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Review

Flame Retardant Polymer Composites

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Abstract: In this review article, different approaches of enhancing flame retardancy of polymeric composite material and their effect on different composite properties are analysed critically. The mechanisms of fire spreading on composite materials are also discussed. Flame retardancy of polymeric composite material can be enhanced either by enhancing the fire performance of constituents of composite i.e. matrices and reinforcing agents or by providing a protective flame retardant (FR) coating around the composite material. Fire performance of reinforcing material is improved by treating with FR-chemicals while the fire performance of polymer matrices can be improved by incorporating micro and nano FR-fillers or by introducing FR-compound into polymer backbone. The flammability of micro and nano filler added polymeric composites and newly developed polymer derivatives and their effect on composite properties like mechanical, thermal have been discussed. However, the development of flame retardant polymer composite is still at nascent stage and for further development, it is necessary to work on the development of non-health hazardous, environment friendly flame retarding agents which will be able to enhance the fire performance of composite materials at very low concentration levels.

Keywords: Polymer composites, Flame retardant composites, Fire performance, Advance composites, Novel composites

Introduction

Composite materials are mainly classified into three categories such as metal composites, ceramic composites and polymer composites. Out of these three types, polymer composites due to their low weight to strength ratio, find mammoth applications in automobiles, aircraft, spacecraft, boats, ships, civil construction, packaging, sporting goods etc. [1-3]. The use of polymeric composite materials rises exponentially due to their good mechanical behaviour, chemical resistance and corrosion resistance behaviour, but their fire resistance behaviour raises a serious safety issue on the uses of polymeric composite materials. Chemically all polymeric materials comprise of hydro-carbon chains and when they are exposed to fire, burn rapidly with the release of high amount of heat, flame and smoke [4,5]. Fire performances of different polymeric matrixes are shown in the Table 1. Fire is one of the greatest invention of human being but every year around 4000 people in USA and 5000 people in Europe die in fire accident and around 0.3 % of gross domestic product lose due to fire accidents [6]. The Aircraft Crashes Record Office (ACRO), a non-government organization based in Geneva, reported that there were 1662 official records of aircraft accidents between 2001-2010 in which total 15,962 people have lose their lives. After analysing the reasons of different air-craft accidents, it was found that improving the fire resistance of polymeric composite materials can reduces the severity of accidents [7,8]. Thus the use of polymeric composite materials without any FR-treatment is dangerous for human safety. Recently all the governments of developed and developing countries including European Community and United States government expressed their concern about the use of FR-composite materials for different applications which enhance the safety awareness in the consumers. In February 1987, a draft of military standard was published for fire and toxicity requirement for material used inside naval submarines. In 1989 another draft was published for fire and toxicity test method for composite material used in hull, machinery and in other structural applications in naval submarine by NAVSEA [9,10].

Presently with increasing environmental consciousness there is a significant effort made by technologist and scientist to replace the non-biodegradable fibres (like Carbons, glass, Aramid etc.) with biodegradable natural fibres (like jute, flax, sisal etc.). Like polymeric materials these natural fibres also burn very rapidly, that is why FR-treatment for the composite material is very essential for its safe service. In this review paper, an attempt has been made to understand the flame propagation and retardancy mechanisms of polymeric composite materials, different approaches of developing FR-composites and the effect of treating with flame retarding agents on other composite properties.

Combustion Mechanism and Flame Retardancy of Composites

Combustion Mechanism

In order to appreciate the flame retardancy mechanism of different polymeric composite materials, it is necessary to understand the combustion mechanism first. Figure 1 shows the schematic diagram of combustion cycle and possible flame retardancy approach for composite materials. Combustion of any material requires three components: heat, oxygen and combusting material or fuel. When heat is applied on any

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Table 1. Flammability of some composite making polymer matrix

Polymer	Ignition temperature (^{o}C)	LOI (%)	Thermal degradation temperature (^{o}C)	Total heat of combustion at 50 flux (kJ/g)	Peak rate of heat release at 50 flux (kW/m^2)	Smoke rerelease at 50 flux (m^2/kg)
Polyethylene	370	18	399	37	1130	362
Polypropylene	330	18	354	44	1300	621
Nylon-6	430	25	424	30	1272	160
Polycarbonate	500	25	476	31	-	-
Poly(styrene)	319	18	356	28	407	546
Poly(acrylonitrile)	480	27	320	28	343	140
Epoxy resin	427	19	427	25	755	866
Unsaturated polyester	330	20	380	23	985	801

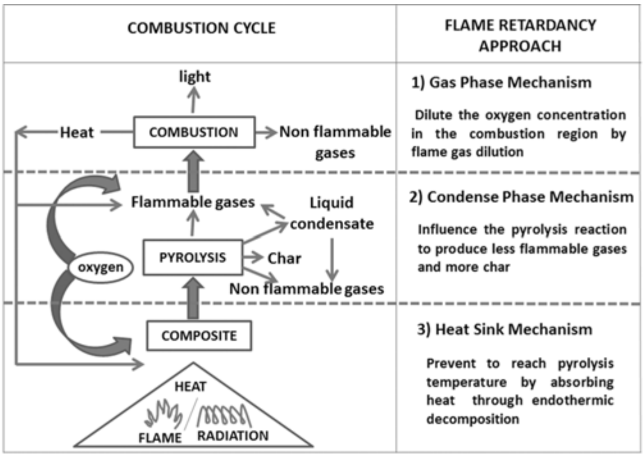

Figure 1. Schematic diagram of combustion cycle and possible flame retardancy approach.

substrate, the temperature of the substrate increases and gradually reaches to its pyrolysis temperature (T_P). At this temperature the material produces some char, liquid condensates and some flammable and non-flammable gases. As the temperature continues to rise, eventually the combustion temperature (T_C) arrives where these flammable gases combine with oxygen and produce large amount of light, heat and smoke. Heat produced by combustion, helps to further continuation of this cycle [5,11,12].

Flame Retardant Techniques

Flame retardancy of the composite materials can be achieved by inhibiting or by disrupting the combustion cycle. Combustion cycle for composite materials can be interrupted in three different ways. Firstly, by incorporating such chemicals that decompose endothermically when exposed to heat and thus these chemicals prevent the temperature to reach the pyrolysis temperature of composite materials. Secondly, by incorporating such chemicals that produce more non-flammable by-products and more char during pyrolysis reaction. This char layer acts as a physical barrier which hinders the heat and mass transfer between gas and condense phase. This mechanism is known as condensed phase mechanism. The third method is known as gas phase mechanism. In this case during combustion, the FR-chemicals release more non-flammable gases leading to reduction in effective oxygen concentration in the flame zone and thus act as a FR-agent [5,11-13].

