Short communication

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

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H I G H L I G H T S

- 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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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-CO₂) 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-CO₂ means high energy cost and equipment requirement, which have become challenges faced by Sc-CO₂ to recycle flame retardants [15]. Solvothermal process is usually conducted at lower pressure in comparison with Sc-CO₂. 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.

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 (Na₂SO₄) 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).

Fig. 1. Schematic diagram of TPPO recovery process.

2.3. Analytical procedures

The energy dispersive XRF spectrometer (XRF-1800, Shimadzu, 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 ¹³C and ¹H 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 ≤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

removed from the PCBs sample. Further treatment showed that only 0.05% of phosphorus was detected by XRF analysis and the dephosphorization efficiency of solvothermal treatment for waste PCBs reached 97.3%. The increase of dephosphorization efficiency after further treatment was mainly relevant to the concentration of TPPO in solvothermal extract. In the initial solvothermal process, TPPO constantly diffused from the polymer into the extraction solvent since the concentration of TPPO in the polymer was higher than the extraction solvent. As the solvothermal process continued, diffusion force decreased with the decrease of TPPO concentration difference between the polymer and the extraction solvent. The increased viscosity of solvothermal extract further limited the increase of dephosphorization efficiency. The foregoing results demonstrated the feasibility of solvothermal procedure for TPPO removal from waste PCBs.

As shown in FTIR spectra (Fig. 2), similar profiles of waste PCBs were obtained before and after solvothermal treatment. The XRD patterns of waste PCBs before and after treatment are described in Fig. 3. The main characteristic peaks of waste PCBs before and after treatment correspond to copper, tin and lead. Similar XRD patterns of waste PCBs were obtained except that the intensity of tin and lead diffraction peaks slightly reduced after solvothermal treatment. This indicated that the inorganic components were greatly maintained. Since waste PCBs were also valuable resources for recovery of chemical feed-stocks and metals such as copper, solvothermal procedure is of great superiority for recovery of flame retardants especially by virtue of less damaged structure and basically unchanged inorganic components.

3.2. Recycled TPPO

The chromatogram of solvent phase after solvothermal treatment reveals that TPPO is the major component of the extract (Fig. 4). After further vacuum rotary evaporating treatment of this phase, brown TPPO powder was obtained, showing the impurity of the product. Fig. 4 illustrates that a small quantity of impurities was observed due to the dissolution of polymeric materials [13]. By comparing the peak areas of the GC/MS profiles for the recycled TPPO and TPPO standard material, it was calculated that the purity of the recycled TPPO was 93.4%.

Obviously, as a practical technique to recycle TPPO from waste PCBs, solvothermal procedure must not significantly affect structure of TPPO. As shown in FTIR spectra of recycled TPPO and pure TPPO (Fig. 5), the band at 3100–3000 cm^{-1} correspond to aryl-H

Fig. 3. XRD patterns of waste PCBs before and after solvothermal treatment. Conditions: solvent methanol; temperature 90 °C; time 120 min; liquid to solid ratio 15:1.

stretching [13]; the strong peak at 1300 cm^{-1} is attributed to the vibration of P=O; the broad band in the region 1220–1165 cm^{-1} and 965–950 cm^{-1} are respectively assigned to the vibrations of C–O and P–O. Similar FTIR profiles of recycled TPPO and pure TPPO were obtained except that the peaks of pure TPPO were sharper.

The ^{13}C NMR spectra of recycled TPPO and pure TPPO (Fig. 6a) show 4 separate signals for 18 carbons present in TPPO. As demonstrated in Fig. 6a, the peak with δ_{C} of 76.90 ppm is related with the carbon of chloroform-d; the relative high chemical shift at 151.83 ppm is assigned to the C (f, k, m); the signal at 129.53 ppm is ascribed to the C (b, d, g, i, o, q); the peak at 125.76 ppm and 120.81 ppm are respectively attributed to the C (c, h, p) and C (a, e, j, l, n, r). This result shows that aromatic carbon in ^{13}C NMR spectra located in the δ_{C} region of 110–160 ppm [19]. The different chemical shifts of carbon on the phenol ring were attributed to the conjugation arising from the phenol ring and oxygen, which resulted in different relative locations between carbon and oxygen. According to the ^1H NMR spectra of recycled TPPO and pure TPPO (Fig. 6b), the relative high chemical shift at 7.26 ppm is assigned to the H (b, d, g, i, o, q); the signal at 7.19 ppm is ascribed to the H (c, h, p) and the peak at 7.15 ppm is attributed to the H (a,

Fig. 2. FTIR spectra of waste PCBs before and after solvothermal treatment. Conditions: solvent methanol; temperature 90 °C; time 120 min; liquid to solid ratio 15:1.

