

RECENT DEVELOPMENTS IN THE FIELD OF FIRE RETARDANCY OF POLYMERIC MATERIALS

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Abstract

The widespread applications of polymeric materials require the usage of conventional flame retardants based on halogen and phosphorous compounds to satisfy the fire safety regulatory standards. However, these compounds, particularly halogen-based, are persistent organic pollutants of global concern and generate corrosive/toxic combustion products. To account for eco-friendliness, ultimate mechanical/physical properties and processing difficulties, the window of options has become too narrow. Although the incorporation of non-toxic nanofillers in polymers shows positive potential towards flame retardancy, there are yet many obstacles to overcome. Moreover, most of the literature on these materials are qualitative and often point to conflicting/misleading suggestions from the perspectives of short-term and long-term fire exposure tests. Hence, this has reinstated the need to fundamentally understand their fire response and complement experimental results with theoretical modelling and/or numerical simulation.

One section of this review will highlight the ecological impacts of using conventional flame retardants, thereby signifying the necessity to use eco-friendly agents. In other sections, we explore the usage of various nanofillers for this purpose, compare their performance with traditional systems, provide insights into different testing standards and combustion mechanisms, modelling aspects of the combustion behaviour, and identify novel approaches that could be considered for meeting the fire safety standards with eco-friendly materials.

List of Abbreviations

General: CAFE, Clean Air for Europe; EEA, European Environment Agency; EPA, Environmental Protection Agency; EU, European Union; FAA, Federal Aviation Administration; FRs, flame retardants; IARC, International Agency for Research on Cancer; NIST, National Institute of Standards and Technology; REACH, Registration, Evaluation, Authorization, and Restriction of Chemical substances; TEF, toxic equivalency factor; TEQ, toxic equivalent; UL, Underwriters Laboratories; WHO, World Health Organization.

Polymers and other organic compounds: ABS, acrylonitrile-butadiene-styrene copolymer; AETMC, 2-(acryloxyethyl)trimethylammonium chloride; AO, antimony trioxide; APP, ammonium polyphosphate; BA, boric acid; EVA, ethylene-vinyl-acetate copolymer; HBCD, hexabromocyclododecane; HDPE, high density polyethylene; HIPS, high impact polystyrene; LDPE, low density polyethylene; MP, melamine phosphate; MPP, melamine polyphosphate; ODA, 4,4-oxydianiline; PA, polyamide; PAA, polyamic acid; PAH, polycyclic aromatic hydrocarbon; PBB, polybrominated biphenyl; PBDE, polybrominated diphenyl ether; PBT, polybutylene terephthalate; PCB, polychlorobiphenyl; PCDD, polychlorinated dibenzodioxin; PER, pentaerythritol; PET, poly(ethylene terephthalate); PLA, polylactic acid; PMDA, pyromellitic di anhydride; PMMA, poly(methyl methacrylate); POP, persistent organic pollutant; PP, polypropylene; PPh, phenyl phosphonate; PPS, polyphenylene sulfide; PU, polyurethane; PVC, poly(vinyl chloride); SAN, acrylonitrile-styrene; SDS, sodium dodecyl sulphate; TBBPA, tetrabromo bisphenol A; TCDD, tetrachloro dibenzo-*p*-dioxin.

Reinforcements: ATH, aluminum tri-hydroxide; Cloisite 25A, dimethyl-dehydrogenated-tallow-2-ethylhexyl quaternary ammonium treated MMT; Cloisite 30B, methyl-tallow-bis(hydroxyethyl)-ammonium treated MMT; CNTs, carbon nanotubes; MH, magnesium di-hydroxide; MMT, montmorillonite; ZB, zinc borate.

Characterization techniques: DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; FTIR, Fourier transform infrared spectroscopy; LOI, limiting oxygen index; NMR, nuclear magnetic resonance; PCFC, pyrolysis combustion flow calorimetry; TGA, thermogravimetric analysis; TEM, transmission electron microscopy; XRD, X-ray diffraction.

Testing parameters: EHC, effective heat of combustion; FIGRA, fire growth rate index; HOC, heat of combustion; HRC, heat release capacity; HRR, heat release rate; MLR, mass loss rate; pHRR, peak of heat release rate; Tg, glass transition temperature; THR, total heat released; TTI, time to ignition.

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1. Background

The interactions among various entities of the eco-system are highly complex and, of particular interest, between the environment and humans are multi-faceted. According to environmental organizations like the USA's EPA and Europe's EEA, the best-known direct impacts are related to ambient air pollution, poor water quality and insufficient sanitation. These are strengthened by the facts from the WHO in that at least 13 million people die every year as a consequence of environmental pollution, which also affects 85 of 102 categories of diseases [1]. The revolutionary development of chemical/polymer technology and nanosciences over the past few decades have added to the seriousness of the issue with many direct and indirect effects including waste control and waste management. The CAFE program also estimates ~348,000 premature human deaths per year as a result of exposure to fine particles.

This review is an effort to demonstrate and highlight such interactions of the widespread usage of conventional petrochemical-based polymeric materials considering the specific facet of 'fire response'. The major objectives of the review are to:

- establish the significance of switching to eco-friendly FRs; and
- streamline various issues associated with facets of flame retardancy behaviour of polymer nanocomposites.

Considering the volume of published literature on fire retardancy of polymeric materials, only a brief overview of the mechanisms of fire retardancy with various fillers is provided here. Major emphasis will be on recent advances in the field. Furthermore, the importance of understanding the fire response of materials from different fire exposure tests and the efforts to model the combustion behaviour of polymers are reviewed, noting alongside a few of the commercially available fire retardant materials.

The analyses of fire retardancy behaviour of polymer nanocomposites from the perception of the aforementioned issues will shed light on the usage of conventional and potentially harmful FRs, and lay the foundation to promote the adoption of "green" and "environmentally benign" materials.

2. Fundamentals of flame retardancy in polymers - conventional FRs and their mechanisms

Combustion of polymeric materials is a complex process involving simultaneous combinations of heat and mass transfer/diffusion, fluid dynamics and degradation chemistry. In general, four major steps comprise polymer combustion: ignition, pyrolysis, combustion and feedback. In the presence of a source of sufficient heat (to induce bond scissions), polymers will decompose or “pyrolyse” evolving flammable volatiles [2-4]. They combine with air (oxygen) and produce the H₂-O₂ scheme, which propagates the fuel combustion by the branching reaction below:



The main exothermic reaction that provides most of the energy to maintain the flame is:



Depending on the flammability limit of the material, ignition occurs (either flash or auto ignition). A self-sustaining combustion cycle will be formed after ignition if the heat evolved by the flame is sufficient to keep the decomposition rate of the polymer above that required to maintain the concentration of the combustible volatiles [5]. So, to protect against fire, it is necessary to (a) reduce the heat evolved to below that required to sustain combustion; or (b) modify the pyrolysis process to reduce the amount of flammable volatiles emitted; or (c) isolate the flame from oxygen; or (d) reduce the heat flow back to the polymer to prevent further pyrolysis [5-8].

Nevertheless, many problems persist in every mechanism mentioned making it impossible for complete protection against fire. But the most common approach to improve the flame retardancy performance of a polymer is to add FRs. Depending on the type/nature of FRs, they act chemically and/or physically in the solid, liquid or gaseous phase and interfere with combustion at different stages (heating, decomposition, ignition, or flame spread). This is reflected in the fire performance of the material evaluated in terms of ignition resistance, flame spread, escape time and containment of flame and combustible/degradation products, etc. The mechanisms of conventional FRs based on halogen, phosphorous and intumescent compounds have been thoroughly discussed in the past [3, 7-20] and therefore, to avoid duplication, the topic will only be reviewed briefly herein.

2.1. Halogen-based agents: They act primarily by chemical interference with the radical chain mechanism (as per equations 4 to 7) in the gas phase during combustion; that is, the amount of combustible matter remains constant but the heat released in the combustion decreases. High-energy OH[•] and H[•] radicals formed during combustion are removed (scavenged) by halogen radicals released from the FRs [2-4, 21].



RX is a hydrocarbon halide.

Generally, halogenated FRs are based on either chlorine or bromine as the carbon-bromine/chlorine bond is relatively weak and thermally-labile. But fluorine-based compounds are highly (thermally) stable to release fluorine radicals compared to polymer decomposition temperatures; and on the contrary, iodine-based compounds are unstable to even go through the processing temperatures of most polymers [14].

In particular, five compounds based on brominated FRs (or BFRs) are widely used due to their outstanding performance: TBBPA, HBCD, penta-BDE, octa-BDE and deca-BDE [22, 23]. Deca-BDE consists of ~97% decabromodiphenylether; octa-BDE contains 10-12% hexabromodiphenylethers, 43-44% heptabromodiphenyl ethers, and 31-35% octabromodiphenyl ethers; and penta-BDE, ~50-62% pentabromodiphenyl ethers and 24-38% tetrabromodiphenyl ethers [24, 25]. Penta, octa and deca correspond to the average bromine content of the various compounds. However, due to their intrinsic toxicity (for instance, octa-BDE and penta-BDE) and their potential to form polybrominated dioxins and furans (like chloro- and bromo- dibenzodioxines and dibenzofurans) and their serious effects on the eco-system (see section 3.1), the use of certain BFRs is restricted. They also have the potential to release massive amounts of corrosive gases (hydrogen halides), corroding metal components and causing damage to sensitive electronics, and in a confined space, such as a typical aircraft fuselage or marine hull compartment, this can have disastrous consequence [26].

2.2. Phosphorous-based compounds: The most widely marketed and available non-halogenated alternatives are based on phosphorous compounds. Common examples of this class of FRs include elemental red phosphorus, phosphines, phosphine oxides, phosphonium compounds, phosphonates, phosphites, phosphinates and phosphates. These compounds mostly act in the condensed phase by altering the pyrolytic path of the polymeric material and reducing the amount of gaseous combustibles (dehydration and char formation are the principle modes of action) [9]. For example, most of the phosphorous-based compounds are converted to phosphoric acid during thermal decomposition, which condenses to produce pyrophosphate and

polyphosphate structures by elimination of water. They can catalyze the dehydration reaction of polymer end chains (and any reactive group) and trigger char formation. The released water dilutes the oxidizing gas phase. In some cases, it is also shown that phosphorus-based FRs can volatilize into the gas phase to form active radicals (PO_2^\cdot , PO^\cdot and HPO^\cdot) and act as scavengers of H^\cdot and OH^\cdot radicals [27]. Some initial studies on the toxicity of phosphorous-based compounds have also pointed out that these FRs are neuro-toxicants after they break down in the environment; and in addition, when they volatilize and condense, stress corrosion cracking of various parts can occur [28].

2.3. Metal hydroxides: ATH, $\text{Al}(\text{OH})_3$ and MH, $\text{Mg}(\text{OH})_2$ are common examples of this class of FRs. These fillers decompose endothermically and release free water to cool the pyrolysis zone [29, 30]. They are also reported to show a diluting effect (to some extent) in the gas phase and formation of a protective layer (consisting of Al_2O_3 or MgO) on the burning surface of the polymer after the water-release mode of action has been exhausted. However, depending on their endothermic decomposition temperatures, polymer systems with suitable decomposition temperatures have to be chosen [14, 31]. For example, endothermic degradation of ATH occurs between 180 and 220 °C and therefore will have a reduced flame retardancy effect (and indeed hydrolysis of polymers) if used in polymers with higher processing temperatures like polyamides. For these systems, MH (with >300 °C endothermic decomposition temperature) is most suitable. The enthalpies of water release are 1.17 and 1.36 kJ/g for ATH and MH, respectively. Besides, recently introduced flame retardant compound based on boehmite chemistry (aluminum monohydrate, AlOOH) is also suitable whenever the processing temperature exceeds 200 °C since its endothermic decomposition temperature is between 340 and 350 °C [32].

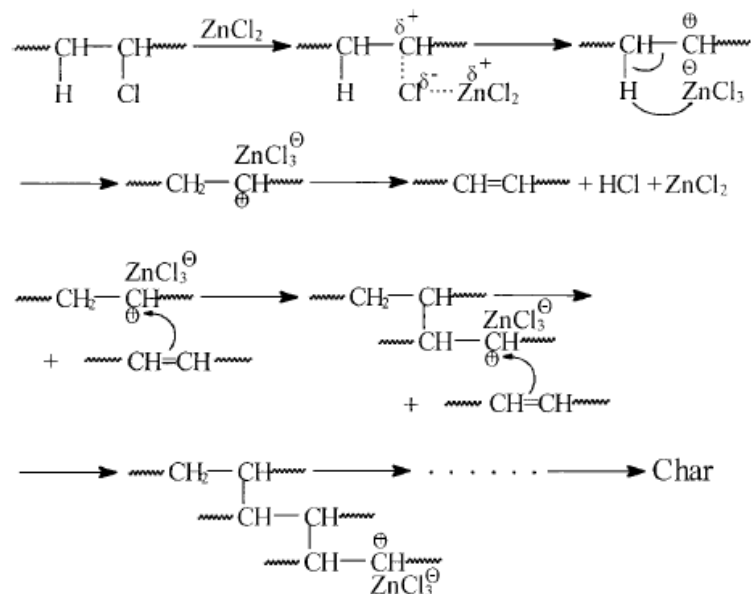
Nonetheless, a well-known major drawback of metal hydroxides is their high levels of loading requirement (generally >40 wt.%) for adequate flame retardancy, which often leads to processing difficulties and deterioration in other critical polymer characteristics.

2.4. Intumescent agents: The concept of 'intumescence' dates back to 1938, but is still used actively in many applications. In this methodology, materials swell when exposed to fire or heat to form a porous foamed mass, usually carbonaceous that acts as a barrier to heat, oxygen and other pyrolysis products [12, 33, 34]. Three agents are generally required in this approach: an acid (or a source yielding acidic species at temperatures in the range of 100-250 °C), a

carbonizing agent (or a char forming agent), and a foaming (spumific) agent. Initially, the released acid esterifies the carbon-rich source and later, the ester decomposes *via* dehydration yielding a carbonaceous residue. The released gases from the above reactions and degradation products cause the carbonizing material to foam. Important points to note are the temperatures at which the acid has to be liberated (should be below the decomposition temperature of the carbonizing agent) and the decomposition temperature of the polymer (should be around that of the dehydration reaction). Best known example of this class is APP in combination with PER in PPs and PAs [35, 36]. Synergists were also used to enhance the efficiency of intumescent FRs. For example, zeolite can effectively enhance mechanical strength of the char layer and stabilize it by Si-O-P-C and Al-O-P-C bonds. Some recent investigations have noted the usage of polymers like PA6 as char-forming agents instead of traditional organic compounds such as polyol to achieve improved mechanical properties and also to avoid problems of exudation and water solubility [12].

2.5. Boron-based flame retardants: From this family of FRs, (hydrated) zinc borates are widely used. Their endothermic decomposition (~503 kJ/kg) between 290 and 450 °C liberates water, boric acid and boron oxide (B₂O₃). B₂O₃ softens at 350 °C and flows above 500 °C leading to the formation of a protective vitreous layer [3, 37]. Several variants of zinc borate exist, differing by the zinc/boron ratio and water content. They are particularly used as synergists to halogenated FRs/polymers due to the interaction of Zn²⁺ ions with halogen radicals. For example, hydrogen chloride generated from PVC reacts with zinc borate to form non-volatile zinc chloride (ZnCl₂) and oxychloride as well as volatile boron trichloride and boric acid (equation 8) [38]. ZnCl₂ is a well-known Lewis acid that promotes cross-linking, resulting in char formation as shown in Scheme 1; that is, ZnCl₂ reacts with PVC by accepting a chloride forming primary carbonium ion. The primary carbonium ion then decomposes into alkene, hydrogen chloride and zinc chloride. The carbonium ions formed react with unsaturated groups in PVC to produce char by a series of cross-linking reactions and, ultimately reducing smoke formation.





Scheme 1. Reaction scheme showing cross-linking of PVC during its decomposition, leading to the formation of char (after [38]).

In another study, 0.5-7 parts by weight of zinc borate ($4ZnO \cdot 6B_2O_3 \cdot 7H_2O$) was used to improve the flame retardancy and oxidative stability of PU [39]. The presence of zinc oxide, an ultraviolet absorber, in zinc borate obviously helped PU to improve its oxidative stability. Additionally, the burning time of PU was significantly enhanced even with 0.5 wt.% of zinc borate, from 15 s in neat PU to 39 s. With 7 % zinc borate, the burning time was further increased to 84 s.

2.6. Nitrogen-based flame retardants: Despite their lower fire retardant efficiency than halogen-based FRs, these compounds are relatively less toxic, release low amounts of smoke during fire, and environmental friendly. Consequently, nitrogenous agents like melamine, triazine, urea (phosphate) and guanidine based compounds are becoming increasingly popular. APP, as mentioned earlier, is another compound that is widely used in intumescent formulations. Among the nitrogen-containing compounds, the use of melamine (or its salts like melamine cyanurate, melamine phosphate, melamine pyrophosphate, melamine polyphosphate) is predominant [40]. Melamine is a stable crystalline product and contains 67 wt.% nitrogen atoms. It undergoes sublimation at $\sim 350^\circ\text{C}$, where a significant amount of energy is absorbed, decreasing the temperature. At further high temperatures, melamine decomposes with the elimination of ammonia and diluting oxygen/combustible gases and results in the formation of thermally stable condensates, melam, melem and melon [14]. It is also noted that these reactions compete with melamine volatilization and dominate if melamine volatilization is

hindered. But unlike the traditional FRs, melamine and its salts promote dripping (with non-burning drips). Triazines (and their derivatives) are also used in several polymers by themselves or in combination with APP as charring or blowing agents with positive results [41]. Other agents based on cyanurate have also been used as FRs primarily because of the presence of nitrogen and their cyclic structure [42, 43].

2.7. Charring agents: Char formation during polymer degradation is generally a complex process and may involve several steps like chemical fragmentation, conjugated double bond formation, cyclization, aromatization, fusion of aromatic rings, turbostratic char construction and graphitization [44]. Char is a highly cross-linked, porous solid and consists of disordered polycyclic aromatic hydrocarbons that become more ordered with increasing temperature (lower amorphous concentration and higher aromaticity). Nevertheless, char formation during combustion is always beneficial whether this points to the materials that are unburnt (therefore, not contributing to heat release) or to the higher fire retardancy effect by serving as a barrier to heat and mass transfer [45]. Some studies have pointed to the importance of rate of char formation towards flame retardancy/flammability [46]. As discussed before, phosphorus-based FRs can effectively result in char formation in oxygen- or nitrogen-containing polymers. In the absence of reactive groups, polyols like pentaerythritol, mannitol or sorbitol were used as char formers, particularly in intumescent formulations. Boron compounds, another topic mentioned before, promote char formation in the burning process. The mechanism is related to the thermal action of boric acid with alcohol moieties. Addition of dehydrogenation or oxidative dehydrogenation catalysts is another interesting field that is not explored. This is based on the concept that the heat of combustion of a reaction consuming only hydrogen of an aliphatic hydrocarbon polymer molecule is only about one-third as compared to both hydrogen and carbon [47, 48].

2.8. Smoke Suppressants: The majority portion of human deaths during fire incidents are related to the inhalation of smoke and toxic combustion gases, and of particular significance is carbon monoxide. It prevents oxygen transport by the formation of carboxyhaemoglobin. While carbon dioxide, within the released quantities during combustion of a polymer, though specifically is not toxic, its presence in blood stimulates hyperventilation, increasing the respiration rate and thus making humans susceptible to the toxic components of the fire gas [49]. It is also important to understand and distinguish the differences between 'combustion gases' and 'smoke' as they have different ultimate effects. The combustion process of polymers,

as explained before, is an endothermic process (pyrolysis) which requires sufficient energy to overcome the dissociation energies of any bonds (to be broken) and any activation energy requirements of the process. This releases flammable gases that combine with air (oxygen) and ignite, leading to exothermic processes of flame propagation and heat release. By contrast, smoke can occur even in the absence of burning, that is, during the smoldering period. Even smoke density (or transparency) is an important factor as it dramatically influences the escape time and the time-to-exposure for harsh gases [6, 31, 50]. This depends on many factors (burning conditions) like oxidant supply, specimen geometry, flame intensity, ambient temperature, chamber volume and ventilation. Moreover, it is also dependent on the inherent properties of the polymers like thermal stability, cross-linking density (of the macromolecules), and types of gases (fuels) formed upon degradation. Although there are exceptions like PVC as it aromatizes due to dehydrochlorination, it is believed, as a general rule, polymers with aliphatic backbones tend towards low smoke generation, while polyenic polymers and those with pendant aromatic groups produce more smoke [5]. The dependency on both inherent and external factors clearly points to its complexity.