Flame Retardant Composites

Flame retardancy behaviour or fire performance of a composite material can be improved in two ways. Firstly, by improving the fire performance of composite making constituents i.e. matrix and reinforcing agent. Secondly by providing protective FR-coating around the core composites. Different methods of improving fire performance of composite materials through component modification as well as through providing protective coating have been discussed below.

Flame Retardant Treatment for Reinforcing Fibrous Materials

Depending on the end uses, different synthetic and natural fibres are being extensively incorporated inside polymeric matrix system, mainly for enhancing the mechanical performance. Presently with increasing environment consciousness, attempts are being made to use the bio-degradable natural fibres where ever it is possible [14,15]. Synthetic fibres like glass, carbon, ceramic fibres are inherently FR in nature but the natural fibres are highly flammable and unlike synthetic polymers they also burn rapidly with the release of heat, light and smoke. Natural fibres (Jute, sisal, ramie, flax etc.) which are being used as reinforceing agent in the polymeric composite are mostly ligno-cellulosic in nature. Compositions of different natural fibres are shown in Table 2 [74]. The flammability of these lingo-cellulosic natural fibres can be improved by treating with suitable FR-chemicals.

FR-treatment of natural fibres was carried out either by i) Pad-Dry-baking method or by ii) Spraying-baking method or by iii) Steeping-drying method [16]. FR-agents can be classified in different ways based on their chemical nature, flame retardancy principle, durability of finish etc. Table 3 shows the list of different conventional FR-chemicals which are generally used for enhancing flame retardancy of natural fibres. Based on durability, FR-chemicals for ligno-cellulosic materials are classified into two main classes. They are non-durable flame retardants and durable flame retardants [11]. Compared to durable flame retardants, non-durable flame retardants are inexpensive and easy to apply. As the reinforced fibres stay inside the polymer matrix system, the non-durable flame retardants are preferable for the flame retardant treatment of reinforcing fibres. Inorganic salts, mixture of borax and boric acid, ammonium salt of strong acids like di-ammonium phosphate, ammonium sulfamate, ammonium bromide are examples of non-durable flame retardant chemicals. Generally 10-15 % solid add-on of these materials makes lingo-cellulosic natural fibres flame retardant.

Table 2. Chemical composition of some common natural fibers [74]

Types of fiber	Chemical component percentage (%)			
	Cellulose	Hemicellulose	Lignin	Wax and minerals
Bast fibers				
Flax	64-71	18.6-20.6	2-5	5
Kenaf	44-57	22-23	15-19	2-5
Jute	61-72	13.6-20.4	12-13	0.5-2
Hemp	70.2-77	17.9-22.4	3.7-5.7	0.8
Ramie	68.6-76.2	13.1-16.7	0.6-0.7	-
Leaf fibers				
Abacca	56-63	15-17	7-10	3
Sisal	67.5-78	10-24	8-11	0.6-1
Cabuya	68-77	4-8	13	1.5-2
Fruit fibre				
Coir	36-43	0.15-0.25	41-45	
Stalk fibers				
Rice	28-48	23-28	12-16	15-20
Wheat	29-51	26-32	16-21	45-9
Oat	31-48	27-38	16-19	6-8
Cane fibers				
Bagasse	32-48	27-32	19-24	15-5
Bamboo	26-43	15-26	21-31	17-5
Grass fibers				
Esparto	33-38	27-32	17-19	6-8
Sabai	-	24	22	6

Tetrakis(hydroxymethyl) phosphonium chloride, a combination of N-methylol dimethyl phosphonopropionamide with trymethylol melamine and phosphoric acid etc. are the example of durable flame retardants [11]. The effect of reinforced fibres FR-treatment on composites flammability and other properties for different fibre-matrix systems with different FR-chemicals are not studied quite extensively. However, Shumao *et al.* [17] treated ramie fibre as well as the poly (lactic acid) (PLA) matrix with ammonium poly phosphate (APP) and prepared composites using three processes (1) PLA was blended with APP, and then the resulting blend was combined with ramie fibres (FPLA-NF); (2) ramie was treated with APP and then compounded with PLA (PLA-FNF); and (3) PLA and ramie, both were treated with APP and blended together (FPLA-FNF). The fire performance of these composite materials was checked by LOI and UL94 test methods. In case of UL94 test, both the FPLA-NF and FPLA-FNF composites achieved a V-0 rating and in both the cases dripping was not observed. The effect of FR-treatment on ramie fibre reinforced composite can be clearly understood by LOI test results. It is observed that the control sample has a LOI value of 19.1 while it reaches to 25 in case of PLA-FNF sample and to 28.1 in case of FPLA-NF sample and when both the matrix and reinforcing agent are treated with FR-chemicals i.e. in case of FPLA-FNF samples the LOI value reaches to 35.5.

Table 3. Different types of flame retardant chemicals and their working principle

Flame retardant chemical nature	Example of flame retardants	Working mechanism
Metal oxides and hydroxide	Magnesium hydroxide, Aluminium hydroxide, alumina trihydrate, calcium carbonate	Heat sink
Boron based	Boric acid, borax, Zink borate, boron phosphate	By forming insulating layer
Halogen based	TCPA, TBPA, Polybrominated diphenyl ethers, Polybrominated biphenyl	Gas phase
Phosphorus based	THPC	Condense phase
Synergistic	P/N, Halogen/Antimony tri-oxide, P/halogen	Flame retardancy of the primary compound enhanced by the presence of another
Intumescent	Acid donor (ex-phosphoric acid, ammonium polyphosphate), carbonizing agent (ex-pentaerythritol), bowling agent (ex-melamine, urea)	Both in gas and condense phase

Flame Retardant Treatment for Polymeric Matrix

Matrices of polymeric composite are broadly classified into two main categories such as thermoplastic matrix and thermoset matrix. Both the thermoplastic and thermoset matrices burn rapidly in fire and the flame retardancy of these polymeric materials can be improved in three different ways. These are (i) by adding flame retarding material to the polymer matrix (ii) by incorporating a flame retardant compound into the polymeric backbone (iii) by intumescent system. Nano particles are being extensively added to polymer systems to improve its mechanical properties but in some studies it was reported that nano particles can improve the fire performance of the polymeric system. Thus addition of nano particle is another approach of improving fire performance of polymer matrixes.

