A Brief Review on Fire Retardants for Polymeric Foams

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ABSTRACT: Fire retardants are briefly reviewed with reference to commonly available polymeric foams. Both physical and chemical aspects of intumescent fire retardants are summarized. New products based on nanocomposites are introduced as well. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 366–376, 2005

Key words: flame retardance; foam extrusion; intumescence; nanocomposites; plastics

INTRODUCTION

Foams are commonly used in sandwich panels as commercial products. There, two coatings or skins, made of reinforced resin or sometimes metal, are solidly glued onto a core of foam. The sandwich composites are used in general-purpose and high-tech applications such as aeronautics, sports and leisure (ski, bicycle, hockey), railway and road transport, body elements for isothermal or cooled vehicles, nautical structural components, blades of wind turbines, and thermal and acoustic insulation in construction. These lightweight composites have a superior stiffness/mass ratio with excellent thermal and acoustic insulating properties.

The foams can be flexible or rigid, with open or closed cells, reinforced or not reinforced. Their properties depend on the polymer; the manufacturing process; the density; and the cell morphology, such as whether the cells are open or closed, diameter of cells, and wall thickness. Polymers commonly used as the core of sandwich composites are poly(vinyl chloride) (PVC) and polyurethane.

Polyurethane foam (PUF) is the one of the most widely used foam materials. Application is split between flexible and rigid foams. In contrast to polyether and polyester foams, PUF has the following properties:

- Better mechanical resistance
- Better behavior with hydrocarbons

- Greater sensitivity to water and hydrolysis
- Better capacity of soundproofing and damping
- More limited resistance to ageing

Examples of applications include the following:

- Sandwich panels for containers or bodies of isothermal trucks (rigid foams), panels for frigorific rooms
- Polyester boats, sailboards
- Walls of prefabricated dwellings
- Self-supporting panels
- Seats in sandwich composite with foamed core and thermoplastic skins
- Soundproofing screens with foamed core and thermoplastic skins
- Insulated doors or double doors for buildings, dwellings, or offices

For special applications, polyolefins, polystyrene, and others are preferred. A summary of other foams is shown in the Appendix.

FIRE RETARDANTS

As shown in some of the data from TownsendTarnell Inc., in Tables I and II on the consumption of plastics additives in 1998, there are tendencies to limit the field to the so-called performance additives. These include plasticizers, lubricants, stabilizers, flame retardants (FRs), and antistatic agents, conferring a specific property or protection on the compounds.

End products involved are housings for consumers and office electronics equipment, wire and cable sheathing, and (as a result of recent tragedies) electrical equipment and rolling stock used for railways.

TABLE I
Consumption of Plastic Additives by Type—1998

Additive	Percentage of total use (%)
Plasticizer	32
Fire retardants	14
Heat stabilizers	12
Impact modifiers/processing aids	10
Antioxidants	9
Others	8
Organic peroxides	6
Lubricants/mold-release agents	6
Liquid stabilizers	3
	Total 100%

Reflecting the importance of fire safety is the largest family of plastic additives, fire retardants, which are usually divided into five major subfamilies, as shown in Table II, that is, Br (39%), Cl (10%), P-based (23%), inorganics (22%), and melamine (6%). Halogen-containing fire-retardant compounds account for 49% of the total (by value, major families of fire retardants, percentage of dollar value—1997).[1]

Recent development of flame retardants has been profoundly influenced by the need to produce systems that not only prevent or retard burning, but also have zero or very low emission of smoke and fumes when exposed to the heat of combustion. There is a general move to nonhalogenated/zero-smoke types (especially among European legislators)[2] to limit or prevent the use of flame retardants based on brominated systems, on grounds of alleged difficulty in recycling.

FIRE RETARDANT FOAMS

Polyurethane foams

Low-cost additive fire retardants used to be incorporated in PUF. The cheaper, improved methods of manufacturing foams have resulted in the increasing use of reactive fire retardants, particularly for rigid foams. In contrast, it is difficult to impart fire retardance to flexible foams because several factors such as open-cell structure, low degree of crosslinking, and chemical structure impair the fire retardance.

Brominated FR compounds for rigid foams are primarily of the reactive type. The change to CFC-free foams has resulted in difficulties in reaching certain FR specifications, which has led to an increase in the use of bromine-based compounds. These include mixed tetrabromophthalate ester of diethylene and propylene glycol (only in the United States), polyether polyol made from brominated diol and epichlorohydrin (in Europe), and dibromoneopentyl glycol and tribromoneopentyl alcohol, all of which are reactive with the isocyanate group and thus are incorporated into the polymer chain.[1,3]

Foams with reduced flammability can also be obtained by modification with aromatic (highly aromatic polyol) or crosslinking agents, such as isocyanurates or carbodiimide, leading to a strong tendency to char.

