formed respectively with ethanol, methanol and isopropanol as solvents, which means a small amount of alcohol solvents participated the reaction. These products were not observed under milder conditions such as lower temperature and less time (Fig. 1(d) and (e)). Five TBBPA calibration solutions were prepared for the quantification and the corresponding bromine contents were calculated according to the chemical formula of TBBPA.

Oxygen bomb combustion-IC analysis of raw plastic indicated that the bromine content accounted for 7.45% of the total plastic
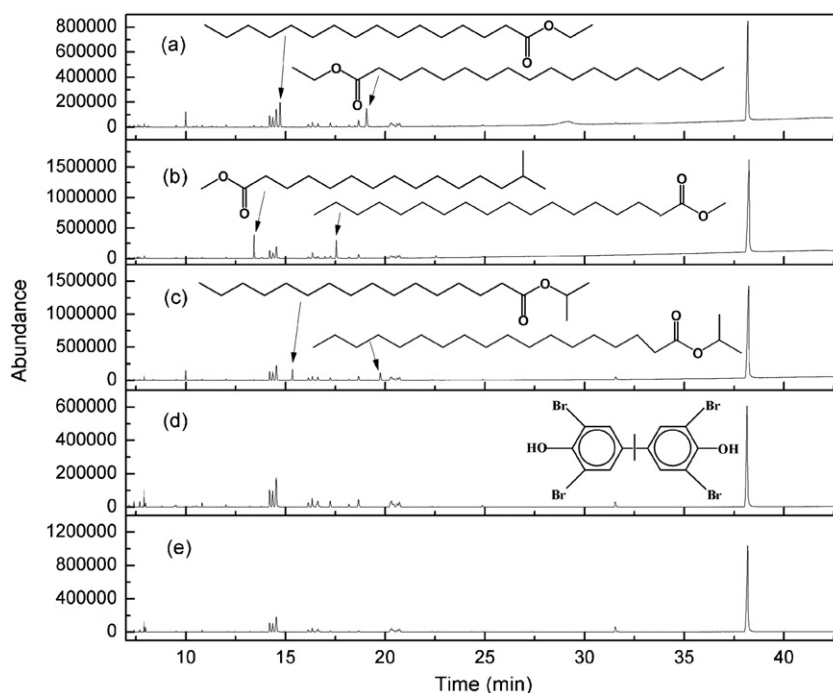
Fig. 1. GC/MS chromatograms of the solvothermal extracts. Solvents, temperature, time and liquid to solid ratio conditions: (a) ethanol, 150 °C, 10 h, 15:1; (b) methanol, 150 °C, 10 h, 15:1; (c) isopropanol, 150 °C, 10 h, 15:1; (d) isopropanol, 50 °C, 10 h, 15:1; (e) isopropanol, 150 °C, 30 min, 15:1.

(wt.%). After solvothermal treatment at 90 °C for 2 h, the residue amount of bromine in the plastic was reduced to 1.87% (wt.%). Further treatment under the same condition showed that no bromine was detected in the plastic. This result confirmed the feasibility of solvothermal procedure for TBBPA removal from E&E waste plastic.

3.2. Optimization of solvothermal procedure

The solvent property plays a critical role in solvothermal treatment of additive BFRs from plastic. The solvent should have high affinity for both BFRs and the plastic, inducing certain swelling effects in the plastic but without causing dissolution of plastic, as also demonstrated by previous studies [2,24]. Meanwhile, the use of hazardous solvents should also be avoided. Alcohol solvents such as methanol, ethanol and isopropanol were thus considered. As can be seen from Fig. 2, all of the selected solvents achieved high TBBPA removal efficiency. Previous reports [24,25] have also indicated that alcohol solvents, which may not perform as good extraction solvent at moderate pressure and temperature, can be efficiently employed for accelerated solvent extraction. The bromine contents in the solid phase were 19.3%, 17.8% and 17.0% of total bromine respectively with methanol, ethanol and isopropanol as solvents. This indicated that there was no significant difference in the removal efficiency of TBBPA between these solvents. Furthermore, the loss of bromine content was calculated by subtracting the bromine content of solid phase and solvent phase from the initial bromine content of raw plastic. It should be noted that there were 2.4%, 29.8% and 12.2% losses of bromine in methanol, ethanol and isopropanol respectively. According to previous reports, these different losses of bromine could be attributed to the different polarities of the solvents [2] and the solubility of TBBPA in the solvents [26–28]. Previous studies have also indicated that the storage of hexabromocyclododecane in *n*-hexane, isooctane and acetonitrile resulted in loss of hexabromocyclododecane [26–28]. All of these findings indicated that the loss of hexabromocyclododecane in solvent was attributed to glass absorbance due to the low solubility of hexabromocyclododecane in these solvents. In this study,

methanol is considered as superior solvent because of the minimum loss of bromine. Accordingly, it is necessary to determine the optimal solvent for maximum recovery and minimum loss of BFRs, as also demonstrated by Bandh et al. [29].

