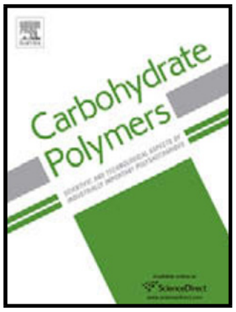

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Review on flammability of biofibres and biocomposites

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Abstract

The subject on flammability properties of natural fibre-reinforced biopolymer composites has not been broadly researched. This is not only evidenced by the minimal use of biopolymer composites and/or blends in different engineering areas where fire risk and hazard to both human and structures is of critical concern, but also the limited amount of published scientific work on the subject. Therefore, it is necessary to expand knowledge on the flammability properties of biopolymers and add value in widening the range of their application. This paper reviews the literature on the recent developments on flammability studies of bio-fibres, biopolymers and natural fibre-reinforced biocomposites. It also covers the different types of flame retardants (FRs) used and their mechanisms, and discusses the principles and methodology of various flammability testing techniques.

Key words:

Flammability, Flame retardants, Biopolymers, Natural fibre, Composite.

Contents **Page Number**

Abbreviations

Abbreviations

APP	Ammonium polyphosphate
ATH	Aluminum tri-hydrate
BAl	Boehemite aluminum
BDP	Bisphenyl A bis(diphenyl phosphate)
DNA	Deoxyribonucleic acid
DTG	Derivative thermogravimetric analysis
EG	Expandable graphite
EVA	Ethylene vinyl acetate
FRs	Flame retardants
FRAs	Flame retardant agents/additives
HPCA	Hyperbranched polyamine charring agent
HBCD	Hexabromocyclododecane
HRR	Heat release rate
HRC	Heat release capacity (η_c)
IFR	Intumescent flame retardant
LOI	Limited oxygen index
LDPE	Low density polyethylene
MA	Melamine
MCC	Microscale combustion calorimetry
MH or MDH	Magnesium hydroxide or Magnesium dihydroxide
MPD	methacryloyloxyethylorthophosphorotetraethyl diamidate
MA-*g*-PP	Maleic acid grafted polypropylene
MMP	Melamine phosphate
MMB	Melamine borate
MMT	Montmorillonite
MLR	Mass loss rate
MWNTs	Multi walled nanotubes
NAs	Normal additives
NFs	Natural fibres

NFRBC	Natural fibre reinforced biopolymer composites
OSU	Ohio State University
PMMA	Polymethyl methacrylate
PCFC	Pyrolysis combustion flow calorimetry
PA6	Polyamide 6
PU	Polyurethane
PC	Polycarbonate
PP	Polypropylene
PE	Polyethylene
PS	Polystyrene
POSS	Polyhedral oligomeric silsesquioxane
PCL	Polycaprolactone
PLA	Polylactic acid
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PBT	Poly(butylene terephthalate)
PBAT	Poly(butylene adipate-co-terephthalate)
PTT	Poly(trimethylene terephthalate)
PPTA	Poly(p-phenylenediamineterephthalamide)
PBDE	Polybromodiphenyl ether
PHRR	Peak heat release rate
PEBAX	Polyether blockamide
PC	Polycarbonate
RAs	Reactive additives
RTM	Resin transfer moulding
SPR	Smoke production rate
SPDPM	Spirocyclic pentaerythritol bisphosphorate disphosphoryl melamine
SEA	Soot extinction area
SEM	Scanning electron microscopy
SWNTs	Single walled nanotubes
TBBPA	Tetrabromobisphenol A
TBPA	Tetrabromophthalic anhydride
TTI	Time to ignition
THR	Total heat release
TPOSS	Trisilanolphenylpolyhedral oligomeric silsesquioxane

UL 94	Underwriter laboratories 94
UV	Ultraviolet
ZB	Zinc borate

1. Introduction

In recent years, the research on biofibre reinforced biopolymer composites has advanced. This development is motivated by factors such as shortage of and high fossil energy cost, and the current shift towards environmentally tolerant or “green” composite materials. The shift towards environmentally friendly biocomposite materials is due to environmental legislation, the REACH Act (Registration, Evaluation, Authorization and Restriction of Chemical substances), comparable properties to synthetic fibre counterparts, green attribution and low cost. Most of the components in biocomposites are based on agricultural products as a source of raw materials. Thus, their use provides solution for waste disposal, reduction in agricultural residues and hence environmental pollution resulting from the burning of these. Additionally, it offers an economical solution for farming and rural areas in developing countries (Anandjiwala et al., 2013; Chapple & Anandjiwala, 2010; Faruk, Bledzki, Fink & Sain, 2012; Horrocks, 2011; Jang, Jeong, Oh, Youn & Song, 2012; John & Thomas, 2008; Kandola, 2012; Sahari & Sapuan, 2011; Satyanarayana, Arizaga & Wypych, 2009).

Biofibre reinforced biopolymer composite materials largely have appealing properties. They are renewable, recyclable (partially or completely), relatively cheap, biodegradable and thus environmentally friendly. However, there are some inherent disadvantages such as their hydrophilic nature and poor flammability properties (i.e. poor fire resistance). The attractive properties clearly outweigh the undesirable ones and the latter have remedial measures. For example, remedies may be chemical and/or physical modifications such as the incorporation of flame retardant additives (FRAs) to improve flammability of biocomposites (John & Thomas, 2008).

Previous research observed limitations in the use of biofibre reinforced biopolymer composites, especially in areas that pose fire hazard and risk.This is because natural fibre reinforced biopolymer composites are largely used in the packaging and automotive industries where fire safety regulatory requirements are not as stringent as those in the aerospace industry. Therefore, to broaden the range of applications of these biocomposites into other sectors of advanced engineering (i.e. aerospace, marine, electronics equipment and construction), both their flammability characteristics and fire retardance strategies need more research (Bourbigot & Fontaine, 2010; Chapple & Anandjiwala, 2010; Kandola, 2012).

There are different strategies that can be demonstrated for fire retardancy of biocomposites. Fire retardancy is the phenomenon in which materials such as plastics and/or textiles are rendered less likely ignitable or, if they are ignitable, should burn with less efficiency (Price, Anthony & Carty, 2001). It may be achieved by use of several approaches. These may be chemical modification of existing polymers, addition of surface treatment to the polymers, use of inherently fire resistant polymers or high performance polymers, and direct incorporation of flame retardants (FRs) and/or micro or nanoparticles in materials. The direct incorporation of flame retardants is achieved through use of various additives. These flame retardance strategies may range from the use of phosphorus additives (e.g. intumescent systems), halogen additives (e.g. organobromine), silicon additives (e.g. silica), nanometric particles (e.g. nanoclays) and minerals based additives (e.g. metal hydroxide). The broader information on flame retardant additives (FRAs) in natural polymers, wood and lignocellulosic materials has been reviewed by Kozlowski and Wladyka-Przybylak (2001). Thus, the primary duty of flame retardant systems is to prevent, minimize, suppress or stop the combustion of a material (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta & Dubois, 2009; Morgan & Gilman, 2013; Price et al., 2001; Wichman, 2003).

Flame retardant systems can either act chemically or physically in the solid, liquid or gas phase. These mechanisms are dependent on the nature of the flame retardant system. The chemical mode of action may be manifested by reaction in the gaseous and condensed phases, whereas the physical mode occurs by a cooling effect, formation of a protective layer or by fuel dilution. FRs may be classified into three classes. They are normal additives (NAs), reactive additives (RAs) and a combination of FRs (Laoutid et al., 2009; Price et al., 2001; Wichman, 2003).

The flammability of fire retarded materials may be tested through different fire testing techniques. The most widely used laboratory flammability testing techniques have been reported in literature (Laoutid et al., 2009; Price et al., 2001; Wichman, 2003). A number of small, medium and full scale flammability tests are used in both academic and industrial laboratories. They are employed for either screening the materials during production or testing the manufactured products. These techniques are cone calorimetry, pyrolysis combustion flow calorimetry (PCFC), limiting oxygen index (LOI), and underwriters' laboratories 94 (UL94) and Ohio State University (OSU) heat release rate tests.These techniques involve the measurement of various flammability parameters by appropriate tests depending on the targeted application of a polymeric material. The flammability of polymers can be characterized by parameters such as ignitability (ignition temperature, delay time, critical heat flux), burning rates (heat release rate, solid degradation rate), spread rates (flame, pyrolysis, and smoulder), product distribution (emissions of toxic products) and smoke production (Carvel, Steinhaus, Rein & Torero, 2011; Laoutid et al., 2009; Price et al., 2001).

