

Alisa Šehić¹, Petra Forte Tavčer², Barbara Simončič²

¹AquafilSLO d. o. o., Letališka 15, 1000 Ljubljana, Slovenia

²University of Ljubljana, Faculty of Natural Sciences and Engineering, Aškerčeva 12, 1000 Ljubljana, Slovenia

Flame Retardants and Environmental Issues

Ognjevarna sredstva in okoljski vidiki

Scientific Review/Pregledni znanstveni članek

Received/Prispelo 07-2016 • Accepted/Sprejeto 09-2016

Abstract

This article reviews the environmental aspects of flame retardant (FR) use for polymeric materials. The most important groups of halogen, phosphorus-halogen, phosphorus, nitrogen-containing and mineral FRs, as well as of nanoparticle FRs are presented in relation to the health concerns and environmental risk. The main toxicological problems resulting from the use of halogenated and formaldehyde-containing FRs are discussed. Moreover, the possibility of mechanical and chemical recycling as well as energy recovery of recycled flame retarded polymeric materials from post-consumer waste are discussed. Some important future directions and trends for the use of FRs are indicated.

Keywords: flame retardants, polymer composite materials, health concern, environmental risk, toxicological issue, recycling

Izvleček

V članku so predstavljeni okoljski vidiki uporabe ognjevarnih sredstev za polimerne materiale. Opisane so najpomembnejše skupine ognjevarnih sredstev na podlagi halogenskih, fosforjevo-halogenih, fosforjevih ter dušikovih spojin, mineralov kot tudi različnih nanodelcev v povezavi z zdravstvenimi vprašanji in tveganji za okolje. Izpostavljene so toksikološke težave, ki izhajajo iz uporabe halogenskih in formaldehid vsebujočih ognjevarnih sredstev. Predstavljene so možnosti za mehansko in kemijsko recikliranje ognjevarnih polimernih materialov kot tudi pridobivanje energije iz odpadkov. Navedene so glavne smernice za uporabo ognjevarnih sredstev v prihodnosti.

Ključne besede: ognjevarna sredstva, polimerni kompozitni materiali, zdravstvena skrb, tveganje za okolje, toksikološki vidiki, recikliranje

1 Introduction

Flame retardants (FRs) represent a group of chemical agents which are added to flammable materials to inhibit combustion and the spread of fire [1, 2]. While FRs could ensure the production of fire safety products, their application is of considerable economic importance in different fields, e.g. transportation, building, electronics, electrical engineering, textiles, wood and paper industries. There are more than 175 different types of FRs in the market, which contain bromine, chlorine, phosphorus, nitrogen, boron, and antimony compounds or their combinations [3–5]. FRs are comprised of inorganic and organic compounds

with gas-phase and/or condensed-phase mechanisms of FR action [5, 6]. According to their chemical structure, FRs, which include reactive groups, can be chemically bonded to the polymer material, whereas the non-reactive FRs can only be physically incorporated into the polymer structure. The latter FRs can easily penetrate into the environment.

Between 1950 and 1980, the fire safety issue and federal regulations in European countries and the USA dictated the development of new, effective flame retardant chemicals to reduce the fire hazards and meet the product flammability standards [5, 7, 8]. During this period, which was appointed as the “golden age of flame retardant research” [5], numerous

Corresponding author/Korespondenčna avtorica:

Prof. DrSc Barbara Simončič

Tel.: 00386 1 200 32 31

E-mail: barbara.simoncic@ntf.uni-lj.si

Tekstilec, 2016, 59(3), 196-205

DOI: 10.14502/Tekstilec2016.59.196-205

nondurable and durable halogen-, phosphorous- and phosphorus-halogen-containing commercial products were synthesised and commercialised without concerns about their potential toxicity and environmental unacceptability. The production expansion of FRs was also influenced by the continuously increased use of synthetic polymers and plastics that replaced other materials in numerous applications due to their excellent functional properties and aesthetic comfort. As the flammability of these materials represents an important limitation in their use, their protection against combustion was of great importance. Since 1977, when an article was published in the journal *Science* [9–11] warning about the carcinogenicity and mutagenicity of the brominated FRs which were widely used in the production of children's sleepwear the toxicological problems of hazardous FRs and their long-term effects on human health and the environment have been increasingly exposed and discussed. The results of toxicity studies revealed the presence of significant concentrations of brominated FR compounds in the environment, including in human and wildlife tissue [3, 9], which caused great concern. Accordingly, a large number of very effective FRs have been prohibited and taken off the market. The market for flame retardant additives is increasing due to raising safety standards worldwide and currently, frequently used additives include organophosphorus compounds. In addition, nanocomposite technology has been recently studied using various nanoparticles, such as organoclay and carbon nanotubes.

