

Flame Retardant Strategies and the Physical Barrier Effect of Nanoparticles to Improve the Thermal Performance of a Polymer

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Abstract—An analysis of various types of flame retardants in polymer nanocomposites is presented. The mechanisms of action of fire retardants and their influence on the thermal stability and fire resistance of polymer composites are considered. The use of nanoparticles of inorganic compounds as flame retardants is shown to be promising. The synergistic effect of the use of nanoparticles together with traditional flame retardants is noted.

Keywords: polymer nanocomposites, fire resistance, thermal stability, flame retardants, inorganic nanoparticles

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INTRODUCTION

The fire resistance and thermal stability of polymeric materials is an urgent problem. The combustion of polymers is a complex physical and chemical process, including chemical reactions of polymer decomposition in the condensed phase and heat and mass transfer processes. Polymeric materials, when exposed to heat, can decompose to form combustible gases, which mix with ambient oxygen to form a combustible mixture. Ignition occurs either impulsively if the temperature is sufficient for self-ignition (defined as the temperature at which the activation energy of the combustion reaction is reached) or at a lower temperature (flash point) due to an external source (flame or spark) [1].

This article discusses the influence and mechanisms of action of various flame retardants on the fire and heat resistance of polymeric materials. Particular attention is paid to inorganic nanoparticles.

1. PRINCIPLES OF REDUCING THE FIRE HAZARD OF POLYMERIC MATERIALS

The main risk factor for people during the combustion of polymeric materials is the release of gaseous toxic products, including carbon monoxide, acrolein, benzene derivatives, and other toxic substances [2–4]. The formation of smoke and the release of toxic gases during combustion is the main cause of deaths [5]. In practice, successful strategies for improving the performance of a polymeric material are achieved either

by mechanically mixing a suitable flame retardant compound with the polymeric material, or by chemically incorporating flame retardants into the polymer during synthesis (by copolymerization), or by chemically modifying the preformed polymer (using reactive component). On the one hand, the first category of flame retardants, which are called additive flame retardants, are not designed to interact with the polymer in the mixing stage at higher temperatures at the start of a fire. On the other hand, reactive flame retardants, which constitute the second category of flame retardants, are integrated into polymer chains. This method has several advantages over those that are simply additives. Due to the fact that their incorporation occurs during polymerization, they can be homogeneously dispersed, preventing the formation of a separate phase, which would cause problems when processing the polymer into the final product. In addition, reactive flame retardants are inherently less susceptible to loss during service. These losses can occur due to migration of the flame retardant on the polymer surface or due to solvent leaching [6–8].

The mechanism of action of fire retardants (additive and reactive) can be associated with physical or chemical processes. The main physical mechanisms preventing combustion are the following:

- endothermic reactions (heat removal), which cool the substrate to a temperature below that required to maintain combustion;
- release of inert gases that weaken the supply of oxygen to the surface of the burning polymer, which

leads to a weakening of the flame and its reduction due to an insufficient amount of oxidizing agent;

- formation of a protective coating that reduces the amount of heat transferred to the polymer, prevents the diffusion of oxygen into the decomposition zone and the release of volatile flammable gases formed during the decomposition of the polymer.

There is also a chemical mechanism in which the flame retardant works.

- Inhibition of oxidation reactions that occur in the gas phase by scavenging free radical particles (especially H and OH) that develop as a result of polymer degradation. Hydrogen radicals are responsible for the chain branching reaction that promotes fuel combustion ($H \cdot + O_2 \rightarrow OH \cdot + O \cdot$), while hydroxyl radicals are involved in the exothermic reaction ($OH \cdot + CO \rightarrow H \cdot + CO_2$) of polymer decomposition, which provides most of the energy needed to keep the flame going. These highly reactive substances react with specific radicals released by flame retardants to form less reactive or even inert molecules.

- Formation of a carbonaceous (or glassy) layer on the surface of the polymer by inducing low-energy solid-state reactions that lead to the carbonization of the polymer instead of the formation of volatiles. This layer acts as a physical insulating barrier between the gas phase and the condensed phase.

- The flame retardant can contribute to the destruction and flow of the polymer and, as a consequence, the release of the polymer from the zone of action of the flame [9–12].

2. TYPES OF FLAME RETARDANTS

The choice of the composition and concentration of flame retardants is a complex task, the solution of which depends on the material and its operating conditions. We will consider the best-known flame retardants.

2.1. Halogen Compounds

Flame retardants based on halogen-containing compounds are one of the most diverse types of additives. They function in the gas phase, removing free radicals and thus reducing the heat release rate [13, 14].

