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With 153 Figures, 5 in Color and 44 Tables

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Foreword

The FLEXIFUNBAR project is an IP SME addressing research issues on emerging technologies for the production of new flexible structures (paper, leather, technical textiles for applications in transport, medical, security and clothing). It will clearly support the development of new knowledge based added value products in textile, leather and paper industries.

The work plan contains work packages tackling simultaneously integrated areas of research and scaling up (nanostructures, materials research for barrier effects, new production processes).

With a critical mass of 45 partners FLEXIFUNBAR project is coordinated by an SME, the PME DUFLOT, manufacturer of technical non wovens for protection and insulation (having 2 ultramodern plants in France). It clearly serves multisectoral needs and industrial leadership is ensured in several work packages (Annebergs, Europlasma, Libeltex, Patraiki, Amkey management).

The strength relies also on the adequacy of the part of the project dedicated to textile perfectly in line with the measures identified in the Communication on the future of the Textiles and Clothing sector adopted in October 2003 by the Commission to improve the competitive position of the Textiles and Clothing sector.

Based on the very high number of partners a particular strong management structure has been adopted (governing board, exploitation committee, scientific committee) providing SMEs to have a decisive role and the majority vote in the decision making structure of the project. This pragmatic management structure is also well adapted to the nature of the project (integration of different activities, different disciplines, stakeholders coming from different industrial sectors). IPR issues addressed in the consortium agreement towards SMEs benefits are clearly defined.

Brussels,
June 2007

Odile Demuth
Program Officer CE

Preface

Everyone relies on barrier structures in one form or another, to protect against extraneous environments such as fire, noise, thermal extremes and microorganisms; to shield from electrostatic or electromagnetic fields; or to filter dust and other matter. In order to meet the technical and economic requirements demanded from this diverse range of applications, barrier structures should ideally be flexible, have multifunctional properties and be easily fabricated at an acceptable cost. Materials used for this purpose are generally based on paper, leather and natural or synthetic textiles, generally modified to enhance their functionality and resulting service properties. Within Europe, products from this sector are, in the main, produced by high-tech SME companies. However, as a consequence of strong foreign competition and imports, particularly in the field of textiles, European industry is facing a familiar scenario: to survive, it must become more cost efficient and increasingly innovative in the development of high performance barrier products.

This challenge forms the underlying driver for the Integrated Project termed FLEXIFUNBAR: "Multifunctional barrier for flexible structure; textile, leather and paper", funded through the 6th European Framework Programme over the period 2004-2008. In this context, the programme partners have proposed fourteen themes concerned with different approaches to functionalising flexible barrier structures, which define the scope of this book. Its aim is to give a complete overview of the present state of the art of these materials, including methods for barrier fabrication and their evaluation. For the first time, this book provides a multidisciplinary approach to the subject, covering a number of industrially relevant topics including: barriers to fire; enhanced antibacterial properties; shielding from electrostatic, electromagnetic and acoustic waves; and means for preventing odour. Particular consideration is also given to developments and opportunities from using nanomaterials and fabrication technologies, together with advanced techniques for characterising their structure and properties.

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June 2007

S. Duquesne,
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Part I

Mono-Functional Barrier Effects - Review

1

The Application of Fire-Retardant Fillers for Use in Textile Barrier Materials

P.R. Hornsby

Summary. Available fire retardant fillers are reviewed with reference to their mechanism of action, both as fire retardants and smoke suppressant additives. Means for enhancing their efficiency are considered using flame retardant synergists and nanoparticulate filler variants of magnesium hydroxide, hydrotalcite and boehemite.

1.1 Introduction

There has been a trend in recent years, driven principally by environmental and safety considerations, towards increasing use of halogen-free fire-retardant systems, including hydrated fillers, such as magnesium and aluminium hydroxides. Their application in textile fibres, however, is limited by the need for high filler levels to confer adequate fire protection and their large particle size, which is generally of the same order as the diameter of the polymer fibre to which they are added. Both these factors significantly limit the spinnability and tenacity of such compositions.

