

Degradation Behavior of Condensed Phosphorus Ester Flame Retardants

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Introduction

Many household products are treated with flame retardants for the purpose of prevention of fire. Home electronics appliances such as television sets and textile such as curtains contain brominated flame retardants (BFRs) at high concentrations. However, some BFRs such as polybrominated diphenylethers (PBDEs) were regulated by RoHS directive (Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment) in European Union or corresponding regulations in other countries. Part of PBDE usages were replaced by other BFRs such as hexabromocyclododecanes or tetrabromo bisphenol A, however, these BFRs are respectively regulated as type I and III monitoring chemical substances by Japanese regulation “Law Concerning the Examination and Regulation of Manufacture, etc of Chemical Substances”. Therefore, non-brominated flame retardants were in demand as alternatives to BFRs.

Phosphate tri-esters are classical plasticizing and/or flame retarding agents. Triphenyl phosphate is one of the most famous flame retardants for printed-circuit board. However, Triphenyl phosphate cannot replace BFRs used in plastic housing material for electronics appliances such as casings of television sets because of its plasticizing property. Condensed phosphorus ester flame retardants (CPFRs) are the new type of phosphorous flame retardants with advanced molecular design, which have condensation oligomer structure of phosphorous ester. Plasticizing properties and emission properties of CPFRs are lower than those of conventional phosphate tri-esters, because of its high molecular weight. However, phosphoester bond in CPFRs oligomer may easily hydrolyzed as have been observed for phosphate tri-esters (Anderson et al. 1993). Hydrolyzed products of CPFR would be ester terminal compounds (phenol or xylenol), cross-linking compounds (resorcinol or bisphenol A) or phosphorous mono/di ester compounds as shown in Figure 1. Some of these compounds possibly have high volatility (Saarikoski & Viluksela 1982) and/or high toxicity (Lemos et al. 2010). Objectives of this study are to determine the degradation behavior and breakdown products of CPFRs under usage condition.

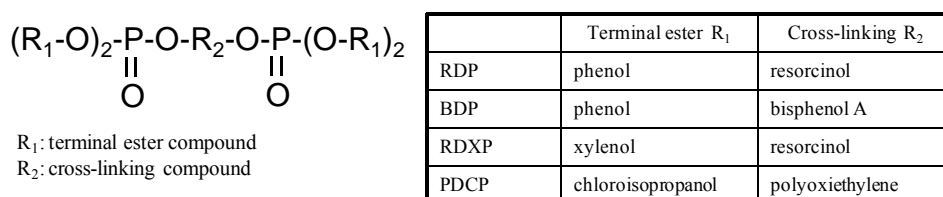


Figure 1 Structure and substituents of CPFRs

Materials and Methods

Four types of CPFRs, resorcinol diphenyl phosphate (RDP), bisphenol A diphenyl phosphate (BDP), resorcinol dixylenyl phosphate (RDXP) and polyoxialkylene dichloroalkyl phosphate (PDCP) were used in this study. Three experiments, which are “hydrolysis experiment”, “sunlight exposure experiment” and “flame retarded material degradation experiment” were carried in this study.

Hydrolysis experiment

3.0 g of each technical CPFRR product was added into Ehrenmeyer flask with 30 mL of pure water. In this experiment, water was directly contacted with CPFRRs. The pH of solution was adjusted to 3.0, 7.0 and 10.0 by 1.0 N HCl and NaOH solution. Then, the flask was shaken at 20°C and 60°C in constant-temperature water bath for 72 hours.

Sunlight exposure experiment

CPFRR was dissolved in dichloromethane at 10 wt %. Quartz plate was coated with 1.0 mL of RDP solution and dried with nitrogen gas. Quartz plate was then placed in a 100-mL quartz flask with a drop of pure water as a moisture source. Flask was sealed and placed under sunlight at room temperature between 23 and 27°C during the experimental period for 28 days. In contrast to hydrolysis experiment, water was just dropped as moisture source to evaluate degradation behavior and identify breakdown products of CPFRRs under usage condition. Blank experiments were also conducted without water addition or/and sunlight exposure to evaluate the influence of sunlight and moisture.

Flame retarded material degradation experiment

The virgin pellet of high impact polystyrene was dissolved by dichloromethane with 10 wt% of RDP. After mixing, solvent was dried at room temperature to prepare flame retarded plastic sample. 10 wt% of RDP were also added to white acrylic textile to prepare flame retarded textile sample. Prepared samples were exposed to sunlight for 28 days with moisture.