The concept of intumescent FR-mechanism relies upon the formation of an expanded carbonized layer on polymer surface during thermal degradation. This layer act as a barrier for heat transfer from heat source to polymer and it also limits the fuel transfer from polymer towards the flame as well as the diffusion of oxygen into the material. An intumescent system mainly consists of three main components: (i) an acid source, (ii) a carbonizing agent and (iii) a blowing agent. When an intumescent system is exposed to fire, depending on the source, some organic acid is released between 150 °C to 250 °C which esterifies the carbon-rich components just above the acid release temperature. During or prior to esterification the acid mixed material melts and then through dehydration the ester decomposes and forms a carbon-inorganic residue and at the same time it also releases some gases which trigger the expansion of carbonized layer. Near completion of this reaction, the melt becomes gel and then solidified in the form of multicellular foam [18,19].

Thermoplastic Flame Retardant Composites

Development of thermoplastic FR-composite is still at nascent stage. Most of the thermoplastic polymers are flammable in nature and help to propagate fire by dripping during burning. Attempts are made to improve the fire performance of these thermoplastic composite materials in different ways. Suppakarn *et al.* [20] have studied the effect of magnesium hydroxide and zinc borate addition to the sisal-polypropylene (Si-PP) composites as a FR-agent. The flammability of these composite materials was checked by horizontal burning test method. It was observed that Si-PP composite burns at a higher rate than neat polypropylene (PP) and when magnesium hydroxide was added to PP matrix, its burning rate decreases with increasing magnesium hydroxide concentration. Zinc borate does not affect the burning rate of PP but the char formation rate increases with increasing zinc borate concentration. However, synergistic effect of zinc borate and magnesium hydroxide was not found when these two were added together to PP matrix. A similar result was observed when magnesium hydroxide with boric acid and zinc borate was added to saw-dust/rice husk-polypropylene (SD-PP/RH-PP) composite [21]. It was found that rice husk filled composites are more prone to flame than saw dust filled composite and when 25 % of rice husk was replaced with magnesium hydroxide, it shows 50 % improvement in the flame retardancy and similar trend was found in case of saw dust filled composite. The composite containing magnesium hydroxide shows a slower burning rate and higher LOI value than the combination of magnesium hydroxide with boric acid or with zinc borate. However, the combination of magnesium hydroxide with boric acid shows lower burning rate than the combination of magnesium hydroxide with zinc borate while the second combination shows the higher LOI value than the first one.

Dvir *et al.* [22] have added pentabromobenzyl acrylate (PBBMA), a halogen based FR-agent and magnesium hydroxide together to glass-PP composite system and it was observed that magnesium hydroxide did not influence the LOI of glass-PP composite but the flaming time in UL94 test decrease significantly with increasing magnesium hydroxide loading percentage. Halogen based compounds are another kind of flame retardants which are quite extensively incorporated inside polymer matrix system for improving FR-behaviour of polymer composite materials. These halogen based flame retardants show very good flame retardancy as compared to metal hydroxide based flame retardants like magnesium hydroxide, aluminium tri-hydroxide etc. To compare the fire performance of magnesium hydroxide and a halogen based flame retardant, Tai *et al.* [23] have added magnesium hydroxide and a mixture of brominated phosphate ester and antimony trioxide to PP composite separately and checked the fire performance of these composite materials by LOI test method. It was observed that 60 % magnesium hydroxide was needed to achieve same degree of flame retardancy offered by 30 % brominated phosphate ester and antimony trioxide mixture.

Chlorinated hydrocarbon (approximate chemical formula $C_{23}H_{28}Cl_{20}$) is another example of halogen based flame retardant. It shows optimum flame retardancy when it was mixed with antimony trioxide at an antimony to chlorine ratio of 1:3. Sheat *et al.* [24] added a mixture of antimony trioxide and chlorinated hydrocarbon to the high density polyethylene and compare its flammability with aluminium tri-hydroxide added high density polyethylene (HDPE) composite. It was observed that antimony trioxide and chlorinated hydrocarbon mixture shows poor synergistic effect due to high crystallinity percentage of HDPE. It provides significant amount of flame retardancy, when 15 % of antimony trioxide and chlorinated hydrocarbon mixture was added to HDPE while about 40 % aluminium tri-hydroxide is required to achieve the same. The metal hydroxides acts as flame retardant through heat sink method while halogen compounds acts through gas phase mechanism and because of the difference in flame retardancy mechanism to achieve

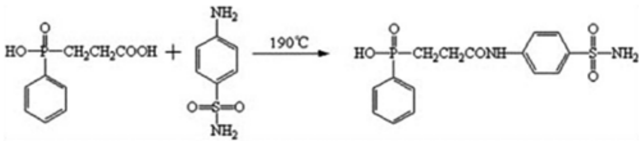

Figure 2. Flame retardant synthesis via melt-condensation [25].

same degree of flame retardancy provided by halogen compound, higher amount of metal hydroxide is required. But, halogen based flame retardants are not environment friendly thus they are being banned in different countries.

Zhao *et al*. [25] have prepared flame retardant glass fibre reinforced poly (ethylene terephthalate) (FR-GF-PERT) composite by incorporating halogen free novel flame retardant. The flame retardant compound contains three flame retardant elements P, N, and Sand was prepared by melt condensation method. Figure 2 shows the novel FR-Agent synthesis route via melt condensation.

It was observed that GF-PET composite achieved V-0 rating in UL94 test when 15 % FR-agent was added while the LOI increases linearly with increasing FR-agent add on upto 26 % where it achieves a LOI value of 32. Matko *et al*. [26] have prepared a series of bio-composites by incorporating alkoxy silane treated wood, corn flake and cotton fibre into polypropylene, polyurethane and starch matrixes and the fire performance of these bio-composites was enhanced by incorporating Ammonium polyphosphate (APP). It was observed that in presence of APP the polysaccharide and polyurethane based bio-composites form more char than the PP based composite and among these three, starch based composite shown more efficient flame retardancy even at lower APP concentration. It was suggested that after their lifecycle these Starch-APP composites can be used as fertilizer.

Another important approach for improving flame retardancy of thermoplastic polymeric composites is by the addition of intumescent flame retardant to thermoplastic polymer matrix. Ammonium poly phosphate (APP) is a well-known flame retardant and extensively used for preparing an intumescent flame retarding (IFR) agent. APP based IFR was prepared by coating APP with hydrophobic Melamine (M) which improves the water resistance and LOI value of APP. Chen *et al.* [27] have added APP and APP based IFR to PP matrix system and compared their fire performance by cone calorimetry, UL94 and by LOI test method. It was observed that the LOI index of IFR-PP composite is 32.5 while in case of APP added composite it was 31. The total time of ignition (TTI), peak heat release rate (PHRR) and total heat release (THR) was lower in case of IFR-PP composite and in both cases V-0 ratting was observed in UL94 test. Wu *et al*. [28] have added APP based IFR to biodegradable PVA/glycerol-plasticized thermoplastic starch (TPS) and checked the combustion behaviour of the composite materials by LOI, UL94 and by micro scale combustion test method. After testing, it was observed that IFR does not affect peak heat release rate of TPS too much but it reduces total heat release significantly. The LOI value for neat TPS was 23 and it cannot pass any rating in UL94 grading system but the addition of 2 % IFS improves its LOI value to 31 and shows a V-0 classification in UL94 grading system. APP is hydrophilic in nature and thus it has poor compatibility with PP and other hydrophobic thermoplastic polymer.