Some of the approaches that were adopted to tackle this problem include the use of fillers/additives, surface treatments, and structural modification of the polymers themselves. The idea behind the incorporation of fillers/additives (or conventional flame retardants), as discussed above is to slow down the thermal decomposition of the polymeric material and reduce the smoke density and gas concentration [51, 52]. However, based on the functionality of smoke suppressant, fillers were categorized as inert and active. Inert fillers mainly act by diluting the amount of combustible material and to a smaller extent by absorbing heat to reduce the burning rate. While active fillers also promote the dilution process and heat absorption, they absorb more heat per unit weight by endothermic processes. Examples of inert fillers are silica, clays, calcium carbonate; and metal hydroxides and oxides are a major class of active fillers.

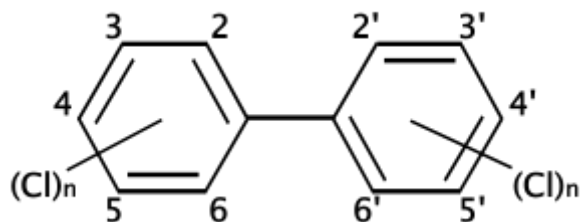
It has been proven that most metal compounds, in particular transition metal compounds like copper, molybdenum and iron compounds, are most effective smoke suppressants [53]. For example, Carty and White [54, 55] have investigated the reactivity of basic iron(III) oxide in blends of PVC (or chlorinated PVC) with ABS and revealed that FeOOH and its synergistic interaction with HCl had the most significant smoke-suppressing activity by increasing char formation. Even reductive-coupling chemistry using Cu(I) compounds was applied to suppress smoke [5]. Further, additives that enhance the cross-linking within the polymer matrix were also

used. Starnes and his co-workers [56-58] did extensive work on copper complexes as smoke suppressants, particularly in PVC. The fundamental concept is to produce zero-valent metal at elevated temperatures as such compounds ideally produce active cross-linking agent(s) only under pyrolytic conditions and without dehydrochlorination of PVC. Several Cu(I) and Cu(II) complexes were prepared for this purpose by using hindered phosphites. They have also examined the usage and smoke suppressing mechanisms of MoO₃ in PVC [58]. Under laboratory-scale measurements (lower enthalpy input), MoO₃ acted as a Lewis acid by catalyzing the dehydrochlorination of PVC at lower temperatures giving *trans* polyene structures rather than *cis*. These *trans* structures are relatively stable and do not undergo the cyclization reaction to form benzene. But for large-scale tests (greater enthalpy input), free radical mechanism dominated to decompose the chains into aliphatic fragments. Hence, although the smoke was reduced, combustion rate was substantially accelerated and also resulted in smaller char residues.

Nevertheless, irrespective of the functionality of various organic/inorganic additives/fillers, the smoke produced (even if little), during burning of polymer composites, is always a mixture of toxic combustion gases along with a suspension of fine particles (mostly inorganic) and soot in the range of nanometres to micrometres depending on the system. This is a particularly dangerous situation for fire-fighters and incident investigation teams. For instance, in aircrafts with fibre-reinforced polymers, in case of fire, the smoke is a mixture of combustible gases and a suspension of fine airborne fibre fragments in the range of 0.3-3 μm in size. There are many reported cases where people doing the post-mortem analyses suffered health problems including eye/skin irritations, breathing difficulties, headaches, etc. even in the presence of protective clothing, masks and goggles [59].

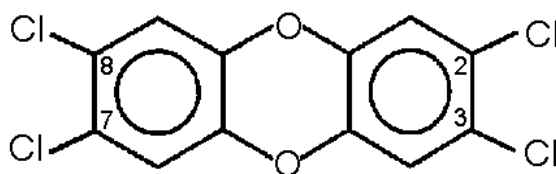
3. Ecological impact of conventional flame retardants

3.1. Background: The global demand for conventional halogen- and phosphorous- based FRs was 2.2 million metric tons in 2011, a 4.7% increase from the previous year. But, these compounds, particularly halogen-based compounds are POPs of global concern and generate corrosive and toxic combustion products (tricyclic aromatic compounds) like dioxins (polyhalogenated dibenzo-*p*-dioxins) and furans (polyhalogenated dibenzo-*p*-furans) [17]. For example, PCBs have two benzene rings (Scheme 2) that can rotate around a carbon-carbon bond and the molecule thus assumes a planar structure resembling dioxins.



Scheme 2. Chemical structure of polychlorobiphenyl.

Although over two hundred halogenated compounds exist, toxicity and persistence are determined by structure, with lateral substitutions (positions 2, 3, 7, and 8) imparting the highest degree of toxicity [60-62]. In Scheme 3, chemical structure of 2,3,7,8-TCDD is shown, which is the most intensively studied and was classified as a human carcinogen by IARC in 1997 because of its potential to disrupt multiple endocrine pathways [63-65]. Owing to the vast range of these compounds, since the early 1990's, the concepts of TEQs and TEFs have been introduced based on *in vitro* and *in vivo* studies to simplify the assessment and regulatory control on an international level [66, 67]. 2,3,7,8-TCDD is considered the most toxic dioxin and has been assigned a TEF value of 1 (that is, a single number which is the TEQ); TEFs for other dioxin-like compounds are based on their activity relative to TCDD. However, this approach only follows an additive rule to calculate the combined toxic effects in a mixture and it does not consider possible synergisms.



Scheme 3. Chemical structure of 2,3,7,8-tetrachloro dibenzo-para-dioxin.

3.2. Direct source and distribution: The source of these compounds can be due to (improper) combustion or incineration of wastes (municipal, hospital, sewage, etc) containing halogenated compounds, as by-products during certain chemicals manufacturing processes (chlorinated compounds in particular), and so on [68]. As these compounds are hydrophobic in nature, they accumulate in soils, sediments, organic matter or waste disposal sites. Besides, their environmental persistence is measured in decades. Their widespread distribution has been a focus of many studies [69-74]. Hence, exposure to humans or other living beings may occur

via several pathways, commonly inhalation, dermal sorption and ingestion (food). More importantly, they are lipophilic compounds, have bio-accumulation potential, and are resistant to metabolism in many of the vertebrate species. In humans, they have been found in blood, serum, adipose tissue, placental tissue, milk and in the brain [75, 76]. Most PCDD and PCDF congeners with a 2,3,7,8-chlorine substitution pattern are in particular strongly retained.

3.3. Indirect effects through improper dumping of consumer products:

Petrochemical-based polymeric materials form a central core of the modern world with broad applications for textiles, furniture, packaging and electrical/electronic devices among others. More interestingly, of the estimated 260 million tons produced each year, more than ~50% are used for short life-term applications (in packaging and electronics/electrical industries) [77, 78]. Despite the recyclability of polymers, the current infrastructure is insufficient to accommodate the production-disposal rates of various kinds of *mixed* polymer wastes [78]. The Great Pacific Garbage Patch (located in the central North Pacific Ocean roughly between 135° W to 155° W and 35° N to 42° N, estimated to be 700,000 km² to more than 15 million km² and 30 m deep consists of 90% of polymer-based materials [79]), Citarum River (Indonesia) or many coastlines around the world and their effects on ecology are a few chapters that necessitate the surge for efficient waste management. It was noted that polymeric materials represent a considerable proportion (50-80%) of shoreline debris and an estimated ~3,520,000 items/km² at the ocean surface [80]. Of particular interest, with the advancements in science and technology, the life spans of electronic products are getting shorter and significant amounts are being discarded worldwide every year. *Greenpeace International* estimates that globally more than 20,000-50,000 million kg of e-waste is generated each year. According to the EPA, an estimated 140 million cell phones were made in 2007 and only 10% were recycled; it was also estimated that over 315 million computers were discarded between 1997 and 2004 in USA alone (National Safety Council).

There is much concern over the disposal of this electronic waste as FRs form a crucial part of these products and are used in printed circuit boards, as connectors, in outer sheaths and cables. Research has shown that their improper dumping/combustion led to pollution of soils and seriously affected the surrounding environment such as farms/fields and rivers by atmospheric movement/deposition [81-83]. Moreover, depending on the environmental conditions, leaching of these additives (as PBDEs are not covalently bound to the polymer matrix) or by-products or the remaining unpolymerized (as the polymerization process is never

100%) monomer building blocks of the polymer, such as styrene and bisphenol-A, along with residual catalysts is another serious issue. For instance, PU foam exposed to ambient outdoor conditions becomes brittle and disintegrates in 4 weeks, and the subsequent emission of penta-BDE containing fragments into the environment is easy [84]. Other issues like the presence of elements such as cadmium, lead, nickel, chromium, antimony and barium in e-waste as part of pigments, performance additives, or stabilizers should also be considered.

Additionally, export of e-waste to different countries (particularly, East and South Asia along with Africa) has led to the development of new sources of environmental PBDEs in these countries [85]. For example, Nigeria imports 60,000 tons of second-hand e-waste annually, which may contain up to 18,000 tons of plastics [86]. Moreover, most of the recycling centres in these countries for electronic wastes often lack sufficient facilities and use crude techniques that endanger environmental and human health [87]. They even include heating printed circuit boards over a grill (using coal blocks) for removing electronic components and burning cables in ambient conditions for recovering metals. Along with these improper techniques, inappropriate disposal of unsalvageable materials in the fields and riverbanks is a major problem. Wong *et al.* [87] did a statistical analyses of concentrations of POPs such as PBDEs, PCDDs/Fs, PAHs, PCBs and also some heavy metals in air, soils and sediments at Guiyu, a traditional rice-growing village located in South-Eastern China, which in recent years became a e-waste recycling site. The concentrations of some of the POPs and heavy metals in different environmental media are alarming; for instance, monthly concentration of the sum of 22 PBDE congeners (from mono- to hepta-BDEs and deca-BDE) of air samples was 100 times higher than any of the previously published data. In fact ~95% of Σ PBDEs contained low bromine compounds, which are relatively more toxic.

3.4. Efforts to control/monitor PBDEs: To balance the potential adverse effects from PBDEs due to their persistence, bio-accumulative and toxic nature, many countries have banned or restricted the use of several organochlorine/bromine compounds, including PCBs/BDEs and some chlorinated pesticides. The EU has banned all uses of penta-BDE and octa-BDE in the EU market, despite their high fire performance. Similarly, the United States has ceased productions of these two BFRs in 2005. The EU Directive on the Restriction of the Use of Certain Hazardous Substances (2002/95/EC, RoHS Directive) also limits the use of PBB and some PBDEs in electrical and electronic equipment along with lead, mercury, cadmium, hexavalent chromium. An upper limit of 1 g/kg for the sum of PBBs and PBDEs was set. But

unfortunately, this list of restricted substances in RoHS 2011 remained unchanged in relation to RoHS Directive 2002/95/EC. However, greater coherence with REACH was called for. Even the introduction of the Kyoto Protocol is a positive step towards the betterment of global climate. According to the protocol, the participating states target a reduction in hydrofluorocarbons and perfluorocarbons (along with four other greenhouse gases) by 5.2% from 1990 levels by the year 2012. Also, the setup of an international treaty, Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal (commonly known as the Basel Convention) to control/reduce the movements of hazardous waste between nations, and specifically to prevent transfer of hazardous waste from developed to less developed countries is another positive stride.

These precautionary ways of monitoring and controlling the production/usage of halogenated compounds are definitely a step towards phasing out of toxic FRs. But there are still many toxic FRs that are currently widely used. More importantly, toxicology information of many BFRs is missing and in particular, their interaction with the eco-system. In fact, as per the WHO, an estimated 95% of chemicals lack some basic testing data on potential health and environmental impacts. With nanoparticles, this information, as expected is at its primitive stage. Without this information, obviously, better estimations of the risks associated cannot be made.

4. Nanofillers as fire retardants in polymers

By considering eco-friendliness, ultimate mechanical/physical properties required for end applications, and processing difficulties, the window of FR options becomes too narrow. To obtain better flame/smoke/toxicity performance, recently, emphasis was laid on using various nanoparticles as FRs, particularly high aspect ratio fillers. Even at low loadings with no additional FRs in the system, both HRRs and MLRs were greatly reduced in addition to huge delay in burning compared to corresponding neat polymers [88]. Despite this, there are many other problems with these materials like the total heat released during flame testing (which is similar to the corresponding neat polymers), inability to meet existing requirements of the ignition resistance tests (e.g., vertical burning UL 94), etc. Moreover, only qualitative terms were used to describe the observed phenomena and little attention was focused on quantitative and physical understanding. This obviously has resulted in conflicting/misleading suggestions on the applicability of materials from the perspectives of short- and long-term fire exposure tests. To avoid unnecessary repetitions/redundancy with other studies published in the literature, herein,

fundamentals and only relatively recent advances on the understanding of fire retardancy behaviour of polymer nanocomposites are briefly reviewed. Also, specific emphasis will be on high aspect ratio fillers. The major issues that are stopping the widespread applications of these materials and the approaches that could be or already adopted to tackle those issues will be discussed in detail in section 5.

4.1. Layered silicates: Different mechanisms that lower the peak HRR of a polymer in the presence of clay (layered silicates like MMT) were proposed [89-91] including radical trapping effect by paramagnetic iron within the clay and catalytic capability of clays to aromatize hydrocarbons and induce char formation. However, char formation is not only catalyzed by protonated silicates formed after the decomposition of the organic modifier/surfactant, it is also promoted by clay itself due to the Bronsted and Lewis acid sites present on the clay lattice. That is, strongly acidic bridging hydroxyl groups and weakly acidic $-\text{SiOH}$, residing at the layer edge, can act as Bronsted acid sites; or iron and aluminium substituted in tetrahedral lattice sites on the clay layers at higher temperatures can act as Lewis acid sites (ability of clay layers to act as radical scavengers). Detailed mechanism of charring is given in [18].

Nevertheless, the major mechanism that was proposed, even in the case of non-charring polymers, is that the structure of the nanocomposite collapses during combustion and a multilayered carbonaceous-silicate barrier will form on the polymer surface that insulates the underlying material from the heat flux of the flame and acts as a mass transport barrier (see Figure 1 [92]). That is, in general, it was believed that flame retardancy performance depends on how fast the clay layers migrate to the burning surface of polymer and form an effective barrier. But recently, it was argued that nano-confinement of polymer chains, at the clay-polymer interface or within the galleries of (intercalated) clay layers (and subsequently formed radicals during degradation) is a more important parameter than the inorganic barrier at the top of the burning surface as the former controls the early stages of degradation [93, 94]. Chen *et al.* [94] supported this reasoning by studying the activation energies of glass transition and thermal degradation as well as the size of cooperatively rearranging region in PS/clay (both intercalated and exfoliated) nanocomposites. For instance, Figure 2 shows the frequency dependence of the glass transition temperature. Evidently, higher activation energy is required for nanocomposites compared to pristine PS, which in turn suggests that nano-confinement of PS chains would result in greater energy barrier to their motion. In fact, this is similar to the concept of confinement/restricted mobility in well-defined geometries *versus* different properties

[95-97]. Although in amorphous polymers, it was believed that the changes were reflected in the T_g of the polymer and the storage/loss modulus or $\tan \delta$ curves, it is important to identify the difference between the presence of nanoparticles during curing and curing under nanoscale constraint. Some studies have shown that, in the former case, T_g of the polymer decreases with increasing loading of nanoparticles; but in the latter case, when nanocomposites were prepared using *sol-gel* technology, T_g increased with particle loading (presumably because of chemical bonding between nanoparticles and matrix) [98, 99]. However, there are many cases in the literature pointing to the opposite behavior; that is, unchanged or decreased T_g even in *sol-gel* developed nanocomposites and enhanced T_g of conventionally prepared nanocomposites or those reinforced with low loadings of nanoparticles [100-102]. Nevertheless, this raises an interesting debate on the confinement issue; also, it is important to understand whether this is system specific or is generally acceptable.

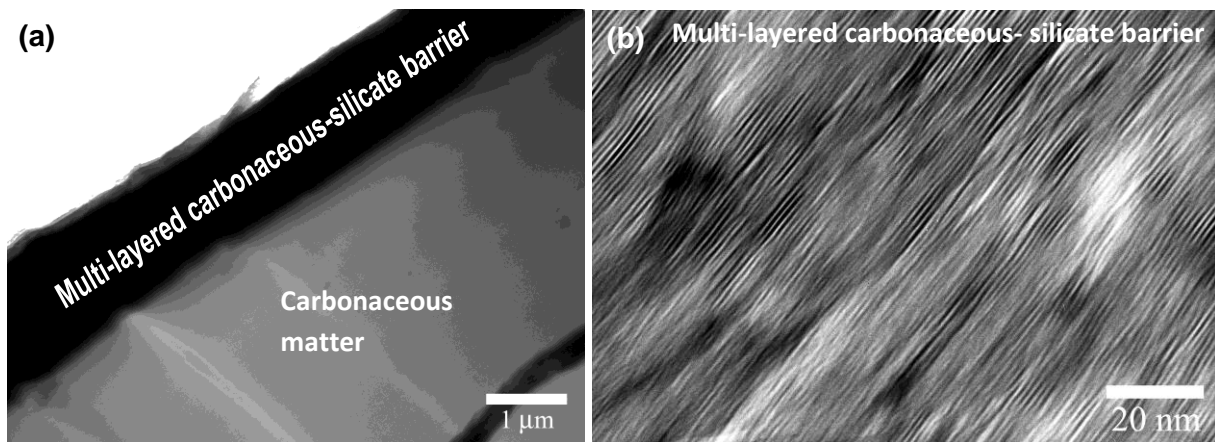


Figure 1. TEM micrographs of the cross-section beneath the top surface of the char layer at different magnification showing the multi-layered carbonaceous-silicate barrier with PA 6/organoclay (70/30) nanocomposite (Reprinted with permission from [92]. Copyright 2007, Institute of Physics).

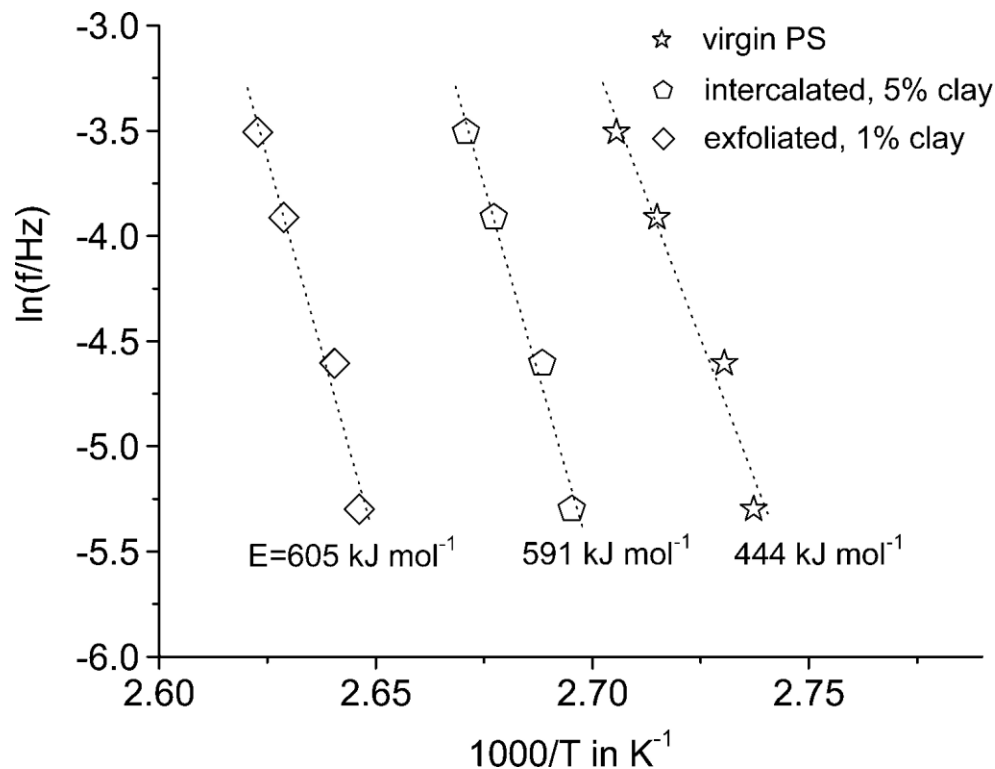


Figure 2. Activation energies of the glass transition temperatures, which were determined from frequency dependence of heat capacity (Reprinted with permission from [94]. Copyright 2007, American Chemical Society).

