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Flammability and Fire Retardancy of Composites

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ABSTRACT

Abstract: The low thermal resistance of composite materials poses a major hindrance in using them for various applications. These limitations are subdued by flame and fire retardants, which when added into polymers and composites provides an enhanced thermal and flame resistance. In this review, the various methods of improving the fire retardancy of composite materials are discussed along with a description of widely used flame retardant additives. The recent progress in the field of flammability and flame retardancy of composite materials is the main focus of this article and considered only recently published works. Additionally, the mechanism of combustion with an emphasis on the flammability of polymer composites is deliberated. The basic idea of improving the fire retardancy of composite is either by enhancing the composite constituents - reinforcement and matrix or by providing a coating to the composite. The flame retardancy mechanism and the methods to improve them are the hot topics for research as the light weight polymer composites are replacing metallic structures. Treatment of reinforcement, matrix, along with the various commonly used flame retardant additives are studied in this article. The circularity, sustainability, and environmentally friendly aspects of composites need to be taken care while considering waste management in the near future.

Keywords: Flammability; Fire retardant; Composites

1. Introduction

The immense growth of the composite market in recent times poses a greater challenge to existing traditional materials. The cost reduction aspect coupled with improved quality and structural performance along with deeper research on emerging composite classes supports the use of composite materials. The concept of using flame retardant material for the first time dates back to 484 BC by the Egyptians. They reduced the flammability of wood and cotton by using Potassium aluminium sulphate. In the year BC 86, the siege of Piraeus used alum with vinegar for improving the combustibility of wooden battleships. The first flame retardant material was patented by O. Wyld in 1735 (Weil & Levchik, 2008). The major disadvantage claimed of using composites is their low resistance to increasing temperatures. Though the invention of fire is regarded as the greatest achievement in human history it also poses danger and mishaps when handled carelessly. In terms of fire-related deaths in the world, India tops the list with 12,474 cases followed by the USA with 3655 deaths (*The CTIF Fire Statistics Issue No 25*, n.d., p. 25). Selecting suitable material for the fabrication of systems plays an important role in reducing such incidents and deaths. One such example is the use of flame retardant composites in almost every field of engineering such as construction, military applications, aerospace, ocean structures, communication, etc. owing to their high specific strength and modulus, good design flexibility, desirable thermal expansion characteristics, facile fabrication, good resistance to fatigue and corrosion and economic efficiency (Kumar et al., 2019; Vijay Kumar et al., 2019). For customization to meet specific applications, the alteration of fiber reinforcement and the matrix is usually done (Gomez et al., 2021). Most of the polymeric materials are chemically made up of hydrocarbon materials which when exposed to fire burn rapidly releasing heat and other by-products. This poses a serious threat in using polymeric materials for fire retardant applications.

A non-government organization named the Aircraft Crashes Record Office based in Geneva investigates the number of aircraft accidents occurring around the globe and as per their official records there were 1637 aircraft accidents between 2010-2021 and a total of 9000 fatalities were reported (*Home | Bureau of Aircraft Accidents Archives*, n.d., Accessed on 15th October 2021). It was further found by analyzing that the material used for aircraft has a direct impact on the incident and improving the fire retardancy of composites used for aircraft could have further helped in reducing the severity. The use of composites without providing any fire retardancy in such applications poses a serious threat. Various countries are now concerned about providing fire retardancy to composites thereby improving safety. The conventional metallic wires can be replaced with high-performance composite wires in future electrical applications (Tran et al., 2020).

Composites with metals like Cu/Composite have good electrical, mechanical, and thermal performance compared to pure Cu (Ali et al., 2021). They need to be safe for use and stable at elevated temperatures and hence require flame retardant properties. Figure 1 shows the trend in the publication that happened from the year 2000 to 2021 on the subject of flame retardants and flame retardant composite. The curve shows an exponential growth in publication trends indicating the importance of the area.

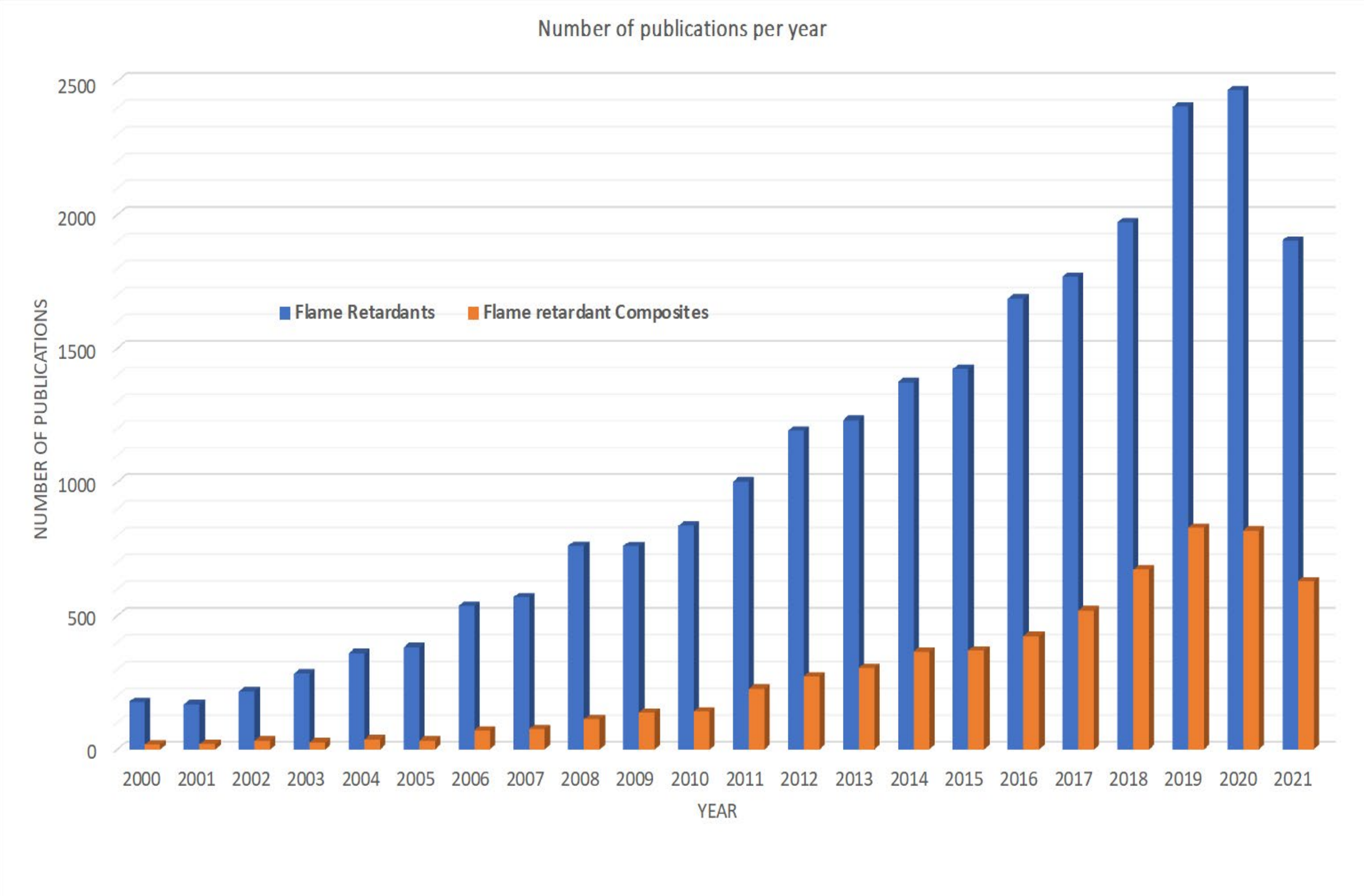

Figure 1: The trend showing the number of publications per year in the field of "Flame retardants" and "Flame retardant composite" – results obtained from the web of science, Accessed on 15th October 2021.