The flammability properties of natural fibrereinforced biopolymer composites have not been studied extensively. The aim of this paper is to review the current research and developments related to flammability of biofibre reinforced biopolymer composites for the period 2000 to 2013. This review will explore aspects such as the different types of flame retardants, laboratory flammability testing techniques and recent studies on flammability of biopolymers and biocomposites.

2. Flame retardants

FRs impart flame retardancy character to materials such as coatings, thermoplastics, thermosets, rubbers and textiles. These FRs may prevent, minimize, suppress or stop the combustion process of materials. They act to break the self sustaining polymer combustion cycle shown in Figure 1, and consequently reduce the burning rate or extinguish the flame in several ways (Guillaume, Marquis & Saragoza, 2012; Grexa & Lübke, 2001; Kandola, 2001; Kandola & Horrocks, 2001; Ke et al., 2010; Kozlowski & Wladyka-Przybylak , 2001; Laoutid et al., 2009; Morgan & Gilman, 2013; Price et al., 2001; Wichman, 2003).

The possible ways to reduce the burning rate or extinguish the flames are:i) the modification of the pyrolysis process in order to lower the quantity of evolved flammable volatiles, with normally an increase in the formation of char (less flammable) serving as barrier between the polymer and flame (stage 'a', Figure 1); ii) the isolation of the flame from the oxygen/air supply (stage 'b'); iii) introduction into the polymer formulations those compounds that will release efficient flame inhibitors (e.g. chlorine and bromine) (stage 'c'); and iv) the lowering of thermal feedback to the polymer to prevent further pyrolysis (stage 'd') (Price et al., 2001).

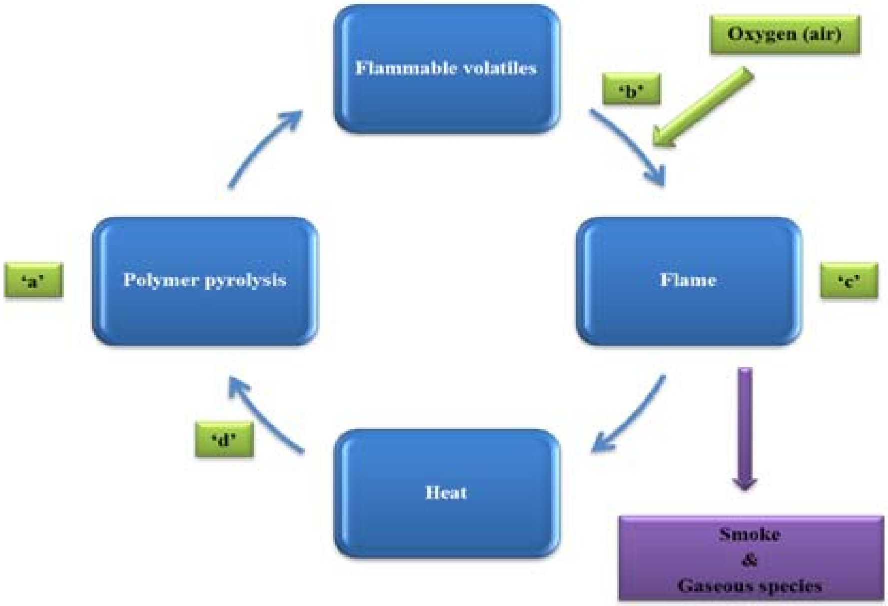

Figure 1. Demonstration of the self sustaining polymer combustion cycle; a–d represent potential modes of flame retardants (adapted from Price et al., 2001) (*Intended for colour on the Web and black-and-white in print*)

To flame retard polymer materials or to protect them from fire, there are three main approaches to be considered. These are the engineering approach, use of inherently low flammable polymers and the use of flame retardant additives (FRAs) (Morgan & Gilman, 2013).

The engineering approach is cost effective and relatively easy to implement. It requires the use of a fire protection shield. However, the method has some limitations such as tearing and/or ripping off (of fire proof fabric), loss of adhesion (in metal fire protection), and scratching away and falling off due to impact or ageing (of intumescent paint). Consequently, the underlying material may be left exposed to fire damage.

The inherently flame retarded polymers can be made in various forms and are easy to implement in different applications. Their use, though, can be limited by high cost and difficulty to recycle (i.e. fibre reinforced polymer composites). As a result, low flammability polymers are less used except for applications demanding their use (e.g. aerospace and military sectors).

The use of FRAs is a well known approach, cost effective and relatively easy to incorporate into polymers. The challenges with this approach, however, include potential for leaching into environment, difficulty with recycling and a compromise in reaching a balance in properties of a polymer. Regardless of these problems, FRAs are still used.

FRs are classified into three categories. They are normal additives (NAs) flame retardants, reactive additives (RAs) flame retardants and combinations of FRs. NAs are incorporated during polymerization or during melt mixing processing and react with the polymer only at higher temperatures at the start of a fire. They are common flame retardant additives and their interaction is physical with the substrate. NAs usually include mineral fillers, hybrids or organic compounds that can include macromolecules. RAs, on the other hand, are usually introduced into polymers during polymerization or in a post reaction process. During polymerization, RAs are introduced as monomers or precursor polymers whereas in a post reaction process their introduction is by chemical grafting. These flame retardants chemically bond to the polymer backbone. Combinations of NAs and RAs can produce an additive (sum), synergistic (higher) or antagonistic (lower) effect. A synergistic effect typically occurs when they are used together with specific flame retardants (Kozlowski & Wladyka-Przybylak, 2001; Morgan & Gilman, 2013; Price et al., 2001; Troitzsch, 1998).

2.1 Mode of action of flame retardants

Flame retardant systems can act either chemically or physically in the solid, liquid or gas phase. Such actions do not occur singly but should be considered as complex processes in which various individual stages occur simultaneously, with one dominating. They are dependent on the nature of flame retardant system in place (Bourbigot & Duquesne, 2007; Laoutid et al., 2009; Morgan & Gilman, 2013; Price et al., 2001; Troitzsch, 1998; Wichman, 2003). Various modes of flame retardants are discussed in subsequent sections.

2.1.1 Physical action

The physical mode occurs by (i) cooling effect, (ii) fuel dilution or (iii) via formation of a protective layer (coating) (Chapple & Anandjiwala, 2010; Jang et al., 2012; Kandola, 2012; Laoutid et al., 2009; Price et al., 2001; Troitzsch, 1998; Wichman, 2003).

(i) Cooling effect: Some FRAs (e.g. hydrated trialumina and magnesium hydroxide) decompose by an endothermic process and trigger temperature decrease in the system. Cooling of the medium to below the polymer combustion temperatures is effected. Such endothermic reaction is known to act as a heat sink.

(ii) Fuel dilution: During decomposition of flame retardants (e.g. aluminum hydroxide), the formation of gases such as H_2O, CO_2, and NH_3 lead to dilution of the mixture of combustible gases. Consequently, this limits both the concentration of reagents and the possibility of materials to ignite.

(iii) Formation of a protective layer (coating): Some FRAs (e.g. phosphorus and boron compounds) form a protective solid or gaseous layer between the gaseous and solid combustible phases. This limits the transfer of combustible volatile gases, excludes oxygen necessary for combustion and thus reducing the amount of decomposition gases.

2.1.2 Chemical action

The chemical mode of action may be manifested by reaction in the (i) gaseous and (ii) condensed phase (Chapple & Anandjiwala, 2010; Jang et al., 2012; Kandola, 2012; Laoutid et al., 2009; Price et al., 2001; Troitzsch, 1998; Wichman, 2003).

