

New prospects in flame retardant polymer materials: From fundamentals to nanocomposites

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ABSTRACT

The objective of this review is to make the field of “flame retardants for polymer materials” more accessible to the materials science community, i.e. chemists, physicists and engineers. We present the fundamentals of polymer combustion theory, the main flame retardant properties and tests used to describe fire behavior, together with the nature and modes of action of the most representative flame retardants and the synergistic effects that can be achieved by combining them. We particularly focus on polymer nanocomposites, i.e. polymer matrices filled with specific, finely dispersed nanofillers, which will undoubtedly pave the way for future materials combining physicochemical and thermo-mechanical performances with enhanced flame retardant behavior.

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Abbreviations: ABS, acrylonitrile butadiene styrene; AN, acrylonitrile; APP, ammonium polyphosphate; APS, aminopropyltriethoxysilane; AS, ammonium stearate; ATH, aluminum tri-hydroxide; BDP, bisphenol A bis(diphenyl phosphate); BPFP, bisphenol fluorenonecarbonate; CNT, carbon nanotube; EVA, ethylene vinyl acetate copolymer; HBCD, hexabromocyclododecane; HDPE, high density poly(ethylene); HIPS, high impact polystyrene; HM, hydromagnesite; LDPE, low density poly(ethylene); MDH, magnesium di-hydroxide; MEPP, 2-methacryloxyethyl phenyl phosphate; MF, melamine-formaldehyde; MMA, methyl methacrylate; MMT, montmorillonite; MWNT, multi-walled carbon nanotube; PA, polyamide; PAN, poly(acrylonitrile); PC, poly(carbonate); PDMS, poly(dimethylsiloxane); PE, poly(ethylene); PET, poly(ethylene terephthalate); PMMA, poly(methyl methacrylate); POSS, polyhedral oligomeric silsesquioxane; PP, poly(propylene); PPgMA, maleic anhydride modified poly(propylene); PPO, poly(phenylene oxide); PS, poly(styrene); PTFE, poly(tetrafluoroethylene); PTME, poly(tetramethylenether); PVC, poly(vinyl chloride); RDP, resorcinol bis(diphenyl phosphate); SAN, styrene acrylonitrile copolymer; St, styrene; SWNT, single-walled carbon nanotube; TBBPA, tetrabromobisphenol A; TCP, tricresyl phosphate; TPP, triphenyl phosphate; VBr, vinyl bromide; CEC, cation exchange capacity; CVD, chemical vapour growth deposition; DTA, differential thermal analysis; EGA, evolved gas analysis; FTIR, Fourier transform infrared spectroscopy; HRR, heat release rate; LOI, Limiting Oxygen Index; pHRR, peak heat release rate; T_g, glass transition temperature; TGA, thermogravimetric analysis; THR, total heat release rate; TOF, time of combustion or extinction; TSR, total smoke released; TTI, time to ignition; XPS, X-ray photoelectron spectroscopy.

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1. Introduction

The massive use of polymer materials in our everyday life is driven by their remarkable combination of properties, low weight and ease of processing. However, polymers are also known for their relatively high flammability; most often accompanied by the production of corrosive or toxic gases and smoke during combustion. Consequently, improving the fire retardant behavior of polymers is a major challenge for extending their use to most applications.

Safety requirements are currently becoming more and more drastic in terms of polymers' reaction to fire and their fire resistance performances, while various flame retardant additives, such as halogenated additives, are being phased out for their proven or suspected adverse effects on the environment. The combined challenge thus consists in developing effective and environmentally friendly flame retardant systems for polymer materials.

The scientific and technical literature contains very diverse and efficient strategies for improving polymer fire resistance, which depend primarily on the nature and chemical structure of the polymer concerned, its decomposition mode and the required level of fire safety, and also the global performances of the resulting materials. The development of flame retardant materials and understanding the phenomena that take place during combustion often require close collaboration between several fields of scientific expertise (macromolecular and physical chemistry, physics of mass and heat transfer, rheology, etc.)

This review, whose aim is to present the keys to the understanding of fire behavior in polymer materials and the main fire control processes, is divided in four sections: (i) the fundamentals of polymer fire behaviour and laboratory fire testing; (ii) the main flame retardant properties; (iii) the most representative flame retardants and their modes of action; and (iv) emerging synergistic effects of combinations of polymer flame retardants.

2. Polymer combustion and flame retardancy

2.1. Polymer combustion

Due to their chemical structure, made up mainly of carbon and hydrogen, polymers are highly combustible [1].

The combustion reaction involves two factors: one or more combustibles (reducing agents) and a combusting (oxidizing agent). The combusting is generally the oxygen in the air. The whole process usually starts with an increase in the temperature of the polymeric material due to a heat source, to such an extent that it induces polymer bond scissions. The volatile fraction of the resulting polymer fragments diffuses into the air and creates a combustible gaseous mixture (also called fuel). This gaseous mixture ignites when the auto-ignition temperature (defined as the temperature at which the activation energy of the combustion reaction is attained) is reached, liberating heat. Alternatively, the fuel can also ignite at a lower temperature (called the flash point) upon reaction with an external source of intense energy (spark, flame, etc.)

The life span of the combustion cycle depends on the quantity of heat liberated during the combustion of the fuel. When the amount of heat liberated reaches a certain level, new decomposition reactions are induced in the solid phase, and therefore more combustibles are produced. The combustion cycle is thus maintained, and called a *fire triangle* (Fig. 1).

This global process is complex and involves several reactions and transport phenomena in the solid, gaseous and interfacial phases. Heating can be caused by a contribution of thermal energy from an external heat source (radiation, convection or conduction), by a chemical process induced inside the material (fermentation, oxidation, etc.) or by the exothermicity of the combustion reaction initiated. In polymers, the amount of energy required to initiate combustion varies in function of the physical characteristics of the material. For instance, during the heating of semi-crystalline thermoplastics, the polymer softens, melts and drips. The energy stored by the polymer during these processes depends on both its

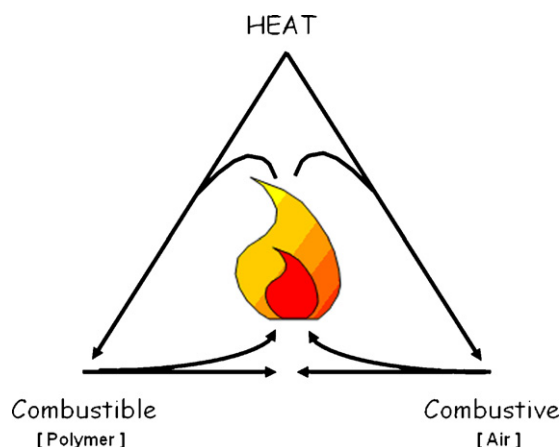


Fig. 1. Principle of the combustion cycle.

heat-storage capacity and its enthalpy of fusion and degree of crystallinity. Therefore, the increase in polymer temperature and the related rate depend primarily on the heat flow, the difference in temperature due to the exothermicity of the reactions involved, and the specific heat and thermal conductivity of the semi-crystalline thermoplastic. In contrast, in the case of amorphous thermoplastics and most thermosets, due to the absence of a melting point, the heating step leads directly to polymer decomposition.

The thermal decomposition of a polymer (i.e. covalent bond dissociation) is an endothermic phenomenon, which requires an input of energy. The energy provided to the system must be higher than the binding energy between the covalently linked atoms (200–400 kJ/mol for most C–C polymers). The decomposition mechanism is highly dependent on the weakest bonds, and also on the presence or absence of oxygen in the solid and gas phases. Generally, thermal decomposition is the result of a combination of the effects of heat and oxygen. We can therefore distinguish between non-oxidizing thermal degradation and oxidizing thermal degradation [1].

Non-oxidizing thermal degradation is generally initiated by chain scissions under the simple effect of temperature (pyrolysis). This scission involves varying degrees of material depolymerization. The initial scission depends on several factors: the presence of oxygen atoms in the chain and catalyst residues, former residues of oxidation, chemical defects in polymer chains and the existence of weak bonds along the chain, particularly at the end, which can initiate unzipping reactions.

Chain scission can occur in two ways:

- by formation of free-radicals ($R_1-CH_2-CH_2-R_2 \rightarrow R_1-CH_2^\bullet + \bullet CH_2-R_2$), in this case, the reaction does not stop at this stage because these radicals start a chain/cascade reaction, which occurs under both oxidizing and non-oxidizing conditions.
- by migration of hydrogen atoms and the formation of two stable molecules one of which has a reactive carbon–carbon double bond ($R_1-CH_2-CH_2-CH_2-R_2 \rightarrow R_1-CH=CH_2 + CH_3-R_2$).

In oxidizing thermal conditions, the polymer reacts with oxygen in the air and generates a variety of low molecular weight products: carboxylic acids, alcohols, ketones, aldehydes, etc. This degradation also releases very reactive species, i.e. H^\bullet and OH^\bullet , particularly in polyolefins. Oxidation can lead to crosslinking through recombination reactions of the macromolecular radicals. However, bond scission usually remains the dominant reaction. The propagation rate of the degradation process is controlled by the wrenching reaction of hydrogen atoms from the polymer

chains. The oxidation stability of the polymer thus depends on the C–H bond energy.

Some researchers [2] suggest that at combustion temperatures above 300 °C polymer degradation takes place via non-oxidizing thermal decomposition. Under these conditions, the rate of pyrolysis is much faster than the diffusion of oxygen in the solid phase. Oxidation therefore only occurs in the gas phase due to the presence of low molecular weight compounds produced by thermal decomposition. The decomposition gases generated by pyrolysis first mix with oxygen by both convection and diffusion into the layer close to the surface, create free radicals, and then ignite. This ignition can be triggered by an external flame (flash-ignition) or self-induced (self-ignition) when the temperature is sufficiently high. Ignition depends on several parameters, in particular oxygen concentration. The combustion of the gases increases the polymer temperature and thus supports the pyrolysis and production of new combustible gases. Combustion thus continues even in the absence of an external heat source.

Flame propagation is also affected by physical factors, more specifically thermal transfers. Conductive and convective transfers are important in the initial phase of fire development when the height of the flame remains limited to a few tens of centimeters. In a more advanced phase, flame propagation on the surface contributes to a rapid increase in radiative transfer.

During these different stages, the development of considerable material heterogeneity can be highlighted, particularly during combustion. A gradient structure tends to form inside the material, arising from the interaction with atmospheric oxygen, coupled with the out-diffusion of reactive species and also concomitant polymer chain breakdown within the material. Several zones inside the material can therefore be identified. Calcraft and Maries [3] were the first to detail this gradient structure and specify the presence of a microporous carbonized layer surmounting a cellular porous underlayer, observed for several polymers. The gaseous decomposition products tend firstly to be located in the cavities of this underlayer, and afterwards migrate (through this microporous underlayer) towards the surface, where combustion takes place. The cellular underlayer is in direct contact with the thermal decomposition zone of the polymer and lies on the top of another layer in which the polymer remains intact even if it may undergo phase transitions. In addition, these authors established an energy balance between the heat transfers occurring in the heterogeneous structure (Fig. 2).

2.2. Flame retardancy

Flame retardant systems are intended to inhibit or to stop the polymer combustion process described in the previous paragraphs. In function of their nature, flame retardant systems can either act physically (by cooling, formation of a protective layer or fuel dilution) or chemically (reaction in the condensed or gas phase). They can interfere with the various processes involved in polymer combustion (heating, pyrolysis, ignition, propagation of thermal degradation). The main modes of action of flame retardant systems are reported and discussed below [4,5].

2.2.1. Physical action

The endothermic decomposition of some flame retardant additives induces a temperature decrease by heat consumption. This involves some cooling of the reaction medium to below the polymer combustion temperature. In this category, we can mention hydrated tri-alumina or magnesium hydroxide, which start liberating water vapor at approximately 200 and 300 °C, respectively. Such a marked endothermic reaction is known to act as a “heat sink”.

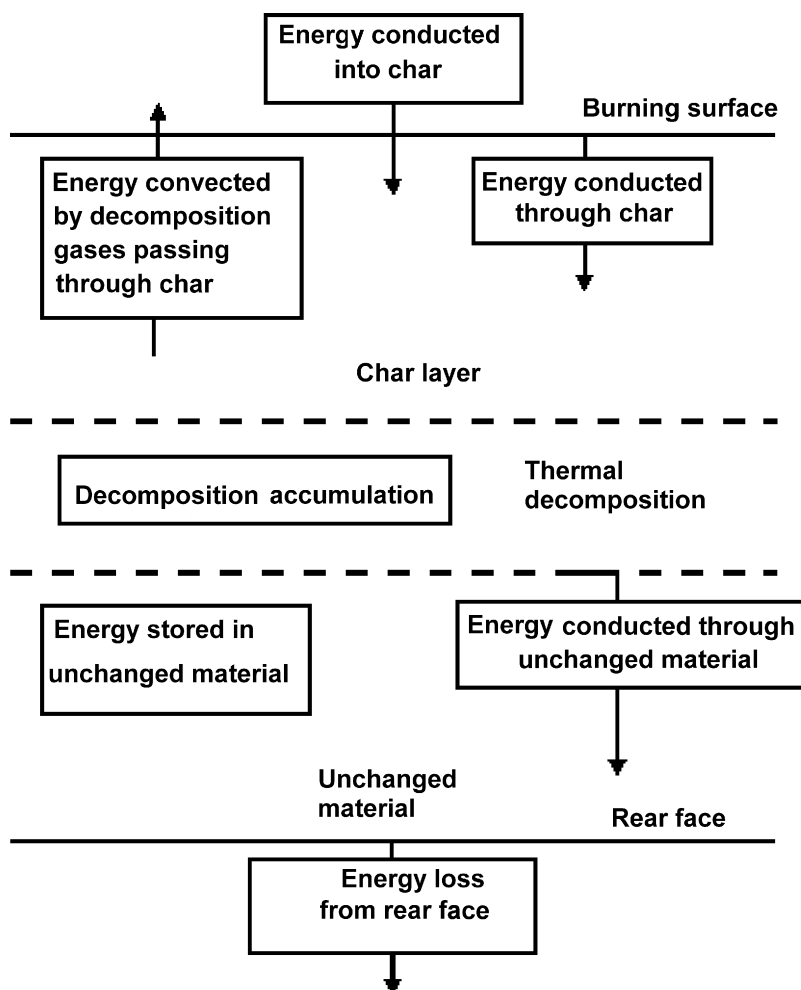


Fig. 2. Identification of thermal transfers during combustion.

When the flame retardants decompose, with the formation of inert gases (H_2O , CO_2 , NH_3 , etc.), the combustible gas mixture is diluted, which limits the concentration of reagents and the possibility of ignition.

In addition, some flame retardant additives lead to the formation of a protective solid or gaseous layer between the gaseous phase where combustion occurs and the solid phase where thermal degradation takes place. Such a protective layer limits the transfer of matter such as combustible volatile gases and oxygen. As a result, the amount of decomposition gases produced is significantly decreased. Moreover, the fuel gases can be physically separated from the oxygen, which prevents the combustion process being sustained.

2.2.2. Chemical action

Flame retardancy through chemical modification of the fire process can occur in either the gaseous or the condensed phase. The free-radical mechanism of the combustion process can be stopped by the incorporation of flame retardant additives that preferentially release specific radicals (e.g. Cl^\bullet and Br^\bullet) in the gas phase. These radicals can react with highly reactive species (such as H^\bullet and OH^\bullet) to form less reactive or even inert molecules. This modification of the combustion reaction pathway leads to a marked decrease in the exothermicity of the reaction, leading to a decrease in temperature and therefore a reduction in the fuel produced.

In the condensed phase, two types of chemical reactions triggered by flame retardants are possible: first, the flame

retardants can accelerate the rupture of the polymer chains. In this case, the polymer drips and thus moves away from the flame action zone. Alternatively, the flame retardant can cause the formation of a carbonized (perhaps also expanded) or vitreous layer at the surface of the polymer by chemical transformation of the degrading polymer chains. This char or vitrified layer acts as a physical insulating layer between the gas phase and the condensed phase.

Flame retardants can be classified in two categories:

- *Additive flame retardants*: these are generally incorporated during the transformation process and do not react at this stage with the polymer but only at higher temperature, at the start of a fire; they are usually mineral fillers, hybrids or organic compounds, which can include macromolecules.
- *Reactive flame retardants*: unlike additive flame retardants, these are usually introduced into the polymer during synthesis (as monomers or precursor polymers) or in a post-reaction process (e.g. via chemical grafting). Such flame retardants are integrated in the polymer chains.

2.3. Laboratory fire testing

The flammability of polymers can be characterized by their ignitability, flame-spread rate and heat release. Depending on the targeted application of the polymeric material, one or more of these flammability criteria need to be measured by appropriate

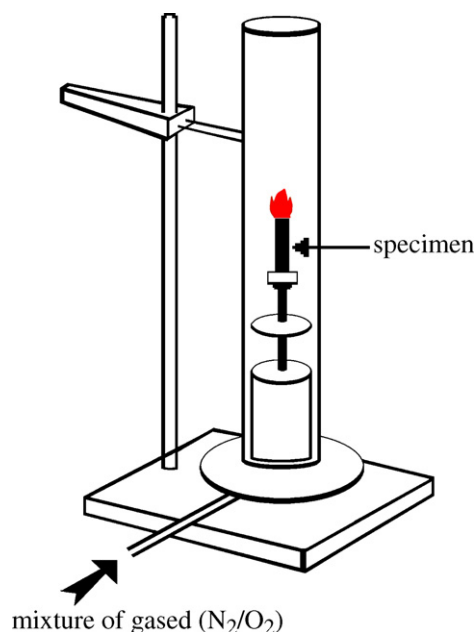


Fig. 3. Experimental set-up for LOI measurement.

flammability tests. There are numerous small-, intermediate- or full-scale flammability tests used in industrial or academic laboratories for either screening materials during product development or testing manufactured products.

Since Troitzsch [4] has already reviewed these flammability tests and standards, this chapter will only cover three of the most commonly used laboratory test methods.

