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Chapter

Nanoscale Configuration of Clay-Interlayer Chemistry: A Precursor to Enhancing Flame Retardant Properties

Sanjiv Sonkaria and Hyun Joong Kim

Abstract

Nanomaterials are proving to be pivotal to the evolution of controllable, cost-effective and environmentally safe technologies. An important concern is the impact of low-dimensional compositional materials and their ability to significantly reduce the hazardous nature of flame retardants that are reputably harmful through unchecked inhalation. While eco-friendly and recyclable alternatives are necessary requirements to function as replacements for the 'Next Generation' of flame retardants, the underlying 'Chemistry' at the nanoscale is unfolding unlocking vital clues enabling the development of more effective retardants. In this direction, the dimensional order of particles in naturally occurring nanoclay materials and their associated properties as composites are gaining increasing attention as important constituents of flame retardants. In this review, we examine closer the compositional importance of intercalated/exfoliated nanoclay networks essential to retardant functionality exploring the chemical significance and discussing underlying mechanisms where possible.

Keywords: nanoclay, flame retardant, nanocomposite, polymer−layered-silicate

1. Introduction

Today, materials are as diverse as the components and methods used to assemble them. Fire safety concerns and regulatory issues have fuelled past efforts to use formulated chemical technologies to help protect against unpredictable fire hazards. Flame retardant technology was introduced fifty years ago as bulk 'additive' materials to effectively reduce flammability of naturally combustible, ignitable or inflammable constituents of products used mainly in household products. An example of such materials include polymers which may be easily ignitable. As synthetic materials, their inclusion in industrial and domestic products has generally been considered essential to the safety of end-users either as chemically uncoordinated additives to the target materials or as chemically bonded with textiles [1], coatings [2] or plastics [3] for example during manufacturing. These additives primarily operate by 'retarding' or resisting the ignition phase of flammables thereby delaying their reactive pyrolytic nature to catch fire by insulating against its spread. However, to be effective in retarding flame progression, high quantities of additives

are required leading to enhanced toxic gas release. They also operate by diminishing flammability when chemically activated or use endothermic processes to drive the suppression of flames. The availability of flame retardants in self-applicable formats such as coatings and sprays has raised concerns on the uncontained exposure of chemicals through inhalation of vapor or through skin contact and other forms of possible contamination. The impact of anti-flame chemicals on the mortality rates [4] has been considerably significant to warrant their widespread use in delaying fire hazards. However in more recent times, health concerns have intensified over the safe use of flame retardants have surfaced— a concern that has emerged more intensified in the era of 'green and environmental chemistry' and authority driven demands for chemical risk to human-health after toxicity related irregularities based material class [5] were highlighted some thirty years ago [6].

There are numerous flame retardant types [7], however halogenated or organohalogen flame retardants containing carbon bonded chlorine (CFRs) or bromine (BFRs) as the major halogen-based constituents are assembled or integrated with polymers forming organic halogenated blends. For example, several flame retardant classes exist [8] as chlorine and bromine polymers while others are composed of phosphorous, nitrogen and sulfur or synergistically made. Others include antimony, aluminum and tin. Since 1992, halogenated flame retardant production has exceeded 20% reaching 25% of the global market and approximately doubling by 1998. The growing demand suggests that flame retardants are a valuable commodity in fire safety and can regulate the combustion process at the heating or decomposition stage, ignition phase and at the level of flame interference curbing its spread by broadly preventing oxygen consumption, heat production and fuel for flame production.

The chemical mode of action occurs at the level of combustion in the gaseous phase through a cooling process that entails curbing the evolution of flammable gases. An alternative action of flame retardants is the deposition of barriers as chemical layers compartmentalizing the supply of oxygen away from the material. Other mechanisms involve additive materials with endothermic properties lowering temperatures below combustible levels or mechanisms that allow the build-up of protective layers cutting off oxygen as essential part of the fueling process. The use of inert materials forming non-combustible gas products also reduce the space for flammable gases entering the ignitable phase. Compositionally, flame retardants are classed by their elementally important counterparts namely bromine, chlorine, phosphorous and nitrogen. The importance of the point of action of flame retardants is shown in **Figure 1** which often depends on the combustion profile of a material and how well it 'fits' with the flame retardant properties of choice [10]. The release of fire hazards are shown in **Figure 2**. In terms of the molecular mechanism of action which are largely unknown, signify only a broad but general based understanding at the bulk scale [11]. It therefore becomes important to re-visit the flame structure partitioned as the outer, middle and inner zones differentiated by color and temperature. Temperatures vary considerably by orders of magnitude in a single flame and temperature variability affects combustibility of materials generating different particle types that originate from different regions in the flame. These regions are further separated by the variable degree of combustibility of vapors dictated by the availability of oxygenated air and critical temperatures needed to ignite unburnt fuels generating high energy propagating particles during flame propagation [12]. It has also been suggested that modeling of flow configuration of flames if adequately understood can help direct particle-particle interactions with multi-scale implications that reside at the gas–solid phase [13]. The contribution of nano- and sub-micrometer particles to flame retardancy is not only dependent on low migration resulting in the surface decomposition of condensed material (char) and the vaporization of particles via surface diffusion at higher temperatures
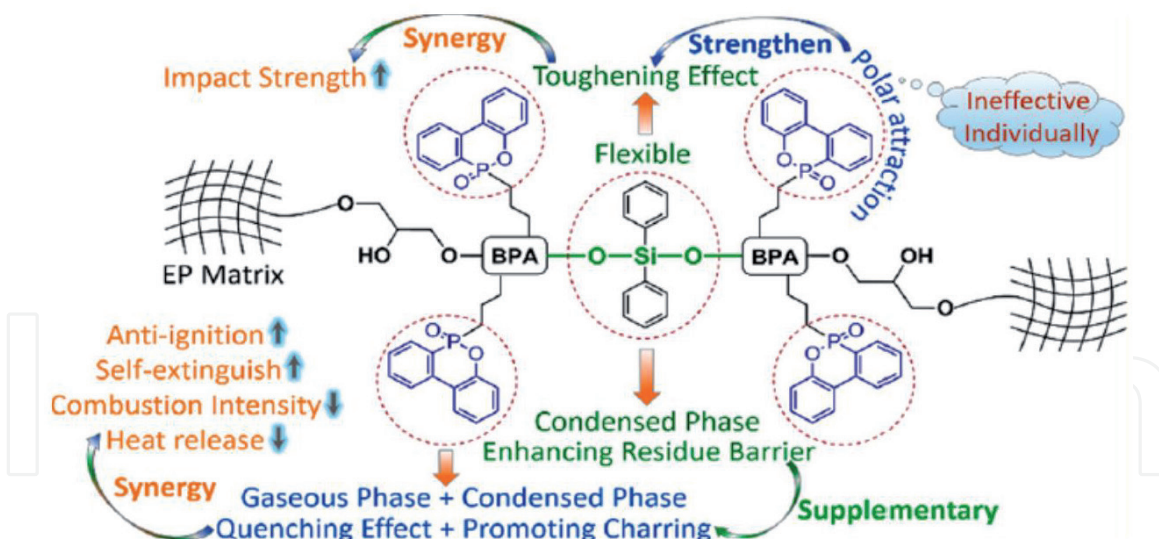
Figure 1.
Flame retardant property and the importance of chemical synergy in the behavior of phosphaphenanthrene retardant chemistry in suppression of flame progression. Reproduced with permission from [9].

phase but also surrounding combustion gaseous conditions. Both particle diameter (geometric mean size) and mass was affected by altered O_2:CO_2 and O_2:N_2:CO_2 ratios during the vapor to particle conversion [14] (**Figure 3**). Given that the pattern of nanoparticle evolution is connected to how a flame is structured, motioned and governed, modeling the underlying features could have important ramifications in reducing or silencing the more turbulent aspects of flames. For example, the size increase of nucleating particles whilst traversing across the flame front rapidly aggregate and particle progression and accumulation can be suppressed by temperature reduction [15].

The basis for the use halogens as flame retardants originates from the production of radicals from the combustion of hydrocarbons such as $H^{\bullet}$, $HO^{\bullet}$ and $O^{\bullet}$ (**Figure 4**). High energy radicals combine with hydrocarbons such as methane to increase radical formation fueling green-house emissions like CO_2 and toxic CO (**Figure 5**) thus considerably contributing to exothermic reactions — a process that is repeated by increasing the chain of radicals during combustion. In particular, hydrogen bromide (HBr) at the ignition phase (decomposes to $Br^{\bullet}$ (bromine radical) and behaves as a quenchers of $HO^{\bullet}$ and $H^{\bullet}$ through protonation forming water and hydrogen respectively. Bromine radicals are able to compete with $HO^{\bullet}$ and $H^{\bullet}$ from hydrocarbons such as methane neutralizing radical hydrocarbon production and instead forming ground state hydrocarbons shown below in **Figure 4**.

Some studies have suggested however that radical recombination although important, constituent CO-H_2 may propagate with differing burning velocities (flame speed progression relative to the unburned state) under conditions of minimal heat loss, particle formation is influenced by the residence time in pre-mixed flames [16].