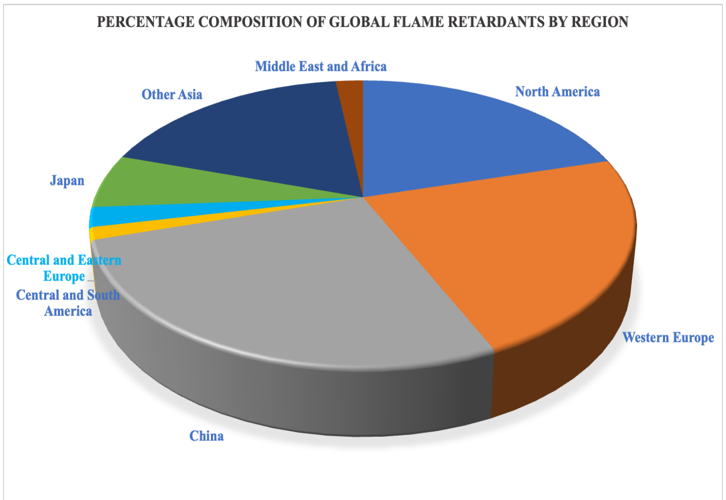

Figure 2: Percentage composition of global FR consumption by region in 2020. Data from I.H.S. Markit. Flame Retardants—Specialty Chemicals Update Program (SCUP), IHS Markit, (https:/ihsmarkit.com/products/chemical-flame-retardants-scup.html)

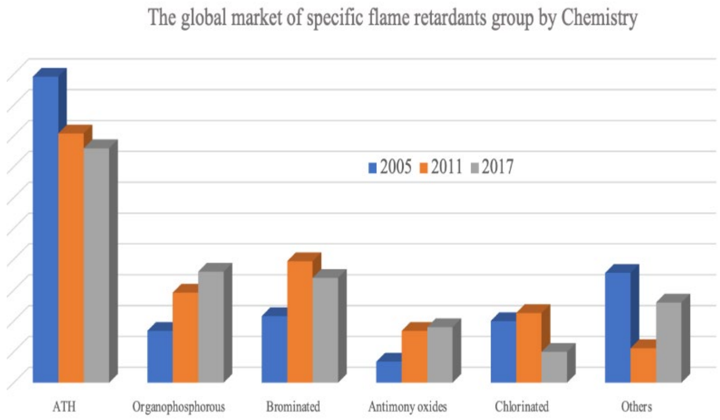

Figure 3: Comparing the global market of specific flame retardants groups by Chemistry. Data from I.H.S Markit,(ihsmarkit.com/products/chemical-flame-retardants-scup.html), EFRA (https://www.flameretardants-online.com/images/itempics/2/9/1/item18192pdf1.pdf)

In the year 2008, the United States, Europe, and Asia consumed flame retardant of about 1.8 million tons which accounted for USD 4.20-4.25 billion. In 2010, Asia-pacific was regarded as the largest market for FR considering its 41% global demand. The percentage composition of global FR demands per region is shown in Figure 2 for the year 2020. The global demand is produced around USD 5.8 billion then. In the year 2013, there were more than 2 million tons of FR consumed by global consumers. In 2019, the market size increased to up to 7 billion USD and is expected to be around 7.2 to 8 billion USD in 2021. Compounding the growth rate annually as 3.6, the market is expected to reach about USD 9.3 billion by 2027 (Retardants, n.d.).

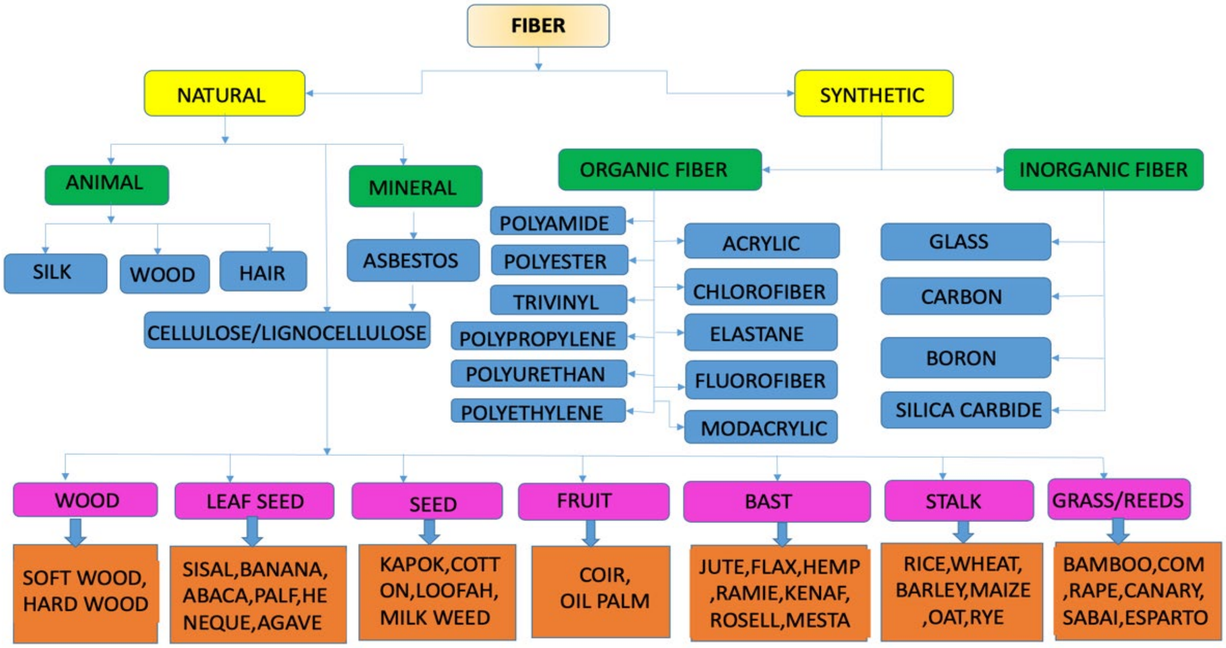

Figure 4: Various types of fiber reinforcements

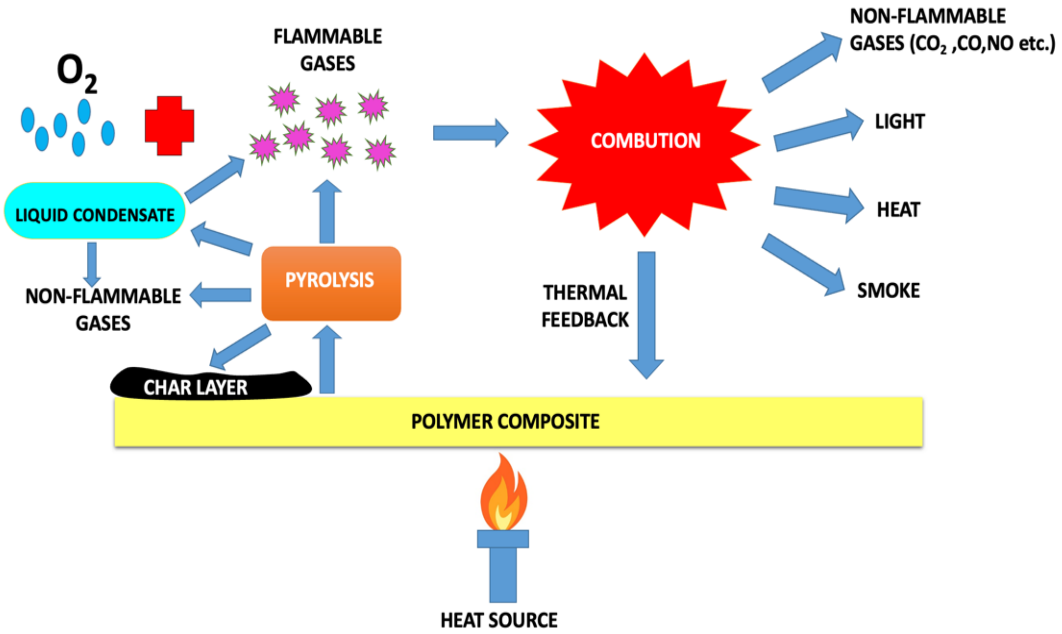

Figure 5: Schematic representing the combustion process in polymeric composites

In the year 2008, the United States, Europe, and Asia consumed flame retardant of about 1.8 million tons which accounted for USD 4.20-4.25 billion. In 2010, Asia-pacific was regarded as the largest market for FR considering its 41% global demand. The percentage composition of global FR demands per region is shown in Figure 2 for the year 2020. The global demand is produced around USD 5.8 billion then. In the year 2013, there were more than 2 million tons of FR consumed by global consumers. In 2019, the market size increased to up to 7 billion USD and is expected to be around 7.2 to 8 billion USD in 2021. Compounding the growth rate annually as 3.6, the market is expected to reach about USD 9.3 billion by 2027 (Retardants, n.d.).

