

Current Advances in the Fire Retardancy of Natural Fiber and Bio-Based Composites – A Review

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Natural fibers and bio-based composites are competitive to conventional materials in structural and transportation industry. Natural fibers reinforced polymer matrix composites are familiar/common materials currently. Various properties of these composites have been explored in the already available literature, and has been continuing with new developments. They have a risk of flammability in most of the applications which is undesirable. Fire retardant natural fiber and bio-based composite materials have recently gained researchers' interest. This paper summarizes recent progress regarding flammability of natural fiber and bio-based composites. The mechanism of fire retardancy has been explained. The factors affecting flammability of such composites and characterization techniques required for evaluating fire retardancy have also been described in detail. The reported effects of fire retardant include practices on the other properties of composites.

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1. Introduction

Environmental concerns, cost and depletion of the synthetic materials have led a way for the development of renewable, economical and eco-friendly materials. The inorganic waste material is generally not biodegradable and cause toxicity to the living being.¹ On the other hand, natural fibers and bio-based polymers and fillers are fully biodegradable materials.²⁻⁴ Due to their light weight and low cost, the natural fiber reinforced composite materials are being preferred in automobiles and construction applications.⁵⁻⁷ These composites; however, have some weaknesses among which high flammability is of critical importance.⁸⁻¹⁰ Currently a limited amount of literature is available on the flammability characteristic of natural fibers and bio-based composites. However more research is needed in this field to extend their applications in automotive, aerospace, marine, construction and electronics industries.^{11,12} In this article a broad review of the recent advances in the flammability of natural fibers and bio-based composites has been presented. The fire-retardant methods, fillers and factors affecting the flammability of such composites have been summarized in this review.

Various methods are being used to enhance the fire retardancy of polymer composites; these methods include engineering approach, less flammable polymers and fire retardant (FR) additives.¹³ Engineering

approach is the inexpensive method but it is not considered safe. Low flammable polymers are durable but expensive method. While incorporation of FR additives in composites is the most common and well accepted method. The FR additives are usually nano or micro powder fillers, which act in different ways to stop fire propagation.¹⁴⁻¹⁷

Ren et al. used zinc borate (ZB), montmorillonite, manganese dioxide and stannic oxide as FR additives synergistic agents in wood flour/polypropylene composites.¹⁸ They have noticed positive synergistic effect of the FR additives on the fire retardancy of the composites. Szolnoki et al. developed hemp fiber reinforced flame retarded epoxy resin composites.¹⁹ Phosphorous based FR additives was used to enhance the flammability properties of hemp/epoxy composites. Jeencham et al. evaluated effect of ammonium polyphosphate, magnesium hydroxide, ZB and their combination on the fire retardant, thermal and mechanical properties of sisal/polypropylene composites.²⁰ Shah et al. used oyster shell powder as organic filler in polypropylene matrix; they enhanced fire retardancy and thermal properties of the matrix.²¹ Umemura et al. used ammonium polyphosphate (APP), melamine polyphosphate (MPP) and aluminum hydroxide to modify flammability of wood-plastic composites.²² More work reported on flammability of natural fibers reinforced composites (NFRC) in the recent literature is listed in Table 1.

The incorporation of FR additives into composites requires special steps in the fabrication processes. The most important factor is homogeneous mixing of the additive particles with other constituents of the composites. The improper distribution of FR additives causes agglomeration which results in undesired decrease in mechanical and water absorption properties.³¹⁻³³ Some methods have been reported in literature to overcome the undesired effects of FR additives.^{34,35}

2. Properties of Polymers

Polymeric matrices are attractive materials and play very important role in composite. Hence, the properties of composites greatly depend upon the polymeric matrices and the fabrication process. The commonly using polymers and some of their physical properties are listed in Table 2. Because of their remarkable properties, massive use of polymeric materials is observed in our everyday life. However, irrespective of their origin both natural and synthetic polymers are very sensitive to flame because of their main constitute element carbon. But in the composites, generally matrix (polymer) plays a role to support the reinforcements against fire propagation and thermal loads.³⁶ Several articles have been published on the flammability of polymers and polymer composites.³⁷⁻⁴² Flammability of polymers is explained based on some parameter e.g. LOI and HRR. Flammability properties of some the commonly used polymers are also listed in Table. 2.

3. Properties of Natural Fibers

Natural fibers are obtained from plants, animals and minerals, which

can be further divided into different categories based on their sources of extraction, as shown in Fig. 1. Flammability and other properties of natural fibers depend upon their chemical compositions. Protein is the main component of animal fibers, but plant fibers are composed of cellulose, hemicellulose and lignin.⁴⁸⁻⁵⁴ Animal and mineral fibers are not known as famous reinforcements while plant fibers have been used globally as well know reinforcement fibers.⁴⁹ This review paper is mainly focused on flammability properties of plants based natural fibers.

Plants based natural fibers are extracted from seed, leaf, bast, fruit, and stalk. These fibers are composed of cellulosic micro-fibrils compounded in lignin matrix, pectin and wax. The flammability of natural fibers mainly depends upon their chemical composition. The compositions of some of the fibers are shown in Fig. 2, while Table 3 shows the role of fiber

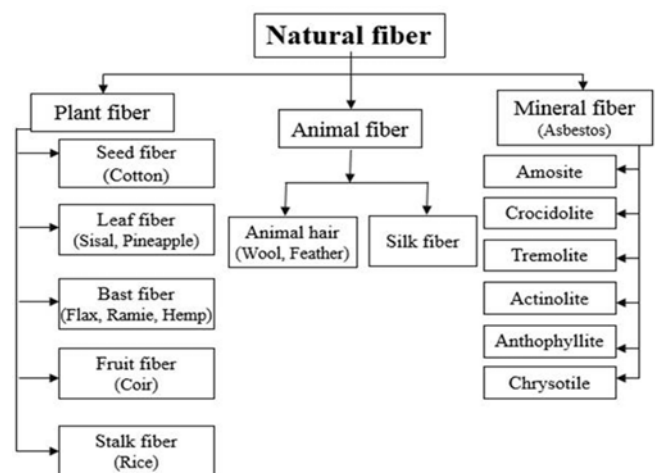


Fig. 1 Types of natural fibers based on their source of extraction^{46,47}

Table 1 List of recently reported work on natural fibers/polymer matrix composites filled with FR additives