These chemical events work synergistically in reducing the propagation of flames through flame suppression and delaying flame ignition via chain termination 'type' reactions. The diverse use of combustible materials and their flammable nature has been at the core of safety and protective concerns to humans and the environment. At the forefront of chemical exposure are fire fighters, a risk assessment case study of this vulnerable group has highlighted chemical exposure through combustion as a leading cause for cancer and thyroid complications [17] among the firefighting population from direct exposure and direct inhalation of chemical constituents of flame retardant materials. Tens of thousands of deaths
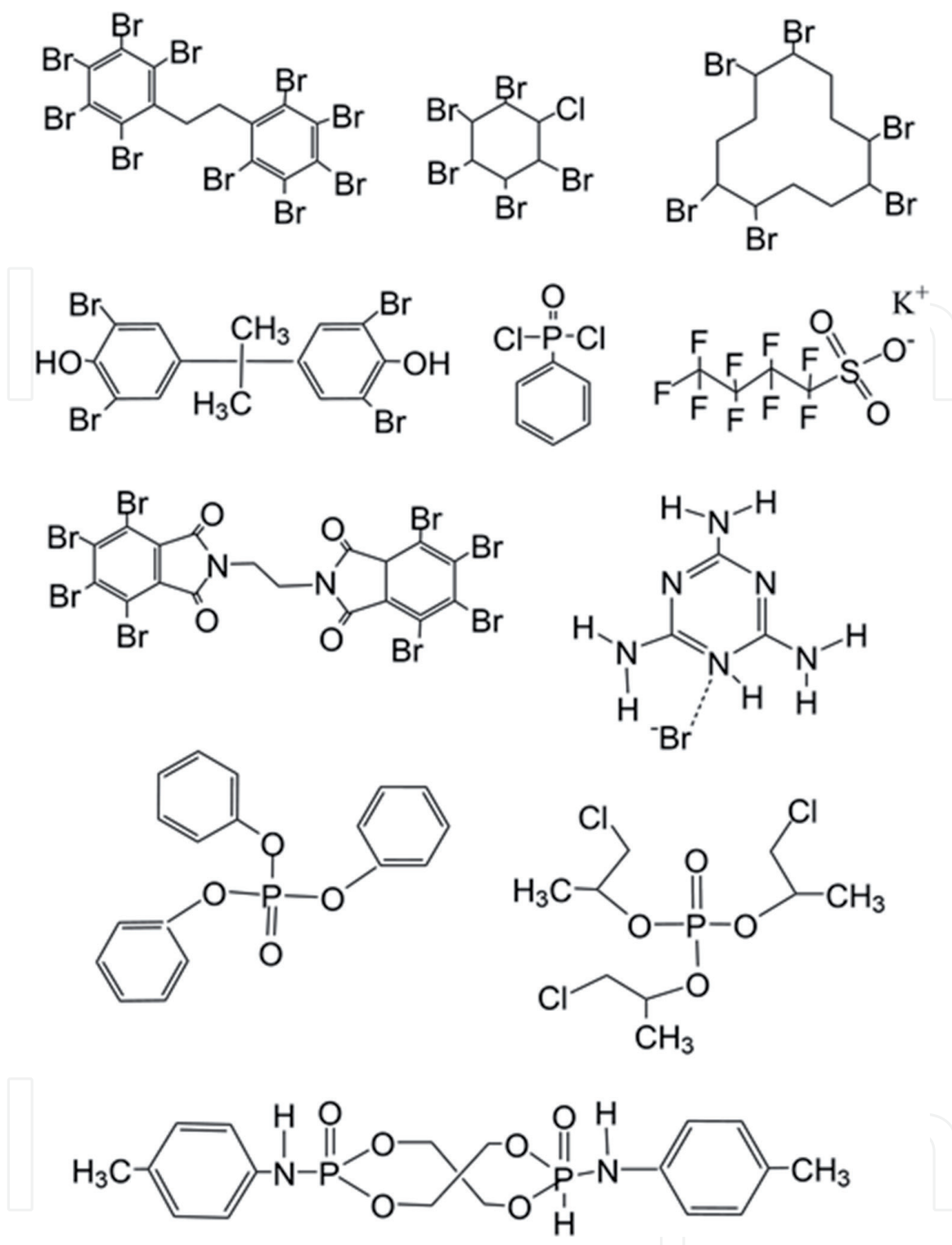
Figure 2.
Halogen derived flame retardants in use.

per year occur through the inhalation of toxic fumes such as carbon monoxide, hydrogen chloride, hydrogen cyanide [18] and dioxins [19] making the effects of smoke toxicity a leading reason for mortality during fire related incidents. The fact that gaseous toxicity release surpasses the ability of flame retardants to suppress fires is a major concern [4] and has shown to persist inside teaching classrooms [20] and college dormitories [21]. Poly-brominated and other halogen-based retardants are shown to be linked to bioaccumulation [22] with child developmental problems effecting child IQ performance, development and intelligence impacting neurologic function in children [23], weakening immune systems through Immunotoxicity [24], reproducibility [25], metabolic [26] and respiratory [27] interference. Such
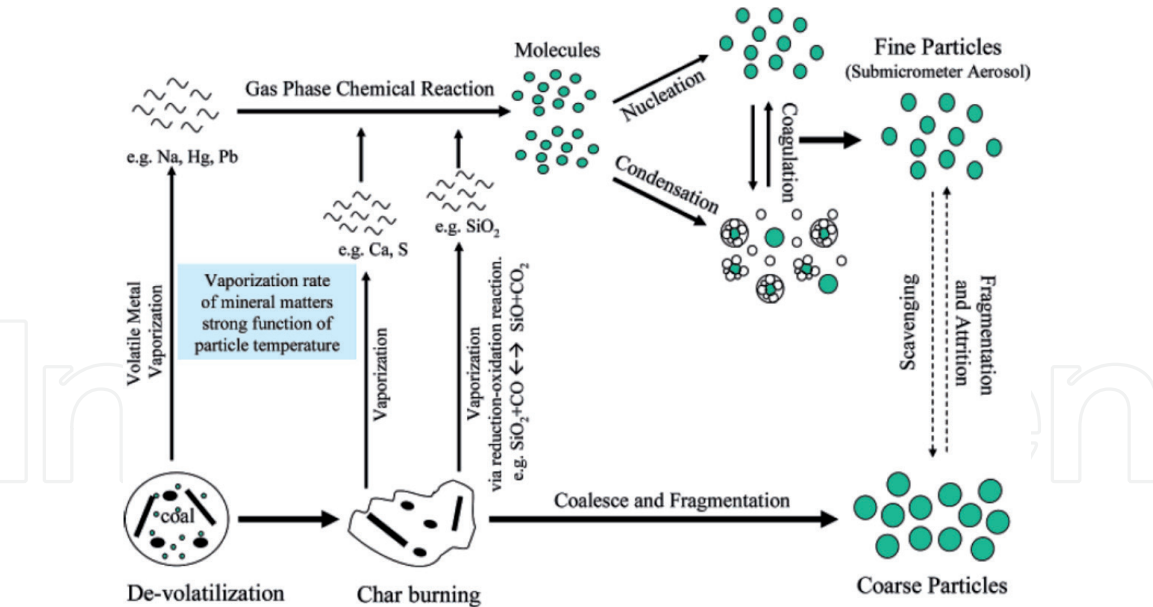
Figure 3.
Condensed to vapor phase particle conversion and associated processes during the combustion. Reproduced with permission from [14].
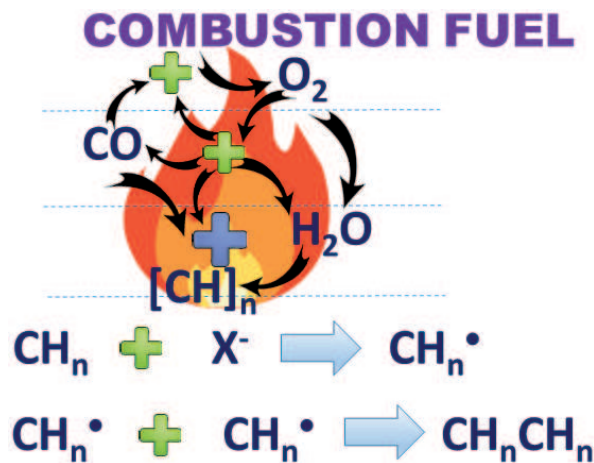

Figure 4.
The global equation of combustion which propagates by a set of chain reactions mediated by high energy radicals that originate from interaction of hydrocarbons with flame retardant halogen anions (Br⁻, Cl⁻ etc.) in a mixture composed of oxygen, carbon dioxide, water and combustion fuels e.g. hydrocarbons.