Considering various FR by their chemical composition, the aluminum trihydroxide (ATH) has been the best-selling one recently with Europe and America contributing 45% of the total market. Considering the brominated FR, Asia tops the market with 28% whereas Western Europe and North America use 6.4% and 12% respectively though they had the largest revenue share of 37.2% in 2019. About 30% of global FR demand is attributed to the construction industry. Considering the non-halogen products, aluminum hydroxide had a 39.4% volume market share in 2019 (Retardants, n.d.). The global market of various FR comparing the years 2005, 2011 and 2017 is depicted in Figure 3.

Although composites are regarded as having low resistance to pyrolysis, their properties can be enhanced using various techniques. Composites inherently possess good thermal insulation properties and slower burn-through nature. The size of reinforcement fibers is adapted to the polymer matrix used and the use of flame retardants that are more polar than the organic polymer matrix results in a degradation of mechanical properties owing to poor fiber-matrix adhesion (Mohammed et al., 2015). Finding a perfect balance for flame retardants between fire retardancy, glass transition temperature, and composite properties is necessary for practical applications. However, they should not interfere with the very basic nature of what application the composite is meant for. However, protective layer formation and charring behavior induced through the fire retardant treatment process poses a threat to post-fire properties of composite resulting in delamination and failure. High-performance applications need a more versatile and fine-tuned composite. The challenge lies in producing a composite having desired functional properties with efficient fire retardancy (Rajak et al., 2019). The addition of retardants in solid-phase sometimes causes a non-uniform distribution through the matrix resulting in uneven fire retardancy (Pomázi & Toldy, 2017). A possible solution for this behavior is to apply a thin layer of multi-functional gel coating with solid flame retardants or a combination of gel coating with liquid flame retardants as well (Pomázi & Toldy, 2019). Figure 4 shows the various fiber reinforcements usually in use.

The review paper is divided into six sections. The first section discusses the mechanism of combustion, followed by the flammability of composite materials. The mechanism of flame and fire retardancy is discussed, and the methods of improving them are also briefed in subsequent sections considering the reinforcement and matrix separately. Various recent studies in the area of flame retardant additives are discussed briefly providing the materials used and the sustainability and circularity aspect is also discussed.

2. Mechanism of combustion

Before discussing the flame retardancy of composites, it is necessary to understand the mechanism of combustion taking place. For combustion to occur, there need to be three components: oxygen, heat source, and combustible material. Combustion usually occurs as a multistage phenomenon; on heating the material temperature rises and gradually attains a value at which it decomposes into char and some other byproducts like gases or liquid condensate at a temperature termed as the pyrolysis temperature. Further increase in temperature causes the flammable gases in the byproduct to combine with oxygen-producing combustion. In order to prevent combustion, the best method is to cut off at least one of the three basic ingredients of combustion. The major step in flame retardancy lies in preventing the main component for combustion. Figure 5 schematically depicts the mechanism of combustion, showing the detailed procedure.

3. Flammability of composite materials

The flammability of material is accounted for by its property to sustain combustion or fire. Polymeric matrices degrade swiftly when in contact with heat sources. Fiber reinforcements might provide improved thermal stability resulting in composite materials. The intensity of heat source, availability of combustible gases and surfaces, conditions for sustained circulation, and various other factors determine the flame spread, mass loss, heat rate reserve, rate of char formation and carbonization, etc. The flammability in polymer composites is inhibited using two techniques: either the application of fire retardants during the manufacturing stage or at the stage of finishing the process.

4. Mechanism of flame and fire retardancy

The flame and fire retardancy properties in composites are usually attained either by inhibiting or by disrupting a change in the combustion phenomenon. This happens basically in three different ways. The first method is to use chemicals that, when exposed to heat or fire, produce an endothermic reaction, thereby reducing the temperature of combustion and inhibiting the decomposition of composite materials. Secondly, chemicals can be incorporated which helps in producing fewer flammable byproducts and more char. The char produced acts as a barrier for further pyrolysis and prevents the exchange of heat and mass occurring between condensed phase and gas. Thirdly, adding flame retardant chemicals causes them to produce non-flammable gases that lead to a depreciation of the total oxygen concentration and prevent further combustion. The flame and fire retardancy mechanism can be accounted for either a single or a combination of the following aspects (Idumah et al., 2015).

- Char formation - The flame or fire retarding happens by the appearance of a carbonaceous char layer on the matrix, preventing further carbon atoms' oxidation and protection from flames. This layer acts as thermal insulation thereby obstructing flammable gases present in the composite.
- Chemical - This method involves the chemical reaction and radical mechanism in which the added retardants or their byproducts imbibe the free radicals generated as a result of polymer decomposition due to combustion. This involves cooling down of the system preventing further reactions and combustion.
- Inert or non-flammable gas - This involves producing inert or non-flammable gases as a result of the vaporization of additives, thereby reducing flammable gas concentrations. The condensation reaction of additives takes place in this method which in turn contaminates the oxygen as well.
- Physical - This mechanism involves the physical interaction of additives having a high thermal capability and capacity against combustion. These reduce the active fuel area and aids them to be below the lower flammability limit. The physical mechanism involves retarding the flame by various means like cooling the medium, forming a barrier, changing the thermal conductivity, heat capacity, and viscosity.
- Thermal - In this, the additives release chemicals to lower the temperature of the substrate quickly. A typical case involves the release of crystal water molecules endothermically, resulting in quenching of composite and swiftly retarding combustibles.

5. Improving the flammability and fire retardancy of composite material

Considering composite materials, the flame retardancy properties can be enhanced or introduced by two different techniques. The first method involves improving the raw materials for fabrication i.e., reinforcement and matrix modifications, and secondly by providing a protective coat around the composite having fire-retardant properties (Bar et al., 2015).

The flame retardants are widely classified into three broad categories: (Speight, 2017)

- Additive: The retardants are added mechanically to the polymer before or during the polymerization process. They bond mechanically to the surface aiding flame retardation. This type of method is usually employed with thermoplastic resins.
- Reactive: This involves one or more chemical substances chemically adhered to the polymer chains. The chemicals react to form a more efficient barrier in protecting the retardants from losing out of the polymeric surface. These types of retardants are more common with thermosetting resins.
- Combination: As the name suggests, it is a combination of both additive and reactive methods to provide a more efficient barrier to flame. They are usually used in some applications requiring areas where a single retardant may not be effective or to get a more effective barrier at a low cost.

5.1 FR treatment for reinforcing fibers

Fiber reinforcements are being used with polymer matrices to improve desired properties. Though synthetic fibers like aramid, carbon, glass, Kevlar, etc. possess an inherent flame retardancy compared to natural fibers like cotton, jute, flax, wood, etc., with an increase in view of circularity, sustainability, and environmental friendliness most of the synthetic reinforcements are either recycled and reused or substituted with natural fibers wherever possible. The flammability of both these classes of reinforcements can be enhanced by suitable treatment with flame retardant additives.

The flame retardancy in fibers are brought about following either by (Bar et al., 2015; Fox et al., 1967);

- Pad-dry-baking method - In this method, the air is removed using vacuuming, and fibers are immersed in the reagent. The impregnation occurs while releasing the vacuum followed by drying, high temperature steaming, and baking resulting in a uniform coating.
- Spraying-baking method - It involves the spray coating of fibers using fire retardant reagent followed by high-temperature baking.
- Steeping-drying-baking method - It involves the treatment of fibers immersed in heated water or solvent to absorb the retardants and followed by drying and baking.

Fire retardants are classified based on various traits like the principle of retardancy, chemical nature, time of action, the durability of finish, etc. Fire retardant lignocellulosic materials based on durability are broadly classified as durable FR and non-durable FR. The former is cheaper and easier to use compared to the former class. Some durable FRs involve: phosphoric acid, tetrakis (hydroxymethyl) phosphonium chloride, N-methylol dimethyl phosphonopropionamide with trimethylol melamine and some non-durable FRs in use are ammonium salts of strong acids like ammonium sulfamate, ammonium bromide, di-ammonium phosphate, a mixture of borax and boric acid, inorganic salts. The non-durable ones are added to compensate for the flammability properties of reinforcing fiber (Bar et al., 2015).

5.2 FR treatment for matrix

The matrices used for fabricating polymer composites are broadly classified into thermoplastic and thermosetting matrices (Zini & Scandola, 2011).