Additive fire retardants can be more easily incorporated in PUF than *reactive* fire retardants. A major disadvantage is that they frequently cause shrinkage, in particular, in flexible foams. Phosphorus-containing fire retardants are used in the form of phosphates, phosphonates, phosphines, and phosphinic oxides. Compounds with high molecular weight are preferred.

Halogen-containing and phosphorus-containing compounds are fire retardants for ready use because of the synergy between both elements.[4,5]

Styrenic homopolymer and copolymer foams

Polystyrene foam (EPS and XPS)

Only *additive* fire retardants are used commercially to make fire-retardant polystyrene homopolymer foams [expandable polystyrene (XPS) and extrusion polystyrene (EPS)]. Bromine compounds are increasingly replacing chlorine compounds. Phosphorus and halogen–phosphorus compounds are used only for special applications because of their cost and low effectiveness.

Hexabromocyclododecane (HBCD), tribromophenyl allyl ester (TBP–AE), and bisallylether of tetrabromobisphenol A (TBBA–AE) are all in use for polystyrene foams. Among them, HBCD at a typical loading between 0.8 and 4.0% is the most commonly used halogen-containing fire retardant. Antimony trioxide is not used as a synergist in fire-retardant polystyrene foam. Higher loadings are necessary to satisfy certain stringent FR standards in Europe to counteract the replacement of low-flammability chlorofluorocarbon (CFC) foaming agent with the much more flammable cyclopentane.

Styrenic copolymers

High-impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene (ABS) are two representatives among

TABLE II
Flame Retardants Used by Value (%)

Flame retardant	Percentage of cost (%)
Brominated FRs	39
Phosphorus-based	23
Inorganics	22
Chlorinated	10
Melamines	6
	Total 100%

the important styrenic copolymers used in the electronics industry (television sets, computers, and office equipment). The traditional halogen fire retardants used in styrenic copolymers are decabromodiphenyl oxide (DECA) and octabromodiphenyl oxide (OCTA), tetrabromobisphenol A (TBBA), bis(tribromophenoxy) ethane, ethylene bis-tetrabromophthalimide, and chlorinated paraffins. Fire retardants are added to these polymers with antimony trioxide as a synergist.[6]

Polyolefins

Polypropylene

The high melt strength PP (HMSPP), the so-called foamable PP polymer is widely used for energy absorber (e.g., automobile damping cores of the car bumpers). FR poly(propylene)s are not so commonly used as styrenics and engineering plastics because there are difficulties in satisfying the fire-retardance requirement in the electronics industry. For example, for complying with UL 94 V-0 rating, 30–40% fire retardant is normally required in formulation; however, only 10–20% FR additives are required for styrenics and engineering plastics. The need for such high levels of fire retardant in poly(propylene) is attributed to its high crystallinity and the flammability of PP. More than 75% of FR polypropylene systems are classified UL 94 V-2 (dripping allowed), rather than V-0.

Most FR additives for PP are often based on aliphatic bromine compounds, which match well with the ignition temperature of PP. Bis(2,3-dibromopropyl ether) of TBBA is the most popular FR additive. However, surface migration of the FR additive has been observed.

Polyethylene

This material has a naturally low fire resistance that can be improved by an adequate formulation. DECA can be used at a level of 20–24% (by weight). Applications in buildings typically contain halogen content in the final products between 4 and 6% (by weight).

INTUMESCENT FIRE RETARDANTS (I)—CHEMICAL IFR

One of the halogen-free fire-retardant approaches is the well-known chemical intumescent fire retardant (IFR). Note that organic compounds would be decomposed to volatile combustible products upon exposure to heat. With respect to the reduction of flammability, polyurethane foam and styrenic polymeric foams can often be exemplified as representative models of great importance. Studies on cone calorimetric analysis of modified PUFs with fire-retardant additives were re-

cently given by Najafi-Mohajeri et al.[7] Besides halogen-free additives, halogen-containing and halogen–phosphorus additives were also tested for comparison. Some conclusions can be drawn as follows:

- Fire retardants had a much greater impact on the reduction of peak heat release rate (p-HRR) of elastomer materials compared to foams. On average, the former had a threefold greater impact than the latter.
- Zinc stearate in 10% by weight loading showed interesting fire performance by prolonging the time to ignition (TTI) by almost 24-fold. Thus, it had the lowest emission value at the possible longest time.
- As expected, the presence of halogen and phosphorus compounds causes a significant increase in smoke and CO production.

The main flame-retardant systems for polymers currently in use are based on bromine, phosphorus, nitrogen, and inorganic compounds. Although the brominated flame retardants represent the most efficient solution for the protection of polymers against fire, there are special concerns on their potential damaging effects to the environment. In the case of traditional nonhalogen alternatives, for example, the inorganic hydroxides [$Al(OH)_3$, $Mg(OH)_2$], silicates, zinc borates, and others are usually used at a loading higher than 50% by weight. This would give problems such as deterioration of polymer properties, difficulty in processing, corrosion, and handling.