2.3.1. Limited Oxygen Index: LOI

This test was first proposed in 1966 by Fenimore and Martin [6] and is used to indicate the relative flammability of materials [7]. Standardized in France (NF T 51-071) and in the United States (ASTM D 2863), the LOI test is now subject to an international standard (ISO 4589). The value of the LOI is defined as the minimal oxygen concentration $[O_2]$ in the oxygen/nitrogen mixture $[O_2/N_2]$ that either maintains flame combustion of the material for 3 min or consumes a length of 5 cm of the sample, with the sample placed in a vertical position (the top of the test sample is inflamed with a burner).

The LOI is expressed as:

$$LOI = 100 \frac{[O_2]}{[O_2] + [N_2]}$$

According to ISO 4589, the LOI is measured on $(80 \times 10 \times 4 \text{ mm}^3)$ specimens placed vertically at the center of a glass chimney (Fig. 3). The mixture of gases flows upstream

through this chimney and is homogenized by being passed through layers of glass beads. After a 30-s purge of the column, the top of the specimen is ignited, like a candle.

As air contains 21% oxygen, materials with an LOI below 21 are classified as “combustible” whereas those with an LOI above 21 are classified as “self-extinguishing”, because their combustion cannot be sustained at ambient temperature without an external energy contribution. The higher the LOI the better the flame retardant property.

Although this test is nowadays considered to be relatively unsophisticated due to the development and standardization of more elaborate methods, it remains one of the most important screening and quality control methods used in the plastics industry.

Table 1 lists flash ignition and self-ignition temperatures for various polymers, together with their LOI values.

2.3.2. UL 94 V

The set of UL94 tests has been approved by the “Underwriters’ Laboratories” as tests of the flammability of plastic materials for parts in devices and appliances. It includes a range of flammability tests (small and large flame vertical tests, horizontal tests for bulk and foamed materials, radiant panel flame-spread test). In terms of practice and usage, the most commonly used test is UL94 V for measuring the ignitability and flame-spread of vertical bulk materials exposed to a small flame. This test is the subject of an international standard (IEC 60695-11-10) for small flames (50 W). It is a simple test of vertical combustion that classifies materials as V-0, V-1 or V-2. The corresponding experimental device is shown in Fig. 4.

The burner is controlled to produce a blue flame with a 20 mm-high central cone and a power of 50 W. The flame is applied to the bottom of the specimen and the top of the burner has to be located at 10 mm from the bottom edge of the specimen. The flame is applied for 10 s and removed. The afterflame time t_1 (the time required for the flame to extinguish) is noted. After extinction, the flame is applied for another 10 s. The afterflame time t_2 is noted, together with the afterglow time t_3 (the time required for the fire glow to disappear).

During the application of the flame, the distance between burner and specimen must remain constant. If drops fall, the burner must be tilted through a maximum angle of 45° or slightly isolated from the specimen flame. During the test, the presence of burning drops, causing a piece of cotton located under the sample to ignite, must be noted.

The standard specifies that five specimens must be tested. The specimen is classified as V_0 , V_1 or V_2 according to the criteria listed in Table 2.

2.3.3. Cone calorimeter

Cone calorimetry is one of the most effective medium-sized polymer fire behavior tests. The principle of cone calorimeter

Table 1

Flash-ignition temperature, self-ignition temperature and correlated LOI values for selected representative polymers [4].

Polymer	Flash-ignition temperature ($^\circ\text{C}$)	Self-ignition temperature ($^\circ\text{C}$)	LOI (%)
Polyethylene	340	350	18
Polypropylene	320	350	18
Polystyrene	350	490	18
Poly(vinyl chloride)	390	450	42
Poly(tetrafluoroethylene)	560	580	95
Acrylonitrile–butadiene–styrene terpolymer	390	480	19
Poly(methyl methacrylate)	300	430	18
Poly(acrylonitrile)	480	560	27
Polyamide 6	420	450	25
Polymaide 66	490	530	24

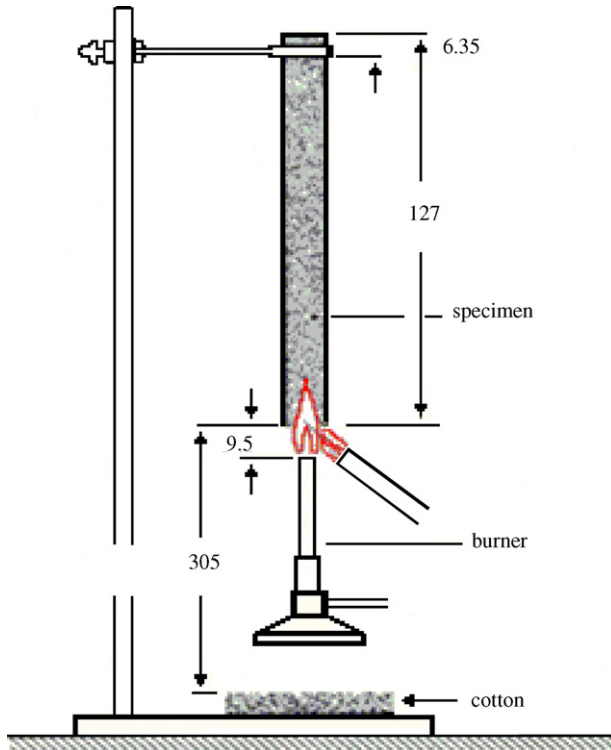


Fig. 4. Experimental set-up for the UL94 V flammability test.

experiments is based on the measurement of the decreasing oxygen concentration in the combustion gases of a sample subjected to a given heat flux (in general from 10 to 100 kW/m²). Fig. 5 illustrates the experimental set-up of a cone calorimeter. Standardized in the United States (ASTM E 1354), the cone calorimeter test is also the subject of an international standard (ISO 5660). The sample (100 × 100 × 4 mm³) is placed on a load cell in order to evaluate the evolution of mass loss during the experiment. A conical radiant electrical heater uniformly

Table 2

Classification of materials for the UL 94 V flammability test.

Fire classification	
UL94 V ₀	t_1 and t_2 less than 10 s for each specimen $t_1 + t_2$ less than 50 s for the five specimens $t_2 + t_3$ less than 30 s for each specimen No afterflame or afterglow up to the holding clamp No burning drops
UL94 V ₁	t_1 and t_2 less than 30 s for each specimen $t_1 + t_2$ less than 250 s for the five specimens $t_2 + t_3$ less than 60 s for each specimen No afterflame or afterglow up to the holding clamp No burning drops
UL94 V ₂	t_1 and t_2 less than 30 s for each specimen $t_1 + t_2$ less than 250 s for the five specimens $t_2 + t_3$ less than 60 s for each specimen No afterflame or afterglow up to the holding clamp Burning drops allowed

irradiates the sample from above. The combustion is triggered by an electric spark.

The combustion gases produced pass through the heating cone and are captured by means of an exhaust duct system with a centrifugal fan and a hood. The gas flow, oxygen, CO and CO₂ concentrations and smoke density are measured in the exhaust duct.

The measurements of the gas flow and oxygen concentration are used to calculate the quantity of heat released per unit of time and surface area: HRR (heat release rate) expressed in kW/m². The evolution of the HRR over time, in particular the value of its peak/maximum (pHRR or HRRmax), is usually taken into account in order to evaluate the fire properties. The calculation is based on Huggett's observation that most organic materials release a quantity of heat practically proportional to the quantity of oxygen consumed while burning. The proportionality factor is constant from one material to another and is equal to 13.1 kJ/g consumed oxygen [8]. Integration of the HRR vs. time curve gives the total heat released (THR) expressed in kJ/m². In addition, the cone calorimeter test also enables characterization of the time to ignition (TTI), time of combustion or extinction (TOF), mass loss

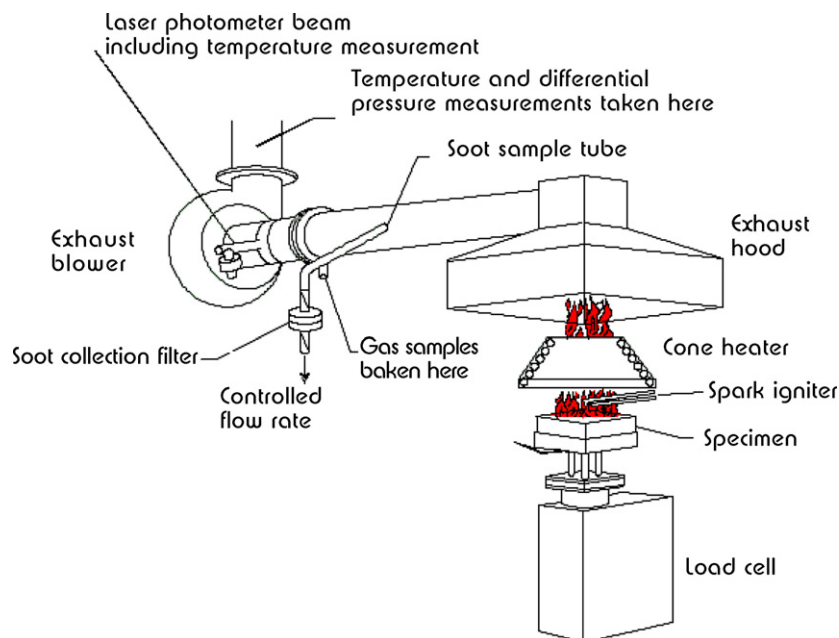


Fig. 5. Experimental set-up for a cone calorimetry measurement.

during combustion, quantities of CO and CO₂, and total smoke released (TSR).

2.3.4. Some comments about laboratory fire tests

The ignitability and inflammation resistance of polymers can be characterized by the LOI test. Nevertheless, it has to be taken into account that LOI measurements are carried out at ambient temperature and LOI values decrease when temperature increases. Consequently, the “self-extinguishing” property cannot be considered as a hard-and-fast rule, since materials with high LOI values at room temperature may burn without self-extinguishing under intense fire conditions.

It is important to note that melting and dripping of the polymer during the LOI test may lead to incorrectly high LOI values. The dripping of flaming polymer drops can take the fire away from the surface of the specimen, causing it to extinguish.

Recently, some other limitations of the LOI test have emerged with regard to the evaluation of flame retardant systems containing nanoparticles. Results given by this test proved to be in contradiction with UL 94 and cone calorimetry data for ethylene vinyl acetate copolymers flame retarded by either magnesium di-hydroxide or a mixture of magnesium di-hydroxide and organo-modified montmorillonite (nanoclay). It transpires that the presence of nanoclay leads to the formation of a barrier layer that limits the propagation of fire inside the material but increases the flame-spread rate over the surface of the specimen. As a result, a decrease in LOI values was measured in the presence of organomodified montmorillonite [9].

The UL 94 V test is widely used both in industry and academic research centers, and is intended to meet industrial requirements as well as to hierarchically classify the polymeric materials. Nevertheless, the information thus obtained remains limited due to its basic and unrefined character. Rather than two successive applications of the burner for 10 s, some users in the academic sphere recommend three applications for 5 s [10], in order to obtain better discrimination between the compositions under investigation. Moreover, this test appears to be less appropriate for specimen samples that flow easily than for more cohesive materials.

Undoubtedly, the cone calorimeter test provides more detailed fire characteristics. The heat release rate (HRR) is certainly the most widely used parameter for evaluating the fire properties of polymers.

In many cases, flame retardant formulations lead to a significant reduction in pHRR values and an increase in the combustion time, but most often without any change in the total heat released. This can nonetheless be considered as an enhancement of the polymer's flame retardant behavior since it enables the same amount of heat to be released over a longer period of time. Consequently it limits the development of the fire and the risk of flash-over, i.e. an extremely high, even explosive, rate of fire spread over the entire area [4].

3. Flame retardant additives

3.1. Mineral flame retardants

Any type of inorganic filler, even inert, can influence the reaction of polymers to fire for several reasons:

- it reduces the content of combustible products;
- it modifies the thermal conductivity of the resulting material and all its thermophysical properties;
- it changes the viscosity of the resulting material;

All these actions have an indirect incidence on the polymer's fire performance.

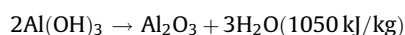
Nevertheless, some minerals are more specifically used as flame retardants owing to their behavior at high temperature. The most commonly used mineral flame retardants are metal hydroxides (especially of aluminum and magnesium), hydroxycarbonates and zinc borates. Besides the aforementioned general effects, these inorganic fillers have a direct physical flame retardant action. As the temperature rises, these fillers decompose endothermically and therefore absorb energy. Moreover, they release non-flammable molecules (H₂O, CO₂), which dilute combustible gases, and can also promote the formation of a protective ceramic or vitreous layer.

3.1.1. Metal hydroxides

To be used as polymer flame retardants, metal hydroxides need to decompose endothermically and release water at a temperature higher than the polymer processing temperature range, and around the polymer decomposition temperature.

The two most commonly used mineral flame retardants are aluminum tri-hydroxide (ATH) and magnesium di-hydroxide (MDH).

The endothermic decomposition of aluminum tri-hydroxide (Al(OH)₃) occurs between 180 and 200 °C and leads to the release of water and the formation of alumina:



As shown by differential thermal analysis (DTA) in Fig. 6, this reaction tends to occur in two stages, which correspond to two endothermic transitions. The intermediate product formed is known as boehmite “AlOOH” [11], which corresponds to the much lower endothermic process energy. The corresponding transition is much more perceptible with increased ATH particle size.

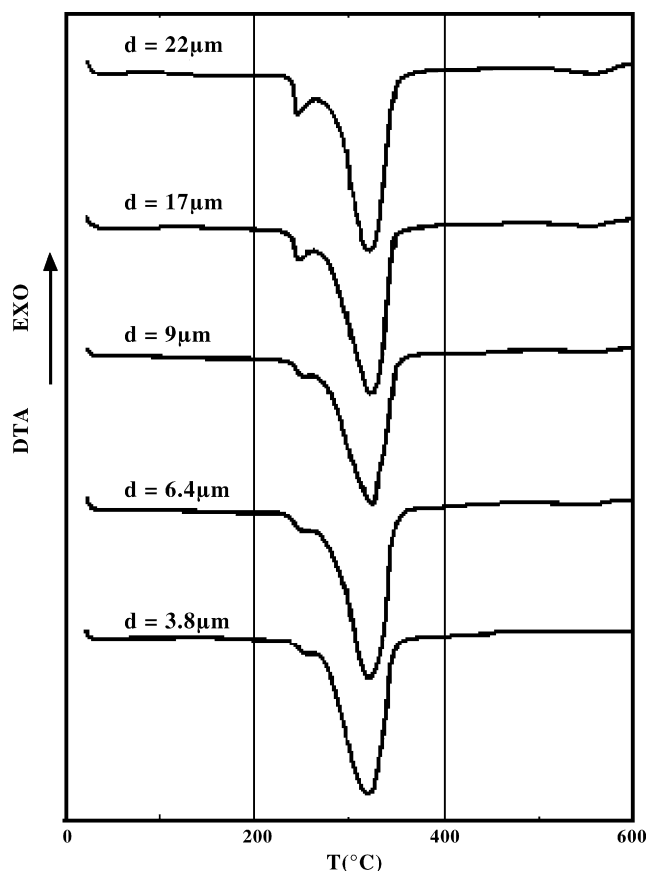


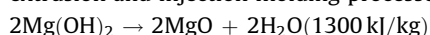
Fig. 6. Effect of mean aluminium tri-hydroxide (ATH) particle size on DTA [11] (heating rate: 20 °C/min).

This reaction has several effects on the combustion of the polymer:

- It absorbs 1050 kJ/kg ATH, i.e. it cools down the polymer material.
- Al_2O_3 forms a thermally insulating protective coating.
- The released water vapor dilutes combustible gases and forms a protective gas layer.

However, the fire properties of ATH-filled polymers are only interesting at high loading levels. For example, the Limiting Oxygen Index (LOI) can reach values higher than 50% for EVA containing 75% (w/w) of ATH [12]. The use of ATH also decreases the HRR peak in the cone calorimeter test and considerably reduces smoke production [13]. Owing to its relatively low degradation temperature, ATH is limited to polymers with low processing temperatures, such as EVA and LDPE.

Magnesium di-hydroxide ($\text{Mg}(\text{OH})_2$) acts in the same way as $\text{Al}(\text{OH})_3$ but its endothermic degradation occurs at a higher temperature ($>300^\circ\text{C}$), which is interesting with respect to the extrusion and injection molding processes of some polymers:



It has to be noted that the flame retardant action of magnesium di-hydroxide is very effective up to 400°C . Beyond this temperature, the exothermic character of degradation predominates.

Metallic hydroxides (ATH and MDH) may also have a catalytic effect on the combustion of the carbonized residues produced, which would explain the incandescence phenomena observed during several flame retardant tests [14].

Interestingly, magnesium di-hydroxide nanoparticles have also been considered as flame retardant additives. Such nanoparticles can be obtained by several methods, via a sol-gel technique followed by a hypercritical drying procedure [15], a hydrothermal reaction using various precursors and solvents [16] or by precipitation of magnesium salts with an alkaline solution [17]. This last method allows for the control of the nanoparticle morphology by fine tuning of the experimental parameters such as the chemical nature of the base used as precipitant, the type of counter-ion, the temperature and the hydrothermal treatment. For example, simply changing the base precipitant (NaOH or NH_4OH) leads to the formation of nanometric magnesium di-hydroxide with needle- or lamella-like morphologies, respectively [18].

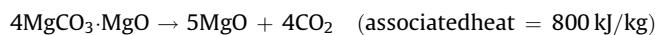
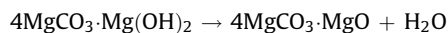
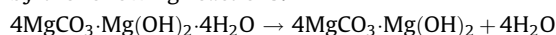
The use of nanometric MDH can enable interesting fire performances to be achieved at lower loading levels. It has been shown [18] that the LOI obtained with EVA containing 50% (w/w) of magnesium di-hydroxide increases from 24% to 38.3% when micronic magnesium di-hydroxide ($2\text{--}5 \mu\text{m}$) is replaced by nanometric $\text{Mg}(\text{OH})_2$. The enhancement of EVA flame retardancy by nanosized $\text{Mg}(\text{OH})_2$ was attributed to the good dispersion of the nanoparticles, which leads to the formation of more compact and cohesive char during the combustion test.

