



A review of flame retardant polypropylene fibres

Sheng Zhang*, A. Richard Horrocks

Centre for Materials Research and Innovation (CMRI), Bolton Institute, Bolton BL3 5AB, UK

Received 12 March 2003; revised 26 August 2003; accepted 5 September 2003

Abstract

Flame retardants for polypropylene (PP) and their potential suitability for use in fibre applications are reviewed. Five principal types of generic flame retardant systems for inclusion in polypropylene fibres have been identified as phosphorus-containing, halogen-containing, silicon-containing, metal hydrate and oxide and the more recently developed nanocomposite flame retardant formulations.

The most effective to date comprise halogen–antimony and phosphorus–bromine combinations, which while having limited performance also are falling environmental pressures. Alternatives are discussed as well as means of enhancing the effectiveness and hence usefulness of phosphorus–nitrogen formulations normally used at concentrations too high for fibre inclusion. Of special interest is the potential for inclusion of functionalised nanoclays and recent observations that certain hindered amine stabilisers are effective at concentrations of 1% or so.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Polypropylene; Flame retardant; Fibres; Combustion; Phosphorus; Halogen; Silicon; Metal hydrate; Nano clay; Nanocomposite

Contents

1. Introduction	1518
1.1. The development of polypropylene fires	1518
1.2. The properties of polypropylene	1518
2. Thermal and combustion behaviour	1519
3. Flame retardants for polypropylene and polypropylene fibres	1520
3.1. Phosphorus-containing and intumescent flame retardants	1521
3.1.1. Effect of heavy metal ions	1525
3.1.2. Effect of silicon-containing species (see also Section 3.3).	1526
3.2. Halogen-containing flame retardants	1526
3.3. Silicon-containing flame retardants	1528
3.4. Metal hydroxides and oxides (metal compounds).	1528
3.5. Nanocomposites.	1529
3.6. Other methods	1531
3.6.1. Grafting and coating.	1531
3.6.2. Hindered amine light stabilisers	1532

* Corresponding author. Fax: +44-1204-399074.

E-mail address: sz1@bolton.ac.uk (S. Zhang).

4. Conclusions	1532
References	1532

1. Introduction

Polypropylene was the first synthetic stereoregular polymer to achieve industrial importance [1] and it is presently the fastest growing fibre for technical end-uses where high tensile strength coupled with low-cost are essential features; it has shown consistent growth of about 5% per annum for the last 10 years [2]. In 1999, worldwide consumption of polyolefin fibres exceeded 5.5 million tonnes and they accounted for 18% of the world's synthetic fibre production [3]. Polypropylene fibres have been widely used in apparel, upholstery, floor coverings, hygiene medical, geotextiles, car industry, automotive textiles, various home textiles, wall-coverings and so on [4].

1.1. The development of polypropylene fibres

The synthesis of highly crystalline isotactic polypropylene using stereospecific catalysts was patented in 1954 by Natta [5]. They used heterogeneous catalysts of the type discovered by Ziegler for the low-pressure polymerization of ethylene to yield linear high-density polyethylene. Commercial polypropylene production was initially undertaken by Montecatini and subsequently expanded by ICI Fibres who introduced their 'Ulstron' product in late 1950s [6]. However, because of patent restrictions associated with fibre production, fibrous polypropylene often appeared in the market in the form of tapes and filaments rather than fibres; it was not until the early 1960s that staple fibres started to be seen on the market [7]. In the early 1970s the emergence of extruded, orientated film technology led to an expansion of polypropylene end-uses, including tapes/slit-film and various fibrillated and fibrous products [1].

The monomer propylene is a hydrocarbon gas mainly produced from petroleum refining. The polypropylene chain comprises a monomer with an asymmetric carbon atom at the C₂ position, $-\text{CH}_2-\text{CH}(\text{CH}_3)-$, and hence the polymer may exist in three types (isotactic, syndiotactic and atactic) of molecular

configurations depending upon the relative orientations of the methyl side groups [7]. Both isotactic and syndiotactic forms have methyl groups situated regularly with respect to adjacent groups along the molecular chain and have fibre-forming character due to their potential for creating order in the polymer structure. Currently, isotactic polypropylene is the main commercially available stereoisomer for use in oriented fibre films and tapes. A very recent EU patent, however, has described the properties of fibres when 0.5–50% by weight of syndiotactic polypropylene having a multi-modal molecular weight distribution is included with at least 50% by weight of an isotactic polypropylene [8].

1.2. The properties of polypropylene

The reason for the rapid expansion in production capacity for polypropylene is its advantage over polyethylene in cost and properties. An economic edge in raw material cost and the high efficiency catalysts have made polypropylene a very low-cost fibre-forming plastic material. A number of properties are responsible for the widespread usage of polypropylene. The general properties of isotactic polypropylene are shown in Table 1 [9].

Table 1
Properties of isotactic polypropylene

Properties	Value
Moisture regain (%)	<0.1
Melting point (°C)	160–175
Softening point (°C)	140–160
T_g (°C)	–19
Density (g/cm ³)	0.90
Specific heat (J g ⁻¹ °C ⁻¹)	1.6
\bar{M}_n	>10 ⁶
Polydispersibility (\bar{M}_w/\bar{M}_n)	9–11
Heat of combustion (kJ g ⁻¹)	44
Heat of fusion (J g ⁻¹)	21
Limiting oxygen index (%)	17.4
Decomposition range (°C)	328–410

Fibre-forming atactic polypropylene is partially crystalline, i.e. it possesses a two-phase system comprising crystalline and non-crystalline regions. The molecular chains of crystalline isotactic polypropylene exist in helical coils having three monomer units per repeating helix with a length of 0.65 nm for each repeat unit. The methyl groups are arranged systematically around the helix forming three lateral rows about 120° apart and thus close packing is possible.

2. Thermal and combustion behaviour

The crystalline melting point of isotactic polypropylene with a crystallinity of around 45% and containing 90–95% isotactic material is quoted as 165 °C [10]. The T_g value of isotactic polypropylene ranges from –30 to 25 °C depending on method of measurement and heat-annealing treatments [10]. Atactic polypropylene has a glass transition temperature (T_g) of –12 to –15 °C and no defined melting point. Table 2 shows the thermodynamical properties of polypropylene.

Because of its wholly aliphatic hydrocarbon structure, polypropylene by itself burns very rapidly with a relatively smoke-free flame and without leaving a char residue. It has a high self-ignition temperature (570 °C) and a rapid decomposition rate compared with wood and other cellulosic materials and hence has a high flammability. The heat of combustion for polypropylene was reported by Einsele et al. [11] to be 40 kJ/g and this is higher than many other fibre-forming polymers. Gurniak and

Kohlhaas [12] investigated the combustibility tests carried out on four different backing fabrics: spunbonded polypropylene, woven polypropylene tape with nylon/polypropylene bonded staple fibre fabrics, spunbonded Bikofilament (polyester core, nylon sheath), and Freudenberg's Lutradur T5012 spunbonded polyester. They found that the lowest flammability was achieved by the spunbonded polyester product. This is a significant observation in that polypropylene competes with polyester in terms of tensile properties and price, but it does have inferior fire performance.

Polypropylene pyrolysis is dominated by initial chain scissions; consequently considerable research has been undertaken in the conversion of waste polypropylene into clean hydrocarbon fuels [13,14] or other valuable products such as lubricants [15,16]. The thermal degradation of both isotactic PP and atactic PP has been investigated under non-isothermal conditions. The maximum volatile product evolution temperature was 420 °C for atactic PP and 425 °C for the isotactic PP. The recovery of carbon as organic volatile products comprised dienes, alkanes, and alkenes. Major compounds are for instance C9 compounds, like 2-methyl-4-octene, 2-methyl-2-octene, 2,6-dimethyl-2,4-heptadiene, 2,4-dimethyl-1-heptene, 2-methyl-1-octene. The hydrogen content of pyrolysis products obtained by flash pyrolysis at 520 °C, indicates the magnitude of the flammability problem in term of its fuel-forming potential [17]. An abundance of unsaturated volatile fuel fragments renders the flame retardation problem even more severe as the longer, less-volatile molecules behave as secondary fuel sources, which decompose further [18,19].

Cool flame combustion of polypropylene at 350 °C leads to the formation of toxic compounds which can cause death in mice, probably because of incomplete combustion and CO formation [20]. While the fire hazard caused by textiles in general has been reviewed by Horrocks [21] and Christian [22], the particular hazard of polypropylene was noted in the Manchester Woolworth Fire of 1979 where polypropylene upholstery covers over polyurethane foam filling in a stacked furniture pile were identified as the first material ignited and were responsible for the rapid growth of that fire. The 12 deaths associated with this fire gave rise to the need to use flame retardant

Table 2
The thermodynamical properties of polypropylene at 230 °C

Property	Value
Heat content relative to 20 °C (kJ/kg)	30.86
Coefficient of thermal diffusion (cm ² s ⁻¹)	0.9 × 10 ⁻³
$\partial H/\partial T_p$ (J °C ⁻¹)	0.55
$\partial S/\partial T_p$ (J °C ⁻¹)	1.10 × 10 ⁻³
$\partial H/\partial P_T$ (J Pa ⁻¹)	0.84
$\partial S/\partial P_T$ (J Pa ⁻¹)	1.0 × 10 ⁻³
Bulk modulus	0.65 × 10 ⁻³
Density (g cm ⁻³)	0.75
Density at 20 °C (g cm ⁻³)	0.90

H, enthalpy; *S*, entropy; *P* = pressure.

textiles in UK domestic furnishings for the first time in 1980 [23].

Hirschler [24] studied the fire hazard and toxic potency of the smoke from burning polypropylene in 1987. Grand [25] investigated the effect of experimental conditions on the evolution of combustion products of polypropylene by using a modified toxicity test apparatus. In 2000, Shemwell and Levendis [26] studied the particulate (soot) emissions from burning polypropylene and four other plastics. Results showed that both the yields and the size distributions of the emitted soot were remarkably different for the five plastics burned. Soot yields increased with an increase of the nominal bulk (global) equivalence ratio (ϕ). Combustion of polystyrene yielded the highest amounts of soot (and most highly agglomerated), several times more than the rest of the polymers. Emissions from PE and PP were remarkably similar to each other, and each produced very low emissions at $\phi \leq 0.5$ where excess oxygen prevails, but emissions increased drastically with ϕ , and most of the soot was very fine (70–97% of the mass was 2 μm or smaller, depending on ϕ).

Subsequently, the pre-combustive oxidative behaviour of commercial PP has been evaluated by simultaneous thermogravimetric analysis (TGA), differential thermal analysis (DTA) and pressure differential scanning calorimetry (PDSC) by Riga et al. [27]. They found that thermal oxidation was a consequence of rapid carbonyl formation initiated at the labile tertiary hydrogen atoms in the chain.

Polypropylene oxidizes more readily than polyethylene because of the lability of its tertiary hydrogen atom. It was reported that the uncatalysed, uninhibited oxidation kinetics and the overall energy of activation of both polyolefins were similar and that the oxidation rate of polypropylene was about 30 times faster than that of polyethylene. Several mechanisms were postulated to account for some of these volatile products [10,28]. The following volatile products have been identified during the oxidation of polypropylene: water, formaldehyde, acetaldehyde, acetone, methanol, hydrogen, hydrogen peroxide, carbon monoxide and carbon dioxide.

Decomposition of the polypropylene chain is also oxidatively sensitized and occurs by breaking the weaker bonds at the polymer surface in the presence of chemisorbed oxygen. The peroxy radicals are

formed by the propagating oxidative reaction at the reaction zone. In the inner oxygen-free zone, C–C bond scission begins resulting in formation of shorter radicals and biradicals. At high temperature ($>350\text{ }^\circ\text{C}$) the dehydrogenation of the polymer radicals occurs yielding alkene species as discussed above.