Fig. 3 shows that bromine in solvent increased with temperature below 90 °C and then basically kept constant in a certain range at higher temperature (90–170 °C). This implies that certain intermolecular bonds between TBBPA and plastic can easily be broken at higher temperatures, and this is probably the decisive advantage of solvothermal procedure. Meanwhile, certain temperature range (>90 °C) cannot promote the further removal of TBBPA remarkably (Fig. 3). According to previous reports [2,24], diffusion rates of BFRs, both in the plastic core and in the boundary layer around the plastic surface were higher at elevated temperatures. The solubility of BFRs in the solvent and the mass transfer from the boundary layer
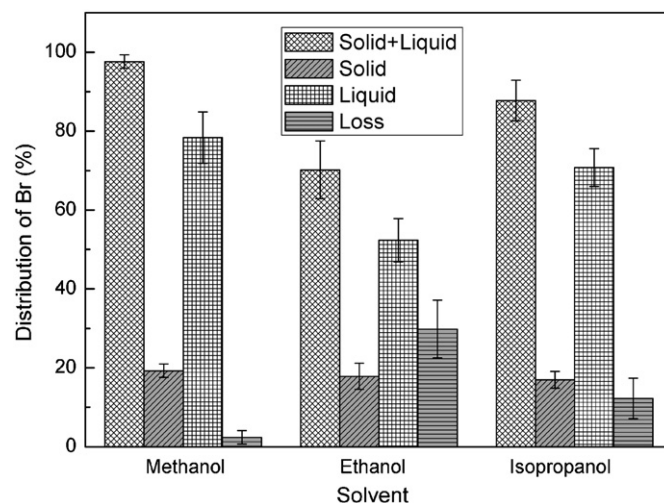

Fig. 2. Effect of solvent type on Br distribution. Conditions: temperature 150 °C; time 10 h; liquid to solid ratio 15:1.
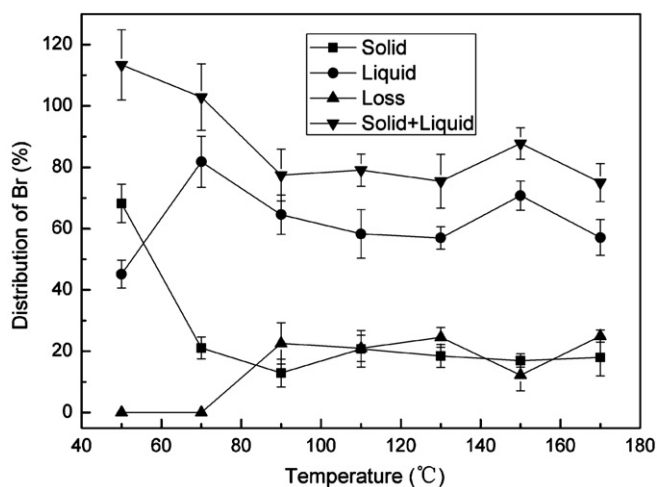
Fig. 3. Effect of temperature on Br distribution. Conditions: solvent isopropanol; time 10 h; liquid to solid ratio 15:1.

Fig. 5. Effect of liquid to solid ratio on Br distribution. Conditions: solvent isopropanol; temperature 150 °C; time 10 h.

to the solvent were enhanced at increased temperatures [2,24]. Moreover, the swelling ratio between the plastic and the solvent was also influenced by temperature [2,24]. Thus, temperature plays an essential role in the extraction process. By contrast, the residue amount of bromine in the solid phase decreased rapidly with a drastic drop at lower temperature (50–90 °C) and then remained almost the same below 170 °C. In this case, 90 °C is considered as optimal temperature with the lowest remaining of bromine in plastic after solvothermal treatment.

As demonstrated in Fig. 4, the effect of time on bromine distribution had similar trend with the temperature. The bromine in solvent increased as the prolonging of time till about 2 h and then remained basically unchanged. The residue amount of bromine in plastic achieved lowest after 2 h treatment. It also should be noted that, the bromine in solid phase decreased rapidly initially and then varied in a certain range as the increase of liquid to solid ratio (Fig. 5). The lowest remaining of bromine in plastic was achieved till the liquid to solid ratio was 15:1. Under this condition, a period of 2 h and a liquid to solid ratio of 15:1 were adequate to obtain maximum removal efficiency.