To enhance matrix-IFR compatibility Ma *et al*. [29] have added etched polypropylene (EPP) as coupling agent to APP based IFR-polypropylene composite system. EPP enhance the compatibility between PP matrix and IFR agents by forming miscible blends with bulk PP through co-crystallization and on the other hand by reacting with available functional groups of IFR like -NH_2 of melamine and -OH of pentaerythritol etc. The fire performance of EPP added IFR-PP composite was checked by horizontal combustion test method which showed that the EPP added IFR-PP composite extinguished within 5s and no dipping was found during burning. The flammability of IFS-polymer composites can be improved further by adding some synergistic agent. It was observed that zeolites, organoboron Siloxane can catalyse the esterification

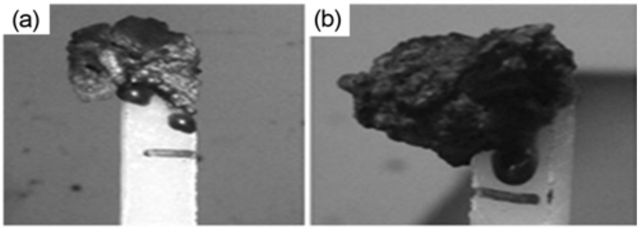

Figure 3. Photographs of LOI test specimen (a) PP/IFR (b) PP/IFR/Sb_2O_3 [34].

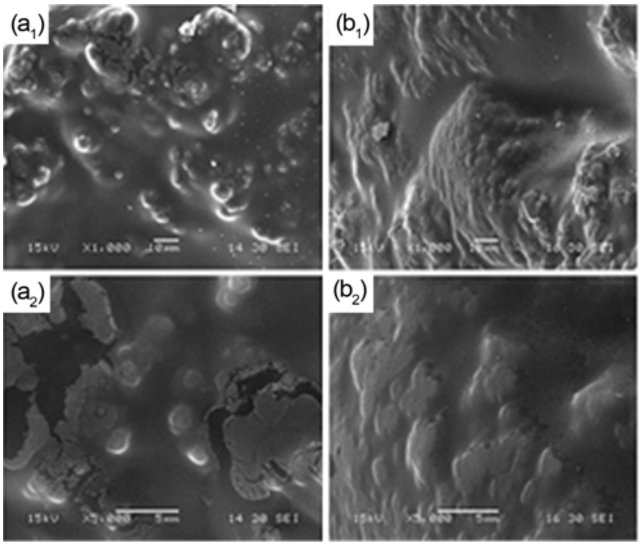

Figure 4. SEM images of the charred layer treated at 400 °C for 30 min in the muffle, (a_1) PP/IFR×1000, (a_2) PP/IFR×5000, (b_1) PP/IFR/Sb_2O_3×1000, and (b_2) PP/IFR/Sb_2O_3×5000 [34].

among IFR components in IFR-PP system while the presence of some synergist like ferric oxide, titanium-di-oxide and aluminium-try-oxide can improve the limiting oxygen index of IFR-PP system effectively [30-33]. Li *et al.* [34] have found that addition of 2 % antimony oxide to PP-APP base IFR (AO-PP-IFR) system improves its LOI from 27.8 to 36.4. Figure 3 shows the photographs of LOI test specimen which indicates that the AO-PP-IFR composite forms more char than the PP-IFR composite. SEM images of charred layer shown in Figure 4 indicate that the char of AO-PP-IFR composite is more compact than PP-IFR composite and some cracks and holes are observed in the charred layer of PP-IFR composite.

Thus during combustion heat and volatiles can easily penetrate through this while the charred layer of AO-PP-IFR composite is less porous and has smoother surface because of possible cross-linked reaction between APP and antimony oxide shown in Figure 5. Similar kind of charred layered was observed by Li *et al*. [35] when lanthanum oxide was added to PP-IFR (APP+ Char Forming Agent (CFA)) matrix. Figure 6 shows the chemical structure of CFA.

Polyol based char forming agents like pentaerythriol, mannitol, sorbitol etc. are hydrophilic in nature and are also associated with migration problem thus these are not compatible with the thermoplastic polymer system. These problems are solved by the synthesis of new types of intumescent.

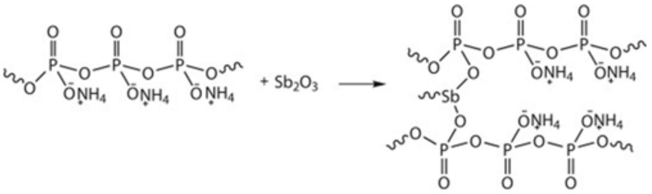

Figure 5. Schematic illustration of the reaction of APP and Sb_2O_3 [34].

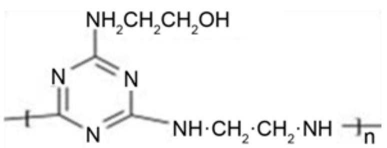

Figure 6. Chemical structure of CFA [35].

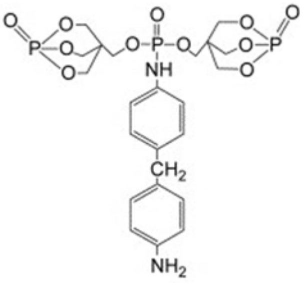

Figure 7. Chemical formula of P-N based novel IFR [36].

Gao *et al*. [36] have prepared phosphorus-nitrogen based novel intumescent flame retardant (NIFR) shown in Figure 7 via the reaction of PEPA, a phosphorous based compound and DDM a nitrogen based compound and added this newly developed compound to poly (butylene terephthalate) (PBT) and checked its flammability by UL94 test method.

It was observed that when 20 % newly developed IFR was added to PBT matrix it achieves V-1 retting in UL94 test but it achieves V-0 retting while 10 % polyurethane was added along with 20 % IFR. Melabis and b-MAP synthesized by the reaction of phosphoryl trichloride, pentaerythritol and melamine shown in Figure 8 are examples of similar kind of novel IFR flame retardants. It was observed that these flame retardants are insoluble in water, having minimum leaching problem and show better flame retardancy than the halide based flame retardants. Because of the long rout three steps synthesis process and lower yields in industry scale production these novel IFR are not so popular [37,38].