3. Flame retardants for polypropylene and polypropylene fibres

While polypropylene fibres may be treated with flame retardant finishes and back-coatings in textile form with varying and limited success [21], the ideal flame retardant solution for achieving fibres with good overall performance demands that the property is inherent within the fibre. This review will concentrate only on systems that can be incorporated within polypropylene polymers, fibres and filaments.

Flame retardant formulations for polypropylene have been established for nearly 40 years and the first patent was probably that published on September 15th, 1964 by Blatz [29], in which polypropylenes were rendered flame retardant by the incorporation of a halogen compound (1,2-dibromo-4-(α,β -dibromoethyl)cyclohexane) and metal oxide (Sb_4O_6) a free radical initiator and a dispersant into the thermoplastic melt.

The flame retardancy of polypropylene may be achieved in one of the following ways [17,30]:

- (1) by changing the pyrolysis reactions to form a carbonaceous char, which will block heat transformation and hence reduce the volatile formation and protect the polymer from further oxidation. This method poses real challenges for polypropylene because the polymer has no reactive side chains thereby preventing char formation following elimination of these groups;
- (2) by inhibiting the initiating radicals in the pre-flame and flame zones; typically, antimony–halogen based additives are effective here;
- (3) by adding some hydrated inorganic additives which decompose endothermically and release water, and hence withdraw heat from the substrate and dilute the combustible volatiles;

- (4) by modifying the chemical structure of the polymer to change its decomposition procedure and/or to improve the compatibility with other flame retardants;
- (5) by addition of char-forming additives preferably having an intumescent property.

An acceptable flame retardant for polypropylene and especially fibre-forming grades, should have the following features:

- It should be thermally stable up to the normal polypropylene processing temperature (<260 °C).
- It should be compatible with polypropylene and have no leaching and migratory properties.
- The additive should retain its flame retardant properties when present in the fibre.
- It should also reduce the toxicity of gas and smoke during burning to an acceptable level.
- It should be present at a relatively low level (typically less than 10% w/w) to minimize its effect on fibre/textile properties as well as cost.

Most flame retardants act either in the vapour phase or the condensed phase through a chemical and/or physical mechanism to interfere with the combustion process during heating, pyrolysis, ignition or flame spread stages. Halogen-containing species, often in combination with some phosphorus and antimony-containing flame retardants, usually act in the vapour phase by capturing the radicals to interrupt the exothermic oxidative flame chemical processes and thus suppress combustion. However, phosphorus-containing species typically act in the condensed phase promoting char formation on the surface initially, which functions as a barrier to inhibit further degradation and hence starve the flame of fuel and protect the polymer surface from heat and air. The poor or zero char-forming ability of PP requires that the additive itself is a source of char; hence high concentrations (typically >20% w/w) are required for acceptable levels of flame retardancy. Furthermore, the incorporation of fillers acts as a polymer diluent and reduces the concentration of decomposition gases. Hydrated fillers also release non-flammable gases or decompose endothermically to cool the pyrolysis zone at the combustion surface. Another major category of flame retardant are intumescent,

which swell when exposed to fire or heat to form a porous foamed carbonaceous char; the expanded char acting as a barrier to heat, air and pyrolysis products.

Like other polymers, there are two main types of flame retardants for polypropylene: namely the additive and the reactive types. Additive type flame retardants, generally incorporated into the polymer by physical means, have been widely used and include many of the commonly used antimony–bromine, intumescent and hydrated filler formulations available [31]. However, a variety of problems may arise, such as poor compatibility, leaching, and a reduction in mechanical properties. The application of reactive flame retardants involves either the design of new, intrinsically flame-retarding polymers or modification of existing polymers through copolymerisation with a flame-retarding unit either in the chain or as a pendant group. At the present time new polymer design lacks sufficient versatility in manufacturing, processing and is uneconomical, due to the expense associated with developing a new material for use. However, the substantial research efforts are centred on this approach and results show that the incorporation of even a few weight percent of the unit into the polymer chains can lead to remarkable improvements in the overall flame retardancy of the polymer [31]. At the present time, however, existing and potentially new flame retardants for polypropylene fibres are additive-based although the latter will be reviewed in Section 3.6.

3.1. Phosphorus-containing and intumescent flame retardants

Phosphorus compounds having flame retardant properties in polypropylene may be both inorganic and organic as shown in Table 3 [32–49]. It is also common for them to be used in the presence of halogen (see Section 3.2) or nitrogen-containing compounds [50] and especially those that generate intumescent char-forming characteristics [31,51].

The range of phosphorus-containing flame retardants is extremely wide since the element exists in several oxidation states. Phosphines, phosphine oxides, phosphonium compounds, phosphonates, elemental red phosphorus, phosphites and phosphate are all used as flame retardants in polymers in general, although, only few of these are applicable to

Table 3
Selected and typical phosphorus-containing flame retardant used in polyolefins

Compound	Reference and date
Halogen phosphate	[32], 1972
Phosphine oxides and ammonium polyphosphates	[33], 1972
Phosphite	[34], 1975
Phosphonitrilic esters	[35], 1975
Phosphonopropionic acid amines	[36], 1974
Alkyl-aryl phosphonates	[37], 1974; [38], 1975; [39], 1976
Cyclic phosphonate esters	[40], 1974
Phosphonateisocyanurate	[41], 1978
Phosphoric acid	[42], 1976; [43], 1978; [44], 1995
Ammonium phosphate and tetrakis(hydroxymethyl) phosphonium hydroxide	[45], 1980; [46], 1977
Inorganic phosphoric acids, such as ortho-, meta-, or pyrophosphoric acids	[47], 1977
Phosphonate ester	[48], 1979
Organic phosphinate	[49], 2002

polyolefins (see Table 3) and especially polypropylene. The reactive type organophosphorus flame retardants, which have attracted more attention in flame retardant chemistry, can be broadly divided into three categories: (a) simple reactive phosphate monomers; (b) linear polyphosphazenes; and (c) aromatic cyclic phosphazenes [31]. However, none of those are used commercially.

The need to have ‘multi-element’ formulations in order to achieve acceptable levels of flame retardancy is illustrated by the work of Istomina et al. [52] who studied the lowering of PE and PP combustibility by introduction of a phosphorus-, nitrogen-, halogen-containing flame-retarding system into the melt polymer. The basic characteristics of the modified PE and PP thermal decomposition were investigated, and LOI values in the range of 27.1–27.5% were obtained thus enabling the modified polyolefins to belong to the category of low-combustible polymers.

While the presence of nitrogen often enhances the flame retardant effect of phosphorus flame-retardants, among the inorganic elements, red phosphorus itself has been claimed to be effective in the absence of

nitrogen and/or halogen compounds [53]. Considerable interest was shown in red phosphorus after the discovery in 1965 of its effectiveness as a flame retardant for most polymeric materials [54]. Flame retardancy is optimized when the concentration of red phosphorus is increased to a level above which no further benefit is observed. The mechanism of flame retardant polypropylene containing microcapsulated red phosphorus has been investigated by Wu [55].

Red phosphorus has the following attractive features:

- (1) the relatively low concentrations required to achieve excellent flammability results in most polymers;
- (2) its stability during process; and
- (3) the negligible effect on the mechanical and electrical properties.

It is claimed to work by both free radical suppression in the vapour phase and char-forming in the condensed phase. Red phosphorus powder can be dust suppressed, stabilized and encapsulated to make it less ignitable and to suppress phosphine formation [49]. However, it has one major disadvantage and that is the derived filament/tapes are red–brown in colour due to the presence of the phosphorus. As a potential FR for use in fibres, its particulate nature is another large disadvantage, causing spinning difficulties and strength loss.

Understanding the role of phosphorus-containing flame retardants in polyolefin environments is key to developing effective systems and while mechanisms have been reviewed in several publications over the 1960–1980 period [56–58], little if any work has been published since. Phosphorus compounds tend to be less efficient in polymers such as polyolefins that do not readily char than in cellulosic materials, unless formulated well with selected char-forming additives. Ammonium polyphosphate (APP) is a very commonly used flame retardant in PP [59], often combined with cyclic urea–formaldehyde resins, hydroxyethylcyanurates or piperazine-base species [60–65], which usually demonstrate phosphorus–nitrogen synergism [66].

The literature mentions various physical modes of action for APP and some other phosphorus-based flame retardants, such as [67–70]:

- (i) the formation of polyphosphoric acid as a surface coating,
- (ii) the heat sink action of the vaporizing phosphorus compound,
- (iii) dilution of the combustible pyrolysates by a less combustible vapour and
- (iv) reduction of melt viscosity to favour a melt drip mode of flame extinction.

However, if a char-former is present, then the additional chemical effect of char promotion exists. This is particularly the case in more complex phosphorus compounds such as pentaerythritol-based phosphates [71], where the polyol present possesses a built in char-forming tendency. This kind of phosphorus-containing flame retardant is usually formulated as the combined acid and carbon source in intumescent systems for polypropylene [51]. An intumescent char-forming system usually acts by combined chemical and physical reaction to form a rigid voluminous foamed residue or char, which offers protection to the underlying substrate from further decomposition [72] and when present in polypropylene should attempt to offset the melt dripping tendency as well [51,72].

Such multi-component formulations are often developed empirically and, with regard to the processing temperature mentioned above, must have high decomposition temperatures of the phosphorus-containing acid source in excess of 260 °C if used in intumescent polypropylene systems. Ammonium polyphosphates [73] and diammonium pyrophosphate [74] have been used or proposed for use with pentaerythritol as intumescent systems for polypropylene, although the water solubility of diammonium pyrophosphate would be a major disadvantage in fibre and textile end-uses. LOI values as high as 25–27 have been claimed at optimum total concentrations of 10–15% w/w although these are still too high for fibre applications.

To understand how these systems might be effective at possibly lower concentrations, requires a greater understanding of the mechanisms operating. These are very complex and have only received close attention recently. Camino et al. [75] in Turin have significantly increased our understanding of the char-forming mechanism in ammonium polyphosphate and pentaerythritol and pentaerythritol diphosphate

systems during the last 20 years. Their results were interpreted in terms of deamination of APP and the release of polyphosphoric acid and ammonia. This former then forms a liquid medium in which phosphorylation of polyol hydroxyl groups occurs followed by cross-linking. The presence of polyphosphoric acid creates a liquid condition whose rheological behaviour determines the char expansion in the presence of a blowing agent such as melamine.

The degree of char expansion is a balance between the effects of the rates of gas/volatile evolution, the viscosity of the liquefied pyrolysis products and the transformation of the latter to solid char in an expanded form. The exact nature of the liquid phase is not well-defined, but will comprise molten pentaerythritol (mp = 185 °C) or other polyols if fusible, decomposing APP, phosphorylated polyols and polyphosphoric acid.

They also found that melamine as a blowing agent could create a continuous blowing action over the char-forming temperature range. Subsequent research showed that intumescent systems comprising melamine salts may decompose to melamine and the parent acid (e.g. melamine cyanurate), promote salt anion dehydration (e.g. melamine borate → melamine boric anhydride) or oligomerise via the salt anion (e.g. melamine phosphate → melamine pyrophosphate → melamine polyphosphate) [75]. Furthermore, reactive extrusion has been reported having been used to synthesize intumescent flame retardants (IFRs) and their master batches by reacting melamine phosphate (MP) and pentaerythritol (PER) [76,77]. The advantages of this technology are: (1) the pelletized IFRs with good flame retardancy have little influence on the mechanical properties of flame retarded material due to the good compatibility of IFRs with PP matrix and their capacities of forming fiber-like structure during processing; (2) the corresponding flame retardant composites also have good water resistance.