Nowadays, there are several different governmental entities that are concerned about the potential hazard and risk assessment of the use of FRs. In the European Union (EU), the most relevant legislation concerning the risks via registration of chemicals is the European Union's Registration, Evaluation and Authorisation of Chemicals (REACH), which is expanding efforts to restrict the use of environmentally unsustainable hazardous substances, including toxic FR compounds [8–10]. However, the restriction and prohibition of the use of halogenated FRs have raised a possibility of new prospects and challenges in the field of FR manufacturing that include the syntheses of non-toxic alternatives, e.g. non-halogenated phosphorous-based FRs, intumescent FR systems and nanocomposite FRs [6, 8, 11–13]. These new prospects and approaches offer opportunities for the development of FR systems that would effectively replace brominated FRs.

2 Environmental risk assessment of flame retardants

2.1 Halogen-containing flame retardants

Halogenated FRs include brominated and chlorinated compounds that have been commercially available since 1960 [5, 6, 14–16]. As a result of higher performance efficiency and lower costs, brominated compounds have been of greater practical importance than chlorinated compounds. There are four main groups of commercially produced brominated FRs: hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), polybrominated biphenyl (PBB) and polybrominated diphenyl ethers (PBDEs), i.e., decabromodiphenyl ether (decaBDE), octabromodiphenyl ether (octaBDE) and pentabromodiphenyl ether (pentaBDE) (Figure 1) [3, 11, 16–19]. The activities of these FRs are based on the gas-phase action by a radical trap mechanism [1, 2]. In the decades when they were allowed for use, brominated FRs were used as one of the most important additives in different plastics and resins, electrical equipment, electronics parts, polyurethane foams and synthetic textile fibres. In textiles, they were mainly applied in fabric back-coatings for residential and commercial upholstered furniture, automotive fabrics, seating in public buildings, curtains, draperies, carpets, floor and wall coverings, and tarpaulins [3, 4, 19]. Resulting from the physical incorporation of brominated FRs into textiles and plastics, they can easily leach during the products' manufacturing, use and laundering. Therefore, significant concentrations of brominated compounds have been detected in the environment [3, 20–26].

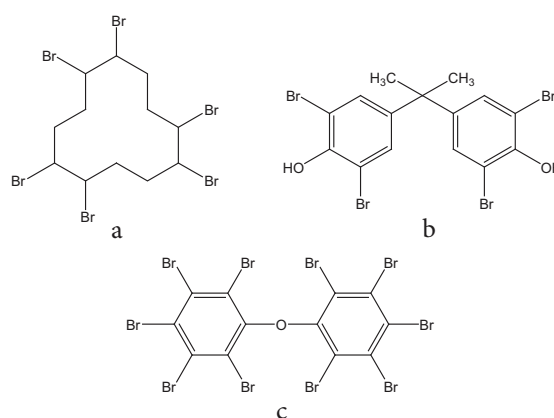


Figure 1: a – hexabromocyclododecane, b – tetrabromobisphenol A, c – polybrominated diphenyl ethers

One of the main toxicological problems and concerns regarding health risks due to the use of brominated FRs is related to their association with long-term carcinogenic and mutagenic effects regardless of their concentration. Namely, during thermal stress, brominated FRs are converted into dioxins and furans [2, 8], which are highly toxic and can cause reproductive problems and damage the immune system. The cause of dioxin formation is often connected with the use of brominated FRs in combination with antimony oxides as synergist additives. Furthermore, brominated FRs are highly resistant to biological, chemical and physical degradation [2, 8, 15, 17]. However, if their degradation occurs under certain environmental conditions, they are converted into even more persistent and toxic lower brominated compounds [2, 8, 14, 15]. With the worldwide use of brominated FRs in the past and their persistence, different brominated substances have been bioaccumulated in the food chain, which represents a serious health risk for the general population. Recent environmental and human monitoring [2, 8, 14, 16, 18, 24] showed that brominated compounds are present in indoor and outdoor air, dust, water, different foods and in the human body despite the fact that the use of brominated FRs is almost completely prohibited.