Fontaine *et al.* [38] have synthesized another novel IFR which is shown in Figure 9 by mixing three starting material in one step which shows very good yield and this newly developed flame retardant shows very good flame retardancy when it is added to polypropylene along with zinc borate.

It was observed that when 30 % NIFR was added to PP matrix its LOI index reached to 30 from 18 (for virgin PP) and when 2 % NIFR was replaced by zinc borate its LOI became 39 and in both cases V-0 rating was observed in UL94 test. To check the leaching/migration effect, NIFR-PP

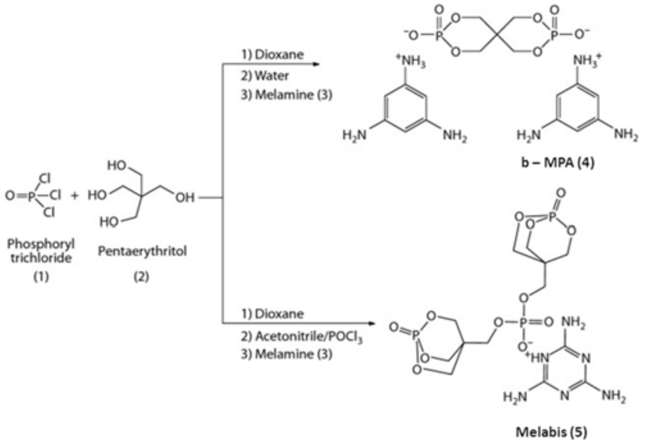

Figure 8. Synthesis method of b-MAP 4 and Melabis 5 [37].

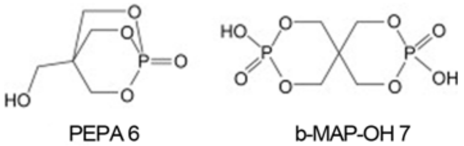

Figure 9. Chemical structure of PEPA 6 and b-MAP-OH 7 [38].

composites were immersed in water at 60 °C for 8 days. It was found that after immersion LOI index of NIFR-PP composite decreases to 28 and in case of 2 % zinc borate added NIFR-PP composite the LOI index becomes 33 and in both cases V-0 rating isobserved in UL-94 test.

Another approach of improving fire performance of thermoplastic composite is by the incorporation of flame retarding agent into polymer backbone or by grafting method. Livshits [39] and Needles [40] have done a lot of work on grafting and express grafting, a novel approach to improve the flame resistance of polymers. Grafting can be done by using different techniques such as grafting initiated by chemical means, by radiation techniques, by photochemical grafting and by plasma radiation induced grafting [41]. Zhang *et al.* [41-43] observed that the fire performance of polypropylene grafted with acryl-amide (AAm) is much better than that grafted with methacrylic acid (MAA) and acrylic acid (AA) and it was also noticed that saponification of grafted sample enhance flame retardancy by promoting the char formation.

Ferry *et al.* [44] have observed that brominated monomer improves fire resistance of glass fibre reinforced polypropylene composite where brominated monomer was grafted either onto the PP matrix or onto the glass fibre by polymerizing around the Sb_2O_3 particles or onto both. It was observed that grafting of brominated monomer dose not strongly modify the fire performance of the composites but when some $Mg(OH)_2$ was added to this system it shows sufficient flame retardancy: an LOI of 31.8 and V-0 classification in UL94 test method.

Thermoset Flame Retardant Composites

Like thermoplastic polymer composites thermoset composites also burn rapidly in fire. Manfredi *et al*. [45] have prepared a series of composites using mod-acrylic and unsaturated polyester as matrices and jute, flax, sisal and glass as reinforcing material and compared the flame retardancy behaviour of these composite materials. It was noticed that flax fibre reinforced composite releases the highest amount of heat while glass fibre reinforced composite shows the lowest release. At the same time flax composite shows large flashover zone which indicates that it will offer longest time to escape or to extinguish the fire and jute composite releases least quantity of smoke volatiles than other composites and burns quicker than other natural fibre composites. Among unsaturated polyester and mod-acrylic resins, the latter shows a longer flashover zone and releases more heat than the first. During burning, mod-acrylic forms a char layer which is not found in case of unsaturated polyester resin. The fire risks of all composites were compared by plotting the total heat evolved against the peak heat release rate divided by time to ignition. It was observed that glass reinforced unsaturated polyester composite shows the least fire risk compared to other composites but none of these were flame retardant in nature.

Like thermoplastic composites, thermoset composites are also still at the nascent stage as far as the improvement in fire retardant properties are concerned and like thermoplastic composites, flame retardancy of thermoset composite materials can be modified in different ways. Boron containing compound like mixer of borax and boric acid have some efficiency in retarding flame spread. In addition to usual char forming catalytic effect, they also have a low melting point and form a glassy film around the burning component when expose to fire.

Baysal *et al.* [46] have treated sapwood with 1 % borax and boric acid (1:1) mixture and then prepared vinyl monomer-wood composites. Styrene, methylmethacrylate and the mixture of Styrene and methylmethacrylate (50:50) was used for vinyl monomer-wood composite preparation. The fire performance of the composite materials was evaluated in terms of weight loss after fire test and the test results showed that the weight loss percentage decreases significantly when sapwood was treated with 1 % borax and boric acid (1:1) mixture. Fernandes Jr. *et al.* [47] have added decabromine diphenyl oxide associated with antimony trioxide as additives to unsaturated polyester matrix to enhance the fire performance of sisal-polyester composite, where the additives were added to the polymer system by high shear mixing prior to the addition of the curing catalyst. The fire performance of sisal-polyester and flame retardant added sisal-polyester composite were checked by UL94V test and it was found that sisal-polyester composite burns completely while the flame retardant added sisal-polyester composite achieved a self- extinguishment in 0.72s which resulted in a V-0 classification, a very high security standard for polymer system.

In another study, Kandola *et al.* [48] have added inherently flame retardant cellulosic fibre visil and Phenol-formaldehyde (keynol) fibre and antiblaze NH, a phosphate based intumescent and combination of flame retardant fibre and intumescent to the glass-epoxy composite and evaluated the flame retardancy behaviour of all composites by LOI test and by cone calorimetric test method. Glass-Epoxy composite shows a LOI of 27.5 and it reaches to 35.2 when 5 % intumescent was added to it, and reaches to 36.2 while 5 % visil fibre was added along with 5 % intumescent, but 5 % kynol and 5 % intumescent combination shows a LOI index of 30.2 which was not so effective. The cone calorimetry test at an incident heat flux of 50 kW/m^2, shows that the time of ignition of all the composites were between 24 to 31s and the peak heat release rate was upto 54 % less and the combustion period is prolonged when compared to control specimen. FR-composites evolve more char than the control sample, this is due to chemical reaction of intumescent and visil fibre with the epoxy resin during thermal decomposition.