Generally, to achieve acceptable levels of flame retardancy and as mentioned above intumescent contents of 15–20% w/w are required which are too high for PP fibres although acceptable for bulk PP. For PP and indeed other fusible polymers like nylons 6 and 66, flame retardant property trends versus concentration are not linear but follows on 'S' shaped curve [78]. Unpublished work by Horrocks et al. [79] (see Fig. 1) suggests that adequate levels of flame

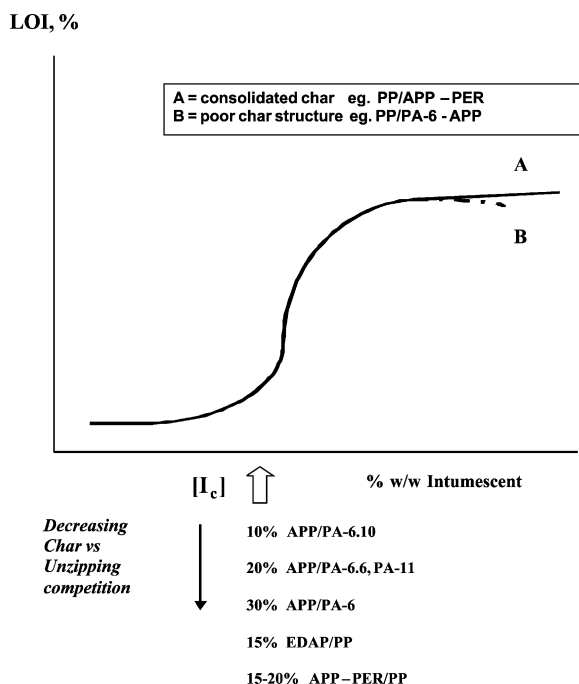


Fig. 1. Schematic trend of FR concentration versus LOI for a number of retardants constructed from various published sources [73,74,79]; APP is ammonium polyphosphate, PER is pentaerythritol and EDAP is ethylene diammonium phosphate.

retardancy occur only when a critical level of intumescent is present which in PP is about 15% w/w. It would appear that this coincides with the ability of the generating intumescent char nuclei to form a coherent network of char through the heated and melting PP matrix. This provides a char structure which prevents melt dripping and is flame retardant.

Horrocks et al. [79] also suggested that at I_c , the flame retardant present was promoting isolated domains of carbonaceous char of sufficient number and size to transform to an extended network of consolidated char. Thus an ‘islands-in-the-sea’ char geometry changes to a network of interlinked domains as schematically shown in Fig. 2. This model was also suggested by the earlier work of Bourbigot et al. [80] who had demonstrated the formation of domains of aromatising char in APP-PER intumescent systems. No attempt has been made to quantify or model this behaviour and therefore understand the flame retardant factors that determine critical char concentration I_c for a given FR–polymer combination. It is evident that any modelling would need to consider the initial

additive particle or domain size and concentration within the surrounding polymer matrix, its change in dimensions with temperature and time as intumescent char forms and the probability that these expanding domains will form a coherent network throughout the matrix. This will be the supportive char which prevents melt dripping, reduces the oxygen supply to the area of burning and reduces overall flammability. The identification of the critical concentration, I_c , would depend upon the flame retardant itself and its initial particle/domain size. Therefore, the objective in generating an appropriate intumescent system for use in polypropylene fibres will require that formation of such an extended and coherent char network is generated by lower retardant

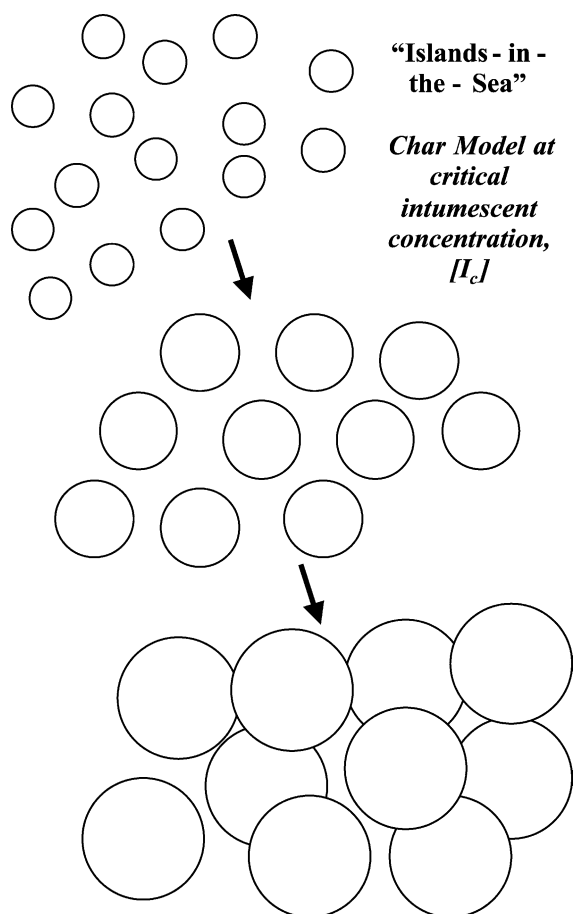


Fig. 2. Schematic representation of the generation of domains of carbonaceous char from a dispersed intumescent and their transformation to an extended network at I_c [79].

concentrations than currently used and preferably less than 10 w/w.

Examples of useful intumescent materials include ammonium polyphosphate (such as that available from Solutia (formerly Monsanto) as Phos-Chek P/40 and P/30), ethylenediamine phosphate (formerly manufactured by Albright and Wilson as Amgard NP and currently available from Unitex Chemical Corp., Greensboro, NC and Broadview Technologies, Newark, NJ), Spin Flam MF82 (Himont), and NH 1511 and NH 1197 (Great Lakes) and mixtures thereof. Very recently, Almeras et al. [81] have investigated the improvement of the fire performance of a polypropylene/ammonium polyphosphate/nylon 6 blend where the minor component, nylon 6 was the charring agent.

The increasing interest in APP-based flame retardants is demonstrated by the announcement that Clariant has expanded production capacity for its Exolit® AP flame retardant products at its plant in Knapsack, Germany. This comes in response to the success of Exolit and increased market demand for halogen-free flame retardants in Europe. These and other APP-based products also have a low smoke density and do not emit corrosive gases in a fire and it has now become possible to use these flame retardant systems in polyolefins [82].

However, none of these commercial products will have application in PP fibre applications unless they can be rendered more efficient at lower concentrations. In addressing this requirement, two possible routes exist that have received recent interest, namely the sensitisation by heavy metal ions and the synergistic activity of silicon-containing species.

3.1.1. Effect of heavy metal ions

Work has been published recently that has demonstrated that the presence of manganese dioxide with ammonium polyphosphate appeared to improve the performance of the flame retardant within polyamide 6 [83] and that an interaction between the manganese dioxide and the ammonium polyphosphate was occurring [84]. More recently, Lewin and Endo [85,86] have published work, which has investigated the addition of small percentages of heavy metal salts to ammonium polyphosphate in combination with pentaerythritol (PER) in polypropylene. It was observed here that the metal salt

addition appears to increase its flame retardant performance of the ammonium polyphosphate as part of a flame retardant system with PER in a polypropylene matrix. The loading required was quite specific and an optimum point was observed for each metal salt at loadings of metal ion/salt of less than 1.5% w/w. Loadings above the optimum reduced resulted in a drop off in the performance in the flame retardant as determined by LOI. Table 4 lists the optimum LOI values achieved at respective metal salt concentrations for zinc and manganese ions which showed the greatest efficiency in improving flame retardancy of the various heavy metal salts studied. It is interesting to note that anion type has a minimal effect when present with a given cation and that cation presence can raise LOI by 4–5 LOI units and often enabled UL94 V-0 ratings to be achieved against a rating of V-2 for the metal ion-free formulation (LOI = 26.5, see Table 4).

Proposed mechanisms of APP-PER- M^{n+} combinations were explained in terms of M^{n+} -accelerated phosphorylation of PER and –OH groups formed on PP molecules following M^{n+} oxidation in parallel with cross-linking. It was also suggested that the improved performance may be due to partial cross-linking (effectively increasing the degree of polymerisation) and increased stability of the ammonium polyphosphate thus reducing the volatility of the phosphorus oxides during pyrolysis and making more phosphorus available for phosphorylation and char formation. In the presence of a polypropylene matrix, this cross-linking will also increase the viscosity of the melt thus reducing the rate of flow to the flaming surface and improve the barrier effect of the char. However, at higher M^{n+} levels, excessive APP

Table 4
Optimal LOI and concentrations of heavy metal ions in APP–PER–PP combinations [85,86]

Salt	Metal ion concentration (%w/w)	Maximum LOI
None	None	26.5
Manganese acetate	0.45	31.0
Manganese sulphate	0.33	32.0
Zinc acetate	0.45	30.5
Zinc sulphate	0.45	31.5
Zinc borate	0.41	32.0

cross-linking occurs with accompanying lower levels of PER phosphorylation and hence reduced char. This hypothesis explains why an optimum level of M^{n+} exists for maximum FR effect as indicated in Table 4.

In a separate but not unrelated study, Marosi et al. [87] have shown that while APP alone in PP does not enable a UL94 V-0 pass to be achieved, with the addition of pentaerythritol (PER) and especially zinc borate at 1.5% level (in the presence of 18% w/w APP and 7% w/w PER) a pass was achieved. The role of the zinc and or phosphate present was not, however, commented upon.

Very recently, Davies et al. [88] have demonstrated that the sensitisation of APP in terms of a reduction in its thermal decomposition temperature occurs in the presence of certain metal ions and that this effect too is greatest at a low concentration of metal ion similar in magnitude to those observed by Lewin and Endo. Clearly, whatever the mechanism, there is the interesting observation that presence of low concentrations of selected metal ions can enhance flame retardant performance and this too could have ramifications for developing more efficient systems for use in fibre grade PP.

3.1.2. Effect of silicon-containing species (see also Section 3.3)

Increased effectiveness of APP-based, intumescent formulations has been claimed by Marosi et al. [89], who show that the encapsulation of both ammonium polyphosphate (21% w/w) and pentaerythritol (PER) (7% w/w) in polypropylene with a borosiloxane polymer at 1–5% w/w presence, enhances fire performance. Reduction in the peak heat release rate and onset of heat release during cone calorimetric exposure is explained by the formation of an organic precursor of an eventual ceramic protective layer to the underlying polymer [90]. In essence, the silicon-containing polymer binds together the APP and PER particles prior to forming a ceramic char at higher temperatures; however, the binding effect is still inadequate to prevent melt dripping and so UL94 V-0 ratings are still not possible. While, the above additive concentrations are too high for possible fibre applications, at even higher concentrations (~34% w/w) including 9.7% w/w borosiloxane polymer, LOI values as high as 33.5 have been achieved [91].

The role of silicon-containing species as possible synergists with APP and similar flame retardants is further demonstrated by the observation that silicotungstic acid ($\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 26\text{H}_2\text{O}$) may be used as a catalyst or synergist in polypropylene (PP) flame-retarded by the intumescent flame-retardants. The results have showed a suitable amount of silicotungstic acid can introduce synergistic effects to the IFR and PP blends resulting in the increase of the LOI value and the thermal stability at high temperature and the promotion of charred structure formation [92,93].

3.2. Halogen-containing flame retardants

Various formulations for the flame retardancy of polypropylene consisting of halogen compounds have been developed over the years. The effectiveness of halogen compounds depends on the ease of liberation of the halogen [94]. The nature of the group to which the halogen atom is attached is very important because it determines the carbon–halogen ratio and carbon–halogen bond energy and hence the amount of halogen released during burning. In general, aliphatic or alicyclic halogen compounds are more effective than aromatic halogen compounds, due to the lower carbon–halogen bond energies, and hence relatively easier halogen-release. The thermal degradation mechanism which take place in the polymer matrix based on halogen fire retardants have been reviewed and discussed by Camino et al. [95] in 1991.