This review will consider current fire-retardant fillers available, their characterisation, application to different polymer types, current understanding of their mechanism of action as fire retardants and smoke suppressants and means for improving their efficiency. This includes combination with other fire retardants as synergists. Emphasis will be given to issues specifically relating to their use in polymer fibres and means for potentially overcoming drawbacks, which may mitigate their application in textile barrier structures. To this end, discussion will also focus on nano-scale variants of these materials with, in particular, magnesium hydroxide, hydrotalcite and boehemite.

1.2 Fire-Retardant Fillers and Limitations for Textile Use

Particulate fillers can strongly influence the combustion characteristics of a polymer, including its resistance to ignition, and the extent and nature of smoke and toxic gas emission products. This may result from simple dilution of the combustible fuel source, slowing down the diffusion rate of oxygen and flammable pyrolysis products and changing the melt rheology of the polymer, thereby affecting its tendency to drip. However, depending on the nature of the filler, the heat capacity, thermal conductivity and emissivity of the polymer composition may also change, giving rise to heat transfer and thermal reflectivity effects, which can also slow the rate of burning.

In general, fillers cannot be classed as totally inert in relation to their effect on polymer combustion, however some, notably metal hydroxides, hydrates and carbonates can confer additional flame retardancy and smoke suppressing qualities being in widespread use for this purpose. These undergo endothermic decomposition, which cools the solid, or condensed phase, and release gases (water and/or carbon dioxide), which dilute and cool flammable combustion products in the vapour phase. The inorganic residue remaining after filler decomposition may also be highly significant in providing a thermally insulating barrier between the underlying polymer substrate and external heat source, in addition to contributing to overall smoke suppression. In this connection, materials, which are currently used or have potential for use as fire-retardant fillers, are listed in Table 1.1, together with relevant thermal properties and gaseous products evolved on decomposition.

In addition to their fire-retarding efficiency, to be commercially exploitable, these fillers should ideally be inexpensive, colourless, non-toxic, free from conductive contaminants, and readily available. Being thermally unstable they must have a sufficiently high decomposition temperature to withstand thermoplastics melt processing temperatures. However, to achieve maximum fire-retarding effect, thermal decomposition should generally occur near the onset of polymer degradation, with subsequent release of flammable volatiles.

When used in load-bearing situations, the presence of the filler generally has an adverse effect on strength and toughness of the composite, which can be limited by judicious formulation, and principally through the use of surface treatments. The implications of filler on polymer viscosity and mechanical properties are exacerbated by the high filler levels normally required to achieve acceptable resistance to combustion. These aspects are not considered in this review.

The size and shape of the filler particles are also important considerations. Filler particle size and the need to use high addition levels to confer adequate fire retardancy create particular limitations on their potential use in textile barrier structures, both in terms of their processability and ultimate physical properties.

Table 1.1. Current and potential fire-retardant fillers [1]

Candidate material (common names and formula)	Approximate onset of decomposition (°C)	Approximate enthalpy of decomposition ($\mathrm{kJ\,g^{-1}} \times 10^3$)	Volatile content (%w/w) Total	H_2O	CO_2
Nesquehonite [$MgCO_3 \cdot 3H_2O$]	70–100	1,750	71	39	32
Alumina trihydrate, aluminium hydroxide [$Al(OH)_3$]	180–200	1,300	34.5	34.5	0
Basic magnesium carbonate, hydromagnesite [$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$]	220–240	1,300	57	19	38
Sodium dawsonite [$NaAl(OH)_2CO_3$]	240–260	Not available	43	12.5	30.5
Magnesium hydroxide [$Mg(OH)_2$]	300–320	1,450	31	31	0
Magnesium carbonate subhydrate [$MgO \cdot CO_{2(0.96)}H_2O_{(0.30)}$]	340–350	Not available	56	9	47
Calcium hydroxide [$Ca(OH)_2$]	430–450	1,150	24	24	0
Boehemite [$AlO(OH)$]	340–350	560	15	15	0
Magnesium phosphate octahydrate [$Mg_3(PO_4)_2 \cdot 8H_2O$]	140–150	Not available	35.5	35.5	0
Calcium sulphate dihydrate, gypsum [$CaSO_4 \cdot 2H_2O$]	60–130	Not available	21	21	0