Nowadays, applying the "sustainable development" concept to this field implies that fire retardants should give low impact on health and environment during the entire life cycle including recycling and disposal. The flammability and poor visibility, corrosiveness, and toxicity of smoke produced in fires are of most concern.

Among the alternatives, the "intumescent" systems come from the original intumescent coating technique as reported by Vandersall in 1971.[8] They undergo charring and foaming upon thermal degradation, yielding an expanded protective cellular char, and have been considered a particularly promising environmentally friendly approach. The regular use of additives to induce the intumescent behavior in polymer materials is more recent. Mechanistic studies on the fire-retardant intumescence process appeared about 30 years ago. Since then, numerous publications have appeared in the literature. The book written by Le Bras et al.[9] is one of the most comprehensive collections.

In spite of the considerable number of intumescent systems developed in the last 15 years, they all seem to be based on the application of three basic ingredients: a "catalyst," a charring agent, and a blowing agent.

Normally, three components are involved in IFR formulation design:

1. The acid source (or catalyst)

The acid source, "catalyst," is usually a phosphorus derivative. Ammonium polyphosphate (APP) is used in most cases, but sulfur derivatives are also used. The function of the APP is to catalyze the dehydration. That means it is not supposed to be a main actual reactant in the system, but to catalyze reactions of other ingredients at specific temperatures. The relatively large amounts (in the range of 10–20% of the weight of the composition) of APP applied are not consistent with the definition of a catalyst. It is therefore possible that the APP has an additional role in the system, serving as an ingredient in the char structure.

Examples are as follows:

- Inorganic acid (e.g., H_3PO_4, H_2SO_4, H_3BO_3)
- Ammonium salts yielding acid at temperature above 100–250°C, such as ammonium polyphosphate (APP), ammonium sulfate, ammonium chloride
- Amine/amide phosphates

2. Char former/self-catalyzing additives [or carbon source (carbonific)]

The polyhydric compound (e.g., pentaerythritol) plays the role of a carbon source, or "carbonific" function. It is possible to design the "carbonific" function and the catalytic function into a single molecule. Pentaerythritol phosphates, which are char-forming, self-catalyzing, and intumescent, were introduced to commercial development in practice.

Examples are as follows:

- Polyhydric materials, such as starch, dextrin, sorbital, pentaerythritol (PER), polyvinyl alcohol, and so forth
- Melamine–formaldehyde, ethylene–urea–formaldehyde, polyurethanes, and so forth.

3. The blowing agents [or gas source (spumific)]

It is assumed that the dehydrating action of the acid and the blowing function arise from the evolution of volatile products formed by thermal treatment of the amines, like melamine. A blowing effect may also arise from products evolved in the charring step. Intumescence occurs only if the chemical reactions and physical processes take place in the appropriate sequence as the temperature increases. The blowing gases must evolve at a correct stage of the gelation process.

Examples are melamine, amine/amides, urea, melamine, dicyandiamide, and their derivatives.

Fire-retarding polymers by intumescence constitute essentially a special case of a condensed-phase mechanism. In intumescence, the amount of fuel produced is also greatly diminished and char rather than combustible gases is formed. The intumescent char, however, has a special active role in the process. It constitutes a barrier, both for hindering the passage of the combustible gases and molten polymer to the flame as well as shielding the polymer from the heat of the flame. More than one of the above three ingredients is required for intumescent behavior. For uncharrable polymers as polyolefins, a charring agent must be present (for example, a charring agent is coated on ammonium polyphosphate as AP750 from Hoechst). Therefore, it is well understood that an intumescent "additive" for polyamide will not be intumescent for polyolefins. Therefore, these tools are more than sufficient to create intumescent formulations for definite applications.

Because intumescence is often created using phosphorus-based compounds, the use of such compounds always leads to intumescence. To create intumescence for a number of possible applications, diverse synergistic systems commercially available for halogen-free systems should be invoked.[1,10–12]

Nitrogen–phosphorus synergism

The P–N synergism in the phosphorylation of cellulose is manifested by an increased rate of phosphorylation and yield of P, by an increased FR effect and improved physical properties. The magnitude of the effect varies from one N compound to another. Usually, amine and amide derivatives are effective, whereas nitriles are antagonistic, allegedly because of their volatility. The synergism in the case of cellulose is ascribed to a swelling effect on the polymer by the N derivatives. P–N bonds are known to be more reactive in phosphorylation than P–O bonds. This consideration would also apply to the case of intumescence in PP during pyrolysis and combustion.

The P–N bonds can also participate in the formation of the crosslinked networks, in which the P will be fixed and its volatilization hindered. Some confirmed the existence of P–N species along with phosphoric or polyphosphoric acids on the surface of char.