(i) Gaseous phase: By incorporation of FRAs that favour the release of specific radicals (e.g. halogen flame retardants, Cl• and Br•) in the gas phase, the free radical mechanism of the combustion process can be stopped. These radicals can react with highly reactive species such as H• and OH• to form less reactive or inert molecules. The exothermic reactions are then stopped; the system cools down and the supply of flammable gases is subsequently reduced.

(ii) Condensed phase: Two types of chemical reaction initiated by FRAs are possible: (a) flame retardants can speed up the rupture of polymer chains and the polymer will drip, thus moving away from the flame action zone; (b) FRs can cause the formation of a carbonized or vitreous layer at the surface of the polymer. This occurs by chemical transformation of degraded polymer chains. The formed char and/or vitreous layer acts as a physical insulating barrier between the gas and condensed phases.

2.2 Types of flame retardant agents

FRAs are based on various chemical compounds. This subsection discusses chemical compounds based on phosphorus, halogen, silicon, nanometric particles and mineral additives. The phosphorus based additives include organic phosphorus, inorganic phosphorus, red phosphorus and intumescent flame retardant systems. The silicon based additives consist of silica and silicones, the nanometric particles based ones may be carbon nanotubes, nanoclays and nanoscale particulate additives, and the minerals based flame retardant additives are hydrocarbonates, metal hydroxides and borates.

2.2.1 Phosphorus based flame retardants

Phosphorus based FRs include phosphorus into their structure. Their structure can vary from inorganic to organic forms, and with oxidation states of 0, +3, or +5. Phosphorus based FRs consist of phosphates, phosphonates, phosphinates, phosphine oxide and red phosphorus. These FRAs are used as NAs or RAs incorporated into the polymer chain during synthesis. They are effective with oxygen or nitrogen containing polymers (cellulose, polyesters, and polyamides). Phosphorated FRs are unique in that they can be condensed phase or vapour phase FRs depending on their chemical structure and interaction with the polymer under fire conditions (Faruk et al., 2012; Jang et al., 2012; Laoutid et al., 2009).

In the *condensed phase*, their thermal decomposition leads to the production of phosphoric acid that readily condenses to give phosphorylated structures and gives off water. Released water dilutes the oxidizing gas phase (physical action: fuel dilution). Additionally, phosphoric acid and pyrophosphoric acid can facilitate a dehydration reaction resulting in the formation of carbon to carbon double bonds and charring. This can then lead to the generation of crosslinked or carbonized structures at high temperatures (Faruk et al., 2012; Jang et al., 2012; Laoutid et al., 2009; Morgan & Gilman, 2013; Troitzsch, 1998).

At high temperatures both ortho and pyrophosphoric acid are turned into metaphosphoric acid (OPOOH) and their corresponding polymers $(PO_3H)_n$. Phosphate anions (pyro and polyphosphates) then partake in char formation (with carbonized residue). This carbonized layer isolates and protects the polymer from the flames, limits the volatilization of fuel, prevents formation of new free radicals, limits the diffusion of oxygen thus reducing combustion, and insulates the polymer underneath from the heat (Faruk et al., 2012; Jang et al., 2012; Laoutid et al., 2009; Morgan & Gilman, 2013; Troitzsch, 1998).

Phosphorus based flame retardants can also volatilize into *vapour phase* forming active radicals (PO_2•, PO• and HPO•) and acting as scavengers of H• and OH• radicals. Volatile phosphorated compounds are among the effective inhibitors of combustion compared to bromine and chlorine radicals. Since phosphorus based flame retardants are significantly effective in oxygen and nitrogen containing polymers, it is thus important to have these atoms in the polymer chain. In case the used polymer lacks these atoms in its chain and cannot contribute to charring, a highly charring coadditive {e.g. polyol (pentaerythritol)} has to be introduced in combination with the phosphorated flame retardant. Polymers such as polyamides and polyurethane can also be used as charring agents in intumescent flame retardant systems (Faruk et al., 2012; Jang et al., 2012; Laoutid et al., 2009; Morgan & Gilman, 2013; Troitzsch, 1998).

2.2.1.1 Organic phosphorus

Many organic phosphorus derivatives show flame retardancy properties. But, those of commercial importance are limited by the processing temperature and the nature of the polymer to be modified. Organic phosphorus based FRs can act as NAs or as RAs monomers or co monomers/oligomers. Their main groups are phosphate esters, phosphonates and phosphinates. Due to their high volatility and relatively low fire retardant efficiency, the use of alkyl substituted triaryl phosphate (i.e. triphenyl phosphate, TPP, cresyl diphenyl phosphate, isopropylphenyl diphenyl phosphate, tertbutylphenyl diphenyl phosphate or tricresyl phosphate) is limited in plastics engineering. Oligomeric phosphates with lower volatility and higher thermal stability than triaryl phosphate can be used for plastics engineering. These may be resorcinol bis(diphenyl phosphate) (RDP) and bisphenol A bis(diphenyl phosphate (BDP). The combination of volatile and nonvolatile phosphates can also lead to a synergistic effect. This may be a positive combination of the condensed phase and gas phase of phosphates. The use of reactive phosphorus flame retardants is also a solution for avoiding volatilization during thermal decomposition and migration towards the surface of a polymer. They can be incorporated directly within the polymer chain structure and can be used either as monomers for copolymerization with one or two co-monomers to get phosphorated polymers or as oligomers that react with polymers to form branched or grafted phosphorated polymers (Faruk et al., 2012; Jang et al., 2012; Laoutid et al., 2009; Morgan & Gilman, 2013).

2.2.1.2 Inorganic phosphorus

A typical example of an inorganic phosphorus salt is a combinationof polyphosphoric acid and ammonia called ammonium polyphosphate (APP). It is either a branched or unbranched polymeric compound with variable chain length (*n*). For short and linear chain APPs (where *n* is less than 100, crystalline form I),they are more water sensitive and less thermally stable, whereas APPs with longer chain (*n* is greater than 1000, crystalline form II) exhibit very low water solubility (< 0.1 g/100 ml) (Jang et al., 2012; Laoutid et al., 2009).

The APPs are stable and nonvolatile compounds. Those with long chains start decomposing at temperatures above 300 °C giving polyphosphoric acid and ammonia, whereas the short chain ones decompose at 150 °C. It is thus important to adapt a crystalline form of APP to the decomposition temperature of a polymer. When an APP is incorporated into a polymer that contains oxygen and/or nitrogen atoms, polymer charring occurs. Thermal degradation of APP creates free acidic hydroxyl groups that condense by thermal dehydration yielding a crosslinked structure of ultraphosphate and polyphosphoric acid with a highly crosslinked structure. Polyphosphoric acid reacts with oxygen and/or nitrogen containing polymers and catalyses their dehydration reaction and char formation. However, the effectiveness of an APP is dependent on the loading concentration. Low concentrations of APP are not efficient in aliphatic polyamides, but at high concentrations it becomes efficient. In non self-charring polymeric materials, the APP can modify the degradation mechanism of the polymer (Bourbigot & Fontaine, 2010; Ke et al., 2010; Zhu et al., 2011).

2.2.1.3 Red phosphorus

This is the most concentrated source of phosphorus for flame retardancy and is used in small quantities (i.e. < 10%). It is effective in oxygen and nitrogen containing polymers (i.e. polyesters, polyamides and polyurethanes). For oxygen containing polymers only, the mode of action involves specific scavenging of oxygen containing radicals leading to the generation of gaseous fuel species. For oxygen and nitrogen containing polymers, red phosphorus turns into phosphoric acid or phosphoric anhydride, which gives polyphosphoric acid upon heating. This happens through thermal oxidation and the formed polyphosphoric acid catalyses the dehydration reaction of the polymer chain ends and triggers char formation (Laoutid et al., 2009; Laoutid, Ferry, Lopez-Cuesta & Crespy, 2006).

Additionally, red phosphorus is also effective in non oxygenated polymers (e.g. polyethylene). Consequently, red phosphorus depolymerizes into white phosphorus (P_4). This white phosphorus can volatilize at high temperatures and act in the gaseous phase or it can diffuse from the bulk of the polymer to the burning surface where it oxidizes to phosphoric acid derivatives. These can come into close contact with the flame and form phosphoric acid. This acid can act as a char forming agent and therefore physically limiting oxygen access and fuel volatilization (Laoutid et al., 2009).