1.3 Mechanism and Application of Conventional Fire-Retardant Fillers

1.3.1 Scope of Application

Substantial industrial use is made of the principal fire-retardant fillers, aluminium hydroxide (ATH), magnesium hydroxide (MH) and, to a lesser extent, hydromagnesite/huntite mixtures. Whereas there is widespread application of ATH in elastomers, thermosetting resins and thermoplastics, its use is generally limited to polymers processed below 200°C. MH is stable to temperatures above 300°C, however, permitting incorporation in polymers such as polypropylene, polyamides and polyketones, in addition to certain elastomers, where increased thermal stability is essential. Its use in thermoplastic polyesters is limited by its tendency to catalytically decompose the polymer during processing [2], whereas unlike ATH, in unsaturated polyester resins MH acts as chain extender adversely affecting resin rheology. Although it has been shown that this effect can be ameliorated by using maleic acid coated grades of MH filler, the long-term stability of these systems is still questionable [3].

Hydromagnesite (usually found in combination with huntite) has intermediate thermal stability, decomposing between 220 and 240°C [4, 5]. Mixtures of these minerals are used in wire and cable applications, due to their higher thermal resistance than ATH and lower cost compared to MH. They have also been considered for use in ethylene–propylene copolymers [6] and PVC formulations, where reduced smoke and acid gas emission are requirements [7].

In thermosets, there is widespread use of ATH in unsaturated polyester resin moulding compounds, for example for automotive parts, epoxy and phenolic resin formulations, especially in electrical applications, and cross-linked acrylic resins where flame retardancy is a key requirement [2]. In thermoplastics and elastomers, applications for ATH have been found in rigid poly(vinyl chloride), high, low and linear low density polyethylene, ethylene–propylene rubber, ethylene–propylene–diene cross-linked rubbers, ethylene–ethyl acrylate copolymers, and ethylene-vinyl acetate copolymers [8–11]. Although it is claimed that ATH can also be used in polypropylene, the limited thermal stability of this filler generally necessitates special compounding and processing measures, which has inhibited its large-scale application in this polymer [12]. In this connection, a modified ATH has been reported with apparent thermal stability up to about 350°C and claimed to be suitable for use in many engineering resins [13]. A major use for both ATH and MH is in low smoke, halogen-free wire, cable and conduit applications, where there has been significant commercial activity [14–18].

1.3.2 Flame Retardancy

The relative performance of hydrated fire-retardant fillers in polymers strongly depends on the nature and origin of the filler type and the chemical characteristics of the host polymer, in particular, its decomposition mechanism. In this regard, specific interactions may exist between certain polymers and fillers, which influence their mechanism of action [19].

However, compared to alternative fire retardants, including phosphorous-based intumescent and halogen-containing formulations, hydrated fillers are relatively ineffective, requiring addition levels of up to 60% by weight to achieve acceptable combustion resistance [20]. For example, with polypropylene, 60% by weight would be required to achieve an oxygen index in excess of 26%. At the same addition level in polyamide 6, however, an oxygen index of nearly 70% can be obtained [21]. Although this might seem more than enough to suppress ignition with this polymer, polyamides are prone to dripping on decomposition. This can be the determining factor when flammability is assessed by the UL94 test procedure widely used in industry for screening purposes. Increasing filler level tends to raise the viscosity of the decomposing polymer, inhibiting its tendency to drip [22].

The following contributing effects may combine to determine the overall mechanism of fire-retardant fillers.

Thermal Effects from Filler

As mentioned earlier, a characteristic of hydrated fire-retardant fillers is that they undergo endothermic breakdown. Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) have been widely applied to study their thermal decomposition [23]. Comparing magnesium hydroxide grades, wide differences have been reported in the magnitude of their decomposition endotherm and decomposition temperature [24]. In addition to inherent characteristics of the filler types, the apparent decomposition behaviour may also be influenced by the analytical procedure adopted [23]. This includes sample size, rate of heating, rate of inert gas flow rate and degree to which the pan is sealed. Furthermore, it has also been reported that different grades of magnesium hydroxide may degrade at different rates, dependent on filler morphology and/or surface area [25].

