

Additives to reduce the flammability of polymers

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ABSTRACT: Introduction. This review article provides data on additives used to reduce the flammability of polymer compositions. It is shown that not individual substances are used for this purpose, but their mixtures, including flame retardants, synergists, and stabilizers. The principle of operation of flame retardants is that when the appropriate degree of concentration of flame retardants in the material is reached, they do not allow it to burn without the presence of an ignition source. Under the influence of fire on the processed material, various chemical and physical processes occur in it, preventing the flame from flaring up. **Main part.** The advantages and disadvantages of the main flame retardants currently used, which include antimony compounds, halogen-containing compounds, phosphorus-containing substances, as well as aluminum and magnesium hydroxides, are analyzed. Various mechanisms for slowing down combustion processes when flame retardants are used are considered. It has been shown that bromine-containing flame retardants are much more effective than chlorine-containing ones. They decompose in a narrow temperature range. In addition, plastics containing bromine compounds as flame retardants are easily recycled due to the high thermal stability of such flame retardants. Phosphorus-containing compounds have a plasticizing ability and increase the fire resistance of plastic compounds. The action in the condensed phase is that during the decomposition of the flame retardant, phosphoric acid residues are formed, which act as dehydrating agents, contributing to the formation of carbonized structures. In this case, an aerosol can also be formed, which contributes to the deactivation of radicals due to the wall effect. Of particular interest are compounds containing halogen and phosphorus. The advantages of these compounds are as follows: by splitting off halogen radicals during decomposition, they deactivate active radicals; contribute to the formation of carbonized structures. Metal hydroxides decompose under the influence of high temperatures with the release of water. The decomposition reaction is endothermic, resulting in cooling of the substrate to temperatures below the flash point. The formation of water contributes to the dilution of combustible gases released during decomposition, weakens the effect of oxygen and reduces the rate of combustion. The effectiveness of hydroxides is directly proportional to their content in the polymer. The greatest efficiency is observed when aluminum hydroxide is introduced into oxygen-containing polymers (polyethylene terephthalate, polybutylene terephthalate, polyamide). Magnesium hydroxide is more expensive than aluminum hydroxide, but has a higher heat resistance (up to 300°C). **Conclusion.** Thus, among the listed flame retardants, aluminum and magnesium hydroxides occupy the first place in terms of the volume of use (more than 40% of the total volume of flame retardants). This is due to their low cost, manufacturability of their application and environmental safety. A well-chosen metal hydroxide system produces a low-cost non-combustible material with little fumes from decomposition. Therefore, the use of metal hydroxides as flame retardants is constantly increasing.

KEY WORDS: flame retardants, flammability, fire resistance, polymer compositions.

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INTRODUCTION

Flame retardants are substances that protect materials of organic origin from ignition and self-combustion [1, 2]. Currently, not individual substances are used, but their mixtures. The composition of the flame retardant includes [3, 4]:

– flame retardants (ammonium phosphates, ammonium sulfate, boric acid, silicates, ammonium chloride);

– synergists - substances that enhance the action of the main moderator;

– stabilizers that limit the flow rate of the moderator.

The principle of operation of flame retardants is that when the appropriate degree of concentration of flame retardants in the material is reached, they do not allow it to burn without the presence of an ignition source. Under the influence of fire on the processed material, various

chemical and physical processes occur in it, preventing the flame from flaring up [5–8].

All means that increase fire-retardant properties are divided into coatings that protect against fire and compounds that penetrate into the material being processed: the first category includes varnishes, pastes, paints and various coatings; to the second – fire-retardant impregnations.

Combustion is a very complex physicochemical process, including both chemical reactions of destruction, crosslinking, and carbonization, as well as chemical reactions of transformation and oxidation of combustion gas products, and physical heat transfer processes [9]. The reactions actually lead to two main types of products: gaseous substances (combustible and non-combustible) and solid products (carbonaceous and mineral). When the reaction proceeds in the pre-flame region, fuel for the flame, soot, etc. are formed.

As a result of thermal degradation of polymers, volatile decomposition products containing C–C and C–H groups are released, which form free radicals that react with oxygen. It is believed that the ability to ignite and the speed of propagation of the flame depend on the rate of formation of HO· radicals. The reactions leading to the formation of CO₂ and H₂O are highly exothermic, i.e. pass with the release of a large amount of heat. This heat creates conditions for self-acceleration of oxidation reactions and subsequent combustion.

MAIN PART

Mechanisms of action of flame retardants

There are several mechanisms for slowing down combustion processes using flame retardants [10]:

– Inhibition of free radical processes that occur during the decomposition of the polymer, due to the formation of substances that can interact with free radicals to form radicals with less reactivity. The introduction of substances containing halogens (chlorine, bromine, fluorine, iodine), nitrogen, phosphorus and boron contributes to the slowing down of combustion. At high temperatures, flame retardants decompose to form halogen radicals, which react predominantly with very active HO· radicals.