Brominated compounds are particularly effective as is demonstrated in two recent reviews [96,97]. However, many halogen-containing agents also contain other elements such as phosphorus, boron and nitrogen. Examples of halogenated flame retardants recommended for use in bulk polypropylene include decabromodiphenyl oxide (DBDPO), dodecachloropentacyclo octadeca-7,15 diene, bis(2,3-dibromopropyl ether of tetrabromobisphenol A), tris(tribromoneopentyl) phosphate, tris-2,3-dibromopropyl-isocyanurate, ethylene bis-dibromobornane dicarboximide and stabilised hexabromocyclododecane; all of these are available as commercial additives [96,97]. Unfortunately, in order to achieve UL94 V-0 passes in polypropylene, the bromine-only containing examples above should be present at 30–40% levels in the absence of synergists such as antimony III oxide. Some copolymers and reactive

monomers are also available for use in addition polymers like PP (as GPP-36 or 39 from Great Lakes Chemical Co.,) and pentabromobenzyl acrylate (as FR-1025M from Dead Sea bromine Group) are examples. Such reactive species, even if they can confer acceptable levels of flame retardancy, will usually reduce potential fibre properties and so would not be prime candidates for textile applications. While the manufacturers claim [98] that this may not be a problem with dibromostyrene-grafted polypropylene retardant types, the 35–37% bromine level in the GPP-36 product, for example, means that they must be added to PP homopolymer in relatively high concentrations to achieve acceptable flame retardancy. These high levels may also adversely affect UV stability of the resulting fibres. The GPP-39 variant, however, has a higher bromine concentration at 39% and this is claimed to be able to achieve V-2 levels of flame retardancy in PP fibre applications [98]. In fact, most of the above formulations mentioned are designed to achieve V-2 (melt dripping) passes in either bulk or, where applicable, fibre applications [96].

While large concentrations, i.e. 40% (w/w) of chloride-containing and 20% (w/w) for bromide-containing compounds are usually required to achieve reasonable levels of flame retardancy when they are used alone [99], the use of synergists can dramatically reduce these concentrations. Typical synergists are antimony, phosphorus, nitrogen, zinc and tin-containing compounds, of which antimony, often as antimony III oxide, is the most common one. Halogen synergists assist in trapping the released halogen and preventing its escape from the flame zone. Thus Sb–halogen systems are considered to act via formulation of SbX_3 [100]. Sb–Br and indeed Sn–Br synergist formulations are claimed to be effective at concentrations in the 5–10% w/w range and so may be used in PP fibres; e.g. Clariant's Sandoflam 5070, 5071 and 5072 have been marketed based on such products, although they are no longer available [101]. It has been reported that PP may be rendered flame-retardant using 0.25 phr dibutyltin maleate (or dibutyltin glutacolate), 2 phr 1,2,5,6,9,10-hexabromocyclododecane, and 4 phr Sb_2O_3 [102]; these low levels are acceptable for use in fibres. In addition, Finck has used a brominated organic FR, a phosphite and an organotin derivative for PP fibres; typical formulations contain

32% Br, 1% P and 1.5% Sn and the flame retardancy was retained through numerous launderings [103].

Orlando and Lavalley [104] patented the use of a broad range of bromobiphenols for use as fire-retardants in numerous polymeric compositions in 1976. The use of pentabromodiphenyl ether in laminate structures was disclosed early in 1975 [105]. A broad range of halogenated hydrocarbons, including decabromodiphenyl oxide in combination with other specific additives such as metal oxides, silicone gum and dibasic lead phthalates were defined for a flame-resistant insulation for an electrical conductor [106,107].

Astoa GmbH, Linz in Austria [4] has been producing flame retardant PP fibres based on halogen flame retardants for about 10 years. Despite the low halogen content (< 1.5%), there are increasing objections against halogenated flame retardants. This is not only because of the possible formation of corrosive hydrogen halide during fire and the formation of small amounts of ultra-toxic halogenated dibenzodioxines and dibenzofuranes, but also their negative interaction with certain UV/thermal stabilisers commonly used for generating acceptable service lifetimes in PP technical fabrics. The most efficient hindered amine stabilisers (HAS) are deactivated by the presence of acidic media and in the presence of brominated organic species may interact with thermally liberated hydrogen bromide acid [4,108].

Chlorinated paraffins have also been used as flame retardants for polypropylene. It was reported that standard chlorinated paraffins used with antimony oxide have successfully achieved a non-drip UL94, V-0 rated polypropylene compound [109]. Chlorez[®] and Hordaresin[®] [110] from Dover and Cereclor [111, 112] from ICI are commercially available chlorinated paraffins used in polypropylene. It is thought they act in the condensed phase and hence produce destabilization of polypropylene at low temperatures. This is a consequence of their dehydrohalogenation and formation of char precursors; released HCl will also act in the vapor phase.

While it is evident that few successful halogen-containing retardants have been commercially successful in polypropylene fibres, FMC Corporation originally marketed a halogen–phosphorus-containing retardant Reoflam FG-372 [113], which was transferred to the Dead Sea Bromine Group as FR-370

and FR-372. This comprises tris(tribromoneopentyl) phosphate, $[\text{CH}_2\text{Br}-\text{C}(\text{CH}_2\text{Br})_2\text{O}]_3 \text{PO}$ [95,96]. FR-370 is designed for bulk PP usage yielding UL94 V-2 performance while FR-372 is a purer form designed for incorporation into fibre grade polypropylenes. This molecule has a high bromine content (70% w/w), which coupled with a 3% phosphorus level ensures that it can be reasonably efficient as a flame retardant at low concentrations. It melts at 181 °C and starts to decompose with mass loss at 309 °C and so it may be melt-blended with polypropylene and is stable at normal extrusion temperatures. FR-372 is claimed to have minimal effect on extrusion behaviour and resulting fibre properties at levels of 3–5% sufficient to yield levels of flame retardancy sufficient for carpets, contract upholstery, office partitions, curtains and drapes and wall-coverings. A major characteristic, apart from the low levels present and the absence of the need for a synergist such as antimony III oxide, is its excellent UV stability and compatibility with HALS stabilisers.

3.3. Silicon-containing flame retardants

Considerable research has shown that the addition of relatively small amounts of silicon compounds, especially when added to intumescent formulations (see Section 3.1 [89–92]) to various polymeric materials can significantly improve their flame retardancy, through both char formation in the condensed phase and the trapping of active radicals in the vapour phase. Silicone-containing flame retardants are considered to be ‘environmentally friendly’ additives because their use is claimed to lead to a reduction in the harmful impact on environment [114–118]; little, if any, scientific evidence exists to substantiate this claim, however. Silicon–oxygen based polymers also have dielectric strength, thermal stability and low and non-corrosive smoke evolution. [105]. Silicone fluids have been widely used in the polymer processing industry as internal lubricants to reduce wear and improving mould release. Although silicones have been used previously as flame retardants, few have been reported to be effective enough to achieve a V-0 rating on the UL94 test for polypropylene [106,119–120]. It was shown that a silicone in conjunction with a metal soap can

provide a degree of flame retardancy for certain thermoplastics [121]. Lower viscosity silicones in combination with a metal stearate show some flame retardancy, but tend to give flaming drips.

The incorporation of silicones often produces slight intumescent char formation in polypropylene, while the polymer itself burns without a char [122]; this solid phase reaction appears to be the main mode for the silicone flame retardant action. It is concluded that a combination of a linear polydimethylsilicone and other optional components can effectively flame retard polypropylene. A now-discontinued commercially available example of silicone flame retardant system for polypropylene is SFR100, a General Electric product, which alone contains no antimony or halogen and provides V-0 ratings at the level of 25% (w/w) [123]. It is a transparent, viscous silicone polymer and is usually used with one or more co-additives, such as ammonium polyphosphate and pentaerythritol that act as synergist both in polypropylene and in the SFR100 resin. The additives also help to mix the two polymers together and aid char formation and both the LOI value and UL94 flame retardant performance are claimed to be improved due to the char formation. These observations have been substantiated by work in our own laboratories in attempts to produce synergistic Si–P retardant combinations at lower concentrations more suitable for fibre applications [79].

Other advantages of the silicone-based additives are that they can improve the impact resistance dramatically and add the conventional silicone properties of improved mouldability, processibility, gloss and electric insulating properties. These attributes are rarely required in fibre end-uses, however.

3.4. Metal hydroxides and oxides (metal compounds)

The main interest for metal hydroxide flame retardants for polypropylene lies in their low toxicity, corrosion properties and emission of smoke during processing and burning. Examples are presented in Table 5 [121,124–129]. These compounds offer an attractive alternative to halogenated formulations for flame-retarding polypropylene. These metal hydroxides decompose endothermically and release water during burning and thus reduce the heat and temperature from the substrate. However, very high

Table 5
Metal compounds used in polypropylene

Chemical	Trade name and/or formulation	Reference and date
Aluminum trihydroxide or alumina trihydrate	Al(OH) ₃	[124], 1989; [125], 1989; [121], 1990
Magnesium carbonate	MgCO ₃	[121], 1990
Magnesium hydroxide	Mg(OH) ₂	[126], 2001
Zinc borates	Firebrake ZB	[127], 2002
	Firebrake RTM. ZB	[128], 1999
	2ZnO·3B ₂ O ₃ ·3.5H ₂ O	
	Firebrake 415	
	4ZnO·B ₂ O ₃ ·H ₂ O	
Calcium borate	Firebreak 500	
	2ZnO·3B ₂ O ₃	[129], 1996

metal hydroxide concentrations are usually required to achieve an acceptable degree of flame retardancy and tend to be poor in mechanical strength [130]. They are, therefore, unsuitable by themselves for incorporation into PP fibres.

Typical metal hydroxide flame retardants are Al(OH)₃ and Mg(OH)₂. Aluminum trihydrate and basic magnesium carbonate are known to have a decomposition temperature in the range of 180–340 °C, with a peak at about 320 °C. Basic magnesium carbonate has a peak decomposition temperature at about 410 °C. Of these three components and relative to each other, magnesium hydroxide is the most endothermic upon burning, basic magnesium carbonate the least and aluminum trihydrate is between the other two. Among the aluminium compounds, hydrated alumina is the most widely used one [131, 132]. Apart from the dilution of the potential fuels in the flame zone, its retardant activity is a consequence of the endothermicity of this dehydration.

Other metal oxides, such as tin oxide (SnO₂) and antimony trioxide have been discussed above because of their roles as synergists with halogen-contained flame retardants to enhance the fire performance of polypropylene [133–137]. Again, a major disadvantage lies in the high loadings required to achieve optimal level of flame retardancy, their high melting points and their difficulty of mixing with the base. Organo-antimony compounds, however, generally have low melting points and also been reported to be effective flame retardants for polypropylene [7].

While flame retardant action in the vapour phase for Sb₂O₃/halogen flame retardant polypropylene [138], organotin compounds work both as free radical inhibitors and as char-former, i.e. both in vapour and condensed phase [139].

3.5. Nanocomposites

While polymer–clay nanocomposites were first reported by Blumstein early in 1961 [140] and their improved thermal stability of a polymer-layered-silicate nanocomposite that combined poly(methyl methacrylate) (PMMA) and montmorillonite clay was reported early in 1965 also by Blumstein [141], their improved thermal stabilities were not studied further until the middle 1990s in both a polydimethylsiloxane–clay [142] and in a polyimide–clay nanocomposite [143]. Subsequent studies suggested that presence of nanoclays can improve the flammability properties relative to pure polymer matrices; for instance characterization of the flammability properties of a variety of polymer–clay nanocomposites, under fire-like conditions, using the Cone Calorimeter [144] has revealed improved flammability properties for many different types of polymer–clay nanocomposites. As a consequence, during the last six years or so, nanocomposites have been considered to be a new class of flame retardant system for polymers.