Red phosphorus is active in both the gas and condensed phase in polyethylene. In the gas phase, the produced PO• radicals quench the free radical process. In the condensed phase, red phosphorus lowers the heat of oxidation and also traps the free radicals. This results in improved thermal stability leading to a decrease in fuel production during burning of a material (Laoutid et al., 2009).

The disadvantage of red phosphorus is that it releases toxic phosphine (PH_3) through reaction with moisture due to its poor thermal stability. However, phosphine formation can be avoided by prior encapsulation of red phosphorus to improve its effectiveness as a flame retardant. Alternatively, phosphine formed at high temperatures can be trapped by taking advantage of its capacity to react with metallic salts (i.e. $AgNO_3$, $HgCl_2$, MoS_2, HgO, PbO_2, CuO, $FeCl_3 \cdot H_2O$) (Laoutid et al., 2009).

2.2.1.4 Intumescent flame retardant system

Intumescent flame retardant systems were initially developed to protect fabrics, wood and coatings for metallic structures from fire. Intumescent materials are classed into thick or thin film intumescent coatings. The thick films are usually based on epoxy resins, contain agents that intumesce when exposed to heat and are available as solvent free systems. Thin films are available as solvent or water based systems, and are applied by spray or brush roller in thin film coats. An intumescent system is based on the formation of an expanded carbonized layer on the surface of a polymer during thermal degradation. This layer acts as an insulating barrier by reducing heat transfer between the heat source and the polymer surface, by limiting the fuel transfer from the polymer towards the flame, and limiting the oxygen diffusion into a material. The formulation of an intumescent system consists of three components: an acid source, a carbonizing agent and a blowing agent. Table 1 tabulates examples of each component category (Bourbigot & Duquesne, 2007). The intumescent FRs are widely used due to their advantages of low smoke and low toxicity (Jimenez, Duquesne & Bourbigot, 2006; Ke et al., 2010; Laoutid et al., 2009; Morgan & Gilman, 2013).

An *acid source* promotes dehydration of the carbonizing agent and results in the formation of a carbonaceous layer. It has to be liberated at a temperature below the decomposition temperature of a carbonizing agent and its dehydration should happen around the decomposition temperature of a polymer. A *carbonizing agent* is generally a carbohydrate that can be dehydrated by an acid to form a char. Its effectiveness relates to the number of carbon atoms and the reactive hydroxyl sites containing carbon source agent molecules. The quantity of char produced is dependent on the number of carbon atoms present. Reactive hydroxyl (OH) sites determine the rate of the dehydration reaction and thus the rate of formation of the carbonized structure. A *blowing agent* decomposes and releases gas leading to expansion of the polymer and formation of swollen multicellular layer. The gas must be released during thermal decomposition of a carbonizing agent in order to trigger the expansion of the carbonized layer (Bourbigot & Duquesne, 2007; Jimenez et al., 2006; Ke et al., 2010; Laoutid et al., 2009; Morgan & Gilman, 2013).

Table 1. Examples of components of intumescent systems. Reprinted from Bourbigot and Duquesne (2007), Copyright 2007, with permission from Royal Society of Chemistry.

Inorganic acid source	**Carbonizing agent**	**Blowing agents**
Phosphoric	Starch	Urea
Sulfuric	Dextrins	Urea-formaldehyde resin
Boric	Sorbitol, mannitol	Dicyandiamide
Ammonium salts	Pentaerythritol, monomer, dimer, trimer	Melamine
Phosphates, polyphosphates		Polyamides
Borates, polyborates	Phosphates, polyphosphates	
Sulfates	Phenol-formaldehyde resins	
Halides	Methylol melamine	
Phosphates of amine or amide	Char former polymers (PA-6, PA-6/clay nanocomposite PU, PC, etc.)	
Products of reaction of urea or guanidyl urea with phosphoric acids		
Melamine phosphate		
Product of reaction of ammonia with P_2O_5		
Organophosphorus compounds		
Tricresyl phosphate		
Alkyl phosphates		
Haloalkyl phosphates		

2.2.2 Halogen based flame retardants

Halogenated FRs are molecules that include elements from group VII of the periodic table (F, Cl, Br and I). Their effectiveness increases in the order F < Cl < Br < I. The type of halogen dictates the effectiveness of the halogenated flame retardant. However, fluorine (F) and iodine (I) are not used because they do not interfere with the polymer combustion process. Fluorinated compounds are more thermally stable than most polymers and do not release halogen radicals at the same temperature range or below the decomposition of the polymers. Iodine compounds are less thermally stable than most commercial polymers and therefore release halogen species during polymer processing. Bromine and chlorine can readily be released and partake in the combustion process because of their low bonding energy with carbon atoms (Chen & Wang, 2010; Laoutid et al., 2009; Morgan & Gilman, 2013; Troitzsch, 1998).

2.2.2.1 Halogenated flame retardant additives

Halogenated FRs differ in chemical structure from aliphatic to aromatic carbon substrates or can come in inorganic forms. Of these, the organohalogen compounds are most used as FRs for polymers due to their effectiveness. Organochlorine and organobromine are the mostly used, with organobromine compounds being the most commonly used. This is because the C–Br bond is stable enough for environmental exposure and yet heat can easily break it to release bromine under fire conditions to inhibit free radical reactions. It is these unique bond strengths that make halogen based FRs mostly vapour phase FRs (Chen & Wang, 2010; Laoutid et al., 2009; Morgan & Gilman, 2013).

Halogenated FR technology has been used since the 1930’s due to advantages of low cost, processability, miscibility and low reduction on the physical/mechanical properties of the FR systems. However, its flaws include increased smoke release under fire conditions, the release of corrosive gases (i.e. HBr in case of brominated FRs) during burning which leaches to the environment and thus brominated products are currently under environmental scrutiny. The increased smoke and corrosive gas release of these compounds is rooted to their flame retardant chemistry. Because it inhibits combustion through the formation of HBr gas, it causes the formation of partially combusted polymer decomposition products as well as carbon monoxide (CO). Halogenated FR systems do not always perform well under very high heat flux conditions because once a halogen is consumed by fire any remaining polymer will burn if exposed to additional heat. This will happen unless a lot of halogen is present in a polymer which results in higher smoke production and corrosive gas release (Laoutid et al., 2009; Morgan & Gilman, 2013).

Mode of action

The thermally induced polymer decomposition (during polymer combustion) releases very reactive free radical species (i.e. H• and OH•). These maintain a combustion process by a series of chain reactions in the gas phase.

$$H\bullet + O_2 \rightarrow OH\bullet + O$$

$$O + H_2 \rightarrow OH\bullet + H\bullet$$

The reactive free radical species H• and OH• formed by chain branching are removed by halogenated FR. Initially the flame retardant breaks down into a halogen radical (see below reaction, where X is either Cl or Br):

$$RX \rightarrow R\bullet + X\bullet$$

The formed halogen radical reacts to form a hydrogen halide:

$$X\bullet + RH \rightarrow R\bullet + HX$$

This hydrogen halide consequently interferes with the radical chain mechanism:

$$HX + H\bullet \rightarrow H_2 + X\bullet$$

$$HX + OH\bullet \rightarrow H_2O + X\bullet$$

The highly reactive H• and OH• free radical species are removed by reaction with HX and replaced with less reactive X radicals. The actual flame retardant effect is therefore produced by HX. The hydrogen halide consumed is regenerated by reaction with hydrocarbon:

$$X\bullet + RH \rightarrow R\bullet + HX$$

As a result, HX is an effective FR species. It is non flammable and can have physical action on the combustion mechanism by forming a protective gaseous layer and/or dilution of fuel gases. Furthermore, HX can catalyse the oxidation of the solid phase and the oxidation products tend to cyclize leading to the formation of a solid protective layer (Laoutid et al., 2009; Troitzsch, 1998).