The heat capacity of these fillers and in particular, their strong endotherm can strongly influence the input of heat required for polymer decomposition and release of combustible volatiles [21]. This effect has been modelled using a heat balance approach which can be applied to the whole combustion process [23]. By this means it can be shown that at sufficiently high filler levels, hydrated fillers can also reduce the mass burning rate by inhibiting the rates of heat transfer from the flame to the underlying matrix, causing the flame to extinguish due to fuel starvation [26]. Hence reductions in applied heat flux or increased surface heat losses will lead to a decrease in the mass burning rate of the polymer, as has been reported for polypropylene/aluminium hydroxide composites [27].

Forced combustion studies provide a method for measuring rates of heat transfer through a fire-retardant polymer composition exposed to an ignition source at its outer surface. In studies involving thermal breakdown of polypropylene, magnesium and aluminium hydroxides decompose to their respective oxides, which together with any carbonaceous char produced, provide an effective thermal barrier, reducing heat transmission to the underlying substrate [28]. Similar behaviour has been observed with other polymer types, including modified-polyphenylene oxide (PPO), polybutylene terephthalate (PBT) and acrylonitrile–butadiene–styrene copolymer (ABS) [20].

Microscopic analysis of the oxide/char residue formed on combustion of magnesium hydroxide-filled polypropylene has revealed an oxide morphology similar in form to the parent hydroxide [29]. In this example, hexagonal platelets appear to align predominantly in the same plane and in some cases overlap, which contrasts with large aggregated structures derived from hydroxide particles formed from association of small crystallites. There is some evidence of increased crystal growth and that the coherency of the oxide particles contributes to the stability of the decomposition residue observed from combustion products arising from oxygen index tests. Although the magnitude of possible inter-particle attractions arising from oxide residues is unknown, the strength of agglomerates containing magnesium hydroxide pseudomorphs has been estimated to be $50\,\mathrm{MN\,m^{-2}}$, arising from physio-chemical association between magnesium oxide and water [30].

Dilution of Combustible Polymer

The presence of up to 60% by weight of fire-retardant filler results in around 35% by volume reduction of combustible polymer (in the case of magnesium hydroxide). In studies using polypropylene compositions containing different grades of magnesium hydroxide, magnesium oxide and glass beads, values of heat release rate (HRR) were determined by cone calorimetry [29]. It was found that rates of heat release were significantly reduced, after allowing for the volume dilution of each of these fillers. However in this regard, magnesium oxide was far more effective than the glass beads, even though both are nominally considered to be inert fillers. This suggests that even with thermally stable and nominally inert fillers, particle geometry, surface chemistry and perhaps thermal conductivity, have an active role in influencing fire retardancy.

Filler Polymer Interaction

TGA and DSC can provide useful information concerning the nature of filler/polymer interaction, together with their relative decomposition temperatures, when used in combination with evolved gas analysis (EGA) and on-line FTIR techniques. It was demonstrated that thermal breakdown of magnesium hydroxide exerts a significant prodegrative action on polyamide 6 (PA-6) and polyamide 66 (PA-66) which has been attributed to water release and resulting hydrolysis of the polymer chain [31]. Evolved gases released from both filled and unfilled PA compositions were shown to be water, carbon monoxide, carbon dioxide, ammonia and various hydrocarbon fragments. PA-6 compositions were found to be significantly more fire retardant than corresponding formulations made using PA-66 and in PA-66, polymer degradation occurred before magnesium hydroxide breakdown, whereas there was much greater overlap in thermal decomposition of PA-6 and this filler.

Despite the high oxygen index values obtained through introduction of magnesium hydroxide into polyamides, achieving a VO rating according to the UL94 test, strongly depends on their tendency to drip during combustion. It has been shown that different magnesium hydroxide filler variants influence the rheological behaviour of thermally decomposing polyamides in different ways and hence their resistance to dripping [32]. In general, plate-like filler particles operate more effectively in this regard [33].

Several comparisons exist on the relative efficiency of magnesium and aluminium hydroxides in the same polymer type. One study, reported for polyethylene, showed that at an equivalent additive loading, these fillers gave the same oxygen index [34]. However in ethylene-vinyl acetate copolymer (EVA) with 30% vinyl acetate content, magnesium hydroxide yielded an oxygen index of 46%, whereas using aluminium hydroxide, this was measured as 37%. From non-isothermal thermo-gravimetric analysis, it was suggested that in this polymer, water release is delayed from aluminium hydroxide, whereas this is accelerated from magnesium hydroxide, possibly arising from acetic acid evolved from the polymer.