Perret *et al.* [49] added 9,10-dihydro-9 oxy-10-phosphaphenanthrene (DOPO) based flame retardants to carbon fibre reinforced epoxy composite (CFREp) system and investigated their fire performance in terms of LOI and UL94 test method. It was observed that DOPO based compounds act in gas phase through flame inhibition as well as in condensed phase through char formation. Addition of DOPO based FR-agent to epoxy matrix achieved a V-0 rating from NR in UL94 test while the LOI index reached to 38 from 25. The incorporation of carbon fibre to DOPO added epoxy resin enhances its LOI from 38 to 43 but it suppressed charring thus in case of CFREp composite DOPO based flame retardants acted only via flame inhibition mechanism.

Abdullah *et al.* [50] have prepared coconut fibre reinforced polyester composite (CFRPC) by incorporating sodium hydroxide and silane treated coconut fibre inside unsaturated polyester resin prepared from waste PET. Dicron, a phosphate based flame retardant was added to CFRPC system to enhance its fire performance. It was observed that silane treatment of coconut fibre increases the hydrophobicity of coconut fibre thus untreated coconut fibre reinforced polyester composite shows better flame retardancy when compared to silane treated coconut fibre reinforced polyester composite. However, when Dicron was added to polyester matrix, saline treated coconut fibre composite shows better flame retardancy over the untreated fibre composite. The burning time and LOI index of silane treated composite increases with increasing Dicron add-on upto 5 wt% but after that it decreases while in case of untreated composite it increases continuously with increasing Dicron add-on.

Another important approach of enhancing flame retardancy of thermoset composite is by incorporating flame retardant compound into the polymer backbone. Series of flame retardant epoxy resin were being developed by incorporating phosphorus based compound into the epoxy polymer backbone where phosphorous based compounds were introduced either as a part of the curing agent or as a part of an epoxy monomer. These newly developed epoxy polymers show excellent flame retardancy even at low phosphorous concentration [51,52].

Lu *et al.* [53] have summarized the chemistry of halogen free FR-polymers where P, N, Si containing compounds and other miscellaneous compounds are being incorporated into the backbone of different polymer or reactive monomer like epoxy, polyvinyl, polyester, polyamide, polyurethane resins etc. These modified flame retardant polymers can be used on their own or added to bulk commercial polymers to enhance fire performance of composite system.

Derouet *et al.* [54] have prepared epoxy-amine resin having good flame retardant property by reacting bisphenol-A with dialkyl(or aryl) phosphate which was followed by curing in the presence of 4,4'-diaminodiphenylsulfone (DDS). Organ phosphorus groups were introduced into the thermosetting epoxy resin structure by formation of stable covalent bond between P-OH groups of dialkyl(or aryl) phosphate and O-glycidyle ring of epoxy resin. Figure 10 shows the reaction of alkyl(or aryl) phosphate with epoxy resin. The flammability of modified epoxy resin was studied with LOI test method and it was observed that modified epoxy resins flammability depends on the nature of the phosphate compound and their concentration in the epoxy resin.

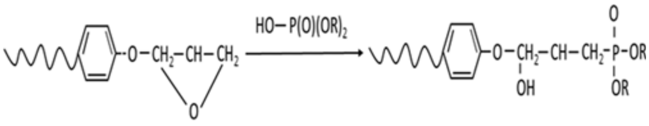

Figure 10. Reaction of alkyl (or aryl) phosphate with epoxy resin [54].

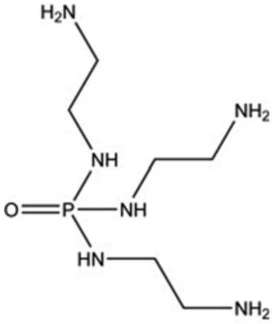

Figure 11. Chemical structure of TEDAP [55].

Toldy *et al.* [55] have developed phosphorus containing reactive amine TEDAP, shown in Figure 11. It is used as a crosslinking agent as well as a flame retardant for aliphatic and aromatic epoxy resins system. Using this newly developed epoxy resin, carbon fibre reinforced epoxy composite was prepared. It was observed that aromatic epoxy has higher LOI value than the aliphatic epoxy resin. But the addition of reactive flame retardant curing agent makes aliphatic epoxy more flame retardant than aromatic and similar kind of result was observed in case of carbon fibre reinforced epoxy composites. In cone calorimetric test it was observed that the incorporation of carbon fibre significantly reduces the PHRR and THR but the incorporation of carbon fabrics layers hinders the intumescent effect of phosphorus thus instead of forming a well charred layer a thin char layer was observed in between carbon fibre plies.

Improving Flame Retardancy by Adding Nano Particles

The mechanical properties of fibre reinforced polymeric composite materials are affected significantly by the addition of conventional micro-sized flame retardant fillers which is not desirable for different uses of composite materials. Nano materials have higher surface energy due to their nano scale dimensions and when these nano particles are dispersed properly into the polymeric matrixes are known to improve thermal, mechanical and fire performance properties of the composite materials. Sometimes it was observed that nano sized flame retardants can reduce the loading percentage for achieving the same degree of flame retardancy. Mainly four types of nano materials are added to the polymer matrices to improve its fire enactments. They are i) Layered nano materials such as nano clays, ii) Fibrous nano materials such as carbon nano tubes, iii) Nano sized polyhedral oligosilsesquioxane and iv) Nano sized metallic oxides and hydroxides. Laoutid *et al.* [56] have recently reviewed the new prospects of flame retardancy of polymer composite materials achieved by adding nano particles to polymer matrixes and also explained the flame retardancy mechanism of different nano particles. It was concluded that nano clay particles improves flame retardancy of nano clay/polymer composites by forming a barrier against heat and volatiles through the migration of nano particle towards the polymer surface which leads to char formation. The fibrous nano materials i.e. carbon nano tubes, multi wall nano tubes and silsesquioxane materials improve the fire performance of the composite material through enhancing char formation only. Nano clays, carbon nano tubes and silsesquioxanes all the three types of nano materials improves the fire performance of composite materials but not so significantly while the nano metal oxides and hydroxides are quite impressive.