health risks also include harm to wildlife [28]. These chemicals discreetly find their way into the surrounding environments spreadable through the air [29] and water or become attached to dirt, soil, sand and powder particles and subsequently into human contact directly through inhalation or through food and water-intake. These health risks shown in **Figure 6** together with unknown and unsubstantiated toxic effects of flame retardants has caused considerable concern in recent risk assessments [31] fuelling demands for the disuse of constituent chemicals by Nanional Oceanic and Atmospheric Administration and the EU driven Restriction of Hazardous Substances Directive [32]. Environmentalists and health risk advisers have particularly focused on finding alternatives for halogenated flame retardants [33] with a view to replacing them with non-halogenic constituents. However, there exists an 'unmet need [34], to make flame retardants toxic free as new technologies emerge. This situation is being addressed by a drive towards policy changes focused on a class of flame retardant types and steps for their replacement [5]. The current
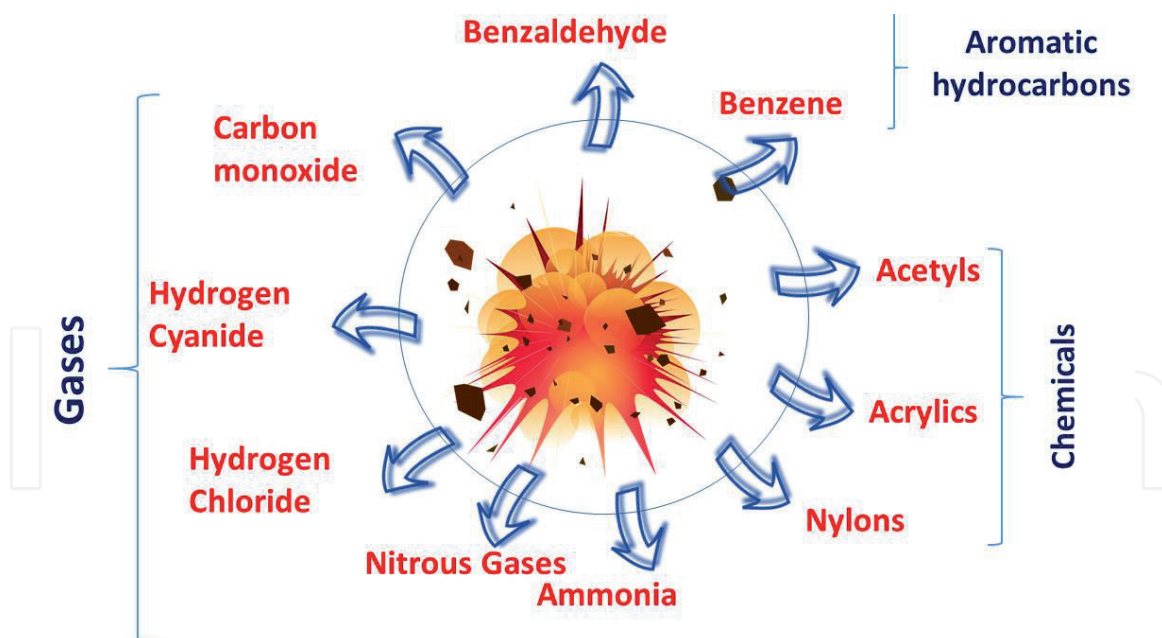
Figure 5.
The release of toxic gases, hydrocarbons and chemicals from polyamide based flame retardants.
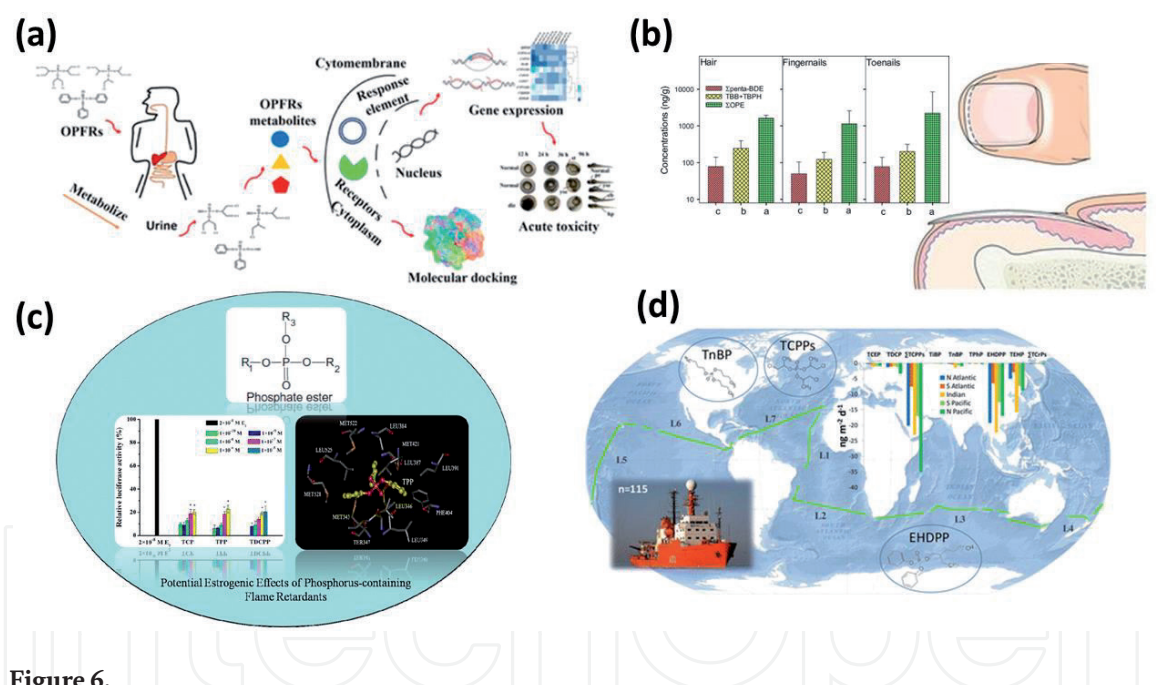

Figure 6.
Prevalence and potential for toxicity of flame retardants (a) metabolic fate of flame retardants affecting gene expression and inducing toxicity (b) accumulation in finger nails and hair follicles (c) hormonal suppression/ activation effects of phosphorous flame retardants modeled through molecule-ligand binding (d) detection of organophosphate esters across tropical and subtropical Atlantic, Pacific, and Indian oceans. The release of toxic gases from polyamide based flame retardants. Reproduced with permission from [30].

challenges weigh on the benefits of flame retardant use in saving lives against death due to toxic inhalation.

In this review, we focus on nanoclay materials and the potential to exploit both their intrinsic and modifiable properties adaptable as flame retardants with a view to make anti-fire materials safer by reducing their potential for toxicity and harm to humans and animals alike. Insight into the technological challenges that confront the flame retardant industry in securing safe and usable chemicals made acceptable by current environmental and health standards is highlighted. The low-dimensional characteristics of nanomaterials is discussed in the context of introducing and

exploiting new flame retardant properties which are absent at bulk scales. Particular attention is directed to polymers as high polymer content and their associated toxicities above ignition temperatures are often the cause of fire related fatalities. In particular, the synergistic role of nanoclays with polymer chemistry offer substantial improvements and the potential of these advancements is presented in the context of the underlying challenges that require new explorations to their development.

2. Igniting low dimensional chemistry to extinguish flame propagation

Increasingly, researchers and regulators of flame retardant use are looking towards the materials used by nanotechnology to improve the risks associated with anti-fire materials. Nanomaterial architectures offer considerable structural and functional control as host modifiers in parent structures. Particles of diminished size at nanoscales represent an important class of materials of technological value in controlling chemical and physical complexity. They hold the potential to offer considerable pyrolytic control as a new class of flame retardants through reinforcement of intercalated low dimensional materials. The effects of increased nanoparticle surface area and surface energy at the nanoparticle-polymer interface [35] caters for diverse orientations at nanoscales that impose changes to the overall microscale structure. Favorable polymer-particle associations can result in interactions that the affect physical and chemical properties of flame retardant behavior. Contributions in this respect may arise from surface interactions (in micro or nano confined spaces), in shape formations affecting polymer spacing and those that result from interfacial compatibility at polymer-filler interfaces. The larger elements of the effects that occur at the micro/nano level translate to globalized effects influencing mechanical properties, permeability and flow behavior of gases through interspaces and structures, thermal property and conductivity. Further, nano based flame retardants utilize less chemicals compared to their bulk counterparts diminishing the production of toxic vapors.

3. Current challenges in flame retardant design

The search for new flame retardants has been intense mainly to make their use safer and more effective. The challenge has been to understand more clearly the underlying mechanisms of pyrolysis particularly in the context of polymers to effectively introduce and to deliver new chemistries and modes of action that manifest at the nanoscale. It has been well-known since the 1960's [36] that the liberation of high energy free radicals play an active role in fire propagation and the broad task of 'chemistry' has been to control heat combustion by limiting radical formation. The emphasis has shifted in controlling the decomposition of flame retardants [37] to limit toxic inhalation and the thermal degradation of polymers [38] and to gain a knowledge-based appreciation of mechanisms prevalent in flame propagation. The broader picture here is complicated by flame retardant mechanistic modes and the overlying chemical synergy with material decomposition. This aspect of flame control has been challenging since polymer chemistry is considerably more diverse than flame retardant chemistry making the alliance of synergistic control intellectually and technologically demanding. Vulnerability to fire-spreading scenarios lies within the combustion process itself aided by a number of processes that lead to the ignition phase. Flame retardants while designed to delay combustion and pyrolysis propmote secondary effects of toxic fume emissions and free radical formation from burning materials such as polymers which may override the ability of retardants to

sufficiently contain fire progression and toxic smoke. The current problems focus not only on the material chemistry but emphasize a shift towards the intrinsic nature of the material itself. Since flame retardants conventionally operate on the principle of delaying fire progression, current objectives require using new material properties for the implementation of multi-functional flame retardants with design features better suited to the thermal properties of particular polymers. This is emphasized in **Figure 6** which seeks to manufacture a 'new generation' of materials effectively suppressing fuels that contribute to flame production such as oxygen, allow carbon dioxide permeability to reach sites to extinguish the birth of new flames and slow combustion, allow the capture and containment of toxic fumes, reduce the population of high energy radicals through quenching mechanisms and lower temperatures below the ignition phase. Health concerns must also be balanced with the dynamics of environmental issues, performance and costings making flame retardants more easily and economically available. The most attractive direction being pursued are low-dimensional materials that act as fillers for polymers bearing the ability to physically and chemically modify the thermal progression of polymers and other materials and to alter critical factors pertinent to fire control more advantageously with minimal damage to the surrounding environment. The additive or synergistic role of nanoclays hold much promise in this direction.

