

# Flame Retardants for Slow-Burning and Fire-Resistant Polymer-Composite Materials

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**Abstract**—Substances used as flame retardants and to produce slow-burning and fire-resistant polymer-composite materials over the past 20 years are overviewed in this work.

**Keywords:** noncombustible binders, slow-burning retardants, flame retardants, fire resistance modifiers, combustibility of polymer composite material, fire safety, phosphorus-containing polymer

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## INTRODUCTION

Polymer-composite materials (PCMs) are actively used in many spheres of people's life and work, for example, in the aircraft, rocket, ship, and automotive industries; railway transport; medicine; sports; and wind energy. PCMs are an inexhaustible source of new materials due to the high variability of starting components for polymer composites, which leads to the displacement of wood, metals, their alloys, and reinforced concrete.

The organic part of the matrix of industrial polymer composites has significant disadvantages: high flammability, smoke emission, and toxicity of combustion products.

An effective way to decrease the combustibility, smoke formation, and toxicity of combustion products for PCMs is to modify their compositions via introduction of flame retardants. The high demand for materials that meet fire safety requirements both indoors and on all modes of transport encourages scientists and developers to develop new, promising, and more effective flame retardants than those currently available on the market.

Currently, there is a wide range of flame retardants for all industrial polymers. In the scientific world, there is a significant number of publications and titles of protection (patents) that consider the problems of combustibility of polymeric materials and their products. Many well-known works, however, focus narrowly and refer only to certain types of flame retardants, and sometimes only to specific compounds.

The aim of this work is to review various flame retardants used in modern polymer-materials science

as modifiers of polymer binders to obtain slow-burning and fire-resistant PCMs on their basis.

## COMBUSTION PRINCIPLES

A decrease in tendency to ignition, the rate of burning, and the formation of smoke and toxic gases during the combustion of polymeric materials is key to reducing the risk of a fire, the rapid development of fire, and manifestation of negative consequences thereof.

Theoretically, the combustion process of polymeric materials can be described by the scheme shown in Fig. 1.

The combustion proceeds as a result of ignition and combustion of gaseous products of thermal–oxidative pyrolysis and is a continuous multistage process. At the first stage (1), a polymer material undergoes the external thermal action that leads to the accumulation of thermal energy from the ignition source. The source can be radiation, friction, an open flame, etc. A polymer material decomposes thermally during the heating to form four groups of intermediate products: noncombustible and combustible gases, liquid products, and solid charred residue (coke).

At second stage (2), an ignitable gas–air mixture is formed in the presence of atmospheric oxygen that leads to effective flame. The heat released by an open flame and the smoldering process of a solid residue provides additional heating of initial burning material and continues until the complete depletion of one or the consumption of all products that support combustion. The total rate of the combustion process is defined by the slowest stages listed.

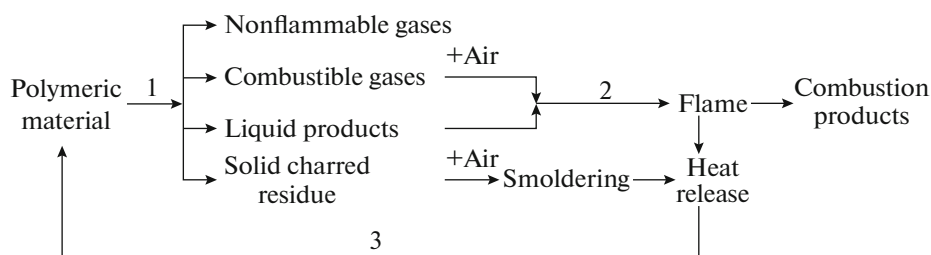


Fig. 1. Schematic representation of combustion stages of polymers.

The complexity of the combustion process of polymeric materials is also because of the fact that its mechanism and kinetics depend on the chemical nature of a burning polymer, the composition of the resulting gas, and the presence of noncombustible products in the gas phase. Particular interest is presented by the relationship between the chemical structure, composition, structural, and morphological properties of polymers and their combustibility.

### FLAME-RETARDANT TYPES

More than 200 different commercial substances are known to be used as flame retardants. Table 1 shows a classification of flame retardants by chemical composition [2].