Laachachi *et al.* [57] have added titanium oxide and ferric oxide nano particles to poly (methyl methacrylate) (PMMA) polymer and studied the flammability by cone calorimetry test method. It was observed that presence of 20 % titanium oxide nano particle reduces 50 % peak heat release rate while same amount of ferrous oxide nano particle reduces only 35 %. The time of ignition increases significantly while titanium oxide nano particle are added to PMMA but Addition of ferrous oxide nano particle does not affect the time of ignition of nano-PMMA composite and at the same time it evolves more smoke than virgin PMMA composite.

Mishra *et al.* [58] found that addition of nano magnesium hydroxide to polypropylene composites improves its fire performance quite significantly where the fire performance of nano magnesium hydroxide-PP composite was checked by assessing burning rate per second. It was observed that as compared to neat polypropylene, a 35 % improvement in the flame retardancy was found when 12 wt% nano magnesium hydroxide was dispersed in polypropylene. Murariu *et al.* [59] have prepared poly (lactic acid) (PLA) based nano composite by adding nano calcium sulphate to PLA matrix. Two organo modified layer silicates (OMLS) i.e. Bentone 104 and closite 30B were further added to nano calcium sulphate/poly (lactic acid) composites for further improvement in flame retardancy. Flammability of OMLS- nano calcium sulphate/poly (lactic acid) composites were evidenced by cone calorimetry and UL94V test methods. Addition of OMLS and nano calcium sulphate to poly (lactic acid) matrix improves the flammability of nano calcium sulphate/poly (lactic acid) composites leading to high time of ignition and to a lower peak heat release rate.

Flame Retardant Composites by Protective Coating

This novel approach can enhance the fire performance of composite material without affecting the matrix-reinforcement interaction. The flame safe coatings are mainly classified into two categories: i) intumescent based coating and ii) non-intumescent coating. FR-coatings are being widely applied on textiles, electrical and electronic devices, building constructions etc. Bourbigot *et al*. [60-63] have done a lot of work on intumescent based flame retardant coating and recently weil *et al.* [64] have reported a review article entitled fire protective and flame retardant coatings- a state of the art which is on intumescent based FR-coating. Liang *et al.* [65] reported a review article on non-intumescent based FR-coating where they described different traditional and new method of flame retardant coating and different new developments in FR-chemistry for coating application. However, FR-coatings on polymeric composite material for enhancing fire performance have not been studied in depth. Fire performance of composite material by providing different protective FR-coatings is discussed below.

Inorganic Coating

Inorganic materials are widely incorporated in macro and nano form for developing flame retardancy behaviour in polymeric composite materials as already discussed above. Metal hydroxides, such as aluminium hydroxide [$Al(OH)_3$], magnesium hydroxide [$Mg(OH)_2$], ammonium polyphosphate [NH_4PO_3] boron salts, inorganic compounds like antimony, tin, zinc etc. are the example of inorganic flame retardants which are being significantly used for coating purpose. Coatings of inorganic materials are mainly carried out by hand layup or by spraying method. Albdiry *et al.* [66] have coated carbon and Kevlar (50:50) reinforced araldite resin composite with zinc borate and antimony trioxide. The fire performance of this coated composite was determined by conducting heat erosion test where the test results were expressed in terms of time required to break down the coated layer. It was observed that time required to breakdown the coated layer increases due to formation of complex char layer formed by the synergistic effect of zinc borate and antimony trioxide.

Intumescent Coating

Intumescent flame retardants are the new types of fire retarding agents which are quite extensively incorporated in polymeric composite system for improving fire performance as already discussed. Intumescent based flame retardants are also coated on composite material for improving its fire performance. Gu *et al.* [67] have prepared an intumescent based FR-coating using polyester and epoxy resin along with APP as an acid donor, melamine as a blowing agent, pentaerythritol as a carbonizing agent and pandable graphite as synergistic agent and its thermal behaviour was checked by DSC and TGA Methods. Kandare *et al.* [68] have applied an intumescent based FR-coating(containing an epoxy base resin, bisphenol F epichlorohydrine, ethyle hexyl glycidyl ether, 2,4,6-tris (dimethylaminomethyl) phenol, triethylenetetramine) on glass-epoxy composite and compared its fire performance with a char forming non-intumescent based coating (containing tricresyl phosphate in propane-2-ol) and with a flame-inhabiting formulation (containing chlorinated paraffin). Fire performance of all the composites were checked by cone calorimetric test at 25, 50 and 65 heat flux. It was observed that intumescent coated composite shows high time of ignition and takes more time to reach 150 ^{o}C on the backside of composite. It also shows lower peak heat release rate (PHRR) and total heat release (THR) when compared to other coated and non-coated composites.

Ceramic Coating

Ceramic materials have poor thermal conductivity and can withstand high temperature thus a protective ceramic layer on core composite can improve the fire performance of core composite materials. Due to high temperature formulation, direct ceramic coating on engineering plastic cause damages like warping, charring, melting etc. To overcome this problem ceramic materials are applied in bond coated form on the polymer composite surface. Hanua *et al.* [69] have prepared a ceramic layer by air-combustion of silicon based polymer and further improved the strength of ceramic by adding some inorganic filler. It was proposed that this silicon based ceramic can be applied as a protective flame retardant on other material. Feih *et al.* [70] have applied a soft flexible ceramic (supperwool 607) on a glass-epoxy composite material which is stable upto 1300 ^{o}C. A thermo-mechanical model was developed using this composite material which can predict the strength loss and time-to-failure of composites with thermal barrier insulation material under combined compressive loading and one-sided heating by fire.

Sorathia *et al.* [71] have developed different types of coated composite configuration and checked their fire performance according to MIL-STD-2031-(SH). In this study glass/vinyl ester, graphite/epoxy, graphite/bismaleimide and graphite/phenolic composites were coated with ceramic coating, intumescent coating, hybridization, silicon foam and with phenolic skin. The flammability of all configurations was determined by cone calorimetric test. The fire performance test result shows that the intumescent and a hybrid of intumescent and ceramic coatings were the most effective fire barrier treatments for composite systems. Using either of these fire barrier treatments, all composite systems met the ignitability requirements of 90 s and 60 s at 75 kWm^{-2} and 100 kWm^{-2} respectively, except glass/vinyl ester composite system.

Effect of Flame Retardant Treatment on Other Composite Properties

Polymeric composite materials are widely used in different areas where flame retardancy is one of the most important requirements. It is observed that flame retardant treatment not only affect the fire performance of composite materials it also affects the other composite properties which are discussed below.