Matrix	Natural fibers	FR additives	References
High density polyethylene	Rice husk & saw dust	Sodium meta silicate & zinc borate	23
Poly butylene succinate	Cellulose, Hemp, Flax, Sugar cane and bamboo	Ammonium polyphosphate	24
Polyvinyl chloride	wood flour	Zinc borate	25
Poly (Lactic acid)	Kenaf	Ammonium polyphosphate	26
Soy protein concentrate	Jute	Halloysite nanotubes	27
Polylactic-Acid & Polypropylene	Coconut & jute	Di-Ammonium phosphates	28
Poly butylene succinate	Flax	Phosphorous compounds	29
Polypropylene	Banana	Nano-Clays	30

Table 2 Physical and flammability properties of polymers⁴³⁻⁴⁶

Polymer	Density (g/cm ³)	Tensile strength (MPa)	Tensile modulus (GPa)	T _m (°C)	Thermal conductivity (w/m °k)	Total HR (kJ/g)	LOI (%)	Bio-Degradation
PE	0.925	15	0.8	105 - 115	0.33 - 0.51	41.6	18	x
PP	0.920	40	1.9	130	0.1 - 0.22	41.4	17	x
PAN	1.184	57	2.7	300	1.0	13.3	27	x
PC	1.2	70	2.6	157	0.19	20.3	26	x
PS	1.04	40	3	240	0.03	38.8	18	x
PMMA	1.18	47	2.2	130	0.20	24.3	17	x
PVC	1.4	51	2.4	160	0.19	11.3	45	x
PVA	1.19	40	1.7	200	0.31	21.6	20.5	x
PLA	1.2 - 1.4	50	3.5	150 - 160	1.13	14.2	21.7	
PET	1.38	55	2.7	260	0.15	15.3	21	

components in its properties. The cellulose content in natural fibers is responsible for their mechanical properties.⁵⁶ Hemicellulose plays its role in moisture absorption, bio and thermal degradation.^{56,57} Hemicellulose is also known as the flammable component of the natural fibers while lignin is the char forming component.^{28,48}

4. Flammability of Composites

Polymer matrix generally degrade rapidly when exposed to heat.⁵⁸ Fibers reinforcement may improve thermal stability of polymer composites at high temperatures. However, the natural fibers are; however more flammable as compared to synthetic fibers, hence NFRC are thermally less stable and more flammable.⁵⁹

The thermal decomposition of polymer composites under combustion is a multistage phenomenon which is explained in Fig. 3. When a composite is exposed to heat generated from fire, it starts decomposing into various volatile gases and char. Some of the volatile gases react to the atmospheric oxygen and carry out the combustion process further. The products of combustion are heat and gases including carbon monoxide, carbon dioxide and smoke. The heat released as a result of combustion supports the decomposition process further and the burning cycle works as self-sustained process. Flammability of polymer composites can be modified by interfering the combustion process at any stage. Most of the available fire retardant methods focus on the stoppage of heat flow by introducing char layers during combustion.⁶¹⁻⁶⁴

5. Effects of FR Additives on Other Properties of NFRC

As mentioned earlier, this review paper is mainly focused on the FR

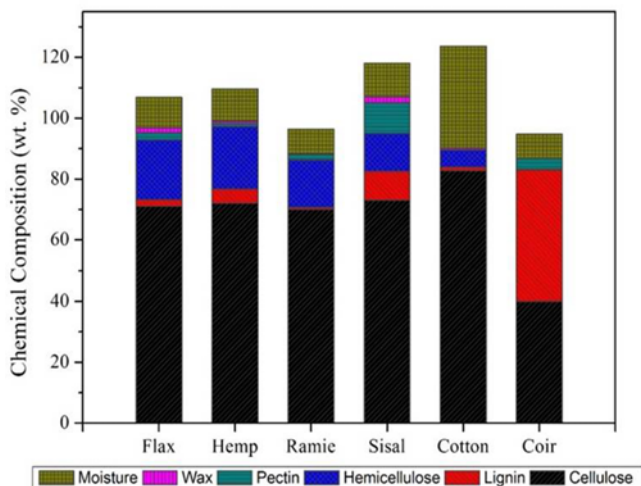


Fig. 2 Chemical compositions of plant fibers^{48,49,55,56}

Table 3 Fiber components and their properties

Components	Properties
Cellulose	Mechanical properties
Hemicellulose	Moisture absorption, Thermal stability, Biodegradation, Flammability
Lignin	Char formation

additives based fire retardant techniques. FR additives enhance the fire retardant properties of composites but it is important to know their effects on other properties. Effects of FR additives on mechanical properties, water absorption and thermal properties of NFRC have been addressed in this paper.

5.1 Effects on Mechanical Properties

If the FR additives have chemically compatibility with the matrix and natural fibers, there is strong interfacial bonding and the mechanical properties are increased. But most of the FR additives have no chemical interactions with composite constituents and act physically only. In such case, the incorporation of FR additives in NFRC may increase fire retardancy but decrease the mechanical strength of NFRC. The decrease in mechanical strength occurs due to debonding, stress concentration and agglomeration of filler powder in the composites. However, the elastic modulus is sometimes increased due to the high stiffness of the composites after FR additives incorporation.

Zhang et al. reported the effect of Ammonium polyphosphate (APP) and silica on the mechanical properties and flammability of polypropylene (PP)/wood-fiber composites.⁸ They have noticed decrease in all of the mechanical properties of PP/wood composites after fillers incorporation. However a little improvement in the tensile strength was observed at lower loadings of silica which disappeared at higher loadings. The authors reported that the decrease in mechanical properties was due to poor compatibility between FR additives and matrix. El-Sabbagh et al. utilized aluminium trihydroxide (ATH) as FR additives in Flax/PP.⁶⁵ They used three different grades of ATH which were Apyral 32, 40CD, and 60CD. Fire retardancy and thermal stability were improved but tensile strength and impact strength were decreased. However elastic modulus was observed to increase which denotes the stiffness of composite. Shumao et al. evaluated the influence of APP filler on the flammability and mechanical properties of ramie fiber/poly(lactic acid) (PLA) bio composites.⁶⁶ The APP has enhanced fire retardancy of ramie/PLA bio composites; also it didn't affect the mechanical properties at lower filler loading. However the mechanical properties of the composites were observed to decrease sharply at higher filler loadings. The decrease in the mechanical properties was caused by hindering the interaction at the polymer/filler interface due