3.1.2. Hydroxycarbonates

All carbonates release CO_2 at high temperatures but only magnesium and calcium carbonates release it below 1000°C , with magnesium carbonate presenting the lowest release temperature (550°C).

Even though hydroxycarbonates are less widely used than other conventional flame retardants, they remain an alternative to metal hydroxides. In addition to the release of water, natural magnesium carbonate (magnesite) and synthetic magnesium hydroxycarbonate (hydromagnesite) also break down endothermically due to the liberation of CO_2 at high temperature.

The thermal decomposition of hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ or $5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$) in air can be described [19] by the following reactions:



Hydromagnesite releases water and carbon dioxide over a wider temperature range than aluminum tri-hydrate and magnesium di-hydroxide. This material has been used as a flame retardant in polypropylene [20] and an LDPE/EVA polymer blend (3:1 blend) [21]. While aluminum tri-hydroxide and magnesium di-hydroxide have water release temperatures around $180\text{--}200^\circ\text{C}$ and $300\text{--}340^\circ\text{C}$, respectively, hydromagnesite releases both water and carbon dioxide between 200 and 550°C [22], which suggests that it may have similar or better flame retardancy effectiveness than ATH and MDH.

3.1.3. Borates

Borates are another family of inorganic additives with flame retardant properties. Among them, zinc borates such as $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ are the most frequently used. Their endothermic decomposition (503 kJ/kg) between 290 and 450°C liberates water, boric acid and boron oxide (B_2O_3).

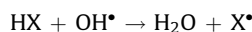
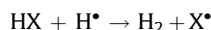
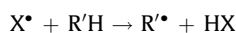
The B_2O_3 formed softens at 350°C and flows above 500°C leading to the formation of a protective vitreous layer. In the case of polymers containing oxygen atoms, the presence of boric acid causes dehydration, leading to the formation of a carbonized layer. This layer protects the polymer from heat and oxygen. The release of combustible gases is thus reduced.

3.2. Halogenated flame retardants

The effectiveness of halogenated flame retardants depends on the type of halogen. Fluorine and iodine-based compounds are not used because they do not interfere with the polymer combustion process. Fluorinated compounds are more thermally stable than most polymers and do not release halogen radicals at the same temperature range or below the decomposition temperature of the polymers [23]. Iodinated compounds are less thermally stable than most commercial polymers and therefore release halogenated species during polymer processing. Bromine and chlorine, because of their low bonding energy with carbon atoms, can readily be released and take part in the combustion process, especially with the previously discussed free-radical mechanism occurring in the gas phase.

3.2.1. Halogenated flame retardant additives

As stated above, thermally induced polymer decomposition releases very reactive free-radical species such as H^\bullet and OH^\bullet , which maintain combustion by a cascade-chain mechanism in the gas phase. Halogenated flame retardants are able to react with these species, stopping the chain decomposition and therefore the combustion of the polymer:



It is worth noting that HX, the effective flame retardant species, is regenerated by the reaction of X^\bullet with RH. In addition, being non-flammable, HX can have a physical action on the combustion

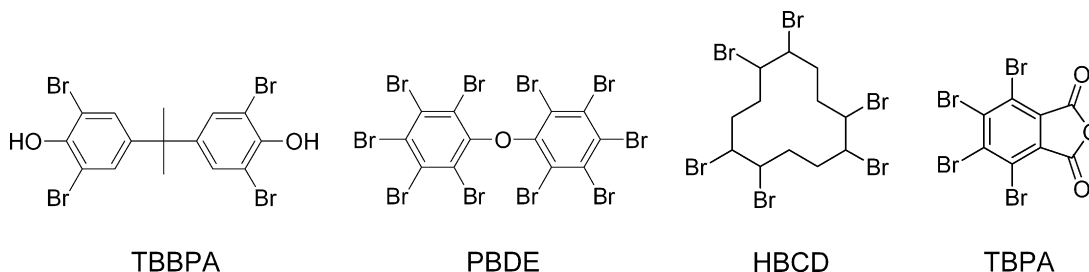


Fig. 7. Chemical structure of classical halogenated flame retardant products.

mechanism (protective gaseous coating, dilution of fuel gases). It also catalyzes the oxidation of the solid phase and the oxidation products tend to cyclize, which leads to the formation of a solid protective layer. It should be noted that X^\bullet is much less reactive than OH^\bullet and H^\bullet . The most common halogenated flame retardant products are given in Fig. 7.

Tetrabromobisphenol A (TBBPA) is the most widely used halogenated flame retardant. It is mainly incorporated as a reactive flame retardant especially in epoxy resins for printed circuit boards. Polybromodiphenylether (PBDE) compounds are the second most used halogenated flame retardant family. They can contain up to 10 bromine atoms attached to a diphenyl ether molecule. The polybromodiphenylethers developed as flame retardant additives are: penta- (5), octa- (8), and deca- (10) bromodiphenylethers.

Penta- and octa-bromodiphenylethers in fact consist of a mixture of different diphenylic ethers containing various bromine atoms, with an average corresponding to the number given, i.e. 5 or 8. They are characterized by high molecular weight and good thermal stability and are mainly used in styrenic polymers, polyolefins, polyesters and nylons. Having been identified as probable dioxine precursors, penta- and octa-bromodiphenylethers have been phased out and only decabromodiphenylether is still used in a limited number of countries outside Europe. Hexabromocyclododecane (HBCD) is a cycloaliphatic halogenated flame retardant. It is currently used in expanded or compact PS and textiles. Tetrabromophthalic anhydride (TBPA) is used as a flame retardant additive in unsaturated polyesters and also as a raw material for the production of other flame retardant agents.

3.2.2. Halogenated monomers and copolymers (reactive flame retardants)

The principal advantage of reactive monomer and copolymer flame retardants, compared to other flame retardant additives, is that they can be used in relatively low concentrations. Since they are directly incorporated in the polymer structure, they can:

- increase the compatibility between the polymer and the flame retardant agent;
- limit the damage caused by heterogeneous additives to the mechanical properties of the materials;
- reduce the migration of the flame retardant agents onto the material surface.

However, these compounds require an additional synthesis step, which can be a disadvantage on the industrial scale.

The monomer and copolymer halogenated flame retardants can be used as condensation or free-radical polymerization monomers, copolymerized with virgin monomers or grafted onto the polymer chain. The action of these reactive flame retardant products is very similar to other halogenated flame retardant additives: they react

with the highly reactive H^\bullet and OH^\bullet species and stop the chain decomposition.

In some cases, other mechanisms can be added to the conventional effect of halogenated derivatives. For example, the incorporation of a low proportion of vinyl bromide (VBr) units into PMMA chains changes the degradation pattern [24]. The thermal degradation of poly(VBr-co-MMA) occurs by intramolecular lactonization [25,26] involving adjacent bromine and esters groups in the copolymer chain and resulting in the release of alkyl bromide as a volatile product (Fig. 8).

The lactone rings formed have a stabilizing effect on the depolymerization reaction and act as “blocking” groups that interrupt the unzipping process, the main thermal degradation pathway for PMMA.

The LOI values of the VBr-based copolymers (Fig. 9) increase with the relative VBr content in the copolymers studied. It is worth pointing out that the more limited increase in LOI value specifically recorded for poly(VBr-co-MMA) copolymers can be directly related to the particle degradation pathway for P(VBr-co-MMA), when only a small amount of HBr is formed.

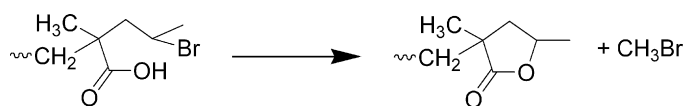


Fig. 8. Intramolecular lactonization of poly(VBr-co-MMA) [26].

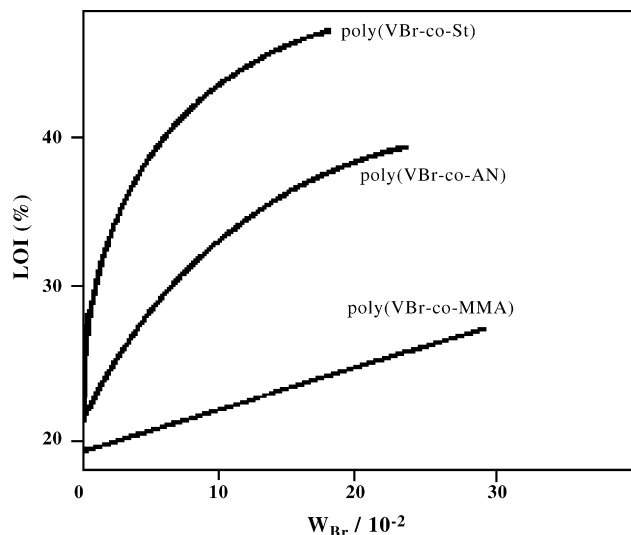


Fig. 9. Dependence of LOI values for vinyl bromide (VBr) copolymers on the mass of VBr in the copolymer. (St: styrene; AN: acrylonitrile; MMA: methyl methacrylate) (adapted from [26]).

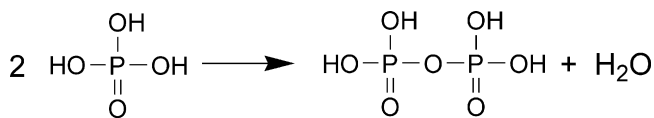


Fig. 10. Pyrophosphate structure formation from phosphoric acid condensation.

Also, the effectiveness of the halogenated monomer depends on the composition of the monomer and the copolymer. As expected, increasing the content of halogen atoms in the monomer leads to more efficient fire retardant behavior.

3.3. Phosphorus-based flame retardants

The range of phosphorus-based flame retardant products is extremely wide, including phosphates, phosphonates, phosphinates, phosphine oxides, phosphates and red phosphorus. These phosphorated flame retardant agents can be used as additives or incorporated into the polymer chain during its synthesis, and are known to be active in the condensed and/or vapor phase.

In the condensed phase, the phosphorus-based flame retardants are particularly effective with polymers containing oxygen [27,28] (polyesters, polyamides, cellulose, etc.) With most of them, thermal decomposition leads to the production of phosphoric acid, which condenses readily to produce pyrophosphate structures and liberate water (Fig. 10).

The water released dilutes the oxidizing gas phase. In addition, phosphoric acid and pyrophosphoric acid can catalyze the dehydration reaction of the terminal alcohols leading to the formation of carbocations and carbon–carbon double bonds (Fig. 11). At high temperature this can subsequently result in the generation of crosslinked or carbonized structures.

At high temperature, ortho- and pyrophosphoric acids are turned into metaphosphoric acid “(O)P(O)(OH)” and their corresponding polymers “(PO₃H)_n”. The phosphate anions (pyro- and polyphosphates) then take part, with the carbonized residues, in char formation. This carbonized layer (char) isolates and protects the polymer from the flames and:

- limits the volatilization of fuel and prevents the formation of new free-radicals;
- limits oxygen diffusion, which reduces combustion;
- insulates the polymer underneath from the heat.

Phosphorus-based flame retardants can also volatilize into the gas phase, to form active radicals (PO₂•, PO• and HPO•), and act as scavengers of H• and OH• radicals. Volatile phosphorated compounds are among the most effective combustion inhibitors since phosphorus-based radicals are, on average, five times more effective than bromine and 10 times more effective than chlorine radicals [29].

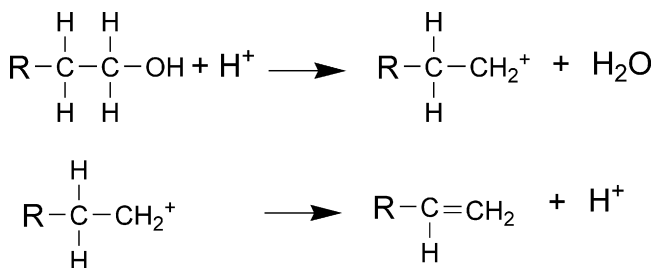


Fig. 11. Formation of double carbon–carbon bonds after dehydration of alcohol end groups.

Phosphorus-based flame retardants are significantly more effective in oxygen- or nitrogen-containing polymers. It is thus important to have oxygen or nitrogen atoms in the polymer chain. If the polymer cannot contribute to charring because of the absence of suitable reactive groups, a highly charring co-additive has to be introduced in combination with the phosphorated flame retardant. This co-additive may be a polyol such as pentaerythritol [30]. Some polymers such as polyamides or polyurethanes can also be used as charring agents in intumescent flame retardant systems (see Section 3.3.4).

3.3.1. Red phosphorus

Red phosphorus is the most concentrated source of phosphorus for flame retardancy. Used in small quantities (less than 10%), it is very effective in polymers such as polyesters, polyamides and polyurethane. A typical example is glass-filled PA-6,6 containing 6–8% red phosphorus, which achieves V-0 classification in the UL 94 test [31].

The first report about the use of red phosphorus as a flame retardant in polyurethane, by Piechota [32], dates back to 1965. However, its action mechanism has not yet been clearly established. Initially, it was believed [33] that red phosphorus exhibited flame retardant properties only in the presence of polymeric materials containing oxygen atoms (polyesters, polyamides, polyurethanes, etc.) It was therefore suggested that its mode of action involved specific scavenging of oxygen-containing radicals, which act as chain carriers in the secondary pyrolysis step leading to the generation of gaseous fuel species [33].

Most researchers [34] now agree that in oxygen- and/or nitrogen-containing polymers, red phosphorus turns, mainly through thermal oxidation, into phosphoric acid or phosphoric anhydride, which upon heating gives polyphosphoric acid. This acid can catalyze the dehydration reaction of polymer end chains and trigger char formation.

In polyesters like PET [34], the flame-retardant effectiveness of red phosphorus is reduced when the sample is burned in an N₂O atmosphere. Accordingly a Nitrogen Oxygen Index can be defined to show whether a given flame retardant acts mainly in the gaseous or conversely the condensed phase. This specific case indicates that some of the flame retardancy imparted by phosphorus involves gas-phase inhibition. Nevertheless, the main flame-retardant action occurs in the condensed phase.

However, it was later found that red phosphorus is also active in polyethylene [35] and other non-oxygenated polymers [36]. Consequently, a different mode of action of red phosphorus was proposed [37,38] where red phosphorus depolymerizes into white phosphorus (P₄). P₄ can volatilize at high temperature and act in the gaseous phase, or it can diffuse from the bulk of the polymer to the burning surface, where it is oxidized to phosphoric acid derivatives that can eventually come into close contact with the flame and form phosphoric acid. This phosphoric acid could act as a char forming agent, thus physically limiting oxygen access and fuel volatilization. Furthermore, Peters [35] found that, in polyethylene, red phosphorus is active both in the gas and the condensed phase. In the gas phase, PO• species produced from the combustion of red phosphorus quench the free-radical processes. In the condensed phase, red phosphorus substantially lowers the heat of oxidation and also traps free-radicals. This improved thermal stability results in a decrease in fuel production during the burning of the material.

However, red phosphorus has a major disadvantage. Throughout the melting process, it can release highly toxic phosphine (PH₃) through reaction with moisture as a direct result of its poor thermostability. Interestingly enough, phosphine formation can be avoided by prior polymeric encapsulation of the red phosphorus

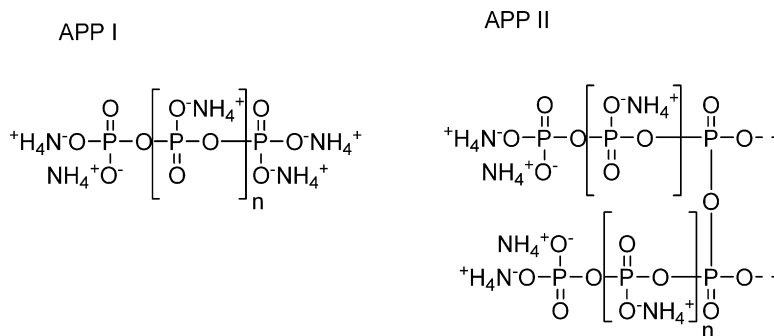


Fig. 12. Chemical structure of APP I and APP II.

[39], which can also further improve its effectiveness as a flame retardant. For instance; in polyethylene [39] the incorporation of micro-encapsulated red phosphorus in melamine–formaldehyde (MF) resin leads to the formation of a compact charred layer upon combustion. The red phosphorus is predominantly oxidized to various phosphoric acid derivatives. These derivatives react with the MF resin to form more stable structures containing “P–O–P” and “P–O–C” chemical bonds. Alternatively to encapsulation in MF resins, there are also systems for trapping the phosphine formed at high temperature. These systems use the capacity of phosphines to react with metallic salts [40,41]. Compounds like AgNO_3 , HgCl_2 , MoS_2 , HgO , PbO_2 , CuO , $(\text{FeCl}_3 \cdot \text{H}_2\text{O})$ have proved very efficient at trapping phosphine in polymers and have accordingly been incorporated in red-phosphorus-based flame retardant formulations.

3.3.2. Inorganic phosphates

Ammonium polyphosphate (APP) is an inorganic salt of polyphosphoric acid and ammonia. The chain length (n) of this branched or unbranched polymeric compound is variable; n can be higher than 1000. Short, linear chain APPs (crystalline form I: APP I) ($n < 100$) are more water sensitive (hydrolysis) and less thermally stable than longer chain APPs (crystalline form II: APP II) ($n > 1000$), which exhibit very low water solubility (< 0.1 g/100 ml) (Fig. 12).

APPs are known to be stable and non-volatile compounds. Long-chain APPs start to decompose into polyphosphoric acid and ammonia at temperatures above 300°C . Short-chain APPs begin to decompose at temperatures above 150°C . It is therefore very important to adapt the crystalline form of the APP to the polymer decomposition temperature.

It is well known that the incorporation of APP in oxygen- and/or nitrogen-containing polymers (polyesters [42], polyamides [43], polyurethane [44], etc.) leads to polymer charring. The thermal degradation of APP creates free acidic hydroxyl groups, which condense by thermal dehydration yielding a crosslinked ultraphosphate and a polyphosphoric acid with a highly crosslinked structure [45]. The polyphosphoric acid reacts with the oxygen- or nitrogen-containing polymers and catalyzes their dehydration reaction and char formation.