4. Polymers - a fire safety perspective

Polymers of varying compositional structures are wide spread in many everyday items [39] both in synthetic and to a lesser extent in biomaterials are a probable source of toxic inhalation during decomposition in fires. Most constitute a fire risk in many household appliances, furniture and wearable materials as the elements of polymer combustion drive fire propagation from the point of ignition. A growing body of evidence suggests that the reinforcement of polymers show a strong correlation with fire resistance while reducing the need for excessive use of fire retardant as single component materials in goods. The physical and chemical relationships between polymer behavior and fire progression has a unique place in engineering with the potential to offer new flame retardants that are both safe and effective. The complexity in the development of effective flame retardants is depicted in **Figure 7** [40] and empathizes the potential for multi-levels of combustibility that lie between the condensed (liquid) and expanded (gaseous) interfaces. As pointed out by Huiqing [40], the combustion cycle of polymer materials subject to a pyrolytic state pass through an [1] initial heating phase, reaching the [2] decomposition phase followed by the [3] ignition phase. Lastly, the combustion phase is triggered by the volatility of the liquid or gaseous products of decomposition at the ignition temperature and the excess heat generated via combustion in the presence of O_2 is utilized at the polymer surface to release more combustible products. This cycle contributes to increasing the free radical population and further increased chain branch reactions as described earlier in **Figure 4** accelerating the cycle of flame growth. Knowledge of the molecular properties of parameters that can be controlled is (shown in the orange box in **Figure 8**) can be applied and incorporated as design features in flame retardants to enable more effective fire suppression. Important targets in flame retardant design are effective suppressors of combustible compounds and their rate of evolution in keeping ignition temperatures below combustible thresholds. Some strategies that have been described include water formation through the use of brominated flame retardants [41] to contain temperature elevation via free radicals operating as inhibitors of flame propagation elements. Other forms of flame resistance includes charring [42] or partial burning
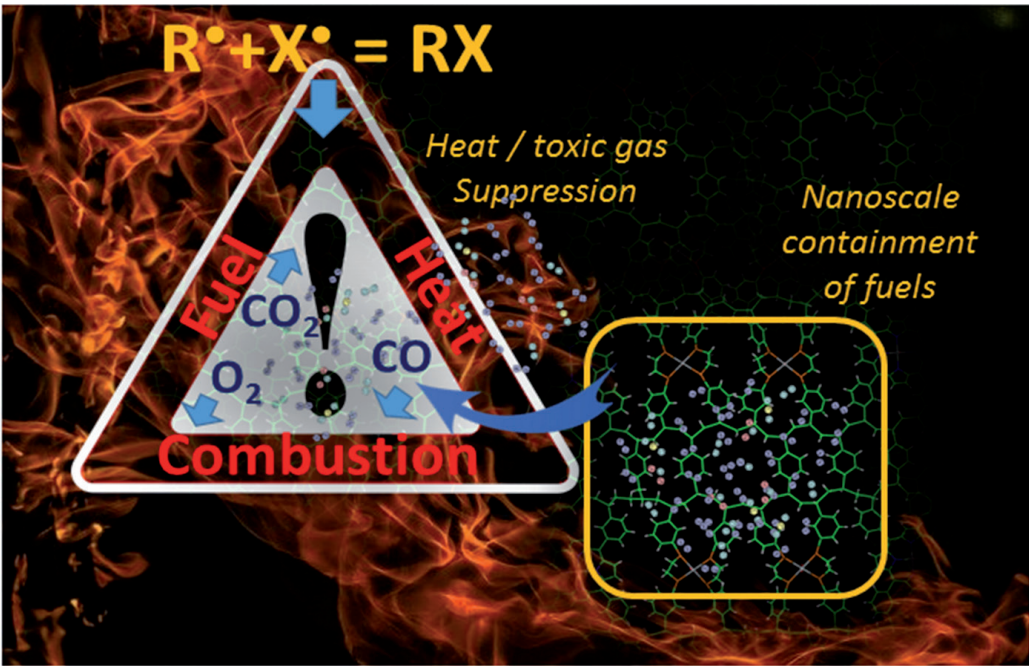
Figure 7.
Low-dimensional materials with multifunctional properties to combat fire hazards on multi-levels.
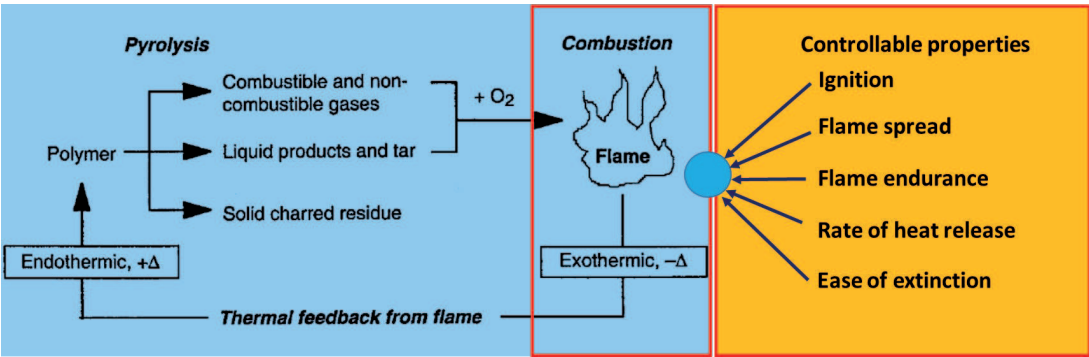

Figure 8.
A schematic showing a general role of polymer pyrolysis in combustion at the gas, liquid and solid interface and the potential for introducing key design features in flame retardants guided by key controllable properties. Modified with permission from [40].

which reduces polymers to black carbon essentially removing oxygen and hydrogen and effectively masking polymer surfaces (as assessed by measuring the limiting oxygen indexes or LOI's) [43] from further combustion through oxygen fuelling and volatile vapor mixing. In the oxidized form, char forms nitrogen oxide and heterocyclic compounds providing a basis for chemical fuel production at higher temperatures. Using two coal types as a carbon based combustion model, peak heat release correlated with the time to ignition showed the char content to decrease or increase with particle size increase [44] of the coal type investigated. Char forming chemistry has been investigated [45] and viewed as a useful alternative to halogen free retardants for polymers exhibiting fire resistance. The widespread application of organic and synthetic polymers in the manufacturing sector and related technologies increases the potential for toxic gas release by decomposition in case of fire demands safer designs of manufacturing protocols and newly improved fire resistant coating materials to replace existing ones. While char formation shows good potential to act as a shield preventing oxygen from mixing with polymers, char chemistry still remains a potential source for flammable gas release under persisting temperatures (**Figure 9**).
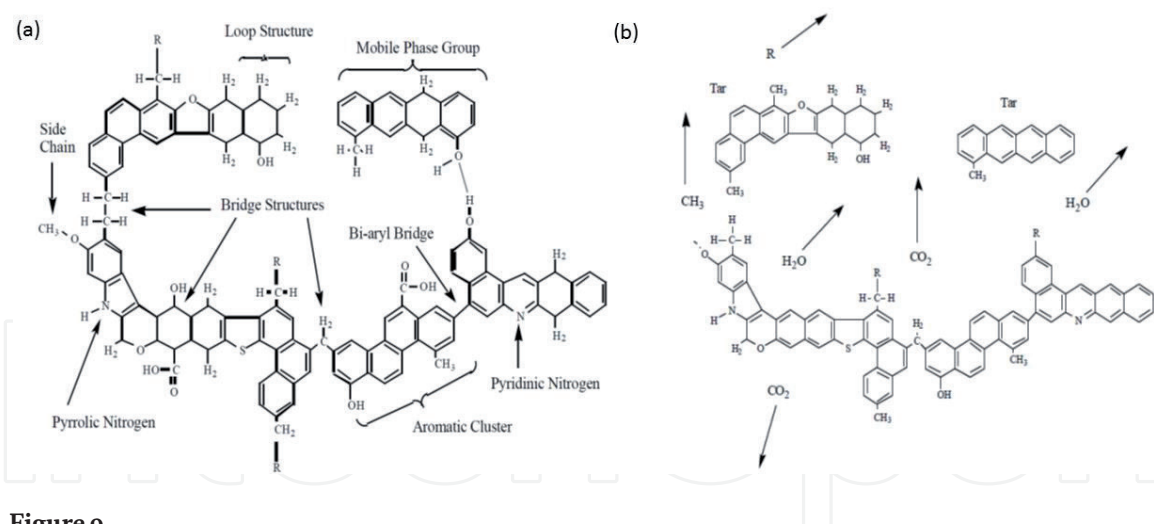
Figure 9.
(a) Likely compositional elements of char (coal) representing (b) possible sources of volatile chemical fuels at ignition temperatures. Reproduced with permission from [46] and modified from [47].

The hazards associated with fire retardant materials arise as a result of fire and the onset of flammable products released could be abated by slowing the decomposition rate of temperature polymer disintegration. Re-tuning the thermal behavioral properties of the primary polymer with other materials as additives that intervene with key elements that regulate combustion related properties to scale-down flame propagation is an important objective. In this direction, compositional integration with nanofillers can provide both structural and functional elements to alter the thermal properties of polymers and opportunities to consider more palatable flame retardants or to introduce new mechanisms to control and limit the harmful effects of existing ones currently in use. The progression of knowledge of the mechanical effects of particles on polymer stability at the nanoscale in terms of the structural harmony between filler-polymer interactions have important implications but have rarely been discussed in the context of polymer matrix, the nanoscale filler and the interfacial region [48]. This is highlighted to be particularly crucial in view of the ability of nanoparticle networks to diminish the combustibility of polymers [49].