In particular, organic–inorganic nanocomposites, comprising organically modified clay dispersed in selected polymer matrices have attracted considerable attention with the advantage that they are efficient at concentrations of 5% w/w or less [145–149]. Several kinds of nanocompounds can be used to enhance the flame retardancy of polymers in general and polypropylene specifically, such as modified montmorillonites [150], TiO₂ [151], Sb₂O₃ [152] and boroxosiloxanes [89,153]. Of these all, the sodium cation exchanged montmorillonite (e.g. Na⁺ grade from Southern Clays Inc.) is the most common one because of its low price. However, to permit their introduction into and dispersion within an organic polymer, these normal sodium cations, found in montmorillonite, a classic aluminosilicate material, must be replaced by cations that are sufficiently organophilic. This usually requires the use of an ammonium or phosphonium salt that contains at least one alkyl chain which is 14 or 16

Table 6
Typical functional group cations used for nanoclay modification

Functionalising groups cations	Reference and date
Alkyl ammonium	[155], 2001
Hexadecyltrimethylammonium (HDTMA)	[156], 2002
Octadecylammonium	[157], 2002
Trimethyloctadecyl, quaternary ammonium chloride, trimethyldodecyl, quaternary ammonium chloride, trimethyltallow, quaternary ammonium chloride	[158], 2001
polyoxypropylene diamines of the type α,ω - $[\text{NH}_3\text{CHCH}_3\text{CH}_2\text{OCH}_2\text{CHCH}_3]_x\text{NH}_3^+$	[159], 2002

carbons in length; the other substituents on the ‘onium’ salt may be freely chosen in order to enhance some particular property of the nanocomposite [154]. Table 6 [155–159] lists a number of examples.

Typical nanocomposites are usually prepared by a blending process or by bulk polymerisation and they may exist in either an intercalated form, in which interlaminar contact is maintained between the aluminosilicate layers, or in an exfoliated form, in which such registry is lost and the layers are completely delaminated by the incoming material and hence result with the silicate layers fully dispersed throughout the matrix [160]. Investigations have shown that the largest increases in mechanical properties are obtained in exfoliated nanocomposite forms although there is some evidence that the intercalated materials show the best fire performance [161]. PP nanocomposite polymers to date are melt-blended and have an exfoliated structure (see Table 7, Refs. [162–166]).

Gilman and co-workers [167] have demonstrated that bulk samples of polypropylene nanocomposites

Table 7
Successfully synthesised polypropylene-nanocomposites

Successful PP-nanocomposites	Reference and date
PP/montmorillonite	[162], 2003
PP/sodium bentonite	[163], 2002
PP/silicate	[164], 2002
PP/calcium carbonate	[165], 2002
PP/boroxosiloxanes	[166], 2002

Table 8
Cone calorimeter data from selected polymer nanocomposites [167, 168]

Sample	Residue yield %	Peak HRR (kw m ⁻²)
Nylon 6	1	1010
Nylon 6-silicate 2%, delaminated	3	686
Nylon 6-silicate 5%, delaminated	6	378
PP	0	1525
PP-silicate 2%, intercalated	5	450
PP-silicate 4%, intercalated	–	305

Heat flux: 35 kW/m², H_c : heat of combustion, peak heat release rate, mass loss rate and specific extinction area SEA data, measured at 35 kW/m², are reproducible to within $\pm 10\%$. The carbon monoxide and heat of combustion data are reproducible to within $\pm 15\%$.

show reduced heat release properties during cone calorimetric experiments (see Table 8). Furthermore, Gilman suggests that the source of the improved flammability properties of nanocomposite materials is due to differences in condensed phase decomposition processes and not to a gas phase effect [168]. For comparison, the flammability properties of various PP nanocomposites in Tables 8a and b show a 70–80% reduction in cone calorimetric peak heat release rates, HRR, relative to the pure polymer for the with only a mass fraction of 2 or 4% clay, respectively [167,168].

The prevalent hypothesis of montmorillonite nanocomposite FR activity is based on gasification and precipitation of montmorillonite [169]; it is considered that the polymer is gasified or burned away and the montmorillonite foils remain and accumulate or precipitate at the surface thereby providing a barrier to oxygen diffusion into the polymer and of volatiles out. Lewin [170] has suggested that the enrichment in montmorillonite concentration at the surface is due to the migration or diffusion of the montmorillonite to it mainly driven by the low surface free energy of the montmorillonite. However, in actual fact, clays have higher surface energies than most organic polymers and so Lewin’s hypothesis would appear to be flawed in this respect [171] although there is clear evidence that migration to the surface of the burning polymer does occur [169, 172]. This proposed enrichment would occur above the glass transition temperature and would be temperature dependent.

Similarly, the mechanism of aluminosilicates as fire retardants is proposed to be the formation of a locally high concentration of the aluminosilicate on the surface of the degrading polymer where it may function as a barrier both to mass transfer from the bulk of the underlying polymer and to the flame transfer to the underlying polymer [173,174] and hence affect the ignition time, ignition temperature, rate of heat release and other flammability characteristics. Recent research has suggested that the presence of iron, substituted for the aluminum or silicon atoms in the clay, can act as a radical trap and hence slow down the rate of combustion [175].

Some nanocomposite polypropylene fibres comprising TiO₂ [176], silver [177] and ceramic and zeolite nanoparticles [178] have been reported, but none of them relate to the possible enhancement of flame retardancy.

Research to date indicates that while nanoclays present in PP and other polymers slow down burning and provide evidence of char-enhancement, they do not reduce ignition tendency or reduce after-flaming properties. Thus, if they are to be successful will require to act with other flame retardants, hopefully at reduced concentration with respect to those when used alone. Nanoclays have also been used together with an IFR additive system. Marosi et al. [89,153] used boroxosiloxanes combined with an IFR additive system, in polypropylene in 2002. This combination is claimed to yield UL94 V-0 ratings at a boroxosiloxane:clay ratio of 10:1 for a Na⁺ grade montmorillonite clay (Southern Clays Inc.) present at only 1.5% w/w. The potential of this for fibre end-uses is interesting. While no commercial nanocomposite PP has been developed, nanoclay manufacturer Nanocor Inc., and compounder Gitto Global Corp. (Lunenburg, MA, USA) have claimed very recently that they are going to expand their joint programme to develop flame-resistant polyolefins by using nanotechnology [179].

3.6. Other methods

3.6.1. Grafting and coating

Grafting and coating techniques have also been used for flame-retarding polypropylene. Coating technology is an economical and effective way to modify the surface of particles and fibres. Usually 5% of the total weight contributes to the coating. It

has been reported recently [180] the ‘masking’ or encapsulating APP with a coating can help significantly reduce the water sensitivity and adjust the polarity and hence improve the compatibility during extrusion. A number of research papers using grafting techniques to impart flame retardancy of polypropylene and other polymers have been published [181–188]. During the period 1966–1977, Livshits and Needles [189,190] mentioned grafting as a novel approach to improve the flame resistance of polymers.

Grafting has reported been used in both modifying the surface and/or bulk of the polymer to enhance the flame retardancy and improving the compatibility of the polymer with additive flame retardants during process. Zhang et al. [191–193] have discovered that surface grafting by electron-beam irradiation can significantly improve the flame retardancy of EVA copolymer, polyethylene and polypropylene. The fire performance of polypropylene grafted with acrylamide (AAm) is much better than that grafted with acrylic acid (AA) and methacrylic acid (MAA). They also found that saponification after grafting can promote char formation and further enhance the flame retardancy.

Very recently, Ma et al. [194] investigated the properties and compatibility of IFR and α -methacrylic acid grafted polypropylene (PP-g-MAA). The results showed that PP-g-MAA was a true coupling agent for IFR/PP blends, but it did not change the flame retardancy. The effect of polypropylene grafting with acrylic acid, PP-g-AA (FPP), on thermal degradation, and limiting oxygen index of Al(OH)₃/PP composites were also investigated [195]. The presence of an interfacial interaction between FPP and Al(OH)₃ was responsible for the increased limiting oxygen index values of composites.

Ferry et al. [196] have found the incorporation of a grafted brominated monomer in glass fibre-reinforced polypropylene to improve the fire resistance. They found the monomer can react either by grafting onto the polymer matrix or onto the glass fibres or by polymerizing around the Sb₂O₃ particles. It was demonstrated that improvement of the fire properties of the composites has been achieved to the detriment of mechanical properties which are strongly affected by the presence of the brominated polyacrylate.

Table 9
Polypropylene fibre NFPA 701 1966 burn test [198]

Additive	Weight loss (%)	Drip burn time (s)	Rating
None	34	97	Fail
2% DBDPO	10	5	Fail
4% DBDPO	7	0.8	Pass
1.0% Flamestab NOR 116	29	0.5	Pass
1% DBDPO + 0.5% Flamestab NOR 116	4	0	Pass

In 1994, acrylic acid (AAc) was grafted onto a polypropylene backbone by a mechano-chemical graft copolymerization reaction initiated by benzoyl peroxide in a twin-screw extruder [197]. Although the flammability of the PP/FR blends was reduced by the addition of the FR, the tensile strength and impact strength were also decreased, while for PP-*g*-AAc/FR blends, the LOI, tensile strength, impact strength, and Young's modulus all increased because of the AAc grafting modification.

3.6.2. Hindered amine light stabilisers

Very recently Ciba company claimed their HAS product, Flamstab NOR 116, requires only a 1–1.5% to confer some degree of flame retardancy to PP fibres and may be used in the presence of brominated compounds like decabromodiphenyl oxide. It is claimed that Flamestab NOR 116 can replace antimony trioxide as synergist for halogen and non-halogen-containing flame retardants and its low level additive can provide better processability, lower density and improved physical and mechanical properties [198]. Table 9 shows its effectiveness alone and with decabromodiphenyl oxide. The obvious synergism between the HAS and bromine-containing species are self-evident and demonstrate effectiveness at relatively low total additive levels. At present, there is no information on the possible mechanisms involved.

4. Conclusions

It is evident that apart from antimony–halogen or in some cases, tin–halogen formulations only one

single flame retardant system, tris(tribromoneopentyl) phosphate, is presently effective in polypropylene when required for fibre end-uses. The recent development of the Ciba hindered amine NOR 116 compound can produce marginal levels of flame retardancy when used alone but also may be used in conjunction with halogen-containing systems at reduced concentration and in the absence of the additional presence of antimony oxide synergist. Such a combination has the value of being perceived to be more environmentally acceptable while technically reducing both the total FR presence and possible negative effects on UV stabilizer behaviour. Presently, the use of phosphorus-based, halogen-free flame retardants in PP fibres is prevented by the need to have at least 15–20% additive presence (see Fig. 1). Since the latter are char-promoting while all halogen-based systems are essentially non-char-forming in polypropylene, the way forward for a halogen-free, char-forming flame retardant conferring acceptable levels of retardancy at additive levels <10% (w/w) will require either completely new FR chemistry or the development of a suitably synergistic combination based on the understanding reviewed above.

References

- [1] Ahmed M. Polypropylene fibers—science and technology. Amsterdam: Elsevier; 1982. p. 10–30.
- [2] O'Day PT. The US manufactured fibre and textile industry. In: 39th International Man-Made Fibres Congress, Dornbirn, Austria, Paper 3, 13–15 Sept. Dornbirn: Austrian Chemical Fibres Institute; 2000.
- [3] Freed W. Polyolefins—major textile market outlook. Chem Fibers Int 2001;51(1):42.
- [4] Gleixner G. Flame retardant PP fibres-lateat developments. Chem Fibers Int 2001;51:422–4.
- [5] Natta G. Italian Patent 1954;53512. Cited in reference 1
- [6] Moncrieff RW. Manmade fibres, 5th ed. London: Newnes–Butterworth; 1967. p. 609.
- [7] Tankard CJ. Flame retardant systems for polypropylene. MPhil Thesis, University of Manchester, Manchester, UK; 1995.
- [8] Demain A. Polypropylene fibres. ATOFINA Res 2002;18(2): 210.
- [9] Wishman M, Hagler GE. Handbook of fire science and technology. Fibre chemistry, vol. 5. NewYork: Marcel Dekker Inc.; 1985. p. 382.