The effectiveness of APP depends also on the level of incorporation. At relatively low concentration, APP is not efficient in aliphatic polyamides [43], however, it becomes very efficient at high concentration, e.g. $>10\%$ in polyamide-6,6, $>20\%$ in polyamide-11, -12, -6, -10 and $>30\%$ in polyamide-6.

In non self-charring polymeric materials, APP can modify the degradation mechanism of the polymer. In PMMA [45], this modification is principally due to reactions of the polymethacrylate chains with polyphosphoric acid due to high acidity and the reactivity of its phosphorus oxygen bonds. These reactions lead to cyclization and the formation of anhydride groups together with

the elimination of ester groups. The modified structures thus produced in the PMMA chains inhibit the chain depolymerization reaction, which occurs quantitatively in pristine PMMA, and catalyzes a partial hydrolysis of the PMMA which can be followed by crosslinking reactions.

3.3.3. Organic phosphorus-based compounds

Even though many organic phosphorus derivatives display flame-retardant properties, the number of them of commercial importance is limited by the processing temperature and the nature of the polymer to be modified. Again, organic phosphorus derivatives can act as additives or as reactive (co)monomers/oligomers. The main groups of organophosphorus compounds are phosphate esters, phosphonates and phosphinates [46] (Fig. 13).

The use of (alkyl-substituted) triaryl phosphates such as triphenyl phosphate (TPP), cresyl diphenyl phosphate, isopropylphenyl diphenyl phosphate, tert-butylphenyl diphenyl phosphate or tricresyl phosphate is very limited in plastics engineering because of their high volatility and relatively low fire retardant efficiency. For instance, the incorporation of TPP in polycarbonate/acrylonitrile butadiene styrene (PC/ABS) blends [47] does not affect the thermal decomposition behavior of the blend. In fact, TPP volatilizes before decomposition of the polymer blend.

For plastics engineering, oligomeric phosphates such as resorcinol bis(diphenyl phosphate) (RDP) and bisphenol A bis(diphenyl phosphate) (BDP) (Fig. 14), with lower volatility and higher thermal stability than triaryl phosphates, can be incorporated. Both BDP and RDP added at a level of 1 wt% of phosphorus in the 5:1 PC/ABS formulation provided V-0 ratings in the UL 94 test [48,49]. In similar experiments, V-0 ratings for poly(phenylene oxide) (PPO)/high impact polystyrene (HIPS)-based formulations were obtained at 2 wt% of phosphorus.

BDP and RDP react with PC phenolic functions, thus promoting crosslinking of the polymer chains and consecutive charring [50,51]. During thermal degradation, the “P–O–C” bonds of BDP react via transesterification with phenolic groups originating from PC, which leads to crosslinking. The char production is enhanced by the presence of PTFE, which releases a significant amount of HF, which supports the esterification, and thus the crosslinking of BDP and PC.

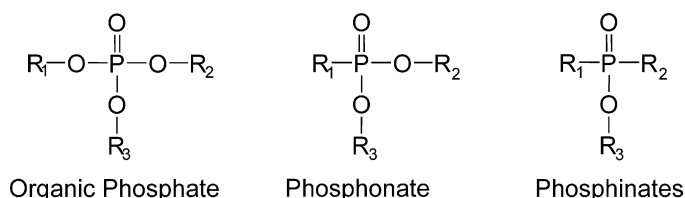


Fig. 13. Chemical structures of some phosphorus flame retardant additives.

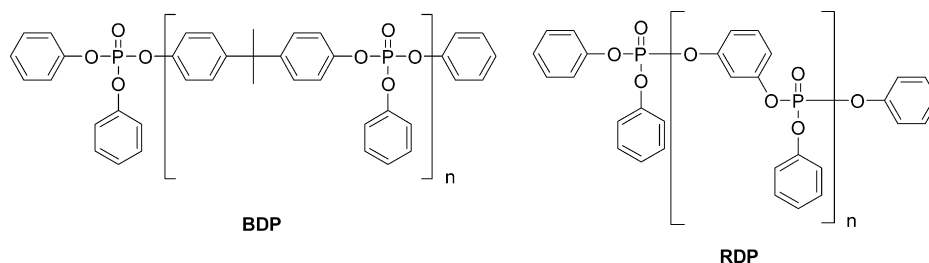


Fig. 14. Chemical structure of bisphenol A bis(diphenyl phosphate) (BDP) and resorcinol bis(diphenyl phosphate) (RDP) [47].

The combination of RDP and PTFE also shows a synergistic effect but the amount of char formed is lower than that generated with BDP. This might be explained by partial volatilization of RDP. Moreover, the combination of volatile and non-volatile phosphates can also lead to a synergistic effect [52]. The combination of RDP or BDP with TPP or even the combination of BDP and RDP are more effective than each additive taken separately. This is most likely due to a positive combination of the condensed-phase and gas-phase actions of the respectively less and more volatile aromatic phosphates.

The use of reactive phosphorus flame retardants is another solution for avoiding volatilization during thermal decomposition and migration towards the polymer surface. They are incorporated directly within the polymer chain structure and can be used either as monomers for copolymerization with one [53] or two comonomers [54] to obtain a phosphorated polymer, or as oligomers that react with the polymer to form a branched or grafted phosphorated polymer.

The copolymerization of a phosphorated monomer such as 2-methacryloxyethyl phenyl phosphate (MEPP) [53] with methyl methacrylate (MMA) leads to the formation of a phosphorated copolymer that is more thermally stable than PMMA and generates char during thermal decomposition. The LOI value of these copolymers increases from 17% for neat PMMA to 21.8% in the presence of 20 wt% of MEPP (2.17 wt% phosphorus), and a V-0 rating in the UL 94 test is also achieved.

MMA has also been copolymerized with a variety of comonomers containing covalently bound phosphorus-containing groups, including vinyl phosphonic acid (VPA), several dialkyl vinyl phosphonates, and various vinyl and allyl phosphine oxides [54]. All these copolymers generate char in both thermogravimetric analysis (TGA) and LOI experiments and some interesting correlations have been observed between the amount of phosphorus in the copolymer and its LOI, and between the amounts of phosphorus in the copolymer and in the char, indicating that the flame retardancy involves condensed-phase mechanisms.

Price et al. [55] studied the thermal behavior of polystyrene copolymers with (meth)acrylate phosphates and phosphonates. For the sake of comparison, the study was also carried out on polystyrene containing phosphate and phosphonate derivatives as simple additives. All the systems contained 3.5 wt% of phosphorus. Very little, if any, char residues were observed when phosphorus compounds were used as additives. The P content in the char formed during cone calorimeter testing at 35 kW/m² was below the detection limit. In fact, the phosphorated compound evolved before polymer decomposition occurred. Thus the main fire retardant mechanism of the phosphorus incorporated as an additive into the polystyrene occurred in the vapor phase. However, in the case of polystyrene-based copolymers, the phosphorus content in the char proved to be substantial for all the copolymers, indicating a condensed-phase fire retardant action of the phosphorus that enhanced crosslinking reactions in the polystyrene during thermal decomposition.

In the cone calorimeter test, the time to ignition was shorter in phosphonate-containing polymers by comparison with those containing phosphate moieties. The phosphoric and phosphonic acids produced in the non-polar environment during the copolymer decomposition catalyze Friedel–Crafts crosslinking of aromatic rings. As phosphonates form rather weak phosphonic acid which is less prone to promote crosslinking reactions, the crosslinking is higher with phosphate-containing copolymers, increasing the thermal stability of the polymer and reducing the release of volatile products.

3.3.4. Intumescent flame retardant systems

Intumescent systems were initially developed to protect fabrics, wood and coatings from fire. The concept of intumescence relies upon the formation of an expanded carbonized layer on the surface of the polymer during thermal degradation. This layer acts as an insulating barrier, reducing heat transfer between the heat source and the polymer surface. It also limits fuel transfer from the polymer towards the flame as well as the diffusion of oxygen into the material.

In general, the formulation of an intumescent system requires three components:

- *An acid source*: an inorganic acid, acid salt or other acid that promotes the dehydration of the carbonizing agent;
- *A carbonizing agent*: a carbohydrate that is dehydrated by the acid to form a char;
- *A blowing agent*, which decomposes and releases gas, leading to expansion of the polymer and the formation of a swollen multi-cellular layer (melamine, guanidine, urea, chlorinated paraffins). The gas must be released during the thermal decomposition of the carbonizing agent in order to trigger the expansion of the carbonized layer.

Thus, acid species catalyze the dehydration reaction of the carbonizing agent, leading to the formation of a carbonaceous layer. The acid has to be liberated at a temperature below the decomposition temperature of the carbonizing agent and its dehydration should occur around the decomposition temperature of the polymer.

The charring agent is generally a carbohydrate that produces char during thermal decomposition. Its effectiveness is related to the number of carbon atoms and reactive hydroxyl sites that contain the carbon source agent molecules. The amount of char produced during thermal decomposition is highly dependent on the number of carbon atoms, whereas the number of reactive hydroxyl sites determines the rate of the dehydration reaction and thus the rate of formation of the carbonized structure.

The most widely used acid source compound is ammonium polyphosphate (APP). In polyolefins, it is necessary to combine APP with a carbonizing agent to generate the char. Pentaerythritol has frequently been combined with APP, but unfortunately tends to migrate, e.g. during the injection molding process. To overcome

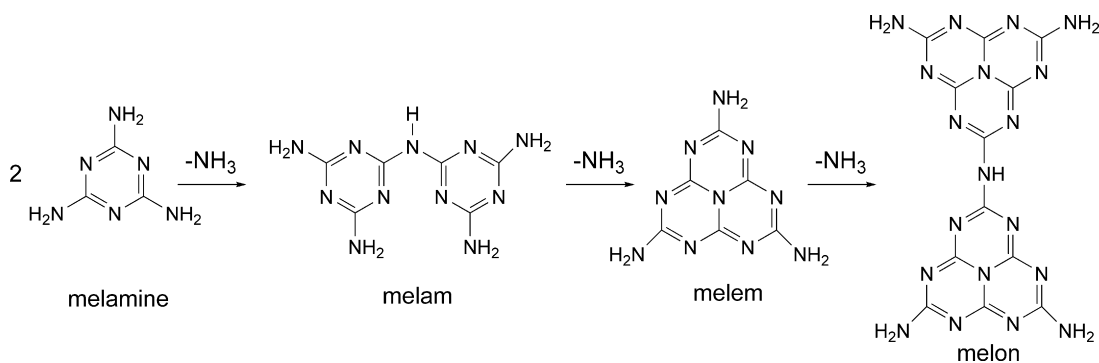


Fig. 15. Thermal decomposition of melamine and related products [63].

this drawback, PA-6 can be used as a carbonizing agent. In fact, a carbonized layer that contains nitrogen atoms linked to carbon atoms is formed during combustion [56,57]. Bourbigot et al. [58] highlighted that PA-6 could advantageously be replaced in intumescent systems by a PA-6 organomodified clay nanocomposite. The presence of such a nanocomposite improves both the mechanical properties and the fire resistance of the materials produced. Clays were found to improve the thermal stability of the phosphorated-carbonated intumescent structure formed during combustion. In addition, the effectiveness of such a system could also be increased by the formation of a protective ceramic layer. It should be mentioned that such intumescent systems have been interestingly reviewed and widely discussed by Bourbigot et al. [59,60] and Camino et al. [61,62].

3.4. Nitrogen-based flame retardants

Melamine is a thermally stable crystalline product characterized by a melting point as high as 345°C that contains 67 wt% nitrogen atoms [23]. Melamine sublimates at about 350°C . Upon sublimation, a significant amount of energy is absorbed, decreasing the temperature. At high temperature, melamine decomposes with the elimination of ammonia, which dilutes oxygen and combustible gases and leads to the formation of thermally stable condensates, known as *melam*, *melem* and *melon* (Fig. 15) [63].

These reactions compete with melamine volatilization and are more pronounced if melamine volatilization is impeded, e.g. by the formation of a protective layer. The formation of melam, melem and melon generates residues in the condensed phase and results in endothermal processes, also effective for flame retardancy. In addition, melamine can form thermally stable salts with strong acids: melamine cyanurate, melamine phosphate, and melamine pyrophosphate. Melamine and melamine salts are characterized by various flame retardant mechanisms. Upon heating, melamine-based salts dissociate and the re-formed melamine volatilizes, like neat melamine, but a large proportion of the melamine undergoes more progressive condensation than in the case of pure melamine [63]. The action of salts in the condensed phase is therefore significantly higher.

The thermal decomposition of melamine phosphate (Fig. 16) leads to the formation of melamine polyphosphate, with the release of melamine and phosphoric acid [43]. The phosphoric acid released is known to phosphorylate many polymers and produce flame retardant effects similar to phosphorus-based flame retardant additives.

The thermal decomposition of melamine polyphosphate leads to the formation of melam ultraphosphate and ammonium polyphosphate, with the release of melamine. However, the melamine in the gaseous phase competes with the formation of

its condensation products, such as melam ultraphosphate. The condensation of melamine is thus accompanied by the formation of polyphosphoric structures. Ammonium polyphosphate can also be formed from melamine polyphosphate. In addition, ammonium polyphosphate tends to dissociate and release ammonia above 300°C and the free condensed hydroxyl groups give crosslinked structures (ultraphosphate) with water elimination. The hydrolysis of the melam ultraphosphate generates a melam phosphate derivative or melam polyphosphate. Above 410°C , the thermal degradation of the ultraphosphate is limited and is followed around 650°C by the formation of a relatively stable residue.

The melamine pyrophosphate evolves to melamine during thermal decomposition but its thermal performances are different from those of melamine and its other salts; the formation of carbonaceous structures is more significant here and its action mode is similar to that of ammonium polyphosphate.

3.5. Silicon-based flame retardants

The addition of a relatively low amount of silicon-based compounds (silicones, silicas, organosilanes, silsesquioxanes and silicates) to polymers has been reported to substantially improve their flame retardancy. They can be used as fillers incorporated in the polymer, as copolymers or as the main polymer matrix. It should be mentioned that the flame retardancy of silicones has been reviewed by Kashiwagi and Gilman [64].

3.5.1. Silicones

Silicones are endowed with excellent thermal stability and high heat resistance, with very limited release of toxic gases during thermal decomposition. Silicones can be used as flame retardant agents through direct blending within the polymer matrix or by synthesizing block/graft copolymers including silicone segments.

Iji and Serizawa [65] investigated several types of silicone polymers as flame retardants in polycarbonate (PC) and studied the effect of the silicone structure on the flame retardant properties of these PC materials. The structural variables were the silicone chain topology (linear type, branched type), the pending groups along the chain (methyl, phenyl, mixture of the two) and the nature of end-groups (methyl, phenyl, hydroxyl, methoxyl, vinyl). As shown in Fig. 17, branched silicone polymers containing a mixture of methyl and phenyl groups along the chain and end-capped by methyl groups proved the most efficient in enhancing LOI values. Furthermore, the branched silicones were observed to be more effective when they were formulated to have a lower molecular weight.

The superior flame-retardant behavior of silicone derivatives was credited by the authors to their excellent dispersion in the PC and migration towards the material surface during combustion,

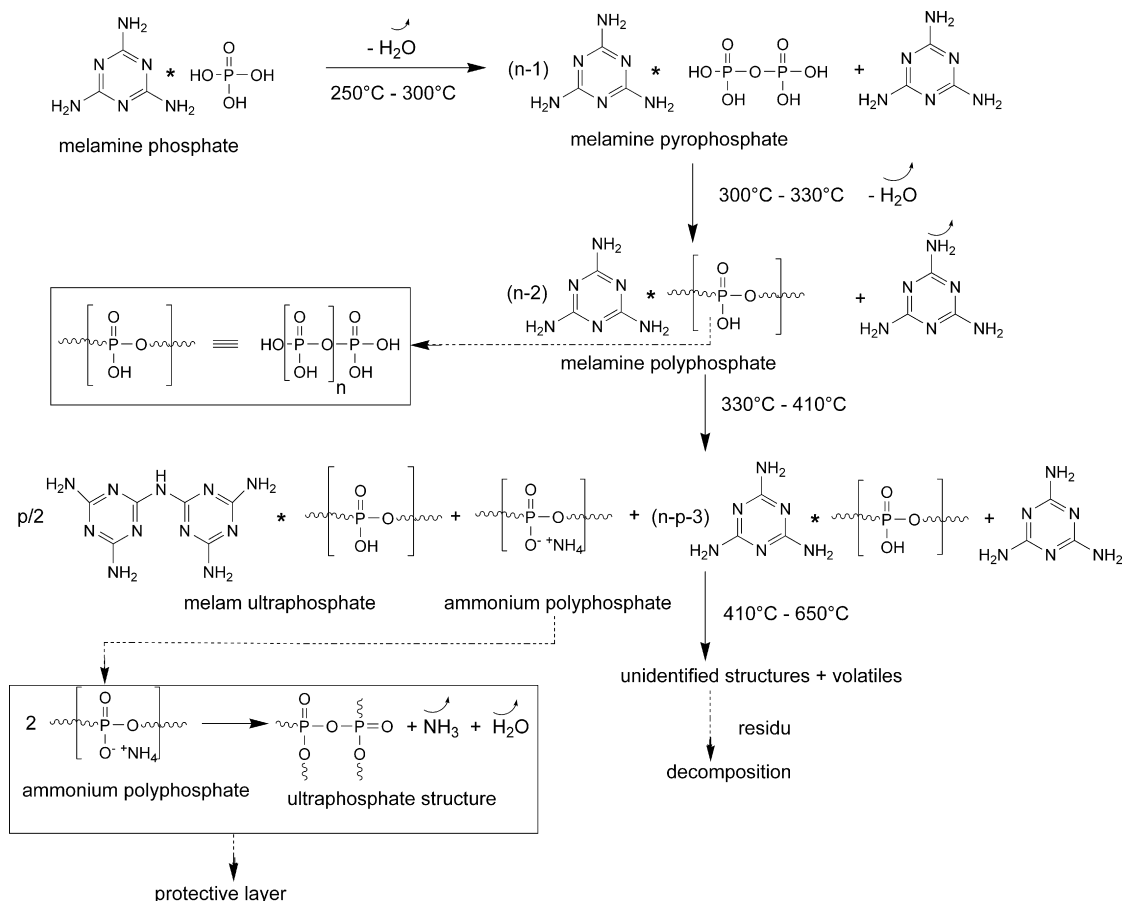


Fig. 16. Thermal decomposition of melamine phosphate [43].