Reinforcement of polymer strength and rigidity through stiffening uni-dimensionally or multi-dimensionally by pushing the chemical equilibrium towards char formation and increasing the barrier properties of chars could lead to new methods for fire retardancy. Hence, efforts have been directed for enabling mechanical stiffening of polymers [50] in a variety of ways that affect the flammability properties [51] closely coupled to ignitability [52] leading to a more controlled combustion arrest phase. For example, addition of co-monomers such as acrylonitrile, butadiene, and methyl methacrylate to the pyrolytic properties of polystyrene and styrene [53] and 2D-MoS_2 nanosheet-containing polyurethane [54] have been fabricated. However, more recently Varol et al. [55] determined that nanoparticle nanofiller quantity and not size determine the strain hardening in polymer nanocomposites (**Figure 10**). Although this study signifies mechanical strength in the context of load bearing application of polymers, tuning strain hardening behavior with nanofillers with a reinforcement magnitude that allows the decomposition of polymers to be critically restrained at high temperatures has much value for tailoring flame retardants. Replacing the characteristics of brittlement of polymeric materials with heat resistant materials [56] by enhancing higher temperature performance in nanocomposites has meritable arguments for the flame retardant industry. A key challenge in the development of environmentally acceptable and low-to-no health risk flame retardant additives for use with conventional anti-fire hazard materials has accelerated in recent years. In line with the growing importance of nanomaterial
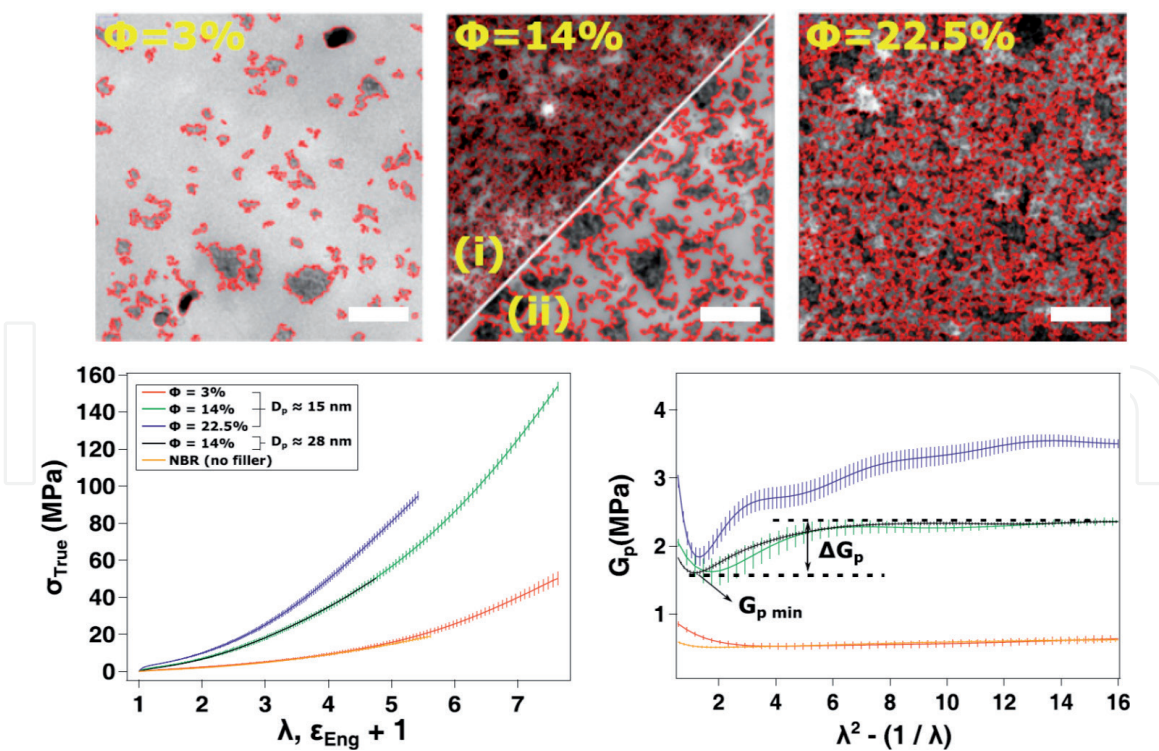
Figure 10.
(Top panel) Transmission electron microscopy images of the volume fraction (Φ) of SiO₂ derived nanocomposites particle size with respect to particle size. (Bottom panel) Plot of the true stress (σ) as a function of the extension ratio (λ) for particles exhibiting different filler volumes and size. Modified with permission from [55].

components for use in flame retardant formulations, the focus of interest has increasingly shifted towards clay based-minerals as nanofillers [57] to address some of the key challenges discussed. Multi-layering of flame retardants in nanocomposites could be an attractive structural feature to allow other additives to interact with flammable constituents that may persist even after part thermal stabilization of polymers with nanoclays. In addition, intercalation between polymer and nanoclay layers offer a level of intervention at the molecular nanoscale scale that may operate synergistically with the polymer and flame retardant chemicals. The possibility of introducing barrier properties, mechanical strength of polymers and hence diminishing volatile decompositions and support flame retardant properties cooperatively.

5. Nanoclays composites: challenging the role of conventional flame retardant mode of action

Nanoclays form a class of inorganic clay based nanomaterials (**Figure 11**) with chemical and structural attributes that enable their integration with diverse materials as clay nanocomposites including polymers [59]. They exist as silicate/aluminum-silicate structures in the form of montmorillonite, bentonite, kaolinite, hectorite, and halloysite. Nanoclays comprise layers of 1 nm thickness separated by interlayer distances between 70 to 150 nm modifiable as nanocomposites through intercalation with guest structures. While compositional mergers of nanoclay result in superior mechanical and tensile strength, properties aligned to reduce gas permeability [60] is achieved through the deposition of thin coated layers, alterations in glass temperature (temperature distortion) of nanocomposites and changes in modulus occur proportionally with increasing amounts of nanoclays and significantly alter material characteristics. Further nanoclays could be attractive additives as anti- combustion materials due to the differential permeability
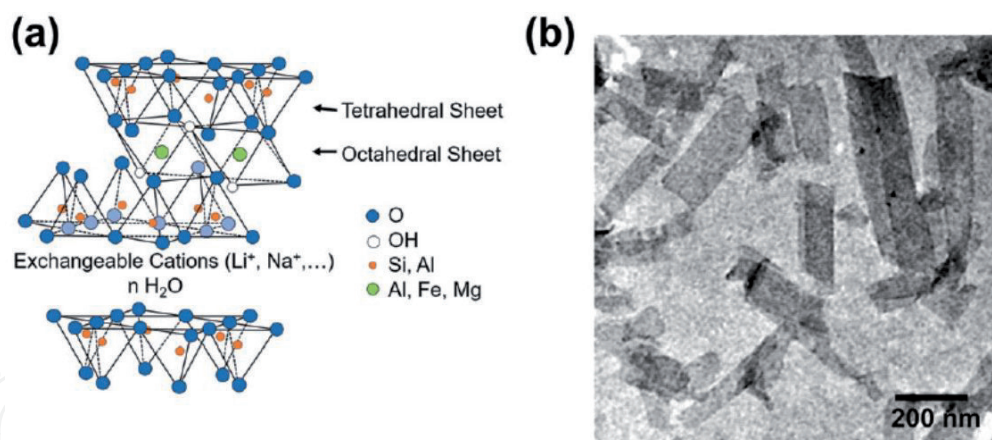
Figure 11.
(a) Structure of nanoclay exemplified by the (b) TEM image of nontronite. Reproduced with permission from [58].

behavior to oxygen and carbon dioxide. Nanoclay exhibits better gas barrier properties against oxygen then carbon dioxide and thus has the potential to limit oxygen as a fuel source to flames [61]. The possible tuning of the molecular spacing of silicon tetrahedral units suggests that gas permeability can be altered to a particular gas through morphological changes to the filler as in the case of nitrogen [60]. With special interest to polymer based flame retardants, the dispersion behavior and orientation properties of nanoclay particles can find significant use in generating intercalated layers with polymers that largely depend on their molecular assembly and ability to interact [62]. Also in the interest of minimizing the release of toxic fumes, nanoclays can be used to generate effective flame resistant barriers by making use of nanometer scale surface adhesion properties that extend across micrometer lengths with aspect ratios between 200 ~ 1000 or indeed higher [63]. Hence a strong correlation of barrier properties to geometric considerations such as orientation, filler morphology and aspect ratios are critical to their functional use as additives in flame retardants to control the spread of fire [64].

To advance fire retardant chemistry however, there exits an underlying need to understand better the molecular transition from the homogenous nanoclay and polymer architectural state to a structurally unified polymer-nanoclay nanocomposite state at the nanometer level. An immiscible state between nanoclays and the surrounding polymer environment lacking a chemical union of bonds as a co-mixture rather than a self-ordered intermixture does not allow ascendency to a superior consolidated mechanically enhanced state. In other words, the filler chemistry must adopt bond, shape, physical and chemical structural characteristics unique to the assembly not shared by the components separately or as a co-mixture. In order to allow the next generation of fire retardants to be of greater general applicability and of broader scope to different polymer populations, the exfoliation of nanoclay inter-layers requires the use of interactants (modifiers such as inorganic minerals, synthetics, hydrophilic or hydrophobic solvents, dispersants, reductants/oxidants and other chemical agents under conducive physical conditions) so that the chemistry and spacing between interlayers is compatible with the polymer environment.

6. Synergistic effects of nanoclays

A well-recognized route for the suppression of flames and probably the best studied process has been described by carbonaceous char formation exhibiting
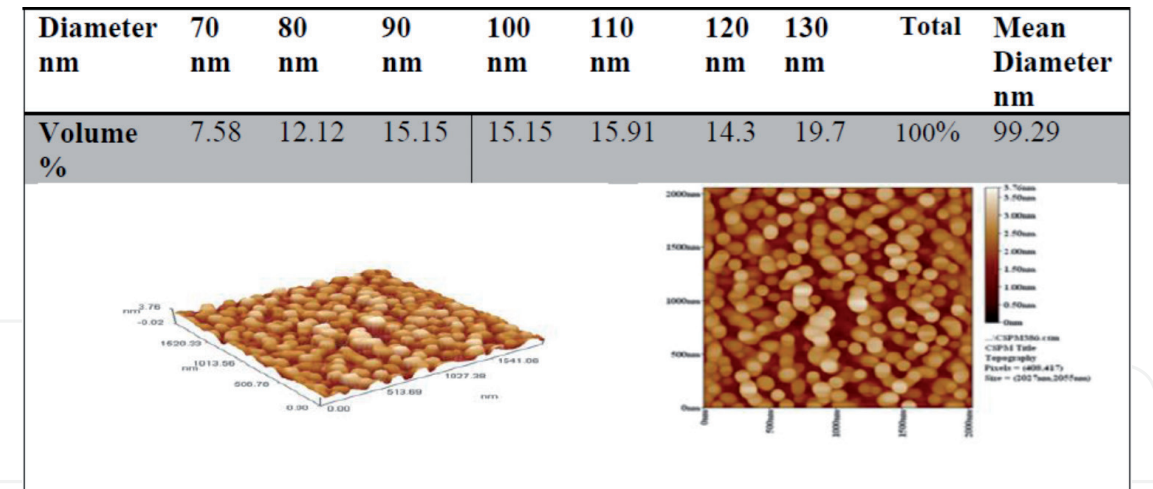
Diameter nm	70 nm	80 nm	90 nm	100 nm	110 nm	120 nm	130 nm	Total	Mean Diameter nm
Volume %	7.58	12.12	15.15	15.15	15.91	14.3	19.7	100%	99.29

Figure 12.
Layered geometry visualization of nanoclay by atomic force microscopy showing the importance of ionic interpenetration at the nanoscale with particle diameter changes from 70–130 nm. Reproduced from [67].

barrier properties [65] that effectively 'cut-off' gaseous fuel supply reducing flame capability. Decade old studies on nanoclay composites have shown to provide 'multistage' insulation during fire progression, however the dependence of fire performance on a measurable quantity of nanoclay was prominent ranging from optimal to infective in delaying and an advancing fire hazard [66]. Such studies have highlighted the complex chemical nature of nanoparticle interpenetration between layers (**Figure 12**) at nanoclay interfaces and the limited knowledge in selecting and activating chemically useful routes that diminish flame growth against accelerating factors. The ambiguity in the nature of these mechanisms is complicated by molecular changes that occur with nanoclays at the surface of different polymers pointing to the nature of interacting species that may be consumed or liberated during different stages of thermal reaction. Char formation is mediated via the catalytic crosslinking of polymers with properties that are identifiably different to their constituent reactants both by their physical and chemical nature. Nitrogen metal complexes have been suggested to counteract barrier char formation by catalytically weakening polymer stability through site specific decomposition by virtue of the metallic catalytic sites accommodated within the clay region [68]. The extent to which these processes operate play a central role in determining polymer stability and the dominant mechanisms that ultimately prevail However, dispersion becomes an important criteria at the nanoscale level in determining effective flame retardant properties [69] while a more informed selection of polymer types forming the nanoclay-composite chemistry can used to increase the carbon content of char [70] likely favoring crosslinking ability and subsequent barrier properties. The ionic nature of nanoclays also plays a significant role in governing the flame retardant properties of complexes.