The foregoing results were in accordance with previous reports [2,25,30,31], which suggested that the extraction efficiency was conditioned by the plastic, as well as the molecular weight and
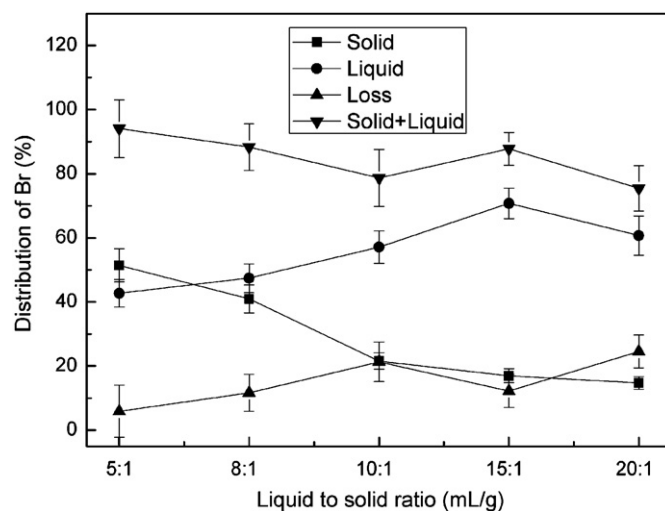
polarity of BFRs. The temperature and time were the most significant factors for extraction process. Meanwhile, other conditions such as solvent and particle size had no significant effects on BFRs removal as discussed for microwave-assisted extraction [2,31].

3.3. Advantages of the solvothermal process

Compared with conventional extraction processes, solvothermal procedure consumes less solvent, shortens extraction time, shows better applicability and broadens the range of solvent type, as also demonstrated by Lou et al. for accelerated solvent extraction [24]. In previous reports [13], toluene has been extensively examined as an efficient solvent in conventional extraction processes to remove BFRs from waste plastic. However, toluene is a kind of highly toxic chemical, thus alcohol solvents obviously show superiority over toluene.

Similar to the process of accelerated solvent extraction [24], the superior removal performance of solvothermal procedure was attributed to the enhanced temperature and slightly higher pressure as compared to conventional extraction processes. In the solvothermal procedure, BFRs are extracted at temperatures above the boiling point of solvents. Contrarily, in conventional extraction processes such as Soxhlet, the temperature is limited by the boiling
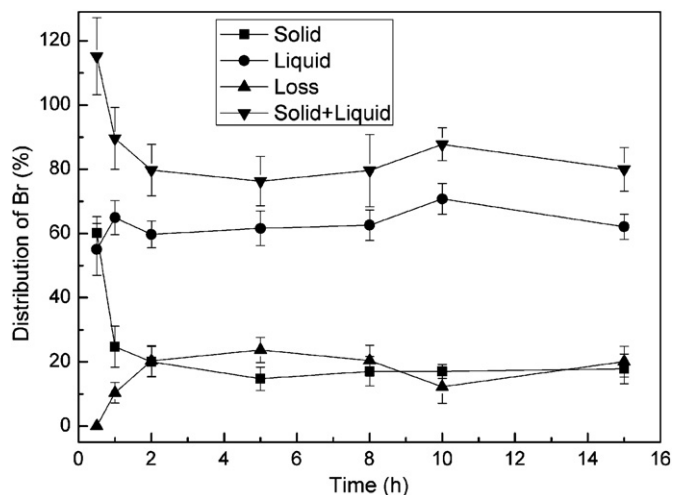

Fig. 4. Effect of time on Br distribution. Conditions: solvent isopropanol; temperature 150 °C; liquid to solid ratio 15:1.
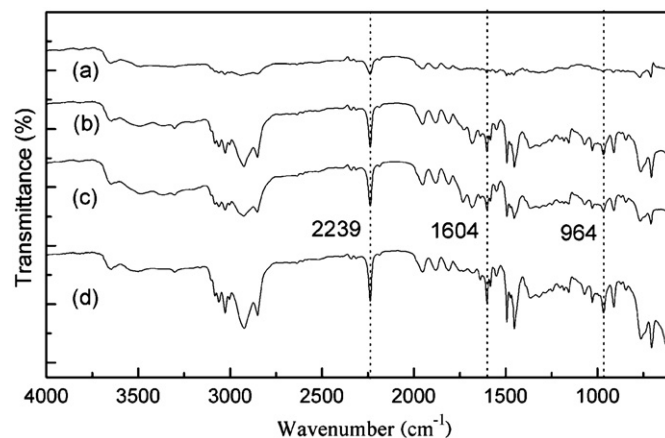