Besides, in our recent investigations, we also pointed that full migration of clay platelets to the top burning surface is a major problem; and so is the formation of a continuous and thick barrier [92, 103-105]. Despite this, peak HRR values of nanocomposites were greatly reduced. Using volume imaging approach, we have shown that after the structural collapse, uniform but intermittent (and thick) inorganic barriers are formed at different thicknesses of the sample (see example in Figure 3a) [105]. These intermittent carbonaceous-silicate barriers might be responsible for the enhanced flame retardancy properties of the nanocomposites (huge reductions, by more than 50%, of HRRs/MLRs of nanocomposites in addition to a large delay in burning compared to their corresponding neat polymers). That is, they force the oxygen or volatiles or heat to traverse a tortuous path in the polymer matrix surrounding these barriers. This obviously increases the effective path length for diffusion. Even the loading does not seem to play a major role in reducing the HRRs/MLRs, since the differences are not significant once a critical composition is reached (see Figures 3b and 3c [11, 92]). This is despite the significant differences that were seen on the surface of the residues. Many discrete island-like structures (with many large cracks) were observed at 10 wt.%, (Figure 4a); in contrast, at higher loadings,

the residues appeared to be solid-like and continuous (Figure 4b) with minimum number of (fine) cracks. Physically, this suggests that the evolution and formation of *sufficient* intermittent structures, as mentioned above, is possibly one of the determining factors. That is, factors such as incoherency and non-uniformity of the char or presence of large cracks on the surface were relatively insignificant in further reducing HRRs/MLRs. Even the nano-confinement concept seems to follow this pattern since it is generally expected to be large at higher loadings of well dispersed/distributed clay. But the results shown in Figures 3b and 3c seem to indicate otherwise. Nonetheless, the approximate relative % reductions in Figure 3b are 40, 65 and 77.5 for 2, 5 and 10 wt% organoclay, respectively, and in Figure 3c, they are ~45% for all loadings (10, 20 and 30 wt%). This by itself is a clear indication that the extent of % reductions in peak HRR depends on other factors such as the matrix viscosity (PA6 used in developing Figure 3b was a low viscosity grade, while that for Figure 3c was a high viscosity grade). So, the structural collapse and formation of intermittent barriers would occur faster in the low viscosity grade compared to the high viscosity grade material giving rise to the observed differences.

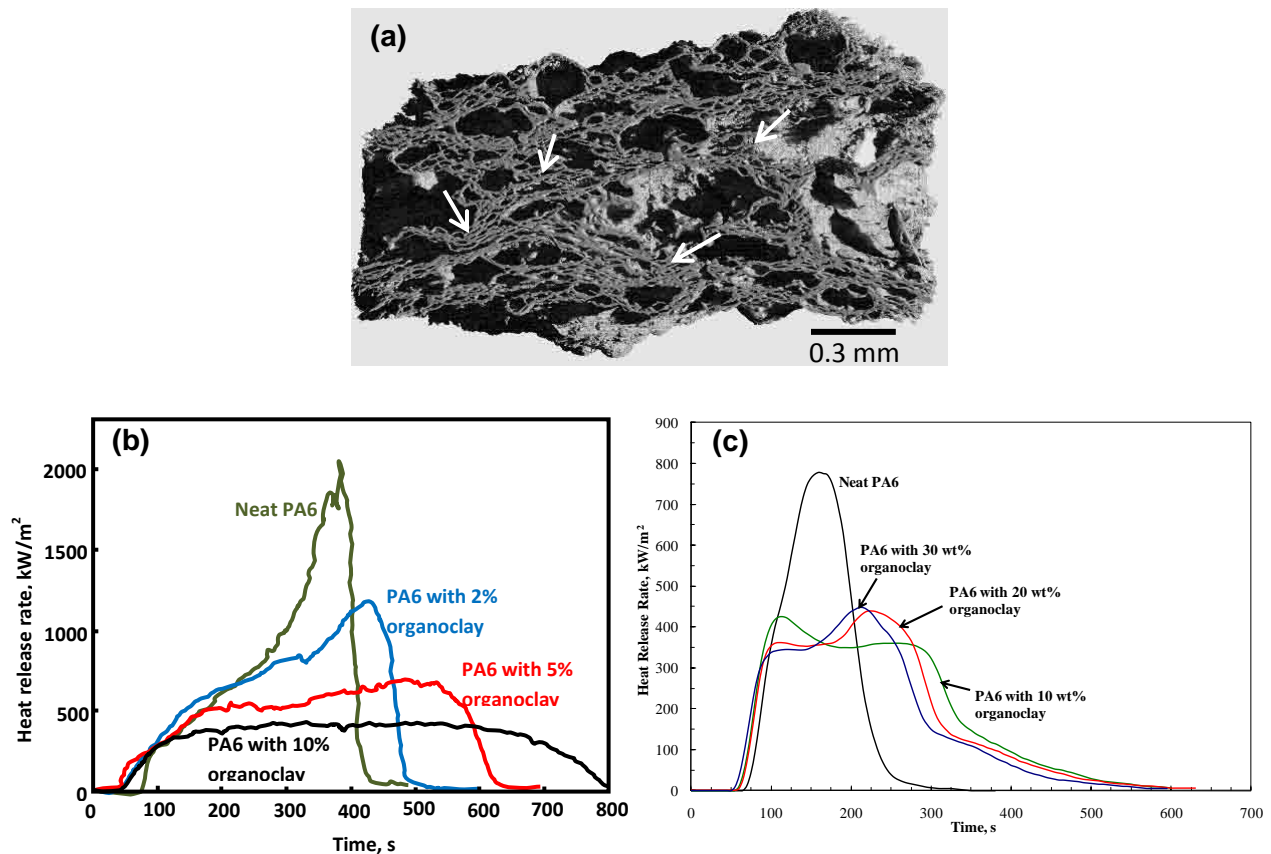


Figure 3. (a) X-ray tomogram of a residue of PLA/silicate nanocomposite showing the internal structural organization of silicates as indicated by arrows (Reprinted with permission from [105]).

Copyright 2012, Elsevier); (b, c) effect of organoclay loading rate on HRR curves for PA 6 nanocomposites at 50 kW/m² (adapted from [11, 92]). Note that (b) and (c) are taken from two independent studies and so the materials by themselves cannot be directly compared. These results are only meant for qualitative comparison.

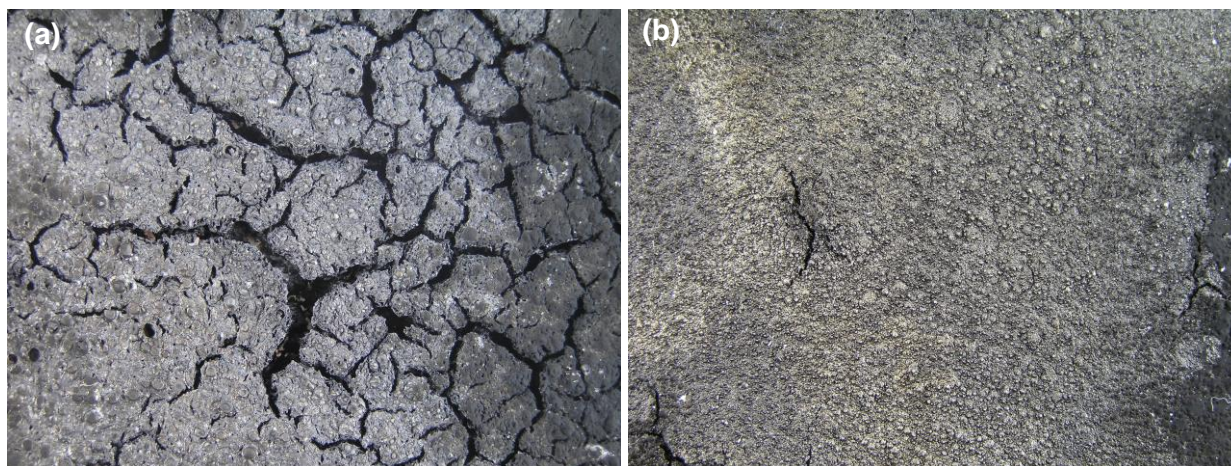


Figure 4. Digital photographs of the residues left after combustion test at an incident heat flux of 50 kW/m² for: (a) PA 6/organoclay (90/10) and (b) PA 6/organoclay (70/30) nanocomposites (Reprinted with permission from [92]. Copyright 2007, Institute of Physics).

Besides, XRD analysis (of the carbonaceous-silicate barrier) of a range of fire exposed polymer/clay nanocomposites revealed that the interlayer spacing was ~1.3 nm, inferring the same nature of the residue irrespective of the matrix (thermoplastics or thermosets), loading, and structure (exfoliated or intercalated) of the original nanocomposite. However, the reductions in HRRs/MLRs depend on the level of exfoliation and aspect ratio of particles. In fact, researchers at the NIST, USA have characterized the surface, middle and bottom layers of PS/clay nanocomposites at different exposure times using XRD and found a 'step decrease' in *d*-spacing from ~3.27 nm (initial spacing of PS/clay nanocomposite) to ~1.3 nm as exposure time increases (Figure 5) [106]. This contraction suggests the loss of polymer from between the clay layers and as the exposure time increases, thermal degradation permeates deeper into the sample. If the thickness of an individual clay layer (completely dehydrated) is taken as 0.7 nm, then ~0.6 nm difference corresponds to the carbonaceous layer intercalated into the clay layers, suggesting that this spacing is a thermodynamically stable form of the clay-carbon material produced by thermal degradation [13, 107]. Besides, in our recent investigation on this aspect, we found that this is valid even with just as-received organoclay (alkyl ammonium treated

montmorillonite) [103]. XRD patterns of this organoclay were collected at various temperatures, which clearly revealed that the initial d_{001} peak at $2\theta \sim 4.5^\circ$ (at 25°C) corresponding to an interlayer spacing of $\sim 1.8\text{ nm}$ starts to shift towards higher angles with temperature (depending on the thermal stability of the modifier) and at 450°C , the peak is located at $2\theta \sim 7.0^\circ$ (d -spacing $\sim 1.3\text{ nm}$). However, beyond this temperature due to the dehydroxylation process of aluminosilicate lattice, this peak is further shifted to higher angles, broadened and with a very low intensity.

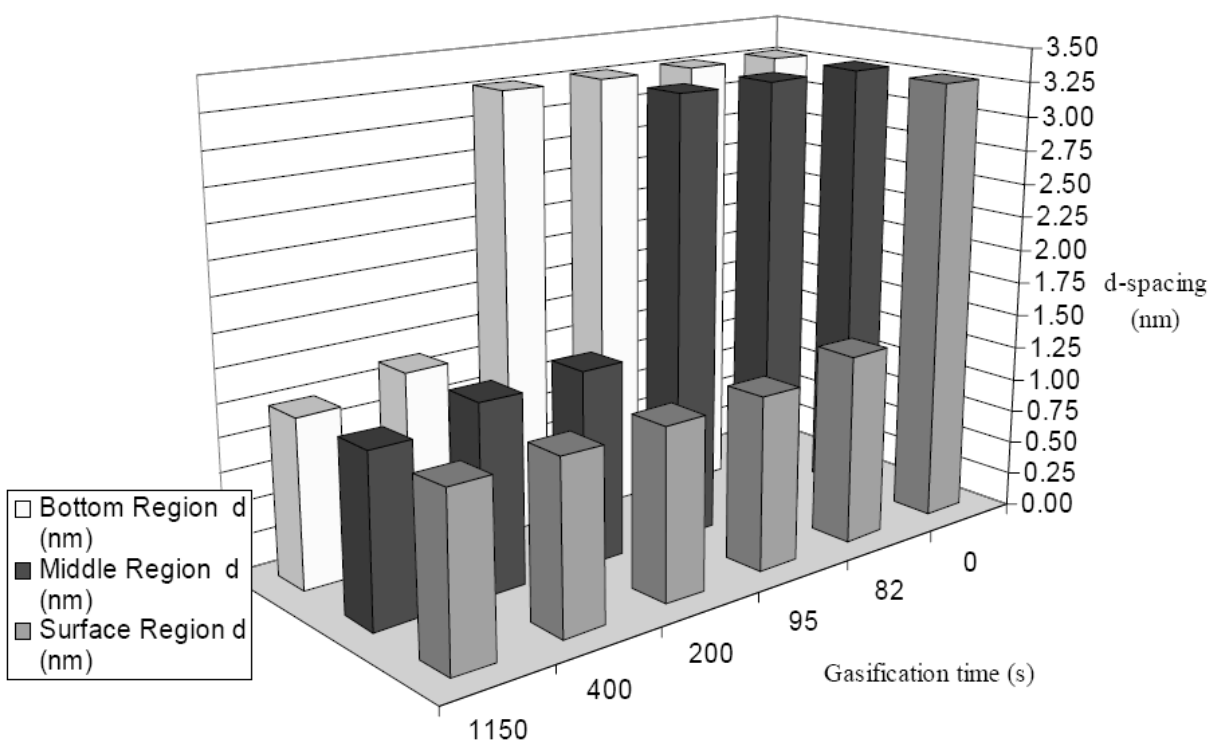


Figure 5. A step decrease in clay-char d -spacings (in different regions) with gasification time (after [106]).

Irrespective of the 50-70% reductions in HRRs/MLRs with polymer/clay nanocomposites, the total heat released was almost similar to the neat polymers, a major disadvantage of these materials in a fully developed fire situation. This is because the nanocomposites do not self-extinguish until most of the fuel has been burnt, i.e., they burn slowly but completely. This raises some critical questions about the homogeneity, physical stability, migration of clay layers to the burning surface and thickness of the carbonaceous-silicate layer. Even when the fire scenario changes from a developing fire (as evidenced in the cone calorimeter) to an ignition scenario, these materials perform poorly. This is clearly reflected by the poor results of the UL 94 vertical

burning and LOI tests. Besides the usage of organic surfactants with poor thermal stability to modify clay layers, the catalytic activity of clay layers by themselves (promoting polymer degradation) may increase the probability of an earlier ignition.

4.2. Needle-like sepiolite: Sepiolite, another phyllosilicate, needle-like with open nano-tunnels, was also used as an FR in a few recent studies [105, 108-111]. Sepiolite particles have an average length of 1 to 2 μm , width ~ 10 nm, and the dimensions of open channels (along the axis of a particle) $\sim 3.6 \text{ \AA} \times 10.6 \text{ \AA}$ (Figure 6). The arrangement of these particles results in loosely packed and porous aggregates with an extensive capillary network. It has a high surface area about $300 \text{ m}^2/\text{g}$ and with high density of silanol groups (-SiOH). Marosfoi *et al.* [110] in an effort to reduce the loading of traditional MH in polypropylene used natural and organically modified sepiolites. Though the % reductions in HRR with just sepiolite (irrespective of modification) alone are not highly promising, in combination with magnesium hydroxide, the results are promising. However, as evident from Table 1, the time-to-ignition decreases drastically with sepiolite. This was explained by considering their inter-channel networks that could hold accumulated heat and use it as a heat source to accelerate the decomposition process in conjunction with the heat flow supplied by the outside heat source. Besides, when combined with organoclay, the peak HRR value was further decreased (see Table 1). The formation of bridges between micro- and nano- scale particles through sepiolite was believed to be the reason for this improvement. In our recent investigation, we noted less prevalence of the abovementioned mechanism of accumulation of heat in sepiolite inter-channel networks. Rather, based on the tomograms of the residues, it was concluded that there was no distinctive migration to the burning surface or grouping at intermittent thicknesses (considering the size of sepiolite particles) (Figure 7).

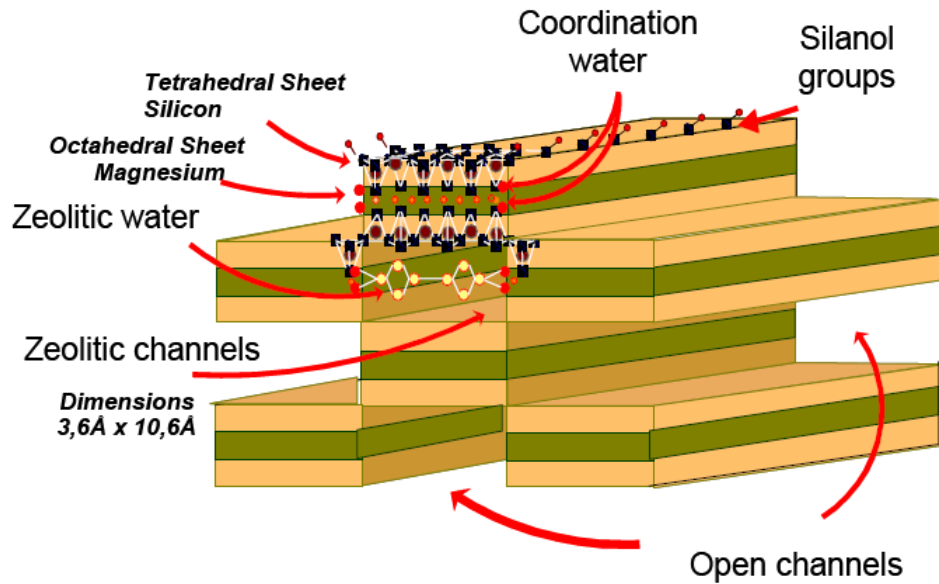


Figure 6. Schematic representation of the crystal structure of sepiolite (Courtesy: Tolsa S.A., Spain).

Table 1. Cone calorimeter results for polypropylene and its composites (after [110]).

Material	Time-to-ignition, s	Peak HRR, kW/m ²	Time to reach peak HRR, s	Total heat released, MJ/m ²
Neat PP	37	584	167	75.6
PP/Mg(OH) ₂ (90/10)	33	471	158	65.9
PP/sepiolite (95/5)	24	533	111	68.1
PP/organo-sepiolite (95/5)	23	515	124	66.1
PP/organo-sepiolite/Mg(OH) ₂ (85/5/10)	29	328	202	62.1
PP/organo-sepiolite/organoclay (95/2.5/2.5)	62	417	213	63.7
PP/Mg(OH) ₂ /organo-sepiolite/organoclay (85/10/2.5/2.5)	54	246	294	56.3

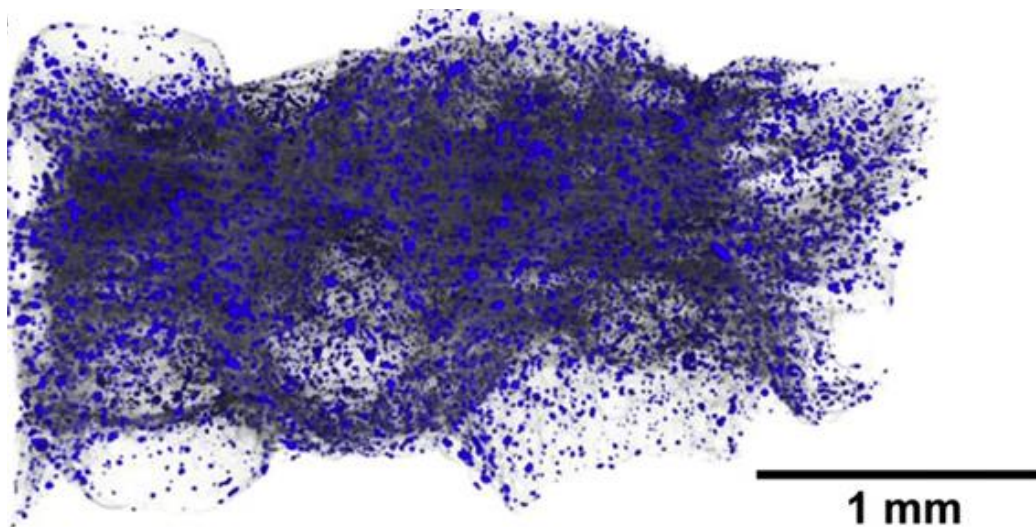
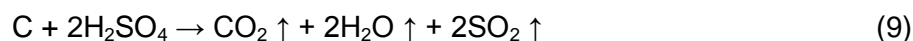


Figure 7. Tomogram showing the uniform distribution of sepiolite particles (blue dots) even in the burned sample (Reprinted with permission from [105]. Copyright 2012, Elsevier).