Phosphorus–phosphorus synergism

The first examples were with combinations of cyanoethylphosphine derivatives with ammonium polyphosphate on PP and HIPS. A clear synergism between melamine salt of pentaerythritol acid phosphate and ammonium polyphosphate on polyurethane elastomers led to a high thermal stability of the char. A

TABLE III
Examples of Layered Compounds Intercalated by a Polymer

Chemical nature	Examples
Element	Graphite
Metal chalcogenides	$(PbS)_{1.18}(TiS_2)_2$, MoS_2, SiO_2
Carbon oxides	Graphite oxide
Metal phosphates	$Zn(HPO_4)$
Clays and layered silicates	Montmorillonite, hectorite, saponite, fluoromica, fluorohectorite, vermiculite, kaolinite
Layered double hydroxides	$M_6Al_2(OH)_{16}CO_3 \cdot nH_2O$; M = Mg, Zn

strong synergism between red phosphorus and ethyl-enediamine phosphate salt was demonstrated in PP by limiting oxygen index (LOI) and UL 94 tests. A synergism was found between a cyclic neopentyl phophonate and a melamine phosphate in an EVA copolymer.

Metal–phosphorus synergism

Divalent or polyvalent metal cations may crosslink polyphosphate chains, in a manner analogous to the crosslinked thermoplastics known as polyionomers. The effective metal compounds also appear to cause a char to be more compact and less penetrable. In the case of MnO_2, the char yield is enhanced, and manganous phosphates appear to be formed. These various hypotheses need further investigation.

The knowledge of the overall reaction scheme is a powerful basis to develop new intumescent additives and/or new intumescent formulations based on commercial additives. It also helps to facilitate performance of the existing intumescent formulations.

NANOCOMPOSITES

Nanocomposite technology originated in the 1980s in Japan. Nylon composites were the focus of increased development, with many patents on related products.

Updated development work suggests that nanocomposites are a unique class of materials having significant improvements in important properties such as modulus, flexural strength, and heat distortion temperature.

The main types of polymer-based materials commonly used in nanotechnology are composites consisting of at least two different substances. At least one of them is a polymer. If one phase in such a composite having forms characterized on the nanometer scale of dimensions, that composite is called a nanocomposite. A host polymer and its partner (filler) would constitute a nanocomposite. A nonexhaustive list of possible layered compounds is given in Table III.

There are several types of such polymeric nanocomposites and a few examples of these materials, subjected to X-ray diffraction measurements, are shown briefly in Table IV.

As reported by the Building and Fire Research Laboratory (BFRL), NIST, semiconductor nanoparticles, such as TiO_2 and ZnO, can be used to optimize the durability of polymeric building materials and provide potential environmental benefits without affecting the appearance of a product. There are other potential benefits of these pigments, such as those related to their quantum mechanical properties, for example, optimal UV absorption.

Polymer-layered silicates (PLS) were first reported in the literature as early as in 1961.[13] A recent review on PLS nanocomposites and fire retatardance was reported by Alexandre et al.[14]

Flammability and thermal stability of PLS (clay) nanocomposites

Two terms, intercalated and delaminated (or exfoliated), are used to describe the two general classes of nanomorphology that can be prepared:

- *Intercalated* structures are well-ordered multilayered structures, in which the extended polymer chains are inserted into the gallery space between the individual silicate layers.

TABLE IV
Several Types of Polymeric Nanocomposites

Type	Example	Comment
Inorganic oxide + conducting polymer (colloidal dispersion)	Δ Polyaniline–silica Δ Polypyrrole–silica Δ Polypyrrole–tin(IV) oxide	Conducting materials
Ultrafine clay + polymer (polymer layered silicates)	Δ Poly(methyl methacrylate)–montmorillonite	Most popular for polymeric systems
Semiconducting nanocrystal + insulating polymer	Δ Perfluorinated ionomer-CdS nanocrystals Δ Poly(methyl methacrylate)–semiconducting TiO_2 and ZnO	Highest scientific interest that may exhibit quantum size effects
Metal particles + polymers	Δ Small gold particles–polymer Δ Nickel nanowires–polyaniline	Usually prepared as emulsions or microemulsions

TABLE V
Relative Comparison Between PLS Nano-blend (5% Clay) and Conventional Blend for Nylon-6

Parameter	PLS nano-Nylon-6	Conventional filled Nylon-6	Comment
Tensile strength	1.4	1.0	↑ ↑
Tensile modulus	1.68	1.0	↑ ↑
Flexural strength	1.6	1.0	↑ ↑
Flexural modulus	2.26	1.0	↑ ↑ ↑
Heat distortion temperature (HDT)	1.26	1.0	↑ ↑ (from 338 to 425 K)
Impact strength	0.9	1.0	↓ (slightly)
Gas permeability	—	—	Improved
Solvent resistance	—	—	Improved

- *Delaminated* (or *exfoliated*) structures result when the individual silicate layers are no longer close enough to interact with the gallery cations of the adjacent layers.