Legislation in the United States prohibited the production of PBB in 1979, when it was partly banned in Europe. In 1983, Switzerland and Austria prohibited the use of PBB additives in the textile industry, specifically for the production of textile materials that come into direct contact with the skin. In 1984, according to Directive 76/769/EEC, the use of PBB was prohibited in textiles, such as clothing, underwear and bedding. Similar restrictions stand for pentaBDE and octaBDE. PentaBDE was banned in Europe in 2004 by the Council Directive 2003/11/EC. Between 1990 and 2005, there was only one factory producing pentaBDE, i.e. Great Lakes Chemical Corporation in the United States, which voluntarily stopped its production on 1 January 2005. Since 1 July 2006, the use of decaBDE was controlled by the Directive on the Restriction of the use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) in Europe. In 2008, the use of decaBDE was prohibited in all Europe [2, 6, 8, 27]. In current REACH, the prohibition of the use of PBB and PBDEs is found in the list of restrictions in Annex XVII [21, 8]. In the case of HBCD,

the Stockholm Convention on Persistent Organic Pollutants listed this product in Annex A in 2013 with specific exemptions for the production and use in expanded polystyrene and extruded polystyrene in buildings [28, 29–31].

2.2 Phosphorus-halogen containing flame retardants

Phosphorous-halogen containing FRs combine the properties of both halogen and phosphorus components, which act synergistically in the polymer system by combining the gas-phase action of halogen species with the condensed-phase action of phosphorus-based compounds [1, 2, 4]. In this group of FRs, tris(2,3-dibromopropyl) phosphate (tris-BP) and tris-(1,3-dlchloro-2-propyl) phosphate (tris-CP) (Figure 2) were the most popular in the 1970s when minimum flammable fabric standards were strictly respected not only for home textiles but also for wearing apparel [32–36]. Tris-BP was the main FR in children's pyjamas, where it was used in high concentrations to meet the children's sleepwear standards. Other compounds, such as tris(1-chloro-2-propyl) phosphate, tris(2-chlorosthyl) phosphate and tretrekis(2-chloroethyl) dichloroisopentyldi-phosphate have also been reported as FRs mainly used for upholstered furniture.

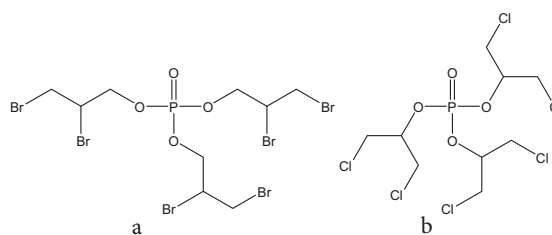


Figure 2: a – tris(2,3-dibromopropyl)phosphate (tris-BP), b – tris-(1,3-dlchloro-2-propyl)phosphate (tris-CP)

Despite the fact that the halogenated phosphorous FRs were introduced as alternatives for the restricted halogenated FRs, it should be noted that some of these compounds have been reported to be toxic [33], since they are structurally similar to neurotoxic organophosphate pesticides [33, 38]. These substances could be released from the products through evaporation and abrasion; therefore, they have been found in indoor air, dust, streams and surface water [33]. Of the halogenated phosphorous FRs, tris-CP has been marked as a persistent or very persistent substance and some studies have reported that tris-CP is at

higher concentrations carcinogenic and a potent mutagenic [33]. Furthermore, tris-CP is not biodegradable and cannot be removed during conventional wastewater drinking water treatments.