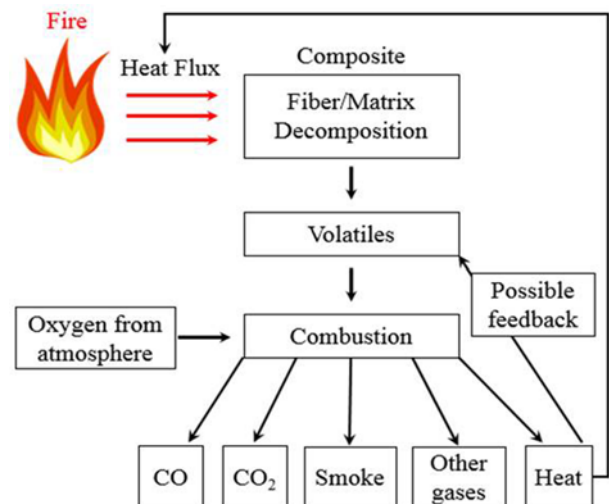


Fig. 3 Thermal decomposition of polymer composites^{54,60}

to the presence of APP. Bocz et al. evaluated the effect of multifunctional additive system on the properties of flax fibers reinforced PLA/TPS bio composites, they used APP as one of the FR additives.⁶⁷ APP decreased HRR rate of the composites to enhance the fire retardancy but it also caused decrease in the tensile and flexural strengths. Shah et al. incorporated various concentrations of oyster shell powder (OSP) as inorganic filler (FR additive) in PP.²¹ The authors reported that fire retardancy of PP has improved but its tensile strength has decreased as a result of OSP addition. The trend of increase in burning time and decrease in tensile strength is shown in Fig. 4. The decrease in tensile strength was caused by the lack of incompatibility between OSP and PP, which resulted in the poor interfacial bonding between the FR additives and matrix.

If a proper compatibilizer is used between the FR additives and matrix, the mechanical properties can sometimes be increased. Better dispersion of filler and chemical bonding between filler/matrix can also increase the mechanical properties. Enhancement of fire retardancy and mechanical properties of NFRC using FR additives is rare, however some cases have been reported in literature. Biswal et al. reported an increase in the tensile and flexural properties of the fire retardant composite made of nano-clay/banana fiber/PP.³⁰ The authors used maleic anhydride grafted polypropylene (MAPP) as a compatibilizer, which facilitated bonding between nano-clay and PP matrix. Additionally, the authors reported that the increase in mechanical properties was due to the insertion of the polymer chains inside the silicate clay layers which caused an increase in the surface area of interaction between the clay and polymer matrix. Paluvai et al. studied the properties of sisal fiber reinforced unsaturated polyester (UP) toughened epoxy nanocomposites, Cloister 30B (C30B) nano-clays were used as FR additives.⁶⁸ They observed an increase in the tensile, flexural and impact properties of Epoxy/UP after the incorporation of C30B and alkali-silane treated sisal fibers. The mechanical properties were reported to improve due to the exfoliation of clays within the Epoxy/UP system and chemical bonding between alkali-silane treated sisal fiber and epoxy/UP system.

5.2 Effects on Water Absorption

Natural fibers are generally hydrophilic; the water absorption capability of NFRC increases more after FR additives incorporation. Due to random shapes of the filler particles and their poor interfacial

bonding with the matrix and natural fiber, there are some micro-gaps and cracks at the interfaces. These flaws are responsible for water absorption. Effect of FR additives on water absorption property of NFRC is reported in literature.

Chindaprasirt et al. analyzed the effects of diammonium phosphate (DAP) on the properties of wood flour/expanded polystyrene waste composites.⁶⁹ The DAP modification improved fire retardancy of the composite, but it also increased its water absorption. The authors described that water absorption was caused by hydrogen bonding between water molecules and free OH groups presented in the DAP structure, also the possible diffusion of water molecules into the composites. Suharty et al. studied the properties of calcium carbonate and DAP filled PP/kenaf composites.⁷⁰ They also observed an increase in the water absorption of the PP/kenaf composites as a result of FR additives incorporation. According to the authors calcium carbonate also absorbs water which causes the composite to gain weight as a result of water absorption.

The water resistance of the FR additives filled nanocomposites can be improved if certain measures are taken. Ayrlimis et al. reported the water absorption properties of wood/PP composites filled with boron and phosphate compounds as FR additives.³³ They have used MAPP as a coupling agent in the composites. The water absorption properties were evaluated with and without MAPP. The authors observed that FR additives addition without MAPP caused a decrease in the water resistance of composites, but water resistance was increased after MAPP coupling. The coupling agents improve the interfaces by filling the internal flaws and cracks in the composites to stop water distribution inside. Alhuthali et al. studied the water absorption of nano-clay filled cellulose fiber/vinyl-ester nanocomposites.⁷¹ They observed reduction in the uptake of water by the composites after nano-clay addition. The high aspect ratio of nano-clay platelets caused this behavior in the water molecules path.

5.3 Effects on Thermal Stability

The FR additives generally produce char residue at high temperatures and combustion. The char layer acts as a heat resistant medium on the composite surfaces. Also, the FR additives have high melting points as compared to matrix polymers; they enhance the crystallization temperature and melting points of polymers. The decomposition temperature of the cellulosic fibers is very low; the fibers are protected by the char layer during combustion. In literature, the thermal stability of composites has been reported to improve with FR additives incorporation.

Jeencham et al. studied the effect of APP, magnesium hydroxide and ZB on the properties of sisal fiber/PP composites.²⁰ PP is originally a low melting point and easily degradable polymer, which loses 100% weight around 500°C. Also the sisal fiber decomposes at lower temperature as compared to PP. However the FR additives used by the authors produced char residues to enhance thermal stability of the sisal/PP composites. The char residue acted as thermal barrier to protect the composite at high temperatures. Nie et al. investigated flammability and thermal behavior of poly(butylene succinate)/bamboo fiber (PBS/BF) biocomposites with microencapsulated ammonium polyphosphate (MCAPP) as a FR additive.⁷² They observed that initially BF reinforcement into PBS decreased the thermal stability of PBS, but

