Effective Approach to Overcome the Problem of Thermal Degradability in Natural Fiber-reinforced Composites is Flame Retardants: A Review

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Abstract

Natural fiber reinforced composites have wide variety of applications due to its large advantageous properties like high specific strength & stiffness, low cost, low density, and non abrasive nature. To employ NFRC material in various sectors like transportation, construction, and industrial field, thermal stability is the key requirement. To enhance the thermal stability of natural fiber reinforced composite, flame retardants is become effective solution. The objective of this review paper is to deals with various flame retardants system which help to protect the material against flammability and thermal degradability.

Key Words: Natural fiber, polymer, thermal stability, flame retardant, flammability.

INTRODUCTION

Increased environmental consciousness, depletion of non renewable natural resources, and recycling and reutilization are the main issues to generate interest among researchers and engineers for developing the biodegradable natural fibers based composite. Natural fiber reinforced composite have many tremendous advantages like high specific strength, low cost, low density, and low abrasiveness during processing that makes enable to substitute glass fiber reinforced composites [1, 2]. Due to its excellent properties, the use of biocomposites as a construction material, automotive parts, electrical parts etc. has generated a great interest. Irrespective of their advantageous properties, some disadvantages like moisture absorption, lower durability, high price fluctuation, lower impact strength, lower processing temperature, and poor fire resistance offered barriers to their application stage. To robust their practice in large number of application, it becomes necessary to elevate thermal stability of NFRC [3]. Many of the fire retardant programs accommodate by researchers to ameliorate the fire retardancy of thermoset, thermoplastic polymers/composites. Kozlowski et al. [4] reported that very limited studies had been discharge out in this area. So the leading objectives of this paper are twofold. On one way is to examine the thermal degradability of biocomposites, and other way is to review the various flame retardants and intumescent system for improving flame retardancy.

THERMAL DEGRADABILITY OF NFRC

Thermal sensitivity and flammability of fiber reinforced composite could limit their use in wide variety of applications. Degree of fire resistance of composite are different compared to individual components. Thermal degradation of natural fibers based composite is highly influenced by structure and chemical composition of fiber and polymer, orientation of fibers, interfacial adhesion between natural fibers and polymeric resin, type of polymer, and type of fillers [5, 6]. The flammability, rate of decomposition, heat release rate etc. are depends upon the physical and chemical properties of polymers. When polymers are exposed to heat, thermal oxidative decomposition occur which results the generation of combustible gases such as hydrocarbon, non combustible residue, solid particles (smoke), and toxic volatiles [7, 8]. During decomposition process, combustible gases combine with oxygen which result reactive $H^{\cdot}$ and $OH^{\cdot}$ Radicals produce, that are involved in sustained burning process [9]. The relative flammability of different polymers is depicted in Table 1. It can be concluded that PTFE have highest value of LOI 90, would appropriate for use as matrix polymer according flammability point of view.

Table 1, LOI of different polymers [51]

Polymer	LOI (vol %)
Polyethylene	17
Polypropylene	17
Polystyrene	18
Polybutylene terephthalate	18
Vinyl ester	20-23
Polyethylene terephthalate	21-33
Polyamide (Nylon 6, 6)	21-30
Polyamide (Nylon 6)	21-34
Polyvinyl chloride	23-45
Epoxy	23-27
Phenolic	25-57
Polyamide (Nylon 11)	25-32
Polycarbonate	26
Acrylonitrile butadiene styrene	29-35
Polysulfone	30

Polyimide	32
Polyphenyl sulfone	34
Polyether sulfone	34-38
Polyether ether ketone	35
Polyamide-imide	42-50
Polyether-imide	44-47
Polyphenylene sulfide	44-53
Polyvinylidene chloride	60
Polytetrafluoroethylene	90