Analytical procedure

The pH of hydrolysis experiment sample was adjusted to 3.0 and liquid – liquid extracted by 10 mL of dichloromethane (DCM) for three times and the extract was dehydrated with Na₂SO₄. A portion of the extract was purified with Sep-Pak plus C18 (Waters co., USA) after solvent exchange by acetone and used for CPFRR analysis. CPFRRs were analyzed by LC-MS/MS. Another portion was purified with Sep-Pak plus silica (Waters co., USA). The eluate was pre-treated with BSTFA to analyze phenol, xylenol, resorcinol and bisphenol A. A part of the eluate was used for phosphorus ester (including phosphorus mono-, di- and tri-ester) analysis. These compounds were analyzed by GC-MS.

The sample of sunlight exposure experiment was extracted with 10 mL of DCM for three times. Extract was analyzed with the same procedure as hydrolysis experiment. In addition, unknown degradation products were scanned by GC-MS analysis.

For the samples of flame retarded material degradation experiment, textile samples were extracted by ultrasonic with DCM. Plastic samples were dissolved with DCM. Solvent of extract was exchanged to acetone and plastic was removed by centrifugation. Supernatant was analyzed with the same procedure as hydrolysis experiment.

Results and Discussion

Hydrolysis experiment

Phosphoester terminal compounds (phenol for RDP and BDP, xylenol for RDXP and chloroisopropanol for PDCP), cross-linking compounds (resorcinol for RDP and RDXP, bisphenol A for BDP and polyoxyethylene for PDCP) and phosphorous mono/di ester compounds (mono/diphenyl phosphate for RDP and BDP) were detected in hydrolysis sample. Cross-linking compounds for PDCP (maybe ethylene glycol or its oligomer) and phosphorous mono/di ester compounds for RDXP and PDCP (maybe mono/dixylenyl phosphate for RDXP and mono/di chloroisopropyl phosphate for PDCP) could not be identified due to the absence of standard compounds.

Figure 2 shows ratio of hydrolysis for terminal ester bond in the hydrolysis experiment. These ratios were estimated using the concentration of terminal ester compounds assuming that CPFR products were pure dimer and ester terminal compounds are stable during the experimental period. Ratio of hydrolysis for terminal ester bond is high under basic pH condition, but the influence of pH was not significant because the solution was neutralized by acidic breakdown products such as phosphoric acid and phenols. The ratio of hydrolysis in 60°C is significantly higher than that in 20°C. This result shows a possibility that CPFR is not suit for articles using under high temperature condition. The ratio of hydrolysis for RDP was significantly higher than those for other CPFRs. This result shows a possibility that RDP is not suit for humid condition. In addition, ratio of hydrolysis for RDXP in 20°C is significantly lower than those for others. It probably due to phase of products. RDXP was solid phase in 20°C and difficult to mix by shaking.

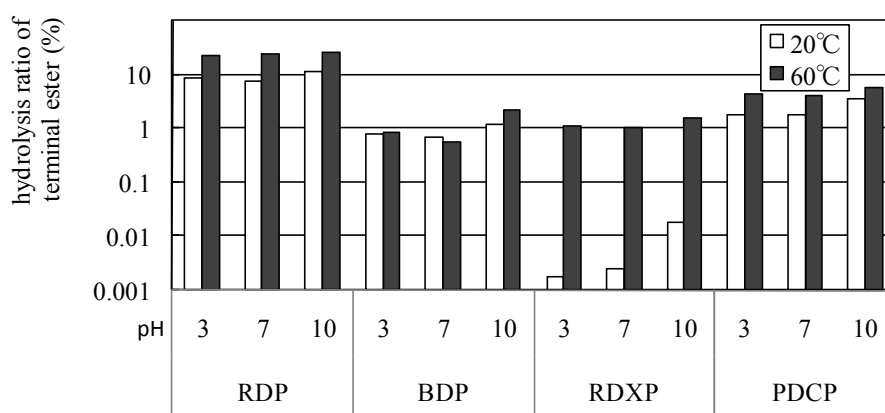


Figure 2 Ratio of hydrolysis for terminal ester bond in the hydrolysis experiment.

Sunlight exposure experiment

Phosphoester terminal compounds (phenol for RDP and BDP, xyleneol for RDXP and chloroisopropanol for PDCP), cross-linking compounds (resorcinol for RDP and RDXP, bisphenol A for BDP) and phosphorous mono/di ester compounds (mono/diphenyl phosphate for RDP and BDP) were detected in the samples of flame retardant product degradation experiment with moisture. On the other hand, no significant increase of these breakdown products was observed in the experiment without moisture. This result shows that moisture is one of the important factors on degradation of CPFRs under usage conditions.