The major types of thermoplastic materials used as matrix include (Kozłowski & Władyka-Przybylak, 2008);

- Aromatic compounds - polycarbonate (PC), phenoxy resins, polysulfone, and polyimide.
- Cellulose derivatives - cellulose nitrate, acetate, butyrate, and propionate
- Poly-vinyl plastics - polyvinyl chloride (PVC), poly- styrene (PS), acrylonitrile-butadiene-styrene (ABS)
- Polyolefins-polyethylene (PE) and polypropylene (PP)

The major types of thermosetting materials for matrix involves (Kozłowski & Władyka-Przybylak, 2008);

- Amino resins: melamine-formaldehyde,
- urea formaldehyde
- Epoxy resins
- Polyurethane
- Phenolic resins - phenol-formaldehyde
- Unsaturated polyesters (UP)

Both these classes are highly prone to fire and their fire retardancy is enhanced by various methods. The flame and fire retardancy in polymeric matrices can be brought about by adding FR materials, modifying polymeric backbone by FR compounds, using nanoparticles into the matrix, and by the intumescent system. Epoxy matrices have good chemical resistance coupled with high corrosion resistance, good thermal and mechanical properties, contraction rate upon curing is considerably less, provides good electrical insulation, bonds excellently well to the substrate surface, and can be processed under a wide range of conditions. The main disadvantage lies in their brittle nature and high sensitivity to temperature changes. The various FR additives are explained in the below sections (Kausar et al., 2016).

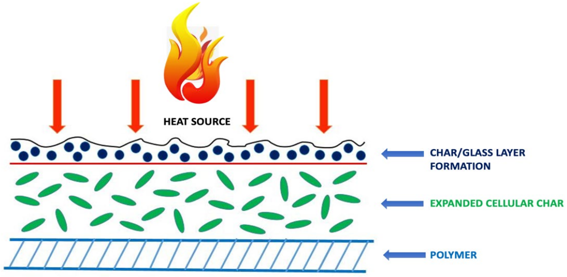

Figure 6: Intumescent systems mechanism

Intumescent systems are broadly classed as thick or thin-film intumescent coatings. The former ones are usually epoxy resins containing additive agents which when exposed to thermal degradation are formed as a solvent-free system whereas the latter are available in solvent or water-based agents applied as a spray coat or using rollers and brushes.
Intumescent FR mechanism depends on the formation of a barrier layer during thermal action thereby preventing heat and mass transfers in and out the polymeric surface. It mainly consists of carbonizing agents, acid, and blowing agents. During pyrolysis, the acid reacts with the carbon components and an esterification reaction happens resulting in the release of some gases and expansion of the carbonized layer. Figure 6 represents the intumescent mechanism of FR

6. FR additives

The flame retardants aids in preventing, minimizing suppressing, or stopping thermal degradation in composite materials. The various additives usually used are discussed below. Table 1 depicts the FR types with examples and the polymer used for fabrication, and the observed properties of FRs.

6.1 Additive flame retardants

The class of additive flame retardants, as the name suggests are added onto the fibre reinforcement or the matrix phase to enhance flame and fire retardancy. We discuss below some of the recent works carried out regarding the additive FR groups.

Peng et.al. (X. Peng et al., 2021) studied a combination of nitrogen /phosphorus FR with nitrile group forming a facile cross-linking strategy thereby enhancing mechanical properties as well as fire retardancy. The above FR is mixed with the EP matrix. Various tests like LOI, TG analysis, UL 94, cone calorimeter, etc. were employed to measure the FR effect. A 20% mixing of FR enhanced the flame retardancy, LOI reached 46.2 % and peak heat release rate dropped to 77.4 %. The cross-linked samples showed superior properties compared to physically mixed ones. Bazan et. al. (Bazan et al., 2021) used the addition of high-strength basalt fiber along with polyolefin and natural fibers like coconut, wood, walnut shell fiber, etc. An addition of 5-10 percent of basalt fibers showed 20-40 percent improved strength and stiffness by 60 percent than pristine polymers. The use of the above mixture in which the natural fiber proved to decline the peak HRR by 20 percent. The work also suggests a potential combination that can sustainably be employed in various sectors.

Chen et. al. (H. Chen, Deng, Zhao, Wan, et al., 2020) prepared novel piperazine containing FR PPBPP. Compared with virgin TPU, the TPU/PPBPP combination increased the LOI to 47.7 %, PHRR and THR reduced by 76.7 and 40.7 % resp in the burning test. The work proves an effective design route for preparing high-performance TPU. The elongation break studied with 12 wt% PPBPP to TPU proved as efficient recovery in elongation at break. The mechanical properties of flame-retarding TPU gradually recovered with increasing the PPBPP. It gives an insight into the design and fabrication of multi-functional additive FR.

Cuong Manh Vu et. al. (Vu et al., 2021) used a Novel Ladder Polymer (NLP) as an additive in vinyl ester resin (VER). Two different silanes were used in fabrication and characterization was carried out using NMR, FTIR, and X-ray diffractometry analysis.

Methyl ethyl ketone peroxide starter was used for the fabrication of NLP composites. A 20 % wt of NLP in VER improved the flexural strength and modulus by 195.6 and 260.6 % resp. a decrease in TSR of 20.7 percent and PHRR of 52.2 percent was observed, proving NLP is a good additive for improving mechanical properties as well as FR behavior.

Lijie Qu et. al. (Qu et al., 2020) used a core-shell FR fabricated from Si(H) micro-capsules with SiO_2 as shell and HPCTP as core and Si(H) / EP composites with coupling agents KH-550 or KH-560 for better interactions. The composite achieved an LOI value of 30.3 % and a V-1 rating in the UL-94 tests. Cone calorimetric results showed a reduced heat and gas release rate. The TTI and THR values of pure EP compared to FR enhanced one was 40,43 s and 148,122.9 MJ/m^2 resp. The residual char was tested and found to be rigid. Raman spectroscopy detections and FTIR tests confirmed the FR enhancement of Si(H) micro-capsules in the EP composite in the solid phase. TGA-FTIR and Py-GC/MS results proved that FR efficiently reinforced properties in the gaseous phase as well. The work gave insight into the microencapsulation method for the P-N-Si synergistic effect on the FR enhancement of EP composite.

Table1: Representing the various FR additives, Examples, polymer, and properties

Types of FR additive	**Common Examples**	**Polymers**	**Properties/Remarks**
Boron compounds	• Zinc borate • Ammonium Pentaborate • Barium Metaborate • Boric Acid • Sodium Borate • Ammonium Fluoroborate	• Cellulose and its derivatives • Polyethylene (LDPE, LLDPE, HDPE) • Ethylene Vinyl Acetate • Ethylene Propylene Diene • Rubber • Ethylene Acrylate • Copolymers (Methyl, Ethyl or Butyl Acrylates)	• Accelerate the formation of char by promoting cross-linking. • Both gas and condensed phase flame retardance. • Prevents the conversion of polymers to flammable gases.
Halogen compounds	• Hydrogen bromide • Polybrominated diphenyl ethers • Brominated polymers • Polyflon	• Polypropylene • Polyethylene • Cellulose	• Bromine is the best among the halogen flame retardants. • Bromine bonds to carbon and prevents the formation of volatile gases during combustion. • The halogen flame retardants are hazardous.

Phosphorous compounds	• Ammonium polyphosphate • Melamine polyphosphate • Aluminum Diethylphosphinate • Red phosphorous	• Polyester • Polyamides	• Accelerate char formation • result intumescent phase inorganic glass formation
Zinc Diethyl Phosphinate		• Polyester • polyamides	• Dense char formation
Silicon compounds	• Polysiloxanes • Silica	• Polypropylene • Poly(methyl methacrylate) • Epoxy resin • Poly(ethylene-co-vinyl • acetate) • Butadiene–acrylonitrile • Rubbers	• Silicon compounds have low heat release rates. • Insensitive to heat fluxes. • During combustion, an inorganic char formed at the surface protects the surface from decomposition.
Nano/Micro particles	• Aluminum hydroxide • Magnesium hydroxide • Magnesium carbonate • Hydrated magnesium • carbonate • Calcium carbonate	• All the polymers	• Nanoparticles assist the formation of an inorganic dense char layer on the surface of the composite. • Often decomposes endothermically.
Melamine compounds	• Melamine Phosphate • Melamine Cyanurate	• Nitrogen-based polymers, • such as Polyamide • Polyurethane	• Melamine compounds are stable at high temperatures • They act as a heat sink to absorb the heat generated during combustion. • Assist char formation and prevents the release of free radicals.