Flammability of natural fibers is greatly dependent upon their chemical composition. Higher cellulose in fiber results lower thermal stability means they have required less activation energy to decompose [13, 14]. Higher lignin content contributes more to char formation which act as a heat barrier, protects the core of material [10, 11]. Lignin starts decomposing at lower temperature (160^0C), relatively weak bonds break, whereas at higher temperature (400^0C) cleavage of stronger bonds in the aromatic ring takes place [12]. According to chemical content, coir with a low cellulose (36-43%) & high lignin (41-45%) should have lower flammability than cotton, which has high cellulose (85-90%) content. Not only chemical composition, flammability of the fiber is dependent upon the crystallinity of fiber, degree of polymerization, and fibrillar orientation [15, 16]. The activation energy of decomposition is about 120 kJ/mol for amorphous cellulose compared to 200 kJ/mol for crystalline cotton. Increased orientation and degree of polymerization result high thermal stability. Orientation of fiber in matrix resin controls the amount of oxygen penetrating into fiber. Higher the orientation, lower the oxygen permeability into fiber [15]. Thermal degradation of composites is largely depends upon the properties of polymer, reinforcing fibers, synergistic or antagonistic effects between them, and construction of the composite [17, 18]. In some cases, flammability of the composite become larger than their components, it may be due to scaffolding effect in which molten decomposition products from the polymer are held in contact with heat source. Melt flow index of polymer is also affect the rate of thermal degradation of polymer [19].

The interfacial adhesion between natural fiber and polymeric resin will greatly influence the thermal stability of composite. Improved

compatibility between them increases the thermal stability of the composite which result high amount of activation energy is required for decomposition [20]. Albano et.al [21] was studied the effect of surface treatment of sisal fiber on thermal stability in polyolefin matrix. He found that acetylated sisal fiber composite had a higher thermal stability than that of untreated fiber.

Rate of thermal degradation of NFRC is also dependent on heat flux, or intensity of fire as depicted in Fig.1. Ignition is the starting point of a fire and it can occur over a long time period which result high production of gases and low heat generation [22, 23]. Ignition of fire may occur over a short period, when sufficient fuel volatiles and air reaches a high temperature.
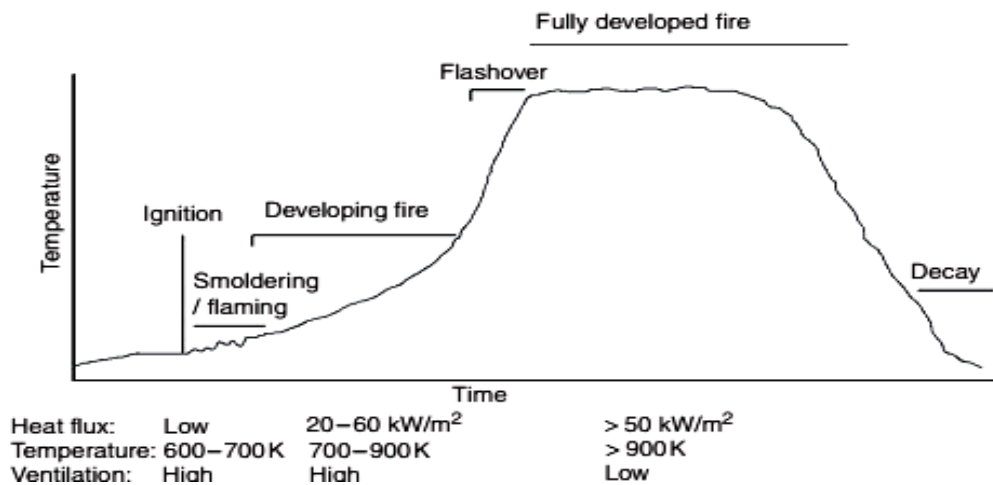

Fig.1 The stages of a typical fire and some fire properties at various stages [22, 53]

FLAME RETARDANTS

Flame retardants are chemicals that are added in combustible materials to inhibit or suppress the combustion process by chemical and/or physical ways during the specific stages of fire process [24]. They are necessary in a wide range of materials to ensure the fire safety. The amount of FRs are added can range from 1% for highly effective to 50% for inorganic fillers to achieve desired level of thermal stability. The principle of FRs is to reduce the propensity of fire when subjected to heat source or open flame. The most effective chemical action may take place by:

- **Reaction in the gas phase:** Flame retardants will interrupt the free radical gas phase combustion process which result cooling of the system, reducing and eventually suppressing the supply of flammable gases. The radicals are
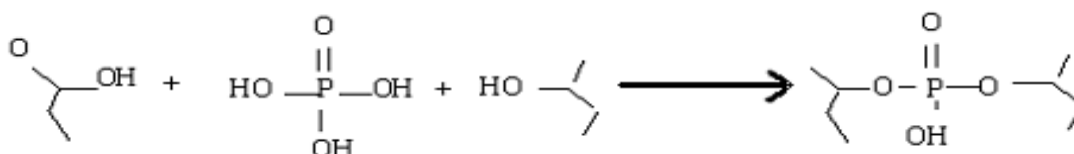
captured by FRs therefore exothermic oxidative flame chemical processes thus stopped resulting in hindrance of combustion [25, 26].