Advantages of the unique properties of PLS over the conventional filled polymer are shown in Table V.

Thermal stability of nanocomposites

One example is given here. TGA data, for example, for a polydimethylsiloxane (PDMS, mass fraction 90%)–clay (mass fraction 10%) nanocomposite shows an improvement in thermal stability. In this case, the nanostructure shows a decomposition temperature more than 140°C higher than that of the virgin PDMS elastomer (as measured at the point of 50% mass loss).[15] Burnside attributed the increased thermal stability to hindered diffusion of volatile decomposition products from the nanocomposite because of the improved barrier properties observed for other polymer nanocomposites.

Another example that can also be exemplified is the TGA data for comparing aliphatic polyimide (PEI), with PEI–clay mixture, intercalated PEI–clay nanocomposite, and delaminated PEI–clay nanocomposite (mass fraction ≈ 10% for all three samples).[16] It can be concluded that:

- The nanostructure is critical to improve thermal stability
- The intercalated PEI nanocomposite is more stable than the delaminated nanocomposite
- For nanocomposites, they were described as self-extinguishing flammability behavior

Flammability properties of nanocomposites

The cone calorimeter is one of the best bench-scale equipments for studying the flammability properties of materials. Data for testing some nanocomposites[17] are shown in Table VI.

The following can be observed from Table VI:

TABLE VI
Flammability Properties (Cone Calorimeter Data)[a]

Sample	Residual yield (%)	p-HRR (Δ%)	av-HRR (Δ%)	Av-H_c	Av-SEA	Av-CO yield
		Nylon-6				
PA-6	1	1010	603	27	197	0.01
PA-6 (PLS) 2% (*exfoliated*)	3	686 (32%)	390 (35%)	27	271	0.01
PA-6 (PLS) 5% (*exfoliated*)	6	378 (63%)	304 (50%)	27	296	0.02
		Nylon-12				
PA-12	0	1710	846	40	387	0.02
PA-12 (PLS) 2% (*exfoliated*)	2	1060 (38%)	719 (15%)	40	435	0.02
		Polystyrene				
PS	0	1120	703	29	1460	0.09
PS silicate-mix 3% (*immiscible*)	3	1080	715	29	1840	0.09
PS (PLS) 3% (*intercalated*)	4	567 (48%)	444 (38%)	27	1730	0.08
PS/DECA/Sb$_2$O$_3$ 30% by weight	3	491 (56%)	318 (54%)	11	2580	0.14
		Poly(propylene)				
PP	0	1525	536	39	704	0.02
PP (PLS) 2% (*intercalated*)	5	450 (70%)	322 (40%)	44	1028	0.02

[a] Data from Gilman et al.[17] Heat flux: 35 kW/m²; H_c (MJ/kg), effective heat of combustion; p-HRR (kW/m²), peak heat release rate; SEA (m²/kg), specific extinction area; CO yield (kg/kg); av-HRR (kW/m²), average HRR.

- Cone data for a variety of polymer–clay nano-composites show that both the peak and average HRR were reduced significantly for *intercalated* and *exfoliated* nanocomposites with low silicate mass fraction (2 to 5%). The nylon-6 nanocomposite has a 63% lower p-HRR than the virgin nylon-6 at 2% mass fraction.
- About the space available for fire-retardant mechanism, a comparison of cone data for nylon-6, nylon-12, PS, and PP nanocomposites reveals that H_c (the effective heat of combustion), SEA (specific extinction area, a measure of smoke yield), and CO yield (toxic gas) are unchanged; this suggests that the source of the improved flammability properties of these materials is a result of the differences in decomposition in the condensed phase rather than in the gas phase.
- For comparison, data for PS fire retarded with decabromodiphenyl oxide (DECA) and Sb_2O_3 show the predominantly gas effect of bromine (i.e., the fire retardant role played in the gas phase). The resulting incomplete combustion is reflected in a lower effective heat of combustion (H_c) and higher CO yield.
- The primary parameter responsible for the lower HRR of nanocomposites is the mass loss rate (MLR, not shown in the table) during combustion. The MLR of the nanocomposite is significantly reduced from those values observed for the virgin polymers. Both sets of data in MLR essentially mirror the HRR data. This is actually an evidence confirming the importance of the condensed phase.

Attempts to use nylon-6 nanocomposite hybrid as a char-forming agent in intumescent formulations were made by Bourbigot et al.[18] The benefits of using PA-6 clay hybrid as a charring polymer in an intumescent EVA formulations were well demonstrated. PA-6 nano allows improvement of both mechanical and fire properties of FR EVA-based materials. It is proposed that the nanodispersed clay allows the thermal stabilization of a phosphorocarbonaceous structure in the intumescent char, which increases the efficiency of the shield and forms a "ceramic" coating acting as a protective barrier to prevent the underlying polymer from heat.