4.3. Carbon nanotubes: Similar results of reduced HRRs/MLRs and delayed burning, and their dependency on aspect ratio of fillers, but negative UL 94 and LOI data were even observed with CNTs (for example, see [112-119]). However, during the combustion of polymer/CNT nanocomposites, although a nanotube interconnected network layer forms which protects the underneath polymeric material from the radiant heat flux, in most cases, the polymer is completely burnt leaving behind only a layer of CNTs (using a conventional cone calorimeter and *not* a gasification apparatus where the results are purely based on the condensed phase mechanisms). Furthermore, in most cases, the mass of the residue is very close to the initial mass of the carbon nanotubes in the original nanocomposites indicating that the network layer (unlike clays) does not enhance char formation. This was true in the measured cases of PP and PA 6 [104, 114]. So, it is believed that CNTs may be addressed as adjuvant in certain systems and scenarios rather than as a general fire retardant. A different behavior was, however, observed in LLDPE, where somewhat thicker combustion residues were left over with CNTs (multi-walled) [113, 117]. But irrespective of the cracks and CNTs loading, that is, highly fragmented *versus* compact residue, a similar reduction in HRRs to PP or PA 6 systems was observed. In LLDPE, the authors noted that CNTs favor the formation of a surface polyaromatic carbon char in thermal oxidative degradation during the first step of LLDPE volatilization. This aromatic char formation was also used to explain the influence of CNTs loading; even at a lower loading of CNTs (0.5 wt%), a thin protective film is rapidly formed and therefore, higher loadings would not add much benefit to decreasing the rate of combustion.

4.4. Graphite oxide: GO or more commonly known as expandable graphite is a pseudo 2D solid-like layered compound where carbon atoms within the layered nano-sheets form hexagonal cells through covalent bonds; and the carbon layers are joined to each other by weak van der Waals forces. It has some oxidants like sulphuric acid, hydrogen peroxide and/or potassium permanganate inserted between the carbon layers of graphite and has various functional groups on it, including hydroxyl, carbonyl and epoxy. It has been shown to be a very efficient intumescent agent as it acts both as a carbonization compound and a blowing agent [120-123]. In fact, even with 10 wt% of expandable graphite in high-density rigid polyurethane foam, Shi *et al.* [124] have obtained a V-0 rating since the filler can benefit from both its layered structure ('physical' barrier mechanism) and intumescent/blowing effect ('chemical' mechanism). According to Camino *et al.* [33], the expansion of GO occurs by a redox reaction (equation 9) between sulphuric acid and graphite that originates the blowing:



During the voluminous expansion, the lamellar structure of GO particles is transformed to a vermicular structure and exfoliates along the *c*-axis of a graphite crystal. It has also been reported that ~10 wt.% blowing agent (water) is liberated at 600 °C [120]. The release of water and expansion of graphite suffocate the flames, and the char layer limits the heat and mass transfer from the polymer to the heat source. This obviously results in a V-0 rating as shown in many studies and huge reductions in HRRs/MLRs. Despite this, it is important to note that the residue is extremely soft which is definitely not beneficial from the viewpoint of safety (may result in the quick collapse of a structure) [103].

4.5 Other miscellaneous FRs: Using melamine (or in combination with other nanoparticles) in polypropylene and polyamides, a V-0 rating was achieved by extinguishing the fire [8, 10, 125]. However, the primary mechanism for this is dripping; that is, they drip away from the flame. So, despite passing the test standard, the commercial application of these materials is restricted as there is every possibility that they will burn completely if exposed to long term flame conditions (forced combustion). On the contrary, the presence of clay layers or CNTs was shown to increase the melt viscosity during burning so that the material as a whole behaved rheologically like a gel (and prevented the dripping and flowing of the nanocomposite) [88, 115, 119]. Therefore, it is essential to thoroughly analyse, understand and compare various parameters

that affect the fire performance of polymer nanocomposites to obtain in-depth information on the applicability of materials.

Compared to cationic clays described above (Section 4.1), LDHs or hydrotalcites or anionic clays are a fairly new class of materials and represented by the formula $[M^{II}_{1-x}M^{III}_x(OH)_2](A^{m-})_{x/m} \cdot nH_2O$ [126-128]. M^{II} represent divalent (or monovalent) cations such as Mg^{2+} and Zn^{2+} , M^{III} trivalent cations Al^{3+} and Cr^{3+} , and A interlayer anion with valency m (like Cl^- , CO_3^{2-} , SO_4^{2-} and NO_3^- etc). In general, LDHs have an octahedral structure similar to brucite - $Mg(OH)_2$ where the partial isomorphous replacement of a divalent cation with a trivalent cation produces positive charges counter balanced by hydrated anions. Similar to cationic clays, LDHs can be modified by intercalating organic ions between the layers to fabricate nanocomposites. Their lamellar structure and anion exchange properties make them attractive for many applications such as ion-exchangers, adsorbents, pharmaceutical stabilizers, thermal stabilizers and flame retardants. However, the strong electrostatic attraction between the hydroxide sheets and short interlayer distance makes LDH materials relatively difficult to exfoliate in a polymer [127] compared to smectitic clays.

Nevertheless, even LDHs, by themselves are not enough to achieve an adequate level of fire performance in polymers. Jiao and Chen [129] pointed to synergistic performance in combination with ZnO in EVA/LDH nanocomposites. Wilkie and co-workers [130] compared the thermal and fire performance of EVA filled with phenyl phosphonate intercalated LDHs, boric acid and MP. Intercalation of LDHs with PPh was carried out by rehydration of the calcined hydrotalcite (MgAl-carbonate) followed by the addition of phenyl phosphonate solution prepared by dissolving phenyl phosphonic acid in a 0.2 M solution of NaOH in water/glycerol (1:2 v/v) under a steady flow of nitrogen to exclude carbon dioxide at 50 °C. It was revealed that 10 wt.% of MgAl-PPh showed the highest enhancement in thermal stability and even relatively good flammability properties in terms of peak HRR value and total heat released. The time-to-ignition and the time to reach peak HRR are reduced in the hybrid materials (Table 2). In another study, Zhang *et al.* [131] pointed out that when PP was directly melt compounded with LDH and an intumescent compound APP/PER, APP and PER segregated and affected the optical properties. For this reason, they used SDS to enlarge the basal spacing of the LDH before melt blending. Following this, APP and PER easily entered the enlarged galleries of LDH in water solution and confining there. The composite of PP/APP/PER/LDH has a higher LOI value of 31 and achieves a V-1 rating in UL 94 test with 30 wt.% of the modified filler.

Table 2. Cone calorimeter results for EVA and its composites at a heat flux of 35 kW/m² (after [130]).

Material	Time-to-ignition, s	Peak HRR, kW/m ²	Time to reach peak HRR, s	Total heat released, MJ/m ²
Neat EVA	65 ± 2	1680 ± 29	204 ± 8	124 ± 2
EVA/BA-10	35 ± 5	899 ± 66	207 ± 8	112 ± 2
EVA/MP-10	47 ± 11	715 ± 47	206 ± 28	112 ± 1
EVA/MgAl-PPh-10	33 ± 3	793 ± 40	140 ± 38	117 ± 1
EVA/MgAl-PPh/MP/BA-2/4/4	29 ± 1	669 ± 34	141 ± 10	114 ± 1
EVA/MgAl-PPh/MP/BA-4/2/4	31 ± 4	680 ± 33	140 ± 8	115 ± 2
EVA/MgAl-PPh/MP/BA-4/4/2	30 ± 2	671 ± 8	118 ± 6	114 ± 1

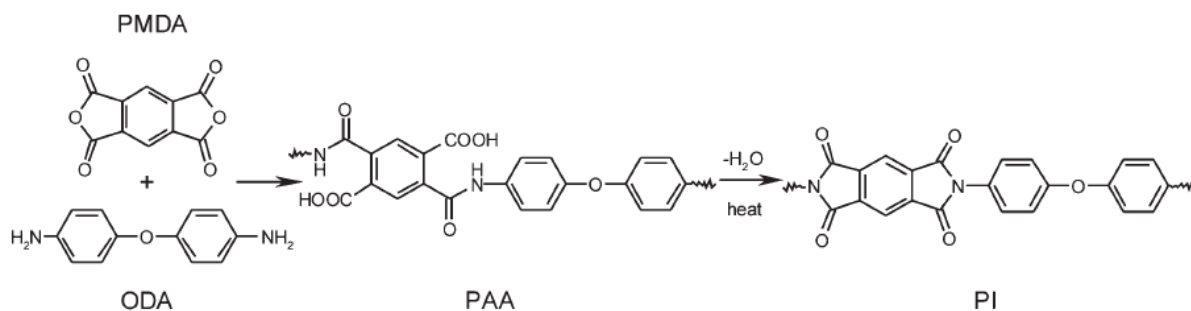
Apart from the high aspect ratio nanofillers, even spherical shaped particles (like TiO₂, SiO₂ or Al₂O₃) or molecular structured particles like POSS were also used for improving the fire resistance of polymeric materials [132-137]. But it is important to note that the general response in the literature with these particles is mixed, showing a dependency on their structure, nature of functional groups attached or the presence of other FRs. Some examples on this behaviour are given below.

Chen and Morgan [137] prepared epoxy/silica nanocomposites under mild processing conditions (low shear mixing) and achieved good dispersion of ~15 nm silica particles even at higher loadings of 30 wt.%. Despite the homogeneous dispersion and high loadings, flammability testing of the resulting materials *via* cone calorimeter suggested minimal reductions in HRRs pointing to the inertness of the filler. With molecular structured POSS compounds, generally, upon combustion and cage degradation, they produce a thermally insulating and oxidatively stable silicon oxycarbide ‘black glass’ (Si-O-C ceramic char), which should theoretically act as an insulating barrier. But when tri-silanol-phenyl POSS was used in PMMA, Jash and Wilkie [138] reported no improvements in flame properties compared to the neat polymer. With the same kind of POSS and even at 15 wt.% loading, we could not achieve any considerable improvements in the fire behaviour of PA 6 [103]. However, with V- and Ti-functionalized cubic silsesquioxanes and an isobutyl substituent on the cage corners, the oxidative degradation was shifted significantly to higher temperatures (around 70-80 °C) compared to metal-free POSS additives (tri-silanol-isobutyl-POSS) [132]. Similarly, Fina *et al.* [135] showed that when 10 wt.% Al-isobutyl silsesquioxane was used in PP, a decrease of

~43% in HRR was noted; but when Zn-isobutyl silsesquioxane was used under similar conditions, no noticeable changes in the combustion behaviour of PP were noted. The authors mentioned that this is probably due to a catalytic effect of the Al moieties, promoting secondary reactions during polymer degradation and resulting in partial PP charring.

Laachachi *et al.* [32] in an attempt to improve the thermal stability and fire retardancy performance of PMMA used aluminium monohydrate (boehmite) and alumina nanoparticles. 2% mass loss temperatures for all materials in the presence of AlOOH or Al₂O₃ (and irrespective of the loadings, up to 15 wt.%) are increased by ~17 °C compared to neat PMMA. Despite this, peak HRR reductions are not promising at lower filler loadings. More than 15 wt.% of AlOOH or Al₂O₃ nanoparticles is required to achieve a 50 % reduction in peak HRR relative to neat PMMA. Camino *et al.* [139] have also concluded that even though AlOOH has a positive effect on char enhancing capabilities, it is not an effective FR as Al(OH)₃ in EVA.

In other approaches, Scharrel and co-workers [140] deposited electrospun fibrous coatings of PI on PA 66 substrates and evaluated their fire behaviour. PI deposition was achieved in two steps, (i) the synthesis of the PAA precursor based on reacting PMDA and ODA (Scheme 4), followed by electrospinning; and (ii) subsequent imidization process to PI by thermal treatment. Although a delay in ignition was noticed with these materials compared to those without the coatings, HRRs (and peak HRRs) were mostly unaffected. This clearly indicates that the fibrous coatings act primarily as sacrificial layers delaying the ignition process of the substrate.



Scheme 4. Condensation reaction between di-anhydride PMDA and di-amine ODA to yield PAA; and imidization of PAA to PI (after [140]).

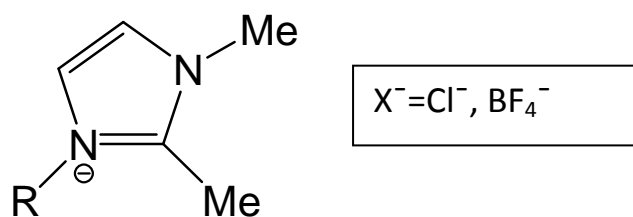
5. Issues with fire performance of polymer nanocomposites

Following from the above section and the data listed in Appendix A (illustrating the magnitude of fire retardancy performance of representative PA6 and EVA based nanocomposites), it is evident that clay platelets (even at relatively low loadings), yield good fire retardancy performance relative to other nanofillers in terms of reductions in peak HRR. Though similar results were noted with CNTs, the absence of physical rigidity of the char and its quality are huge disadvantages. Thus, in this section, emphasis will be mostly on layered silicates.

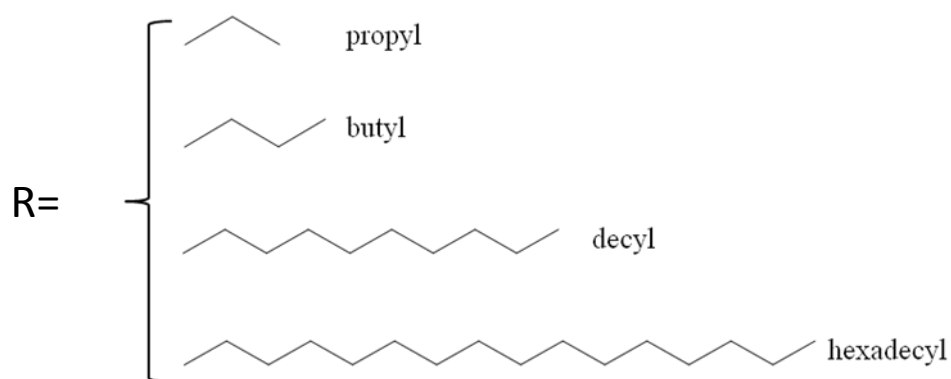
5.1. Thermal stability: Before we discuss this topic, it is important to note that improving the thermal stability of polymer nanocomposites does *not* guarantee superior flame retardancy performance. The purpose is to improve the onset decomposition temperature of the system, which might influence the ignition. It is customary to modify clay layers with organic surfactants by replacing the inter-layer cations with hydrophobic cations to enhance their compatibility with polymers. Based on the cation-exchange capacity of clay, the alkyl ammonium surfactant content in organic clay is usually over 30 wt.% [141, 142]. But these compounds are thermally unstable and decompose usually from ~180 °C. As the processing of most engineering polymers requires a temperature much higher than this, thermal decomposition of the organic salts is unavoidable and adversely affects the thermal stability of the nanocomposites. The decomposition (*via* Hoffman's elimination reaction) could also be one of the sources of fuel for ignition. But in some cases, it was also noted that once the organic treatment is decomposed, as the acidic site on clay surface has a direct interface with the remaining polymer, this results in hydrocarbon cracking and/or aromatization [91]. Though this char enhancement behaviour is a positive sign for fire performance of nanocomposites, it depends on many factors like silicate structure, acidity, etc.

Many efforts have been directed towards developing alternative routes to produce nanocomposites without using the conventional alkyl ammonium surfactants. Some of these approaches include: (i) partially exchanged systems that decrease the amount of surfactant required [143]; (ii) sol-gel technology consisting of direct crystallization of organically modified layered silicates by hydrothermal treatment with a gel containing organics and organometallics [144]; (iii) usage of thermally stable compounds based on imidazolium, phosphonium, pyridinium, and iminium to increase the initial decomposition temperature [145, 146]; (iv) water-assisted approach [147, 148]; and (v) surfactant-free method [149].

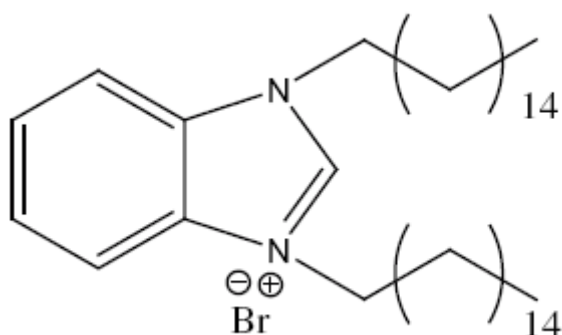
In particular, the treatment of clay with aromatic compounds based on imidazolium salts via standard ion-exchange methods shows tremendous improvement in thermal stability of modified clays. This is due to the higher bond energy of rigid rings (aromatic) than chain-like (aliphatic) molecules. An obvious drawback of this methodology, however, is the lack of compatibility of modified clay(s) with different polymeric systems and the high costs associated with these salts. Gilman *et al.* [145] prepared several trialkylimidazolium salt derivatives with propyl, butyl, decyl, and hexadecyl alkyl chains (Scheme 5) and used them to treat clay layers (montmorillonite). They obtained an improvement of ~100 °C (in terms of peak decomposition temperature) by using 1-alkyl-2,3-dimethylimidazolium-treated clay in nitrogen compared to common alkyl ammonium clay. The disadvantage for this method is that the synthesis cycle is very long; to add an alkyl on to 1, 2-dimethylimidazole, it takes 7-10 days refluxing under nitrogen atmosphere, which may restrict the practical application of this surfactant. As the enhanced thermal stability of imidazolium surfactants was attributed to the delocalization of the positive charge over the imidazole ring [150], Costache *et al.* [151] attempted to increase the charge delocalization by fusing a benzene ring to imidazole and synthesized two types of benzimidazolium (1,3-dihexadecyl-3H-benzimidazol-1-ium and 2-methyl-1,3-dihexadecyl-3H-benzimidazol-1-ium) modified clays and used them in PS, ABS and HIPS. They observed mostly intercalated structures of these modified clays in all polymers at the meso-scale pointing to a negative aspect of these clays. However, thermal stability of the nanocomposites was enhanced similar to alkyimidazolium-modified clays. Moreover, the reaction time was shortened to less than 1.0 h. In another study, Cai *et al.* [104] used similar benzimidazolium modified clay in PA 6 system and also found that the dispersion of the layers was poor. This was attributed to the higher (or increased) steric hindrance partly in the presence of (another) long tail in benzimidazolium (Scheme 6) and partly due to fusing of benzene ring to imidazole affecting the rigidity of the aromatic ring. The higher steric hindrance makes it more difficult for the polymer chain to enter the interlayer.