Fig. 6. FTIR spectra of the residues after solvothermal treatments by (a) no solvent, (b) ethanol, (c) methanol, (d) isopropanol; conditions: temperature 150 °C; time 10 h; liquid to solid ratio 15:1.
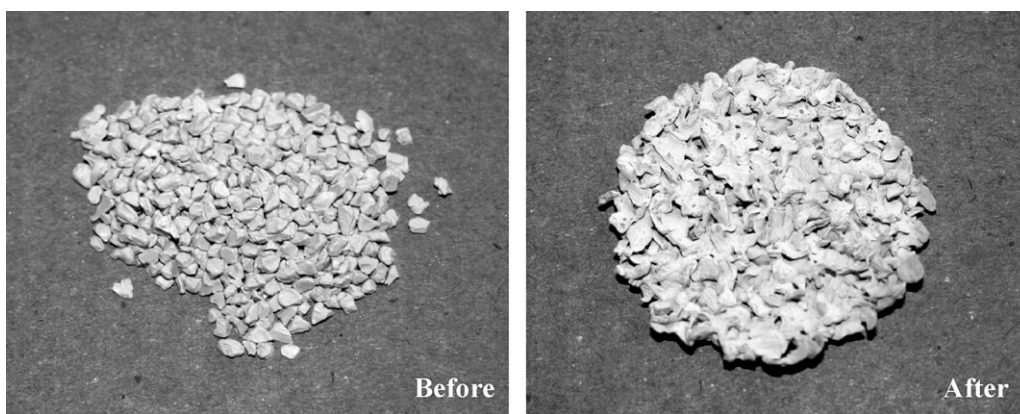
Fig. 7. Morphology of the plastic before and after solvothermal treatment. Conditions: solvent isopropanol; temperature 90 °C; time 2 h; liquid to solid ratio 15:1.

point of solvents. Since the kinetics of mass transfer are greatly improved at elevated temperature, a poor solvent in conventional extraction can thus be a good solvent in solvothermal process at higher temperatures. Although pressure had no effect on the accelerated solvent extraction [24], the role of pressure was important in that a slight higher pressure kept the solvent in the liquid phase at a high temperature as described by Gan et al. [32] for accelerated solvent extraction.

Obviously, as a practical technique to remove BFRs from plastic, solvothermal procedure must not significantly affect structure of the plastic. As shown in FTIR spectra of raw plastic (Fig. 6), the broad band in the region 2800–3000 cm^{-1} are assigned to vibrations of saturated C–H or CH$_2$; the band at 3000–3100 cm^{-1} correspond to aryl-H stretching. The strong peak at 1604 cm^{-1} is attributed to vibration of styryl (C=C aromatic), and the peaks at 964 cm^{-1} and 2239 cm^{-1} are respectively assigned to the vibration of butadienyl and nitrile group [13]. This result confirms that the sample is typical ABS resin. Fig. 6 further indicates that similar profiles were obtained before and after solvothermal treatment except that the peaks were slightly sharper after treatment. Additionally, the morphology of plastic (Fig. 7) was almost the same before and after treatment except for slight agglomeration of plastic. Since halogen-free plastic were valuable resources for recovery of energy and chemical feed-stocks, solvothermal procedure is of great superiority for safety disposal of plastic especially by virtue of less damaged structure.

3.4. Debromination of TBBPA in the presence of copper

According to the GC–MS profiles (Fig. 8), copper powder has significant effects on the debromination of TBBPA in methanol. TBBPA residue was less than 12.3% after the reaction stirred at room temperature with metallic copper, and was not detected after reaction with metallic copper in solvothermal reactor at 150 °C. It means that metallic copper in alcohol solvents is highly effective for the debromination of TBBPA. This is consistent with previous reports [15,16], which demonstrated that the dechlorination of polychlorinated biphenyls easily took place by a simple stirring procedure at room temperature for 24 h using metallic calcium in ethanol. Luo et al. [33,34] also described the degradation behavior of TBBPA in Fe–Ag suspension solutions under ultrasonic radiation and revealed that TBBPA was completely degraded over Fe–Ag nanoparticles. The HPLC analysis further shows that no TBBPA peak was observed after reaction in solvothermal reactor. The presence of metallic copper is thus an efficient and environmental-friendly method for complete debromination of TBBPA in alcohol solvents.