The reactions in the vapour phase mechanism are as follows:

$H \cdot + HX = H_2 + X \cdot$

$HO \cdot + HX = H_2O + X \cdot$

$RH + X \cdot = R \cdot + HX$
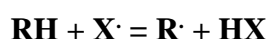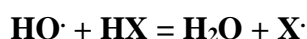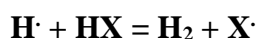
- **Reaction in the solid phase:** FR chemicals in the condensed phase builds

The chemical Reaction shown below:

Less effective physical action may takes place by:

- **Cooling:** Cooling effect triggered the endothermic reaction which cools the substrate to a temperature below that required for sustaining the combustion process. Alumina trihydrate (Al (OH)$_3$) work with this way [27, 28].

- **Formation of protective layer:** FRs should be able to shield the material from heat and oxygen with a solid or gaseous protective layer. Also they

- Phosphorous

- Nitrogen

- Halogens (Bromine and Chlorine)

- Others (like antimony trioxide, nanocomposites)

up a carbonaceous char layer and produce shielding effect against penetration of oxygen which led to decrease the heat and mass flow rate, flame propagation etc. Dehydration and cross linking form the carbonaceous char on the polymer surface which act as a heat insulation, serves to reduce the gases [25, 26]. Most phosphorous based FR compounds possess this kind of action to impart thermal stability.

prevent the supply of flammable gases to the material surface [27, 28].

- **Dilution:** These FR additives dilute the fuel in solid and gaseous phase by evolving non-combustible decomposition gases which result concentration of flammable gases reduced and falls under the ignition limit.

The main families of flame retardants are based on compounds containing:

- Intumescent systems

- Minerals (Based on Al & Mg)
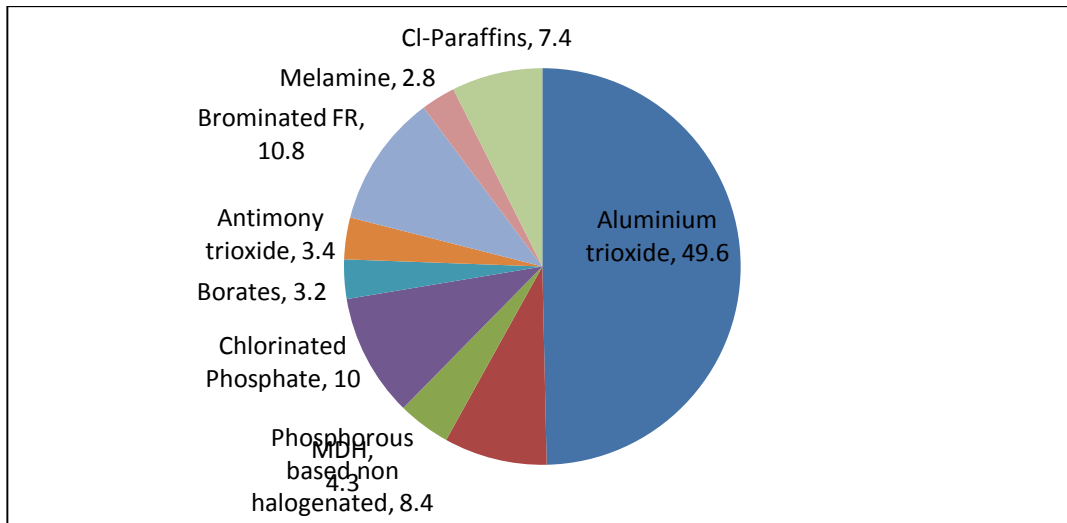
Fig.2 EFRA survey showing consumption of FRs

*Ammonium Polyphosphate (APP, $(NH_4)_{n+2}P_nO_{3n+1}$)*

Ammonium polyphosphate is a popular inorganic salt of polyphosphoric acid and ammonia which is extensively used as a flame retardant in biocomposite because of its low cost, low toxicity, and higher thermal stability [29, 30]. In most polymers, APP is able to cross-link carbonaceous structure and thereby enhance the amount of residue formed. When APP heated, it decomposes and evolves NH_3, H_2O, and polymeric phosphoric acid. Decomposition temperature mainly depends on the length of polymeric chain, long chain APP start to decompose at temperature above 300^0C but short chain at around 165^0C. The thermal degradation of APP produces free acidic hydroxyl group, which yield the cross linked structure of polyphosphoric acid and ultraphosphate. APP acts mainly in condensed form where polyphosphoric acid catalyzes char formation and dehydration reaction which creates a barrier in combustion process [31]. Incorporation of ammonium polypropylene in nitrogen and/or oxygen containing polymer i.e. polyamide [32] and polyurethane [33] leads to intumescent effect. Sz. Matko et al. [34] studied the effect of APP flame retardant on plasticized starch thermoplastic. He found that LOI=60 value can be achieved with 30% FR additive.