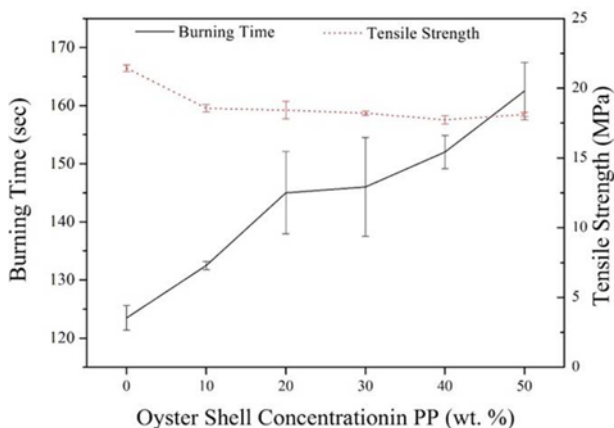


Fig. 4 Effects of OSP on flammability and tensile properties of PP²¹

MCAPP incorporation controlled the thermal degradation of PBS/BF composites. MCAPP produces more char residue at high temperatures which makes the composites thermally stable as compared to non MCAPP composites. Nikolaeva et al. evaluated the effect of melamine, ZB, APP, ATH, natural flake graphite and expandable graphite on the reaction-to-fire properties of wood/PP composites.⁷³ The authors calculated the mass loss rates of the composite specimen at high temperatures. They found that the wood/PP composites with FR additives have higher char residues than the standard wood/PP specimen without FR additives. The mass loss rate of flame retardant based wood/PP composites was lower than the non-flame retardant based wood/PP composite. They found that wood/PP composite filled with combined APP and expandable graphite has highest thermal stability. Pan et al. studied the synergistic effect of APP and nano silicon dioxide on flammability of wood fiber/polyethylene composites.⁷⁴ The authors also conducted thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) to calculate the weight loss of composites at high temperatures. They observed that the addition of APP and nano-SiO₂ has decreased the thermal degradation of composite. Both the FR additives produced char residue and increased thermal stability. Kovacevic et al. studied the influence of montmorillonite nanoclay on the properties of Spartium junceum L. short fibers reinforced PLA bio composites.⁷⁵ The authors observed higher thermal stability of nanoclay treated bio composites as compared to non-treated composites and pure PLA. Nanoclay acted as charring agent to reduce the weight loss rate at higher temperatures. Shah et al. reported properties of OSP filled PP composites.²¹ OSP was used as FR additive in the composites but it also increased thermal

stability of the matrix. Pure PP has a very low thermal stability which is reported to increase prominently after OSP incorporation. The TGA thermograms of OSP/PP composites in air (as medium) are shown in Fig. 5. The results suggest that PP degraded in a single step while OSP/PP composites degradation took place in two steps.

6. Types of Flame Retardant (FR) Additives

FR additives imparts flame retardant characteristic to materials such as coatings, thermoplastics, thermosets, rubbers and textiles. These FR additives may prevent, minimize, suppress or stop the combustion process of materials. They act to break the self-sustaining polymer combustion cycle and consequently reduce the burning rate or extinguish the flame in several ways. According to a 2012 market study of Townsend,⁷⁶ the consumption of FR retardant has grown substantially in the past 4 years as shown in Figs. 6 and 7.

6.1 Halogenated FR Additives

These FR additives are specially used for making consumer articles which are important part of our daily life. They are very effective in capturing the free radicals and easy release of halogen atom which depends on the ratio and bond energy of halogen and carbon, hence it can efficiently reduce or prevent the propagation of fire.⁷⁷ The halogenated FR additives mainly works on the principle of gas phase mechanism for the extinguishing of the fire. In atmosphere, these FR additives reduce flammability because its free radicals bond with atmospheric oxygen and hydrogen, as a result decrease both oxygen and fuel concentration in the air. Due to the bond energy, aromatic halogen FR additives are less effective than aliphatic and alicyclic. Among halogens, fluorine and iodine can't be use as a FR additives because of high electronegativity and large size molecule respectively.

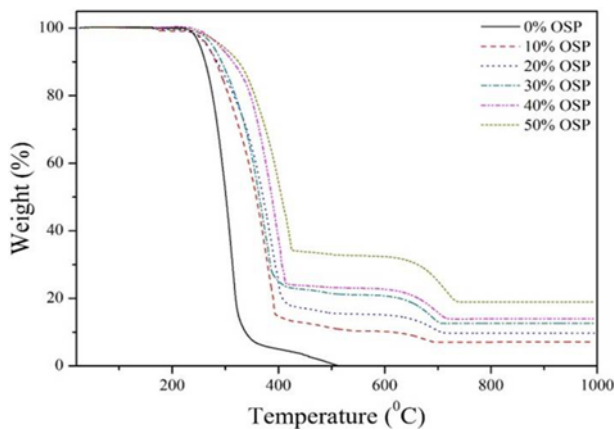


Fig. 5 TGA thermograms of OSP/PP composites²¹

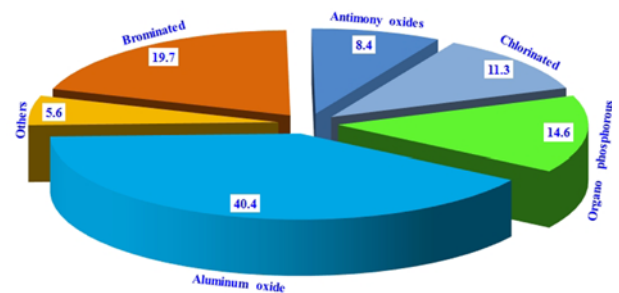


Fig. 6 Global consumption of FRs in plastics by type, Tonnes-2011⁷⁶

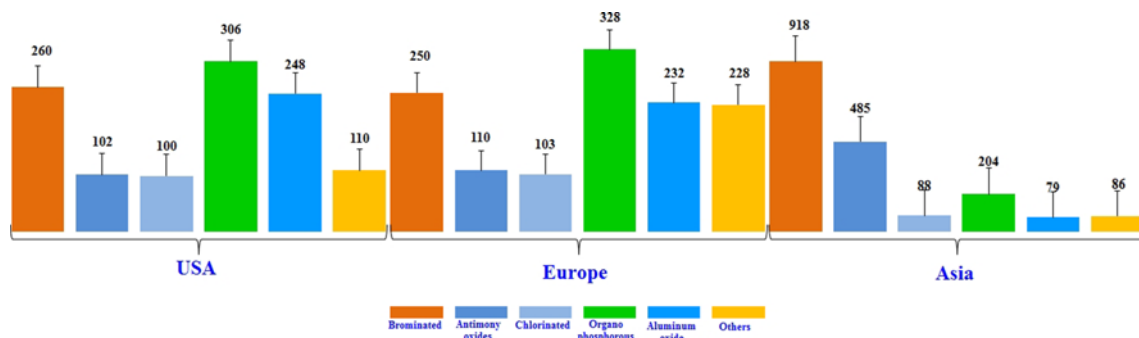
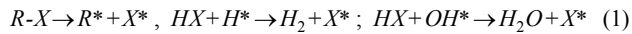


Fig. 7 Sales of FRs by region (Million \$US, with a total of 4.2 billion \$US)⁷⁶

However, chlorine and bromine are more effective FR additives, but bromine easily forms free radicles at higher temperatures than chlorine. Reaction mechanism of halogenated FRs on decomposition is shown in Eq. (1).