In studies on the ignition and incandescence of filled polymers, both ATH and MH were found to increase the self-ignition temperature of an EVA copolymer, with magnesium hydroxide being more effective [35]. Using TGA, in these systems it was concluded that the solid-state afterglow effects observed were due to oxidation of carbonaceous residues.

Vapour Phase Action

The release of water and/or inert gas into the vapour phase on decomposition of hydrated fillers, also contributes to the overall fire retardation mechanism. Although little detailed analysis has been undertaken in this area, it is generally considered that water release into the vapour phase exerts a beneficial effect through dilution and cooling of volatiles produced on polymer degradation [21].

Effects of Filler Particle Size and Morphology

It has often been observed that different grades of the same fire-retardant filler can give significantly different effects, despite apparent similarities in their endothermic decomposition or release of inert gas. Whilst this may, in part, be an outcome of the flammability test procedure applied, distinct particle size and particle morphology effects have been reported. These factors also have a significant bearing on the mechanical properties and melt rheology of polymer composites containing hydrated fillers.

In relation to flammability, however, it has been shown using the UL94 vertical burn test that the effectiveness of magnesium hydroxide in polypropylene increased with decreasing particle size [36]. Similarly, in studies involving PMMA modified with ATH, fine grades ($< 1\,\mu\text{m}$) gave markedly higher oxygen index values than coarser ($45\,\mu\text{m}$) grades, particularly at filler loadings above 50% by weight [23]. ATH is reported to be less thermally stable as the particle size increases [37]. Early in the decomposition process the alumina produced is very reactive, readily combining with water vapour to rehydrate to ATH. In larger particles, water escaping nearer the centre of the particle has a larger diffusion path, giving more time to react with alumina formed near the surface of the decomposing particle. During this process boehmite or pseudo-boehmite is formed and, being a partial decomposition product, is more stable than ATH, decomposing at about 450°C. In relation to the effects of particle size on thermal stability, it has been shown that there is a greater transition from gibbsite to pseudo-boehmite as the particle size increases [38]. These observations on particle size effects are especially significant in the context of nano-sized hydrated fillers, considered later, and whether at this scale, further improvements in efficiency are achievable.

The thermal stability of magnesium hydroxide is also influenced by particle morphology. Spherical particles have been shown to decompose more slowly than platy structures, when heated isothermally at 390°C [21].

1.3.3 Smoke Suppression

Since most fatalities in fires arise from smoke-related effects, it is important to consider the influence of hydrated fillers on smoke emission during polymer combustion. An early study discussed the effects of calcium carbonate, ATH and MH fillers on smoke production from styrene butadiene (SBR) foams [39]. It was evident that all the fillers reduced soot formation relative to unfilled foam with the hydrated fillers being more effective than the calcium carbonate, which was considered to act merely as matrix diluent. ATH and MH were found to give enhanced char formation and promotion of solid-state cross-linking as opposed to pyrolytic degradation. The occurrence of afterglow, after extinction of the flame, was noted with MH and attributed to slow combustion of carbon residues. There have been a number of other reports demonstrating the smoke suppressing tendencies of hydrated fillers in various polymers including ethylene–propylene–diene elastomers [40], polypropylene [20], polystyrene [41], modified polyphenylene oxide, polybutylene terephthalate and ABS [28]. Not only do these hydrated fillers reduce overall levels of smoke released, but they can delay the onset of smoke evolution, potentially allowing more time for escape from the vicinity of a fire [21].

Although there has been extensive analysis of the composition and formation of soot from polymers undergoing combustion [42,43], only limited work has been published on the mechanism of smoke suppression using hydrated fillers. It seems likely however, that the process is a consequence of the deposition of carbon onto the oxide surface, produced on decomposition of the hydrated filler [20]. Volatilisation of carbonaceous residue as carbon oxides subsequently occurs, which do not contribute to the obscuration effects of smoke. On hydroxide decomposition, these oxides have high surface areas [20] and being catalytically active [44], can promote both carbon deposition and subsequent oxidation processes [45]. The reduced combustion rate arising from the effects of the fire-retardant filler will also play a part in lowering the rate of smoke evolution and also improving oxygen to fuel ratios, further limiting the obscuration effect [23].