Polymer variability in terms of composition, structure and intrinsic properties are defining features that determine the degree of material inflammability. Understanding the mechanistic role of nanoclay particles in subduing polymer vulnerability to thermal heating and volatility becomes a challenging problem in the field of flame retardancy. **Figure 13** shows the chemical integration of polymer-nanoclay surface where the interface chemistry is a key factor in deciding flame retardant properties of the resulting nanocomposite. Some generalized insights into possible mechanisms have emerged from fire retardant investigations. As mentioned, much effort has been directed in uncovering the complexities surrounding char deposition pathways to improve mechanisms that have an obvious advantage in blockading the mass transport of fire enhancers (e.g. free radicals, gases,
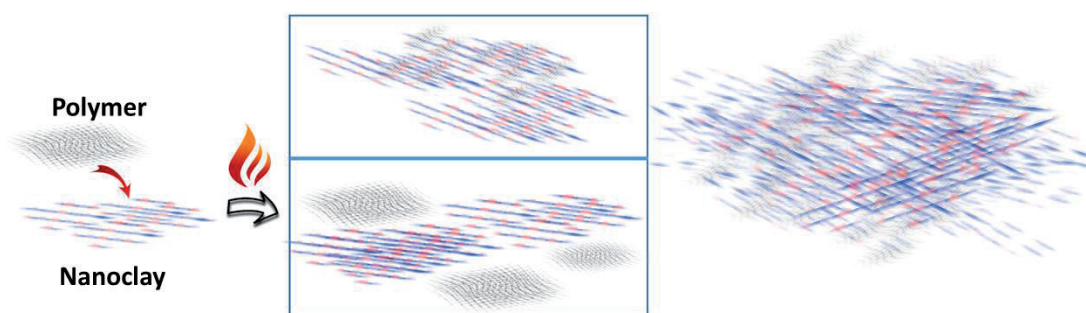
Figure 13.
Clay-polymer assembly processes under thermally elevated conditions determine fire retardant potency driven by nanoscale chemistry.

hydrocarbons etc.) that can be released from clay surfaces via an initial pyrolytic state. Barrier properties become progressively more effective during the condensed phase as more material is retained and cross-linked leading to enhancement with subsequent layers. The synergistic cooperation between nanoclay layers and mineral addictive's has attracted much attention in recent years and has rapidly become the most favored approach in the field of flame retardancy.

While the immobilization of decomposed components aided by low migration at the surface of silicate layers is an important mechanistic approach to barrier creation and polymer modification, the unrestricted migration of the more volatile degradation products can release free radicals with the ability to passivate halogen radicals through the chemical association with hydrocarbon radicals. Such radicals may take the form of metals embedded or chemically attached to the nanoclay polymer matrix. The intrinsic and selective nature of the polymer materials modifiable by thermal processes potentially embody exploitable synergistic characteristics particularly at the nanoscale. For example, improvement in interfacial adhesion has been correlated to a change in thermal decomposition to elevated temperatures during the merger of nanoclays with flame retardant supporting the synergism of nanoclays to char layer enhancement [71]. Hence, the chemical synergy between the reactive nature of starting materials (nanoclay, polymers and minerals), the initiation temperature and pathway for thermal activation of condensed and volatile degradation products and the knowledge of key mechanistic events in terms of mapping structure to flame retardant function and performance still need to be resolved. Certainly, the correlation between clay composition and decompsition kinetics ohas been identified to be a key factor in charring [72]. Despite the hidden challenges which persist in the field, the effects of scale are slowly emerging using a number of experimental approaches. Some observations that form the basis of well-accepted outcomes coupled to unresolved mechanistic ideas are generalized in **Figure 14**.

The potential for polymer-layered nanoclay composites for applications as flame retardants has been recognized in earlier studies [73]. A common objective in nanocomposite design has been the search for effective interacting agents for the alignment of polymers along the corridor-like arrangement in stacked layers of nanoclays to improve mechanical strength, thermal stability and gas barrier properties. Diagrammatically, the stacking is described as intercalated in which polymers lie between inorganic layers in well-ordered arrangements or adopt exfoliated patterns represented by disordered arrangements within the layers exemplified by poly(ethylene oxide) adsorption on nanoclay surfaces (**Figure 15**). In similar studies [75], the use of polypropylene-graft-maleic anhydride and polystyrene-layered-silicate nanocomposites in their ability to suppress flames was mechanistically similar and it was established that the behavioral properties depended on the degree
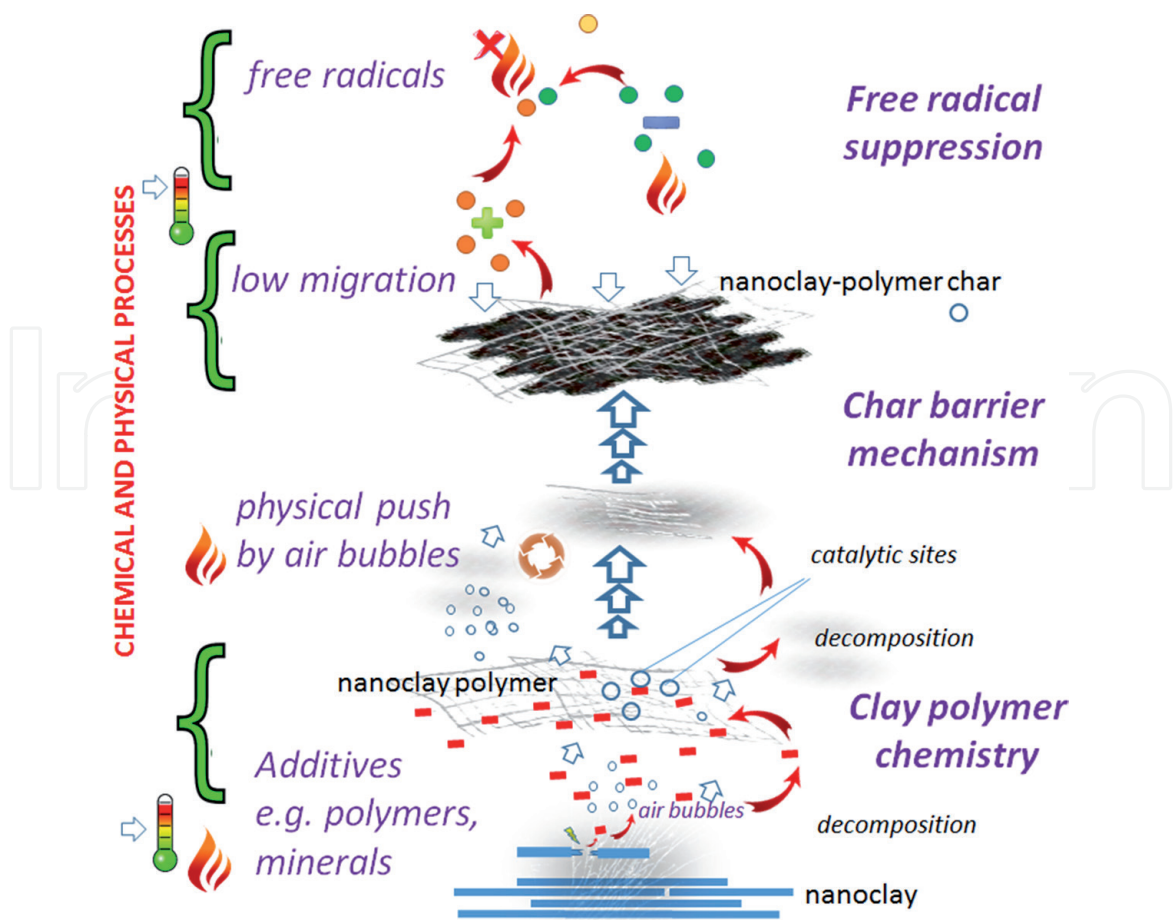
Figure 14.
General mechanistic routes to fame retardancy by char barrier formation and free radical suppression mediated by catalytically induced sites at the nanoclay polymer interfaces. Migration of particles formed by degradation products originating from pyrolytic chemical processes are assisted by air bubble movement pushing particles upwards and low migration of condensed phased char particles.
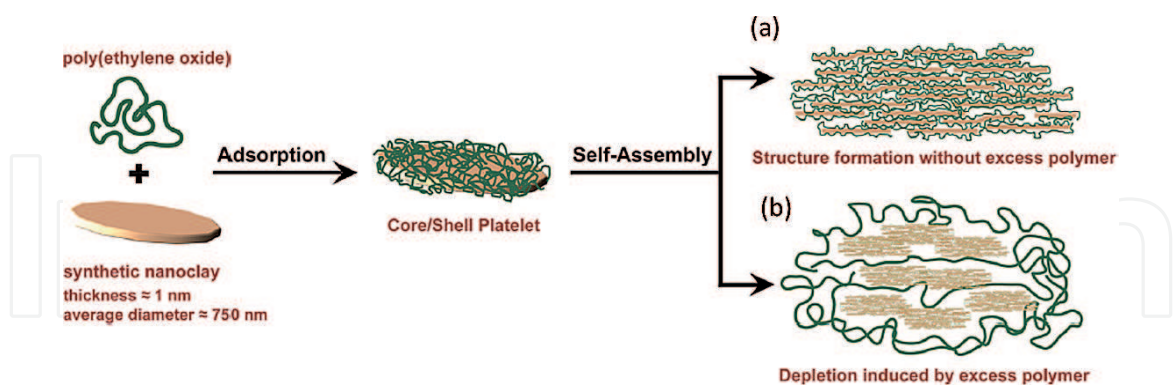