Aluminium Trihydrate (ATH, $2Al(OH)_3$)

Aluminium trihydrate (ATH) is active filler which is widely used at high loading in polymers to achieve adequate flame retardancy. It starts to decompose at around 220^0C, so it is most suitable for that polymer having processing temperature below 200^0C [6, 8]. The use of aluminium trihydrate reduces HRR peak

and smoke production. In most of the cases, ATH requires at higher loading up to more than 60% because its flame retardant mechanism is based on the release of water.

$$2Al(OH)_3 \xrightarrow[+1050kJ/Kg]{200^0C} 3H_2O + Al_2O_3$$
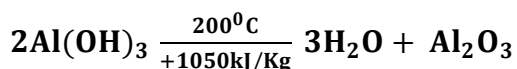
This reaction has wide effects on the combustion of the polymer:

- It absorbs 1050 kJ/Kg i.e. it cools down the polymer material.
- It dilutes the conc. of flammable gases.
- Restrict oxygen access to the composite surface.
- Al_2O_3 forms a thermally insulating coating on polymer surface.
- Aluminium hydroxide also produces catalytic effect on carbonized residues formation

Magnesium Hydroxide (MDH, Mg(OH)₂)

Magnesium hydroxide [$Mg(OH)_2$] is the acid and halogen free flame retardant which is most widely used in polymers. Like ATH, magnesium hydroxide decomposes endothermally by absorbing heat energy, but it decomposes at a higher temperature (300-320^{0}C) than ATH (200^{0}C).

$$Mg(OH)_2 \rightarrow MgO + H_2O$$
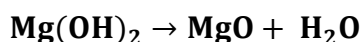
Similar to ATH, magnesium hydroxide releases a significant amount of gaseous water phase which envelop the flame, thereby excluding oxygen and diluting flammable gases.

Important factors determining the performance of magnesium hydroxide as a flame retardant:

- The endothermic decomposition of magnesium hydroxide starts at about 320^0 C, withdraw heat from the substrate, slowing the rate of thermal degradation of the plastic.
- The decomposition products provide insulation from heat source.
- Producing a char during burning that results flame retardant protection and less smoke generation.

Sain et al. [35] investigated the effect of magnesium hydroxide FR on sawdust and rice husk filled polypropylene composites. He found that magnesium hydroxide reduced the horizontal burning rate (ASTM D 635). The LOI was higher for composites with flame retardant compared to the without flame retardant.

Red Phosphorous

Red phosphorus is found to be effective flame retardant which is mainly used for phenolic and polyamide applications to meet UL 94 V0 fire safety level [36]. The flame retardancy effect of red phosphorus is due to oxidation of elemental phosphorus during combustion cycle to phosphoric acid or phosphorus pentaoxide. Fig. 3 represents polymeric structure of red phosphorus. More applications are in EVA,

polyurethane foams, and thermosetting resins (unsaturated polyesters and epoxies).
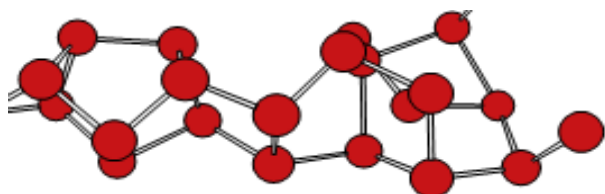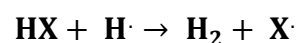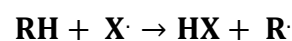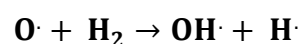

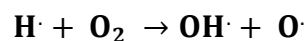**Fig. 3 Polymeric Structure of Red Phosphorus**