- [10] Allen NS. Degradation and stability of polyolefins. London: Applied Science Publishers; 1983. Chapter 1.
- [11] Einsele U, Koch W, Herlinger H. Investigations into the development of heat when textiles burn in air. *Melliand Textilberichte* 1984;65(3):200–6.
- [12] Gurniak U, Kohlhaas O. The effect of backing materials on the combustion behaviour of tufted carpets. *Melliand Textilberichte* 1993;74:632–3.
- [13] Ballice L. Classification of volatile products evolved during temperature-programmed co-pyrolysis of low-density polyethylene (LDPE) with polypropylene (PP). *Fuel* 2002;81(9):1233–40.
- [14] Ballice L, Reimerta R. Classification of volatile products from the temperature-programmed pyrolysis of polypropylene (PP), atactic-polypropylene (APP) and thermogravimetrically derived kinetics of pyrolysis. *Chem Engng Process* 2002;41(4):289–96.
- [15] Ding W, Liang J, Anderson LL. Thermal and catalytic degradation of high-density polyethylene and commingled post-consumer plastic waste. *Fuel Process Technol* 1997;51:47.
- [16] Ochoa R, Woert HV, Lee WH, Subramanian R, Kugler E, Eklund PC. Catalytic degradation of medium density polyethylene over silica–alumina supports. *Fuel Process Technol* 1996;49:119.
- [17] Jha NK, Misra AC, Bajai P. Flame-retardant additives for polypropylene. *J Macromol Sci Chem* 1984;24(1):69–116.
- [18] Loan LD, Winslow FH. In: Hawkins WL, editor. *Polymer stability*. New York: Wiley; 1972. Chapter 3.
- [19] Pearce EM, Khanna YP, Raucher D. *Thermal characterization of polymeric materials*. London: Academic Press; 1981. Chapter 8.
- [20] Chaigneau M, Le Moan G. Toxicity of products resulting from the cold combustion of polypropylene. *Comptes Rendus des Seances de l'Academie des Sciences. Serie III. Sciences de la Vie* 1982;295(3):223–5.
- [21] Horrocks AR. Flame-retardant finishes and finishing. In: Heywood DH, editor. *Textile finishing*. Bradford: Society of Dyers and Colourists; 2003. p. 214–50.
- [22] Christian SD. Suggested flammability performance requirements for the contents of public buildings. *J Soc Dyers Colour* 1983;99:78–85.
- [23] The Upholstered Furniture Safety Regulations. SI 725: 1980. HMSO, London, UK
- [24] Hirschler MM. Fire hazard and toxic potency of the smoke from burning materials. *J Fire Sci* 1987;5(5):289–307.
- [25] Grand AF. Effect of experimental conditions on the evolution of combustion products using a modified University of Pittsburgh toxicity test apparatus. *J Fire Sci* 1985;3(4):280–304.
- [26] Shemwell BE, Levendis YA. Particulates generated from combustion of polymers (plastics). *J Air Waste Mgmt Assoc* 2000;50(1):94–102.
- [27] Riga A, Collins R, Mlachak G. Oxidative behavior of polymers by thermo-gravimetric analysis, differential thermal analysis and pressure differential scanning calorimetry. *Thermochim Acta* 1998;324(1–2):135–49.
- [28] Philippart JL, Gardette JL. Thermo-oxidation of isotactic polypropylene in $^{32}\text{O}_2$ – $^{36}\text{O}_2$: comparison of the mechanisms of thermo- and photo-oxidation. *Polym Degrad Stab* 2001;73(1):185–7.
- [29] Blatz PS. French Patent 1964;1,355,064. Cited in: Lyons JW. *The chemistry and uses of fire retardants*, Wiley–Interscience, New York, London, Sydney, Toronto; 1970
- [30] Zhang S. PhD Thesis. Flame retardancy of polymers modified by electron-beam irradiated grafting, Beijing Institute of Technology, Beijing, China; 1996
- [31] Lu S-Y, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. *Prog Polym Sci* 2002;27(8):1661–712.
- [32] Listner GJ. Fire retardant polymers. US Patent 3,650,300; 1972
- [33] Murray RW, Savides C. Tertiary phosphine oxide–ammonium polyphosphate combinations as flame-retardants for propylene polymers. US Patent 3,663,502; 1972
- [34] Versnel J. Fire retardant polypropylene compositions containing a halogenated flame retardant and a phosphate adjuvant. US Patent 3,893,970; 1975
- [35] Wolf R. Phosphonitrilic esters. US Patent 3,894,121; 1975
- [36] Nachbur H, Maeder A. Phosphonopropionic acid amide derivatives. US Patent 3,800,010; 1974
- [37] Golborn P, Duffy JJ. Dialkyl aromatic amidomethyl phosphonates. US Patent 3,803,269; 1974
- [38] Golborn P, Duffy JJ. Dialkyl alkyl and aromatic sulfonamidomethyl phosphonates. US Patent 3,870,771; 1975
- [39] Golborn P, Duffy JJ. Phosphorus containing amides flame retardants. US Patent 3,976,620; 1976
- [40] Anderson AL. Fire retardant polymers containing thermally stable cyclic phosphate esters. US Patent 3,849,368; 1974
- [41] Den Otter MJAM, Van Geenen AA, Te Nijenhuis A. Phosphonate-isocyanurates. US Patent 4,085,283; 1978
- [42] Brady DG. Nonburning, nondripping, char-forming, polypropylene composition. US patent 3,936,416; 1976
- [43] Login RB. Phosphorus-containing polyester and size compositions. US Patent 4,098,741; 1978
- [44] Landoni G, Neri C. Flame-resistant polyolefinic fibres and films. US Patent 5,447,991; 1995
- [45] Bertelli G, Roma P, Locatelli R. Self-extinguishing polymeric compositions. US Patent 4,193,945; 1980
- [46] Miller GT. Durably flame proofed textile materials. US Patent 4,063,884; 1977
- [47] Miller GT. Durably flame proofed textile materials. US Patent 4,024,308; 1977
- [48] Hancock H. Fire retardant polyolefins. US Patent 4,139,476; 1979
- [49] Nass B, Schacker O, Schlosser E, Wanzke W. Phosphorus containing flame retardants-containing and material properties. In: *Flame retardants 2002*. London: Interscience Communications; 2002. p. 63–74.
- [50] Boyer NE. Flame retardant polymers with 1,3,5-triazines having halo- and halo-aryl substitutes. US Patent 4,104,250; 1978

- [51] Camino G, Delobel R. Intumescence. In: Grand AF, Wilkie CA, editors. Fire retardancy of polymeric materials. New York: Marcel Dekker; 2000. p. 217–43.
- [52] Istomina EI, Zubkova NS, Butylkina NG, Gordeeva SA, Tjuganova MA, Khalturinskaya NA. Lowering of polyethylene (PE) and polypropylene (PP) combustibility. Fire Safety J 1996;26(2):185.
- [53] Peters EN. Flame-retardant thermoplastics. I. Polyethylene-red phosphorus. J Appl Polym Sci 1979;24(6):1457–64.
- [54] Broadbent JRA, Hirschler MM. Red phosphorus as a flame retardant for a thermoplastic nitrogen-containing polymer. Eur Polym J 1984;20(11):1087–93.
- [55] Wu Q, Lü J, Qu B. Preparation and characterization of microcapsulated red phosphorus and its flame-retardant mechanism in halogen-free flame retardant polyolefins. Polym Int 2003;52(8):1326–31.
- [56] Weil ED. Flame retardants, 3rd ed. In: Kirk–Othmer Encyclopedia of Chemical Technology, vol. 10. New York: Wiley; 1980. p. 396–419.
- [57] Granzow A, Savides C. Flame retardancy of polypropylene and impact polystyrene: phosphonium bromide/ammonium polyphosphate system. J Appl Polym Sci 1980;25:2159–204.
- [58] Savides C, Granzow A, Cannelongo JF. Phosphine-based flame retardants for polypropylene. J Appl Polym Sci 1979; 23(9):2639–52.
- [59] Anna P, Marosi GY, Bourbigot S, Le Bras M, Delobel R. Intumescent flame retardant systems of modified rheology. Polym Degrad Stab 2002;77(2):243–7.
- [60] Chiu S-H, Wang W-K. Dynamic flame retardancy of polypropylene filled with ammonium polyphosphate, pentaerythritol and melamine additives. Polymer 1998;39(10): 1951–5.
- [61] Lewin M. Synergistic and catalytic effects in flame retardancy of polymeric materials. J Fire Sci 1999;17(1):3–19.
- [62] Landoni G, Fontani S, Cicchetti O. Self-extinguishing polymeric compositions. US Patent 4,336,182; 1982
- [63] Bertelli G, Locatelli R. Self-extinguishing polyolefin compositions. US Patent 4,420,577; 1983
- [64] Scarso L. Self-extinguishing polymeric products based on polyolefins. US Patent 4,727,102; 1988
- [65] Marciandi F. Self-extinguishing polymeric compositions. US Patent 4,198,49; 1980
- [66] Cullis CF, Hirschler MM, Tao QM. Studies of the effects of phosphorus–nitrogen–bromine systems on the combustion of some thermoplastic polymers. Eur Polym J 1991;27(3): 281–9.
- [67] Delobel R, Le Bras M, Ouassou N, Alistiqsa F. Thermal behaviour of ammonium polyphosphate–pentaerythritol and ammonium pyrophosphate–pentaerythritol intumescent additives in polypropylene formulations. J Fire Sci 1990;8: 85–108.
- [68] Delobel R, Ouassou N, Le Bras M, Leroy J-M. Fire retardance of polypropylene: action of diammonium pyrophosphate–pentaerythritol intumescent mixture. Polym Degrad Stab 1989;23:349–57.
- [69] Delobel R, Ouassou N, Le Bras M, Leroy J-M. Fire retardance of polypropylene: action of diammonium pyrophosphate–pentaerythritol intumescent mixture. Polym Degrad Stab 1989;23(4):349–57.
- [70] Brad DG, Moberly CW, Norell JR, Walters HC. Intumescents: a novel effective approach to flame retarding polypropylene. J Fire Retard Chem 1977;4:150–64.
- [71] Albright JA, Kmiec CJ. A novel class of halogenated phosphate fire retardants for use in polypropylene. Appl Polym Sci 1978;22(9):2451.
- [72] Berlin AA, Khalturinskii NA, Reshetnikov IS, Yablokova MYu. Some aspects of mechanical stability of intumescent chars. In: Le Bras M, Camino G, Bourbigot S, Delobel R, editors. Fire retardancy of polymers—the use of intumescence. London: Royal Society of Chemistry; 1998. p. 104–12.
- [73] Bourbigot S, Duquensne S, Leroy JM. Modeling of heat transfer of a polypropylene-based intumescent system during combustion. J Fire Sci 1999;17:42–56.
- [74] Delobel R, Le Bras M, Ouassou N. Fire retardance of polypropylene by diammonium pyrophosphate–pentaerythritol: spectroscopic characterization of the protective coatings. Polym Degrad Stab 1990;30(1):41–56.
- [75] Costa L, Camino G, Luda di Cortemiglia MP. Mechanism of thermal degradation of fire-retardant melamine salts. In: Nelson GL, editor. Fire and polymers. ACS Symposium Series, Washington: American Chemical Society; 1990. p. 211–38.
- [76] Chen Y, Liu Y, Wang Q, Yin H, Aelmans N, Kierkels R. Performance of intumescent flame retardant master batch synthesized through twin-screw reactively extruding technology: effect of component ratio. Polym Degrad Stab 2003; 81(2):215–24.
- [77] Wang Q, Chen YH, Liu Y, Yin H, Aelmans N, Kierkels R. Performance of intumescent flame retardant master batch synthesized through twin-screw reactively extruding technology: effect of carrier resin, polypropylene. Polym Int, submitted for publication
- [78] Levchik SV, Weil ED. Combustion and fire retardancy of aliphatic nylons. Polym Int 2000;49(10):1033–73.
- [79] Horrocks AR, Price D, Tankard C. Unpublished results. See also Tankard C. MPhil Thesis, University of Manchester; 1995
- [80] Bourbigot S, Le Bras M, Delobel R. Carbonization mechanisms resulting from intumescence association with the ammonium polyphosphate–pentaerythritol fire retardant system. Carbon 1993;31(8):1219–30.
- [81] Almeras X, Dabrowski F, Bras MLe, Poutch F, Bourbigot S, Marosi G, Anna P. Using polyamide-6 as charring agent in intumescent polypropylene formulations I. Effect of the compatibilising agent on the fire retardancy performance. Polym Degrad Stab 2002;77(2):305–13.
- [82] Anon, Clariant increases capacity for halogen-free flame retardants. Addit Polym 2002;2002(10):4.
- [83] Levchik SV, Levchik GF, Camino G, Costa L, Lesnikovich AI. Mechanism of action of phosphorus-based flame retardants in nylon 6. III. Ammonium polyphosphate/manganese dioxide. Fire Mater 1996;20:183–90.
- [84] Levchik GF, Levchik SV, Sachok PD, Selevich AF, Lyakhov AS, Lesnikovich AI. Thermal behaviour of ammonium