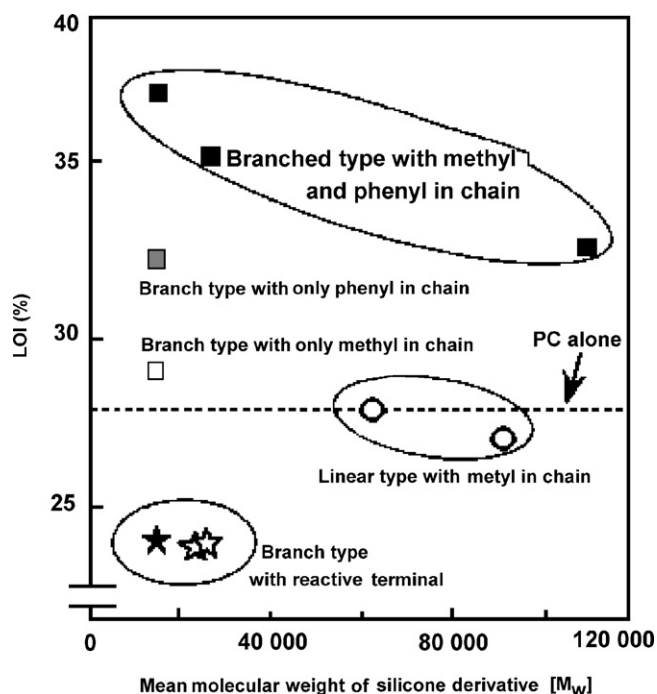


Fig. 17. LOI values for PC containing 5 phr of silicone polymers of various compositions and/or architectures and molecular weights (reproduced from [64] with permission).

followed by the formation of a highly flame-resistant char issued from the combination of polysiloxane and condensed aromatic compounds.

Zhou and Yang [66] used TGA to investigate the thermal decomposition of PC containing branched-structure methyl phenyl-silicone. They suggested that the hydroxyl groups present in the PC degradation products could react with the carbon-silicon bond in the silicone yielding a crosslinked structure (as shown in Fig. 18a) and a condensed aromatic structure by means of a dehydrogenation reaction between phenyl groups (Fig. 18b).

Nodera and Kanail [67] incorporated block copolymers of PC and PDMS (PC-*b*-PDMS with degree of polymerization – DP ~ 40) as a flame retardant agent in PC. By comparison with simple PC/PDMS blends, the copolymerization of PC and PDMS blocks leads to better flame retardant properties in both the LOI (Fig. 19) and cone calorimeter tests (pHRR = 500 kW/m² for the blend and only 235 kW/m² for the copolymer). The combustive behavior of PC-*b*-PDMS copolymers appeared totally different from that of the PC/PDMS blends, generating large amounts of gas bubbles and promoting significantly more intensive charring.

Nodera and Kanail [67] also investigated the effect of PDMS block size (DP from 15 to 350) and PDMS content (from 0 to 2.5 wt%) on LOI values recorded with PC-*b*-PDMS copolymers. The LOI values and the amounts of residues for each PC-*b*-PDMS copolymer increased rapidly until ca. 1.0 wt% in PDMS, then started leveling off at higher silicone block content. The authors showed that PDMS block size influences the dispersability of the PDMS in the PC, and that moderate PDMS dispersion (i.e. 50 nm mean inclusion size) resulted in high flame retardancy. They

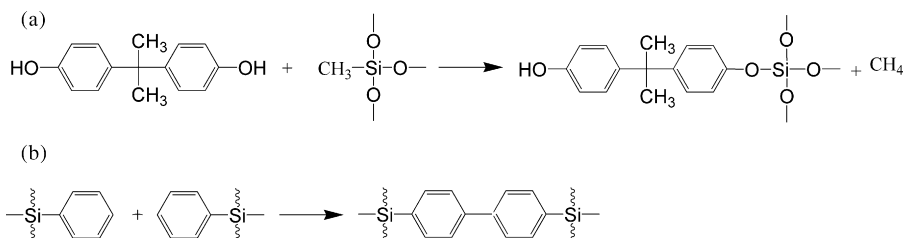


Fig. 18. Formation of a cross-linked structure at high temperature in PC-siloxane blends (a) and dehydrogenation reaction between two silicone phenyl groups (b).

assumed that PC-*b*-PDMS block copolymers with moderate PDMS dispersion could form numerous fine bubbles through reaction of PC and PDMS during combustion, which behave as good thermal insulation domains spread throughout the material. Furthermore, silica particles *in situ* formed by thermal degradation of PDMS mostly remained within the char layer, thus increasing the quantity of highly oxidation resistant char. The resulting char layer therefore had a structure that prevented volatile fuel production and served as an additional thermal insulator.

3.5.2. Silica

The effect of silica gel structure on the flammability properties of polypropylene has been investigated by Gilman et al. [68]. They studied the effect of three silica gels with different pore volume, particle size and surface silanol concentration. Cone calorimeter tests revealed the dramatic effect of silica gel pore volume on the heat release rate (HRR) of PP containing 10% wt. in silica. The incorporation of high pore volume silica led to a marked reduction in the HRR. There was no noticeable effect of particle size on the flammability properties but a significant effect of the surface silanol concentration was observed. The authors explain the reduction of the flammability at higher silica gel pore volume by the possibility offered by larger pores to accommodate macromolecular PP chains or by the increase in molten viscosity during pyrolysis, which can trap or slow down volatilization and the evolution of degradation products.

In another study, Kashiwagi et al. [69] also investigated the performances of various types of silica, silica gel, fumed silica and fused silica as flame retardants in non-char-forming thermoplastics (e.g., polypropylene) and polar char-forming thermoplastics (e.g., polyethylene oxide). The addition of low density, large surface area silica, such as fumed silica (140 and 255 m²/g) and silica gel (400 m²/g) to polypropylene and polyethylene oxide significantly reduced the heat release rate and mass loss

rate. However, the addition of fused silica with lower surface area did not reduce the flammability properties as much as the other silica samples. The flammability reducing mechanism is based on the physical processes taking place in the condensed phase rather than chemical reactions. The balance between the density and the surface area of the additive, together with the polymer melt viscosity, determine whether the additive accumulates near the sample surface or sinks through the polymer melt layer. The fumed silica and silica gel used in this study accumulated near the surface and acted as a thermal insulation layer and also reduced the polymer concentration near the surface in contact with the flame. However, the fused silica studied mainly sank through the polymer melt layer and did not accumulate near the surface.

The accumulation of silica on the surface of the burned polymer has been also observed in PMMA [70]. In this study, two types of silica (fused silica and silica gel) were incorporated in two different molecular weight PMMA samples. In this case, the specific surface area of the silica and its porous volume affected the thermal stability and flame retardant properties of the polymer by modifying the viscosity of the system in the molten state. Viscosity control proved to be a key-factor in the formation of the protective layer.

3.6. Nanometric particles

Nanometric particles when individualized and properly dispersed in polymer matrices are known to contribute to the enhancement of properties such as thermal, mechanical or fire resistance. They enable a considerable reduction of the loading rate as the interfacial area between the polymer and the nanofiller is greatly increased.

More precisely, the contribution of each type of nanoparticle to flame retardancy varies and strictly depends on its chemical structure and geometry. The aim of the following section is therefore separately to describe and discuss the flame retardant effects and flame retardant mechanism(s) of three widely investigated nanoparticles:

- *layered materials*, such as nanoclays (e.g., montmorillonite: MMT), which are characterized by one nanometric dimension, referred to as 2D nanoparticles;
- *fibrous materials*, such as carbon nanotubes and sepiolite, which are characterized by elongated structures with two nanometric dimensions and referred to as 1D nanoparticles;
- *particulate materials*, such as polyhedral oligosilsesquioxane (POSS) and spherical silica nanoparticles, which are characterized by three nanometric dimensions and sometimes referred to as 0D nanoparticles.

3.6.1. Nanoclays

In order to favor the dispersion of the clay nanolayers within the polymer matrix, a modification of natural clays using organic cations (alkylammonium, alkyl phosphonium and alkyl imidazol(idin)ium

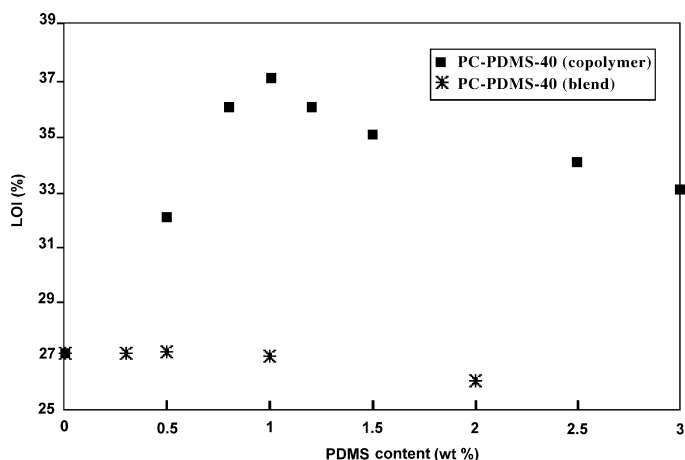


Fig. 19. LOI values of PC-*b*-PDMS copolymers and PC/PDMS blends in function of relative PDMS content (adapted from [66]).

cations) is often carried out, leading to the formation of organo-modified nanoclays.

The incorporation of a relatively low quantity of (organo-modified) nanoclay in the polymer matrix creates a protective layer during combustion [71,72]. Upon heating, the viscosity of the molten polymer/layered silicate nanocomposite decreases with increasing temperature and facilitates the migration of the clay nanolayers to the surface. Moreover, heat transfer promotes thermal decomposition of the organomodifier and the creation of strongly protonic catalytic sites onto the clay surface, which can catalyze the formation of a stable char residue [73,74]. Therefore accumulation of the clay on the surface of the material acts as a protective barrier that limits heat transfer into the material, volatilization of combustible degradation products and diffusion of oxygen into the material. Furthermore, nanoclay migration is enhanced by the formation of gas bubbles, initiated by the decomposition of both the quaternary ammonium organomodifiers and the polymer chains. Such gas bubbles may in fact be nucleated by the surface of the MMT. These gas bubbles could also help in the convection of the MMT sheets to the surface.

Concerning EVA layered silicate nanocomposites, Camino and co-workers [71] have proposed a chemical mechanism to explain why conventional microcomposites (with no MMT exfoliation/intercalation) burn in the same way as unfilled EVA, whereas heat release is reduced by 70–80% when nanocomposites (with high

level of clay delamination) filled with tiny amounts of organoclays (2–5%) are burned (Fig. 20). Heat transfer from an external source or from the flame itself promotes the thermal decomposition of the organomodifier and the formation of acidic onium ions on the clay layers [75], which catalyze the loss of the acetic acid. The polyene obtained from EVA deacetylation undergoes several chemical reactions resulting in the formation of conjugated and crosslinked polyenes creating the charred surface layer, as proposed by Costache et al. [76]. To summarize, the combination of the charred structure and the reassembling of the silicate layer generates a ceramic char-layered silicate nanocomposite at the material surface.

Camino et al. [77] also studied and monitored the evolution of the (nano)structure of EVA-clay nanocomposites during thermal treatments under inert and oxidizing atmospheres (Fig. 21). At low temperature (under 225 °C), in both nitrogen and air atmospheres, the interlayer distance of the organoclay decreased. At higher temperature, the nanocomposite structural modification depended on the atmosphere investigated. Under nitrogen, the decomposition of the organomodifier made the silicate layers less organophilic and EVA deacetylation reduced the polarity of the polymer. Polymer–clay compatibility was reduced and segregation of the two phases occurred, leading to a further decrease in the interlayer distance. In air, partial oxidation of the polymer chains triggered an increase in matrix polarity thereby enhancing

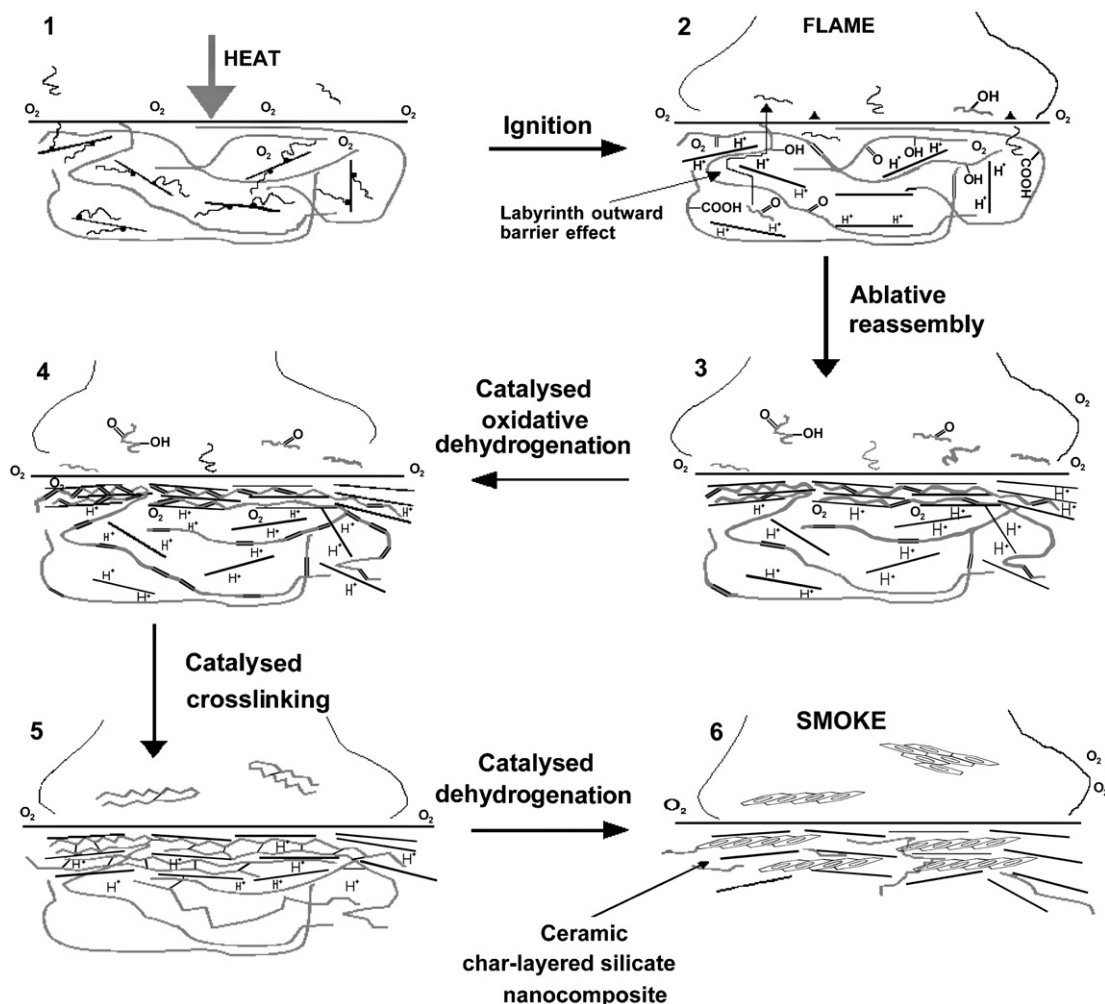


Fig. 20. Schematic representation of the combustion mechanism and ablative assembly of a nanocomposite during the cone calorimeter test (reproduced from [70] with permission).

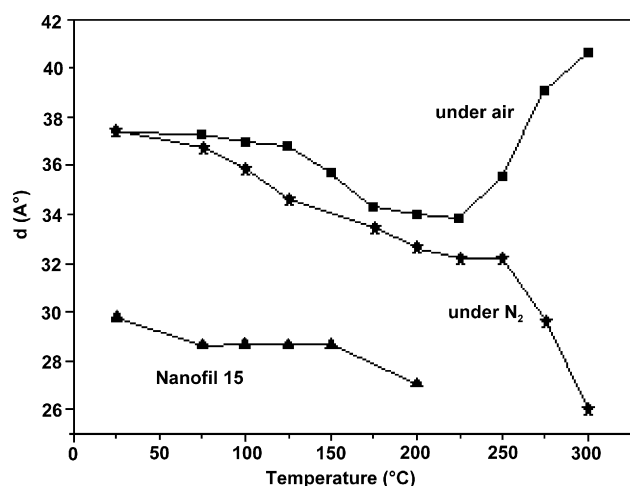


Fig. 21. Interlayer distances as a function of temperature for an EVA-clay nanocomposite compared to the pure nanoclay (Nanofil 15) (adapted from [76]).

polymer-clay compatibility and maintaining and improving the intercalation of the layered silicate. This study stressed the crucial role that the atmosphere can play in the flame retardant mechanism within polymer nanocomposites.