Matrix Viscosity and Fibre-Matrix Interaction

Melt viscosity (for thermoplastic polymer) or resin viscosity (for thermoset polymer) plays an important role on different composites properties like void content, matrix-reinforcement interaction, mechanical properties etc. It was observed that addition of flame retardant compound to polymeric matrix system influences its rheological properties quite significantly. The shear viscosity of thermoplastic polymer melt increases with increasing micro sized flame retardant content and this rate of increase, decreases with increasing load or temperature. In case of PP matrix system when particle size of $Al(OH)_3$ or $Mg(OH)_2$ is smaller than 5 μm, melt viscosity increases with increasing particle size after that it decreases with increasing particle size [72]. Fibre matrix interaction of fibre reinforced polymer composite system is mainly expressed in terms of its tensile property. Generally it was observed that a composite having good fibre matrix adhesion shows good tensile property and vice a versa. In case of fibre reinforced polymer composite when polymer matrix was modified by incorporating micro sized FR-filler, its tensile strength decreases and when the reinforced fibre or both the matrix and reinforced fibre were modified then its tensile strength increases [17]. FR-treatment of reinforce fibres makes the fibre surface rough which leads to better fibre matrix adhesion and better tensile strength of composites.

Mechanical Properties

The mechanical behaviour of a composite material is mainly expressed in terms of their tensile behaviour, flexural property and impact property. It is observed that the mechanical property of a composite material is greatly affected by different FR-treatment. Metal hydroxides are being extensively used for improving fire performance of composite material which is already discussed above but the addition of these materials has a negative impact on mechanical behaviour of composite materials. Suppakaran *et al.* [20] found that in 30 % sisal-PP composite if 15 % sisal is replaced by Magnesium hydroxide ($Mg(OH)_2$) or a mixture of $Mg(OH)_2$ and zinc borate its tensile strength decreases due to poor compatibility between PP and flame retardants.

It was found in case of flexural property that the flame retardant added composite shows higher impact strength than

30 % sisal-PP composite. The impact strength of a composite material is greatly affected by high loading of fillers because they disturb matrix continuity and each filler is a site of stress concentration and initiate micro-cracks. The particle size of flame retardants is smaller than sisal fibre thus flame retardant has a lower impact on impact strength. Sain et al. [21] tried to improve the compatibility between matrix and flame retardant by adding coupling agent E-43. It was observed that despite the presence of coupling agent, addition of Magnesium hydroxide to rice husk and saw dust filled PP composite shows a reduction of 15 % and 17 % in flexural and tensile properties respectively while the impact behaviour was not affected too much by magnesium hydroxide addition. Misra *et al*. [56] have found that with increasing nano filler loading percentage the tensile strength of nano-$Mg(OH)_2$ to PP composite system increases continuously and it shows 86 % improvement in tensile strength at 4 % loading while 433 % improvement was observed in case of Young's modulus. Impact property of nano-$Mg(OH)_2$-PP composite decreases with increasing nano filler concentration upto 4 % and after that it becomes stable. It was observed that to achieve a same degree of flame retardancy less amount of halide based flame retardant is required when compared to metal hydroxide based flame retardant. In case of composites made of same matrix having same degree of flame retardancy, metal hydroxide added composite shows lower tensile and impact property than halide based flame retardant added composite due to low add-on percentage of halide based flame retardant. But with same add-on percentage, metal hydroxide added composites show better tensile property than halide based flame retardant added composites [23].

Addition of antimony oxide to PP-IFR system shows that its tensile strength increases upto addition of 1 % antimony oxide and after that it decreases with increasing antimony oxide concentration while same kind of result was observed in case of bending strength and impact strength [34]. Kandola *et al*. [73] found that the addition of phosphate based intumescent and the mixture of intumescent and inherent flame retardant fibre to glass-epoxy composite dose not reduce the flexural modulus and in some cases it increases slightly while its tensile modulus decreases with additives. It was concluded that the addition of additives does not affect composite's tensile property; the lower tensile strength of additive added composites is due to lower glass fibre content. Mechanical property of core composite material is not affected by protective flame retardant coating but post heat mechanical property gives the idea about coating property. It was generally observed that composite's mechanical property deteriorates with increasing applied heat flux and exposure time.

Thermal Property

Thermal analysis of polymer composite plays an important role in the study of flame retardant composite. This provides important information for the evaluation and development of flame retardant composites through thermal decomposition profile [47]. Thermal behaviour of composite materials is mainly analysed by Thermo-gravimetric analysis (TGA). It was observed that among all the natural fibres which are being extensively incorporated inside the polymer matrix, flax shows highest thermal stability due to its lowest lignin content [45].

It was observed that addition of flame retardants to polymeric matrix system greatly affects its thermal property. Suppakaran *et al*. [20] observed that virgin PP start thermal degradation at 390 ^{o}C in nitrogen atmosphere and at 270 ^{o}C in oxygen atmosphere. The addition of $Mg(OH)_2$ to PP matrix increases its starting degradation temperature to 394 ^{o}C and 272 ^{o}C in nitrogen and oxygen atmosphere respectively. While the addition of natural fibre to PP matrix system decreases it's starting degradation temperature as the hemicellulose and lignin part of natural fibre start degradation at lower temperature. Mishra *et al.* [58] found that with the addition of nano $Mg(OH)_2$ to PP matrix initially decreases its melting temperature about 0.2 ^{o}C at 4 % loading and after that it increases 0.8 ^{o}C at 12 % loading. The difference in melting temperature is mainly due to even distribution of nano particle in PP matrix. Chen *et al*. [27] have found that APP based IFR added PP composite degraded at a higher temperature when compared to APP added PP composite. But the addition of APP based IFR to PP matrix decreases its starting degradation temperature as APP starts to degrade at lower temperature [29].

Conclusion

In this review, a broad range of flame retardant systems used for polymer composites that have been studied and reported in the literature have been analysed and categorized critically. Attempt has been made to understand the mechanisms of flame propagation and different fire extinguishing approaches. Various approaches that can be adapted for improving fire performance behaviours of the composite materials have been studied and how properties of the composite materials change with the addition of FR-materials have been studied.

Although significant amount of work has been done for improving fire performance of polymeric composite material but still lot of scope is there for further improvement. From literature it is observed that for obtaining good quality FR-composites more than 15 % flame retardants (micro sized) have to be added to polymer matrix system which deteriorates its mechanical property quite significantly. However halogen based flame retardants can improve composite flame retardancy at lower concentration (when compared to metal hydroxide compounds) but presently these are being banned for their environment hazarding behaviour. Nano sized flame retardants are providing good flame retardancy at lower concentration but these are also being banned for their health hazardous nature due to nano sized dimensions. Intumescent flame retardants are the new types of flame retardant materials which improve composite materials flame retardancy significantly but still a lot of research is required for further improvement of this kind of materials.

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