2.3 Phosphorus-containing flame retardants

Phosphorus-containing FRs include numerous inorganic and organic compounds, *inter alia* triaryl-phosphates, e.g. triphenyl phosphate (TPhP), tricresylphosphate (TCP), diphenylcresylphosphate (DCP), resorcinol-bis(diphenylphosphate) (RDP), bisphenol-A diphenyl phosphate (BADP) (Figure 3), which are mainly used as flame retardants for textiles, plastics, electronic equipment, furniture and construction [33, 39–43]. Furthermore, polyphosphates, phosphonate esters phosphonic acid (PA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivatives are also of commercial importance. Depending on their chemical structure, phosphorous FRs can be active in condensed and/or in gas phase [1–5]. They are very effective for materials that contain oxygen, such as cellulose. Phosphorus formulations in various oxidation states (0, +3, +8) change the degradation mechanism of the material and promote the formation of carbonised residue and they tend to reduce the formation of volatile

products. Most often phosphorus additives cause the formation of phosphoric acid, which in the condensed phase, eliminates water.

In general, the toxicity potential of triaryl-phosphates is related to the content of o-phenolic residues in commercial products, where the maximal potential is reached when o-phenolics are 33%. The most pressing health and environmental problem with the use of triaryl-phosphates arises from their ability to induce delayed polyneuropathy. This rare neurotoxic toxic effect in humans and experimental animals has been determined for TCP, whereas in the literature, there are contradictory arguments about the toxicity of TPhP [33]. Some papers namely report possible neurotoxicity of TPhP, while some papers deny these claims [33, 43, 44]. For TPhP, the contact allergenic effects on humans and possible toxicity to water organisms have been documented [33, 43, 44]. The toxicological studies of other triaryl-phosphates are very rare with insufficient data available in the literature.

Among polyphosphates, ammonium polyphosphate (APP) and melamine polyphosphate (MPP) are the most documented FRs [2, 5, 43–45], and are used in the treatment of commercial upholstered furniture, automotive interior fabrics, draperies, as a

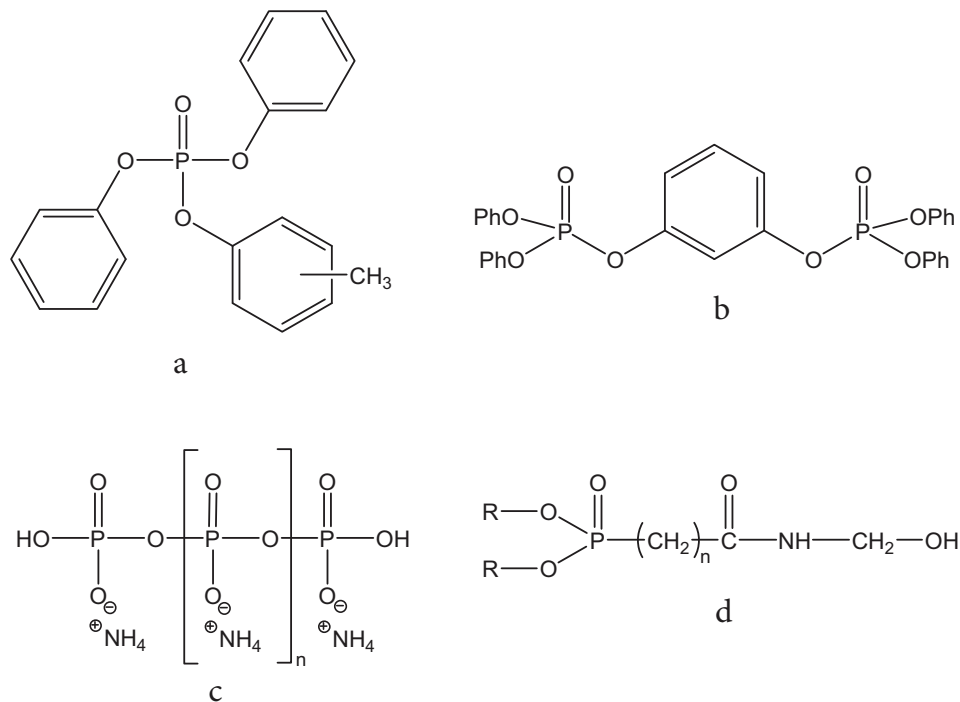


Figure 3: a – diphenylcresylphosphate, b – resorcinol-bis(diphenylphosphate), c – ammonium polyphosphate, d – dialkylphosphonocarboxylic acid amide

food additive, emulsifier and as a fertiliser. APP and MPP have low bioaccumulation. There is no data in the literature on the toxicological, immunological, neurological, or carcinogenic and mutagenic effects of oral exposure to APP, ammonium ions, or polyphosphates. The only documented negative environmental effect of APPs is the algal toxicity. In the few studies, low ecotoxicity of MPP to algae, dolphin and fish has been reported [43–47]. As a result of low environmental risks, APPs and MPP could represent a good alternative to brominated FRs [1, 2, 5].