- polyphosphate–inorganic compound mixtures. Part 2. Manganese dioxide. *Thermochim Acta* 1995;257:117–25.
- [85] Lewin M, Endo M. Catalysis of intumescent flame retardancy of polypropylene by metallic compounds. In: Proceedings of the American Chemical Society Division of Polymeric Materials: Science and Engineering, Fall Meeting, August 20–24, Washington, DC, vol. 83.; 2000. p. 38–9.
- [86] Lewin M, Endo M. Catalysis of intumescent flame retardancy of polypropylene by metallic compounds. *Polym Adv Technol* 2003;14:3–11.
- [87] Marosi G, Anna P, Balogh I, Bertalan G, Tohl A, Maatong MA. Thermoanalytical study of nucleating effects in polypropylene composites. *J Therm Anal* 1997;48:717–26.
- [88] Davies PJ, Horrocks AR, Alderson A. Do heavy metal ions sensitise flame retardant activity in ammonium polyphosphate? In: Proceedings of 14th Annual BCC Conference, Recent Advances in Flame Retardant Polymeric Materials. Norwalk, CT: Business Communications Co.; 2003.
- [89] Marosi G, Anna P, Márton A, Bertalan G, Bóta A, Tóth A, Mohai M, Rácz I. Flame-retarded polyolefin systems of controlled interphase. *Polym Adv Technol* 2002;13:1103–11.
- [90] Marosi G, Márton A, Anna P, Bertalan G, Marosfői B, Szép A. Ceramic precursor in flame retardant systems. *Polym Degrad Stab* 2002;77(2):259–65.
- [91] Marosi G, Bertalan G, Balogh I, Tohi A. Silicone containing intumescent flame retardant systems for polyolefins. In: *Flame retardants 96*. London: Interscience Communications; 1996. p. 115–32.
- [92] Wang Q, Qu B. Synergistic effects of silicotungstic acid on intumescent flame-retardant polypropylene. *Polym Degrad Stab* 2001;74(2):255–61.
- [93] Xie R, Qu B. Synergistic effects of expandable graphite with some halogen-free flame retardants in polyolefin blends. *Polym Degrad Stab* 2001;71(3):375–80.
- [94] Lyons JW. The chemistry and uses of flame retardants. New York: Wiley–Interscience; 1970. Chapter 7, p. 289.
- [95] Camino G, Costa L, Luda di Cortemiglia MP. Overview of fire retardant mechanisms. *Polym Degrad Stab* 1991;33(2):131–54.
- [96] Georlette P, Simons J, Costa L. Halogen-containing flame retardant compounds. In: Grand AF, Wilkie CA, editors. *Fire retardancy of polymeric materials*. New York: Marcel Dekker; 2000. p. 245–84.
- [97] Georlette P. Applications of halogen flame retardants. In: Horrocks AR, Price D, editors. *Fire retardant materials*. Cambridge: Woodhead Publishing; 2001. p. 264–90.
- [98] Great Lakes. Technical information on flame retardants. <http://www.e1.greatlakes.com>
- [99] Pitts JJ. Antimony–halogen synergistic reactions in fire retardants. *J Fire Flamm* 1972;3:51–84.
- [100] Costa L, Camino G, di Cortemiglia MP. Effect of the metal on the mechanism of fire retardance in chloroparaffin–metal compound–polypropylene mixtures. *Polym Degrad Stab* 1986;14(2):113–23.
- [101] Bill R, Wolf R. Use of flame retardants on base polymers. *Selezione Tessile* 1986;7/8:31–5.
- [102] Hill GR, Needham DG. Flame-proofing additives and resins containing the same. US Patent 3,432,461; 1969
- [103] Finck HW, Tscheulin G. Novel flame retardant for polypropylene fibres. *Kunststoffe* 1981;71:320.
- [104] Orlando CM, Lavalley F. Fire-retardant polymeric compositions containing brominated biphenols. US Patent 3,989,531; 1976
- [105] Franz A, Stein W. Process for the manufacture of flame-resistant laminates. US Patent 3,922,459; 1975
- [106] Betts JE, Holub FF. Flame-resistant composition, and electrical product thereof. US Patent 4,123,586; 1978
- [107] MacKenzie JBT, Rothenberg S. Electric conductor product having a flame resistant insulation. US Patent 4,022,945; 1977
- [108] Sinturel C, Lemaire J, Gardette J-Luc. Photooxidation of fire retarded polypropylene. III. Mechanism of HAS inactivation. *Eur Polym J* 2000;36:1431–43.
- [109] Camino G. Mechanism of fire-retardancy in chloroparaffin–polymer mixtures. In: Grassie N, editor. *Developments in polymer degradation-7*. London: Elsevier; 1987.
- [110] Dover Chemicals. Technical information on chloroparaffin retardants <http://www.doverchem.com/>
- [111] Camino G, Costa L. Thermal degradation of polymer–fire retardant mixtures. Part III. Degradation products of polypropylene–chlorinated paraffin mixtures. *Polym Degrad Stab* 1982;4(2):133–44.
- [112] Camino G, Costa L. Thermal degradation of polymer–fire retardant mixtures. Part I. Polypropylene–chlorinated paraffin. Evidence of interactions. *Polym Degrad Stab* 1980–1981;3(6):423–30.
- [113] Buszard DL. Inherently flame retardant polypropylene fibres. In: Proceedings of Conference Textile Flammability: Current and Future Issues, 30–31st March 1999. Manchester: Textile Institute; 1999.
- [114] Lomakin SM, Zaikov GE, Artisis MI. New types of ecologically safe flame retardant systems for polymethylmethacrylate. *Int J Polym Mater* 1996;32(1–4):213–20.
- [115] Lomakin SM, Zaikov GE, Artisis MI. Polypropylene flame retardant system based on Si–SnCl₂. *Int J Polym Mater* 1996; 32(1–4):203–11.
- [116] Zaikov GE, Lomakin SM. Polymer flame retardancy: a new approach. *J Appl Polym Sci* 1998;68(5):715–25.
- [117] Jayakody C, Nelson GL, Sorathia U, Lewandowski S. A cone calorimetric study of flame retardant elastomeric polyurethane modified with siloxanes and commercial flame retardant additives. *J Fire Sci* 1998;16(5):351–82.
- [118] Hubber M. Silicone flame retardant for polyolefins. Conference Proceedings of papers presented at Fire Retardant Chemicals Association Meeting, New Orleans, March 25–28. 1990. p. 237.
- [119] Moody AG, Pennick RJ. Polymeric blends containing a monoorganic polysiloxane resin. US Patent 4,265,801; 1981
- [120] Frye RB, Zembayashi M. Flame retardant thermoplastic compositions. US Patent 4,536,529; 1985.
- [121] Maclaury MR, Holub FF. Flame retardant compositions and coated article. US Patent 4,273,691; 1981.

- [122] Frye RB. A new silicone flame retardant system for thermoplastics. *Polym Mater Sci Engng* 1984;51:235–9.
- [123] Hubber M. Silicone flame retardant for polyolefins. *Silicones Plastic Compounding* 1990;Sep/Oct:124.
- [124] Harrell JR, Muschiatti LC. Ethylene copolymer compositions. US Patent 4,839,412; 1989
- [125] Opsahl AW, Watson LD. Ethylene copolymer compositions having improved fire retardancy. US Patent 4,851,463; 1989
- [126] Tai CM, Li Robert KY. Studies on the impact fracture behaviour of flame retardant polymeric material. *Mater Des* 2001;22(1):15–19.
- [127] Leeuwendal R, Shen K, Ferm D. New application developments in halogen-free flame retardant polyolefin and polyamide engineering plastics using firebrake zinc borates. *Flame Retardants 2002*. London: Interscience Communications; 2002. p. 95–106.
- [128] Bourbigot S, Le Bras M, Leeuwendal R, Shen K, Schubert D. Recent advances in the use of zinc borates in flame retardancy of EVA. *Polym Degrad Stab* 1999;64(3):419–25.
- [129] Slusher CC, Ogren EA. Flame retardant modified asphalt-based material and products therefrom. US Patent 5,516,817; 1996
- [130] Rothon R. The emergence of magnesium hydroxide as a fire retardant additive. In: The Plastic and Rubber Institute, editor. *Flame Retardants 1990 Conference*. London: Elsevier; 1990.
- [131] Gree J. In: Lewin M, Atlas SM, Pearce EM, editors. *The flame retardation of polyolefins*. Flame retardant polymeric materials, vol. 1. New York: Plenum Press; 1982. Chapter 1.
- [132] Anon, The flame retardant and smoke suppression mechanisms for alumina trihydrate and magnesium hydroxide. *Addit Polym* 1994;1994(6):9–10.
- [133] Dvir H, Goldraich M, Gottlieb M, Daren S, Cuesta JL. Distribution of a brominated acrylate flame retardant in polypropylene. *Polym Degrad Stab* 2001;74(3):465–74.
- [134] Hirschler MM. Reduction of smoke formation from and flammability of thermoplastic polymers by metal oxides. *Polymer* 1984;25(3):405–11.
- [135] Anon. Great Lakes Chemical, High Performance Textiles; June 1995
- [136] Jha NK, Bajaj P, Misra AC, Maurya PL. Flame retardation of polypropylene: effect of organoantimony compounds on the flammability and thermal behaviour. *J Appl Polym Sci* 1986; 32(4):4393–403.
- [137] Cline BL, O'Mahony GM. Flame retardant polyolefin fiber. US Patent 4,774,044; 1988
- [138] Costa L, Luda MP, Trossarelli L. Mechanism of condensed phase action in flame retardants. Synergistic systems based on halogen–metal compounds. *Polym Degrad Stab* 2000; 68(1):67–74.
- [139] Kutner A. Flame retardant polymers. US Patent 3,717,609; 1973
- [140] Blumstein A. Memoires presentes la societe chimique. *Bull Soc Chim de Fr* 1961;899–905.
- [141] Blumstein A. Polymerization of adsorbed monolayers. II. Thermal degradation of the inserted polymer. *J Polym Sci Part A* 1965;3(7):2665–72.
- [142] Burnside SD, Giannelis EP. Synthesis and properties of new poly(dimethylsiloxane) nanocomposites. *Chem Mater* 1995; 7:1597.
- [143] Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O. Synthesis and properties of polyimide–clay hybrid. *J Polym Sci Part A: Polym Chem* 1993;31(10):2493–8.
- [144] Gilman J, Kashiwagi T, Lichtenhan J. Nanocomposites: a revolutionary new flame retardant approach. *SAMPE J* 1997; 33:40–6.
- [145] Bourbigot S, Devaux E, Flambard X. Flammability of polyamide-6/clay hybrid nanocomposite textiles. *Polym Degrad Stab* 2002;75(2):397–402.
- [146] Zanetti M, Camino G, Müllhaupt R. Combustion behaviour of EVA/fluorohectorite nanocomposites. *Polym Degrad Stab* 2001;74(3):413–7.
- [147] Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Mater Sci Engng: Rep* 2000;28(1–2):1–63.
- [148] Chiang C-L, Ma C-CM. Synthesis, characterization and thermal properties of novel epoxy containing silicon and phosphorus nanocomposites by sol–gel method. *Eur Polym J* 2002;38(11):2219–24.
- [149] Wang J, Du J, Zhu J, Wilkie CA, An XPS. study of the thermal degradation and flame retardant mechanism of polystyrene–clay nanocomposites. *Polym Degrad Stab* 2002;77(2):249–52.
- [150] Lepoittevin B, Devalckenaere M, Pantoustier N. Poly (ϵ -caprolactone)/clay nanocomposites prepared by melt intercalation: mechanical, thermal and rheological properties. *Polymer* 2002;43(14):4017–23.
- [151] Li CJ, Yang GJ, Wang Z. Formation of nanostructured TiO₂ by flame spraying with liquid feedstock. *Mater Lett* 2003; Uncorrected Proof, Available online <http://www.sciencedirect.com> 3 October 2002.
- [152] Ye C, Meng G, Zhang L, Wang G, Wang Y. A facile vapor–solid synthetic route to Sb₂O₃ fibrils and tubules. *Chem Phys Lett* 2002;363(1–2):34–8.
- [153] Marosi G, Márton A, Anna P, Bertalan G, Marosfői B, Szép A. Ceramic precursor in flame retardant systems. *Polym Degrad Stab* 2002;77(2):259–65.
- [154] Kandola BK. Nanocomposites. In: Horrocks AR, Price D, editors. *Fire retardant materials*. Cambridge: Woodhead Publishing; 2001. p. 204–19.
- [155] Liu X, Wu Q. PP/clay nanocomposites prepared by grafting–melt intercalation. *Polymer* 2001;42(25):10013–9.
- [156] Lee SY, Kim SJ. Expansion characteristics of organoclay as a precursor to nanocomposites. *Colloids Surf A: Physicochem Engng Aspects* 2002;211(1):19–26.
- [157] Wang KH, Choi MH, Koo CM, Choi YS, Chung IJ. Synthesis and characterization of maleated polyethylene/clay nanocomposites. *Polymer* 2001;42(24):9819–26.
- [158] Xie W, Gao Z, Liu K, Pan WP, Vaia R, Hunter D, Singh A. Thermal characterization of organically modified montmorillonite. *Thermochim Acta* 2001; 367–8:339–50. see also p. 367–8.
- [159] Triantafyllidis CS, LeBaron PC, Pinnavaia TJ. Thermoset epoxy–clay nanocomposites: the dual role of ω,ω -diamines