Dimethyl alkyl imidazolium salts

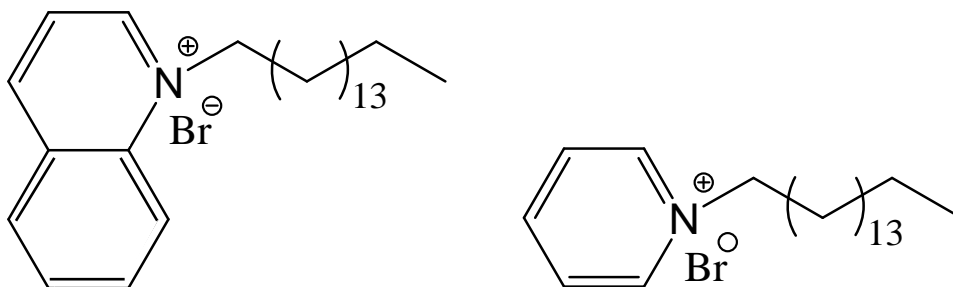


Scheme 5. Structures of various imidazolium salts used to treat sodium montmorillonite (after [145]).



Scheme 6. Structure of benzimidazolium surfactant used to modify silicate layers (after [104]).

In another attempt, pyridine and quinoline-containing salts (Scheme 7) were employed to modify clay layers [146]. Although enhanced thermal stabilities were achieved for modified clays/PS-based nanocomposites and the synthesis of quinolinium/pyridinium salts is relatively simpler than imidazolium salts, the yield rates are very low (around ~5%), which is a huge disadvantage.



Scheme 7. Structures of quinoline- (left) and pyridine- (right) salts (after [146]).

Very recently, Shi *et al.* [149] used a surfactant-free method to tackle the problem of degradation of low molecular weight surfactants. They used a masterbatch approach where firstly, vinyl acetate was copolymerized with AETMC to give cationic polyvinyl acetate containing different % of cationic units; secondly, these cationic polymers were used to synthesize PVAc/clay nanocomposites; and finally, using these nanocomposites as masterbatches to prepare EVA nanocomposites *via* solution blending. The authors observed good dispersion of nanoparticles in EVA along with improved thermal stability, particularly when cationic comonomers were used (that is with AETMC over those prepared without AETMC). The improved dispersion of clay layers with cationic moieties was attributed to the increased polarity of cationic vinyl acetate copolymers due to the presence of the higher amount of the cationic comonomer contents (on top of clay layers). Even the radiative gasification tests indicated a huge reduction in peak mass loss rate and more than twice the gasification time when the clay layers were homogeneously dispersed (Figure 8).

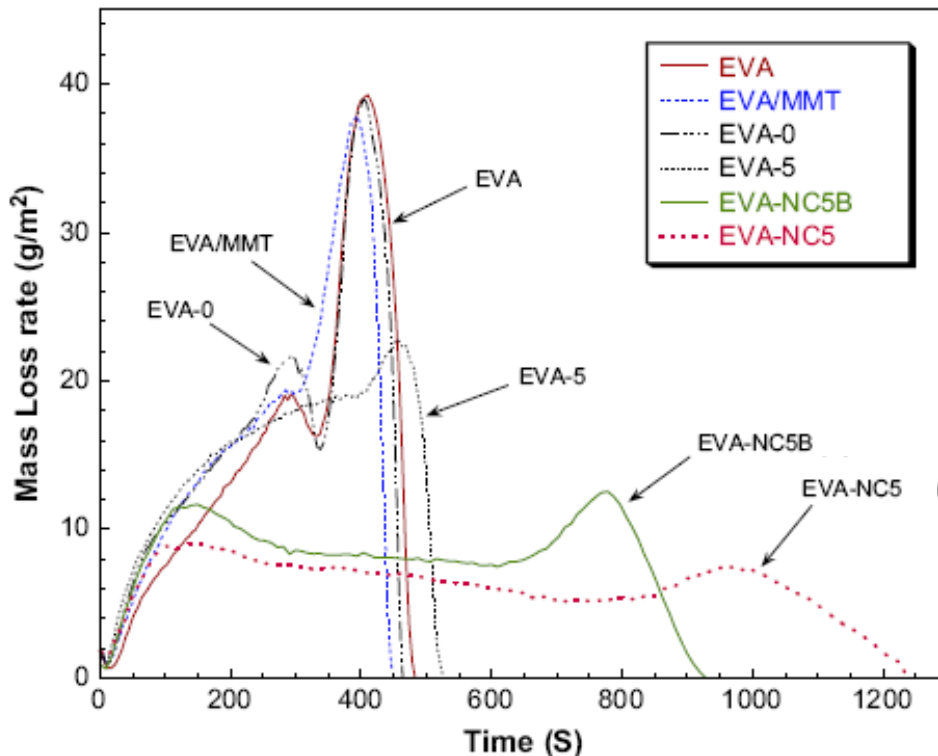


Figure 8. Mass loss rates of EVA and its composites measured at a heat flux of 50 kW/m². EVA/MMT has 5 wt.% of unmodified MMT; EVA-0 contains 20 wt.% of cationic vinyl acetate

homopolymer and is the reference sample for EVA-5 containing 5 wt.% of unmodified MMT; EVA-NC5B is prepared according to the master batch process with 20 wt.% of cationic vinyl acetate containing 2 mol.% of cationic moieties and 5 wt.% MMT; and EVA-NC5 was prepared similar to EVA-NC5B, but with only 1 mol.% of cationic moieties (Reprinted with permission from [149]. Copyright 2009, Elsevier).

In a few studies, water was also used as a substitute to organic agents [147, 148]. Since water is a powerful swelling agent for pristine clay and a natural plasticizer of polyamide, it will assist in intercalation/exfoliation of the clay layers *in situ* in the extruder during compounding. Yu *et al.* [148] injected water into the extruder barrel downstream with a mass flow rate of 9 g/min during melt extrusion of polyamide 6/pristine clay composite. After mixing, water was removed from the composite further downstream *via* a venting gate before the composite exited from the extruder die. Although good results in terms of dispersion and thermal stability were achieved with the water-assisted approach, it is too early to apply commercially. The difficulty of applying this method to other polymers is another major disadvantage. For example, Kato *et al.* [152] prepared PP/clay nanocomposites using a modified clay-slurry method in which the clay-slurry was obtained by pumping water into the extruder containing the PP melt and clay mixture. Exfoliated structure of clay in PP was successfully obtained, but they used two types of organic compatibilizers in order to stabilize the nano-morphology.

5.2. Time-to-ignition and thickness of samples: Generally, for non-charring polymers in radiative heating, it is assumed that TTI is independent of the imposed heat flux [153]. Some models correlating TTI and heat flux have also been proposed assuming no changes in the physical constants of the material prior to ignition [154]. Due to the lack of considerations like melting/decomposition of the polymer during heating and others such as changes in the surface absorption/emission properties (affecting the heat flux), there is always uncertainty in predicting the TTI. This is particularly true for polymer nanocomposites whose TTI is completely unpredictable and variable trends have been observed relative to neat polymers (see for e.g. [14, 15, 18, 20]). But qualitatively, in most of the studies on polymer/clay nanocomposites, an early ignition was observed for nanocomposites compared to their corresponding neat polymers.

As discussed before, thermal instability of nanoparticles (or their modifying agents) was attributed as one of the possible reasons for early ignition. But apart from this, in a recent study,

it was concluded that clay nanoparticles catalyze the oxidation of gases produced by the volatilization of polymer inducing early ignition [155]. For example, consider Figure 9 which shows the surface temperature plots of PET and its nanocomposites during cone calorimeter testing. Surface temperatures were measured by placing thermocouples in contact with the upper surface of the specimen throughout the combustion experiment. With neat PET, as expected, after the steep increase in temperature initially, it stabilizes upon reaching the melting temperature (~ 255 °C) for about 250 s owing to absorption of latent heat of melting. After completion of melting, a sharp increase in temperature was noted to a new plateau at about 400 °C. The authors correlated this with TGA (isothermal condition in air) and attributed to the decomposition of PET at about 0.13 wt.%/s. Interestingly, this surface temperature remained almost constant for 420 s until ignition at 730 ± 80 s (corresponding surface temperature 413 ± 9 °C). While the surface temperature plot of nanocomposite shows an increase in temperature after complete melting at ~ 300 s, suggesting that heat was available to increase the temperature and decompose polymer. Unlike neat PET, which required several minutes of heat transfer before ignition (around 420 s or 7 minutes), in nanocomposite, ignition occurred (at 380 ± 16 s) as soon as polymer volatilization temperature was reached. Also, the measured ignition temperature for the nanocomposite (407 ± 20 °C) is similar to neat PET. This suggests that the gases evolved from the top area of the specimen were sufficient for ignition, that is, nanoparticles can catalyze oxidation of the gases generated at the surface by volatilization of the polymer. Indeed, cross-sectional pictures of the residues from interrupted tests immediately after ignition clearly showed that only 1 mm of the sample from the top surface is involved in the process of ignition in nanocomposite, whereas the whole sample (3 mm) participates in the ignition of neat polymer.

Unlike neat PET, in neat PP, complete melting was observed at times longer than ignition time. That is, the specimen is not completely molten before ignition [156]. This in turn indicates that in neat PP ignition was a result of decomposition of thin surface layer producing the critical mass flux of volatile fuel. The authors attributed this to the order of magnitude difference in viscosity of PP and PET above melting, 40 Pa-s (at 260 °C) for neat PET compared to 1300 Pa-s for neat PP (experiencing completely different flow behaviour). The high viscosity in PP reduced the heat exchange by convection.

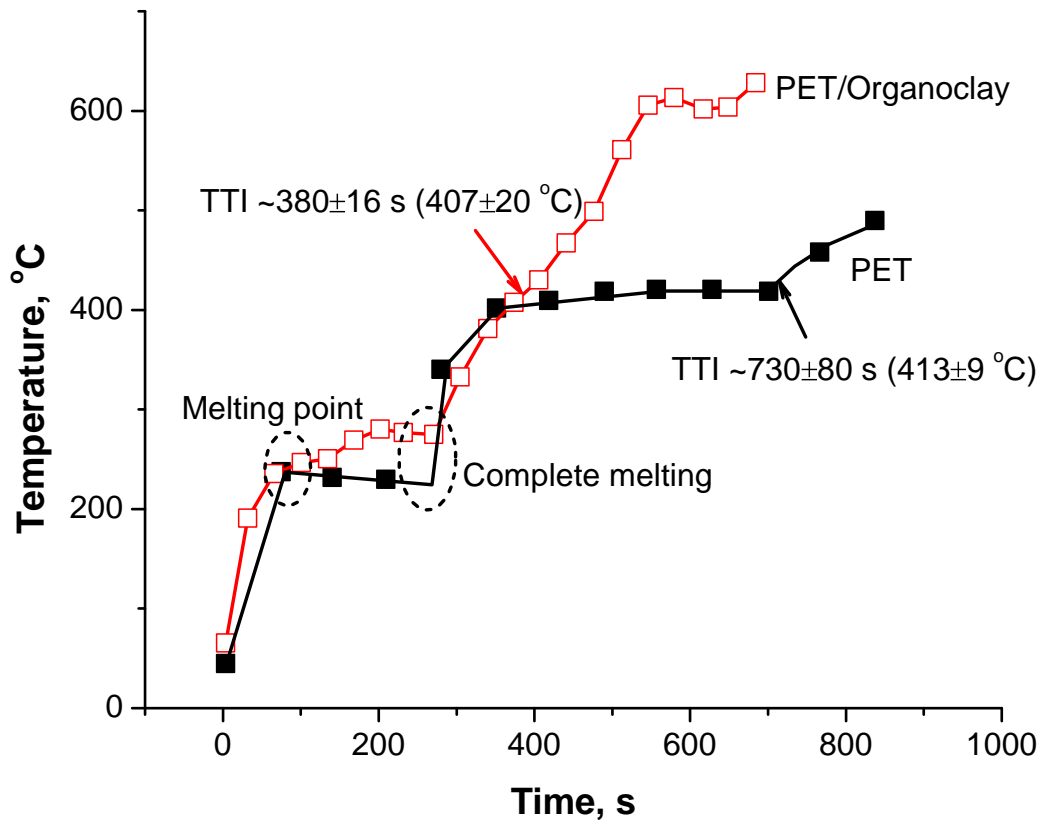


Figure 9. Surface temperature *versus* time for PET and PET/organoclay nanocomposite (adapted from [155]).

Besides, after the thermal decomposition of organic surfactants through the Hoffman degradation reaction, the acidic clay site formed on the layered clay surface will have a direct interface with the remaining polymer. Layered silicates in acid form are generally known to cause hydrocarbon cracking, which will further degrade the polymer. Hence, a combination of different parameters can be attributed to the early ignition of nanocomposites, particularly for layered silicates.

Differences in sample thickness will result in significant mechanistic changes and must be considered. For instance, in our recent investigation [105], we noted that with thermally thin polymer nanocomposite samples (for example, 1 mm thickness), despite the excellent dispersion of clay layers, no reductions in peak HRR values were observed compared to neat polymer (Figure 10). But with 3 mm thick samples, the HRR curves were as expected for nanocomposites with layered silicates; that is, considerable reduction in peak HRR and a delayed burning was noted. These results point to crucial mechanistic changes during combustion of thermally thin and thick nanocomposites. In thermally thin samples, due to the

limited volume, the whole sample is pyrolyzed at the same time and there cannot be any dependency on the conductivity of the material to control the heat transport into the material (and therefore no or little viscosity gradients). For thermally thick samples, the surface temperature is dictated by the thermal gradient within the sample and so the thermal conductivity and viscosity gradients are important. This in turn indicates that the fire performance (or HRRs) of thermally thin and thick materials can be related to the competition between the formation of a surface carbonaceous-silicate shield and the volatilization to fuel (polymer). Obviously, in thicker materials, the competition seems to favour barrier formation, while for thinner materials, volatilization dominates.

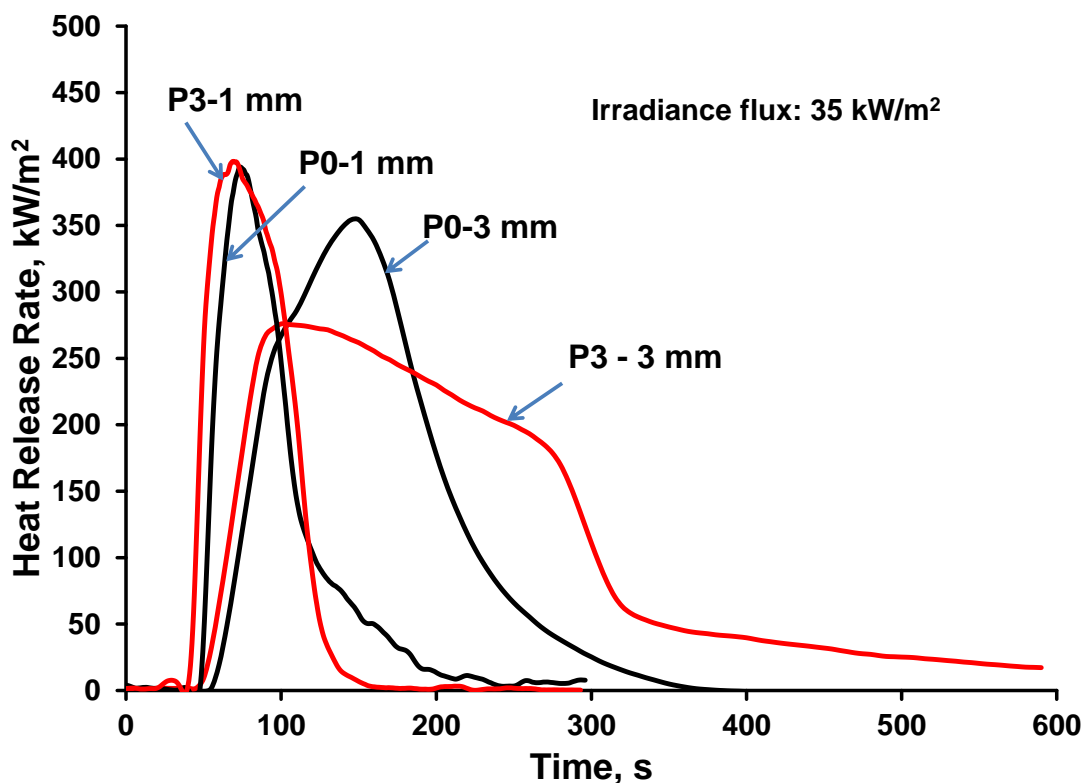


Figure 10. Comparison of the HRR curves of neat PLA (P0) and its clay-based nanocomposite (P3) with varying thickness tested at an irradiance flux of 35 kW/m^2 (adapted from [105]).

5.3. Migration of nanoparticles: Irrespective of the nano-confinement concept, structural collapse and migration of nanoparticles to the burning surface is another issue that influences the uniformity and stability of the nanoparticles/carbonaceous network structure formed. Many plausible driving forces for the migration of nanoparticles were considered including convection forces from the temperature gradient (which may accelerate the migration of clay particles in the

direction of the heat source), melt viscosity gradients (from the burning surface to the bottom), and lower surface free energy of the clay layers than carbon-based polymers. Apart from these, a rising bubbles theory was also considered. This process initiates when the polymer surface temperature becomes sufficiently high and degradation generates pyrolysis products, which are monomers, linear and cyclic oligomers, and small quantities of gas volatiles (depending on the polymer). These products are superheated, nucleate and form bubbles in the melt as the degradation temperature of the polymer is much higher than the boiling temperature of the monomer [2, 157]. The bubbles rapidly rise and burst at the heated surface evolving their contents into the gaseous phase as fuel vapour. To improve the fire performance, a simple solution is to suppress the bubbling rate and retard the fuel supply. However, during the travel of the bubbles to the top surface of the sample, they also push the nanoparticles with them and form a protective heat shield [13]. In addition, bursting of bubbles at the sample surface may also push any accumulated clay particles on the melt surface outwards from the bursting area promoting agglomeration to island-like floccules (e.g., see Figure 4a).

It should be noted that any or all of the above suggested theories can simultaneously occur during the combustion. There are no specific correlations among them that give an insight on their extent of contribution. Besides, irrespective of the driving forces for migration, there are other factors that influence this process like the interfacial interactions between polymer and clay layers and degradation temperature of the organic surfactants relative to the polymer. It should also be noted that only a portion of the nanoparticles are migrating to the top surface and evidence revealed the presence of numerous clay layers stacked together in the middle and bottom portions of the residue [92]. That is, if the clay structure collapses completely before their migration, it is possible that these clusters/stacks cannot be pushed by the rising bubbles or cannot migrate based on any of the other driving forces. As discussed earlier, these intermittent (and thick) inorganic barriers at different thickness of the sample were useful in reducing the peak value of HRRs and imparting a reinforcing effect on the char.

Tang and Lewin [158] studied the migration aspect of clay layers from a different perspective. They annealed PP/clay composites at different temperatures and times in controlled environments from 100% N₂ to 100% air. Using the attenuated total reflectance FTIR spectroscopy, the surface concentrations (to 4 μm deep) of clay (-Si-O- intensity) and carbonyl groups were recorded on the original and annealed samples. It was observed that the value of R₂ that characterized the change of clay concentration at the surface after annealing or the

extent of migration of clay layers, increased with increasing %O₂ in the stream and the highest value was recorded when the stream was just air (ambient). R₂ is the ratio of R₁ to R₀, where R₀ and R₁ are the normalized intensities of –Si-O- peak at room temperature and after annealing. Since the presence of carbonyl groups on the surface represents the extent of thermal oxidation, R₄ can also be calculated in a similar manner, which is the ratio of concentrations of carbonyl groups before and after annealing. As shown in Figure 11, the migration of clay layers increases with increase in concentration of carbonyl groups or thermal oxidation. However, this methodology (where heating is non-directional and slow combustion occurs due to the diffusion of oxygen from the top surface) cannot be directly compared to the traditional cone calorimetric or gasification tests (where heating is directional and produces temperature/viscosity gradients).