Carbon materials	• Fullerene • Carbon nanotubes • Graphene • Carbon black • Graphene quantum dots graphite	• Poly (methyl methacrylate) • Polypropylene • Polyurethane • Polyether ether ketones • Poly (vinyl alcohol) • Polyacrylonitrile • Poly(acrylonitrile-butadiene styrene) • Epoxies	• Dense network type char later formation during combustion prevents the propagation of flame to the interior of the surface.
Molybdenum compounds	• Molybdenum trioxide • Sodium molybdate	• Cellulosic polymers • Poly(vinyl chloride) • Unsaturated polyesters	• Flame retardants and smoke suppressants • Acts as a heat sink
Antimony Compounds	• Antimony trioxide • Antimony pentoxide • Sodium antimonate	• Polyethylene • Polypropylene • Polyvinyl Chloride • Polystyrene • Cellulosic polymers	• Works well with halogenated compounds • Antimony oxide reacts halogen highly volatile antimony oxy-halogen

Hu et.al. (J. Hu et al., 2012) used a novel phosphonamidate, DEMEMPA as an FR additive for Li-ion batteries. It was found that when they use above 10 percent of phosphonamidate in the electrolyte, the flammability is reduced significantly and the electrochemical stability is also enhanced as well. The major drawback lies in the fact that it had electrochemical compatibility issues with natural graphite electrodes with the addition of DEMEMPA. Chen, et.al. (H. Chen, Deng, Zhao, Huang, et al., 2020) fabricated an alkynyl-containing PPBP oligomer and PPBOP. Thermal analysis showed residual char of the PPBP with C-C triple bonds increased to 45.0 percent, much higher than 1.6 percent for the PPBOP without C-C triple bonds, and greatly increased by 27 folds. Adding PPBP to thermoplastic polyurethane (TPU) improved FR and anti-dripping characteristics, as well as low HRR and smoke production rate, declined by 70.7 and 53.9 % respectively.

6.2 Reactive retardants

Reactive FR is bonded chemically to the base material, and they cannot migrate out easily after fabrication. Below is a discussion of various reactive FR papers that have been published recently. In a work conducted by Hamidov et.al. (Hamidov et al., 2021) phosphorus and nitrogen-containing FR were synthesized and added to PUF at different ratios of 2.5, 5, and 10 percent. The fabricated ACRFRs showed good catalytic activity, moderate FR properties. High char yields and moderate LOI values were observed for ACRFR containing PUFs. The combination is considered to be innovative and environmentally friendly. Wang et.al. (H. Wang et al., 2021) used polyester diol containing phosphorus, which is based on 9,10-dihydro-10-(2,3-di(hydroxycarbonylydroxycarbonyl)propyl)-10-phospha phenanthrene-10-oxide (DDP) with PU elastomers. On adding 0.72 wt % of Phosphorus increased the LOI from 19 to 24.1 percent, passing UL-94 rating to V-0 and reducing total heat release by 25 percent. Also, FR-PUEs showed higher tensile strengths of 40.0 MPa based on MDI and 1,4-BDO. The work provides a suitable and effective way of producing FR PUE. Eco-friendly FR warm-mix epoxy asphalt binders (WEABs) for road tunnel pavements were introduced by an embodiment of reactive polymeric FR (RPFR) by Chen et.al. (R. Chen et al., 2021) which contained reactive polymeric brominated epoxy oligomer (BEO) and antimony oxide. The RPFR improved the Tg, thermal stability, LOI and provided more construction time for WEAB by reducing the viscosity. An addition of 8 wt % RPFR increased the tensile strength but slightly decreased the break elongation compared to pure WEAB.

Cheng et.al. (Cheng et al., 2020) used GBCAE containing reactive Boron and combined it with silk textiles. Higher LOI values of 28.6 percent were obtained and showed self-extinction behavior. GBCAE combines silk with ester covalent bonds and electronic attraction, helping in stable char formation during combustion. Reduction in smoke and heat release rate was also recorded with FR modification in silk. Bio-lignin-based vanillin and guaiacol were added to DOPO to form BDB which was converted into epoxy monomer DGEBDB. It showed greater potential as FR for DGEBA. UL-94 V-0 was achieved with a phosphorus content of only 1.27 wt %. It showed superior FR properties but poses toxic epichlorohydrin involved in the process which is non-eco-friendly. DOPO-based hindered amine-containing phosphaphenanthrene and piperidine groups for EP thermosets were fabricated by Huo, et. al. (Huo et al., 2017) the TGA values of EP/DDM/DPT thermosets showed a higher level (162–173°C) compared to non-treated ones. Better char yielding was observed and the addition of DPT significantly enhanced the FR properties of EP Thermosets. The phosphaphenanthrene and piperidine groups jointly exert the FR effect in the gaseous and condensed phases.

Yang et.al. (R. Yang et al., 2017) synthesized an HDPCP containing cyclophosphonate and phosphazene group by P-H addition reaction and combined with polyurethane foams. Studies noted a reduction in thermal conductivity when the addition of HDPCP was below 20 %, thermal conductivity reduced. During pyrolysis, P containing char layers were formed as the HDPCP decomposed first and the layer secured the internal material from further deterioration and hence reduced the weight loss rate of RPUF/HDPCP. A maximum LOI value of 25 % was attained by incorporating 25 % HDPCP. Cotton fabric was made FR using a highly reactive and efficient FR containing P, N, and S in a work by Wan et.al. (Wan et al., 2020), They studied the durability, thermal degradation behavior, heat resistance, and mechanical strength of cotton. A 30 % FR treatment improves the FR properties of raw cotton and volatile degradation products are reduced while increasing the residue rate. The FR showed little effect on mechanical properties. Zhang Qiu et.al. (Qiu et al., 2019) used a DOPO-based reactive FR (PBI) composed of multiple hetero-aromatic groups for EP. The Tg values of EP thermosets were reduced slightly but the PBI induced catalytic decomposition and charring behavior. EP/DDS/PBI-0.75 wt % of Phosphorous achieved LOI value of 34.6% and passed UL94 V-0 rating. Also, pk-HRR, av-HRR, and THR values were reduced by 48.7, 31.1, and 28.3%, respectively compared to EP/DDS thermoset.

6.3 Char forming

Zhiyu et.al. (Xia et al., 2020) fabricated a chemically modified tannic acid with terephthaloyl chloride into Nylon 6 at 235°C making it thermally more stable and improving its extrusion efficiency. During thermal degradation, the char formation nature is enhanced and reduces the mass-loss rate. Tests conducted in combustion calorimeters comparing plain and treated Nylon 6 showed a 52 percent reduced heat capacity, 36 percent peak HRR and 17 percent THR for 15 percent that modified Nylon 6. TGA, FTIR analysis of gas emission proved that more ammonia was released than primary and secondary amine/amide, thereby diluting the gas phase formed, providing more char yield, and lowering heat release rate. Flame tests revealed a reduction after flame time and swift extinguishing nature, improving oxygen index to about 25 %. Another advantage of using tannic acid is its good chemical resistance and sustainable nature.

Xua et.al. (Xu et al., 2018) used SCTCFA-ZnO, which is a novel organic-inorganic hybrid material that aids in char formation. On adding 25 percent of APP/SCTCFA-ZnO, the sample of PP composite got an LOI value of 31.1 percent. It showed enhanced FR property and smoke suppression properties owing to the development of a dense intumescent char layer. The residue analysis proved the development of graphitic char layers that supports the view of improved FR properties of the PP composite.

Feng et. al. (Feng et al., 2016) synthesized and characterized a novel CNCA-DA containing triazine and benzene rings which showed an efficient char formation behavior. The combination of APP and CNCA-DA, which is a good IFR on 2:1 ratio with LDPE composite on 30 wt % of composite had LOI value of %. With 25 wt %, LOI was measured to be 26.8 % and UL-94 V-0 rating was reached. Calorimetric studies revealed that the IFR reduced HRR, THR, SPR, TSP, CO2P, and mass loss significantly, compared to LDPE, LDPE/APP, and LDPE/CNCA-DA. The Raman and FTIR spectroscopy revealed that the APP and CNCA-DA showed the char forms graphitic structure and aids in FR effectively. The char residue of APP/CNCADA (2:1) attained 41.0 and 18.2 wt % at 600 and 700 °C resp. under air, whereas it was 40.8 and 6.6 wt % in the calculation. The GA/MS results showed chain fragmentation and synergistic effects between APP and CNCA-DA could improve the char formation capability of the APP/CNCA-DA system.