Reaction mechanism of halogenated FRs ($R-X = FR$; $X^* = Cl, Br$)

6.1.1 Bromine FR Additives

Because of low cost and high performance efficacy, bromine FR additives are generally used as additives in manufacturing commercial and domestic products such as construction materials, electronic equipments and upholstery for protecting the property damage and injury. These FR additives have lower decomposing temperature which is sufficient to get effective results and their flame retardancy appliance is alike for all compounds.⁷⁸⁻⁸⁰

(1) Examples: The main brominated FR additives are brominated bisphenols, diphenyl ethers, cyclododecane, phenols, and phthalic acids derivatives.

6.1.2 Chlorine FR Additives

The chlorinated FRs are being commonly used as additive for polyalkene compounds. Higher amounts are required for efficient working, because these have lower stability and partial plasticizing at higher temperatures than brominated FR additives. The mixture of metal chloride can further enhance the flame retardancy nature as compared to chloride FR additives.⁸¹⁻⁸²

(1) Examples: There are two main classifications of chlorinated fire retardants include Chlorinated paraffins, and chlorinated alkyl phosphate.

(2) Mechanism: The mechanism of resisting the fire propagation mainly depends on the liberation of hydrochloric compounds in a gaseous phase; further this HCl decomposes and release chlorine free radicals, also with these radicals propagating the oxidation of the volatile products during thermal degradation of the polymers.

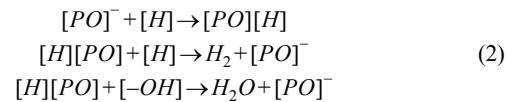
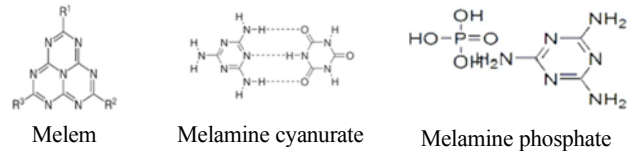
6.2 Phosphorous FR Additives

Due to the ecological concerns, phosphorous FR additives are used as halogen free FR additives which have similar flame retardant mechanism as that of halogenated FR additives.⁸³⁻⁸⁷ They act in the condensed phase (char former and char enhancers) while metal phosphates may also act in the gas phase. The importance of these FR additives is high effective mode of action on fire with low concentration amounts. They completely rest on the matrix structure and very active with the polymer which contains rich oxygen in their structure.

(1) Examples: The famous phosphorus containing FR additives are phosphate esters, phosphonates and phosphinates. Examples are Tributyl phosphate, Triphenyl phosphate, Tri phenyl phosphine oxide, Tris-(2-chloroethyl) phosphate, Tri (chloropropyl) phosphate, Resorcinol-bis(disphenyl phosphate), Red phosphorous, Ammonium polyphosphate, Melamine phosphate.

(2) Mechanism: Phosphorous FR additives are works efficiently in the solid phase of polymeric materials. First these phosphoric FR additives are converted into their relative acids and then to polyacids by the process of thermal decomposition. Acids esterify and dehydrate the

pyrolysing polymer to form un-satured compounds with char. Poly phosphoric acids inhibit further pyrolysis process to form carbonaceous layer, this will protect the polymer materials from oxygen and radiant heat in high temperatures. General reactive flame retardant mechanism of phosphorus additives is as shown in Eqs. (2) and (3).

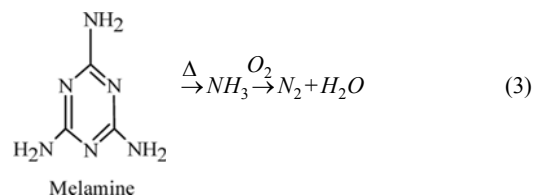


6.3 Nitrogen FR Additives

Ecologically, nitrogen FR additives are very safer and effective because of their low toxicity, low evaluation of smoke with fire and suitable for easy recyclability. They are stable compounds even at elevated temperatures; therefore, they can inhibit the decomposition of the materials at higher temperature. Nitrogen itself has very limited flame retardancy, compare to nitrogen FR additives efficiency, nitrogen containing additives (nitrogen-phosphorous) have superior flame retardancy efficiency because of synergistic action. Moreover, they liberate hydrogen cyanide on combustion, it has lower tendency to corrosion, due to liberation of hydrogen cyanide at combustion which is weak acid and has less tendency to corrosion, and therefore they are well suitable for manufacturing of electrical installation materials.⁸⁸⁻⁹¹

(1) Examples: The major nitrogen FR additives include melamine and melamine compounds such as melamine cyanurate, melamine polyphosphate, melamine poly (zinc/ammonium) phosphate, Melamine based hindered amine light stabilizer, melem, melon. Melamine cyanurate (structures as shown in the text) is also used in olefin intumescent compounds in conjunction with ammonium polyphosphate. The combination of both nitrogen and phosphate compounds i.e., pyrophosphates of melamine is used in amides. Urea, isocyanurates, triazines, guanidine and cyanuric acid derivatives are used as reactive compounds.

(2) Mechanism: Nitrogen FR additives are works on several mechanisms; among them gaseous and condensed phase mechanisms are important. In gases phase, may resist the fire propagation by releasing the stable nitrogen based molecules, and in the case of condensed phase, forming the complex nitrogen compounds, which are capable of producing char to protect the decomposition of polymer materials under fire. These materials can release the nitrogen mixed gases, which weak the vapor phase and thus suppressed the combustion process. The reaction mechanism of melamine as demonstrated in the Eq. (3).



6.4 Silicon FR Additives

Various forms of silicon compounds have been explored as potential flame retardants to polymeric materials, such as silicones, silica, organosilanes, silsesquioxane, and silicates.

6.4.1 Silicones

Silicones and silicon co-additives have been considering as useful eco-friendly FR additives for a long time. Lower amounts are sufficient for effective performance, because these compounds dilute more organic materials and make barrier on the surface of the materials to an evolving flame. Due to their lower surface energy property, they can move on the surface of the material during degradation and enhance the flame retardancy. These can also improve the mechanical properties especially impact resistance dramatically.