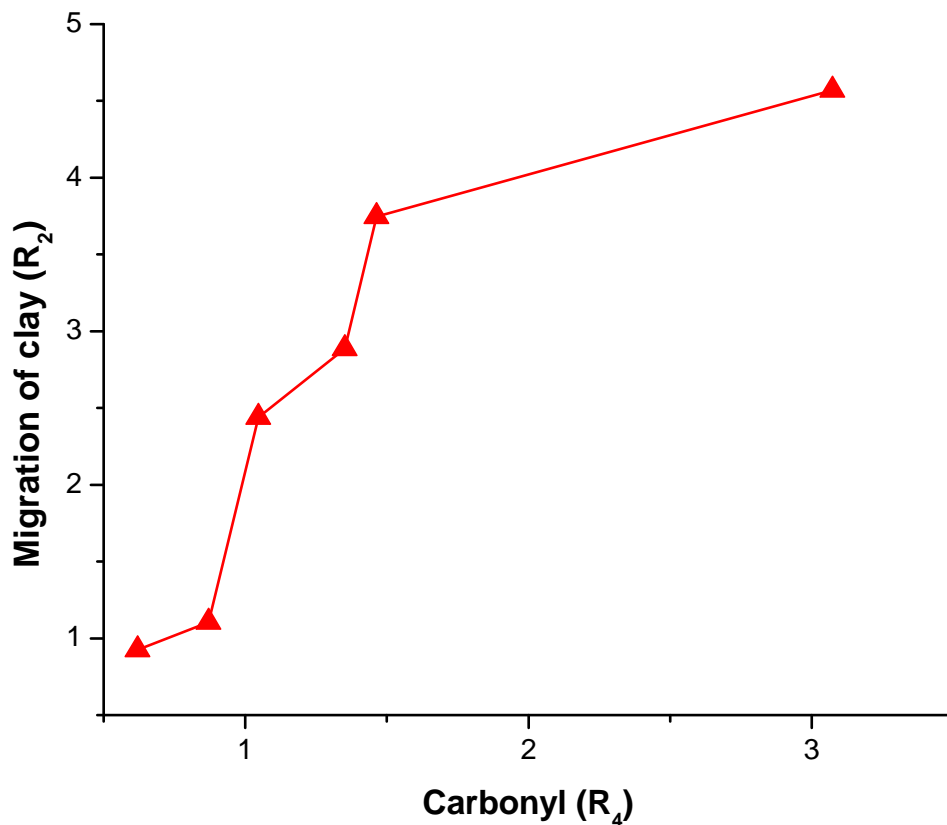


Figure 11. The value of migration (R₂) versus carbonyl (R₄) of samples annealed at 190 °C under different concentration of air for 1 h (adapted from [158]).

5.4. Homogeneity/uniformity of the barrier: Apart from the migration, for most effective flame retardancy performance, the protective barrier should (a) cover uniformly the entire sample

surface in order to fully shield/protect the polymer melt; (b) have sufficient physical strength (packing density) not to be broken or disturbed by bubbling; and (c) remain intact over the entire burning period. However, as discussed before, nanoparticles by themselves, irrespective of the loading and huge reductions in HRRs/MLRs, are unable to extinguish the fire under forced combustion. This indicates that the protective barrier, even if it appears smooth with no major cracks, is always permeable to mass/heat transfer, probably due to the presence of fine cracks. Therefore, as the degradation products evolve through such cracks to the gas phase, they will compromise the reductions in HRRs. Kashiwagi *et al.* [159] using a gasification apparatus showed that, particularly at the early stages of the (gasification) process, the physical strength of a clay particle network structure was not strong enough to prevent the formation of many small cracks in the surface layer (Figure 12). They thought that this might be due to the stiffness and less entangled nature of the clay platelets.

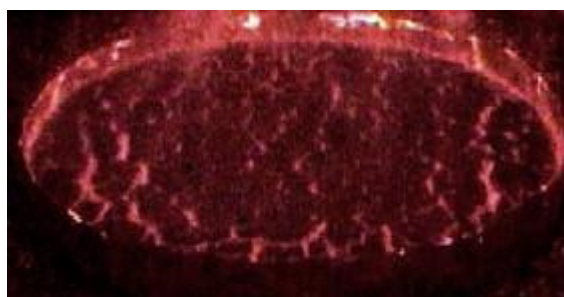


Figure 12. Formation of cracks at about 70 s from the start of the test in a gasification apparatus for an acrylonitrile-styrene/organoclay (95/5) nanocomposite. Test was conducted at a flux of 50 kW/m² in nitrogen atmosphere (Reprinted with permission from [159]. Copyright 2009, Elsevier).

To tackle this problem, some suggestions and efforts were made like the usage of high temperature silica precursors to modify nanoparticles, adding small amounts of inorganic additives like low melting glass and zinc borate during melt compounding, and the usage of compounds like POSS as a sealant [37, 103, 160]. These compounds transform to a partially ceramic-like material, coupling all silicate layers to each other upon firing and enhance the structural integrity of the char by effectively providing a continuous coating or fill the voids in the char. Nevertheless, either their effectiveness was not yet confirmed and still needs thorough testing/understanding or the results are not entirely positive. For example, with POSS, as the cage degradation temperature (used in [103]) was ~550-680 °C, its conversion to a thermally

insulating and oxidatively stable silicon oxycarbide “black glass” (Si-O-C ceramic char) is delayed. This delay significantly downgraded its effectiveness as many small cracks already appear on the surface.

5.5. Char enhancements: Another approach that was adopted to further reduce the HRRs and total heat released is to enhance the formation of char. This is based on a simple logic, that is, to divert the burning polymer to carbon rather than to fuel the gas phase combustion. The significant amount of carbon in the condensed phase in the form of char thus helps to decrease the HRRs/total heat released. Generally, Lewis acids or Friedel-Crafts alkylation and reagents were used as char enhancing catalysts in some polymers like polystyrene [161, 162]. Zinc borate and PVA were also used for this purpose in a few cases [17, 37, 38]. Zinc in the condensed phase favours the production of aliphatic hydrocarbons which, together with an increase in cross-linking reactions, result in both smoke reduction and increased char formation. PVA is a well-known char enhancing agent and acts through intermolecular cross-linking.

The effectiveness of the char enhancers depends on many parameters including the host polymer decomposition temperature. Very recently, Kashiwagi *et al.* [159] provided an insight on this process. They prepared SAN/clay nanocomposites by the solvent casting method and used zinc chloride ($ZnCl_2$) as a char enhancing catalyst (to react with the resin/degradation products). A similar approach was demonstrated in [163] with PP/clay nanocomposites by producing char using a nickel catalyst. Nevertheless, in [159], the resin contained 25 wt.% acrylonitrile component. It was found that the addition of 3 wt.% $ZnCl_2$ to SAN reduced its thermal stability (particularly in the initial stages) and the flammability results (gasification in N_2) at 50 kW/m² flux were also not so promising. This is despite the significant enhancement of char, which initiated at higher temperatures of ~400 °C. Furthermore, this behaviour is independent of the presence of clay. The authors have also tried using resins with 30 wt.% and 40 wt.% acrylonitrile components, but similar degradations in thermal stability of the materials were observed (see for example, Figure 13a). However, higher residue yields of about 22 wt.% (with SAN containing 40 wt.% acrylonitrile component) in the absence of clay layers and 30 wt.% in the presence of clay layers were obtained. See Figures 13b and 13c where the MLR curves were shown along with the residues. Further, the total heat release is reduced with the addition of $ZnCl_2$ (by about 17%) and with the combination of $ZnCl_2$ -clay (by about 29%), but no synergisms or reductions in the peak HRR were noted. Therefore, it is vital to use agents that induce char formation at lower temperatures when the cracks tend to start.

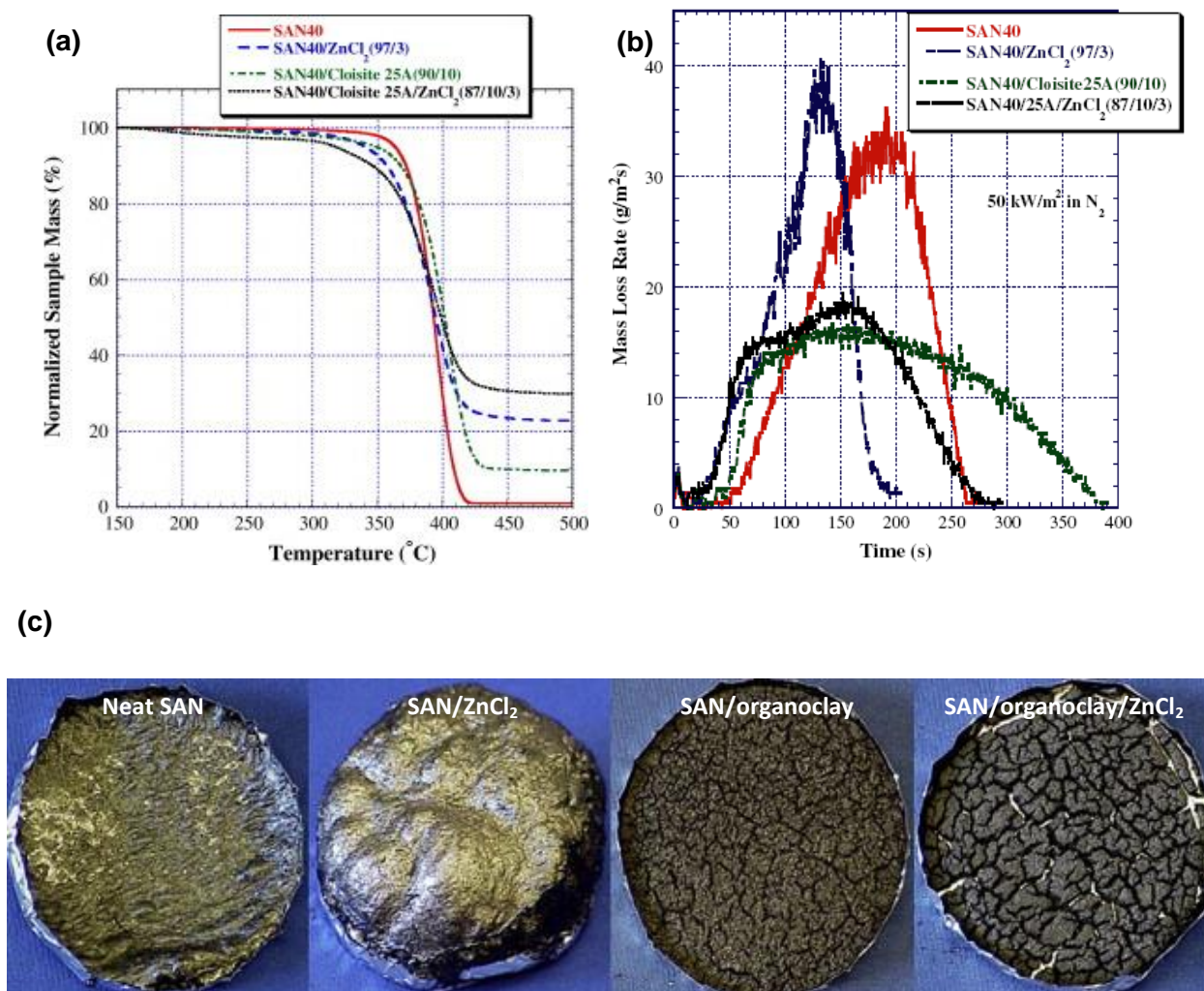


Figure 13. (a) TGA and (b) mass loss rate curves of SAN (containing 40 wt.% acrylonitrile component) and its composites – SAN/ZnCl₂ (97/3), SAN/organoclay (90/10) and SAN/ZnCl₂/organoclay (87/10/3) and (c) corresponding pictures of the residues (from left to right) after gasification testing conducted at an external radiant flux of 50 kW/m² in nitrogen atmosphere (Reprinted with permission from [159]. Copyright 2009, Elsevier).

In summary, analysing the literature data on the fire performance of polymer/clay nanocomposites, it can be concluded that: (i) the differences in reductions in HRR/MLR of nanocomposites with different loadings of nanoparticles are not significant once a critical composition is reached (for modified layered silicates, it was ~ 8-10 wt.%); (ii) irrespective of the dispersion of nanoparticles, the presence of low molecular weight surfactants (like quaternary alkyl ammonium salts) adversely affects the thermal stability and thereby TTI (as these

surfactants decompose usually from ~ 180 °C); and (iii) quick migration of nanoparticles to the burning surface, their coupling upon fire and packing density (to yield homogeneous, physically stable and thick barrier) are problematic issues. Subsequently, these parameters yield unsatisfactory flame performance, that is, polymer/clay nanocomposites burn completely, despite reducing HRRs/MLRs and extending the burning time compared to the corresponding neat polymers.

6. Short-term *versus* long-term fire exposure tests

Before ranking fire performance of candidate materials, it is important to understand the inherent differences between short-term and long-term fire exposure tests. To illustrate this point, consider layered clay and GO as FRs in polymers. As discussed before, with just clay as an FR in polymers, V-0 rating in UL 94 test is far from real; but with GO, many studies have shown a V-0 rating as it benefits from both its layered structure ('physical' barrier mechanism) and intumescent/blowing effect ('chemical' mechanism) [120-123]. But under forced (or long-term) combustion conditions, HRR/MLR data indicate that the performance of GO is similar to clay layers [103]. Additionally, with GO, the residue was extremely soft and even a puff of air could blow it away; while the residue was physically rigid in the case of polymer/clay nanocomposites.

The above example demonstrates the necessity to thoroughly analyse, understand and compare the various parameters that affect the fire performance of polymer nanocomposites based on various fire exposure techniques in order to obtain in-depth information on the applicability of materials under fire. This is due to the inherent differences in various testing standards (for simplicity, we consider only cone calorimeter, UL 94 and LOI testing techniques here), the principles of evaluation, ambient conditions, orientation differences of the samples, and so forth. Some of these differences will be highlighted below:

- (a) **Inherent differences** - Cone calorimeter evaluates the material response to a constant heat flux with time (forced combustion), whereas in UL 94, the response of a material to a removed fire and its self-extinguishing behaviour *versus* time are measured. That is, UL 94 provides information in a local ignition fire scenario, but their safety level is not so clear when exposed to a more aggressive fire scenario [125]. Besides, the test operator has to 'follow' the polymer with the Bunsen burner flame during the test, and therefore, maintaining a steady ignition source on a moving/curling/dripping thermoplastic is

difficult [164]. This obviously induces fluctuations and a degree of uncertainty in the UL 94 test data. While in LOI, the relative flammability of a material is evaluated under controlled conditions, whereby the percentage oxygen required in sustaining a candle-like burn is measured. The sample is also burned in the least challenging configuration (candle-like). So, even a material with higher LOI number than 22 may burn in ambient if ignited at the bottom edge [165].

- (b) **Horizontal versus vertical configuration** - Another parameter that is of high relevance is the horizontal (cone calorimeter) *versus* vertical (V-UL 94 and LOI) configuration; this is particularly important for injection moulded polymers with 2D nanofillers like clays. The differences in the orientation of clay layers will affect the fire performance of the sample. Moreover, in the vertical configuration, dripping should be considered; while in cone calorimeter, the bottom of the material is securely wrapped in an Al-foil.
- (c) **Melt viscosity** - Misleading data can be obtained if the melt viscosity is affected during the test fire scenario; for example, melamine (or in combination with other nanoparticles) if used in polypropylene and polyamides, a V-rating is achieved by extinguishing the fire [8, 10, 125]. However, the primary mechanism for this is dripping; that is, they drip away from the flame. So, despite passing the test standard, these materials are not ideal choices for use in practical applications as there is every possibility that they will burn completely if exposed to long-term flame conditions (forced combustion). Even with the same sample (PA 66), Wharton [166] obtained two different LOI values depending on whether the burning/non-burning border was approached from the low oxygen side or the high oxygen side. That is, when the flame was large, significant melt flow occurred and that resulted in a high LOI.
- (d) **Chemical structure of polymer** - This is another factor that has a significant influence on the fire data. Examples include oxygen- or nitrogen-rich materials like polyformaldehyde, cellulose, poly(vinyl acetate), polyethylene terephthalate and polyacrylonitrile or polymers which decompose to give aliphatic *versus* aromatic hydrocarbons (due to the requirements of more energy to decompose and combust aromatic hydrocarbons).
- (e) **Miscellaneous** – Other parameters like sample thickness, edge conditions, ignition source, and phenomena such as glowing and flaming drip complicate the correlations among various tests.

Nevertheless, some efforts have been made to correlate cone calorimeter and V-UL 94/LOI or V-UL 94 and LOI results in order to ensure a good futuristic prediction of a material's behaviour in different fire tests. Wharton [167] correlated V-UL 94 vertical burning and LOI tests data and concluded that V1 covered the LOI range from 23 to 34, while V0 between 24 and 52. These large fluctuations obviously do not lead to any particular correlation or conclusion. Some studies also suggested a linear relationship between LOI and FR concentration; but it applies to only some cases and is not universal when compared to data in most of the published literature.

Similarly, LOI results failed to correlate with HRR data from the cone calorimeter; even worse, a qualitative general trend revealed that the inverse of the LOI made sense for some systems [164]. By comparing LOI and TGA results of many polymer systems, Cullis and Hirschler [48] concluded that there is no correlation between LOI and thermal stability. It is important to reinstate that though thermal stability is an important parameter in the fire performance of polymeric materials, it does not mean or indicate that improvements in thermal stability will cause reductions in HRR/MLR or achievements of higher ratings in a UL 94 test or higher LOI numbers.

Some investigators used a parameter, critical HRR or HRR_0 , obtained from the cone calorimeter to correlate with V-UL 94 data. HRR_0 for any material is calculated by taking steady-state HRRs at three different heat fluxes, and using the slope of the straight line extrapolation of these points to resolve the HRR at a zero heat flux [168, 169]. Though, in some cases, this parameter has shown good correlation with V-UL 94 data for neat polymers, it cannot be taken as a real indicator. There are many problems associated with this parameter including large uncertainties when selecting the 'steady-state' burning heat flux due to the variations in HRR curves [125]. An example of this behaviour is shown in Figure 14 for polycarbonate with a brominated FR at different heat flux, 30, 50 and 90 kW/m². Even large differences exist in time-to-ignition at low and high heat fluxes because of higher onset decomposition temperature for polycarbonate. With nanocomposites forming a physical barrier at the burning surface, the effect will again be different at different heat flux; that is, the formation of cracks differ with heat flux, which will influence the HRR curves. Usually, lower heat flux (25-35 kW/m²) represents only small fires, 50 kW/m² indicates a medium-scale fire with propensity for propagation and develop into a full-scale fire, and a heat flux of 90 kW/m² is related to fully developed 'room' fires near flashover.

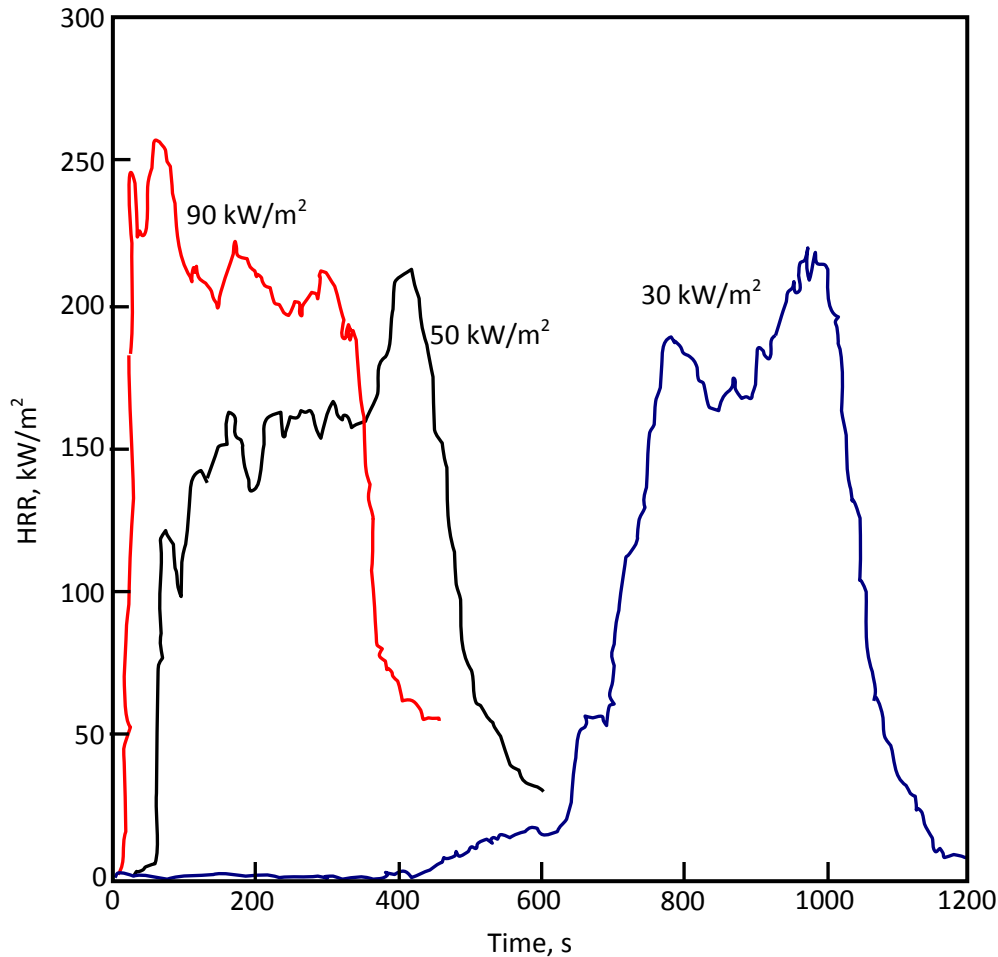


Figure 14. Variations in HRR curves of polycarbonate with a brominated FR at different heat flux (adapted from [125]).