Liu et.al. (Liu et al., 2007) synthesized a novel poly (2-hydroxy propylene spirocyclic pentaerythritol bisphosphonate) (PPPB) with polyethylene terephthalate (PET) fibers and characterized using FT-IR and XPS. The results showed that with the rise in temperature, P–O–C group of PPPBP disintegrate progressively, and species containing C=C appears and the PPPBP produced phosphoric or poly-phosphoric acid during XPS spectra studies which eventually develop the evolution of unsaturated carbonaceous species, suppress C oxidation and forms effective charring and good FR properties.

Chen et. al. (D.-Q. Chen et al., 2005) used PET fabrics with 8.7 % PPPBP and found excellent FR and anti-dripping characteristics in the vertical burning test. The composite showed good thermal stability at high temperatures and was characterized using FITR, XPS, and SEM imaging. The char formed is a critical factor and aids in the FR and dripping resistance.

6.4 Mineral

Minerals are a popular class of FR in use. The hydrated minerals gibbsite and goethite having 51.9 percent of GKGW are used as FR in UPR matrix, which reduced the burning rate by 60 and 86% in composites having 20 and 30% filler, resp. The added GKGW reduced the initial degradation temperature of UPR by 30 ◦C. The wastes formed due to pyrolysis poses various advantages as remaining metal oxides in the solid act as thermal insulators, it’s environmentally friendly as byproducts are water vapors and that also reduces the burning. The waste product generated: gibbsite-kaolinitegoethite inorganic material can be used as a co-product and raw material thereby providing sustainability (Santos et al., 2020).

Mineral-based FRs like clay are widely in use with PP due to their cost-effectiveness and good thermal resistance. Aluminum trihydroxide (ATH) and magnesium dihydroxide (MDH) are some of the important minerals in use and ATH has been the best-selling FR recently. Even at a low % of addition, they provided higher FRI values. Metal hydroxides, such as magnesium hydroxide ($Mg(OH)_2$) and aluminum hydroxide ($Al(OH)_3$) are other minerals FRs that produce water vapor when thermally degraded and that helps in diluting the fuel and aiding FR properties (Arao et al., 2014). A study by El-Sabbagh et al. (El-sabbagh et al., 2013) showed 20–30 wt % $Mg(OH)_2$ in composite increased the LOI values significantly. A 50 wt % flax fiber and 30 wt % FR showed about 27 % LOI value and passed the UL-94 test V-2 rating.

6.5 Clay

Layered clay is extensively studied as a reinforcement for polymer matrices. The presence of clay is likely to improve the mechanical strength & barrier properties of the polymer composites, but a slight increase in thermal resistance. Clay modified with intumescent forming organic compounds can create protective barriers on the surface, thus one can observe a significant amount of residue during high-temperature combustion. Clay is often intercalated or exfoliated by the polymeric chains as it is reinforced in a polymer matrix to form 2D nanostructures in the matrix. All the nanostructured clay reinforcements are not excellent flame retardants, however, they can be modified or combined with other FRs to alter the thermal degradation properties of the polymer. Particularly, if the second additive is supporting the former for enhancing the char formation and reducing the amount of heat released by the composite. Additionally, nanoscale clay additives do not change much of the inherent properties of pristine polymers such as aesthetics, eco-friendliness, processing abilities, etc. During combustion, nanoscale clay reinforcements can react more rapidly than microsized FR counterparts due to the high surface area of the nanomaterials. In general, the nanostructured FRs can achieve a significant improvement in flame retardancy with a small quantity of filler loading (Araby et al., 2021).

The hybrid FRs of clay and organic char forming agents can increase flame retardance significantly. For instance, a hybrid system constituting fish DNA-modified clays in an epoxy matrix increases the thermal stability of the parent matrix. During combustion, the formation of a densely packed char of aggregated clay–char layer restricts the further propagation of the flame to the interior of the composite. Interestingly, DNA molecules can significantly contribute to the formation of dense condensed char layers as they can release effective suppressant agents during decomposition (Zabihi et al., 2016).

Similarly, DOPO/organoclay-loaded epoxy composite exhibits flame retardance through a similar mechanism as discussed earlier. Here, the synergistic FR effect DOPO and organoclay led to a decrease in pHRR by 40 % and smoke production rate by 46 %, when compared to pristine resin. Clay is also used as a hybrid FR filler for bionanocomposites of rice husk and recycled HDPE/PET blend. In the presence of a compatibilizer, interfacial interaction between polymer blend and the clay. The addition of compatibilizer to the clay/polymer blends not only improves the mechanical properties but also the thermal and flame retardance (R. S. Chen & Ahmad, 2017).

6.6 Nitrogen

Nitrogen is an inherent FR. During combustion, nitrogen remains inactive to any reactive species, thus it functions as a protective barrier. The nitrogen-containing or phosphorous/ nitrogen-containing compounds are commonly proposed as FR additives in polymers. 9,10-dihydro-9-oxa-

10-phosphaphenanthrene-10-oxide(DOPO) is a phosphorus/nitrogen compound that can be grafted to bisphenol A bis(phthalonitrile) containing benzoxazine, and the new compound is DOPO-BAPh. DOPO-BAPh is a potential FR for epoxies. Blending DOPO-BAPh in epoxy (EP) results in the acceleration of curing reaction due to the presence of phenolic hydroxyl groups in the structure of DOPO-BAPh. The cross-linked aromatic heterocycle networks formed by the self-curing of the nitrile group in DOPO-BAPh augment the constancy of the protective char layer formed during combustion. DOPO-BAPh embedded EPs show an LOI of 35.8 percent and a V-0 rating for the UL 94 test by the addition of 0.26 wt. % DOPO-BAPh. This reveals the ability of DOPO-BAPh as an FR enhancer in both the gaseous and condensed phases (D. Wang et al., 2021).

DOPO-N-(4-hydroxyphenyl) maleimide (DOPO-HPM) obtained by addition reaction is also a nitrogen/phosphorus-containing FR additive for epoxies. The resulting epoxy resin systems formed by copolymerization of diglycidyl ether of bisphenol-A (DGEBA), DOPO-HPM, triglycidyl isocyanurate (TGIC), and 4,4′-diamino-diphenyl sulfone (DDS) exhibit excellent flame retardancy. Most importantly, the new epoxy resin has the physical properties of the parent resin with an LOI value of 31 % when the P-content in the resin was only 0.25wt.%. By varying the phosphorus content to P-1 and P-1.25, the LOI value increased to 37 and 38.5 %, resp. and V-0 rating in a UL94 test. The calorimetric test reveals a significant reduction in the peak of HRR (pk- HRR), an average of effective heat of combustion (av-EHC), and total heat release (THR) (S. Yang et al., 2015).

The intumescent char layer on the surface forms a sealed non-combustible layer on the surface, thus creating a protective coating. Interestingly the synergic action of phosphaphenanthrene and triazine-trione groups inhibits rapid combustion in the condensed phase. Phosphaphenanthrene undergoes rapid decay during combustion, which can induce decomposition to the EP matrix to form a protective char layer. However, the presence of rigid and thermal stable maleimide groups prevents the deterioration of the EP matrix. As a result, a sealed crosslinked char coating is created across the surface which serves as shielding for the EP matrix underneath the surface. The components released by the FR systems during combustion act as quenchants in the gaseous phase. Additionally, the char layer at the surface decreases the emission reactive species that may take part in the combustion chain reaction.

Adjusting the ratio of phosphorus/nitrogen in organic/inorganic hybrid FRs exhibits good water repellency and tuned flame retardancy. The network of organic/inorganic is playing a vital role in the water-resistance of hybrid FRs. When hybrid FRs with different P/N ratios are mixed with epoxy resins the intumescent char formation on the surface of the epoxy material during combustion as discussed earlier. The calorimetric studies show that the inclusion of N results in a reduction of THR as compared with compositions with higher TGIC-KH loadings. But the hybrid FRs exhibit an increased THR, revealing the synergistic effect of P/N on the flame retardant properties. Here also the formation of intumescent char on the surface by FRs acts as a mechanism of flame retardance of the composite material in gaseous and condensed phases (S. Yang et al., 2015). Likewise, organic/inorganic hybrid FRs containing phosphorus, nitrogen, and silicon also exhibit high resistance to water and a significant enhancement in the flame retardance of epoxy composites (Qian et al., 2014).

6.7 Phosphorous

Phosphorus-containing compounds are widely used as FR additives in polymer matrices. The selection of the phosphorus compound for flame retardance depends on the nature of the polymer. The following table lists phosphorus-containing FRs (Green, 1992).