The most popular phosphonate ester is the reactive, functional phosphoramidate, which is chemically dialkylphosphonocarboxylic acid amide. Its main limitation and health and environmental risk represents the formaldehyde generation due to the presence of reactive methylol group in the structure, as well as its combination with methylolamine precondensates that are also formaldehyde-containing products [2, 5, 8]. Formaldehyde is namely classified as a possible carcinogen for humans. Due to the negative effects of formaldehyde on health, Japan was the first country to introduce limits in the amount of formaldehyde allowed in textiles in 1973. The Act No. 112 (Supervision of products for home and household containing harmful substances), published in 1974, laid down the maximum allowable concentrations for five compounds, including formaldehyde. The content of formaldehyde in finished textile products should not exceed 20 mg/kg in textiles for children and textiles that will be in direct contact with the skin and 300 mg/kg for other textile products [2, 5, 8]. Formaldehyde is clearly genotoxic in vitro and may be genotoxic at the site of contact in vivo. Overall, formaldehyde is considered to have weak genotoxic potential. The emission of formaldehyde to the atmosphere, especially during curing, is also restricted to be less than 20 ppm. Phosphonic acid (PA) has been used in various applications, residential furniture, draperies, and work clothing. PA and its derivatives are affixed directly to textile fibres by the application of high heat in the presence of cross-linking agents, such as melamine and glyoxal. The cross-linking imparts resistance to laundering through several washings, but the applied PA can undergo slow ambient hydrolysis and release from the fabric over a period of years. In the literature, there is no evidence about the toxic effect of PA on the health and environment.

Nowadays, DOPO and its derivatives are identified as non-neurotoxic and with no inflammatory activation potential. They also have no effect on the algae growth or daphnia viability at low concentrations [48]. Therefore, they are very promising candidates for the replacement of currently applied flame retardants.

2.4 Nitrogen-containing flame retardants

Typically, nitrogen FRs are melamine and various melamine derivatives, such as melamine cyanurate (Figure 4) and melon, and are primarily used in polymers containing nitrogen, such as polyurethane and polyamide [2, 3, 49]. Separately, they have little effect on the flame retardancy; therefore, they are often used in combination with phosphorus FRs, such as MPP. The main advantages of these compounds are their low toxicity, solid state and in the case of fire, the absence of dioxin and halogen acids, and their low evolution of smoke [49–51].

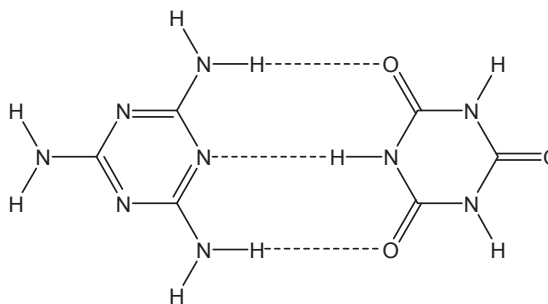


Figure 4: Melamine cyanurate

2.5 Mineral flame retardants

Few inorganic flame retardant additives are useful for fire-proofing as they must be effective at temperatures from 150 to 400 °C, which is a relatively low temperature for their activity. Inorganic flame retardants are various metal hydroxides, e.g. aluminium or magnesium hydroxide, calcium carbonate and silica compounds [4–6, 10]. These additives work in the condense phase, have a physical effect on the combustion of the material and act by preventing the access of oxygen and heat [4–6]. There is limited information about the environmental issue of any mineral flame retardant compounds.

