Progression in Fire Retardant Properties of Polymer Composites – A Review

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Abstract: Emerging new composite materials from existing materials is the actual challenge for the greater part of the material engineers. In this way, there are enormous inspections, attempts rising in the field of composites to compose new materials with the updated mechanical, electrical and thermal properties. The available articles dependent on the thermo-mechanical investigation of epoxy polymers and other polymer matrix composites with various fibre reinforcement methods are deficient and are less useful. Therefore, this survey focuses on the use of thermal investigation tests and parameters to contemplate thermal properties of (Glass Fibre Reinforced Epoxy Polymer Composites) GREP composites. This survey additionally refreshes the exploration that has been acted in the ongoing years on the frontage of thermal behaviour of advanced materials for various applications.

1 Introduction
In recent days, the application of glass fibre based reinforcement in composite structures are seems to be wide and large due to its improved mechanical behaviour in polymer composites. Due to high mechanical properties, it is used in several developing industries such as: Automotive, Aircrafts, Ships, Electrical & Electronics appliances and Sporting products. The reason for GREP usage is, the most fascinating because of its sufficient consumption in various applications which fit in various structural components [1-3].

Epoxy Polymer (EP) resin has become the most used polymer matrix with glass fibre. EPs are generally utilized as matrices in advanced composites because of their great impregnation and adhesion to fiber strengthening, bringing about incredible mechanical execution; chemical and electrical resistance and low shrinkage on cure. Their utilization is specifically advocated in application zones where their specialized points of interest balance their greater expenses contrasted with other thermosetting polymers, for example in aviation industry. However, due to its restricted advantage of inherent lower thermal conductivity and stability, their wide range of application is restricted, especially where excellent heat dissipation and low thermal expansion are necessarily required [4-5].

In the recent years, scientists made intentional endeavours so as to change the properties of epoxy with the consideration of added substances or fillers to expand the framework commanded composite
properties. Anyway the flammability/combustibility of EPs despite everything speaks to a confinement in basic applications as an incidental fire occasion includes wellbeing dangers, yet in addition loss of mechanical properties.

So, the natural flammability of epoxy polymer matrices prompts fire risk for GREP composite products. It brings large concern of need for improving the fire retardant property of GREP.

2 Combustion of Polymers and Various Fire retardants

Combustion of polymers is a multi-staged process and it is due to its physical and chemical reactions. As shown in Figure-1, the three factors: Heat, Fuel and Oxygen are coexisting to initiate and sustain the combustion of polymers. So the interruption or retard of combustion process is also realized by its physical actions and chemical actions as in the same way.

The physical action of retardant can be applied by sustaining the combustion through (i) an endothermic process; (ii) formation of protective char layer; and (iii) addition of fillers/additives [6-7].

These methods are work as follows:

- Through an endothermic process, cooling is allowed to the underlying polymer to a certain amount of temperature below the critical temperature to sustain the combustion level.
- The protective char layer serves as heat shield to prevent the transfer of both combustible fuels and oxygen between the flame and pyrolysis zone.
- The addition of fillers and additives can change inert non-combustible gases to dilute the fuel.

Other than, addition of flame retardants, can hunt and terminate the active H• and HO• radicals in the gas phase [7-9]. There are six more fire retardant chemistries for selection which is having more advantage than each other individually, as listed in table-1.

### Table 1. Various fire retardant categories and its characteristics

| Flame Retardants (FR) | Additives | Advantage | Disadvantage | PMC used | Ref |
|-----------------------|-----------|-----------|--------------|----------|-----|
| 1. Halogenated (Organobromine, organochlorine) | - Brominated FR | - soluble in polymer | - unacceptable losses in mechanical properties | - Epoxy - Vinyl esters | [10] |
| | | - tendency to lower $T_g$ | - Release large smokes and CO | | |
| | | - ignition resistance and self-extinguishing behavior | - Release corrosive gases | | |
| | | | | | |
| 2. Phosphorus | - intumescent additives | - based on polymer, chemical structure it will be act as vapor-phase and condensed-phase active flame retardants | - some phosphorus-based are plasticize the matrix | - | [8] |