Intumescent System

Intumescent systems have increased interest as flame retardant during the last decades because of its excellent capability to forms an insulating layer over the surface of polymer composite which result retards heat transfer and oxygen accessibility [38]. Intumescent system are used as coatings to increase the thermal stability of combustible materials like wood and plastics, but also increase strength of steel structure at high temperature. The intumescent effect is achieved by incorporating acid source like APP, a source of carbonizing substance, and spumific (foaming) agent for blowing the foam and resin binders to stabilize foam [39]. An intumescent char is formed from decomposition products of carbonizing agent and non-flammable gases. Fig.4 depicts the formation of intumescent char. Foaming agent of intumescent system produce protective layer which cools the solid phase and limits the transfer of flammable volatiles. Most of the intumescent systems are based on phosphorous-nitrogen combinations, such as
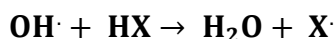
ammonium polyphosphate (APP) + pentaerythritol (PER), APP + triazine, APP + melamine + PER, diammonium pyrophosphate + PER etc [40, 41]. Typical advantages of intumescent systems are high thermal stability, high UV stability, and less smoke density. Phosphorous compounds used alone in polypropylene are not effective (except red phosphorous) but phosphorous based intumescent system is highly effective solution to achieve thermal stability of polypropylene.

Halogenated Flame retardants

Halogen based flame retardants consist of I, Br, Cl, or F elements. Their efficiency in the order of: I> Br> Cl> F. Fluorine and iodine based FRs are rarely used because fluorine derivatives decompose too late and iodine compounds have very low thermal stability, means in most of the cases iodine compound already decompose during polymer processing [42, 43]. The efficiency of halogen compounds is dependent on the balance between two reactions, i.e. the formation of $H^.$ and $OH^.$ radicals and the consumption thereof when they react with HX.

$$H^. + O_2 \rightarrow OH^. + O^.$$

$$O^. + H_2 \rightarrow OH^. + H^.$$

$$RX \rightarrow R^. + X^.$$

$$RH + X^. \rightarrow HX + R^.$$

$$HX + H^. \rightarrow H_2 + X^.$$

$$OH^{.} + HX \rightarrow H_2O + X^{.}$$

Halogenated FR can be divided into three categories: aromatic, aliphatic, cycloaliphatic. Halogen flame retardants vary in their thermal stability. Thermal stability: brominated aromatic > chlorinated aliphatic > brominated aliphatic.

Halogenated FRs is either additive or reactive with base polymer. Reactive type flame retardant is become a part of polymer and they are more complex and costly as compared to additive types. In order to reduce the amount of halogen, synergists such as ATO are widely used with halogenated flame retardants [44, 45].
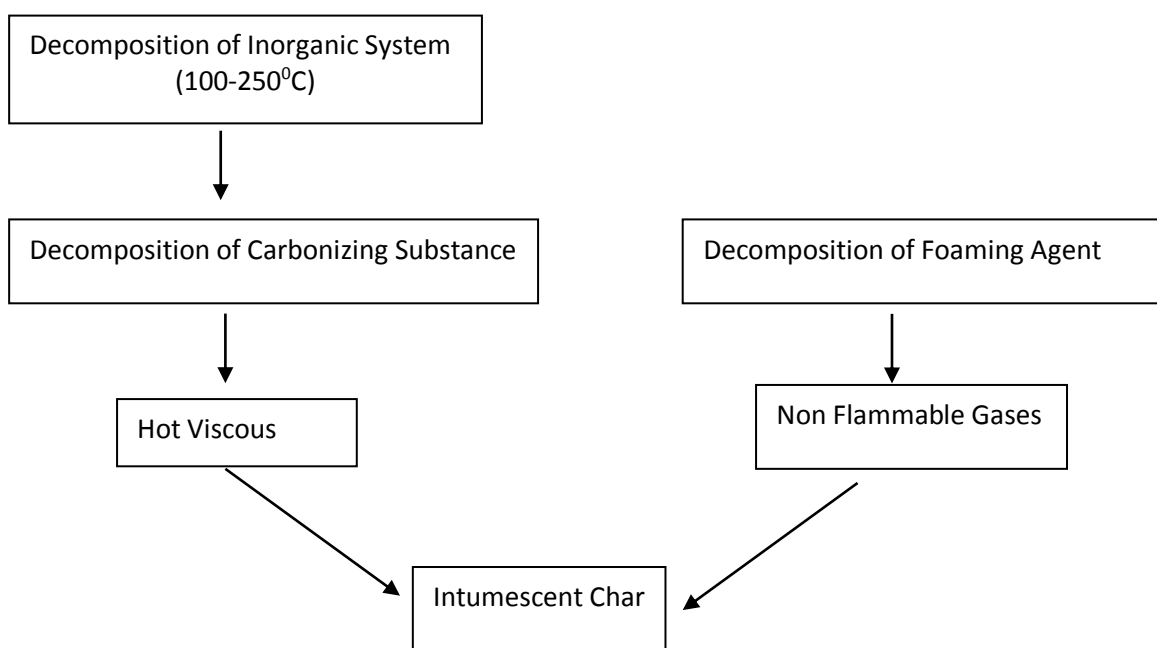