The most common halogen FRA compounds are tetrabromobisphenol A (TBBPA), polybromodiphenyl ether (PBDE), hexabromocyclododecane (HBCD) and tetrabromophthalic anhydride (TBPA) (Chen & Wang, 2010; Laoutid et al., 2009; Morgan & Gilman, 2013; Troitzsch, 1998).

2.2.2.2 Halogenated monomers and copolymers

The advantages of reactive additive FRs are their ability to be used in relatively low concentrations, and that they can be directly incorporated in the polymer structure. Consequently they can increase compatibility between a polymer and an FRA, they can limit the damage caused by heterogeneous additives to the mechanical properties of the resulting materials, and can reduce the migration of FRAs onto the material surface (Laoutid et al., 2009).

Nevertheless, they need an additional synthesis step that may be a limiting factor on an industrial scale. They can be used as condensation free radical polymerization monomers, copolymerized with virgin monomers or grafted onto the polymer chain. Their action is very similar to other halogenated FRAs. In some cases, other mechanisms can be added to the conventional effect of halogenated derivatives and thus changing the degradation pattern of a polymer. The effectiveness of a halogenated monomer depends on the composition of the monomer and the copolymer. Increasing the content of halogen atoms in the monomer leads to more efficient fire retardance (Laoutid et al., 2009; Morgan & Gilman, 2013).

Reactive halogenated FRAs may be an alternative to halogenated FRAs that seem to pose some toxicological risk to the environment. However, they are less used due to high cost, and most of them are limited to a few polymers such as styrenics, acrylates, urethanes and epoxies (Morgan & Gilman, 2013).

2.2.3 Silicon based flame retardants

The addition of a relatively low amount of silicon based compounds to polymers substantially improves their fire retardancy. These silicon based compounds are silicones, silicas, organosilicates, silsesquioxanes and silicates. They can be used as fillers incorporated into polymers, as copolymers or as main polymer matrices and are discussed in the following sections.

2.2.3.1 Silicones

Silicones {typically polydimethylsiloxane (PDMS) polymers} are known to have excellent thermal stability, high heat release (i.e. 60 to 150 kW m^{-1}) and very limited release of toxic gases (i.e. CO) during thermal decomposition. They exhibit a slow burning rate without a flaming drip and, when pure, they do not emit toxic smokes. Silicones have been commercialized since the 1940's. They are used in various applications in civil engineering, construction building, electrical, transportation, aerospace, defence, textile, and cosmetics industries. They can be used as flame retardants through direct blending with a polymer matrix or by synthesizing block/graft copolymers including silicone segments. Their superior flame retardant behaviour is the result of excellent dispersion in polymer matrices and migration towards the material surface during combustion followed by the formation of a highly flame retardant char. Their main advantage as flame retardants is that they have a minimal environmental effect due to their inorganic structure. They are expensive and hence used sparingly (Cheng & Wang, 2010; Hamdani, Longuet, Perrin, Lopez-Cuesta & Ganachaud, 2009; Laoutid et al., 2009; Morgan & Gilman, 2013).

2.2.3.2 Silica (silicon dioxide, SiO_2)

The flammability reduction mechanism of silica is based on a physical process rather than a chemical reaction. Its effectiveness is dependent on several factors including pore size, particle size, surface silanol concentration, surface area, density and viscosity. Large pore volumes may accommodate macromolecular polymer chains, or the presence of silica may increase the melt viscosity during pyrolysis, which can trap and/or slow down volatilization and evolution of degradation products. The balance between density and surface area of the additive, together with the polymer melt viscosity, determine whether the additive accumulates near the surface of a sample or sinks through the polymer melt layer. If additives accumulate near the sample surface, the possibility is that the additive acts as a thermal insulation layer and also reduces the polymer concentration near the surface in contact with the flame. The specific area and porous volume can modify the viscosity of the system in the molten state. The control over viscosity seems to be the key factor in the formation of a protective layer (Cheng & Wang, 2010; Kashiwagi et al., 2000; Laoutid et al., 2009).

Several studies have been conducted where silica was used as flame retardant in thermoplastics (Kashiwagi et al., 2000; Li, Jiang & Wei, 2006; Zhang et al., 2012). Kashiwagi et al. (2000) used various types of silica (i.e. silica gel, fumed silica and fused silica) in polypropylene (PP) and polyethylene oxide (PEO). Their effectiveness and mechanisms were determined. Li et al. (2006) synthesized flame retardants that contain silicon elements (together with phosphorus and nitrogen), applied them in PP, and investigated their fire performance. Zhang et al. (2012) investigated the use of silica and ammonium polyphosphate flame retarded wood fibre in polypropylene composites. In all these studies, the silica flame retarded systems showed reduced heat release and burning rates. The mechanism of the reduction in the heat release rate and mass loss rate was due to physical action of the silica in the condensed phase.

2.2.4 Nano metric particles

Nano metric particles contribute to the enhancement of thermal, mechanical or fire resistance properties when used separately and well dispersed within polymer matrices.They allow considerable reduction in loading content as the interfacial area between the polymer and nanofiller is greatly increased. The contribution of each type of nanoparticles to flame retardancy varies anddepends on its chemical structure and geometry. These nano-metric particles are classified as layered, fibrous and particulate materials (Laoutid et al., 2009).

Layered materials:	represented by nanoclays (e.g. montmorilonite, MMT); one nanometric dimension.
Fibrous materials:	e.g. carbon nantubes (CNTs), sepiolite; elongated structured materials with two nanometric dimensions.
Particulate materials:	e.g. nano scale particulate additives; polyhedral oligosilsesquioxane (POSS), spherical silica nanoparticles; three nanometric dimensions.

2.2.4.1 Nano-clays

A lot of work has been done on nanoclay-based polymer composites and some reviews have been published (Bordes, Pollet & Avérous, 2009; Hapuarachchi & Peijs, 2010; Kiliaris & Papaspyrides, 2012; Morgan, 2006; Morgan, Harris Jr., Kashiwagi, Chyall & Gilman, 2002). Morgan (2006) reviewed the flame retarded polymer layered silicate nanocomposites for commercial and open literature systems. Bordes et al. (2009) discussed the recent research and developments in biopolyester/nanoclay systems, whereas Kiliaris and Papaspyrides (2012) presented recent developments on the use of layered silicates (clay) for designing polymer nanocomposites with enhanced flame retardancy. Natural clays must be chemically modified in order to favour the dispersion of clay nanolayers within the polymer matrix. This is achieved by using organic cations such as alkylammonium, alkyl phosphonium and alkyl imidazol(idin)ium, and leads to the formation of organo-modified nanoclays (Laoutid et al., 2009).

Incorporation of low amounts (~10 wt.%) of organomodified nanoclay in a polymer matrix creates a protective layer during combustion. During heating, the viscosity of a molten polymer/layered silicate nanocomposite decreases with increasing temperature. This facilitates the migration of clay nanolayers to the surface. Heat transfer promotes thermal decomposition of an organomodifier and creates strongly protonic catalytic sites onto the clay surface, which can catalyse the formation of a stable char residue (Kiliaris & Papaspyrides, 2012; Laoutid et al., 2009).

Consequently, the accumulation of clay on the surface of a material acts as a protective barrier that limits the heat transfer into the material, limits the volatilization of combustible degradation products, as well as the diffusion of oxygen into the material. Additionally, nanoclay migration is enhanced by the formation of gas bubbles initiated by the decomposition of both quaternary ammonium organomodifiers and polymer chains. Such gas bubbles may be nucleated by the surfaces of the nanoclay sheets and could also help in the convection of nanoclay sheets to the surface (Kiliaris & Papaspyrides, 2012; Laoutid et al., 2009).