Typical representatives of halogenated flame retardants are chlorine-, bromine-, fluorine-, and iodine-containing compounds, with chlorine and bromine being the most widely used representatives of this group. This is because efficiency and stability depending on the type of halogen are the two main factors that determine the type of compound that can be used as a fire retardant. Compounds based on fluorine and iodine are not used because of their inability to interfere with the combustion process of the polymer, since fluorinated organic substances are more stable than

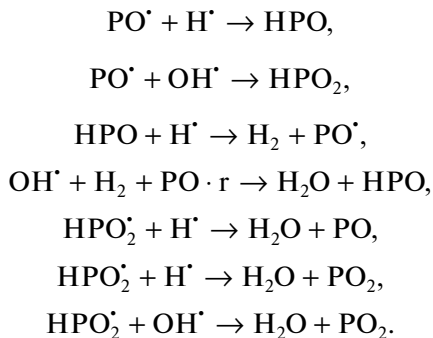
most commercial polymers and do not emit fluorine or hydrogen fluoride radicals at the temperature of polymer decomposition [15–17]. Halogen-containing compounds are used with other flame retardants, which are synergists that improve the characteristics of the flame retardant. There are a significant number of such synergists, for example phosphorus-based flame retardants [18], and the most common ones with antimony trioxide-halogen synergism-based compositions are widely used to increase the fire resistance of various polymers, such as polyolefins, polystyrene, polyesters, polyamides, polyurethanes, etc. Antimony trioxide mainly works in the gas phase. During pyrolysis, hydrogen halides, which are released during self-decomposition of the halogenated compound or during interaction with antimony trioxide and/or polymer, react with antimony halides Sb_2O_3 [19]. Due to environmental concerns and toxicity concerns, the use of halogen compounds has been limited. As an example, polybrominated diphenylesters are classified as persistent organic contaminants that can accumulate in dangerous concentrations in the human body and exhibit hepato-, nephro-, gonadotoxic properties [20], and brominated dibenzofurans are modulators of gene expression associated with the nuclear X-steroid receptor responsible for the biosynthesis of sex hormones [21]. Chlorine-containing flame retardants can form toxic products during combustion. In [22–24], it was shown that halogen compounds separate a large amount of toxic substances formed both during combustion and during operation. Halogen-containing flame retardants not only do not solve the main problem of the fire hazard of polymer materials associated with the toxicity of combustion products, but even aggravate it.

2.2. Phosphorus-Containing Compounds

Phosphorus-based flame retardants are widely used with thermoplastics and thermosetting materials [25]. Phosphorus-based fire retardants include various products, such as elemental red phosphorus, inorganic phosphates, phosphites, phosphates, phosphine oxides, and organochlorine phosphates, which are active in the condensed and/or gas phase [26]. Phosphorus compounds can function in the condensed polymer or in the gas phase, and possibly in both phases simultaneously. With regard to condensed phase operation, it is generally accepted that phosphorus flame retardants are markedly more effective in oxygen-containing or nitrogen-containing polymers, which can be either heterochain polymers or polymers with these elements in pendant groups. By generating phosphoric anhydrides of phosphoric and related acids, which act as dehydrating agents, phosphorus compounds react with these polymers to promote the formation of coke (dehydration reactions lead to the formation of double bonds, which at elevated temperatures lead to cross-linked or carbonized struc-

tures) [1]. In general, the chemical reactions involved in the decomposition of the matrix are redirected to form carbon rather than CO or CO₂. Thus, the phosphorus charring process can be used even in the case of weak char-forming polymers such as polyolefins and styrenes, which form coke by adding an additive. Acids released during the decomposition of phosphorus-based chemicals can form a thin glassy or liquid protective coating on the condensed phase, thereby reducing oxygen diffusion as well as heat and mass transfer between the gas and the condensed phase. This glassy residue can also coat the coke, making it stronger and cohesive, thereby delaying its destruction [27, 28]. In addition to slowing the spread of fire in the condensed phase, phosphorus additives can work well in the gas phase, exhibiting free radical scavenging properties. Volatile phosphorus compounds are among the most effective flame retardants. They contain products that reduce the concentration of hydrogen atoms in the flame, thereby extinguishing it.

In fact, at the same molar concentration, phosphorus is a much more effective radical scavenger than bromine and chlorine, since they control the gas-phase action of phosphorus-based additives [29–31]:



Phosphorus compounds can be inorganic or organic. The most commonly used inorganic compounds are red phosphorus, ammonium polyphosphate, ammonium dihydrophosphate, phosphine, phosphorus oxides, etc. [32, 33]. Ammonium polyphosphate is used in intumescent compositions [34, 35].