All flame retardants can be conditionally divided into two types according to the method of interaction with polymers: additive and reactive.

### ADDITIVE-TYPE FLAME RETARDANTS

Additive flame retardants are not able to chemically bond with components of a polymer binder. Often, they are evenly distributed in the volume of a material and between the layers of a reinforcing filler or are shifted closer to the ignition surface. The basic principles of action of additive flame retardants are as follows: they (1) increase the temperature of the start of thermal degradation of a composition; (2) release a large amount of gases during the decomposition process that do not support combustion (vapors of water and nitrogen); (3) inhibit free-radical reactions in the condensed phase; and (4) formation a protective layer (noncombustible coke) on the surface of a material, which is capable of isolating the combustible polymer from the source of heat and oxygen and interrupting the propagation of the flame in the gas phase, acting as a heat sink to avoid heat supply.

Additive-type flame retardants include mineral, less often organic, substances and compounds in a

Table 1. Classification of flame retardants

Flame-retardant groups	World-production volume, %
<i>Inorganic substances:</i> silicon dioxide, metal hydroxides (e.g., magnesium and aluminum hydroxides), antimony compounds (e.g., antimony trioxide), boron compounds (e.g. zinc borate), and other metal compounds (e.g., molybdenum trioxide)	50
<i>Halogenated (brominated and chlorinated) substances:</i> halogenated paraffins, halogenated alicyclic and aromatic compounds and halogenated polymeric materials. They can contain other heteroelements such as phosphorus or nitrogen. • There are three chemical classes: (a) aromatic, including tetrabromobisphenol-A (TBBPA), polybrominated diphenyl ethers (PBDEs), and polybrominated biphenyls; (b) aliphatic, including dibromomethane, dichlorobromomethane, and trichlorobromomethane; and (c) cycloaliphatic, including hexabromocyclododecane (HBCD)	25
<i>Phosphorus organic substances:</i> organic and inorganic phosphates, phosphonates, phosphinates, and red phosphorus. They can contain chlorine or bromine	20
<i>Nitrogen-containing substances:</i> melamine and its derivatives (e.g., melamine cyanurate and melamine polyphosphate). They do not contain heteroatoms except nitrogen	5

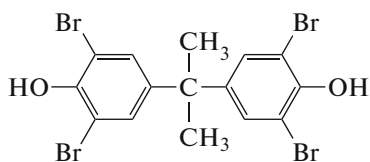


Fig. 2. Structural formula of tetrabromobisphenol-A.

highly dispersed form, such as oxides and hydroxides of alkaline earth metals and phosphates and phosphites of organic substances. Aluminum hydroxide, for example, is used to create a fire-resistant polymeric binder and composite material used to produce printed circuit boards [3]. Magnesium hydroxide is included in a low-combustibility and environmentally friendly epoxy composition that is in demand in the electronics industry [4]. The active use of flame retardants of such type is based on their ability to decompose with the absorption of thermal energy (endothermic) to cool the material and to slow down its combustion, whereas water (as steam) forms a layer of noncombustible gas near the surface of a material to suppress the flame.

There are low-combustible nanocomposites, materials that can be obtained via introduction of various nanomodifiers into composite materials, including nanoclay, graphite, carbon nanotubes, metal nanoparticles, and polyhedral oligosilsesquioxanes. The use of such effective nanomodifiers can also improve other performance properties of PCMs, increasing the strength characteristics, electrical conductivity, and UV resistance and reducing weight, density, cost, etc. Such flame retardants exhibit multifunctionality, because they are able to improve performance, and their use seems to be much promising.

Indeed, a nanopowder based on aragonite sand (a natural biogenic polymorph of calcium carbonate  $\text{CaCO}_3$ ) with a crystal size of 30–100 nm is as a flame retardant in a fire-resistant polyester binder (Stekloplastik) [5]. Filling with aragonite helps to protect against burning and to decrease the emission of smoke and harmful volatile substances. The coke residue of the decomposition of a nanomodified polyester binder is 50–60%, whereas the noncombustible residue of the profile is 95%. Aragonite particles in the polymer matrix of a glass composite also lead to a significant decrease in the development of microdeformations (impact strength increases to  $32 \text{ kJ/m}^2$ ) and an increase in fatigue strength (ultimate compressive strength is up to 240 MPa) and static bending strength (increase up to 1050 MPa in cross section).