In summary, the nanocomposite approach is a novel direction to improve both fire retardancy and mechanical performances of the final formulated products at low level, say 5% by weight. Recently, it is reported that nanoeffect exerts obvious influences on both LOI values and HRR maintaining good mechanical performance.[19] It may be accomplished either as a single fire-retardant additive or more likely in combination with other fire-retardant additives. In other words, the potential synergy between traditional fire retardants

and nanocomposites could further extend the use of nanocomposites as fire retardants or nanofiller. The work ongoing toward the direction is approaching to prove the latter as highly promising.[20,21]

INTUMESCENT FIRE RETARDANTS (II)—PHYSICAL IFR

Chemical intumescent systems have been used as fire retardants for over 50 years. Their performance depends on the heat-induced decomposition of the organic components, and the creation of a char layer that insulates the underlying polymeric substrate from the heat source. To meet more severe and diverse applications, the new approaches of intumescents with improved performance over conventional IFR systems are required.

Intumescent additives are playing a larger role, often providing improved performance when used in combination with other FRs. An example is using expandable graphite gray-black with a metallic gloss. The system has been used in many applications such as giving special effect of pigment.

Nord-Min from Nordmann, Rassmann, Hamburg was developed from flame-retarding plastics in China. It is a halogen-free fire barrier additive, based on natural graphite flakes with intercalcated acids. Depending on the raw material and acid treatment, the expansion rate is up to 250 times the original volume. Grades treated with sulfuric acid begin to expand at around 200°C; with nitric or acetic acid treatment expansion starts at about 150°C. This is too low for many technical thermoplastics and a key development target is to raise the expansion point to, say, 300°C.

It can be used alone as a smoke suppressant with a heat insulation effect as well. For some applications, however, the expanded carbon layers are not too stable. Other flame retardants, such as zinc borate, ammonium polyphosphate, or ethylene diamine phosphate, are used as stabilizers to give a good span of properties and applications.

A new intumescent product that just appeared in the market is Noflan (a classified product). It is an additive developed from space technology in Russia and distributed by Isle of Man–based CFB. The material is being tested by many companies in Europe. However, details have not been revealed because of confidentiality agreements. No substantial details have been released, except it is a fine white crystalline powder, initially soluble in water but microencapsulated and water repellant for normal use. It acts by forming a carbonized top layer on the polymer, reducing the building up of heat and retaining the decomposition products. It can be used with a variety of polymers, including polyolefins, polyamides, and acrylics, and also with thermosets such as polyesters and epoxies, and with elastomers such as butadiene

styrene (SBS) and isoprene. Loadings are in the range 14–20%, with 30% recommended for polyamide. The limiting oxygen index is 26 to 30%, rising to 35% for epoxies. CFB claims that it does not release toxic substances when exposed to external fire and can even reduce smoke and fumes. It has a melting temperature of 200°C and is thermally stable up to 250°C. Treated polymer waste is easier to dispose because thermoplastic polymers can be recycled.

Expandable graphite (EG) has been used in a substantial number of applications in polymeric composites that deal with a number of resins, such as polyolefins (PP, PS, HIPS, PP, EVA, EPDM, etc.), phenolic resins, epoxy resins, melamine–formaldehyde resins, polyesters, and engineering plastics (PBT).

In construction applications, expandable graphite distributed in the outer layers of *oriented strandboard* has been shown to reduce the flame spread. Most intumescent putties, caulks, and firestop systems now rely on expandable graphite to provide the expansive force necessary to close off gaps and holes during the course of a fire. The performance of the resin systems with and without expandable graphite is reported by Penczek et al.[22] Based on the cone calorimeter results for each resin system, the addition of expandable graphite improved the performance by increasing the amount of char developed. Formulations using expandable graphite were found to increase the time to ignition, reduce the heat release rate and mass loss rate, and reduce smoke and flame spread.

When added into many materials, the expansive force of chemical intumescents is often insufficient to generate an effective char layer. For example, rigidized thermoset phenolic or unsaturated polyester resins cannot be protected by the incorporation of chemical intumescents. However, the expandable graphite flake could decrease the flammability of the crosslinked polyester resin when added at a level of 10 phr. Expandable graphite was particularly effective when used in conjunction with red phosphorus and ammonium polyphosphate as a synergist.

Sometimes, as revealed in a recent patent (e.g., USP 6,410,122), the resin composition has sufficient flame resistance, from the perspective of oxygen index, but, when molded into a sheet and used as a wall backing in construction, for instance, it failed to meet the flame retardancy or fire protection test requirement when the face side is heated to 1000°C. The temperature of the reverse side should not rise over 260°C without dropping off. To satisfy the demand, it is imperative that synergistic fire-retardant additives, such as red phosphorus and/or a phosphorus compound, be incorporated together into formulations accompanied with thermally expandable graphite. The combined effect of GRAFGUARD® and APP on the fire behavior of unsaturated polyester (UPR) is shown in Table VII as an example.