Meanwhile, HPLC profiles imply that bisphenol A was the main debromination product, in accordance with previous reports
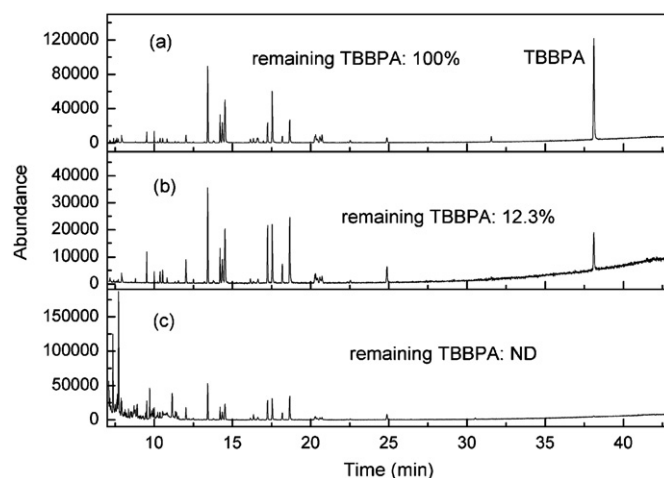

Fig. 8. GC/MS chromatograms of the extracts after reaction with (a) no copper; (b) copper stirred at room temperature; (c) copper heated at 150 °C.

[21,33,34]. The XRD pattern of spent metallic copper is described in Fig. 9. The three peaks, which appeared at 43.29 (main peak), 50.42 and 74.16°, correspond to copper diffraction peaks. The characteristic peak of cuprous bromide (CuBr) was clearly observed, indicating that bromine was mainly in the form of cuprous bromide. The identification of bromine in the spent copper powder was also confirmed by Mohr's titration method. According to previ-
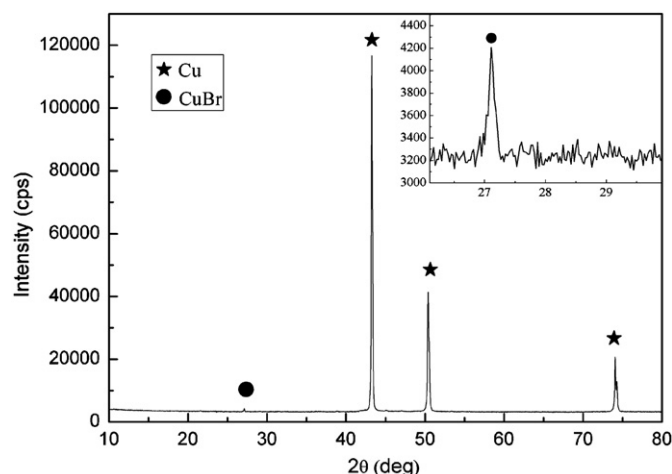

Fig. 9. XRD pattern of spent copper powder.

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ous reports [15,16], chlorine was also identified as calcium chloride after polychlorinated biphenyls, metallic calcium and ethanol were stirred at room temperature for 24 h. The formation of bisphenol A and cuprous bromide in this study was attributed to the Ullmann reaction [17,19]. It has been reported that under conditions of the Ullmann reaction, the presence of organic acids, alkanols and water as hydrogen donors result in formation of hydrodehalogenation products [19]. The following dehalogenation reactions were thus represented [19]:

$$ArX + 2Cu \rightarrow ArCu + CuX$$

$$ArCu + H^+ \rightarrow ArH + Cu^+$$
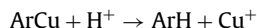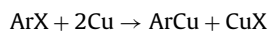
4. Conclusions

This study demonstrated that solvothermal process was a practical and efficient technique for BFRs-containing E&E plastic disposal. A complete removal of BFRs with wide range of solvent type, low solvent consumption, and short extraction time was achieved. Alcohol solvents, such as methanol, ethanol and isopropanol have no significant difference on the removal efficiency of BFRs, but resulted in different bromine losses. Methanol was the optimal solvent for solvothermal treatment to remove TBBPA and the optimum temperature, time and liquid to solid ratio were 90 °C, 2 h and 15:1, respectively. Metallic copper was effective for debromination of TBBPA in alcohol solvents, while bisphenol A and cuprous bromide were the main products. The structure of the plastic was maintained after the solvothermal process, which could be easily recycled as common plastic.

Acknowledgements

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