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Short communication

Recovery of triphenyl phosphate from waste printed circuit boards by solvothermal process

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HIGHLIGHTS

- A process for triphenyl phosphate (TPPO) recovery from PCBs was established.
- The structure of recycled TPPO was in good agreement with TPPO standard material.
- The PCBs became phosphorus-free with structure and inorganic components maintained.
- The kinetics analysis of solvothermal process was evaluated and better understood.

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ABSTRACT

Organophosphorus flame retardants (PFRs) have been largely used in waste printed circuit boards (PCBs) because of the regulation of brominated flame retardants (BFRs) in recent years. In the present study, triphenyl phosphate (TPPO), a typical PFR, contained in waste PCBs was tentatively subjected to solvothermal treatment in order for efficient recycling of this type of valuable resource. Experimental results showed that the optimum operation temperature, time and liquid to solid ratio for TPPO removal were 90 °C, 120 min and 10:1, respectively. After solvothermal treatment, TPPO was transferred into the solvents and solid TPPO powder was easily recovered through vacuum rotary evaporation. The TPPO recovery efficiency reached 84.4% in a purity of 93.4% and dephosphorization efficiency of waste PCBs reached 97.3%. Shrinking core model (SCM) indicated that both interface transfer and internal diffusion affected the recovery rate of TPPO in the solvothermal process. Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) profiles of the recycled TPPO were in good agreement with TPPO standard material indicating that the structure of the recycled TPPO maintained after the recovery process. This work provides a clean and applicable process for PFRs recovery from waste PCBs.

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1. Introduction

Organophosphorus flame retardants (PFRs) have been largely used in waste printed circuit boards (PCBs) because of the regulation of brominated flame retardants (BFRs) in recent years [1]. In 2004, for example, the global production volume of PFRs amounted to 14% of total flame retardants, while that of BFRs accounted for 21% [2]. These PFRs including arylated, alkylated and chloroalkylated phosphate esters are extensively used in industrial polymeric materials such as plastic, lubricants, hydraulic fluids and electrical and electronic equipments [3]. In most cases, PFRs are used as additive chemicals and not covalently bound to polymeric materials [1,2], which may migrate out from the materials, emit into the surrounding environment and pose a threat to human health [1,4]. Take triphenyl phosphate (TPPO) as example, which is widely used as a plasticizer and flame retardant in waste PCBs, it is a potent inhibitor of human blood monocyte carboxylesterase and has shown hemolytic toxicity [3]. Owing to these negative biological effects of PFRs in polymeric materials, treatment of PFRs before recycling polymeric materials is urgently desired.

Various technologies, including biotransformation [5], photochemical transformation [6] and thermal decomposition [7] have been developed for treatment of flame retardants, which mainly focused on the characterization of degradation products [8] using flame retardant chemicals without consideration of matrix effects. The reported treatments for polymeric materials containing flame retardants mainly include landfills [9], incineration [10], pyrolysis [11] and mechanical recycling [12]. Among these techniques, contamination by harmful compounds is inevitable [9–12]. Obviously, transferring flame retardants from polymeric materials to the solvent and recycle flame retardants through rotary evaporation procedure is a simple and practicable technique for disposal of flame retardants in polymeric materials.

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Supercritical carbon dioxide (Sc-CO_2) extraction is a promising way to remove flame retardants from polymeric materials, in which harmless polymeric materials and high-priced flame retardants were recycled [13,14]. But it is noteworthy that, high pressure of Sc-CO_2 means high energy cost and equipment requirement, which have become challenges faced by Sc-CO_2 to recycle flame retardants [15]. Solvothermal process is usually conducted at lower pressure in comparison with Sc-CO_2. Recently, we have revealed that solvothermal process was a powerful method to remove BFRs from electrical and electronic waste plastic [16]. As a consequence, we applied this technique to transfer TPPO from waste PCBs to the solvent followed by recycling TPPO through rotary evaporation procedure. To our knowledge, only limited works focused on the occurrence and behavior of PFRs in water, indoor air and the atmospheric environment as well as analytical methods for the determination of PFRs from environmental samples [17,18]. There is no report focused on application of solvothermal procedure for the recovery of PFRs from waste PCBs.

The primary objective of this study was to evaluate the effectiveness of solvothermal procedure for the recovery of PFRs from waste PCBs. Effects of various conditions on the recovery of PFRs were evaluated, and a suitable procedure for PFRs recovery was established.