TABLE VII
Combined Effect of GRAFGUARD® and Ammonium Polyphosphate (APP) on Fire Behavior of UPR

Fire retardant (phr)		Self-extinguishing	Afterglow time (s)	Nonburnt length (mm)
GRAFGUARD®	APP			
5	0		365	0
5	5	No	13	73
5	10	No	10	75
5	15	Yes	0	80
10	0	Yes	0	80
10	5	Yes	0	80
10	10	Yes	0	80
10	15	Yes	0	80
0	15	Yes	40	55

As seen in Table VII, phosphorus in the form of ammonium polyphosphate (APP) exhibited the best self-extinguishing properties when combined with expandable graphite in UPR. Whereas APP by itself at 15 phr was not self-extinguishing and had an afterflame time of 40 s, the addition of 5 phr GRAFGUARD® gave immediate self-extinguishing. No sparks were observed at this concentration of additives. In addition, at a loading level of 10 phr GRAFGUARD® + 15 phr APP, the amount of smoke produced was reduced significantly. Thus, the combination of GRAFGUARD® and APP is distinctly synergistic in this unsaturated polyester resin system.

It is considered that cellular materials manufactured from flammable polymers are more flammable than the solid materials because the insulating effect of their cellular nature allows a rapid buildup of heat at the heating surface with a consequence of high rate of pyrolysis. Polyurethane foams (flexible and rigid) have the highest value of R, implying the lowest thermal conductivity than the other foams.

The use of EG incorporated in flexible PU foams was first patented by Dunlop Limited, a British Company (GB) in 1987 (U.S. Pat. 4,698,369). Since then, there had been rapid development in the technology with many patents and publications. Reasons for the rapid development are as follows:

- They are very effective in fire retardancy, better than the traditional chemically intumescent flame retardant (IFR) in many aspects.
- They are very effective in smoke suppression.
- No toxic and corrosive gases are emitted while burning.
- There are no dripping and migrating problems.

In the European industry, the alternative blowing agents most extensively used for PU foaming are *n*-pentane and cyclo-pentane.[23] Those are characterized by zero ozone depletion potential (ODP), as required

by the Montreal Protocol and the following revisions. The use of pentanes as blowing agents makes the flammability of the foams significantly worse. The recent more strict requirements for materials fire safety have led to an extensive use of flame-retarded polyurethane (PUR) or polyisocyanurate–polyurethane (PIR–PUR) foams.

Flame-retarded polyisocyanurate–polyurethane (FR PIR–PUR) foams have been synthesized by the use of a new flame retardant, expandable graphite (EG foams), never used on an industrial scale in polyurethane rigid foams, and a mixture of expandable graphite and triethylphosphate (EG–TEP foams). The effect of triethylphosphate in EG–TEP foams and PIR–PUR foams was investigated by Modesti et al.[24]

Their study indicated that increasing the amount of triethylphosphate would not influence the thermal conductivity, but an increase in the quantity of expandable graphite would affect the insulating properties, probably because of the bigger dimensions of the foam cells. The oxygen index (LOI) increases in a linear way and the highest LOI values are obtained for EG–TEP foams. The results from the cone calorimeter are in agreement with those of LOI. EG and EG–TEP-filled foams show a considerable decrease in the rate of heat release (RHR) with respect to unfilled foams. The only hazard observed is an increase of CO/CO_2 weight ratio in the presence of very high content (25%) of expandable graphite; this effect is not shown when increasing the TEP amount.

The effect of red phosphorus on the system of EG–TEP was also studied by Modesti et al.[25] The fire behavior characterization has demonstrated that the introduction of such flame retardants as fillers leads to substantial improvement, particularly for foams filled with expandable graphite and triethylphosphate. Also, significant improvement has been observed in thermal stability because of the presence of flame retardants.

The effect of melamine cyanurate (MC) on the above-mentioned systems was also studied by the same group.[26] It has been observed that the best results, that is, the lowest rate of heat release and the highest oxygen index, are achieved with expandable graphite. In contrast, ammonium polyphosphate promotes a slight improvement in fire behavior, whereas the effect of melamine cyanurate is negligible.

It was announced that Chemtron fire retardant for foam uses EG as the key ingredient, which is a halogen-free retardant that complies with environmental protection requirements and could be applied on such materials as PU, EVA, LDPE, EPDM, SBR, phenol, and so forth. The product is pH neutral and delivered in powder (light gray) form. The product series could meet fire resistance standards such as UL-94 HBF.[27]

Because intumescence is a halogen-free technique, it could be a good way to replace halogenated compounds or to decrease their amount for some applications to satisfy some environmental considerations.