Figure 3 shows ratio of hydrolysis for terminal ester bond in sunlight exposure experiment. These ratios were estimated from the same assumption in Figure 2. The trend of hydrolysis ratio of terminal ester was almost as same as that shown in Figure 2. Room temperature during this experiment ranged from 23°C to 27°C and were lower than melting point of RDXP. As a result, hydrolysis ratio of RDXP was lower than those for other CPFRs. BDP has higher resistance to hydrolysis than RDP and PDCP.

Hydrolysis of terminal ester was slightly accelerated under sunlight except PDCP. Sunlight exposure may increase temperature of tested materials and accelerated vaporization of moisture. These may accelerate hydrolysis of CPFRs, but inverted trend of PDCP was not explainable. Furthermore unknown peaks of the breakdown products were found in the total ion chromatogram of all samples exposure to sunlight (chromatogram not shown). These compounds were apparently photo-degraded

products of CPFRRs because these compounds were detected only in the sample exposure to sunlight. However, molecular structure of these compounds was still unclear.

flame retarded material degradation experiment

Phosphoester terminal compound (phenol), cross-linking compound (resorcinol) and phosphorous mono/di ester compounds (mono/diphenyl phosphate) were detected in the textile and plastic samples flame retarded with RDP. The photo-degraded products detected in sunlight exposure experiment were also detected. Therefore, same breakdown reaction was occurred in textile and plastics.

Figure 4 shows ratio of hydrolysis of terminal ester and degradation of RDP in textile and plastic material. Ratio of hydrolysis was estimated from the same assumption in Figures 2 and 3. Degradation of RDP include hydrolysis, photo-degradation and other all reaction of RDP. Both ratios in textile and plastic were lower than that for RDP product. Especially, ratio of hydrolysis and degradation of RDP in plastic were 6 and 10 times as low as those for RDP product, respectively. This result shows that degradation of RDP was significantly reduced in plastic, but 1.1% of terminal ester phenol was hydrolyzed in 28 days.

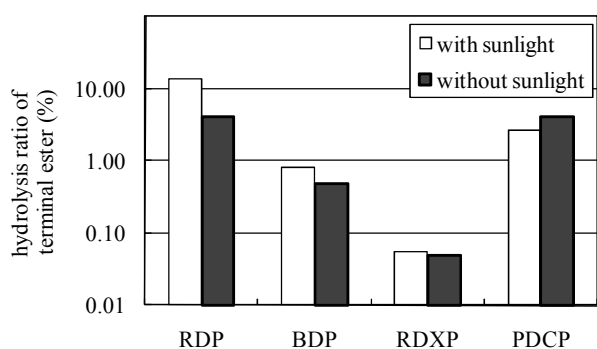


Figure 3 Ratio of hydrolysis for terminal ester bond in flame retardant product degradation experiment

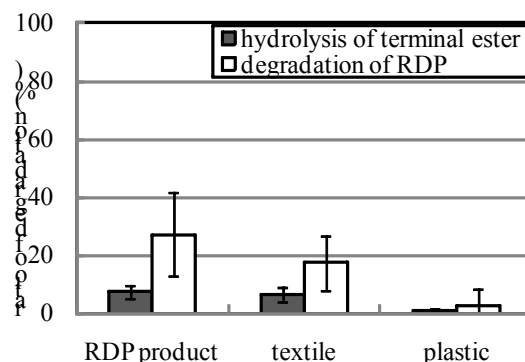


Figure 4 Hydrolysis of terminal ester and degradation of RDP in textile and plastic material

In conclusion, four types of commercial CPFRRs; RDP, BDP, RDXP and PDCP were hydrolyzed and produce low molecular weight breakdown product under humid condition. Hydrolysis was significant for RDP and PDCP. Unknown photo-degraded compounds were produced under sunlight exposure. Hydrolysis of terminal ester and degradation of CPFRRs were prevented in textile and plastic materials.

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References

- Anderson C, Wischer D, Schmieder A, Spittler M. 1993. *Chemosphere* 27:869
- Lemos MFL, van Gestel CAM, Soares AMVM, 2010. *Chemosphere* 78:907
- Saarikoski J, Viluksela M. 1982. *Ecotoxicology and Environmental Safety* 6:501