There are several factors that play a key role in determining the flammability behaviour of polymer/silicate layered nanocomposites. These may be char formation, morphology of the nanocomposites (intercalated or exfoliated), and the ability of nanoclays to disperse, contents of organomodifier in nanoclays, nanoclay loading and melt viscosity. The main fire retardancy mechanisms in polymer/silicate layered nanocomposites may be the formation of a barrier against heat and volatiles by migration of clay nanolayers towards the material surface, followed by char formation together with increased melt viscosity for exfoliated nanocomposites. These mechanisms may modify the fire properties of nanocomposites differently depending on the fire test applied. In general, incorporation of nanoclays retards and reduces the peak heat release rate (PHRR), but does not lower the total heat release (THR). This may mean that almost all of the fuel released is combusted, hence almost no change in THR. However, the fuel is released so slowly that HRR stays throughout the burning process (Morgan, 2006). It may also reduce the time to ignition (TTI). In addition, it reduces the melt viscosity in exfoliated nanocomposites and thus prevents dripping and promotes char formation (Kandola, 2001; Laoutid et al. 2009).

Manfredi, Rodríguez, Wladyka-Przybylak & Vázquez (2010) investigated various properties including fire resistance of organically modified clay on jute reinforced vinyl ester and resol composites. The composites showed an improvement in their fire performance. Lower fire risk and low heat evolution were observed. Barbosa, Araújo, Melo & Ito (2007) used Brazilian clay [montmorillonite (MMT)] and two types of commercial flame retardants with a polyethylene matrix to evaluate their flammability behaviour. Polyethylene flame retarded nanocomposites were produced via direct melt intercalation. The flammability resistance of PE/Brazilian clay nanocomposites was improved due to the barrier effect of the organoclay during the combustion. The nanocomposites were more effective than conventional PE/flame retardants systems, and only 3 wt.% MMT reduced the burning rate of the nanocomposites by 17%.

Wei, Bocchini and Camino (2013) addressed the combustion behaviour of PLA nanocomposites based on organomodified MMT clays (i.e. Closite 30B and 20A) with N-alkoxy hindered amine as a flame retardant. Si et al., (2007) prepared self-extinguishing polymer nanocomposites using Closite 20A with PMMA matrix, decabromodiphenyl ether and antimony oxide as flame retardants. Ribeiro, Estevão, Pereira, Rodrigues and Nascimento (2009) imposed some organic chemical treatments on natural Brazilian MMT clay and then evaluated the effect of treatments on flame retardancy potential of ethylene-buty acrylate copolymer composites in the presence of APP and PER (pentaerithritol). In all these studies, samples were prepared by melt mixing process and then subjected to various characterization tests on morphological, thermal, mechanical and flammability performance (i.e. UL94, LOI, cone calorimetry).

From these studies, it is generally reported that the incorporation of clays into polymer matrices led to reduced burning rate with respect to neat polymers. The effect was attributed to the ability of clay to form stable char on the surface of the burning nanocomposites. This insulated the underlying polymer from heat transfer due to flames, thus lowering the rate of volatilization (Wei, Bocchini and Camino, 2013). Furthermore, Wei, Bocchini and Camino (2013) concluded that the combination of nanoclays and flame retardant did not exhibit remarkable additional influence on fire behaviour of PLA nanocomposites except for improved resistance to self-sustained combustion. However, Ribeiro et al., (2009) and Si et al., (2007) have concluded that the combination resulted to lower PHRR, average MLR and HRR than those with only clay or the FRAs. This indicated some synergistic effect between nanoclays and FRAs. Ribeiro et al., (2009) also reported that the modifications to natural Brazilian MMT clay did not change their flame retardancy performance.

Tai, Yeun, Song and Hu (2012) incorporated the organic nanoclay into polyphosphoramide (PDEPD) by in-situ polycondensation to prepare flame retardant/clay nanocomposites. These were then introduced to both polystyrene (PS) and polyurethane (PU) by solvent blending method. From the MCC tests, it was found that both PDEPD and mostly PDEPD/clay nanocomposites FRAs improved the flammability performance of PS and PU matrices by reducing both PHRR and THR. Moreover, the reduction in THR with the inclusion of PDEPD was attributed to the enhancement of char residues after combustion thus leading to less evolution of combustible fuel gases.

2.2.4.2 Carbon nanotubes

Carbon nanotubes (CNTs) are the most widely studied nanofibrous materials with respect to polymer flame retardancy (Gao, Beyer & Yuana, 2005; Hapuarachchi & Peijs, 2010; Laoutid et al. 2009; Ye, Wu & Qu, 2009).They may be synthesized in several ways such as arc discharge, laser ablation and thermal or plasma enhanced chemical vapour growth deposition (CVD). Direct arc discharge and laser ablation require the use of small quantities of a metal catalyst and very high temperatures. The CVD technique, on the other hand, enables the synthesis of CNTs at lower temperatures but leaves significant amounts of catalysts residues on the recovered sample. These nanotubes show exceptional properties that can be used in many applications ranging from macroscopic material composites to nanodevices. They have high aspect ratios and as a result percolate to form networks at very low loadings in a polymer matrix. This leads to a substantial improvement in a number of properties such as mechanical, rheological and flame retardancy (Laoutid et al. 2009).

There are two different types of carbon nanotubes, i.e. small diameter (1-2 nm) single walled nanotubes (SWNTs) and large diameter (10-100 nm) multi walled nanotubes (MWNTs). CNTs are an interesting alternative to the use of conventional flame retardants and nanoclays. Their incorporation at low contents (< 3wt.%) has resulted in enhanced flammability for several polymers {PP, polystyrene (PS), ethylene vinyl acetate (EVA), polymethyl methacrylate (PMMA), low density polyethylene (LDPE) and polyamide 6 (PA 6)}. Several factors influence the flame retardant properties of polymeric material nanocomposites: nanotube dispersion, nanotube loading rate, mean size of nanotubes and large aspect ratio. Large aspect ratio can lead to the formation of an efficient and compact layer (Laoutid et al. 2009).

The presence of CNTs may increase thermal conductivity of a polymer and thus increase the time to ignition (TTI) and peak heat release rate (PHRR) where MWNTs are used. Several studies based on CNTs with nanoclays in different thermoplastic matrices were reported. Gao et al. (2005), Hapuarachchi and Peijs (2010) and Ye et al. (2009) investigated the role of MWNTs with clays (Hapuarachchi & Peijs, 2010; Ye et al., 2009) and magnesium hydroxide (MH) (Gao et al., 2005) in the fire retardancy of PLA and EVA nanocomposites. In all these studies, it was reported that the incorporation of MWNTs in the presence of other additives resulted in a remarkable reduction in heat release rate (HRR), PHRR, mass loss rate (MLR) as well as a prolonged combustion in the cone calorimetry test. Ye et al. (2009) concluded that there was a synergistic effect which was driven by factors such as increased melt viscosity, improved thermo oxidation stability and the formation of compact charred layers due to MWNTs acting as heat barriers and insulation. Furthermore, Gao et al. (2005) concluded that the addition of clay into a CNTs/EVA composite enhanced the formation of graphitic carbon. Additionally, nanotubes reduced the surface cracks of chars to increase the barrier resistance to the evolution of flammable volatiles and the oxygen ingress into the condensed phase.

Peeterbroeck et al., (2004, 2007) used MWNTs with EVA copolymers, in the presence of commercial organoclays (Peeterbroeck et al., 2004) and high density polyethylene (HDPE) coated-MWNTs (Peeterbroeck et al., 2007). In the latter study, the authors demonstrated the significant effect of the HDPE coating on the mechanical properties of nanocomposites and explained the flame retardant efficiency of MWNTs in EVA matrix. Furthermore, improved flammability performance of coated MWNTs containing EVA nanocomposites was reported. This followed the reduction in HRR and enhanced cohesion of the combustion residue, which was attributed to high quality of dispersion of HDPE-coated nanotubes and the chemical structure of the combustion products. In the former study (Peeterbroeck et al., 2004), it was concluded that simultaneous addition of both modified clay and CNTs displayed a synergistic effect. The enhanced thermal and mechanical properties in the presence of nanofillers were also reported.