Fig. 4. GC/MS chromatogram of the solvothermal extract. Conditions: solvent methanol; temperature 90 °C; time 120 min; liquid to solid ratio 15:1.

Fig. 5. FTIR spectra of the recycled TPPO and pure TPPO. Conditions: solvent methanol; temperature 90 °C; time 120 min; liquid to solid ratio 15:1.

Fig. 6. NMR spectra of the recycled TPPO and pure TPPO in chloroform-d: (a) ^{13}C and (b) ^1H . Conditions: solvent methanol; temperature 90 °C; time 120 min; liquid to solid ratio 15:1.

e, j, l, n, r). This indicated that the ^1H NMR signals of protons on phenyl ring located in the δ_{H} region of 6–8.5 ppm [19]. Similar ^{13}C and ^1H NMR profiles of recycled TPPO and pure TPPO further confirm that the obtained product is typical TPPO.

3.3. Optimization of operating parameters

Solvent property is an important factor for flame retardants removal from waste polymeric materials [20,21]. The solvent should have high affinity for both flame retardants and the polymeric materials and induce certain swelling effects in the polymeric materials without causing dissolution of polymeric materials [21]. Moreover, the use of hazardous solvents should be avoided. Recently, we have revealed that methanol was optimal solvent for maximum recovery and minimum loss of BFRs [16] and the range of solvents applicable in solvothermal process was much wider than conventional extraction processes due to higher temperatures and pressures, e.g., alcohol solvents, which may not perform as good extraction solvents at moderate pressure and temperature [20], were efficiently employed for solvothermal process. Methanol was thus considered for the recovery of TPPO especially due to its low toxicity.

Temperature has a dramatic effect on the removal of flame retardants from polymeric materials due to its synergistic effect on both polymeric structure and extraction kinetics [22]. And the swelling ratio between the polymeric materials and the solvent was significantly influenced by increasing temperature [22]. However, temperature should be controlled in order to avoid dissolution of polymeric materials in the solvent or collapse of polymeric structure [22]. Fig. 7 shows that the increase of temperature resulted in a remarkable increase in the extraction efficiency of TPPO from 50 °C. This is mainly because solid TPPO melts into liquid at the temperature of 50 °C resulting in the increase in solubility of TPPO as the melting point of TPPO is 50 °C [23]. Further increase of temperature (90 °C–170 °C) declined the recovery efficiency of TPPO, which was attributed to degradation of TPPO. Accordingly, 90 °C was considered as optimal temperature with the highest TPPO recovery efficiency of 77.9%.

As demonstrated in Fig. 8, the recovery efficiency of TPPO increased as the prolonging of time till about 120 min and then reached a plateau. The highest recovery efficiency of TPPO was achieved after 120 min treatment. According to the phosphorus contents in the solvent phase (Fig. 9), it also should be noted that, the recovery efficiency of TPPO increased rapidly initially and then varied in a certain range as the increase of liquid to solid ratio. The highest recovery efficiency of TPPO in waste PCBs was achieved at 84.4% till the liquid to solid ratio was 10:1. The phosphorus contents in the solid phase were 20.1%, 8.1%, 10.4% and 10.0% of total phosphorus respectively with the liquid to solid ratio of 8:1, 10:1, 15:1 and 20:1. The loss of phosphorus content was calculated by

Fig. 7. Effect of temperature on TPPO recovery. Conditions: solvent methanol; time 120 min; liquid to solid ratio 15:1.

subtracting the phosphorus content of solid phase and solvent phase from the initial phosphorus content of waste PCBs. These losses of phosphorus were attributed to the solubility of TPPO in methanol [24–26]. In this case, a period of 120 min and a liquid to solid ratio of 10:1 were adequate to obtain maximum recovery efficiency.