There are many organic phosphorus-containing compounds that have flame retardant properties, but few have achieved commercial success. The three main groups of organic phosphorus fillers that are commonly used are:

(1) phosphinates, (2) phosphonates, and (3) phosphate esters (Fig. 1) [36].

Inorganic phosphorus-containing flame retardants include: ammonium polyphosphate, red phosphorus, ammonium dihydrogen phosphate, phosphine, phosphorus oxides, etc. Examples of phosphorus-containing fire retardants can be alkyl phosphonates, esters of phosphoric acids (tricresyl phosphate, cresyl diphenyl phosphate, etc.), triaryl phosphates [37, 38]. Every year an increasing number of phosphorus-containing flame retardants appear,

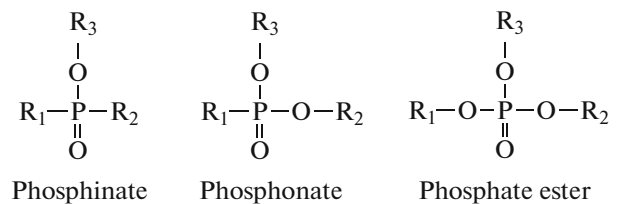


Fig. 1. The chemical structures of organic phosphorus flame retardants [36].

this is a consequence of the desire to more effectively reduce the flammability of polymeric materials. At the same time, there is a clearly expressed tendency towards the complication of substances that combine these elements [39, 40]. It is important that this tendency is not always effective, since it is still impossible to avoid the isolation of low-molecular-weight reaction products. It is also not possible to completely exclude the deterioration of the physical and mechanical characteristics and the increase in the corrosion aggressiveness of the compositions.

2.3. Nitrogen Compounds

Nitrogen-containing compounds are one of the most environmentally friendly classes of flame retardants that produce a small amount of smoke and do not contain by-products of dioxin and/or halogen during combustion [41]. Melamine and melamine derivatives are the most important fire retardants based on nitrogen compounds. Nitrogen-containing flame retardants have been used to increase the fire resistance of, firstly, polyamides and, secondly, polyolefins (and polyurethanes), but they are usually not very effective for other polymers [42]. Melamine is a thermostable product containing 67% nitrogen by weight. It has high thermal stability and is used in polyurethane foams and intumescent coatings [43]. Melamine decomposes the released ammonia (which dilutes oxygen and combustible gases) and leads to the formation of a thermally stable condensate melam (2,5,8-triamino-1,3,4,6,7,9,9b-heptaazaphenalene), melam ((N-4,6-diamino-1,3,5-triazin-2-yl)-1,3,5-triazine-2,4,6-triamine) and melon (Poly (8-amino-1,3,4,6,7,9,9b-heptaazaphenalene-2,5-diyl)imino). The evolution of melam, melam, and melon is accompanied by the formation of residues in the condensed phase, leading to the occurrence of endothermic processes, and is also effective for slowing combustion [44]. Melamine flame retardant is used as a blowing agent and flame retardant in intumescent coatings, elastomers and plastic formulations, and in flexible polyurethane foams [45]. Melamine is a weak base that can form well-defined heat-resistant salts with both organic and inorganic acids. These salts, such as melamine cyanurate, melamine phosphate and melamine pyrophosphate, have been found to have

flame retardant characteristics and for this reason are commonly used in practice to improve the flame retardance of a polymer. Melamine phosphate and melamine pyrophosphate act as intumescent compounds upon combustion [46]. Melamine cyanurate, oxalate and melamine phthalate are polyamides that decompose under combustion conditions, promote enhanced droplet flow of noncombustible liquid; therefore, the polymer is removed from the flame source without providing fuel to feed the fire. It also has a physical effect on the combustion cycle, acting as a heat sink and source of inert gas. More specifically, its initial endothermic dissociation followed by sublimation of the resulting melamine and subsequent decomposition of the melamine vapor absorbs the heat generated, cooling the substrate. In addition, the formed inert gases additionally contribute to the retardation of combustion due to the dilution of oxygen and combustible gases [47–49]. Most melamine salts work in the condensed phase. Another nitrogen-containing composition exhibiting flame retardant properties is oxazene resin; it can be used as a homopolymer or as a reactive additive in epoxy resins. Polyisocyanurate also has a certain fire resistance. It is most effective in combination with phosphorus-containing epoxy resins [50].