When the synergistic effect of CNTs, MMTs and decabromodiphenyl oxide/tin oxide in enhancing flame retardancy performance of PS was investigated, Lu and Wilkie (2010) found that nanotubes were more efficient than clay in improving flame retardancy of materials. These CNTs are said to have promoted carbonization in the polystyrene matrix. On the other hand, Isitman and Kaynak (2010) evaluated the potential synergistic flame retardancy action of filler nanoparticles (i.e. nanoclays and CNTs) combined with organophosphorus flame retardant in PMMA. In this case, it is reported that nanoclays showed improved effect on fire properties of intumescent nanocomposites compared to CNTs containing ones. This was explained in terms of suppressed intumescent character of organophosphorus FRA exerted by strong and continuous CNTs networks formed on the flaming surface during combustion. Nanoclays on the other side are said to have physically reinforced and consolidated the phosphate barriers without interfering with its intumescent character.

2.2.4.3 Graphene

Graphene is an emerging two dimensional material with unique mechanical, electrical and thermal properties. It consists of monolayer of sp^2-hybridized carbon atoms (carbon – carbon bond length of ~ 142 pm) packed in a honeycomb lattice. Its current scientific research interest results from marked enhancement in polymer properties at low filler contents. This is due to high aspect ratio of graphene platelets, homogenous dispersion of graphene platelets in a polymer matrix, and the filler-polymer interactions at interface. Similar to other types of nanofillers such as CNTs and MMTs, it is also used to impart flame retardancy character to polymeric materials. This beneficial flame retardancy property may be attributed to the physical barrier effect of layered graphene that slows down the release of volatile flammable gases and protects the underlying material from further burning (Mittal, 2014; Premkumar & Geckeler, 2012; Hong et al., 2014; Wang, Wei, Qiang & Liu, 2014).

Numerous works on graphene-based nanocomposites have been done with focus mainly on various properties other than flammability. The graphene-based nanocomposites may be manufactured in four main routes. These may be a) template synthesis, b) intercalation from solution, c) in situ intercalative polymerization and d) melt intercalation. Mittal (2014) reviewed graphene materials in functional polymer nanocomposites, and has elaborated on these fabrication methods. Premkumar and Geckeler (2012) looked at graphene-DNA hybrid materials. Most studies on graphene nanocomposites mainly involved petroleum-based polymer matrices such as EVA, PP, PVA, PMMA and epoxy (Wang, Wei, Qiang & Liu, 2014; Hong et al., 2014; Huang, Chen, Tang & Gao, 2012; Huang, Gao, Wang, Liang & Ge, 2012; Huang et al., 2012; Dittrich, Wartig, Hofmann, Mülhaupt & Schartel, 2013), whereas studied biopolymers included poly(D, L-lactic-co-glycolic acid), chitosan and cellulose (Pandele et al., 2014; Yoon et al., 2011; Feng, Zhang, Shen, Yoshino & Feng, 2012; Ryu, Mahapatra, Yadav & Cho, 2013; Lee, Marroquin, Rhee, Park & Hui, 2013). Form these studies, the flammability performance of graphene nanocomposites were based on petroleum polymer matrices and so far non on biopolymer matrices.

Huang et al., (2012a, b, c) investigated the flame retardant properties of graphene containing nanocomposites in EVA and PVA polymer matrices. In these studies, authors used graphene alone (Huang et al., 2012a) and incorporated flame retardant additives such as melamine polyphosphate (MMP) (Huang et al., 2012b) as well as an intumescent FR (i.e. poly(piperazine spyrocyclic pentaerythrito bisphosphonate) (PPSPB) grafted onto the surface of graphene oxide (Huang et al., 2012c). From all these studies, the presence of graphene and other FRAs led to improved flammability character of the investigated nanocomposites. This was indicated by increased TTI and reduction of values of PHRR, THR, ASEA and average MLR (Huang et al., 2012a, b) compared to neat PVA. This was attributed to the condensed phase flame retardancy through forming a compact, dense and uniform char during combustion (Huang et al., 2012a). Furthermore, the combination of MMP with graphene in PVA achieved the LOI value of 29.6 vol.% and UL94 V-0 grade (Huang et al., 2012b). Similarly, the graphene grafted PPSPB were reported to have enhanced the flammability performance of EVA by reducing the PHRR of the nanocomposites by about 56% at 1 wt.% filler content (Huang et al., 2012c).

Dittrich et al., (2013) used various carbon additives with different particle sizes and shape to investigate their influence on both flammability and mechanical properties of isotactic PP. Authors compared thermally reduced graphite oxide and multi-layer graphene with carbon black, MWNTs and expanded graphite. The flammability properties of PP were mainly enhanced in the presence of thermally reduced graphite and multi layer graphene which formed residue layers that protected the underlying polymer during combustion. These led to a reduction PHRR up to 74% with respect to neat polymer.

2.2.4.4 Nano scale particulate additives

Nano scale particulate additives form another family of additives made up of nanoparticles of metal oxides, silica and polyhedral oligomeric silsesquioxane (POSS). They are distinguished by their isometric dimensions.

2.2.4.4.1 Silsesquioxane

Polyhedral oligomeric silsesquioxane (POSS) cluster is an inorganic silica like nanocage (general formula $RSiO_{3/2})_n$ where $6 < n < 18$. The inorganic core of POSS is surrounded by organic ligands (i.e. hydrogen, halogen, alkyl groups, organofunctional groups) covalently bound to the Si atoms placed at the vertices of the polyhedral cage. A general concern about POSS is the high level of interactions existing between clusters. This makes some POSS immiscible with some monomers or polymers. Consequently, the nature of the organic ligands of POSS clusters is an important element to choose, since it controls the behaviour of clusters during processing and polymerization, and thus allows tailoring the desired microstructure for the POSS hybrid polymer systems. POSS is given by methyl phenyl polysilsesquioxane, aluminumisobutyl silsesquioxane (Al POSS) and zinc isobutyl silsesquioxane (Zn POSS). They can play a role of metal dispersing agent, and it is possible to include a metal atom at one corner of the POSS nanocage structure. These inorganic nanocages are also referred to as preceramic compounds (Franchini, Galy, Gérard, Tabuani & Medici, 2009; Waddon & Coughlin, 2003).

There are two types of POSS that have been studied with respect to flame retardancy; those that bear either i) eight identical R groups (R = methyl, phenyl, isobutyl or isooctyl), or ii) seven R groups of the same nature and one functional R′ group (R′ = ester, silane, isocynate, methacrylate, alcohol, epoxide or amine). This wide range of R and R′ groups allows for the selective use of functionalized POSS according to the chemical nature of the polymer matrix. The functionality of the R′ group can improve the compatibility between the dispersed nanocages and the polymer matrix. It can also allow either chemical grafting of reactive polymer chains or initiation of polymerization reactions from the POSS surface via the socalled “grafting from” technique (Franchini et al., 2009; Laoutid et al. 2009; Waddon & Coughlin, 2003). Devaux, Rochery and Bourbigot (2002) used montmorillonite (MMT) clay together with POSS to process polyurethane nanocomposites, and they concluded that the nanoadditives appreciably reduced the harmful effects of fire. Additionally, the study showed the importance of the choice of nanoadditives on the results of fire retardant behaviour with two notable factors: the nature of the chemical groups grafted onto POSS and the conditions of the coating synthesis.

The presence of POSS in polymers modifies both the viscosity and mechanical properties of the molten polymer. It also affects the thermal stability and fire performance by reducing the amount of heat released upon combustion. On combustion, POSS acts like a precursor forming thermally stable ceramic materials at high temperatures. For example, Franchini et al. (2009) showed that POSS nanoclusters resulted in the improvement of fire retardancy of epoxy materials and the mechanism involved the formation of a rigid char structure during combustion. Furthermore, He, Song, Hu and Zhou (2009) prepared a series of flame retardant hybrids based on bisphenol A polycarbonate (PC), trisilanolphenylpolyhedral oligomeric silsesquioxane (TPOSS) and oligomeric bisphenyl A bis(diphenyl phosphate) (BDP) by a melt blending method.The group found enhanced thermal oxidative stability and fire resistance of the char layer which built upon the surface of the burning polymer when both BDP and TPOSS were introduced. A synergistic effect was established in the system consisting of 2 wt.% TPOSS and 3 wt.% BDP.