Additive-type fire retardants have the following disadvantages despite their relatively low cost and their ability to significantly increase the fire resistance of polymer-composite materials. (1) It is necessary to introduce a significant amount of flame retardant (up to 60%) into the composition of polymer compo-

sitions or in combination with other more effective types of flame retardants to achieve high incombustibility and fire resistance. This has a critical effect on the strength characteristics of PCM resulting products to prevent their use in critical areas technology. (2) A high amount of additive flame retardants requires the addition of various modifiers to polymer binders that increase wettability and aggregative stability for uniform distribution of additive flame retardant in the material to avoid delamination, phase inversion, and large agglomerations. (3) The high viscosity of polymeric binders filled with additive flame retardants complicates their processing into semifinished products or PCM products and limits their use in transfer technologies of PCM molding.

Additive-type flame retardants are widely used due to the optimization of production methods with their use (new methods of mixing and processing are developed and old ones are modernized) despite all the disadvantages described. Such compositions are widely used in lightly loaded decorative products in various fields of construction and technologies.

## REACTIVE FLAME RETARDANTS

More promising reactive flame retardants, which have reaction centers in their structure that allow them to bind to a polymer matrix of a composite through chemical bonding both during the preparation of PCMs directly and during chemical modification of a binder, are used to impart fire resistance and incombustibility to medium- and high-loaded PCMs. Flame retardants of this type include halogen-, phosphorus-, phosphorus-nitrogen-, and nitrogen-containing flame retardants with functional groups.

### *Halogen Flame Retardants*

Halogenated flame retardants (organic compounds containing chlorine or bromine atoms that slow down or prevent the combustion process and excessive heat generation) are widely produced among the components that decrease combustibility.

Brominated flame retardants are the most common due to their cost effectiveness and their ability to be used for various polymers. Currently, almost 75 types of flame retardants containing bromine are produced industrially, with the most common being decabromodiphenyl oxide (DBDPO), tetrabromobisphenol-A (TBBPA, Fig. 2), and hexabromocyclododecane (HBCD) [6].

The most common reactive flame retardant used to produce self-extinguishing epoxy and epoxy vinyl ester resins is TBBPA, which is a crystalline solid with  $T_{\text{melt}} = 179\text{--}181^\circ\text{C}$  in an amount of Br of 58.5 wt %. TBBPA is added to the resin part during the production of a polymeric binder. The finished epoxy bromine resin typically contains 18–21% of bromine.

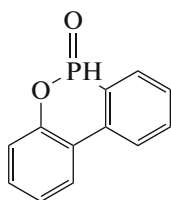


Fig. 3. Structural formula of DOPO.

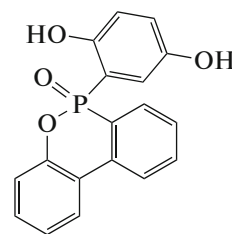


Fig. 4. Structural formula of DOPO-HQ.

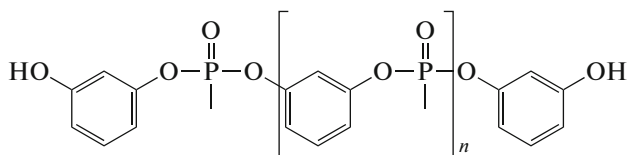


Fig. 5. Structural formula of Fyrol PMP.

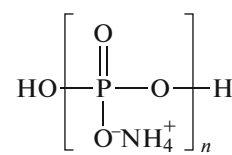


Fig. 6. Structural formula of APP.

Halogen flame retardant compounds are often combined with antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) to decrease their concentrations and to achieve a synergistic effect of interaction of various chemical compounds [7].

Recently, there has been a tendency to replace halogen-containing flame retardants with promising, less toxic, and environmentally friendly materials.

#### *Phosphorus-Containing Flame Retardants*

Phosphorus-based flame retardants can be divided into inorganic and organophosphorus ones. The main representatives of inorganic phosphorus flame retardants are red phosphorus and ammonium polyphosphate (APP).

Organophosphorus flame retardants currently include phosphoric-acid esters and polyols containing phosphorus [8–13].