2.4. Intumescent Flame Retardants

An intumescent fire retardant system is another popular class of fire retardant additives that functions by creating swollen coke that acts as an insulating barrier. This barrier reduces heat transfer between the polymer and the heat source. An intumescent system typically consists of three components, namely a charmer or carbonizer, an acid source, and a blowing agent. During combustion, acids catalyze the dehydration reaction, which leads to the formation of coke [51]. The foaming agent (melamine, urea, or guanidine) decomposes and foam is released [52]. The development of swollen coke occurs through a multi-stage physical and chemical process. Noncombustible gases released during the decomposition of the blowing agent form a foam and a carbonized layer [53, 54]. Several synergistic agents have been proposed to enhance the fire properties of intumescent formulations. As an example, it has been found that by adding it together with ammonium polyphosphate (APP)/pentaerythritol (PER) a small amount of zeolite in polyolefins, their flame retardant properties can be significantly improved. Zinc borate or a combination of zinc oxide and borate also improve the protection provided by typical intumescent systems. In addition, intumescent coatings can be made more effective in terms of protective properties by incorporating Ti or Zr or other metal borides, nitrides or carbides [55–58].

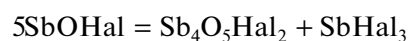
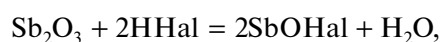
2.5. Metal Compounds

Metal compounds are used as flame retardants and belong to the group of inert additives; they can be divided into two types [59, 60]:

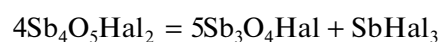
— substances resistant up to a temperature of 1000°C (carbon black, silicates, inorganic glass, metal oxides, etc.);

— substances that decompose at temperatures below 400–500°C, while absorbing heat with the release of CO₂, NH₃ or water vapor (carbonates, hydroxides, ammonium phosphate, metal hydrogen carbonates, etc.).

To date, antimony oxide is the most effective flame retardant. As mentioned earlier, antimony oxide has synergistic activity with halogens and other types of fire retardants. The hypothesized mechanism of action is as follows [61]:



at a temperature of about 270°C,



at a temperature 450°C;

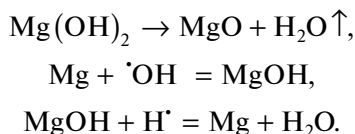


at more than 500°C.

At the final stage, the formation of antimony oxide makes an additional contribution to the retardation of combustion, creating obstacles to flame propagation. Gaseous antimony trichloride limits the supply of oxygen to the combustion zone [62].

Metal hydroxides remove heat by liberating a large amount of water in the same temperature range or at a temperature lower than that at which the polymer decomposes. Thus, by absorbing heat, they slow the polymer pyrolysis process. In addition, the resulting water vapors dilute the combustible gases of polymer decomposition, thereby preventing exothermic radical reactions in the combustion zone. Moreover, a non-combustible layer is formed on the surface of the material, which protects the substrate [63, 64]. Smoke suppression is another contribution of metal hydroxides to fire resistance. Studies have shown that the amount of carbon monoxide released during the combustion of polymers containing inorganic hydroxides is usually lower than in a pure matrix. The most likely explanation for the mechanism of action of hydroxide-based fire retardants is that the carbon formed as a result of polymer decomposition is deposited on the resulting oxide by hydroxide decomposition, and then it evaporates in the form of carbon dioxide without emitting smoke. As well, because water is their only decomposition product, inorganic hydroxides do not significantly increase the corrosive nature of the smoke emitted during the combustion of polymers containing them.

The two most commonly used mineral flame retardants are aluminum and magnesium hydroxides. More than 40% of the production of industrial fire retardants are metal hydroxides. This is due to their low cost and low toxicity compared to halogen-containing additives [65]:



The main disadvantage of both aluminum and magnesium hydroxide is that at least 60 wt % of these substances must be included in the polymer to achieve good flame retardant properties. However, an increase in the efficiency of the produced material negatively affects the mechanical properties of the resulting material [66]. To increase their effectiveness, metal hydroxides are often used in combination with other types of fire retardants. As an example, aluminum hydroxide, together with antimony oxide, is used for fire-resistant flexible PVC wires and cables. PVC-based materials exhibit improved flame retardant properties when mixed with inorganic hydroxides and molybdenum-containing compounds [67–69]. More recently, it has been shown that an improvement in fire resistance at significantly lower loads on the additive can also be achieved using nanoparticles (aluminum and magnesium hydroxides) [70].