– Formation of a protective layer on the surface of the polymer, impermeable to oxygen or insulating from further heating. The mechanism of action of a number of fire retardants (silicates and aluminosilicates, metal borates, phosphates, their organic derivatives) is due to the predominant influence on the combustion process of the protective layers formed on the surface. These layers consist of non-volatile residues (mainly metal oxides) formed during the decomposition of inorganic compounds. Flame retardants, which are capable of creating dense surface protective layers, create a kind of physical

barrier to the action of the flame on the polymer, making it difficult for the diffusion of combustible gases into the flame. Such flame retardants include barium metaborate, zinc borate, and ammonium tetrafluoroborate [11]. Flame retardants containing phosphorus compounds reduce the oxygen permeability of the material. An example of such a flame retardant would be diammonium phosphate. One of the effective inhibitors of the processes of combustion and smoldering of various polymers are organic phosphorus compounds, the action of which is explained in the following way [12]. During the pyrolysis of polymers containing phosphorus compounds, phosphoric acid and its anhydrides are formed, which catalyze dehydration and dehydrogenation.

– Emission of non-combustible gases that prevent the supply of oxygen to the combustion zone. When halogen compounds are used as flame retardants, the combustion of polymers can be slowed down by the following mechanism. Ammonium chloride or bromide at temperatures above 200 and 250°C, respectively, decompose into ammonia, hydrogen chloride and hydrogen bromide. Gaseous (hydrogen chloride and hydrogen bromide) suppress combustion. In addition, the percentage of oxygen in the gas phase decreases, which also slows down combustion.

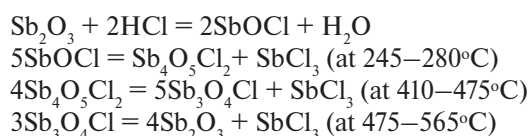
– Decomposition of flame retardants or interaction of flame retardants and their degradation products with other substances with heat absorption, which helps to reduce the temperature of the material below the flash point. A large group of substances used as fire retardants are substances that decompose endothermally to form non-combustible products. These include hydroxides of aluminum, magnesium, zinc, hydrated metal carbonates, urea and other substances. The mechanism of action of such flame retardants is associated with a purely physical effect on the heat balance of the combustion process.

– Prevention of flame propagation during the combustion process, due to additional costs of thermal energy for heating the powdered filler. The introduction of non-combustible fillers into materials can reduce the content of the combustible component. For this purpose, in addition to dispersed fillers (chalk, sand), fibrous (glass fibers, asbestos) can also be used. Potassium or sodium silicates are of great importance as a fire-preventive agent, since the materials coated with them ignite with great difficulty. For this purpose, the material is covered several times with a solution of silicate, to which a little chalk, bone ash, mineral paint, or some other crushed, non-fusible mineral substances are added. Processed materials do not burn with a flame, but only char and smolder.

Synergistic mixtures of flame retardants

It should be noted that in fact the mechanism of action of flame retardants is not limited to any one effect, but is a more complex process. The simultane-

ous presence in the mixture of two or more substances that prevent the formation of a flame contributes to the achievement of a significantly greater effect compared to the effects observed when using the same substances separately. The joint action of two substances is called synergism. The most effective flame retardant at present is antimony oxide in combination with halogen-containing organic compounds (optimum molar ratio $Sb/Cl = 1/3$). This mixture has a synergistic effect [13]. The proposed mechanism of action of this mixture is as follows. The hydrogen chloride released during the combustion of the polymer from the holoenoorganic compound interacts with antimony oxide to form antimony oxychloride, which, in turn, can decompose with the release of antimony trichloride:



The antimony oxide formed at the final stage, being a powdered filler, contributes to the retardation of combustion, creating additional obstacles to the spread of flame. Gaseous antimony trichloride, in turn, limits the supply of oxygen to the combustion zone. The widespread use of antimony oxide is also facilitated by the fact that it is not a carcinogenic compound.