6.4.2 Silica

Silica is a combination of silicon and inorganic materials, which is generally used as filler in general, but some particular situations it also used as a FR additive as well. It has been also using as to various commodity polymers. The chemical reaction of silica and organic alcohols with catalyst, result in multi co-ordinate organo siliconate compounds, which form protective char layer on the polymer surface on combustion.^{92,93}

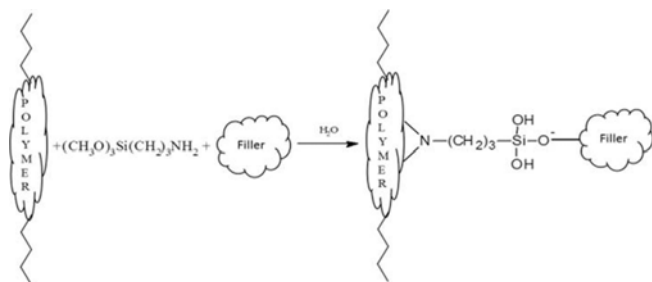
6.4.3 Silanes

Silanes are the compounds of silicon atom bound to reactive functional groups (rarely carbon atom) with different chemical structure. Poly silanes, Poly carbosilanes, Poly silazanes are some of the important silane compounds. Silanes act as coupling agents (scheme 1); they can bind the fillers and polymer matrix very easily with little energy by simple synthetic rote, moreover a great contribution to forming a compact and dense char layer during combustion and also improves the physical and dynamic properties.^{94,95} Schematic representation of silane coupling agent bonded with filler and polymer matrix shown in Scheme 1.

(1) Examples: Tetraethoxy silane, diglycidylether terminated poly dimethyl siloxane, dimethyldichlorosilane, methyltriethoxysilane, methyltriacetoxysilane, Polyhedral Silsesquioxanes, etc.

6.4.4 Silicates

Silicates are compounds containing anionic silicon as oxides (clay), which can improve the flame retardancy and physical properties of polymers. These are inexpensive, environmentally benign nano filler



Scheme 1 Schematic representation of silane coupling agent bonded with filler and polymer

materials with unique mechanical properties. Lower amounts of silicates incorporation make a gas barrier over polymer matrix which decreases flammability significantly. They mostly manage to rise the thermo-oxidative stability by reducing the permeation of oxygen. The main mechanism of flame retardancy of these FR additives was the mechanical improvement of char, in addition with the presence of silicates improve the viscosity of the polymers which lead to decreasing the dripping nature, hence reducing the flammability.⁹⁶⁻⁹⁸

(1) Examples: Ammonium silicon tetra polyphosphate ($\text{Si}(\text{NH}_4)_2\text{P}_4\text{O}_{13}$), Silicon oxomonophosphate ($\text{Si}_5\text{O}(\text{PO}_4)_6$), Talc ($3\text{MgO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$), Montmorillonite (phyllosilicate).

(2) Mechanism: Silicon FR additives work on both condensed phase and vapour phase mechanism. In condensed phase, thermally stable silica has the ability to move to char surface at high temperature and stop the degradation process, dilution of organic gases and caching of active radicals in the flame zone, and make barrier to heat and mass transfer in the vapour phase. The fire-retardant behaviour of these alone have not much efficient, but with other FR additives the fire-retardancy enhances to higher.

6.5 Carbon FR Additives

6.5.1 Carbon Nanotubes

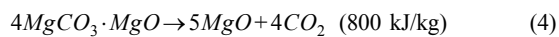
Carbon nanotubes are cylindrical nano topological structure compounds of carbon allotropes, they consist of single, double and multi-walled graphite sheets, which have good mechanical, thermal, electrical and flame retardant properties and also with polymer matrix as additive. However, the cost of carbon nanotubes quite high, compare to carbon fibers/fabric or fillers, but they have a special ability of flame retardancy in relatively lower concentration. Additionally, they enhance the material mechanical properties of materials and are more effective than nano-clays. Moreover, these can reduce the polymer matrix decomposition rate due to the trapping of free-radicals, hence increasing its thermal stability. The practical unique advantage of carbon nano tubes with hydrocarbon polymers compare to hydrophilic additives is their organophilic nature, they can be dispersed directly in to the polymer matrix without any organic treatment and compatibilizer.⁹⁹⁻¹⁰³

6.5.2 Hydroxycarbonates

Hydroxy carbonate FR additives are alternative to metal hydroxides flame retardants and which are relatively low cost and environmentally compatible. These produce non-toxic products such as H_2O and CO_2 on combustion through an endothermic reaction followed by release of water in gas phase so that flame suppress and releases 20 times lesser amount of smoke compare to halogenated FR additives. These works both gas phase and condense phase. They also act as oxidizing agent for carbon containing compounds and decomposes, this can contribute the formation of an insulative protection chard layer to the matrix polymer. The commonly used hydroxy carbonate FR additives are Magnesium carbonates (Natural (magnesite) and synthetic (hydro magnesite)) and Calcium carbonates. The combination with other FR additives especially clay nano particles, can observe the improvement in the flame retardancy as well as better mechanical properties.¹⁰⁴⁻¹⁰⁶

(1) Mechanism: The flame retardancy and thermal stability strongly depend on the type of carbon nanotubes, polymer matrix and dispersion

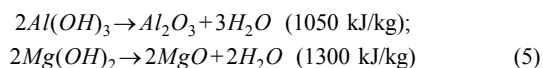
of nanotubes in the polymer matrix. Carbon nano tubes form three dimensional crosslink network structures and also increase the melt viscosity of the polymer matrix in combustion process through condensed phase mechanism. This network structure protects the polymer matrix as protective barrier and reduces the propagation of flame. The nano tubes also do not show effective flame retardant properties with polymer; however, combined with other flame retardant additives showing synergistic effect to make significant amount of char layer over the matrix, enhancing the thermal stability and flame retardancy of the polymer. Reaction mechanism of aluminium trihydroxide on decomposition is shown in Eq. (4).



6.6 Metallic Oxides and Hydroxides

Metals react with oxygen in the air to form Metallic oxides. These FR additives have proven that; they are efficient additives for improving the thermal stability and morphological structure of char residues and the FR of the polymers because of not only strong interactions between polymer and nano-particle surface and also the degradation temperature of these particles are higher than the polymer processing temperature.¹⁰⁷⁻¹¹⁰ Reaction mechanism of aluminium trihydroxide on decomposition is shown in Eq. (5). Examples are magnesium oxide (MgO), zinc oxide (ZnO), and ferric oxide (Fe₂O₃), Titanium oxide (TiO₂).

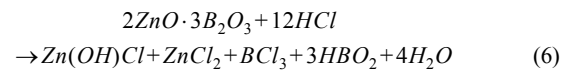
Metal hydroxides are nothing but mineral FR additives with combination of hydroxides and carbonates. They are commonly used for low smoking FR additives, because of low cost and abundant availability in nature. These flame retardants work through endothermic reaction and gives water in the form of vapour (one third of total metal hydroxide) and fire protection inorganic residue, these metal oxides absorbs heat and resist the oxygen which can reduce the propagation of flame. These are generally not used as synergists, but rarely mixed with to other flame retardants for beneficial effect on the polymer flammability.¹¹¹⁻¹¹³ Examples are aluminium tri-hydroxide (Al(OH)₃), Magnesium di-hydroxide (Mg(OH)₂), Antimony trioxide (Sb₂O₃), Expandable graphite, etc.