The char formed during thermal degradation of the polymer matrix is an important factor that considerably improves the flame retardant behavior of the nanocomposite. The incorporation of sodium layered montmorillonite (Na-MMT) and organomodified montmorillonite (oMMT) in PP/PPgMA (Polypropylene grafted Maleic Anhydride) can create a char layer only in the presence of organomodified montmorillonite (oMMT) [73]. In the presence of Na-MMT, whatever the amount of incorporated clay, no trace of char could be observed. The difference between PP/PPgMA/Na-MMT composites and PP/PPgMA/oMMT nanocomposites with regard to the formation of char has been attributed to the fact that Brønsted acid sites only form on the oMMT surface. After decomposition of the organomodifiers, the creation of Brønsted acid sites has been reported to catalyze the thermal degradation of PP via a cationic mechanism, which leads to char formation via a hydrogen transfer reaction occurring during combustion. The char content and cone calorimetry behavior depend on the organomodifier content: increased organomodifier content leads to a more pronounced catalytic effect and more intensive char formation. As an illustration, two organoclays with different organomodified contents (oMMT(80) and oMMT(150)) incorporated in polypropylene actually resulted in the same nanoclay dispersion state [73]. The factual adsorption levels of the organomodifier were 51%CEC and 122%CEC for oMMT(80) and oMMT(150), respectively (where CEC = the cation exchange capacity of the clay). The amount of char formed after combustion at 700 °C increased and the cone

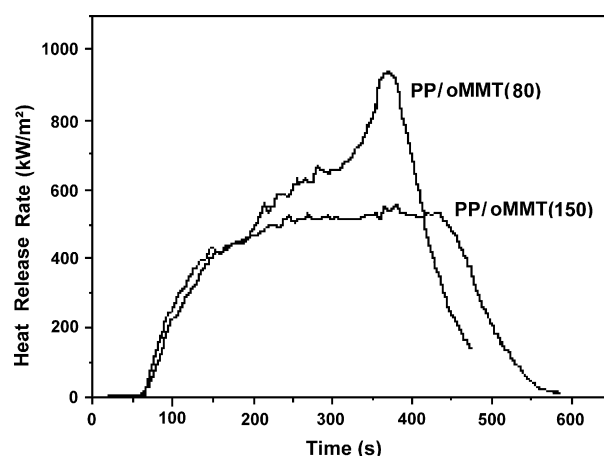


Fig. 22. Effect of oMMT organomodifier content on the heat release rate (35 kW/m²).

calorimeter HRR decreased (Fig. 22) for the nanocomposite containing oMMT(150), i.e. the larger amount of organomodifier.

Interestingly, Wilkie and co-workers [74] correlated the change in the degradation pathway of a polymer by incorporation of nanoclay to the heat release rate peak measured by cone calorimetry (Table 3). Indeed, polymer nanocomposites with good fire retardancy (i.e. large reduction in pHRR) exhibit significant intermolecular reactions, such as inter-chain aminolysis/acidolysis (PA-6), radical recombination (PS) or hydrogen abstraction (EVA), whereas polymers showing moderate reduction in HRR (SAN, ABS, PE and PP) only present limited intermolecular reactions. Furthermore, when no significant HRR reduction was observed no change in polymer degradation pathway was noticed (PAN, PMMA).

It is generally accepted that the formation of a nanocomposite (whether intercalated or exfoliated) enables good flame retardant properties to be achieved. For instance, in cone calorimetry experiments, it has been shown that the peak heat release rate decreases only by 25% for EVA/5% Na-MMT microcomposite compared to 50% for EVA/5% Cloisite® 30B nanocomposites; by comparison with the unfilled polymer [78]. However, some other studies investigating the importance of the exfoliation of clay nanoplatelets with respect to flame retardant performances have concluded that simple intercalation could give similar or even better flame retardant properties than exfoliated nanocompositions, leaving the question open. For instance, Morgan et al. [79] have shown that the HRR curves of intercalated and exfoliated PA-6 nanocomposites, as obtained by cone calorimetry (Fig. 23) are not significantly different from each other. However, they revealed a clear-cut difference in ignition times between the

Table 3

Effects of the incorporation of nanoclay on the thermal degradation pathway of the polymer and reduction of HRR values [74].

Polymer	Degradation pathway of virgin polymer	Degradation change (increase) in the presence of clay	HRR reduction (%)
Polyamide 6	Intra-aminolysis/acidolysis, random scission	Inter-aminolysis/acidolysis, random scission	50–70
Polystyrene, high-impact polystyrene	β-Scission (chain end and middle)	Recombination, random scission	40–70
Ethylene-vinyl acetate copolymer	Chain stripping, disproportionation	Hydrogen abstraction, random scission	50–70
Styrene-acrylonitrile copolymer,	β-Scission (chain end and middle)	Random scission, recombination	20–50
Acrylonitrile-butadiene-styrene terpolymer			
Polyethylene	Disproportionation	Hydrogen abstraction	20–40
Polypropylene	β-Scission, disproportionation	Random scission	20–50
Poly(acrylonitrile)	Cyclization, random scission	No change	<10
Poly(methylmethacrylate)	β-Scission	No change	10–30

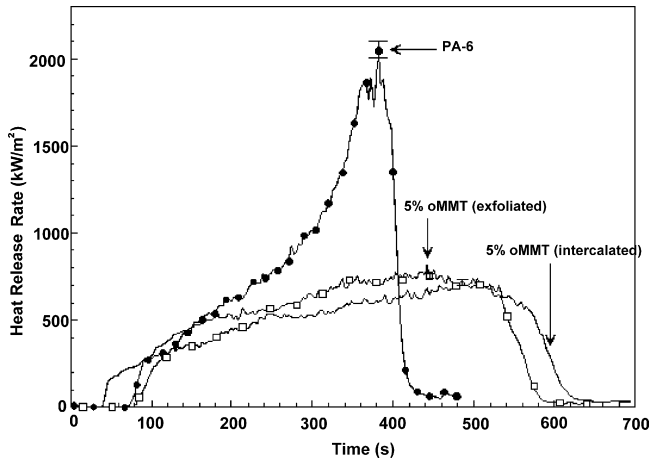


Fig. 23. HRR curves for pure PA-6, intercalates and exfoliated PA-6/5 wt% MMT(50 kW/m²) (adapted from [78]).

intercalated and exfoliated nanomorphologies (40 s for the intercalated sample compared to 80 s for the exfoliated nanocomposite).

Another study suggests, however, that the dispersion state of the clay particles in the polymer matrix may have a considerable influence on flammability [77]. With two different nanoclays (oMMT(80) and oMMT(150)) containing different amounts of the same organomodifier (an ammonium salt bearing long alkyl chains), two morphologies were revealed (intercalated and exfoliated) in PP depending on whether or not PPgMA was used to improve the nanoclay dispersion [73].

For the same organomodified content (oMMT(80) – Fig. 24a, or oMMT(150) – Fig. 24b), the improvement of the clay dispersion (i.e. the increase in the degree of exfoliation), in the presence of PPgMA acting as a compatibilizer, triggers a significant reduction in the HRR value. However, this reduction is more visible when a larger amount of organomodifier is incorporated in the clay interlayer space (Fig. 24b), highlighting that the flame retardant effect of the clay depends not only on its ability to disperse through the nanocomposite but also, and more fundamentally, on the organomodifier content, which can promote more intensive formation of catalytic acid sites on the surface of the clay at high temperature. It is worth noting that the better dispersion of oMMT in the compatibilized PP matrix may also generate a continuous MMT-rich carbonaceous surface layer upon combustion [73].

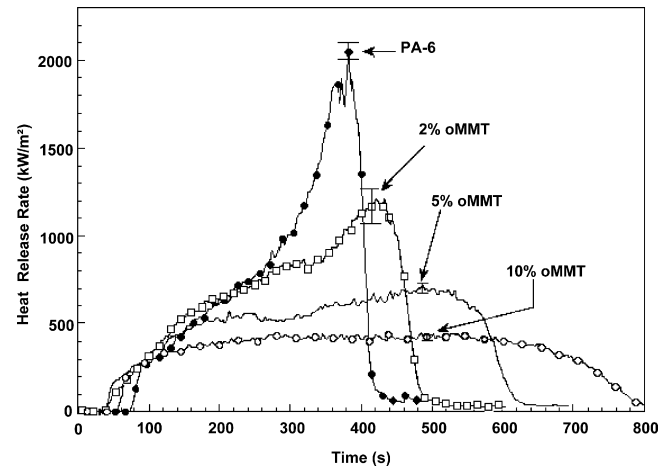


Fig. 25. Effect of nanoclay loading rate on HRR curves for PA-6 nanocomposites [78] (50 kW/m²).

Increasing the nanoclay content of the polymer also influences the HRR curves and leads to a sharp decrease of the HRR peak (Fig. 25). However, the time to ignition tends to decrease while the total heat release rate does not change.

With regard to PA-6 clay nanocomposites, the increase in melt viscosity arising from the nanocomposite structure has shown to slow down the formation of the melt state. The solid state having a lower thermal conductivity than the melt state, the temperature at the surface of the nanocomposite rises more rapidly than with unfilled PA-6, increasing the rate of fuel production and therefore decreasing the time to ignition [80]. The rapid temperature increase at the sample surface is also thought to be due to the presence of clay nanoplatelets, which reduce thermal diffusion into the sample.

The main fire retardancy mechanisms in polymer/clay nanocomposites seem to be the formation of a barrier against heat and volatiles by migration of the clay nanolayer toward the material surface, followed by char formation, together with increased melt viscosity for exfoliated nanocomposites. These mechanisms modify the fire properties of the polymer nanocomposite, sometimes improving them and in some other cases worsening them, depending on the type of fire test applied and the nature of the measurements recorded. For example, in cone calorimeter tests, the incorporation of nanoclays generally retards and decreases the peak heat release rate, but does not reduce the total heat involved and may also decrease the time to ignition. The increased melt

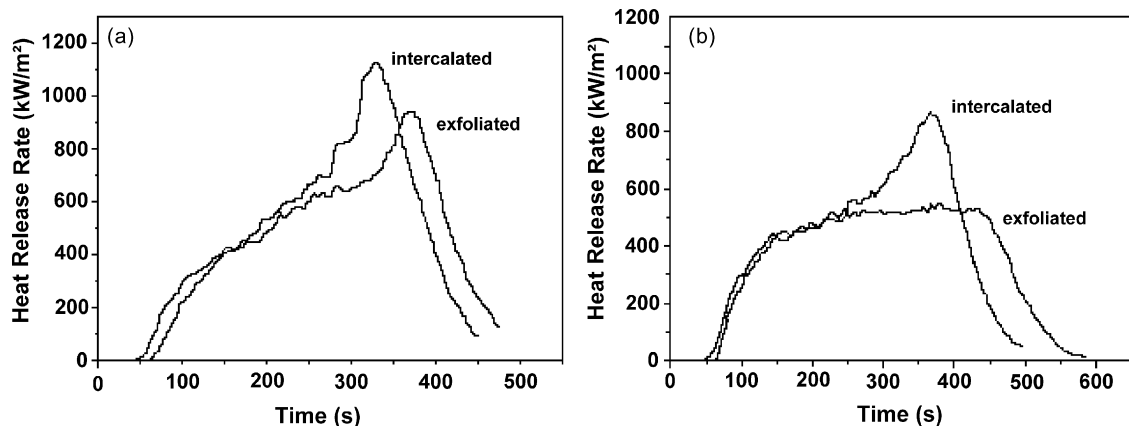


Fig. 24. Effect of clay dispersion on HRR: (a) oMMT(80) based nanocomposites; (b) oMMT(150) based nanocomposites (35 kW/m²) (adapted from [72]).

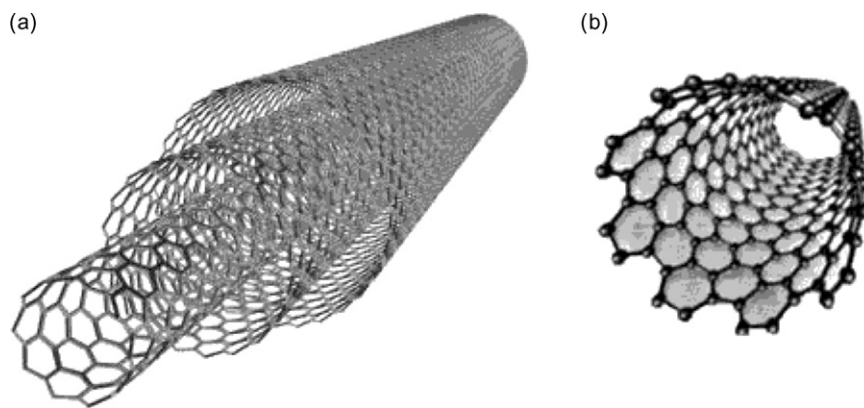


Fig. 26. Schematic representation of multi-walled (a) and single-walled (b) carbon nanotubes.

viscosity in exfoliated nanocomposites prevents dripping and promotes char formation. However, the char formed at the surface of the burning sample in UL 94 and LOI tests is not effective enough to stop the flame and the sample continues to burn slowly, ultimately displaying poor flame retardant performances.

3.6.2. Carbon nanotubes

The most widely studied nanofibrous materials with respect to polymer flame retardancy are carbon nanotubes (CNTs). They can be synthesized in several ways: arc discharge, laser ablation and thermal or plasma enhanced chemical vapor growth deposition (CVD). Direct-arc discharge and laser ablation require the use of a small quantity of metal catalyst and very high temperatures while CVD techniques enable the synthesis of CNTs at lower temperatures but usually leave significant quantities of catalyst residues within the recovered samples.

Carbon nanotubes display exceptional properties that can potentially be used in many applications ranging from macroscopic material composites down to nanodevices. Thanks to their high aspect ratio, CNTs percolate to form a network at very low loading in the polymer matrix and lead to substantial enhancement of several functional properties such as mechanical [81], rheological [82,83,84] and flame retardant [85,86,87] properties. There are two different types of CNTs (Fig. 26), small-diameter (1–2 nm) single-walled

nanotubes (SWNTs) and larger-diameter (10–100 nm) multi-walled nanotubes (MWNTs).

CNTs are an interesting alternative to the use of conventional flame retardants and nanoclays. Their incorporation at low loading rate (<3 wt%) has been reported to improve the flammability of a large range of polymers such as EVA [81], PS [84], PMMA [85], PA-6 [86], LDPE [87] and PP [88].

Kashiwagi et al. [85] studied the effect of the nanotube dispersion state on the flame retardant properties of PMMA nanocomposites. They showed that the incorporation of only 0.5 wt% of SWNT correctly dispersed in PMMA led to a marked decrease in the HRR (Fig. 27a), liberated over a much longer time range in comparison to neat PMMA. However, the combustion behavior of PMMA nanocomposites containing poorly dispersed SWNT proved to behave similarly to unfilled PMMA, without any significant reduction in the heat release rate. It is worth pointing out that the total heat release (THR) did not vary for all the samples tested, indicating that nanocomposites filled with relatively well dispersed nanotubes burn more slowly than compositions in which nanotube aggregation is still observed. Both types of samples burned almost completely.

The nanotube loading rate affected the flammability of the PMMA nanocomposites. For nanocomposites characterized by good nanotube dispersion, the addition of 0.1 wt% SWNT did not

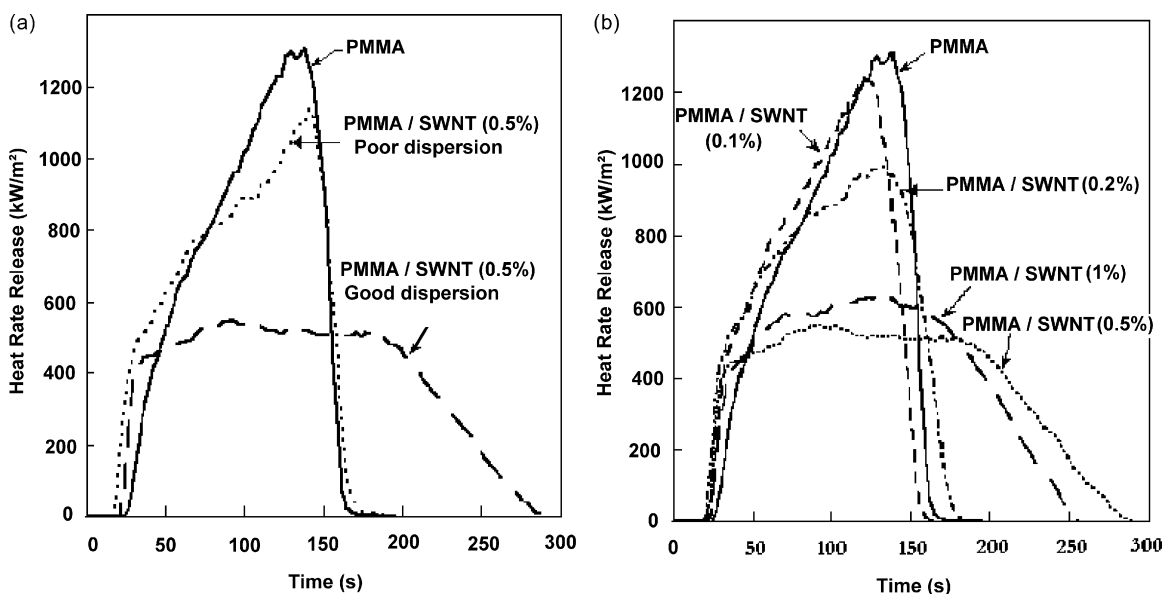


Fig. 27. HRR of PMMA containing SWNT; effects of SWNT dispersion (a) and SWNT concentration (b) (50 kW/m²) [84].

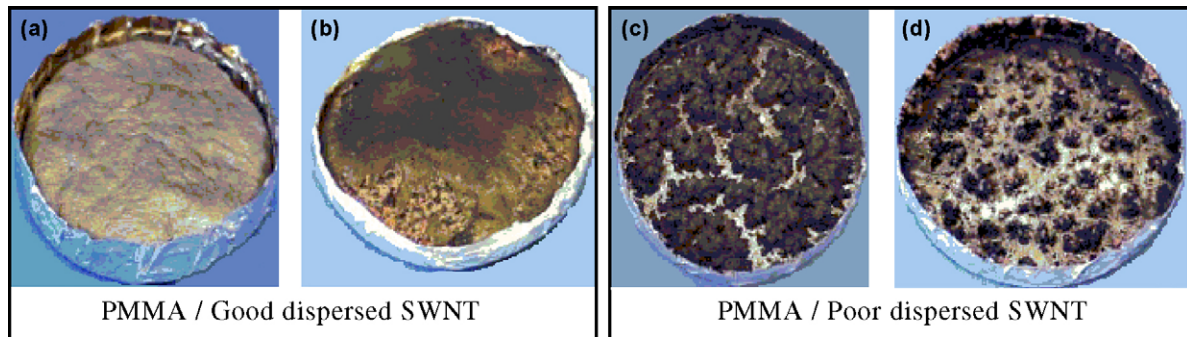


Fig. 28. Effect of carbon nanotube dispersion on PMMA/0.5 wt% SWNT residues formed during the nitrogen gasification test (a and c), and cone calorimeter test (b and d) (reproduced from [84] with permission).

significantly reduce the HRR of the PMMA while a 25% reduction was attained by the addition of 0.2 wt%. More than 50% reduction in HRR was even achieved, by the incorporation of 0.5 wt% of SWNT (Fig. 27b).