Like thermoplastics as listed in the above table, the addition of nano- and micro-sized FRs to the thermosets imposes flame retardancy in the respective matrix. For instance, glass fiber reinforced epoxy matrix loaded with phosphorus-containing FRs such as ammonium polyphosphate and/or tris (tribromoneopentyl) phosphate exhibit superior flame retardance. The presence of FRs alters the nature of combustion of the above composite through the formation of dense char networks. Interestingly, the addition of double-walled carbon nanotubes (DWCNTs) does not alter the flame retardance of the composite, however, the flexural strength of the composite improves after exposure to the flame as compared to the one without DWCNTs (Katsoulis et al., 2012).

Table 2: List of Important phosphorus-containing FRs

Name of the FR additive	polymer/matrices	Advantages
Phosphates of Ammonium	Cellulose, wood and paper	Cheap ,inhibits smouldering combustion
Red Phosphorus	Polycarbonate, polyethylene terephthalate, polymethyl methacrylate and Nylon	Most efficient in oxygen containing polymers through the formation of P–O bonds. Enable the formation of cross-linked char as protective barrier
Trialkyl Phosphates and Phosphonates	Unsaturated polyester	Used in highly FR reinforced saturated polyesters to lower viscosity and improve flame retardancy.
Aryl Phosphates	Polyvinyl chloride, cellulose acetate, Poly(p-phenylene oxide), Polycarbonate/ABS Blends, etc.	The aryl phosphates replace the highly flammable organic plasticizers in PVC. Alkyl di-aryl phosphates give lower LOI. Small quantities are enough for substantial flame retardancy
Chloroalkyl Phosphates and Phosphonates	Flexible polyurethane foam	Scorch resistant. Higher concentrations are necessary to a good degree of flame retardancy if aromatic halogens are used.
Brominated Phosphates	Polycarbonate/polyester blends	Effective flame retardant than brominated polymers. Burn with significantly lower LOI.

6.8 Silicon

Silicon-containing materials can act as FR when they are reinforced/blended in a polymer matrix. Silicone polymers, SiO_2, silsesquixanes, and organic and inorganic silicates are some representative silicon-containing potential FR compounds. Silicon compounds are considered environmentally benign FR reinforcements/additives because many of these compounds have natural origins and they don’t release any detrimental products to the environment. The term silicones represent a group of polymers with silicon in their backbone, one such example is polydimethysiloxane. Silicones exhibit exceptional resistance to heat, are highly exothermic when burned, and have a very low release of harmful gases during their thermal decomposition. Silicone is blended with highly flammable polymer matrices to impart flame retardancy to the polymer. The flame retardancy of silicone-containing blended polymers is due to the uniform and smooth blending of silicone in polymer matrices and the tendency of silicone to migrate towards the surface as the combustion commences. Thus, forming a highly flame-resistant char layer covering the material which can undergo rapid combustion. Additionally, such a char layer can prevent the highly reactive species from reaching the surface that is undergoing combustion. Similarly, co-polymerizing silicone polymer monomers to a flammable polymer backbone can bestow flame retardancy in the new polymer. For instance, a co-polymer of polyamide 6 (PA6) and poly-dimethyl phenyl silicone (PDPS) is flame resistant and anti-dripping in nature.

The silicon-containing PDPS is introduced to PA6 backbones using ethylene glycol (EG) as the chain linker. Interestingly, EG plays a double role as a ‘chain linker and charring agent, which ultimately induce flame retardancy to PA6. The tests revealed that the PDPS-PA6 composite exhibited an LOI of 28.3 percent, and no flammable dripping during the burning tests. As discussed earlier, the ability of silicone-containing compounds to form silicon-rich char as a protective coating resulted in a tremendous improvement in the flame retardancy of PDPS-PA6 copolymer (Fan et al., 2020). Such techniques can be adopted for the synthesis of flame-resistant polymers at a large scale without much affecting the properties of the parent polymer. Silica (SiO2) and its polymorphs, for instance, quartz, silica gel, and fumed and fused silica also exhibit flame retardant properties. However, the efficacy of silica in flame retardancy mainly depends on the particle size, aspect ratio, pore size, surface area, density, etc.. The addition of silica to highly combustible polymers results in reduced heat release and mass loss rate owing to the unique properties of silica in the polymer phase when the polymer is undergoing combustion.

A layer-by-layer (LBL) nanocoating of phosphorus/nitrogen/silicon assembly prepared using colloidal silica and polyphosphates can reduce the flammability of polyester/cotton blend (T/C) blends significantly. This nanocoating can be easily deposited on the surface of the T/C blends. The T/C blend coated with 15 by layers of nanocoatings is self-extinguishing in a vertical flammability test. In the meantime, the blend with FR coating exhibits a slight delay in the ignition and a remarkable reduction of heat release rate. The LBL-FR nanocoating release non-flammable volatiles and the subsequent formation of char from the nanocoating endued an outstanding flame retardance for the T/C blend. This approach is suitable for the manufacturing of flame retardant fabric (B. Wang et al., 2020).

Tri(2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxo-4-hydroxymethyl)phenylsilane (TPPSi) is an organic silicon-containing material and an excellent FR material. TPPSi exhibits high stability at a wide temperature range and can effectively suppress the generation of smoke during combustion. The high char formation of TPPSi resulted in its increased FR characteristics. Most importantly the addition of TPPSi does not compromise the mechanical properties and the aesthetics of the polymer matrix. For example, TPPSi loaded PA6 exhibits the qualities of pure PA6, but the blend is flame-retardant and suppressed smoke. The addition of TPPSi prevents the whole matrix to act as a fuel during the combustion by altering the thermal degradation pathway of PA6. With the mutual interaction of TPPSi and PA6 as the combustion prevails, a cross-linked char that contains phosphorus and silicon is formed and this char acts as a barrier to prevent the reactive species from entering the flame front thus inducing flame retardance. Additionally, the primary FR element of TPPSi, i.e., Silicon-containing components can easily migrate the surface of polymer matrix as it is a general characteristic of silicon-containing materials due to low surface tension that provides an additional barrier effect to PA6. Altogether the barrier effect of residues determines the FR behavior of TPPSi (J. Chen et al., 2011, p. 6).

The silicon and phosphorus-containing FRs are grafted to the bulk reinforcements such as glass fiber to enhance the flame retardance of the composite. For instance, glass fiber (GF) fabric (PHSi-g-GF) grafted with phosphorus-containing hyperbranched polysiloxane (PHSi) reinforced modified vinyl ester (PHSi mixed VE) matrix improve the flame retardancy as compared to the composite containing GF without any grafting. Such a modification simultaneously increases the impact and inter-laminar shear strength in addition to the flame retardance, making it a high-performance GFRC (Z. Zhang et al., 2016).

6.9 Nanomaterials

Nanostructured materials are extensively used as multi-functional reinforcements in polymer composites. In general, nanomaterials lead to a remarkable increase in the mechanical properties of the composites. Often nanomaterials themselves result in an improvement in thermal properties of the parent matrix. Nanostructured hybrids with FR components are also a well-accepted strategy for the obtention of flame retardant composites. A small quantity of nanomaterial is sufficient for a remarkable enhancement in the properties of the polymers, without compromising the prominent properties of the pure polymer. Most importantly, the nanomaterials can significantly contribute to the formation of dense char layers during combustion. Nanostructured $Mg(OH)_3$, $Al(OH)_3$, etc. are the most common FRs in the polymer, which can release water during combustion. When the hierarchical nano assembly of Zn–Co Zeolitic Imidazolate Framework (ZIF) on MoS_2 nanosheets is used as a reinforcement, PAN improves the flame-retardant efficiency of MoS_2 layers. The barrier properties of the nanolayers and the ability of Co-Zn ZIF/MoS_2 nanosheets as a catalyst for the char formation result in the flame retardancy of PAN composite fibers. Interestingly, the Co-Zn ZIF/MoS_2 hybrid nanosheet reinforcement leads to the growth of CNTs from PAN, which ultimately results in dense char layers (H. Peng et al., 2020).

The titanium nanotubes (TNTs) and Ce ion-doped TNTs influence the flame retardance of bamboo fiber/high-density polyethylene (HDPE) (BH). The presence of TNTs in BH increases the flame retardance of the composites besides the improvement in thermal stability and thermal oxidation behavior. The network-like structure formed by TNTs and BH is likely to act as a thermal barrier which ultimately leads to the improvement in thermal properties and flame retardance. Additionally, the capillary effect of TNTs leads to the absorption of combustion products and the highly reactive species which may otherwise undergo a chain reaction. The char formed by carbon and TNTs on the surface of the composite prevents the propagation of flame to the interior of the composite. The addition of Ce doped TNTs exhibits better thermal stability than the pure TNTs in the composite (Wu et al., 2012). Similar to TNTs, Halloysite nanotubes (HNTs) are tubular nanomaterials that exhibit flame retardance when reinforced in a polymer matrix. HNTs and formed by the weathering of clay. While reinforcing HNTs in a polymer matrix, functionalized HNTs or a compatibilizer is used for good dispersion. Alike TNTs, the thermal stability of HNT reinforced polymers can also be corroborated by the capillary action of the nanotubes, besides the formation of network-like char formation (Goda et al., 2018).