The role of evolved water from hydroxide decomposition is of interest, since water can also oxidise carbon. In this connection, smoke yields from polypropylene compounds containing magnesium hydroxide and magnesium oxide were compared [20]. These results showed little difference in levels of smoke evolution, suggesting that water has limited effect on the smoke suppression mechanism. These data are supported by CO emissions from burning ABS, which again demonstrate little distinction between oxide and hydrated forms of this magnesium compound [28] and also by the fact that the so-called water–gas oxidation reaction occurs at temperatures and pressures well in excess of those normally found at the burning surface of a polymer [46].

The afterglow or incandescence effect mentioned earlier, commonly observed following combustion of polymers containing hydrated fillers has been studied in EVA copolymer [35]. Using a heated quartz reactor purged with air, oxidation, self-ignition and incandescence were monitored as a function of temperature and filler loading. With magnesium and aluminium hydroxides, self-ignition temperature was raised progressively with increasing filler level, whereas the onset temperature for incandescence decreased. It was concluded that afterglow was due to catalytic oxidation of carbonaceous residues by surface active oxides produced from filler decomposition, with magnesium oxide showing greater activity [47].

1.3.4 Synergism

The challenge to improve the efficiency of hydrated fillers as fire retardants and thereby enable reductions in filler levels, has prompted much interest into the use of co-agents or synergists. As shown in Table 1.2 and in the following examples, significant improvements in overall performance can be achieved by this approach, although the mechanisms of interaction are frequently unclear.

Combinations of MH and ATH can give improved performance when used together [48, 49], due to the increased range of endothermic reaction (180–400°C) and release of water in the vapour phase. The different metal oxides produced on dehydration may also contribute to this effect.

ATH and red phosphorus (3–5%) have also been used in synergistic mixtures with to increase fire retardancy and enable lower filler loadings [50].

The addition of melamine and novolac (∼1%) to PP/MH mixtures has been found to reduce the burning time and give a UL94 VO rating at lower filler levels (30–50%) as opposed to a more usual value of around 60%, allowing the formulation to be mechanically more flexible. The novolac causes a structurally stabilising effect above the melting point of PP. Thermal evidence suggests that a novolac magnesia gel may be formed [51].

Metal hydroxides in combination with various formulations of silicon-containing compounds have been used to reduce the amount of additive required to achieve a required level of flame retardancy in a variety of polymeric materials, including polyolefins [52,53]. Systems, which have been used, contain a combination of reactive silicone polymers, a linear silicone fluid or gum and a silicone resin, which is soluble in the fluid, plus a metal soap, in

Table 1.2. Examples of synergists for metal hydroxides

Co-additives	Hydrated filler(s)	Polymer(s)	Effect(s)	References
Antimony trioxide	ATH, MH	PVC (flexible), Polyolefins, EVA	Reduced overall filler level/reduced smoke	[47,60,61]
Antimony trioxide/zinc borate	ATH	PVC (flexible)	Reduced overall filler level/lower smoke	
Borate compounds (zinc borate/calcium borate)	ATH	EVA	Enhanced flammability resistance at low co-additive additions, increased char promotion	[65]
MH/ATH combinations	ATH, MH	PVC	Reduced flammability, wider range of endotherm and water release, enhanced oxide thermal barrier (?)	[48,49]
Molybdenum compounds (molybdenum oxide/molybdate salts)	ATH, MH	PVC	Reduced flammability and smoke emission, increased char promotion	
Red phosphorus	ATH, MH	–	Reduced overall filler levels, suppression of phosphine formation by metal hydroxide, coloured formulations, low co-additive additions	[50]
Silicon-containing compounds (organo-silicones)	ATH, MH	Polyolefins	Enhanced flammability resistance/reduced smoke, improved processability and physical properties, handling issues	[52,53]