Borates, namely zinc borates, constitute another group of inorganic additives that have been found to improve the combustion characteristics of polymeric materials. There are two forms of zinc borates that have good thermal stability, which allows them to be used as flame retardants: $4\text{ZnO}\cdot 6\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$ and $2\text{ZnO}\cdot 2\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$. Zinc borate, in the second category, is the most used. It operates predominantly in the condensed phase, promoting coke formation, but also acts as a smoke suppressor [71]. The main use of zinc borate is in PVC and halogenated polyester, either as a complete or, more commonly, partial replacement for antimony oxide. Unlike antimony oxide, which is a flame retardant in the vapor phase, zinc borate significantly increases the amount of coke formed during the combustion of the polymer. In particular, it reacts with hydrogen chloride released during the decomposition of PVC to form zinc hydroxychloride and zinc chloride, as well as boron oxide and boron trichloride [72]. Zinc borate is often used in combination with other flame retardants, such as magnesium hydroxide, causing the formation of a porous ceramic layer during polymer combustion, which insulates the substrate [73, 74]. It is also used as a synergist to phosphorus- and halogen-containing compounds. One great advantage is that zinc borate retains water of crystallization up to a temperature of 300°C, due to which it is used to create compositions based on a copolymer of ethylene and vinyl acetate [75], polyvinyl chloride,

polypropylene [76], polyester resins, and polyurethane [77].

2.6. Nanoparticles of Metal Compounds

Recently, nanoparticles of metal compounds have attracted great attention as flame retardants [78–80]. Nanoparticles of zinc borate [81], magnesium hydroxide [82], zinc oxide [83], aluminum oxide [84], iron(III) oxide [85, 86], and layered double hydroxides [87, 88] are used as fire retardants.

Zinc borate nanoparticles have been used as flame retardants for polyvinyl chloride [89], polyurethane [90], polyethylene [91], and polyethylene terephthalate. The effect of zinc borate is associated with the formation of a protective layer on the surface of the polymer, which protects the material from combustion [92].

Magnesium hydroxide nanoparticles are used as an additive that reduces the flammability of polymeric materials [93–96]. They are attractive because of their relatively low cost. Magnesium hydroxide mainly acts by cooling the polymer due to the reaction of endothermic decomposition of magnesium oxide [97].

In a number of works [98–100], the use of zinc oxide nanoparticles as a flame retardant in polymeric materials was presented. In [101], the use of aluminum oxide nanoparticles to reduce the combustibility of a polymer was studied. It was found that, on the one hand, aluminum oxide nanoparticles catalyze the processes of thermal-oxidative degradation and accelerate the process of decomposition of macromolecules; on the other hand, they form a protective layer that increases the thermal stability of the polymer.

Polymer composites with inorganic nanoparticles have great potential as materials with high fire and heat resistance. Nanoparticles in polymer nanocomposites demonstrated a simultaneous decrease in the heat release rate and an increase in thermal stability [102, 103]. The combustion characteristics of polymer nanocomposites due to the addition of nanofillers are due to a dual mechanism, namely, the effect of a physical barrier and the effect of catalytic charring [104]. The physical barrier effect, also known as the surface ceramization process, is observed during combustion when the nanoparticles form a network of flakes. These flakes are combined with a small portion of carbonaceous coke. This coke or ceramic layer is thermally stable and acts as a barrier, preventing heat transfer between the material and the flame, and also serves as a screen between combustion and decomposition products [104].

3. SYNERGISTIC EFFECTS OF FLAME RETARDANTS

The concept of synergy is very often used in the optimization of flame retardant formulations. The term synergy refers to the combined effect of two or

more additives. Synergistic phenomena can be obtained either by a combination of flame retardant mechanisms, such as char formation by a phosphorus flame retardant in combination with gas phase action by a halogenated flame retardant, or by a combination of flame. Fire retardants that enhance the same mechanism, such as nanoclays and phosphorus fire retardants, act in the condensed phase. [105] studied the effect of using nanosized oxides and ammonium polyphosphate synergistically with polystyrene and polymethyl methacrylate. The result of the cone calorimeter showed a reasonable reduction in the maximum heat release rate, a reduction in opaque smoke, and an increase in the limiting oxygen index value. In [106], the effect of the synergistic use of ammonium polyphosphate, melamine phosphate, and aluminum oxide trihydrate with a layered silicate polyester resin was studied. In [107], using the example of plasticized polyvinyl chloride and polymethyl methacrylate, the effect of particle size on the fire-resistant characteristics of composites was shown. Based on the presented works, it can be concluded that synergism between various flame retardants can increase the fire-resistant properties of polymer composites.

CONCLUSIONS

The paper considers various groups of flame retardant additives in polymeric materials, such as halogen-containing, phosphorus-containing, metal compounds, which are used to increase the fire resistance of polymeric materials. The mechanisms of action of flame retardants are discussed, and the concept of a physical barrier of nanoparticles is described. The prospects of using nanoparticles of metal compounds are noted.

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