![Figure 1 Fire Triangle](image)

- [Image](image)
| 3. Mineral Fillers | Metal hydroxides, carbonates | good to face the most fire safety criteria | smoke release and fire performance shortcomings exist | Epoxy \([7,12]\) |
|-------------------|-----------------------------|------------------------------------------|--------------------------------------------------|---------------------------------|
|                   | - by use of non-flammable gases it will dilute total fuel at combustion | - low smoke release rates | - limited use during fire | |
|                   | - Effective fire resistant | | - effectively resist fire at early stage but not after | |
|                   | | | - cannot use alone, as fire retardant | |

| 4. Intumescent Flame Retardants | Carbon based char, pentaerythritol | protect the flame affected area | Cannot blend directly, can apply at the surface only | Epoxy \([7,9]\) |
|-------------------------------|-----------------------------------|--------------------------------|--------------------------------------------------|---------------------------------|
|                               | - good ignition resistance, self-extinguishment | - lowered heat release | - Absorb water and durability of the coating is questionable, | |
|                               | - yield good time-to-temperature | | - corrosion and weight issues due to water absorption | |

| 5. Inorganic/Ceramic Forming | zinc stannate, zinc hydroxyl stannate, ammonium molybdenate, | can form ceramic reinforced thermally stable chars on the top surface | Since it is inorganic, are not phase-miscible with many polymers |  |
|-----------------------------|-------------------------------------------------------------|-------------------------------------------------|------------------------------------------------|---------------------------------|
|                            | | | | |

| single molecules | - DOPO \((9,10\text{-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide})\) | - having a mix of vapor-phase and condensed-phase activity | - difficult to process | [7-8] |
|-----------------|---------------------------------------------------------------|---------------------------------------------------------------|----------------------------------------------------|------------------|
|                 | - very good hydrolytic stability | - higher heat leads to loss in mechanical properties | | |
|                 | | - more vapor-phase active produces more smoke and corrosive gases | | |
|                 | | - difficult to synthesize | | |
|                 | | - more expensive | | |

| Oligomeric Species | - Fyrol ™ PMP (Poly methylphenyl phosphinate) | - oligomeric phosphorus act as condensed-phase active flame retardants | - If not encapsulated, it leads to health and corrosion issues | Epoxy | [11] |
|-------------------|---------------------------------------------------------------|---------------------------------------------------------------|--------------------------------------------------|---------------------------------|
|                   | - red phosphorus | - good hydrolytic stability | - Proper encapsulation leads good flame retardancy at low loadings | - provide protection in time-to-temperature | - Epoxy Polyurethanes | |
|                   | | | - works through a char formation mechanism during burning | - protect from structural failure types of fires | | |

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Zinc borates - resistance - reduced flame spread - improved heat release performance - problem in processings - loss of mechanical properties - sometimes act as co-cured fire protection barrier

- geopolymers - superior fire performance - high level of fire safety performance - FRP, aerospace applications

6. Polymer nanocomposites - Lower heat release rate - Provide anti-drip behavior to thermoplastics - Some are have worse ignition resistance - Polymer viscosity cause challenge in fabrication - Chance for voids and dry-spots is usual

Although the fire property of composite is not only depending on the added filler, also by its own constituent materials that is fibre as well as resin, which is supposed to have a negative response to the heat.