Figure 15.
Schematic showing two types of silicate-polymer composite layering either as (a) ordered (intercalated) or (b) disordered (delaminated) arrangements. Reproduced with permission from [74].

of dispersibility and type of silicate material. The effects of flammability reduction were inferred through a protective insulation surface slowing down the decomposition rate of the underlying material and thus preventing exposure to the decomposition products. Mechanistic insight has been better aided by knowledge of the molecular orientation of nanoclays that have resulted in establishing three types of nanoclay geometries. Understanding the geometrical orientations of nanoclay shown in **Figure 16** may help in our decipher the barrier properties exhibited by these class of materials which exist as (a) phase separated (immiscible), (b) intercalated or (c)
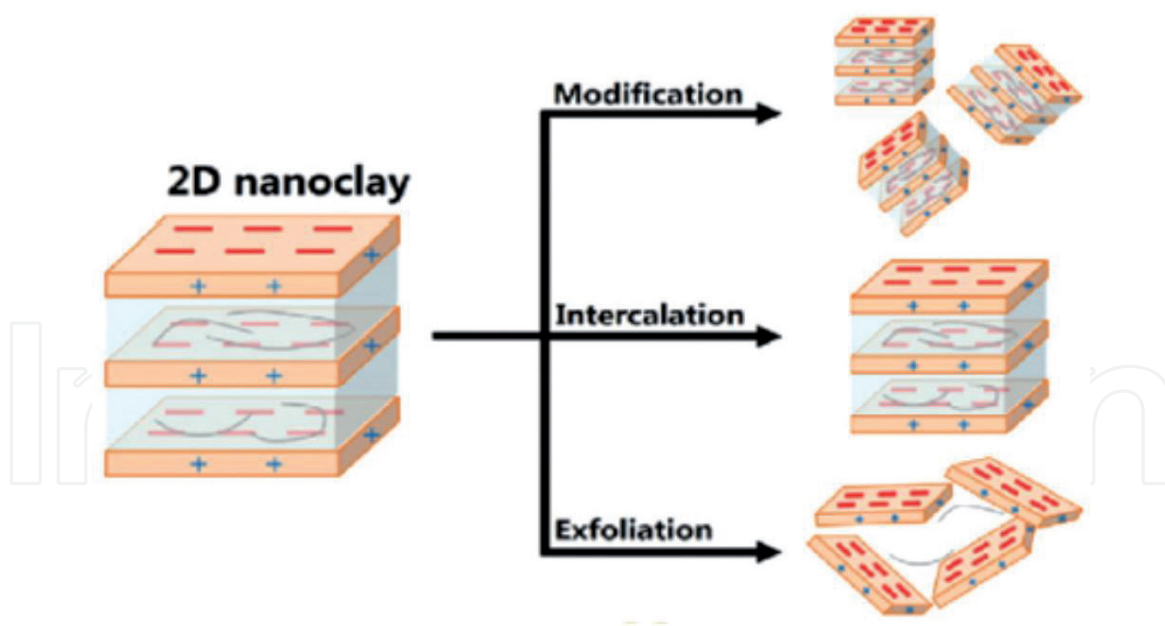
Figure 16.
Differing morphological states of polymer–nanoclay structure of nanoclay. Reproduced with permission from [76].

exfoliated as polymer nanocomposites. In (a), polymers do not reside inside the inorganic layers that may exhibit conventional silicate layer properties as layered blocks while (b) shows interlayer distancing of a few nm between silicate layers which is a result of polymer intervention within the layers by the surrounding polymer. Finally (c), shows an exfoliated structure where clay layers are singularly separated by the polymer. Polymer matrix and nanofiller interactions play an important role for atomic-scale nanoclay dynamics. The interaction of the cationic surface of nanoclays with organic layers of polymers is identifiably important in the advancement of flame retardant nanotechnology. There are many reported studies that have pursued the effects of polymer matrix/nanofiller (nanoclay) associations and while there are benefits to the formulations, the precise role of nanoparticle ambulation during surface modification remains unknown. Current knowledge however, stipulates that organic components of polymers can sufficiently reduce excess energy (surface energy) [77] by minimizing cohesive and adhesive forces at the solid-wet interface between cationic and polymer states of matter respectively while supporting the stabilization of interlayer spacing. Spacing serves a useful purpose in reducing surface energy and preventing nanoparticle aggregation generating enhanced dispersion and the level of ordered intercalation largely dictate the nanocomposite structure. In context to **Figure 12**, it might be expected that separation achieved in exfoliated nanocomposites generate maximum space and hence maximum surface area allowing polymer migration to occur and spread along interfaces unperturbed between silicate layers. Schartel et al. [78] demonstrated differing morphologies of phosphonium-modified layered silicate epoxy resin nanocomposites but structures closer to exfoliated forms (**Figure 16**) with silicate as a nanofiller revealed a barrier effect but had little effect on the suppression of decomposition products and combustion of volatiles. The current perception of exfoliated surfaces yielding superior surface and mechanical properties is a phenomenon that is now less clear and conflicting evidenced by experimental interpretations. By its nature, exfoliation generates better dispersity between the nanoclay surface in an uninterrupted polymer matrix. Variability in experimental observations often uncovered inconsistency from glass transition values and suggest that a state of higher thermal stability depends on other factors and not solely on the visible state of a structure. Hence, the level

of unpredictability associated with well-separated exfoliated layers of separation could reside with the degree of variability in interfacial patterns that may ultimately determine polymer mechanics and further complexities introduced by compatibilizers as components for in epoxy adhesives [79] for example, or as thermally reactive additives. The lack of understanding of these factors could be contributing factors to discrepancies among related samples and more insightful explanations are needed to develop favorable material properties.

The use of non-halogenated flame retardant materials have recently come into effect like aluminum diethylphosphinate (ADP) [80] improving char yield. It has been reported that the multi-phase use of ADP in the vaporized and condensed phase [81] significantly contributes to flame inhibition. Investigations by Kaynak and Polat [82] further established the role of path driven intercalated/exfoliated NC layers that contributed to the emergence of insulative barrier properties as judged by the increased limiting oxygen index. Chemical synergy between nanoclay layers and ADP likely favored the retainment of aluminum phosphinate at the clay surface forging the incorporation of the mineral within the layers of the carbonized char residues within the mechanically strengthened polymer structure of diminished chain flexibility. Thermally activated vapourization of ADP triggered the oxidation of surface unbound minerals in the gaseous phase to phosphinate radicals $HPO_2\bullet$, $PO\bullet$, $PO_2\bullet$ creating opportunities to neutralize the toxic effects of $H\bullet$ and $OH\bullet$ curbing flame growth. Here, the use of 5% silicate layers was effective in combination with 15% ADP.

In an attempt to better elucidate the mechanistic impact of nanoparticles during pyrolysis, two-dimensional transient-state models based on nanoclay layering using carbon nanotubes as potential polymer reinforcement additives. The study revealed a number of nanoscale effects between charred and uncharred regions that span the clay network serving as the major interface in regulating the transportation of surface degraded and diffusive particles that affect thermal transfer [83]. However, the synergistic shift in surface chemistry at the clay-nanoparticle that permits mass transfer loss via polymer degradation by addition of carbon nanotubes during the initial stages of pyrolysis suggests that improved stability around structured nanoclay layers will be pivotal to controlling flame retardant properties in future nanocomposite designs. Tuning the thermal stability of nanoclays with compatibilizers can provide access to the incorporation of smarter materials such nanopolymer confined quantum sized TiO_2 [84] that demands better exfoliation of silicate layers improving immiscibility of layers with TiO_2 [85].