Observation of the residues recovered after cone calorimeter experiments and gasification tests (Fig. 28) clearly revealed the presence of a continuous dark layer covering the residues of the nanocomposites based on fine nanotube dispersion. By contrast, only poorly cohesive and discontinuous residues were isolated in case of nanocomposites containing aggregated CNTs. The authors suggested that the reduction in HRR and improvement of polymer flammability were essentially due to physical processes in the condensed phases. Observations carried out during gasification under a nitrogen atmosphere showed that at low SWNT concentration (below 0.2 wt%) many small, discrete black islands were generated after the initial apparition of small bubbles which burst at the specimen surface. Some bubbling was observed to take place between the islands, pushing nanotubes toward the islands, gradually increasing their mean size and eventually connecting them to each other, with the formation of a discontinuous residue. At relatively higher loading rates (0.5 and 1 wt%), a continuous

layer was formed, entirely covering the sample surface without any major visible cracks, as shown in Fig. 29.

A relatively uniformly structured network layer, without any cracks or holes, is also generated during the combustion of PP containing finely dispersed MWNT [88] resulting in a significant decrease in the peak HRR (MWNT content varied from 0.5 to 4 wt%).

Based on the above observations, the flame retardant properties of PP/MWNT nanocomposites appear to be governed by two distinct physical processes. Firstly, the structured network layer acts as a shield and re-emits much of the incident radiation back into the gas phase, decreasing the polymer degradation rate. Secondly, the presence of carbon nanotubes increases the thermal conductivity of the polymer. As a result, the time to ignition and the peak heat release rate of the PP/MWNT increase with the MWNT content. The lowest heat release rate is attained with the sample containing 1 wt% MWNT, most likely due to a balance between thermal conductivity and shielding effects.

The formation of such an efficient and compact layer is favored by the use of MWNT with a high aspect ratio, i.e. length-to-outer diameter ratio. Kashiwagi and co-workers [84] studied the effect of

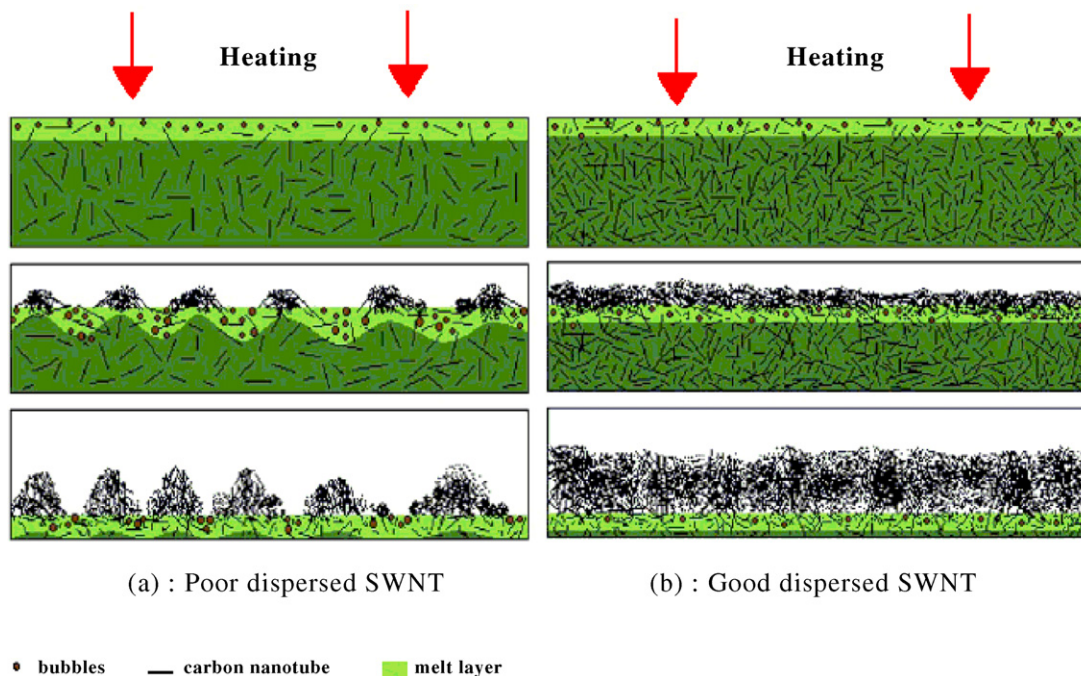


Fig. 29. Schematic representation of the formation of islands (a) and a structured continuous network layer (b) (reproduced from [84] with permission).

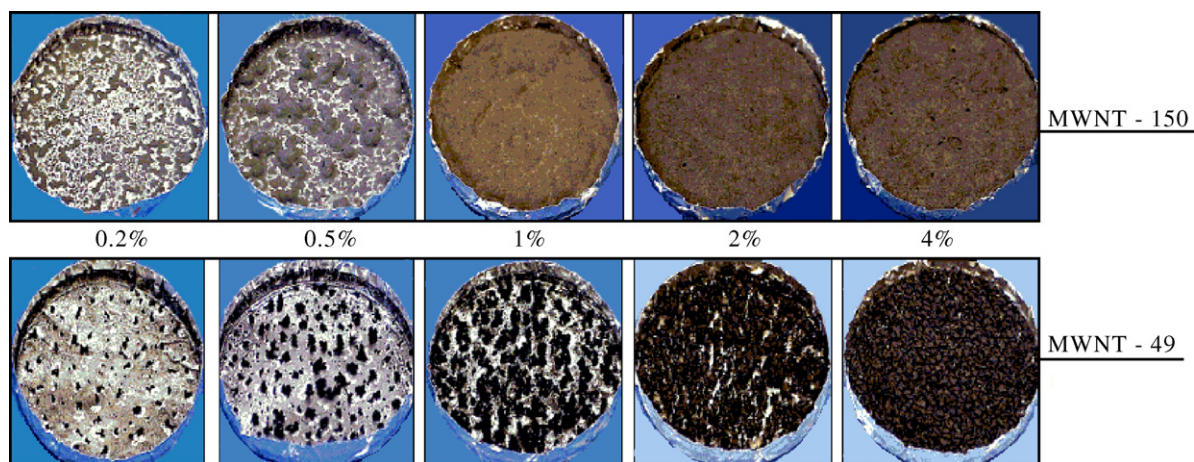


Fig. 30. Gasification residues of PS/MWNT nanocomposites based on MWNT – 150 and MWNT – 49 (reproduced from [83] with permission).

two different MWNT samples characterized by average aspect ratios of 49 (MWNT-49) and 150 (MWNT-150) on the flammability of polystyrene/MWNT nanocomposites. During gasification tests under nitrogen, the solid-like network structure was achieved at 2 wt% of MWNT-150 and 4 wt% of MWNT-49 (Fig. 30). The mass loss rate of PS/MWNT nanocomposites appeared to be reduced more by CNTs with a high average aspect ratio (MWNT-150), while no significant effects of MWNT aspect ratio on the thermal stability of PS/MWNT nanocomposites was detected by thermogravimetric analysis.

The effect of the MWNT mean size on EVA flammability has recently been studied by Dubois and co-workers [89]. 3 wt% MWNT and crushed MWNT were incorporated in an ethylene-vinyl acetate (EVA) copolymer and the resulting materials submitted to a cone calorimeter test at 35 kW/m². The results obtained showed a marked increase in time to ignition when crushed MWNT was used (Fig. 31). Interestingly, partial substitution of MWNT by crushed MWNT also led to an increase in time to ignition (Fig. 31). The authors attributed this behavior to the chemical reactivity of radical species (or precursors) existing at the surface/extremities of such crushed carbon nanotubes, and formed during the nanotube crushing process. However, the exclusive use of crushed MWNT resulted in the generation of thermally unstable char that finally degraded and decomposed (Fig. 32)

Dubois and co-workers [81] also used HDPE-coated MWNT obtained by a polymerization-filling technique [90] to produce

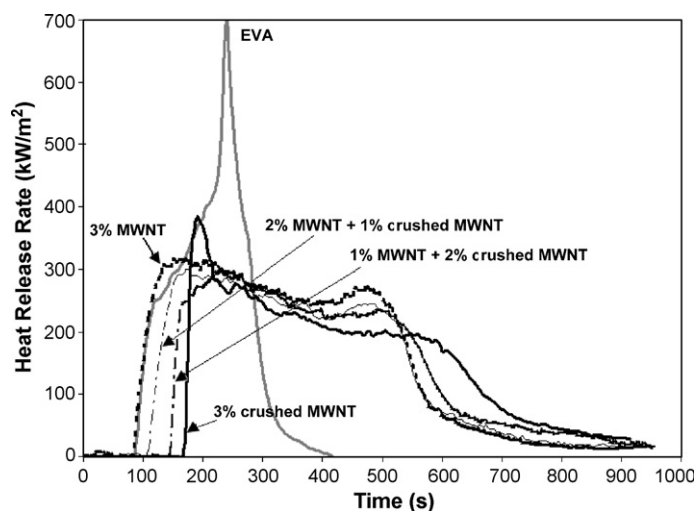


Fig. 31. Evolution of HRR during the cone calorimeter test (35 kW/m²) for EVA containing MWNT, effect of the crushing of CNTs.

nanocomposites within an EVA copolymer. The dispersion of the coated MWNT was considerably improved by comparison with EVA filled with uncoated-MWNT but no difference was observed between the HRR values of EVA containing 3 wt% of MWNT, whether coated or uncoated. However, in the presence of finely

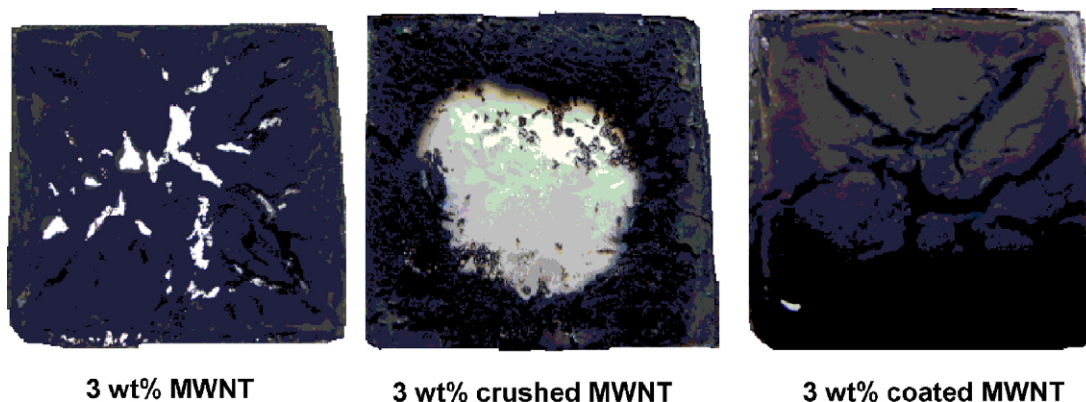


Fig. 32. Cone calorimeter residues for EVA containing MWNT, crushed MWNT and HDPE-coated MWNT.

dispersed HDPE coated-MWNTs, a more cohesive and homogeneous char was recovered after the cone calorimetry test (Fig. 32).

3.6.3. Nanoscale particulate additives

Another family of additives consists of nanoparticles of metal oxides, silica and polyhedral oligomeric silsesquioxane (POSS). These nanoscale particulate additives are characterized by their isometric dimensions and have also proved to be very interesting with regard to flame retardant polymer systems.

3.6.3.1. Silsesquioxane. POSS is an inorganic silica-like nanocage ((RSiO_{1.5})₈) surrounded by eight organic groups located at the corners that enhance its compatibility within organic polymers. On combustion of such a polymer composite, POSS acts as a precursor forming thermally stable ceramic materials at high temperature. These inorganic nanocages are also referred to as pre-ceramic compounds.

While a wide variety of nano-structures are described in the literature, essentially two types of POSS have been studied with respect to flame retardancy: bearing either eight identical R groups (R = methyl, phenyl, isobutyl or isooctyl) or seven R groups of the same nature and one functional R' group such as an ester, silane, isocyanate, methacrylate, alcohol, epoxide or amine. This wide range of R and R' groups enables the selective use of (functionalized) POSS according to the chemical nature of the polymer matrix. The (reactive) functionality of the R' group can not only improve the compatibility between the dispersed nanocages and the polymer matrix but also enable either chemical grafting of reactive polymer chains or initiation of polymerization reactions from the POSS surface via the so-called "grafting from" technique.

The incorporation of POSS in polymers modifies both the viscosity and the mechanical properties of the molten polymer. In addition, it also affects the thermal stability and fire performances by reducing the quantity of heat released upon combustion. For instance, the incorporation of 10 wt% of methyl phenyl polysilsesquioxane in polytetramethylenylether-glycol-*b*-polyamide-12 (PTME-*b*-PA) leads to a 70% decrease in peak HRR during cone calorimetry tests carried out at 35 kW/m² [64].

In addition, POSS can also play the role of metal dispersing agent [91,92]. In fact, it is possible to include a metal atom at one corner of the POSS nanocage structure. It has been shown that

finely dispersed metal-bearing POSS nanoparticles, at tiny concentrations (ca. 1 wt%), can markedly enhance the char yield in PP. This char formation has been explained by catalysis of the dehydrogenation reaction by the metal-bearing POSS. However, some experiments have measured an increase in flammability with metal-bearing POSS nanoparticles, as revealed by lower LOI values [91,93].

Fina et al. [93,94] studied the effect of the incorporation of dimeric and oligomeric Al- and Zn-isobutyl silsesquioxane (Al- and Zn-POSS) (Fig. 33) in polypropylene. For the sake of comparison, PP/octaisobutyl POSS was also prepared and investigated. The thermoxidative degradation of PP-based compositions was strongly affected by the presence of metal-containing POSS, resulting in an improvement in the thermal stability of the nanocomposite. The presence of Al-POSS led to a decrease in the heat release rate (decrease by 43% at 10 wt% POSS loading) as well as a reduction in CO and CO₂ production rates. Zn-POSS did not significantly affect the PP combustion behavior. The effect of Al-POSS is most probably related to its chemical catalytic activity, which favors the formation of a moderate amount of char residue during polymer combustion.

3.6.3.2. Metallic oxide particles. Laachachi et al. [95] investigated the effect of the incorporation of nanometric titanium oxide (TiO₂) and ferric oxide (Fe₂O₃) particles on the thermal stability and fire reaction of poly(methyl methacrylate) (PMMA). The incorporation of a small amount (5 wt%) of nanometric TiO₂ or Fe₂O₃ enhanced the thermal stability of PMMA nanocomposites [96]. HRR values, as determined by the cone calorimetry test (irradiance of 30 Kw/m²), were found to depend on the filler content and to decrease at higher loadings (Fig. 34). Even though the Fe₂O₃ nanoparticles had a similar particle size (23 nm) and surface area (48 m²/g) to the TiO₂ (21 nm and 50 m²/g), their incorporation led to a different behavior in the cone calorimeter test. The combustion of PMMA/Fe₂O₃ nanocomposite produced more smoke than virgin PMMA. The peak HRR was reduced by about 50% in the presence of 20 wt% TiO₂ while it decreased by only 37% when the same quantity of Fe₂O₃ was used. Time to ignition increased significantly (more than 20 s) in the presence of TiO₂ and remained largely unchanged at higher TiO₂ loading rate. By contrast, no significant change was observed with Fe₂O₃, which has tentatively been explained by the lower thermal diffusivity of iron oxide (0.74 × 10⁻⁶ m²/s) compared

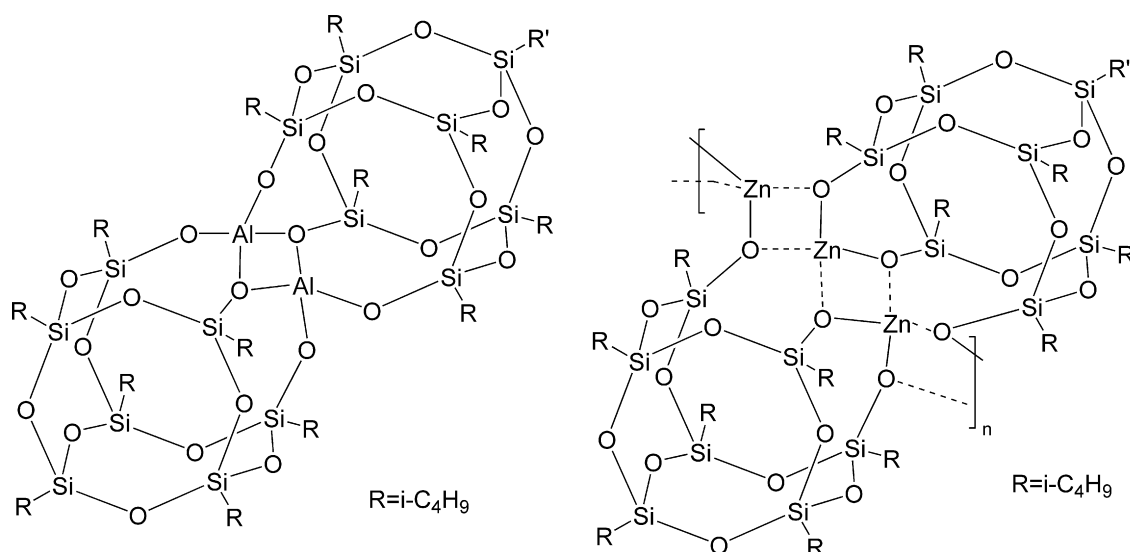


Fig. 33. Structure of Al- and Zn-isobutyl silsesquioxane [92].