2.1 Effect of Fibres in Fire Retardants

In general, even though the flammability in polymer matrix composites is more over controlled by the selection of polymer, the choice of fibre and the quantity can have the effects on the fire safety performance and flammability during various firing circumstances. Most reinforcing fibres are carbon, glass and aramids in PMCs for high performance industrial applications usually in aerospace, automotive applications. Exotic fibers such as metals, ceramic, basalt materials are also used but not frequently as compared to the usual one because of inadequate reach of end demands and level of performance. Eventually the fibre is used to attain the mechanical performance nevertheless flammability is not a design requirement for the choice of fibre in the development of PMC. The effect of kind of fibre on flammability in PMC may quite simple or difficult based on the type of test the flammability [7, 10].

| Type of Fiber | Flammability Characteristics | Ref |
|---------------|-------------------------------|-----|
| Glass         | Generally non-combustible    |     |
|               | Poor thermal conductivity    |     |
|               | At very high heat flux it can melt-decompose-degrade | 13  |
| Carbon        | Not fully non-combustible, but decreased heat release rate | 13  |
|               | Thermally conductive along its axis |     |
|               | At very high heat flux it will burn |     |
|               | Difficult to extinguish the fire flow |     |
|               | Cause inhalation and exposure hazards |     |
| Aramid        | fibers tend to char or ash when exposed to fire | 13  |
|               | Burn away faster than carbon fiber |     |
|               | Low peak Heat release rate    |     |
|               | Burning time is large compared to carbon and glass fiber |     |
| Thermoplastic | Rapid deformation due to melt and deform process when exposed to heat and flame | 14  |
|               | Worse flammability            |     |
|               | Increased flame spread / fire flow |     |
Will destroy the mechanical properties easily

- Natural (Cellulosic) fibers will burn when exposed to flame
- Negative contribution to flammability performance
- Addition of fire retardants is must required for better flammability performance

2.2 Effect of Polymers in Fire Retardants

The chemical structure of the polymer is the basic key to resolve the combustion and heat release rate of polymer with its atoms whether it drips or chars during burning. For the most PMCs thermoset polymers are the dominated material over the thermoplastic polymers. The reason is thermoset polymers tend to hold in place when exposed to fire whereas thermostos tend to deform and flow and in some cases drip, while exposed to fire. Meanwhile there is also some exceptional cases on both thermosets and thermoplastic polymers, like PEEK (Poly ether ether ketone), PVC (Poly vinyl chloride) etc. [10].

2.3 Effect of Fillers in Fire Retardants

Flame retardants (FR) are the chemicals that are added to composite materials focused to prevent or/and slower the further development of ignition by various physical and chemical procedures. There are three wide categories of flame retardant additives as listed in table-3.

| Category | FR type | Mechanisms |
|----------|---------|------------|
| I        | vapor phase reactants | Includes FR chemistries that inhibit combustion through chemical reaction. eg. Halogenated additives, Phosphorus |
| II       | endothermic decomposing diluents | Cools the decomposing polymer by means of releasing non-flammable gas that dilutes the fuel. eg. Mineral fillers that releases water and CO₂ |
| III      | condensed phase char formers | Comprise FR chemistries for cross linking the decomposing polymer into a more thermally stable char |

Based on the working mechanism each category has its own advantage and limitation, however it is the need of time to propose and suggest eco-friendly form of fire retardants which may release no or less hazardous, corrosive gases and as well as decreased effect on mechanical property degradation.

3 Thermo mechanical Analysis of Recent Epoxy Polymer Blends

Thermo mechanical analysis is a technique to study the thermal behaviour of designed material using several tests with the application of heat/temperature. It is to be necessary to evaluate the fire behaviours of designed composites to improve its thermal behaviour. To evaluate the fire behaviors of composites, cone calorimetry test is performed. Several important detailed data such as time to ignition (TTI), peak heat release rate (pHRR), total heat release (THR), total smoke production (TSP), peak smoke production rate (pSPR), peak CO production (COP) and peak CO₂ production (CO₂P) were derived from the test. [16-18]

Some researchers used more than one filler to improve fire retardant properties and that is too blended with epoxy to result better properties during combustion. Tie Zhang and et Al., proved that the results obtained using synergism of more than one retardant fillers produces better LOI values compared with single filler added. Also it reveals organic compounds and metal oxides synergism for fire retardant effectively reduces the heat release rate and promotes char formation [12]. Another researcher recently experienced addition of graphene oxide and titanium-di-oxide synergism result the improvement on mechanical and thermal behavior against fire which exposed to prove significantly. Focusing on thermo mechanical behavior is the compromising method adopted now days to improve the existing composite structure synthesized with polymers. By the effect of adding more than one additive/filler it disclose that existing polymers such as epoxy are increased twice in its mechanical behavior as well as peak load carrying ability at elevated temperatures [4, 11].