3.4. Kinetics analysis

Similar to typical liquid–solid leaching processes [27,28], five subsequent steps was identified in the solvothermal process of removing flame retardants from polymeric materials, i.e., diffusion of solvent towards the polymer particles, diffusion of solvent through the polymer layer to the flame retardants (internal diffusion), dissolution of flame retardants into the solvent (surface dissolution), diffusion of flame retardants through the polymer layer (internal diffusion) and transfer of flame retardants from the polymer boundary into the solvent. The shrinking core model (SCM) considers that surface dissolution, internal diffusion, both the interface transfer and internal diffusion are rate controlling steps of leaching processes. Assuming that TPPO particles are spherical and the leaching process is first order reaction, the SCM could be used to illustrate the kinetics analysis of solvothermal process for TPPO removal. When the rate controlling steps are surface dissolution, internal diffusion, both the interface transfer and internal diffusion, the shrinking core model can be respectively illustrated by Eqs. (1)–(3) as follows [27,28]:

$$1 - (1 - \alpha)^{1/3} = k_1 t \quad (1)$$

$$1 - (2/3)\alpha - (1 - \alpha)^{2/3} = k_2 t \quad (2)$$

$$(1/3) \ln(1 - \alpha) + (1 - \alpha)^{-1/3} - 1 = k_3 t \quad (3)$$

where α is recovery efficiency of TPPO, k_1 , k_2 , k_3 are rate constants, and t is treatment time.

As can be seen from Eqs. (1)–(3), when the process is controlled by surface dissolution, internal diffusion, both the interface transfer and internal diffusion, the corresponding plots of $1 - (1 - \alpha)^{1/3}$, $1 - (2/3)\alpha - (1 - \alpha)^{2/3}$ and $(1/3)\ln(1 - \alpha) + (1 - \alpha)^{-1/3} - 1$ versus time are straight lines with different slopes. For the kinetics analysis of solvothermal process in the present study, $1 - (1 - \alpha)^{1/3}$, $1 - (2/3)\alpha - (1 - \alpha)^{2/3}$ and $(1/3)\ln(1 - \alpha) + (1 - \alpha)^{-1/3} - 1$ were plotted with respect to the treatment time and the correlation of the kinetics data with these models were assessed by using correlation coefficients in Fig. 10. As can be observed from Fig. 10, Eq. (2)

Fig. 8. Effect of time on TPPO recovery. Conditions: solvent methanol; temperature 90 °C; liquid to solid ratio 15:1.

Fig. 9. Effect of liquid to solid ratio on P distribution. Conditions: solvent methanol; temperature 90 °C; time 120 min.

Fig. 10. Plots of $1 - (1 - \alpha)^{1/3}$, $1 - (2/3)\alpha - (1 - \alpha)^{2/3}$ and $(1/3)\ln(1 - \alpha) + (1 - \alpha)^{-1/3} - 1$ versus time. Conditions: solvent methanol; temperature 90 °C; liquid to solid ratio 15:1.

fitted better compared with Eq. (1) and the correlation coefficient for Eq. (2) was 0.90 ($p < 0.05$), which meant that internal diffusion was of great significance in controlling the recovery rate of TPPO. Compared with Eq. (2), Eq. (3) takes into account the factor of interface transfer and the higher correlation coefficient of Eq. (3) ($p < 0.05$) indicates that interface transfer also plays a role in controlling the recovery rate of TPPO.

4. Conclusions

This study demonstrated that solvothermal process followed by vacuum rotary evaporation was a practical and efficient technique

for recovery of additive flame retardants from waste PCBs. For waste PCBs containing flame retarded TPPO, high TPPO recovery efficiency of 84.4% with a purity of 93.4% and dephosphorization efficiency of waste PCBs at 97.3% were achieved. The optimum temperature, time and liquid to solid ratio were 90 °C, 120 min and 10:1, respectively. The recovery rate of TPPO in the solvothermal process was mainly controlled by interface transfer and internal diffusion. The structure of recycled TPPO was maintained after the recovery process, which could be easily utilized as chemical feed-stocks.

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