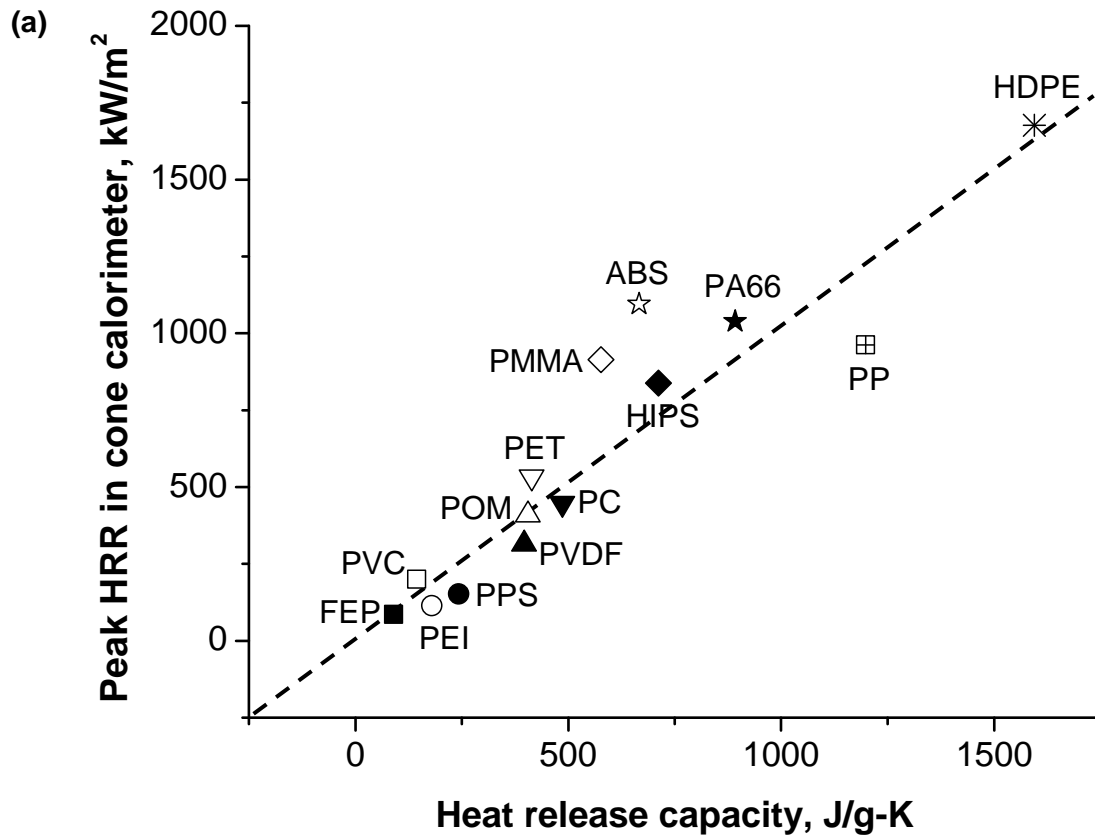
Morgan and Bundy [125], comparing the fire performance of different polymeric systems *via* cone calorimeter and UL 94 vertical burning techniques, showed that in some cases, similar to HRR_0 , average HRR at 60 s also agreed with V-UL 94 data, but only in a large sense; that is, it was hard to differentiate between V0/V1 or V2/fail ratings. However, it should be noted that as discussed earlier in this section, a V0 ranking material may also mean heavy non-flaming dripping. In turn, this will make it hard to understand and correlate the true response of these materials. However, parameters like the rate of burning (an indication of after-flame time) and the extent of sample burnt derived from UL 94 tests could throw some more light on the flame response of the material. For instance, PP with a brominated FR exhibited V2 rating with an average HRR at 60 s of 727 kW/m²; while for another V2 rated PP/BFR system, the average

HRR at 60 s was only 219 kW/m². In fact, the mean burn length during UL 94 test was similar for both cases, but the mean total after-flame time differed by almost 3 orders of magnitude. In another system, PP with non-halogenated additive, V0 rating was achieved and the average HRR at 60 s was 361 kW/m². These results clearly suggest the difficulties in correlating different test data. While the most common parameter of cone calorimeter, peak HRR can only provide slight indications whereas time to ignition does not correlate at all with UL 94 test ratings under any heat flux. In general, it was shown that lowering the peak HRR and delaying time to peak HRR could qualitatively point to higher UL ratings.

Recently, PCFC was introduced to measure heat release rates of small amounts of samples, which was based on the oxygen consumption principle (see [168, 170] for full description of the technique). Compared to cone calorimeter, in PCFC, the combustion of volatile and non-volatile components of a sample can be measured separately. In PCFC, the sample is first heated at a constant rate in a pyrolyzer. The pyrolyzed (fuel) gases are swept by an inert gas from the pyrolysis chamber to a tubular furnace where they are mixed with excess oxygen at ~900 °C so that the decomposition products are completely oxidized (non-flaming combustion). An oxygen sensor will then record the oxygen depletion. Evidently, only species that are volatile at the pyrolysis temperature may contribute to the O₂ depletion signal. In another case, the sample is heated in the presence of excess oxygen, followed by routing the gas flow through the furnace to the oxygen sensor. Here, both volatile and non-volatile species from the sample will contribute to the oxygen depletion signal. The instantaneous heat of combustion and the heat release rates of the flowing gas stream are measured based on the signal.

In contrast to cone calorimeter, PCFC has limited sensitivity to gas phase FRs and obviously cannot provide any information on dripping, intumescence or any other physical phenomena. Lyon and Walters [170] used HRC, defined as HRR/heating rate, derived from PCFC to compare with other flammability test methods and found good agreement with the polymers systems investigated. An example of this is shown in Figure 15. Peak HRC data from PCFC correlates well with the peak HRR determined in cone calorimeter; LOI also has a reciprocal correlation with HRC; whilst V-UL 94 rating can also be derived based on the HRC data. Materials with HRCs below 200 J/g-K does not ignite after brief exposure to small flames (UL 94) and have LOI > 35; whereas materials with HRCs above 400 J/g-K continue to burn in a UL 94 test and have low LOI values of <21. However, there are very few studies correlating the results obtained from this technique with other tests data for polymer nanocomposites. Shi *et al.*

[149] indicated that PCFC could not identify the differences between intercalated and exfoliated nanocomposites as they obtained similar HRC and THR values. But as discussed before, with cone calorimeter, HRRs/MLRs depend on the level of exfoliation and aspect ratio of nanoparticles. They attributed this difference to the milligram quantities of samples used in PCFC where the barrier effect of clay layers is expectedly hard to prosper. Wilkie *et al.* [171] also evaluated their polymer nanocomposites with both PCFC and cone calorimeter and suggested good correlations between HRC and peak HRR, but poor correlations with other parameters including average mass loss rate and time-to-ignition.



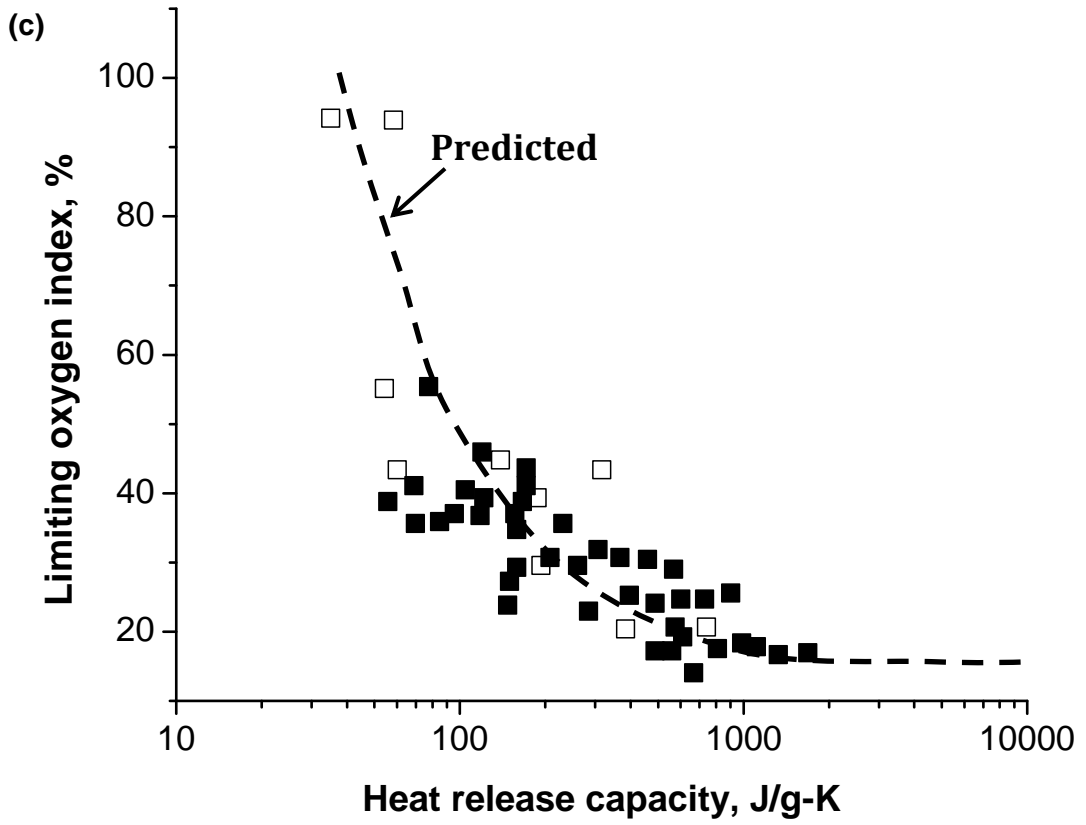
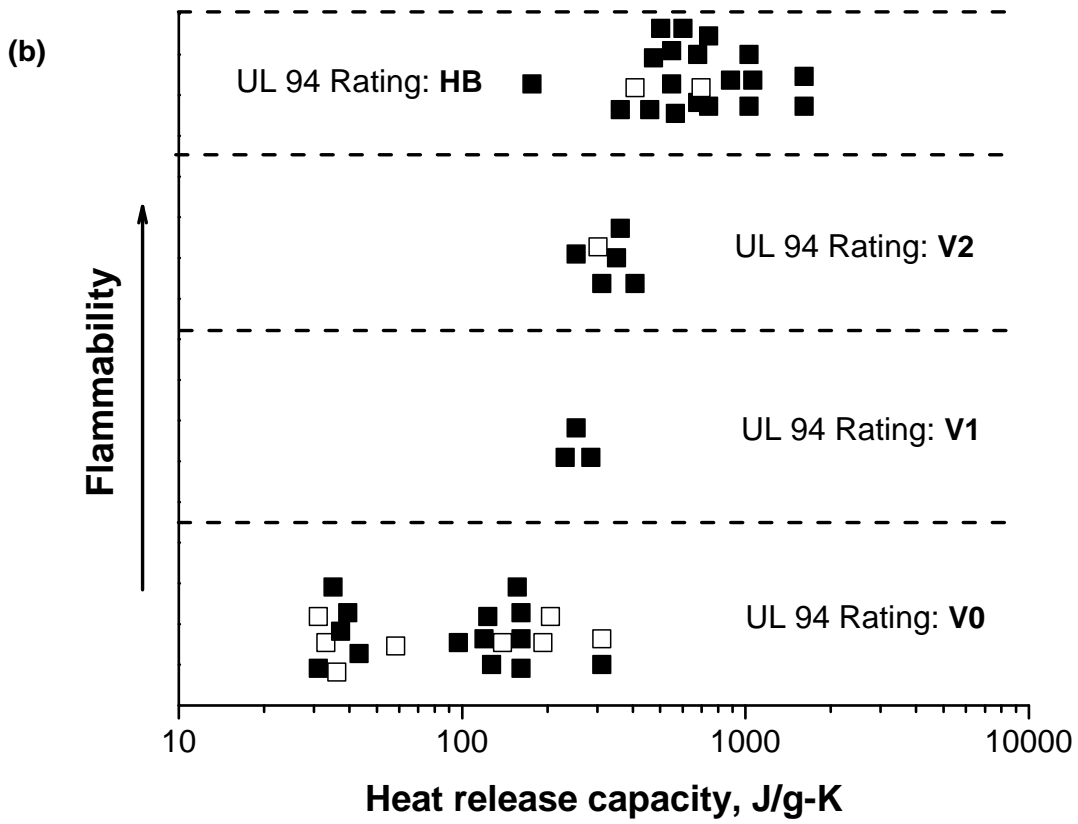


Figure 15. Comparison of heat release capacity data of different polymeric materials with results obtained from various fire testing techniques: (a) peak HRR from cone calorimeter; (b) UL 94 vertical burning results; and (c) limiting oxygen index data. Open squares in (b) and (c) represent halogen-containing samples (adapted from [170]).

7. Modelling of combustion behaviour

As explained in the above sections, there are vast differences in the fire response of polymeric materials, which depend greatly on the type of tests performed. Therefore, ranking materials or their relative flammability does not have any intrinsic scientific meaning, albeit physically, relatively meaningful deductions can be drawn if the same technique is used to rank the materials within the realm of test applicability. Put simply, generalizing the fire performance of a material is not practical. Besides, the qualitative nature of many fire tests makes it difficult to obtain an approximation of the necessary parameters to build a model. Few preliminary attempts to model the transport of volatiles through a melt were available [172-175]; moreover, these solid-phase mathematical models did not consider many of the important factors like subsurface pyrolysis, volume changes, gas-phase chemistry and heat transfer in the gas-phase and even made simplified assumptions [176-178]. For example, it was assumed that the volatiles formed from the polymer escaped from the solid as soon as they are formed and decomposition of the polymer occurred in a single step, according to a first-order Arrhenius process in which:

$$-\frac{dm_1}{dt} = A \exp\left(\frac{-T_A}{T}\right) m_1 \quad (10)$$

where m_1 is instantaneous mass of a small amount of polymer, t is time, A is a pre-exponential factor, T_A is absolute activation temperature and T is absolute temperature. Interested readers can refer to [179-182] for extensive reviews of the modelling efforts concerned with solid- and gas-phase processes for neat polymers.

In another study, Staggs incorporated the change of volume in his model, but assumed that the volatile species escaped as soon as they were formed even in the presence of fillers (albeit micro-scale) which were considered inert [172]. Whilst this can be used to obtain the upper limit of a model, when considering nanocomposites, it is important to note that as the multi-layered char thickness increases, the residence time of combustible volatiles produced from the degradation of the polymer becomes increasingly long. This may in turn increase the chance of

oxidation of the volatiles depending on the local oxygen concentration. Moreover, as described earlier, nanoparticles, particularly layered silicates, are not always inert; but they participate in the catalytic degradation of polymers. Kashiwagi [180] also reviewed the difficulties to model the pyrolysis of a polymer by considering the production and transportation of volatiles.

Recently, researchers at FAA developed a thermal-kinetic numerical modelling program called ThermaKin that simulates the pyrolysis and combustion of materials [183]. It includes transient energy transport, chemical reactions and mass transport, but simulates only one-dimensional burning rate of an object and also does not consider the effects of charring and composite materials. The physical properties like density, thermal conductivity and heat capacity are fed into the programme to identify the chemical effects of FRs.

It is also unfortunate that only qualitative terms like 'uniform' or 'coherent' or 'continuous' were mostly used to describe the carbonaceous-silicate layers. Till now there are neither explicit correlations between the suggested driving forces responsible for the migration of nanoparticles (rising bubbles, viscosity gradients, and convection forces due to the temperature gradient) nor any attempts to physically understand or simulate the migration phenomena (except for a few efforts to model the physical processes of bubble dynamics for intumescent systems). Clearly, it is extremely hard to model the processes as they involve simultaneous fluid dynamics, heat and mass transfer, and degradation chemistry. Furthermore, understanding the thermal properties of polymer blends is even more complicated, since the properties of the blend can change continuously as the blend is heated to high temperatures and phase separation accelerates [184]. The segregation of FRs or nanoparticles into one of the phases should also be considered.

Wichman [173] described the individual bubble characteristics by considering both translational velocity and growth rate, and subsequently determined the bubble distribution function for coupling with the equations for the thermoplastic (PMMA) melt layer. To determine the translational velocity, it was assumed that surface tension forces are dominant compared to buoyancy and based on the steady-state momentum equations (low Reynolds numbers). The expression for the growth rate was then obtained by an approximate balance between the rate of heat flow into the bubble from the liquid and the latent heat required to supply bubble vapour. Staggs and Whiteley [182] described a mathematical model for the early to mid stages of gasification to assess ignition resistance in cone calorimeter-type experiments (either by

coupling with an appropriate gas-phase model, or using some simplified ignition criterion). Different models have also dealt with the intumescent behaviour as a problem in one-dimensional heat transfer, with the physical properties of the intumescent layer changing as a function of time to reflect foaming and out-gassing [185]. Furthermore, Butler *et al.* [186] modelled the intumescent system three dimensionally, by incorporating bubble and melt hydrodynamics, heat transfer and chemical reactions. They treated the system as a highly viscous and incompressible fluid whose viscosity is a function of temperature and contains a large number of expanding bubbles.

Zhang and Delichatsios [187] made an effort to quantitatively evaluate the surface layer formed after pyrolysis of PA 6- or EVA- or PBT-based clay nanocomposites in a cone calorimeter. They concluded that the heat flux ratio (defined by equation 11) is proportional, by a factor K , to the depth of the pyrolysed material (or equivalently the amount of the nanoparticles accumulated on the surface). K varies with the type of polymer and the type/loading of fillers. This correlation was subsequently incorporated into a numerical model to predict the MLRs of PA 6 nanocomposite at different heat flux and different sample thickness, which was in good agreement with experimental results. The numerical model was based on a standard non-charring model based on the ignition temperature concept and one-dimensional conduction equation. The heat flux ratio is defined by:

$$ratio_{flux}(t) = \dot{q}_{net_0}'' / \dot{q}_{net}''(t) \quad (11)$$

where \dot{q}_{net_0}'' represents the net heat flux on the surface of the polymer for the case with no surface layer, and \dot{q}_{net}'' the actual heat flux imposed on the interface of the surface layer and the unpyrolysed polymer. This ratio is, however, independent of the external heat flux and sample initial thickness, which actually raises a few questions as many polymers and their nanocomposites are reported to deviate from their usual behaviour at high heat flux.