Halogen-containing flame retardants

Halogen-containing flame retardants have proven themselves well [14–18]. For compounds of the same type, the effectiveness of halogen-containing flame retardants decreases in the series $J > Br > Cl > F$. Compounds with a reduced carbon-halogen bond energy have the highest efficiency. The effectiveness of halogen-containing compounds is determined by how easily C–G bonds can dissociate. That is, the effectiveness of the fire retardant depends not only on the halogen content, but also on the radical to which it is attached. These are halogen-containing aliphatic compounds. Most often, chlorinated paraffin ($C_nH_{2n+2-x}Cl_x$, where $n = 10\text{--}30$; $x = 1\text{--}7$) containing up to 70% of combined chlorine is used. Less often, aromatic chlorine or bromine containing compounds are used, for example, decabromodiphenyl oxide, ($C_{16}H_{10}Br_{10}O$), tetrachlorophthalic anhydride ($C_8C_{14}O_3$). Aromatic compounds are more stable and therefore reduce flammability to a lesser extent. Fluorine and iodine compounds are not used as flame retardants, since fluorine compounds are ineffective, and iodine compounds have low thermal stability during processing. The use of chlorine has recently been greatly reduced due to pressure from public organizations concerned about the toxicity of these compounds. And when burning bromine-containing fire retardants,

toxic compounds (dioxins and furans) are not released. The range and volume of use of bromine-containing flame retardants is greater than that of chlorine-containing ones. Bromine-containing flame retardants are much more effective than chlorine-containing flame retardants, since their combustion products are less volatile. In addition, chlorine-containing fire retardants emit chlorine over a wide temperature range, so its content in the gas phase is low, and bromine-containing fire retardants decompose in a narrow temperature range, thus ensuring the optimal concentration of bromine in the gas phase. You should also pay attention to such an important factor as the recycling of materials containing fire retardants. According to recent data, plastics containing bromine compounds as flame retardants are easily recycled due to the high thermal stability of such flame retardants.

Polybromodiphenyl oxide and its derivatives. Suitable for most plastics except EPS. Currently, the use of such compounds is declining due to pressure from environmental organizations.

Dibromoneopentyl glycol and its derivatives. It is applied to polyester pitches in the course of synthesis. Contains 60% bromine. They have high thermal stability and chemical resistance. High performance fire retardant. High light fastness. Can also be used in rigid polyurethane foams.

Dibromostyrene and its derivatives. Including graft copolymers with polypropylene. Recommended for acrylonitrile butadiene styrene plastics, polystyrene, engineering thermoplastics, unsaturated polyesters and polyurethanes. Not recommended for use in PVC, EPS and rigid polyurethane foams.

Hexabromocyclododecane is used in high impact polystyrene and polyolefins, including foamed ones.

Pentabromobenzyl acrylate is designed for engineering thermoplastics. Used in reactive extrusion to copolymerize with polyamides, thermoplastic polyesters, and polycarbonate to achieve UL-94 V-0 (self-extinguishing in less than 10 seconds after flame removal; burning droplets are not allowed) without compromising the physical and mechanical properties of the polymer.

Can also be used for filled polypropylene. Due to its high molecular weight, it does not migrate, it has high thermal stability and chemical resistance. Improves the compatibility of the filler (fiberglass) with polypropylene.

Brominated epoxy oligomers (BEO) are used for engineering thermoplastics (polyethylene terephthalate, polybutylene terephthalate, polyamide 6, 66, etc.), thermoplastic polyurethanes and polycarbonate/acrylonitrile butadiene styrene blends. Due to its high molecular weight, it does not migrate, it has high thermal stability and chemical resistance.

Tetrabromophthalic anhydride and its derivatives. It is used in thermoplastics and polyurethanes. Can be used in PVC and thermoplastic elastomers.

Tribromineopentanol contains 70% aliphatically attached bromine, is introduced at the stage of synthesis, chemically interacts with the polymer. It has very high thermal and light resistance. Not subject to hydrolytic degradation. It is highly soluble in polyols, making it particularly suitable for the manufacture of non-flammable polyurethanes.

Tribromophenol and its derivatives. Used for polystyrene and its copolymers (high impact polystyrene, acrylonitrile butadiene styrene), polycarbonate, polyamide, polyurethane foam and thermoplastics. Not suitable for polyolefins and PVC.

Brominated trimethylphenyl indane (developed by Dead Sea Bromine Group). Contains 73% aromatic bromine, providing excellent thermal stability, which is especially important in the processing of engineering plastics. Allows you to increase the impact strength and fluidity of the thermoplastic melt.

Phosphorus-containing flame retardants

Phosphorus-containing fire retardants are organic and inorganic compounds [19, 20]. They are active in the gas or condensed phase, and sometimes in the ejection. It is believed that phosphorus compounds occur in the gas phase through the formation of $PO\cdot$ radicals, which absorb active $H\cdot$ and $OH\cdot$ radicals, the spread of which is propagated by flames.

The action in the condensed phase occurs in the fact that during the decomposition of the flame retardant, phosphoric acid residues accumulate, which act as dehydrating agents, contributing to the repetition of carbonized structures. In this case, an aerosol can also be formed, which contributes to the deactivation of radicals due to the tissue effect.

The nomenclature of phosphorus-containing compounds is quite wide, they can be divided into 2 groups – halogen-containing and halogen-free.