CONCLUSIONS

The future of fire-retardant polymers and composites is to produce at reasonable cost fire-retardant materials mainly from polymers of commodity with the preservation and/or the improvement of their mechanical properties.

The "nanocomposite approach" is worth exploring as a novel direction to improve both fire retardancy and mechanical performances. The intumescent concept using charring polymers as additives through blending leads to acceptable materials, which can pass tests in different industrial sectors. New materials with the properties of interest can be designed at the nanoscale with the aid of chemical and physical intumescence and synergistic effect.

Further improvement of metal hydroxides–based formulations, which have been widely used in practice, can maintain fire-retardant performances at lower loading with the same cost. Better use of novel ideas and potential technologies with considerations on design criteria and safety concerns should be the promising route to attain good products.

APPENDIX: SUMMARY OF FOAMS

Polyethylene

Generally, the properties of polyethylene foams used as cores are the following:

- Densities from 25 to 330 kg/m^3
- Semirigid to flexible
- Closed cells
- Crosslinked or linear. Often, the crosslinking improves the mechanical properties and chemical resistance.

Polyethylene foams have

- Insulating and damping properties
- Correct mechanical characteristics
- A low absorption and permeability to water or moisture and an excellent hydrolysis behavior
- A naturally low fire resistance that can be improved by an adequate formulation

Examples of applications

- Panels and sandwich structures for protection of wellhead of oil.
- Multilayer composites for damping, sometimes in combination with poly(propylene) (PP) foam. Some helmets, for example, are made of thermoplastic skins and a core of one layer of PE foam with, eventually, a second layer of PP foam.

Poly(propylene)

Generally, the properties of the polypropylene foams used as cores are as follows:

- Densities from 23 to 70 kg/m^3
- Lightweight
- Closed cells
- Crosslinked or linear. Often, the crosslinking improves the mechanical properties and chemical resistance.

Polypropylene foams have

- Insulating and damping properties
- A good resistance to multicycle impacts
- Correct mechanical characteristics
- A low absorption and permeability to water or moisture and excellent hydrolysis behavior
- The major application is in the damping cores of car bumpers.

Polystyrene

Examples of applications

- Insulated panels for refrigerated warehouses and other cold storages
- Structural insulated panels
- Sea sailboards or surfboards with laminate skins UP/FV or EP/FV
- External panels of house or building with laminate skins UP/FV
- Decorating beams for the interior house with laminate skins UP/FV

Generally, the properties of the polystyrene foams used as cores are as follows:

- Low densities, usually from 10 to 50 kg/m^3
- Damping and insulating properties (thermal and acoustic) that allow their use in building and packing.
- A low absorption of water and a low permeability to water vapor, a good behavior with hydrolysis
- Sometimes weak mechanical properties

- A limited or weak resistance to solvents and hydrocarbons

Polymethacrylimide

This specific foam, named "Rohacell," was specially developed by Röhm to be used as cores in the lightweight sandwich composites for transport.

The main properties of this rigid and closed-cell foam are as follows:

- A broad range of densities: from 30 to 300 kg/m^3
- Excellent mechanical properties
- A high thermal stability
- A high resistance to solvents used for the transformation of composites
- A low thermal conductivity
- Excellent damping properties and shock absorption
- A low X-ray absorption
- Low oxygen indexes of 19 to 20

Examples of applications:

- Aeronautics: parts for Airbus, ATR, Eurocopter, Dassault, McDonnell Douglas, radomes
- Automobile: parts for Matra, Volvo
- Railways: 2 floors TGV, front end of the Italian Pendolino
- Medical: radiography table (low X-ray absorption)
- Naval: race boats, yachts, catamarans
- Sports and leisure: parts for skis, rackets, and the like (Head, Dynastar, Atomic), wheels and frames for racing bikes

Polyethersulfone

This low-density specific foam, named "Airex R80.90," is specially developed by Airex associates. The main properties are as follows:

- A good fire resistance
- A high thermal behavior
- Transparency to radar frequencies

The major applications of this foam are sandwich structures for

- Aeronautics
- Space technology
- Transmissions and telecommunications (transparency to radar frequencies)

Polyetherimide

This low-density specific foam with closed cells, named "Airex R82," is specially developed by Airex associates. The main properties are as follows:

- A wide range of service temperatures: -194 to $180°C$
- A good fire resistance
- A high thermal behavior
- A high impact strength
- Low water absorption
- Useful dielectric properties

This foam is used as the core of composites for the following principal applications:

- Aeronautics: equipments for planes, radomes, and communication systems
- Automobile and transport: structures for railway and road vehicles
- Industry: structures working in temperature, cryogenic applications

This article is focused on the widely used commodity plastic foams, such as PU, PS, PP, and PE foams.

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