Figure 16 plots the calculated heat flux ratio, $ratio_{flux}$ versus the pyrolysed depth, δ_{pyro} , for EVA nanocomposite at 50 kW/m². δ_{pyro} is calculated from the experimental instantaneous mass loss rate from equation 12 below. During the pyrolysis process, $ratio_{flux}$ increases linearly with δ_{pyro} implying that the former is proportional to the amount of nanoparticles accumulated on the

surface that is proportional to the pyrolysis depth. This is obviously based on the assumption that the nanoparticles remain on the surface after pyrolysis. Hence,

$$\delta_{pyro} = \int \dot{m}'' dt / \rho \quad (12)$$

where $\dot{m}''(t)$ is the 'instantaneous experimental MLR'. From the best fit lines in Figure 16, the value of $ratio_{flux}$ can be obtained for different regime of δ_{pyro} :

$$ratio_{flux} = 1.2 \quad \text{for } \delta_{pyro} < 4 \times 10^{-4} \text{ m; and} \quad (13a)$$

$$ratio_{flux} = 500 \delta_{pyro} + 1.0 \quad \text{for } \delta_{pyro} > 4 \times 10^{-4} \text{ m} \quad (13b)$$

Subsequently, these correlations are incorporated into the numerical model to calculate the MLR at different heat flux as:

$$\dot{m}''(t) = \frac{\dot{q}_{cone}'' + \dot{q}_{flame}'' - \sigma T_{ig}^4}{ratio_{flux} \cdot L} \quad (14)$$

where \dot{q}_{cone}'' is the nominal heat flux from cone, \dot{q}_{net}'' the heat flux after ignition (10 kW/m² is assumed), σ density, T_{ig} ignition temperature, and L latent heat of pyrolysis (derived from the experimental cone calorimetric data and assumed to be the same for neat polymers and their nanocomposites). Figure 17 shows good agreement between predicted and measured MLRs at different heat flux for EVA/clay nanocomposites. However, it is doubtful whether the model can predict MLRs accurately once a critical composition of clay is reached.

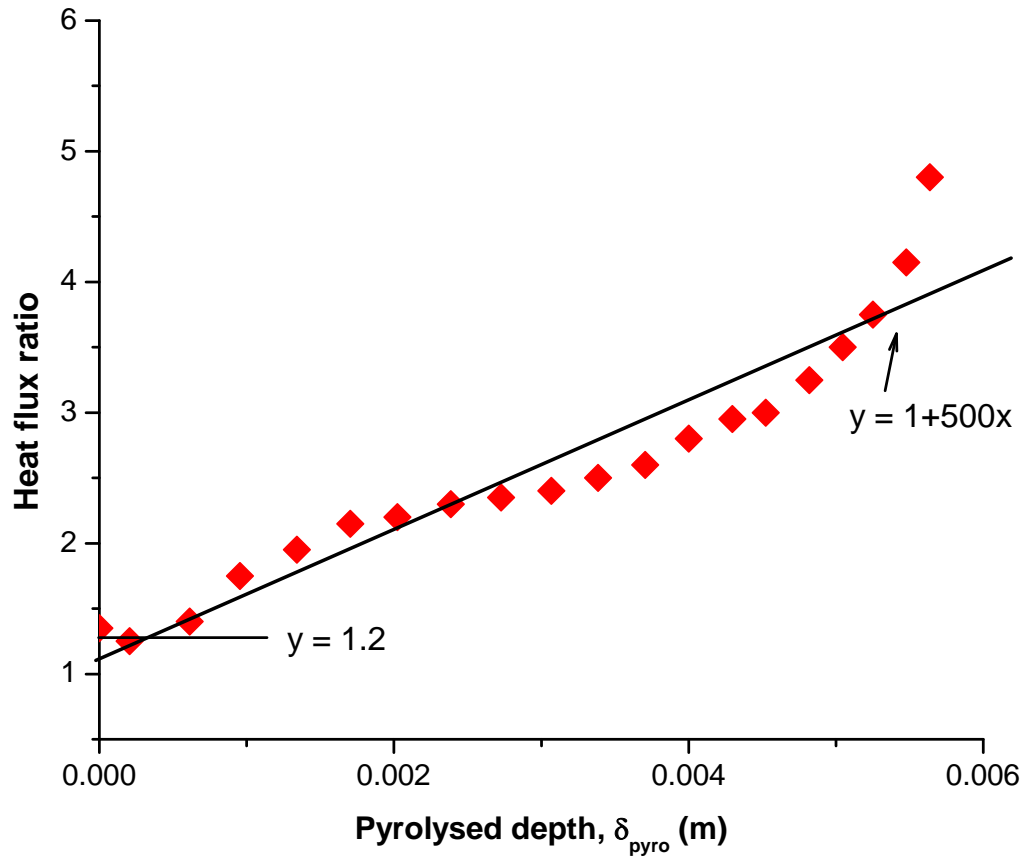


Figure 16. Calculated heat flux ratio *versus* pyrolysed depth for EVA/clay nanocomposite (adapted from [187]).

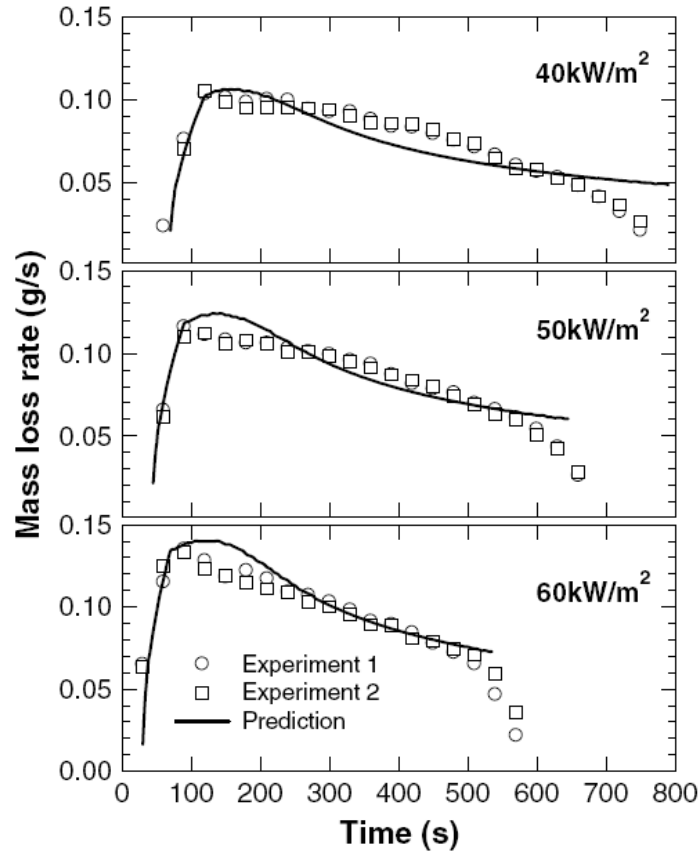


Figure 17. Comparisons of predicted and experimental MLRs for EVA/clay nanocomposite at different heat flux (Reprinted with permission from [187]. Copyright 2010, Springer).

Oñate *et al.* [188] developed a computational procedure, particle finite element method (PFEM), which combines Lagrangian particle-based techniques with the integral formulation of the finite element method (FEM), to understand the melting (track the motion of the polymer as it melts, flows over the surface, and drip) and flame spreading of polymers. For example, they have used this technique to simulate a vertical burning experiment (Figure 18) where the sample is exposed to uniform heating on one face from a radiant cone heater; as the sample is insulated on its lateral and rear faces, the melt flows down the heated face and drips onto a surface below. The mass loss and the melt collected are monitored. In the simulation, they adopted an approach to incorporate viscosity degradations in the sample as a function of temperature. Figure 19a shows a couple of snapshots of the time evolution of the melt flow into the catch pan from a sample when exposed to a heat flux of 20 kW/m^2 . Comparison of these simulation results of mass loss rate as a function of incident heat flux to experiments also reveals a similar trend despite the higher simulation values (Figure 19b).

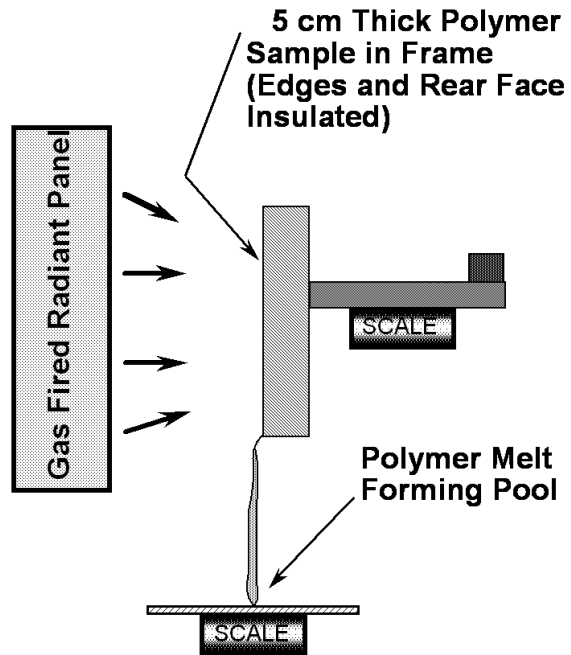
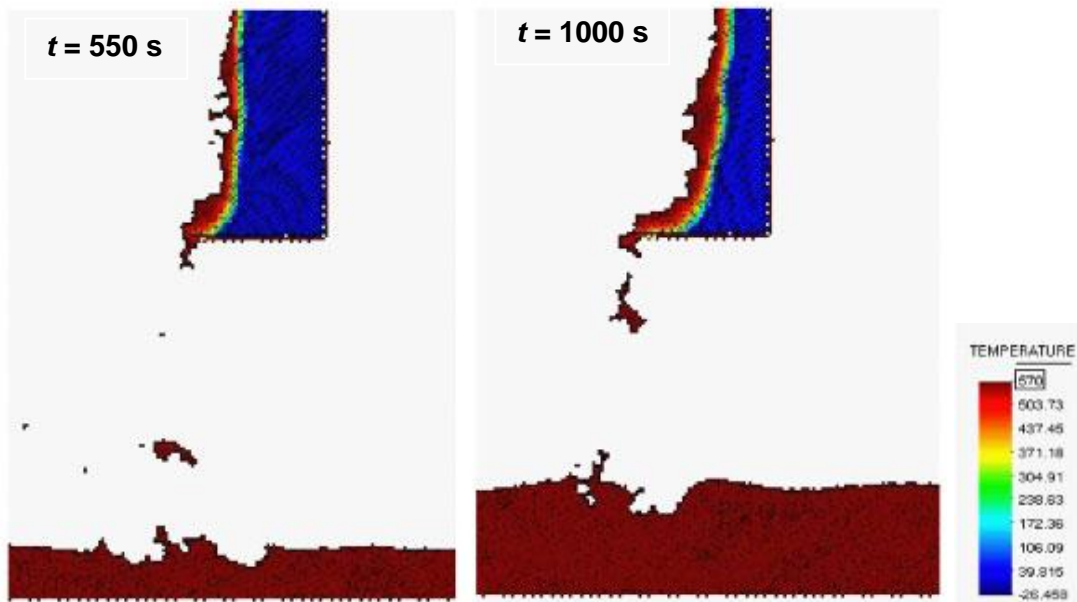


Figure 18. Schematic of vertical burning polymer melt experiment setup (Reprinted with permission from [188]. Copyright 2009, John Wiley and Sons).

(a)



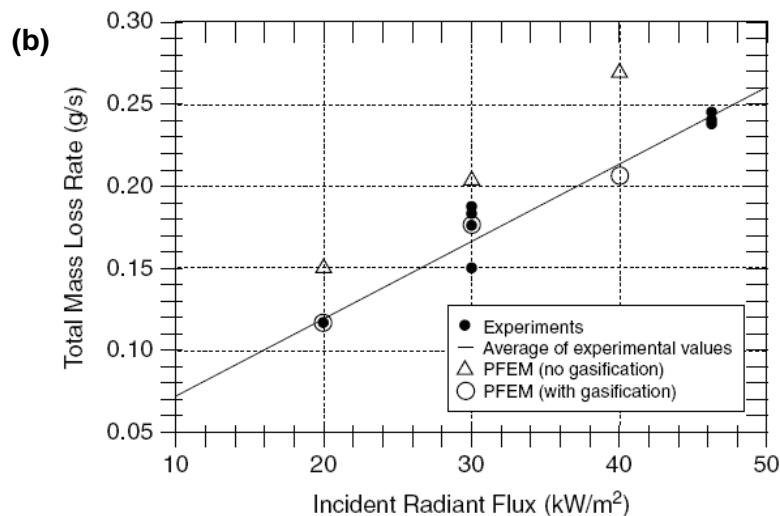


Figure 19. (a) Snapshots of the time evolution of the melt flow into the catch pan from a 25x2.5 cm² sample at $t = 550$ s and 1000 s; and (b) comparison of PFEM results to experiments for mass loss rate as a function of incident radiant flux (Reprinted with permission from [188]. Copyright 2009, John Wiley and Sons).

8. Commercial flame retardant polymeric materials

Even in 450 BC, alum was widely used to reduce the flammability of wood by the Egyptians; while the Romans started using synergistic approaches like a mixture of alum and vinegar to protect their boats in 200 BC or the technique of using a mixture of clay and gypsum on theatre curtains as early as 1638 [189]. In the current world market, there is a huge demand for FRs which are heavily consumed additives by the plastics industry. These agents have an estimated market share of ~\$2.3 billion (according to Eurobrom BV) making up about 27% of the ~\$8.6 billion “performance” additives market [190]. As discussed earlier, in the absence of additional conventional FRs, polymer nanocomposites are unable to meet the existing fire safety standards for commercial applications. This is the reason why commercially available flame retardant materials from various companies are simply based on conventional FRs to meet the safety requirements or with a reduced loading of these FRs when polymer nanocomposites were used. For example, products like Maxxam[®] FR from PolyOne (USA), Reofos, an organo-phosphorous flame retardant from Great Lakes Chemical Corporation (USA) and Exolit OP, an organo-phosphorous FR from Clariant (Switzerland) are based on conventional FRs for different consumer applications. By contrast, Sud-Chemie, a Germany based company’s product ‘Nanofil’ (in cooperation with Kabelwerk Eupen, Belgium) for cables has 52-55% ATH or MH in

addition to 5% clay in EVA copolymer. Similarly, US based Foster Corp's nylon 12 used for tubing contains 25% loading of halogen/antimony oxide in addition to 14% clay.

Some others like Albemarle Corporation, USA, Sabic Europe, The Netherlands, and ICL Industrial Products, Israel have introduced many combinations of fire retardant additives for polymers resulting in attractive multi-functional properties like colour stability, ease of processing and lower processing temperatures, high melt flow, etc. These products are particularly targeted for high flow applications such as complex, thin-wall parts. ICL-IP has also introduced the SaFRon series, proprietary polymeric FRs with anti-drip properties, and for improved conveying and feeding.

Besides, the switch to lead-free solder systems in electronics (mandated according to the EU's RoHS) requires polymers with higher thermal stability. This is due to the fact that lead-free solder systems typically run 30-50 °C higher than traditional lead systems [191]. Therefore, to meet the requirements of fire safety standards, traditional FRs based on halogen/phosphorous compounds are incorporated. Although the RoHS directive bans some PBDE FRs, particularly deca-, octa- and penta-BDE, still many congeners of halogenated and phosphorous compounds are used.

9. Summary and future work

The usage of conventional FRs to meet the fire safety standards is of serious importance as they ultimately yield POPs of global concern. Considering eco-friendliness and other required properties, unsatisfactory fire performance is a major obstacle. The various facets associated with this issue are highlighted in this review from the viewpoints of both materials and fire exposure techniques. The complexities involved in investigating the fire retardancy behaviour of polymer nanocomposites and the limited systematic studies on the different parameters involved (materials/mechanisms/ methodologies and techniques) are discussed. These have led to mostly qualitative observations, and the near absence of specific correlations among the various parameters responsible for the fire performance of these materials substantiates this. Moreover, some of the literature on these materials often points to conflicting and/or misleading suggestions from the perspectives of short- and long- term fire exposure tests.

Hence, it is necessary to understand fundamentally and thoroughly the steps involved in the combustion process of polymer nanocomposites (both qualitatively and quantitatively) and not just to pass the fire testing standards. This will facilitate insights into the mechanisms of fire retardancy, accurately delineating the boundary conditions and transport phenomena. Ultimately, this knowledge can be used to integrate with mathematical models and simulation techniques to have accurate predictions on the applicability of the material.

It is also worth referring to the topic of replacing conventional polymeric materials to some extent, at least in short-life applications, with biodegradable polymers. Despite the huge demand for biodegradable polymers in recent years, there are still several hurdles: (i) lack of infrastructure for their efficient disposal in bioactive environments and bioconversion facilities; (ii) limited knowledge and awareness among consumers, leading to the disposal of these products in dry landfills generally designed to retard biodegradability; and (iii) relatively poor performance/functionality of the current commercially available biodegradable polymers in concerned applications. To address these problems, much attention was diverted on the development of water soluble polymers based on acrylic acid, maleic anhydride, etc. These polymers, however, are not biodegradable, but persist in water systems and hard to realize their effects on the marine life/eco-system. In addition, progress has also been made on water soluble biodegradable polymers based on starch and cellulose; nevertheless, all these materials (biodegradable, water soluble and water soluble biodegradable) generally have low thermal deformation tolerance and, obviously, the incorporation of performance additives/FRs will make things more complicated.

Acknowledgements

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Appendix A.

Representative examples of PA6 and EVA based nanocomposites with platelet, spherical and fibrillar reinforcements subjected to cone calorimeter testing at a heat flux of 50 kW/m² (unless otherwise stated). % relative differences in TTI and peak HRR compared to their corresponding neat polymers along with information on microstructure of the composites before combustion and the final left over char quality is tabulated. ↑ Indicates an increase while ↓ point to the reduction.

Reinforcement geometry	Polymer	Reference	Reinforcement and its loading	Microstructure	% Relative difference in TTI	% Relative difference in peak HRR	Char quality
Platelet based materials	PA 6	[92]	10 wt.% organoclay*	Excellent dispersion	16 ↓	45 ↓	Physically rigid despite large cracks
			20 wt.% organoclay*	Excellent dispersion	14 ↓	44 ↓	Physically rigid and fine cracks
		[103]	15 wt.% GO	Good dispersion	15 ↓	57 ↓	Intumescent and not rigid
		[192]	5 wt.% hexadecyl-trimethylammonium treated MMT	Intercalated structure	26 ↓	44 ↓	No information
		[193]	5 wt.% organoclay	Well dispersed	36 ↓	43 ↓	Only a powdery residue
	EVA	[194]	5 wt.% organoclay*	Intercalated	25 ↓	50 ↓	Cracked char
			10 wt.% organoclay*	Well dispersed	8 ↓	59 ↓	Rigid char with cracks
[116]		5 phr organoclay*	No information	20 ↓	19 ↓	Island like structures	
Spherical fillers	PA 6	[103]	15 wt.% POSS	Good dispersion	1.5 ↑	2 ↓	Thin layer from POSS degradation/non-uniform

	EVA	[195]	25 wt.% TPPSi*# (based on silicon and caged bicyclic phosphate groups)	No information	No information	78 ↓	dense and continuous vitreous char
		[196]	55 wt.% MH	No data	51 ↑	60 ↓	No data
			60 wt.% MH	No data	70 ↑	82 ↓	No information
Fibrillar/tubular fillers	PA 6	[104]	5 wt.% CNTs	Excellent dispersion	27 ↑	58 ↓	Only a thin layer (mostly CNTs) left behind
		[197]	5 wt.% halloysite	Good dispersion	1.5 ↑	15 ↓	Cracked char
			10 wt.% halloysite	No information	8 ↓	40 ↓	Cracked but thick char
		[198]	15 wt.% of short glass fiber (flux: 35 kW/m ²)	No information	similar	42 ↓	No information
	EVA	[199]	5 wt.% zirconium phosphate (flux: 35 kW/m ²)	No information	5 ↓	16 ↓	No information
		[116]	5 phr purified CNTs	No data	1 ↑	30 ↓	Thin layer of CNTs/non-uniform

*Cloisite® 30B

*#TPPSi: tri(2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxo-4-hydroxymethyl) phenylsilane

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