The advantage of compounds, halogen-containing and phosphorus:

- splitting off halogen radicals during decomposition, they deactivate the active radicals $H\cdot$ and $OH\cdot$ according to the usual mechanism for halogens;
- contribute to the formation of carbonized structures according to the mechanism described above.

The second group includes red phosphorus, water-soluble inorganic phosphates, insoluble ammonium phosphate and polyphosphates, organophosphates and phosphonates, as well as phosphine oxides.

Red phosphorus is an excellent flame retardant for heterochain polymers (polyethylene terephthalate, polycarbonate, etc.). Specially processed red phosphorus is used for fire protection of electrical products made of polyamides. Used in combination with foaming and carbonizing agents in intumescent fire retardants.

The use of phosphorus is limited by its toxicity and red color.

Triaryl phosphates. Triphenyl phosphate (TPP) is used in polycarbonate/acrylonitrile butadiene styrene and polyphenylene oxide blends. Tricresyl phosphate (TCP) is mainly used in PVC as a flame retardant plasticizer and in styrene-containing polymers.

Diaryl phosphates (RDP and BDP) are colorless liquids used primarily in polycarbonate/acrylonitrile butadiene styrene, polybutylene terephthalate, polyphenylene oxide blends. These are low-volatile, heat-resistant products, with a lower plasticizing effect compared to triaryl phosphates. Typically 10–15% of these compounds are sufficient to achieve the appropriate UL-94 fire rating. They have high resistance to hydrolytic degradation.

Alkylphosphonates. The high efficiency of compounds of this class is due to the high content of phosphorus. However, the high volatility of these flame retardants limits their use in rigid polyurethane foams and highly filled polyesters.

Oligomeric cyclic phosphonates. The high viscosity of such compounds complicates their use in pure form. The most commonly used superconcentrates. They are mainly used for the manufacture of non-combustible fibers from polyethylene terephthalate, with a content of 6% of the active component in polyethylene terephthalate, they satisfy all the requirements for such products. Due to their low volatility they can be used in rigid polyurethane foams.

Metal hydroxides

Aluminum hydroxide (ATH) is used in elastomers, thermoplastics and thermoplastics. It decomposes at temperatures of 190–230°C, depending on the particle size of 0.25–3 μm . The main areas of application are styrene-butadiene latex, for carpeting, the manufacture of non-combustible elastomeric cable insulation, conveyor belts, roofing materials and hoses. The greatest efficiency is observed when aluminum hydroxide is introduced into oxygen-containing polymers (polyethylene terephthalate, polybutylene terephthalate, polyamide).

Magnesium hydroxide (MH) is a white powder with a particle size of 0.5 to 5 μm . To achieve a fire-retardant effect, it is introduced in an amount of 50–70% by weight of the polymer. Magnesium hydroxide is more expensive than aluminum hydroxide, but has a higher heat resistance (up to 300°C). Mainly used in polypropylene, acrylonitrile butadiene styrene plastics and polyphenylene oxide, it is not recommended for use in thermoplastic polyesters (polyethylene terephthalate, polybutylene terephthalate), as it accelerates the degradation of such polymers.

Metal hydroxides decompose under the influence of high temperatures with the release of water. The decom-

position reaction is endothermic, resulting in cooling of the substrate to temperatures below the flash point. The formation of water contributes to the dilution of combustible gases released during decomposition, weakens the effect of oxygen and reduces the rate of combustion. The efficiency of hydroxides is directly proportional to their content in the polymer [21].

In some tests used to evaluate electrical products and cable insulation, the main parameters are material self-extinguishing and fire resistance. Metal hydroxides are suitable for use in these areas. Moreover, after decomposition, a heat-insulating layer is formed, which also prevents the emission of smoke.

Zinc borate can be used for fire protection of PVC, polyolefins, polyamides, elastomers and epoxy resins.

In halogen-containing systems, it is used in conjunction with antimony oxide, and in halogen-free systems, with metal hydroxides or red phosphorus.

CONCLUSION

Thus, among the listed flame retardants, aluminum and magnesium hydroxides occupy the first place in terms of the volume of use (more than 40% of the total volume of flame retardants). This is due to their low cost, manufacturability of their application and environmental safety. A well-chosen metal hydroxide system produces a low-cost non-combustible material with little fumes from decomposition. Therefore, the use of metal hydroxides as flame retardants is constantly increasing.

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Ilnaz I. Zaripov – methodology development; writing the draft; follow-on revision of the text.

Irina N. Vikhareva – research concept.

Evgeniya A. Buylova – collection of materials.

Tatyana V. Berestova – participation in the development of the material.

Aliya K. Mazitova – scientific management; final conclusions.

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