Fig.4 Formation of Intumescent Char

Antimony Compounds

Antimony trioxide is not a flame retardant, but it is used as synergist. ATO is commonly used for synergism action because it acts both in condensed and gas phase. In the condensed phase, they promote char which work as a barrier to flame propagation and access of oxygen. These compounds formulate an inert gas blanket over the polymer surface which leads to reduction the ease with which oxygen can combine with material. To achieve UL94 V0 rating in PP, deca-BDE should be present in at least 20 wt% together with 7 wt% of antimony trioxide [47]. Antimony trichloride and antimony oxychloride reduces the oxygen attack and energy content of flame. Hydrogen bromine (HX) released during pyrolysis of halogenated FR forms antimony oxide bromide (SbOX) upon reaction with antimony trioxide (Sb_2O_3) which promote C-X bond scission in the condensed phase.

$$2HX + Sb_2O_3 \rightarrow 2SbOX + H_2O$$
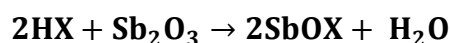
Halogen-antimony trioxide synergism [46]

Boron Compounds

Boron containing compounds as flame retardants are primarily used for cellulosic materials. Boric Acid (H_3BO_3) and sodium borate ($Na_2B_4O_7.10H_2O$) are two main type of boron based FR which are soluble in water, so they are not preferred in those cases where durable flame retardancy is required. Zinc borate is water insoluble compound which is usually used in conjunction with antimony oxide for halogen containing systems and in conjunction with aluminium trihydroxide for halogen free system. Boron containing compounds act by stepwise release of water and formation of glassy coating protecting the surface.

Expandable Graphite

Expanded graphite consists of graphite layers with a blowing agent like sulphuric acid or nitric acid which trapped between the layers. When heated up in a fire, EG starts to expand due to the evaporation of blowing agent which results formation of worm-like protective layer on the surface of polymer composite. This layer acts as heat insulation system for the underlying material. Expandable graphite expands up to 300 times its initial volume at around 900^0C. The impact of EG is based on condensed phase mechanism but expansion of graphite leads to disruption of thermal barrier, so to get a better flame retardancy effect EG is utilized with other flame retardants which act by condensed phase mechanism which results stabilization of the residue. Expandable graphite acts as a thermal barrier which reduced fire risk, fire hazard and dripping. The addition of 15% or 25% EG to the composite instead of APP, resulted in enhanced char formation [48].

Nitrogen based flame retardants

Nitrogen based compounds, i.e. melamine, melamine salts can be employed as flame retardant or form part of intumescent system. Melamine is thermally stable crystalline product that contains 67 wt% nitrogen atoms. At high temperature about 350^0C, melamine decomposes with the elimination of ammonia, which dilutes flammable gases and leads to the formation of cross linked thermally stable char. Nitrogen based FRs are mostly used in nitrogen containing polymers like polyurethanes, polyamides. Melamine is widely used in polyurethane foam whereas Melamine cyanurate is used in nylons or in formulation of intumescent system with APP [49, 50].

Conclusion

After reviewing this paper, it can be concluded that for successfully implementation of natural fiber reinforced composite in large number of application, thermal stability is the key requirement. It is also required that material

should be highly resistive against low temperature ignition, flame & fire propagation, emission of smoke and toxic gases. Recent research has shown that fire resistance, THR, PHRR, CO yield etc. can be improved by application of flame retardants. Thermal stability of polymer composite has been achieved by flame retardants that tend to char production and protective coating on the polymer surface which result reduction of volatilization of flammable material, access of oxygen, and propagation of flame. To innovate and develop application area of thermoplastic, thermoset, natural fibers, and biocomposite; more work will be required to understand their thermal behaviour and techniques to elevate their thermal stability.

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