The following table intimates that the results of synergistic effects for epoxy polymers in recent years. All the results are showing as in table-4 is that additive materials with FR properties improved
the fire retardancy in positive high direction but the limitation is to be considered under the releasing agents which are harmful to the environment while burning or firing with respect to table-1.

Table 4. Fire retardant behaviors of various combinations and their recent highlights

| Epoxy composite blends                        | FR additives                                | Highlights in FR properties | Refs |
|----------------------------------------------|---------------------------------------------|----------------------------|------|
| Epoxy with nano materials (octaMethyl-polyhedral oligomeric silsesquioxane, ammonium polyphosphate) | 1 wt% OM-POSS +4 wt% APP                   | 30% ↓ 50% ↓ -              | [8]  |
| Epoxy with carbon nanotubes poly (phenylphosphonic-4,4’-diaminodiphenyl-methane) | 5 wt% CNT-PD                               | 29% ↓ 47% ↓ -              | [9]  |
| Epoxy with organically modified MMT; OM-POSS | 2.5 wt% OMMT intercalated withDNA           | 31% ↓ 21% ↓ 32%           | [10] |
| Epoxy with layered double hydroxides + melamine polyphosphate | 5 wt% LDH + 15 wt% MPP                      | -                          | [16] |
| Epoxy with layered double hydroxides + butylene succinate | 6 wt% LDH intercalated with cardanol-BS   | 19% ↓ 62% ↓ 29.2%         | [20] |
| Epoxy with layered double hydroxides hydroxypropyl-sulfobutyl-beta-cyclodextrin sodium+ dodecylbenzenesulfonate | 6 wt% LDH intercalated with sCD/DBS     | 35% ↓ 66% ↓ 26.8%         | [21] |
| Epoxy with Graphene nanofillers              | 5 wt% FRs-rGO                               | -                          | [22] |
| Epoxy with aluminum trihydroxide             | 4 wt% DPP-GO                                | 35.6% 30.8% 25.2%         | [23] |
| Epoxy with polydopamine                      | 2wt% ATH/EP                                 | 21% ↓ -                    |      |
|                                              | 10wt% ATH/EP                                | 6% ↓ 50.7% ↓ -            | [24] |
|                                              | 2wt% PDA/EP                                 | 16.6% ↓ 53.5% ↓ -        |      |
|                                              | 10wt% PDA/EP                                | 15% ↓ 61.3% ↓ -          |      |

Study of flammability properties through thermal gravimetric analysis (TGA) and Differential thermal analysis (DTA) curves along with cone colorimeter provide detailed behavior of designed composite under firing. TGA and DTA curves [26-27] will show the moss loss and residual weights during combustion which expose the characteristic of thermal decomposition.

4 Conclusion

The flame retardant property is additionally considered with the mechanical behaviour of new composites now a day. All the research findings are explicitly showing that the addition of fire retardant additives and the modified version of the same matrices revealed a positive increment in the thermal behaviour of existing constituents of the composite structure. There is a need to develop various synergistic approaches to design composites based on eco-friendly and null effect on the environment. Therefore, it is concluded from this survey that FRs based on natural sources either via bio-based / mineral-based products such as metal hydroxides have a good impact on both thermal and mechanical behavioural conditions and less impact on the environment during design material fire. Still, there is no compromise with the degradation of the matrix and fibre property during combustion.

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