6.7 Borate FR Additives

These are one of the commercial inorganic family additives, environmentally friendly, low mammalian toxicity and low volatility fillers. These additives mainly using as a synergist for halogenated, phosphorus and mineral fillers because of their poor charring performance if used alone. In combustion process, these decompose via endothermic reaction and give fire suppress products i.e., crystal water, boric acid and boron oxide (endothermic decomposition (503 KJ/Kg) between 290 and 450°C), which leads to the formation of glassy shield layer, which blocks the fire propagation and stops the polymer chain oxidation.¹¹⁴⁻¹¹⁷ Reaction mechanism of zinc borate on decomposition is shown in Eq. (6). Examples of most frequently and commercially used borates include zinc borate (2ZnO. 3B₂O₃. 3.5H₂O), ammonium

pentaborate (NH₄B₅O₈.4H₂O), melamine borate (C₃H₉N₆O₃B), barium metaborate.



6.8 Nano-Clays

Nano-clays are abundantly available naturally occurring eco-friendly inorganic material consisting of fine grained minerals (phyllosilicates) such as rocks, sediments and soils. These nano clays have higher thermal stability; hence it's reduces the heat release rate and increase the smoke and CO yields. In combustion, nano-clays migrate to the surface of the polymer matrix and to form a dense silicate layer, which resist against the fire as protective layer that slow down the polymer composite for further degradation. Moreover these materials have the ability to form carbonaceous layer during combustion which will resist the permeability of oxygen but it does not stop the flame. Nano clays decreases the polymer viscosity at high temperature, which prevents the dripping of melt polymer composite and promotes char forming. Nano clays also act more efficiently as flame retardants if they are combined with other FR additives. These sometimes also increase the mechanical properties, scratch resistance, glass transition temperature and stiffness of the polymer composites.¹¹⁸⁻¹²¹

6.9 Natural FR Additives

6.9.1 Chitosan (CS)

Chitosan is a natural and abundantly available renewable biodegradable polymer obtained from the fully or partially deacetylated form of chitin, which is extracted from exoskeleton of living organism such as fungi (cell walls), crustaceans (shrimps and crabs) and cuticles of insects; moreover, it is a non-toxic, highly biocompatible organic polymer. Chitosan chemically [β -(1,4)-2-amino-2-deoxy-D-glucopyranose] is an amino polysaccharide with multy hydroxyl groups and potential to be used in carbonization. Hence, chitosan has the capacity to promote the formation of char during combustion. Due to this unique property of chitosan, it is being used as a natural FR additive to polymer matrix and intumescent flame retardant in polymer composites. In combustion chitosan, can produce char layer on the surface of the polymer materials which acts as heat insulator or thermal shield to suppress the fire propagation.¹²²⁻¹²⁴

6.9.2 Oyster Shell Powder (OSP)

Oyster shell is renewable and naturally available (abundance on seashores of many countries), nontoxic, not accumulated in the environment and biodegradable mineral filler which mainly consist of calcium carbonate (about 96% of about 96%, as crystals of calcite and aragonite (pH 9.8)). Oyster shell thermally stable around 800°C, above which it decomposes to give CaO and CO₂, the produced inert gas carbon dioxide has the ability to put off fire by stopping the entry of oxygen and the fire-retardant mechanism is environmental friendly, it totally depended on carbon dioxide. Oyster shell powder is being used as FR additive to the plastic materials and polymer based composites for environment friendly fire retardant plastics. Moreover, oyster shell powder reinforcement improves stiffness, flexural properties and dielectric properties of plastics.²¹

6.9.3 Egg Shell

One among the renewable biological and calcium rich materials is egg shell, produced as waste by-product of food industry, poultry industry, and domestic household and could be found littering dustbins in our big cities, and farm yards in villages. According to the survey, the statistical data in 2013, China is the rank one for producing the egg it is nearly 484.6 billion. The exclusive chemical composition of egg shell is 96 wt% calcium and magnesium carbonate in the form of calcite and 4 wt% X collagen, sulfated polysaccharides and other proteins (high levels of Gly and Arg). On the application of heat this calcium carbonate present in the egg shell decomposes into CaO and CO₂, carbon dioxide does not support combustion because it is good fire extinguisher. The more quantity of egg shell additive is incorporated into the polymer matrix, the more quantity of CaCO₃ in the composite and less tendency of the composite to burn. The considerable amount of availability with unique composition and structure makes egg shell a potential source and it is efficiently useful as bio-filler reinforcement material as well as FR additive for polymer nanocomposites.¹²⁵⁻¹²⁷

6.9.4 Lignin

Lignin is from plant constituent around 20 - 30 by wt%, chemically polyphenolic and structurally amorphous. Its degradation temperature is around 450°C in nitrogen environment and leave stable dense crosslinked char, increases with increasing temperature up to 900°C. It is well known that the ability to form char during the thermal degradation is a basic aspect of flame retardant additives since the char reduces the combustion rate of polymeric materials because it does not allow the oxygen to reach the combustion zone easily. Hence, lignin can also be incorporated in polymeric materials to improve the thermal properties because its cross-linked structure with phenolic groups is capable of generating the high char yield after decomposition.^{128,129} Moreover, improvements in thermal properties and flame retardant properties of lignin based composites can be strengthened by chemically modifying lignin with phosphorus and nitrogen elements.¹³⁰

6.9.5 Bio Char

The name biochar describes any charcoal that is composed from biomass. It is a renewable, microporous, carbon-rich product which also contains nitrogen, hydrogen, oxygen and ash. It is a carbon rich by-product that is produced when organic waste treating by thermo-chemical process then at high temperatures through pyrolysis. Even it is carbonaceous material, holds the physical shape and form honeycomb structure which also has various functional groups on its exterior surface. Because of these characteristics, current polymer industries and academic institutions are showing interest for its vital part in many purification systems due to ability of pollutant corrective assistant and as a sustainable means for carbon detachment.