Polyacrylonitrile fibres	ATH, MH	Polyolefins	Char promotion, reduced filler levels can be pigmented	[64]
Transition metal oxides (nickel oxide/cobalt oxide)	ATH, MH	Polyolefins	Reduced overall filler levels, colour limitations, possible adverse toxicity effects	[54]
Metal nitrates (copper nitrate/iron nitrate)	ATH	EVA	Enhanced flammability resistance with low co-additive additions	[55]
Melamine	ATH, MH	PP	Improved fire retardancy, reduced afterglow	[51, 60]
Tin compounds (zinc stannate/zinc hydroxystannate)	ATH, MH	PVC, Cl-Rubbers, EVA	Enhanced flammability resistance/ reduced smoke especially with ZH/ZHS-coated filler variants	[57, 58]
Nano-clays	ATH, MH	EVA	Lower heat release rates/ reduced smoke emission used in combi- nation with tin compounds	

particular magnesium stearate. However, there is little insight into how these formulations work.

Some recent work has shown that required loading levels of metal hydroxides to flame retard polyolefins, could be reduced by addition of transition metal oxides as synergistic agents. For example, combination of 47.6% MH modified with nickel oxide in PP gave a UL94-VO flammability rating which would require $\sim$55% of unmodified MH [54]. These systems, however, can only be used where colour of the product is not important.

The addition of metal nitrates to improve the flame retardancy of metal hydroxides and EVA has been reported [55]. Synergistic behaviour was observed by addition of 2% of copper nitrate to EVA containing only 33% ATH, in which the oxygen index was raised from 19.9 to 30.0%.

The flammability properties of an intumescent fire-retardant PP formulation with added MH has been investigated [56]. The results show that the intumescent flame retardant ammonium polyphosphate-filled PP has superior flammability properties but gives higher CO and smoke evolution. The addition of MH was found to reduce smoke density and CO emissions, in addition to giving superior fire resistance. PP filled with ammonium polyphosphate, pentaerythritol and melamine has improved flammability performance, without reducing its mechanical properties [56].

In halogen-containing polymers, zinc hydroxystannate- or zinc stannate-coated hydrated fillers can give significantly improved flame resistance and lower smoke emission compared with uncoated fillers [57, 58]. The efficiency of the coated fillers was found to be superior to simple admixtures of these components, reflecting improved dispersion and possible synergism in these systems.

Addition of silane cross-linkable PE copolymer to PE/metallic hydroxide systems can significantly improve the flame retardant properties of these materials allowing lower filler levels to be used [59].

The combination of melamine with hydrated mineral fillers can improve the fire retardancy behaviour of PP, eliminating at the same time the afterglow phenomenon, associated with these fillers used in isolation [60]. Similarly in EVA copolymer, antimony trioxide used in combination with metal hydroxides has been reported to reduce incandescence [47]. Chlorinated and brominated flame retardants are sometimes used in combination with metal hydroxides to provide enhanced fire-retardant efficiency, lower smoke evolution and lower overall filler levels. For example, in polyolefin wire and cable formulations, magnesium hydroxide in combination with chlorinated additives was reported to show synergism and reduced smoke emission [61].

A natural mineral filler, containing mainly huntite and hydromagnesite, has been used, together with a blend of antimony trioxide (Sb_2O_3) and decabromodiphenyl oxide (DPDPO) to reduce the flammability of an ethylene–propylene copolymer [62].

The addition of very small amounts of fine carbon fibre [63] or polyacrylonitrile fibres [64] can reduce the level of inorganic hydroxide required to achieve UL94-VO flammability ratings in polyolefin compounds. These secondary additives are thought to function as char promoters.

The addition of low levels (∼3%) of zinc borate to metal hydroxides can give synergistic effects [65]. For example in an EVA/MH formulation, LOI was found to increase from 39 to 43%, together with a significant reduction in heat release rate. Solid-state NMR of carbon in the residues showed that polymer fragments were in the char layer. It was suggested that zinc borate slows the degradation of the polymer, creating a vitreous protective physical barrier to combustion.

1.4 Nano-Size Fire-Retardant Fillers

Nano-particulate fillers have been shown to significantly increase the properties of polymers using only small levels of additive, typically between 3 and