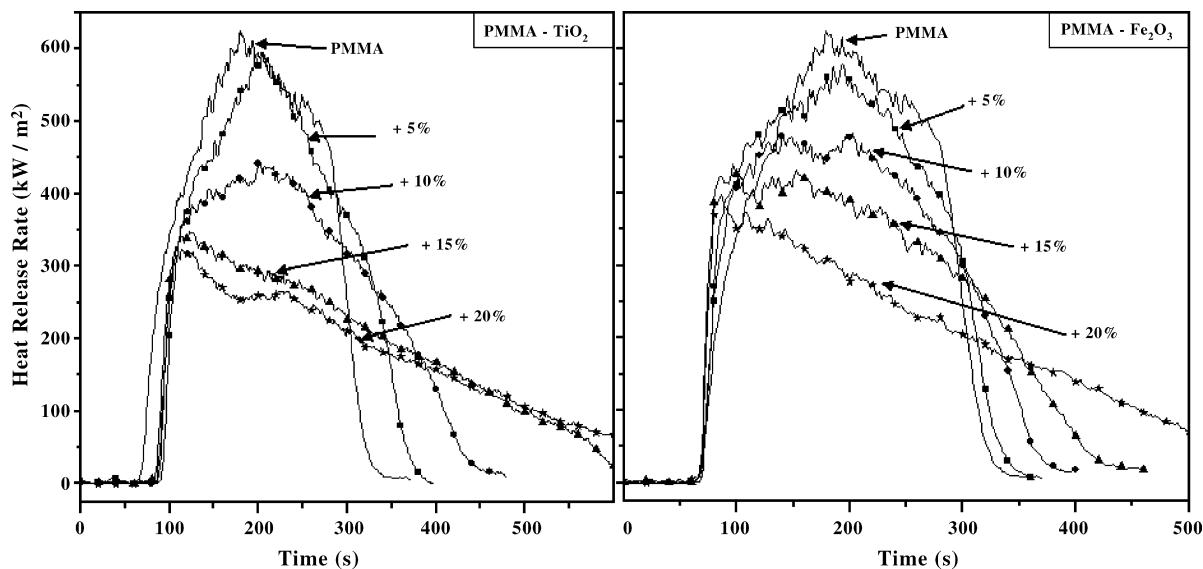


Fig. 34. HRR for PMMA nanocomposites (left, TiO_2 and right, Fe_2O_3) during the cone calorimeter test at 35 kW/m^2 .

to TiO_2 ($1.96 \times 10^{-6} \text{ m}^2/\text{s}$), leading to a more rapid rise in temperature at the surface of the samples filled with iron oxide.

The improved flame retardancy of PMMA- TiO_2 and PMMA- Fe_2O_3 nanocomposites was attributed to a restriction of the mobility of polymer chains resulting from strong interactions between PMMA and the nanoparticle surface. In fact, it was demonstrated that both the glass transition temperature (T_g) and LOI increased with metal oxide content. Furthermore, it was shown that the flame retardant effect of both TiO_2 and Fe_2O_3 depends on their particle size and surface area (Fig. 35). By comparison with virgin PMMA, the pHRR value was reduced by ca. 45% when 15 wt% nanometric TiO_2 was used and only by 39% when the same amount of micrometric TiO_2 was introduced. In both cases the time to ignition increased by about 20 s. With regard to iron oxide-filled PMMA, a 30% reduction in pHRR was recorded in the presence of 15 wt% nanometric Fe_2O_3 . This reduction was limited to 20% with the same quantity of micrometric Fe_2O_3 . The TTI value increased from 69 s for the nanometric filler to 99 s for the micrometric one. The TTI reduction recorded when nanometric fillers are used was

attributed to heat transfer between the metal oxide nanoparticles and the polymer chains, which is enhanced by the increased metal oxide/polymer contact interface at lower particle size. The polymer temperature therefore increases more rapidly, particularly at the surface, decreasing the time to ignition.

The incorporation of nanoparticles such as organoclay, carbon nanotubes or POSS reduces polymer flammability by several mechanisms (limiting fuel transfer to the flame, formation of a protective char layer, etc.) However, these polymer nanocomposites still burn with very little, if any, reduction in total heat release, and time to ignition is generally not improved and can even decrease for some nanocomposites. In other words, nanoparticles have to be used in combination with other flame retardant agents in order to achieve the required fire performance levels.

4. Flame retardant synergy

In general, flame retardant additives are used to limit the risk of fire and its propagation. They are incorporated in the polymer

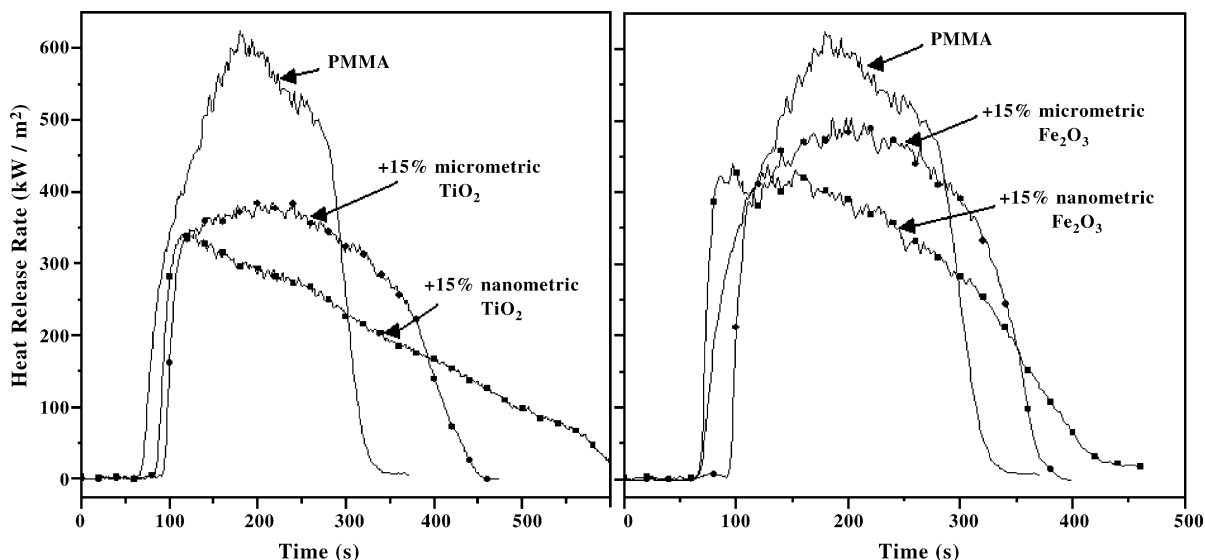
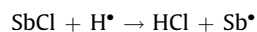
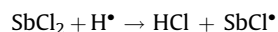
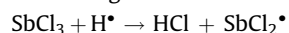


Fig. 35. HRR values for PMMA containing 15 wt% nanometric and micrometric TiO_2 and Fe_2O_3 (35 kW/m^2).

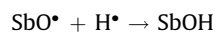
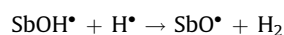
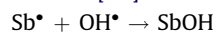
matrix to increase the time to ignition, improve the self-extinguishability of the polymer, decrease the heat release rate during combustion and prevent the formation of flammable drops. In order to achieve high fire performance levels, it is necessary to develop a flame retardant system based on a combination of different flame retardant agents. The concept of synergism is used to optimize flame retardant formulations and enhance the performance of mixtures of two or more additives. Synergism is achieved when the performance level due to a mixture of additives $x\text{A} + y\text{B}$ ($x + y = 1$) for a given property (P) is greater than that predicted for the linear combination ($xP_{\text{A}} + yP_{\text{B}}$) of the single effects of each additive (P_{A} and P_{B}). Conversely, antagonistic effects can be detected.

As discussed above, polymer flame retardancy can be achieved through one or more chemical and/or physical mechanisms taking place in either the gas or the condensed phase. Synergistic phenomena can be obtained either by a combination of flame retardancy mechanisms, such as char formation by a phosphorated flame retardant combined with a gas phase action by a halogenated flame retardant, or by a combination of flame retardant agents reinforcing the same mechanism, e.g. nanoclays and phosphorated flame retardant agents, both acting in the condensed phase.

For example, the gas-phase flame retardant action of halogenated additives can be improved by the incorporation of antimony oxide (Sb_2O_3). Antimony oxide reacts with the hydric acids (HCl or HBr) generated by the halogenated flame retardants to form antimony oxyhalides, which are much heavier than the native hydric acids, thus prolonging their residence time in the flame. All these oxyhalides lead to the formation of SbCl_3 or SbBr_3 , which act as scavengers of “hot” radicals such as H^\bullet :



Moreover, antimony oxide and Sb^\bullet can also react by a parallel oxidation mechanism and participate in the scavenging of “hot” radicals [97]:



Synergistic effects can also be obtained by combining the gas-phase action of halogen species with the condensed-phase action of phosphorus-based compounds. Improved fire performances can thus be achieved by the use of mixtures of halogenated and phosphorated flame retardant compounds, or by incorporation of substances containing both phosphorus and halogen groups in their molecular structure. Indeed, Phosphorus halides or oxyhalides are excellent free-radical scavengers, better than hydrogen halides (HX), and can release more halogen-based radicals due to the P–X bond being weaker than the C–X bond. In addition, the phosphorus contained in phosphorus halides or oxyhalides can also act in the condensed phase to promote the formation of a protective char layer.

However, due to toxicological and environmental concerns, halogen flame retardant additives are currently being phased out and replaced, and the latest research trends mostly focus on the development of new halogen-free flame retardant systems together with combinations of traditional flame retardant additives exhibiting enhanced efficiency when combined together.

For instance, the use of nitrogenated additives combined with phosphorus flame retardants can produce interesting synergistic

effects [98]. The formation of phosphorus–nitrogen intermediates can accelerate the *in situ* production of phosphoric acid and therefore polymer phosphorylation. P–N bonds are more reactive than P–O bonds in the phosphorylation process. They maintain phosphorus in the condensed phase, yielding crosslinked networks that promote more intensive char formation. Phosphorus–nitrogen synergism is not a general phenomenon but depends on the nature of the phosphorus and nitrogen flame retardants, as well as the chemical structure of the polymer.

Other types of synergism can be considered. For example, in order to preserve the flame retardant effect beyond 400 °C and decrease the total filler loading rate, the endothermic effect of metallic hydroxides can be improved by the use of other flame retardant systems. More specifically, metal borates and particularly zinc borates have frequently been used as synergistic agents for metal hydroxides in polyolefin matrices. Partial substitution of 3 wt% of MDH by zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$) in EVA (8 wt% vinyl acetate at a global filler percentage of 40 wt%) [99] increases the LOI value from 38.5 to 43% and decreases the peak HRR recorded by cone calorimetry. In this system, the thermal decomposition of MDH catalyzes the decomposition of zinc borate, generating boron oxide at lower temperature. A vitreous layer is then formed in combination with MgO located at the material surface [100]. Moreover, interestingly, the combination of both fillers triggers a physical effect corresponding to the formation of an expanded vitreous layer more mechanically resistant than the crust formed with magnesium di-hydroxide alone. The physical barrier effect of the protective layer formed can be improved by the addition of lamellar talc particles to magnesium di-hydroxide and zinc borate in ternary systems [101]. The combination of a small fraction of organomodified montmorillonite and talc together with magnesium hydroxide also considerably reduces the pHRR value and generates a cohesive residue [9].

The action in the polymer of nanoparticles alone proves to be insufficient for ensuring adequate fire resistance to meet the required standards. However, their association with other flame retardant systems such as phosphorated compounds could potentially be a very interesting approach. Several recent works have focused on such methods.

For example, Laachachi et al. [96] combined the flame retardant action of nanometric metallic oxides (TiO_2 , Al_2O_3) with the char formation induced by phosphorated flame retardant systems (ammonium polyphosphates and phosphinates) in PMMA. In the case of aluminium phosphinate supplied by Clariant under the trade name Exolit OP930 (hereafter noted phosphinate), cone calorimeter results showed that partial substitution of phosphinate by alumina nanoparticles promoted synergistic effects, with a marked decrease in pHRR (Fig. 36a). However, no significant effect could be achieved with TiO_2 nanoparticles (Fig. 36b).

Although Al_2O_3 and TiO_2 promote positive flame retardant effects in PMMA, their combination with phosphinate does not automatically lead to a synergistic effect. Observation of residues involving alumina nanoparticles essentially shows a continuous solid layer, as typically illustrated by the Al_2O_3 9 wt%–phosphinate 6 wt% sample. However, with TiO_2 –phosphinate combinations, the char residues do not cover the entire sample surface, leading to a poor barrier effect, which explains the limited performances displayed by these compositions. It has been shown that there is no chemical reaction between Al_2O_3 (or TiO_2) and phosphinate but only the formation of a vitreous layer, promoted by the phosphorated compound and reinforced by alumina particles. It appears that, in addition to their role in char reinforcement, alumina particles also have a positive catalytic effect on the formation of the protective layer with phosphinate (not provided by titanium oxide particles).

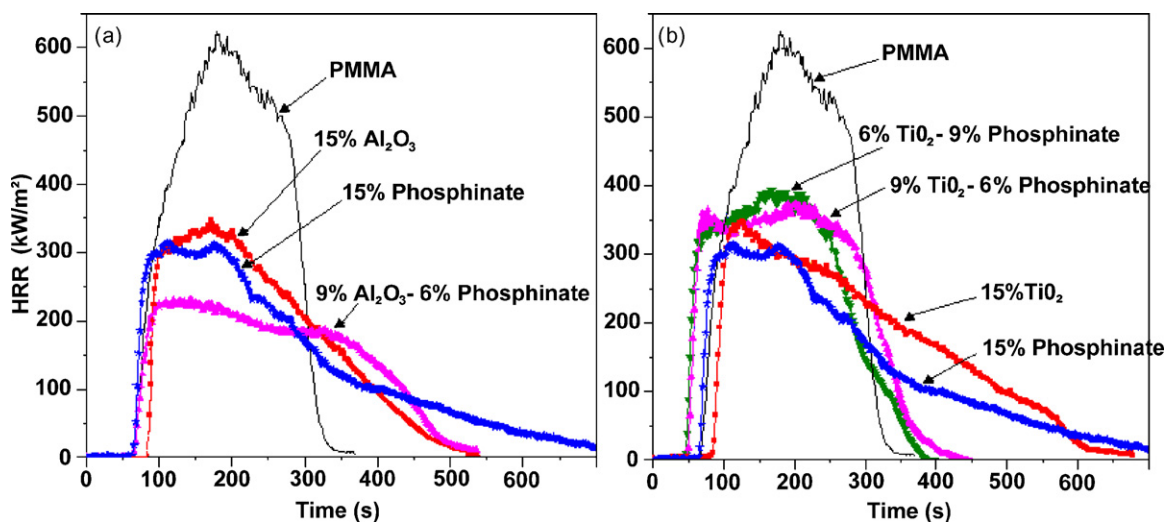


Fig. 36. Cone calorimeter curves for combinations of phosphinate (Exolit OP 930, Clariant) with Al₂O₃ (a) and with TiO₂ (b) in PMMA (35 kW/m²) [95].

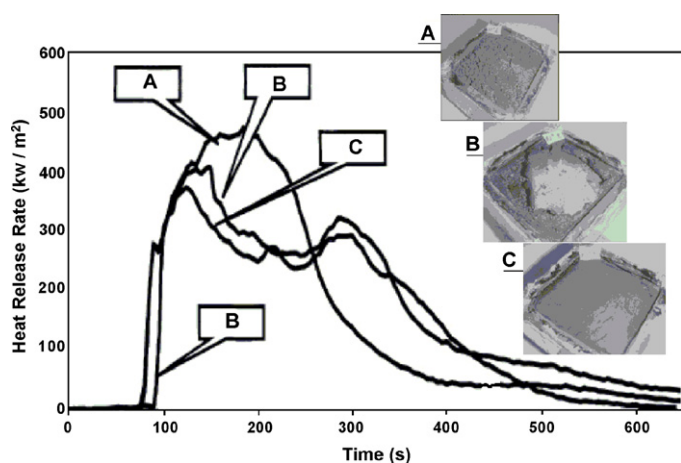


Fig. 37. Evolution of RHR for flame retardant EVA formulations; (A): EVA + 5 phr MMT; (B): EVA + 5 phr MWNT and (C): EVA + 2.5 phr MMT + 2.5 phr MWNT, and corresponding residues formed (35 kW/m²), adapted from [102].

As mentioned above (cf. Section 3.6, nanometric particles), depending on their nature and geometry, nanoparticles can contribute in various ways to improving the flame retardant performances of polymer materials. In this respect, a combination of two different types of nanoparticles can be expected to promote some synergetic flame retardant effects. For instance, Beyer [102] combined organomodified silicates (Nanofil 15) with multi-walled carbon nanotubes (MWNT) in EVA. The evolution of the HRR measured by cone calorimeter tests showed a synergistic effect when 2.5 phr organomodified silicates (MMT) were combined with 2.5 phr MWNT compared to EVA containing either 5 phr MMT or 5 phr MWNT (Fig. 37).

Moreover, the combination of both nanoclay and MWNT has been shown to improve the cohesion of the residues recovered, which are much less cracked than those isolated separately from either organoclay or carbon nanotube-based EVA nanocompositions (Fig. 37).

5. Conclusions

This review has shown that a broad range of flame retardant systems have either already been studied or are currently under

development to ensure greater safety in a world where plastic materials are being increasingly used in transportation and buildings, and where fire prevention remains a major issue. While some systems, such as halogenated compounds, are in the process of being banned due to health and environmental concerns, other systems such as the use of relatively low amounts of nanoparticles or the synergistic effects of flame retardants from various families show very promising results. Among non-halogenated fire retardant additives, phosphorus and nitrogen-based compounds have proved to be very powerful solutions, especially in matrices containing oxygen or nitrogen atoms in their backbone, while silicon-based additives also appear to provide efficient solutions. We have demonstrated that the flammability of plastic materials remains a very complex scientific problem for which no single solution can be found, especially with regard to the extensive diversification of polymer matrices available. However, with the advent of new techniques such as cone calorimetry, TGA-EGA or gasification studies, research into fire retardancy is becoming a less and less empirical science, and a much better understanding of the phenomena related to flammability and how to fight it is arising from the scientific studies carried out, enabling the effective selection of the most appropriate additives for producing fire resistant polymers.

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