- as clay surface modifiers and polymer curing agents. *J Solid State Chem* 2002;167(2):354–62.
- [160] Becker O, Varley R, Simon G. Morphology, thermal relaxations and mechanical properties of layered silicate nanocomposites based upon high-functionality epoxy resins. *Polymer* 2002;43(16):4365–73.
- [161] Gilman JW, Kashiwagi T, Nyden M, Brown JET, Jackson CL, Lomakin S. Flammability studies of polymer layered silicate nanocomposites: polyolefin, epoxy, and vinyl ester resins. In: Al-Malaika S, Golovoy A, Wilkie CA, editors. *Chemistry and technology of polymer additives*. Oxford: Blackwell Scientific; 1999. p. 249–65.
- [162] Li J, Zhou C, Gang W. Study on nonisothermal crystallization of maleic anhydride grafted polypropylene/montmorillonite nanocomposite. *Polym Test* 2003;22(2):217–23.
- [163] García-López D, Picazo O, Merino JC, Pastor JM. Polypropylene–clay nanocomposites: effect of compatibilizing agents on clay dispersion. *Eur Polym J* 2003;39(5):945–50.
- [164] Kaempfer D, Thomann R, Mülhaupt R. Melt compounding of syndiotactic polypropylene nanocomposites containing organophilic layered silicates and in situ formed core/shell nanoparticles. *Polymer* 2002;43(10):2909–16.
- [165] Chan CM, Wu J, Li JX, Cheung YK. Polypropylene/calcium carbonate nanocomposites. *Polymer* 2002;43(10):2981–92.
- [166] Marosi G, Márton A, Anna P, Bertalan G, Marosfői B, Szép A. Ceramic precursor in flame retardant systems. *Polym Degrad Stab* 2002;77(2):259–65.
- [167] Gilman JW, Kashiwagi T, Lichtenhan J. Recent advances in flame retardant polymer nanocomposites. In: *Proceedings of Conference on Fire and Materials*, Jan 22–24. London: Interscience Communications; 2001. p. 273–84.
- [168] Gilman JW. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. *Appl Clay Sci* 1999;15(1–2):31–49.
- [169] Wang J, Du J, Zhu J, Wilkie CA. An XPS study of the thermal degradation and flame retardant mechanisms of polystyrene–clay nanocomposites. *Eighth European Conference on Flame Retardant Polymers*, Alessandria, Italy, June 24–27. 2001.
- [170] Lewin M. Recent advances in flame retardancy of polymeric materials. In: *The 13th Annual BCC Conference on Flame Retardancy*. Norwalk, CT: Stamford, Business Communications Co.; 2002.
- [171] Weil E. Personal communication; 2003
- [172] Kashiwagi T, Harris B, Shields J, Quintiere JG, Liu X. FR mechanism of polymer–clay nanocomposite. In: *Proceedings of the 14th Annual BCC Conference on Flame Retardancy*, Recent Advances in Flame Retardancy of Polymeric Materials. Norwalk, CT: Business Communications Co.; 2003.
- [173] Gilman JW, Kashiagi T. Recent advances in flame retardant polymer nanocomposites. In: Pinnavaia TJ, Beall GW, editors. *Polymer–clay nanocomposites*. New York: Wiley; 2000. p. 193–206.
- [174] Gilman JW, Morgan AB, Harris RHJ, Manias E, Giannelis EP, Wuthenow M. Polymer layered-silicate nanocomposites: polyamide-6, polypropylene and polystyrene. New advances in flame retardant technology. In: *Proceedings of Fire Retardant Chemicals Association*, October 24–27, 1999, Tucson, AZ. Lancaster, PA: Fire Retardant Chemicals Assoc.; 1999.
- [175] Zhu J, Uhl FW, Morgan AB, Wilkie CA. Studies on the mechanism by which the formation of nanocomposites enhances thermal stability. *Chem Mater* 2001;13:4649.
- [176] Dong W, Huang G. Study on properties of nano polypropylene/TiO₂ composite fiber. *Fangzhi Xuebao* 2002;23(1):22–3.
- [177] Yeo SY, Lee HJ, Jeong SH. Preparation of nanocomposite fibers for permanent antibacterial effect. *J Mater Sci* 2003;38(10):2143–7.
- [178] Ma X, Cui H. The preparation of nano polypropylene/ceramic and zeolite fibres. *Hecheng Xianwei Gongye* 2002;25(1):4–7.
- [179] News and Views, Nanocor and Gitto Global expand joint development of flame-resistant polyolefins. *Addit Polym* 2002;2002(8):9–10.
- [180] Nass B, Schacker O, Schlosser E, Wanzke W. Phosphorus containing flame retardant-compounding and material properties. *Flame retardants 2002*. London: Interscience Communications; 2002. p. 63–74.
- [181] Chiang WY, Hu CH. Approaches of interfacial modification for flame retardant polymeric materials. *Compos Part A: Appl Sci Manufact* 2001;32(3–4):517–24.
- [182] Ferry L, Lopez Cuesta JM, Chivas C, Mac Way Hoy G, Dvir H. Incorporation of a grafted brominated monomer in glass fiber reinforced polypropylene to improve the fire resistance. *Polym Degrad Stab* 2001;74(3):449–56.
- [183] Shi LS. Characterization of the flame retardancy of EVA copolymer by plasma grafting of acrylic acid. *Eur Polym J* 2000;36(12):2611–5.
- [184] Wilkie CA, Suzuki M, Xiaoxing D, Deacon C, Chandrasiri JA, Xue TJ. Grafting to achieve flame retardancy. *Polym Degrad Stab* 1996;54(2–3):117–24.
- [185] Chatelin R, Gavet L. Process for imparting flame retardancy to textile materials. *US Patent* 5,281,239; 1994
- [186] Simionescu CI, Denes F, Macoveanu MM, Negulescu I. Surface modification and grafting of natural and synthetic fibres and fabrics under cold plasma conditions. *Makromol Chem Suppl* 1984;8:17–36.
- [187] Zahran AH, Stannett V, Liepins R, Morosoff N. Radiation grafting to polyesters, cotton and their blends to impart flame retardancy. *Radiat Phys Chem* 1980;16(4):265–76.
- [188] Nablo SV. Process for imparting durable flame retardancy to fabric, fibers and other materials and improved product produced thereby. *US Patent* 4,211,622; 1980
- [189] Livshits RM, Stanchenko GI. Treatment of cellulose fibres by grafting binary mixtures of monomers. *Nauch-Issled Tr* 1969;22:317–23.
- [190] Needles HL. Novel approaches to flame retardant finishing. *J Cons Prod Flamm* 1977;4(2):156–9.
- [191] Zhang S, Wang J. Electron-beam irradiation initiated grafting to improve flame retardancy of PE. *Gaofenzi Cailiao Kexue Yu Gongchong* 2000;16(6):99–101.

- [192] Zhang S, Wang J, Xie LQ, Wen CL. Electron-beam (EB) irradiation and grafting of acrylic monomers onto EPDM copolymer. *Chin Sci Bull* 2000;45(4):322–5.
- [193] Zhang S, Wang J. Approaches to the flame retardancy of polymers. I. Electron-beam preirradiation and grafting of acrylic monomers onto EVA copolymers. *J Fire Sci* 1997; 15(1):68–86.
- [194] Ma ZL, Zhao M, Hu HF, Ding HT, Zhang J. Compatibilization of intumescent flame retardant/polypropylene composites based on α -methacrylic acid grafted polypropylene. *J Appl Polym Sci* 2002;83(14): 3128–32.
- [195] Mai K, Li Z, Qiu Y, Zeng H. Thermal properties and flame retardance of $\text{Al}(\text{OH})_3$ /polypropylene composites modified by polypropylene grafting with acrylic acid. *J Appl Polym Sci* 2001;81(11):2679–86.
- [196] Ferry L, Lopez Cuesta JM, Chivas C, Mac Way Hoy G, Dvir H. Incorporation of a grafted brominated monomer in glass fiber reinforced polypropylene to improve the fire resistance. *Polym Degrad Stab* 2001;74(3):449–56.
- [197] Chiang WY, Hua CH. The improvements in flame retardance and mechanical properties of polypropylene/FR blends by acrylic acid graft copolymerization. *Eur Polym J* 1996;32(3): 385–90.
- [198] Kaprinidis N, Shields P, Leslie G. Antimony free flame retardant systems containing Flamestab NOR 116 for polypropylene modling. *Flame retardants 2002*. London: Interscience Communications; 2002. p. 95–106.