2.6 Nanoparticles

Nanoparticles (NPs) that are used as FRs mainly include nanoclays, carbon nanotubes (CNTs), graphene, polyhedral oligomeric silsesquioxanes (POSS),

and spherical silica nanoparticles [50–57]. It has been found out that NPs act in the condense phase where they, in low loadings (<10%), influence dripping behaviour of the polymer. NPs reduce the burning temperature, prevent the oxygen supply from the atmosphere, and promote char formation. NPs do not have an influence on the limiting oxygen index (LOI) and are only added as synergistic to other flame retardants. The disadvantage of NPs creates difficulties in achieving uniform dispersion. As the viscosity of the polymer decreases during the heating, nanoclays migrate to the surface and create a protective layer. Montmorillonite (MMT) platelets are accumulated as the clay migration was pushed by numerous rising bubbles of degradation products. Layered double hydroxide (LDH) is a class of anionic clays and as a heat sink, the material improves flame retardant properties and works as a hydrated material, very similar to mineral flame retardants. It has the potential to release water under firing conditions. Carbon nanotubes have applications in many materials for memory storage, electronics, batteries and fibres. CNTs have the ability to reduce the heat release rate (HRR) due to polymer degradation. Some scientists have concerns about carbon nanotubes due to unknown harmful impacts to the human body by inhalation, and some papers suggest that carbon nanotubes have similar toxicity as asbestos fibres. Nanoparticles have higher surface areas than bulk materials, which can cause more damage to the human body and the environment compared to the bulk particles, since the mobility of nanoparticles is more possible [50–57]. Another problem is the lack of information and methods of characterising nanomaterials, making the existing technology extremely difficult to detect the nanoparticles in air for environmental protection.

3 Recycling of flame retarded materials

There are several economic and ecological reasons that endorse and support polymer recycling [2, 8]. In general, polymer waste product recycling importantly contributes to the reduction of post-consumer waste, among them apparel, domestic and technical textiles, plastic bottles and electronic equipment. This is also the main reason that different manners of polymer recycling, including mechanical and

chemical recycling and energy recovery, have been greatly broadened in the last decade.

When introducing recycling of polymer materials with incorporated FRs, technological, economic and environmental aspects of this process should be discussed. The implementation of flame retardant additives in polymers affects especially the mechanical recycling of final products. Therefore, the recyclability of polymers from post-consumer plastic goods depends on different factors, such as the polymer nature, presence of additives for light stabiliser, flame retardant additives and colour pigments [58–63]. For an open loop, where different materials with different additives are returned from the market, mechanical recycling is difficult to reach the quality of the virgin polymer. For a closed loop, mechanical recycling is much easier as the composition and the origin of the material is known. Contrary to mechanical recycling, there are no technological limitations for using chemical recycling of flame retarded polymers [8, 59, 60]. Furthermore, as FRs incorporated into products are usually more expensive than the origin polymer, these products have added value, which could be an economic advantage in the recycling process.

Nevertheless, recycling of flame retarded polymers is also accompanied by some pressing ecological problems. It is documented that during waste recycling activities, especially if they are carried out in a non-professional primitive manner, high concentrations of brominated and chlorinated FRs, mainly PBB and TBBPA, as well as highly toxic brominated and chlorinated dioxin-related compounds were present in air and house dust [8, 50, 58, 63]. Therefore, only certain and strictly controlled experimental conditions are appropriate for recycling of polymers with incorporated FRs. In this concept, energy recovery of recycled flame retarded polymers, especially of those with incorporated halogenated FRs, raises concern due to the release of toxic and corrosive halide-containing polymers during the burning of polymers.

4 Future trends

In the EU, future research directions and activities in the field of the use of FRs for polymer materials are guided by sustainable development goals, which are included in the REACH legislation. Flame retardant products have difficulties in obtaining eco-labels, and

some of them cannot obtain it. The most important objective comprises a complete replacement of halogenated FRs with phosphorus and phosphorus-nitrogen “greener” FR formulations for achieving efficient flame retardancy with minimal health and environmental hazards. According to this objective, the introduction of novel intumescent FR systems represents a major scientific and technological challenge; however, this will enable a breakthrough in the production of flame retarded polymer materials, which would follow the principles of “eco-designing”. Adding two or more flame retardants in products that work in combination and have a synergistic effect is another novel and efficient way of achieving efficient flame retardant polymers.

Acknowledgments

This work was supported by the Slovenian Research Agency – Slovenia (Program P2-0213). Alisa Šehić would like to thank AquafilSLO d. o. o., for her PhD grant.

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