The exception properties of bio char contain uniform composition, high porosity, anti-bacterial and anti-fungal, breathability, thermal regulation, and odour control and odour control control and absorption. During heating process, the constituents of Biochar suppress the reactive compounds and decrease the weight loss of the composites. The thermal stability of the biochar filled composite is observed to be enhanced in the literature, found out from thermogravimetric and differential scanning calorimetric analysis.¹³¹

6.9.6 Human Hair

The main portion of hair is protein keratin about 91% with mostly alpha-helix structure contains long chain of amino acid molecules by peptide (-CO-NH-) bond. Amino acid present in hair contain cytosine, serine, glutamine, threonine, glycine, leucine, valine, and arginine. The average composition of normal hair is composite of 45.68% carbon, 27.9 oxygen, 6.6% hydrogen, 15.72% nitrogen and 5.03% sulphur. This is easily, economically, abundantly available and collectable than any other bio material, and easy to transport and store. It has been used as indicators of human exposure to heavy metals and drugs for years. In addition, a few studies have explored the use of hair for assessing human exposure to persistent organic pollutants, especially to flame retardants, because of the structure contains nitrogen and hydroxyl groups which might be responsible.¹³² Chai et al. are over and done with the thermal properties of human hair and tried to wind up the flammability of bio-derived composite materials with human hair as the fiber.¹³³

6.9.7 Deoxyribonucleic Acid (DNA)

DNA is a structurally very complex natural bio polymer (two polymer strands, bound together in a helical fashion by non-covalent bonds) consisting of millions of repeating units/monomers of nucleotide units called polynucleotide, which is responsible for carrying genetic information (development, functioning and reproduction) in all living organism and viruses. The nucleotide monomer consists of either cytosine, guanine, adenine or thymine along with monosaccharide (deoxyribose) and phosphate group through covalent bond between deoxyribose and phosphate backbone.¹³⁴ On the other hand, DNA is a capable of intumescent flame retardant, because of the monomers containing large amount of the elements like nitrogen, phosphorus and carbon. Moreover it consist of acid source (ammonium phosphate give phosphoric acid), carbon source (polysaccharide has multiple hydroxy compounds gives char) and blowing agent (guanidine, melamine give nitrogen gas) like intumescent flame retardant system. When DNA is subjected to heat, it releases inert gases such as water vapour, ammonia or carbon dioxide and carbonaceous char layer which is act as protection layer from heat (flame), fuel (polymer), and oxygen. Because of this unique nature of DNA, many researchers are using it as a FR additive to polymer matrix in polymer composites area for enhancing the thermal stability and flame retardancy of the polymers.¹³⁵⁻¹³⁹

7. Influence of Surface Treatments on Flammability

The surface treatments apart from influencing mechanical properties of the fiber, also has an impact on the thermal properties too. During the process of the surface treatment, maximum percentages of amorphous contents like hemicellulose, pectin, lignin and waxes from the fabric are washed away eventually resulting in enhancement of crystallinity in the fiber. The randomly aligned linkages in the fiber before, tends to exhibit in an organized form resulting in the amplification of surface area of the fabric. Due to this reason, wettability and the bond ability between the fabric and the resin is improved making the composite thermally stable in comparison with untreated natural fiber composites.¹⁴⁰

8. Mechanism of Flame Retardancy

The mechanism of flame retardancy of FR additives mainly follows one of the following five routes to suppress/reduce the flammability of the polymer matrix composites, such as physical dilution, chemical interaction, inert gas dilution, thermal quenching and protective (char-formation) coatings.

8.1 Physical Dilution

In the mechanism, the FR additives itself acts physically as inert compounds and it has thermal capacity against flame, so that these have the ability to reduce the fuel content to a level below the lower limit of flammability. Moreover, in physical dilution mechanism, the flame is suppressed by cooling, barrier formation, changing the heat capacity, thermal conductivity and viscosity. Chemical mechanisms are always accompanied by one or several physical mechanisms such as endothermic dissociation dilution of fuel. Nano clays, glass filler compounds function in this way when used as FR additives.

8.2 Chemical Interaction

This is radical mechanism, in which FR additives or their by-products interferes and catch the free radicals which are produced by decomposing polymers through combustion. The free radicals are seized so that the system cools down and resist/reduce the flammability. Halogenated (brominated) FR additives usually act by this mechanism. The free radicals i.e., OH^* and H^* formed from polymers react with halogen free radicals in gases phase so that the flame inhibition occurs.

8.3 Inert Gas

In this mechanism, FR additives in this mechanism, vaporize and evolve large quantities of non-flammable gases/inert gases such as nitrogen, ammonia, carbon di-oxide) into the gas phase or by condensation reaction. These inert gases contaminate the oxygen which is nearer to the combustion source, so that it dilutes the flammable fuel concentration. Metal hydroxides, metal carbonates and some nitrogen producing compounds function in this way.

8.4 Thermal Quenching

The FR additives in this mechanism release crystal water molecules on combustion (high temperatures) through endothermic chemical reaction. It thermally quenches (sudden cooling) the materials (polymer matrix) and dilute the combustion process. Halogen free FR additives, metal hydroxides and carbonates usually act by this mechanism.

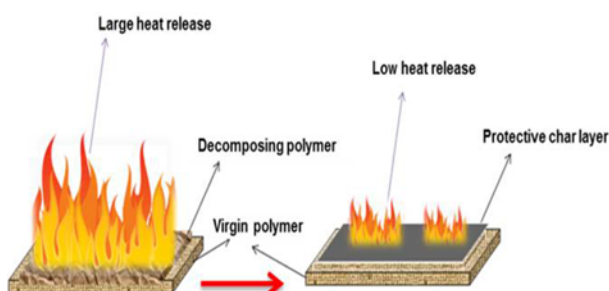


Fig. 8 Charring mechanism in polymers

8.5 Char-Formation

The FR additives in this mechanism form carbonaceous char layer on polymer matrix, which can inhibit the oxidation of carbon atoms in the polymer, so that it is protected from the further action of flame. Carbonaceous char layer also reduced mass volatiles, increase thermal insulation, obstructs the flammable gases and increases the thermal capacity. Halogen free FR additives such as phosphorus, nitrogen etc., usually act by this mechanism. Schematic representation of char forming mechanism is as shown in Fig. 8.

9. Summary

In this review, we have presented a broad range of flammability of natural fiber reinforced polymer composites and flame retardant additive systems. Flammability of natural fiber reinforced polymer composites remains a very complex scientific problem for which no single solution can be found, especially with regard to the extensive diversification of polymer matrices available. The selection of suitable FR additives supports to create flame resistant composites, and prolongs the variety of their uses. The use of relatively low amounts of additives with polymers shows very promising results. Among non-halogenated FR additives, phosphorus and nitrogen-based compounds have proved to be very effective solutions, especially in matrices containing oxygen or nitrogen atoms in their backbone, while silicon-based additives also appear to provide efficient solutions. However, the improvement of flame retardancy in natural flame reinforced composite materials is being a great task, but the effective selection and addition of most appropriate FR additives will hopefully contribute to producing flame resistant natural fiber reinforced polymer composites.

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