Suter et al. [86] have more recently used a novel multiscale modeling to shed light on the mechanisms driving exfoliation behavioral properties of clay-polymer nanocomposites. The results show how molecular simulation techniques targeted around clay interfaces using free energy profiles and structure based coarse-grained iteration processes to understand clay layer exfoliation and how such interactions lead to experimentally observed changes. This was achieved by simulating the interactions of montmorillonite clay, a polymer (PEG) and a quaternary ammonium dimethyldioctadecylammonium ionic surfactant. **Figure 17(a)** shows molecular dynamics simulations of models predicted I, II and III after a simulation of 3 μs with model II and III forming partially and fully exfoliated single layers respectively. **Figure 17(b)** shows the radial distribution as a function of sheet distance and provides evidence supporting a completely dispersed system. In the bottom panel of **Figure 13**, different stages of the molecular dynamic simulation of model II is presented illustrating (a) the clay structure prior to the interactive state with PEG (b) intercalated nanoclay-PEG formation resulting in increased gallery separation and the (c) departing motion of neighboring of layers favoring an exfoliated increases in Young's modulus derived from the stress–strain behavior models of II and III. The
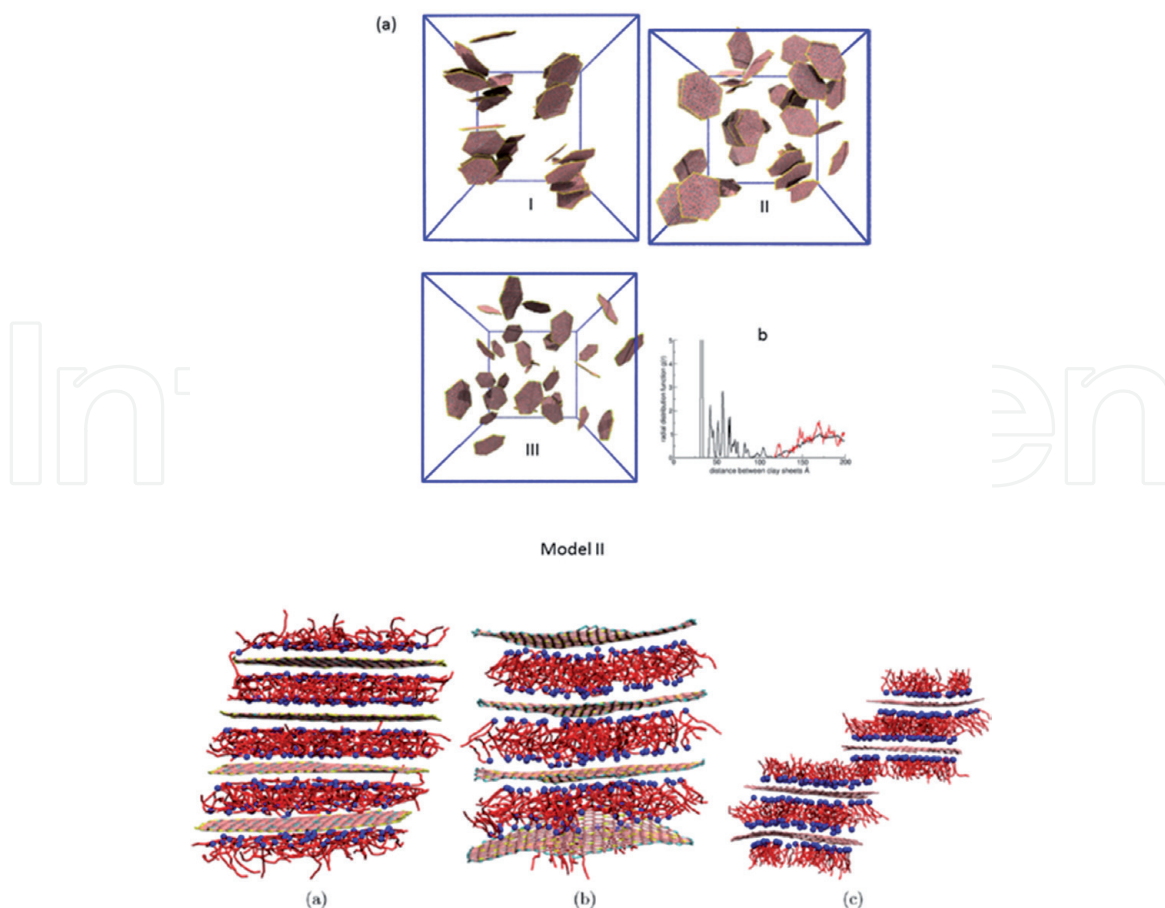
Figure 17.
Dynamic simulation models of (a and b) of (c) partially and fully exfoliated nanocomposite state. The exfoliated models are found to exhibit considerable elastic properties with substantial structures based on model II as described in the text. Modified with permission from [86].

density charge increase around the polymers attributed to the surfactant molecules rendering the nanoclay structure to an exfoliated state by inhibiting a diffusive state which is assisted by a transversally sliding motion of clay. Such simulations provide plausible clarity on the dynamics of nanoclay sheets and important mechanistic clues that can be evidenced and supported by experimental findings with additives. As simulation tools become more powerful, it will become easier to assign definitive structure–function relationships to earlier observations that have been more phe-nomenological in their explanatory findings. The re-organization of intercalated or exfoliated states in nanoclay based nanocomposites is a promising way to better regulate not only polymer behavior but also the behavior of flame retardants under nanoconfinement signifying the functional role of clay particle size [87].

Nanoconfinement of polymer chains in nanoclays can influence polymer behav-ior affecting the chemical and physical behavior with additives in the melt, altering decomposition, thermal degradation and intermolecular interactions kinetically of components globally determined by the local morphological states that adapt to intercalated or exfoliated or indeed partial intermediate states. Over the last two-to-three decades, polymer research has intensified the use of nanofiller materi-als to form polymer bends into tunable nanocomposites. Nanofillers in the form of layered silicates have enabled a considerable reduction in the use of conventional load bearing modifiers in comparison to their low dimensional counterparts by as much as 3 ~ 8 fold of the total content normally used by conventional processes. A significant trend that continues to be a promising pathway for the future use of flame retardants is the chemical synergy driving nanocomposite assembly while extinguishing the properties of its individual components in the blend. Some of

these examples include the synergistic effects of clay-organic intumescent hybrid systems. Distances among silicate layers in nanoclay modified with organic surfactants show functional significance in the absence and presence of intumescent agents. Irrespective of whether nanoclays adopt an exfoliated or intercalated state of matter, increase in the layer distance from 9.8 to 13.8 Å revealed that the stacking morphological architecture of the nanocomposite was important to its role in reducing heat release rate through the formation of dense char layer [88].

Here, we provide a summary of some of the more recent approaches and strategies in flame retardant design used for targeting flammable plasticizers widely used industrial polymers with reference to some key studies on nanoclay-polymer nanocomposites from pervious works. In earlier work, quin et al. [89] in their investigation with nanoclay-polypropylene aimed to clarify some unresolved aspects of key mechanisms of flame retardancy. The fundamental problem related to the dispersion state of the nanocomposite and addressed its influence on flammability which tied in with the underlying role of nanoclay in thermal oxidative degradation and combustion. It was concluded the delay to combustible ignition of volatiles was in fact due to the char barrier formation and the route to char deposition occurred via catalytic dehydrogenation and crosslinking of the nanocomposite which was mainly assisted by acid sites of the silicate. The process is summarized in **Figure 18**. An important component in this mechanism that is most relevant to the liberation and availability of silicate catalytic sites was the addition of the alkyammonium salt which in itself decomposes leading to the pyrolytic release of ammonia and olefin hydrocarbons and the accompaniment of rich acidic cations on silicate surfaces. While this mechanism was effective in suppressing flammability, evidence continues to accumulate and support increased mechanical strength and hardness capacity of nanoclay modified polymers enhanced by significant increases in tensile strength and stiffness using tetramethylammonium chloride but may decline with suboptimal quantities [90]. For example, the addition of nanoclays have shown to disadvantage the working performance of flame retardants as noted for a phosphorous-based retardant [91] comprising a Diglycidyl Ether of Bisphenol A (DGEBA) resin composite. This emphasizes the importance of tailoring the cooperativity between the filler and polymer space and dispersion which facilitates the nanoscale chemistry of the retardant components in the composite in response to parametric changes affecting interactions at the molecular level.

A future direction in the controlled degradation of polymers using regulated by filler amounts is the prediction of degradation products. In a recent investigation,
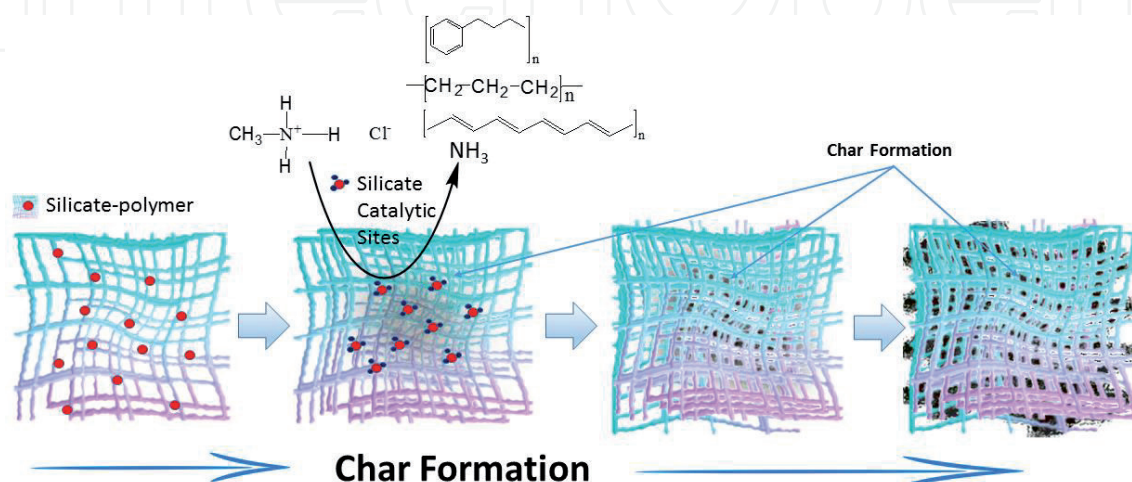

Figure 18.
Active-site catalytically induced char formation during combustion on clay surfaces supported by polypropylene as the polymer matrix.

Saha et al. [92] applied reactive force field molecular dynamics simulation to poly-acrylester in which clay nanofillers in conjunction with graphene was used to modify the elastomer polymer characteristics. The model developed using this approach very reliably predicted the effect of adding graphene oxide (GO) in relation to the evolution of degradation products which agreed well with the experimental outcome. Improving the knowledge base of volatile materials originating from different polymer compositions computationally will certainly have meritable consequences in implementing better control strategies against flame enhancing volatile materials [93] and predicting combustion behavior such as ignition times [94], char oxidation and particle sizes [95]. The differences in melting and shrinking behavior that arise from physical conditions affecting ignition performance for example and other important parameters may not be easily accurately measured by micro-scale tests [96] will significantly shift the burden for reliability more towards computation methods.

7. Concluding comments

The current perspective on nanoparticle driven flame retardant performance specific to nanoclay materials emphasizes their growing importance as fire regulatory materials and reduced toxicity. At the nanoscale, clay interactions with different polymer types hold the potential to steer nano-driven mechanisms to more effective outcomes in retarding the spread of flames. In the generality of flame retardant mechanisms to the formation of chemical barriers and passivation of fire enhancers such as free radicals, nanoclay makes important contributions to polymer structure and mechanics, catalysis and kinetics of production degradation and acceleration of stability of factors in slowing down flames. The thermal activation of new catalytic sites at the clay-polymer interfaces will crucial be in developing a more effective class of retardants in the future particularly in the context of target specific modifiers. The lack of detailed mechanistic knowledge of nanocomposites is often hindered by the limitation of experimental approaches and computational approaches will become important predictive tools for guiding areas of new insight.

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