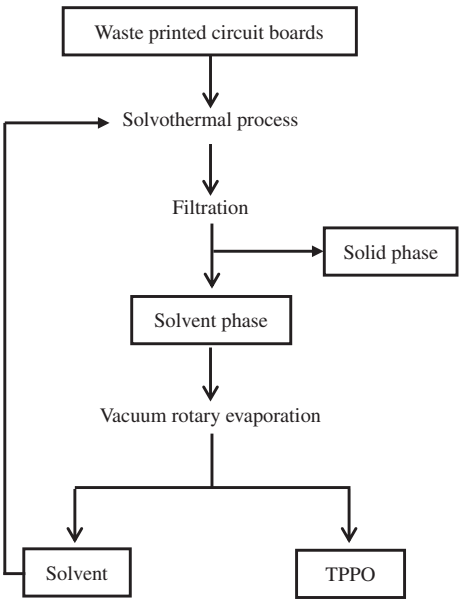

Fig. 1. Schematic diagram of TPPO recovery process.

2. Experimental section

2.1. Materials

Waste PCBs used in this work were supplied by XIAMEN OASIS Sources Co., Ltd. The PCBs with TPPO as additive flame retardant were cut into small pieces and ground to powder by a grinder after the electronic components such as capacitors, relays were disassembled. HPLC grade acetone and methanol were purchased from J&K Chemical Ltd., USA. Standard of TPPO was obtained from Accu-Standard Inc., USA. Anhydrous sodium sulfate (Na_2SO_4) was analytical reagent from domestic manufacturer.

2.2. Experimental procedures

Fig. 1 shows the schematic diagram of TPPO recovery process. Solvothermal experiments were carried out by using a series of reactors consisted of 100 mL Teflon interiors and stainless exteriors. In a typical run, weighed PCBs and a certain amount of methanol were introduced into the reactor. The reactor was sealed, placed into an oven and held at the desired temperature for a specified time. On the termination of the reaction, the reactor was cooled quickly to room temperature. The mixture was separated by centrifugation (10,000 g, 10 min, TG16-WS, China). The solid phase was allowed to air-dry overnight and subjected to analyses of X-ray diffraction (XRD) and X-ray fluorescence (XRF). The solvent phase was first concentrated on the vacuum rotary evaporator for solvent substitution with acetone and dehydrated by anhydrous sodium sulfate. Then the solvent phase was transferred to Kuderna–Danish (K–D) concentrator and evaporated to 1 mL using evaporation with gentle stream of nitrogen for gas chromatography–mass (GC/MS) analysis of TPPO.

Different treating temperatures (50, 70, 90, 110, 130, 150, 170 °C), times (15, 30, 45, 60, 75, 90, 105, 120, 180, 240 min) and liquid to solid ratios (5:1, 8:1, 10:1, 15:1, 20:1) were performed so as to optimize the parameters of solvothermal process. The solvent phases were collected and evaporated on the vacuum rotary evaporator to obtain recycled TPPO powder. The recycled TPPO powder was subjected to analyses of Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR).

2.3. Analytical procedures

The energy dispersive XRF spectrometer (XRF-1800, Schimadu, Japan) was applied for the analysis of phosphorus content in waste PCBs before and after treatment. TPPO in solvent phase was analyzed by an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass spectrometry detector and autosampler (USA). Chromatographic separation was accomplished with a HP-5 capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) using splitless injections. High purity He was used as carrier gas with a constant flow rate of 1 mL/min. The column temperature of chromatographic analysis was programmed as follows: the initial temperature was set at 50 °C and then ramped to 150 °C at 20 °C/min, increased to 180 °C at 10 °C/min, finally increased to 280 °C at 3 °C/min holding for 2 min. The purity of TPPO was characterized by peak area ratio method of GC/MS analysis. The FTIR analysis was accomplished by in situ FTIR spectrometer (Bruker-Tensor27). The ^{13}C and ^{1}H NMR spectra were used to identify the recycled TPPO, which were tested in chloroform-d on a JEOL 600 MHz spectrometer (Tokyo, Japan) at room temperature. XRD analyses of waste PCBs before and after treatment were carried out using Philips PW 1700 X-ray diffractometer.

Each experiment was carried out in triplicate for parallel test, and average values with standard errors were reported. Procedure blanks were run to determine background levels. Blank levels for the solvothermal procedure were typically $\leqslant$1% of the contents of TPPO in the samples. The presented values were corrected accordingly. Statistical analysis of the results was performed in SPSS 19.0 (SPSS Inc., USA).

3. Results and discussion

3.1. Dephosphorization efficiency

XRF analysis of waste PCBs indicated that the phosphorus content accounted for 1.83% of the total waste PCBs (wt.%). Based on chemical formula of TPPO, it was calculated that TPPO content amounted to 19.3% of the original waste PCBs (wt.%). After solvothermal treatment at 90 °C for 2 h, phosphorus in the residue was reduced to 0.19% (wt.%), indicating that 89.6% of TPPO was

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