A reactive flame retardant in thermoset systems may be chemically incorporated into the main chain during the formation of a polymer structure. It is also possible to use phosphorus-containing hardeners based on ester compounds of phosphorus-containing acids. Developers use usually both of these strategies during the preparation of slow-burning thermosetting materials from phosphorus-containing flame retardants [14, 15].

The most promising products based on red phosphorus are superconcentrates produced by Italmatch (Masteret<sup>®</sup>, Italy), Clariant (Exolit<sup>®</sup>, PP, Switzerland), and Shinde (FR, China) [16].

Phosphinates are new flame-retardant modifiers, consisting of phosphinates of organic and metal salts. The most commercially used hydrophosphate is a DOPO flame retardant (9,10-dihydro-9-oxa-10-phosphophenanthrene-10-oxide) obtained for the

first time from decorative phenyphenol and trichloride in the 1970s (Fig. 3).

DOPO is a good alternative to halogenated flame retardants, because it is considered a “green” flame retardant in the EU countries, and its effectiveness is comparable to that of TBBPA. Indeed, a fire-resistant epoxy binder containing DOPO, developed by Schill & Seilacher Struktol AG [DE], possesses higher protection ability of polymeric materials based on it against flame: V-0 of UL94 standard, which is achieved with a phosphorus amount of 1% [17].

Another competitive DOPO-based adduct obtained by its interaction with benzoquinone, DOPO-HQ (10-(2,5-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phosphophenanthrene-10-oxide), is widely used (Fig. 4).

Another important commercial alternative to DOPO is a Fyrol PMP reactive flame retardant (Israel Chemicals Ltd, Israel) (Fig. 5), oligo(1,3-phenylene-methylphosphonate).

Fyrol PMP oligomeric resorcinol methylphosphonate with end hydroxyl groups is a solid compound with a melting point from 45 to 55°C, an amount of phosphorus of 17.5%, thermal stability, and a weight-loss onset temperature higher than 300°C [18, 19].

#### *Phosphorus–Nitrogen-Containing Flame Retardants*

The most effective flame-retardant characteristics of thermosetting polymers are provided by the use of ammonium polyphosphate (APP), in which the amount of phosphorus is up to 30% and that of nitrogen is up to 15% (Fig. 6).

Ammonium polyphosphate transforms into phosphoric acid via thermal decomposition under the action of heat. The degradation of the material contin-

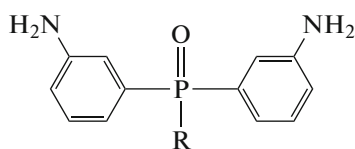


Fig. 7. Structural formula of bis(aminophenyl)alkyl or arylphosphine oxides.

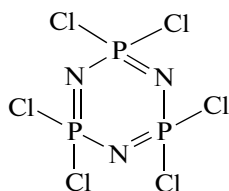


Fig. 8. Structural formula of hexachlorocyclotriphosphazene.

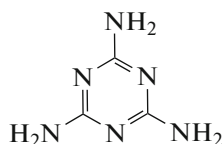


Fig. 9. Structural formula of melamine.

ues to form polyphosphoric acid, which contributes to the degradation of a polymer during the pyrolysis step, to give unsaturated compounds that form a carbonaceous structure (coke). This flame retardant is widely used as a foaming component in compositions, which makes it possible to obtain thermosetting compositions with even lower flammability due to enhancement of intumescent properties [20–24].

Amino-functional phosphine oxides are also used as reactive components to impart fire resistance to curable epoxy compositions. These chemical substances are capable of forming moisture-resistant systems during interaction with epoxy resins, and bis(aminophenyl)alkyl- or arylphosphine oxides (Fig. 7) are widely used as curing agents for this reason [4].

Cyclophosphazene compounds and their derivatives are used as flame-retardant modifiers due to the synergistic effect of phosphorus and nitrogen atoms involved into their composition (Fig. 8).

This product possesses high temperature resistance and low polarity (an unusual property for phosphorus compounds), so that it is of great interest for materials used to produce electronic devices. Flame retardants based on cyclophosphazenes are produced by many foreign companies under the following trademarks: SPB-100 (Otsuka, Japan), Rabitle FP-110 (Fushimi Pharmaceuticals, Japan), PhireGuard HPTCP (Jiansu Yoke, China), etc.