6.10 Halogen

Flame retardants comprising halogen have been used for decades and the majority of them are developed over time as sediments. The naturally existing halogenated FRs are likely to release the halogen and the resulting compound may not exhibit FR nature. Chlorinated and brominated compounds are the most widely used FRs due to their availability at a large scale and low cost. The most used brominated FRs are tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and polybrominated diphenyl ethers (PBDEs). Tris(l,3-dichloro-2-propyl) phosphate (TDCCP), tris(2- chloroethyl) phosphate (TCEP), chlorinated paraffins, and Dechlorane plus are the most common chlorinated FRs (Venier et al., 2015). These class of FR have been in use for decades and resulted in a very high accumulation as waste and sediments. A study conducted by Guo et.al. (Guo et al., 2020) showed that the trend for input legacy of PBDE and PBB showed an decreasing trend as replacements like DBDPE and DEC604 are increasing. Due to long range transportation and disposal into settlements, the dehalogenation of HFR might happen resulting in more and more accumulation of halogens in the environment. Various mechanism pathways need to be sorted to understand safe disposal without harming nature. HU et.al. (Y. Hu et al., 2020) discussed the bio-accumulation aspect of PBDE and AHFR in the Futian National Nature Reserve of Shenzhen. AHFR, BTBPE, DBDPE, HBB, pTBX, PBT, PBEB, etc. in natural mangroves are investigated. These studies showed HFR with higher hydrophobicity have a decreased transportation from root to stem to leaves. It also gave insight on the vitality in pertaining PBDE and AHFR in mangrove wetlands. The e-waste recycling resulting in plastic debris that contains HFR are studied in detail by Zhang et.al. (J. Zhang et al., 2021) High concentrations were detected in soils and BDE 209 was the most important in soil and plastics. The mechanism that results in plastic to soil transfer of HFR is still unclear. The paper suggested looking into human exposure and ecological results in e-waste recycling sites. Nowadays, the use of halogenated FRs is highly discouraged due to the environmental impact and the health hazard associated with those chemicals.

7. Summary

Composite materials are a superior class of materials having various applications. The main disadvantage of using them lies in their low thermal resistance. Various incidents are being reported and many mishaps happened due to the thermal degradation of composites. Studies were conducted to overcome this and one of the possible and practical solutions appeared to be the addition of flame and fire retardants to the composite. The addition takes place in the reinforcement or matrix or the composite can also be coated with FR materials. The introduction of FR materials made a boom and the manufacturers were forced to use them owing to various regulations and growing awareness among consumers. The market for various FR globally is discussed in this review and also the different FRs based on their chemical composition on the global market is also discussed. ATH tops the chart followed by halogenated FR. The FR industry is aimed to attain a revenue of about 9.3 billion by the year 2027 considering the current market growth rate.

Considering the environmental effects and sustainability into account, halogenated FR poses a serious threat. Consumer awareness of the advantages & effectiveness of FR has compelled the producers to promote FR usage in items. Also, the various fire safety standards and regulations are expected to have a positive impact on FR demands. The Waste Electrical and Electronic Equipment Directive discouraged the use of halogenated FR owing to their bioaccumulation and environmental contamination. Restriction of Hazardous Substances Directive imposes the use of more environmentally friendly FR and degrades the use of hazardous materials like halogenated FR in electrical and electronic instruments. The European Union in March 2021 prohibited the use of halogenated FR in plastic enclosures and stands of electronic displays. Growing awareness for more eco-friendly options and circularity & sustainability approach reduces the use of hazardous FR and promotes alternative solutions.

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Conflicts of Interest

The authors declare no conflict of interest.

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ABBREVIATIONS

ATH	Aluminum Trihydroxide
ABS	Acrylonitrile-Butadiene-Styrene
APP	Ammonium polyphosphate
BDB	Benzodioxolylbutanamine
BDO	Butanediol
BEO	Brominated Epoxy Oligomer
CNT	Carbon nanotubes
DDS	Diaminodiphenyl sulfone
DEMEMPA	bis(N,Ndiethyl)(2methoxyethoxy) methyl phosphonamidate
DGEBA	Diglycidyl ether of bisphenol-A
DDM	4,4′-methylenedianiline
DPT	Dimethyl phosphite
DOPO	9,10-dihydro-9-oxa-10-phosphaphenanthrene- 10-oxide
DPT	N,N-Dipropyltryptamine
DWCNT	Double-walled carbon nanotubes
EG	Ethylene glycol
EHC	Effective heat of combustion
FPI	Fire Performance Index
FR	Fire Retardant
FTIR	Fourier Transform Infrared
GF	Glass Fiber
GFRC	Glass fiber reinforced concrete
GBCAE	Glycerol Borate Citric Acid Ester
HBCD	Hexabromocyclododecane
HDPCP	Hexa-[2-(2-hydroxy-ethoxy)-Ethylamino]-Cyclotriphosphazene
HDPE	High Density Polyethylene
HFR	Halogenated Flame Retardants
HNT	Halloysite nanotube
HRC	Heat Release Capacity
HRR	Heat Release Rate
Si(H)	Hydrogenated amorphous silicon
IFR	Intumescent Flame Retardant
LBL	Layer by layer
LOI	Limiting Oxygen Index
LDPE	Low-density polyethylene
LLDPE	Linear Low Density Polyethylene
MDI	Maximum Demand Indicator
MDH	Magnesium dihydroxide
NLP	Novel Ladder Polymer
NMR	Nuclear Magnetic Resonance
PAN	Polyacrylonitrile
PBDE	Polybrominated Diphenyl Ethers
PC	Polycarbonate
PCTP	Phenoxycyclophosphazene

PDPS	Poly-dimethyl phenyl silicone
PE	Polyolefins – Polyethylene
PEMEMPA	Phosphonamidate, bis(N,N-diethyl)(2 methoxyethoxy) methylphosphonamidate
PET	Polyethylene Terephthalate
PHRR	Peak of Heat Release Rate
PHSi	Phosphorus-containing hyperbranched polysiloxane
PBI	Phosphaphenanthrene, benzothiazole and imidazole
PP	Polypropylene
PPA	Phenylphosphinic Acid
PPBOP	Poly(1,4-Butanediol Phenylphosphonate)
PPBP	Poly(2-Butyne-1,4-Diol Phenylphosphonate)
PPBPP	Poly (2-Butyne-1,4-Diol Piperazine Bisphosphonate)
PPPBP	2-Phenyl-3,3-Bis(4-Hydroxyphenyl)Phthalimidine)
PPPB	2-hydroxy propylene spirocyclic pentaerythritol bisphosphonate
PS	Poly- Styrene
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PUE	Polyurethane elastomer
PUF	Polyurethane foam
PVC	Poly Vinyl Chloride
RoHS	Restriction of Hazardous Substances
RPFR	Reactive Polymeric Flame
RPUF	Rigid polyurethane foams
SPR	Smoke Production Rate
TBBPA	Tetrabromobisphenol A
TCEP	Tris(2- chloroethyl) Phosphate
TDCCP	Tris(l,3-dichloro-2-propyl) Phosphate
TGA	Thermogravimetric Analysis
TGIC	Triglycidyl isocyanurate
TNT	Titanium nanotubes
THR	Total Heat Release
TPPSi	Tri(2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane-1-oxo-4 hydroxymethyl)phenylsilane
TPE	Thermoplastic Elastomers
TPU	Thermoplastic Polyurethane
TSP	Total Smoke Production
TSR	Total Smoke Release
TTI	Time to Ignite
UP	Unsaturated Polyesters
UPE	Urethane-Based Phosphonate Ester
UPR	Unsaturated Polyester Resin
VER	Vinyl Ester Resin
WEAB	Warm-Mix Epoxy Asphalt Binders
WEEE	Waste Electrical and Electronic Equipment Directive
XPS	X-ray photoelectron spectroscopy
ZIF	Zeolitic Imidazolate Framework