### Nitrogen-Containing Flame Retardants

Nitrogen-containing flame retardants decrease flammability through several chemical mechanisms. Their main advantages are low toxicity and smoke formation, whereas the best effectiveness in decreasing combustibility when these materials are used is manifested by halogen compounds and alkaline earth metal hydroxides. A large group of nitrogen-containing flame retardants are commercial products based on melamine (Fig. 9).

The preparation of binders and PCMs based on them using the Exolit® AP 462 promising flame retardant (Clariant, Switzerland), which consists in ammonium polyphosphate particles with melamine coating, is described in a patent of the American company Cytec Industries Inc. Structural composite materials developed for use in the aviation, automotive, and railway industries possess high fire resistance characteristics that meet the fire safety requirements of the FAR 25.853 App. F Part-I (a) (1) (i) aviation standard and toxicity of combustion products according to DSS 7239 [25].

### USE OF FLAME RETARDANTS IN THE FIELD OF PCMs

A flame retardant is chosen according the technology to obtain PCMs. There are no strict restrictions on flame-retardant type for PCMs obtained by prepreg technology. Another situation is with flame retardants used for PCMs obtained by liquid molding technologies.

Liquid composite molding (LCM) technologies impose strict requirements regarding the technological properties of polymer binders used for molding PCMs. Indeed, they should have a long shelf life without increasing the rheological characteristics and a low initial viscosity, as well as taking a long time to maintain necessary technological properties during the impregnation of a filler, homogeneity of the composition, and a short curing mode.

The French SICOMIN company produced a two-component epoxy flame retardant system for infusion technology based on an SR 1125 resin component in 2015. The nonhalogenated system provides low smoke transparency and smoke toxicity and meets fire-protection standards for construction, automotive, and railway equipment, including class A ASTM E84.

The American company Hexion Inc. produced the EPON™ FlameX Resin 9600/EPIKURE™ FlameX Curing Agent 9700 two-component low-viscosity fire-resistant composition system in 2017, which provides fire safety with low smoke density and toxicity. It can be used in aviation to produce structures used in cargo spaces, saloons, lavatories, galleys, or anywhere else where heat control-requirements are not needed.

The Japanese company Nippon Kayaku KK offers a highly effective modified low-viscosity epoxy com-

position consisting of a mixture of bisphenol F epoxy resin, phenolic resin, Kayahard MCD anhydride hardener (methyl endomethylene tetrahydrophthalic anhydride), 2E4MZ imidazole catalyst, and a phosphorus-containing compound as a flame retardant [26].

The British company Hexcel Composites LTD developed an epoxy composition suitable for processing by liquid technology into PCM products. Phosphorus organic substances are used as flame retardants, which are toxicologically harmless even in the case of fire, under the Polyphlox<sup>®</sup> trade name, supplied by the German company Schill & Seilacher Struktol, or products under the Exolit<sup>®</sup> EP 150 and Exolit<sup>®</sup> EP 200 trade names supplied by the Swiss company Clariant AG [27].

### CONCLUSIONS

The international flame-retardant market is large and growing at a steady pace. Significant progress has been made abroad in the development of thermosetting binders for PCMs with low flammability. There are complex compositions created during the chemical modification of a polymer matrix with flame retardants based on the concept of combining two or more different components to obtain a new material with a synergistic or additive set of properties. Halogen-free solutions (phosphorus- and nitrogen-containing flame retardants), which are inferior in some flame-resistance indicators, have significant advantages in foreign developments in terms of fire safety and environmental characteristics.

Promising flame retardants used for slow-burning PCMs began to appear in Russia according as part of an import-substitution program: for example, epoxy resin modified with epoxyphosphazenes (Mendeleev University of Chemical Technology of Russia), ethoxylated polyesters of methoxymethylphosphonic acid (GosNIIOKhT), phosphorus-containing methacrylate (FOM-II) (Volgogradpromproekt), etc.

The current program for the development and subsidization of the PCM area allows for the process of innovative development of the composite industry and significantly approaches, and even outstrips, the developments of foreign companies in some aspects.

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