In their investigation where POSS and talc fillers were incorporated in vinyl ester resins and tested for different properties including flammability, Glodek, Boyd, McAninch and LaScala (2008) reported slightly improved fire retardancy and material property. There was a slight increase in fire resistance of methacryl POSS relative to other fillers and this was attributed to successful dispersion and reaction of this POSS into the polymer matrix. However, its overall fire resistance performance was reported as poor relative to brominated FRAs used in the study. Fina, Tabuani and Camino (2010) prepared PP/POSS blends using POSS with different organic groups (methyl, vinyl or phenyl) by melt mixing method. Authors reported improved performance in both thermal and combustion rate. This was said to be as a results of formation of a ceramic superficial layer that protected the underlying material from degradation. The conclusion made was that better results were obtained when vinyl-POSS was used as seen from maximum HRR reduction and increased LOI value. In another study on the effect of flame retardance of isotactic PP/aminopropylisobutyl POSS composites, Bouza et al., (2014) reported improved fire retardance as determined by LOI test. In this study, authors incorporated maleic anhydrite grafted PP (MA-g-PP) coupling agent and such composites led to remarkable increase in LOI values when 2% POSS and 10% MA-g-PP were compounded with PP matrix. Furthermore, the presence of these additives in PP matrix gave composites with high thermal stability than neat matrix as reported from TGA test.

When biopolymers such as poly(butylenes succinate) (PBS) (Wang et al., 2012) and PLA (Fox et al., 2014) were used with POSS materials, improved materials properties were reported. Wang et al., (2012) used POSS and graphene as nanofillers to flame retard PBS prepared by melt blending. It was reported that the addition of graphene led to superior flame retardance to POSS. Authors concluded that the presence of both POSS and graphene improved the char yield with graphene incorporation into PBS leading to better thermo-oxidative resistance in char layer. In a latest study, PLA was extruded with intumescent FRAs based on APP, nanofibrillated cellulose fibre, POSS modified nanofibrillated cellulose fibre and PER by Fox et al., (2014). The authors found that the cross-linked network formed between cellulose, POSS and PLA produced composites with superior flame retardant, rheological and mechanical properties with respect to other intumescent formulations.

2.2.4.4.2 Metallic oxide particles

Metal oxide particles have been studied as reinforcing fillers for polymeric materials. These particles may be nanometric titanium oxide (TiO_2), ferric oxide (Fe_2O_3), aluminum oxide (Al_2O_3) or antimony oxide (Sb_2O_3) particles. Flammability performance of these metallic oxide nanoparticles is dependent upon filler content, particle size and surface area of the nanoparticles (Gallo, Braun, Schartel, Russo & Acierno, 2009; Gallo, Schartel, Acierno & Russo, 2011; Laachachi, Leroy, Cochez, Ferriol & Lopez-Cuesta, 2005, 2007; Laoutid et al., 2009; Lewin, 2011).

Laachachi et al. (2005, 2007) looked at the influence of different nanoparticles (Al_2O_3, TiO_2 and Fe_2O_3) in combination with organoclays (organomodified MMT) and phosphinate additives on the thermal stability and fire retardancy of poly(methyl methacrylate). In both studies, a synergistic effect on the thermal stability and fire performance of these systems was reported. This resulted in enhanced ignition times, reduced total heat, reduced smoke release and a significant increase in the total burning period. The metal oxide particles seemed to promote carbonaceous layer/char formation. They also modified the heat transfer properties of the polymer nanocomposites due to their good thermal properties and large specific area. Depending on the system, the metal oxide particles may (Laachachi et al., 2005) or may not (Laachachi et al., 2007) improve the fire performance of the composites.

Gallo et al. (2009, 2011) investigated the flame retardancy synergy between aluminium phosphinate and metal oxides for different polymers. In the first study (Gallo et al., 2009) Al_2O_3 and TiO_2 were used for poly(butylene terephthalate) PBT. In the second study (Gallo et al., 2011), they used Fe_2O_3 and Sb_2O_3 for a commercial poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/poly(butylene adipate-co-terephthalate) PHBV/PBAT biodegradable blend system. They reported better fire retardancy which was ascribed to increased intermediate char formation. A synergistic effect due to the phosphorus and the nanofiller components was observed in the flame retardancy mechanism, where the phosphorus acted as flame inhibition in the gas phase, and the nanofiller promoted crosslinking in the solid phase (Gallo et al., 2009). In both studies a combination of metal oxides and aluminium phosphinate resulted in better classification in the UL94 test due to the combination of the different mechanisms.

Wang, Han and Ke (2006) prepared flame retardant nanocoatings of nanometer layer double hydroxides (nano-LDHs) and titanium oxide nanoparticles to ammonium polyphosphate-pentaerythritol-melamine intumescent FR system. Authors studied the improvement of nanoparticles in fire resistance and anti-ageing properties of the intumescent flame retarded system. It was reported that the thermal decomposition of nano-LDHs promoted formation of the char by the IFR system, which was said to be intercalated nanostructure with mixed resultant metal oxides (Al_2O_3 and $MgAl_2O_4$). This intercalated structure was thought to have improved the anti-oxidation character of the char structure. It was further reported that inclusion of nano titanium oxide particles improved the anti-ageing of the IFR coated system. The conclusion made was that nanocoating has the good expanding effect and fire resistance property even after 500 hours accelerated ageing.

Shen, Chen and Li (2012) and Li et al., (2012) used PP to investigate the influences of metal oxides on flammability properties of nanocomposites. Lanthanum oxide in the presence of magnesium hydroxide were extruded with PP matrix and their flammability performance tested via LOI and microscale combustion calorimeter (Shen, Chen and Li, 2012). On the other hand, Li et al., (2012) compounded the intumescent system based on APP and PER with antimony oxide by melt mixing method. LOI and UL94 were employed for flame resistance tests. In this study authors reported increased LOI values from 27.8 to 36.6 vol.% in the presence of antimony oxide. The FR system also recorded UL94 V 0 rating at the 2 wt.% content of Sb_2O_3. This was attributed to the reaction of antimony oxide with APP to form crosslinked charred layers. Lowered mechanical properties were also reported in the presence of a metal oxide due to poor compatibility between PP and Sb_2O_3. In the former study (Shen, Chen and Li, 2012), it was found that the presence of La_2O_3 could remarkably improve the flame retardancy of magnesium hydroxide filled PP flame retarded composites. It was indicated by the obtained UL94 V-0 rating and reduced HRR, THR and HRC values of the PP/MH/ La_2O_3 composites. This was attributed to enhanced quality of condensed phase charred layers deposited on the surface of formed magnesium oxide particles through the participation of PP chains in char formation due to a catalytic effect of lanthanum oxide. The authors further proposed some flame retardancy mechanisms which may be obtained from the source.

In general, the incorporation of nanoparticles (organoclays, CNTs, or POSS) decreases polymer flammability through several mechanisms. Amongst others, limiting the fuel transfer, formation of protective layers (char and/or ceramic like materials) and prevention of dripping via reduced melt viscosity can be mentioned. These polymer nanocomposites still burn with little reduction in THR and TTI is generally not improved, which can even decrease for some nanocomposites. This may somehow necessitate the use of nanoparticles in combination with other flame retardant agents for a synergistic effect.

2.2.4.5 Hybrid nanofillers

The hybrid materials refer to the class of materials whereby inorganic and organic components are mixed intimately at a nanometric or molecular scale. Hybrids may be either homogeneous systems of miscible organic and inorganic components or can be heterogeneous. The properties of the resultant material do not only depend on individual properties of the materials, but also on the scale of interaction between the two components that contributes noticeably to the properties of the resultant material. These materials have the potential to improve, amongst others, thermal, mechanical and photochemical stability (http://www.dstuns.iitm.ac.in/teaching-and-presentations/teaching/undergraduate%20courses/vy305-molecular-architecture-and-evolution-of-functions/presentations/presentations-2007/seminar-1/P4.pdf).

A number of studies have been done on the use of hybrid materials in thermal, mechanical and flame resistance performance (Wang, Wei, Qian & Liu, 2014; Bonnet, Bounor-Legaré, Boisson, Camino & Cassagnau, 2012; Marras, Zuburtikudis & Panayiotou, 2007; Nurul & Mariatti; 2013; Messori et al., 2003; Wang, Pang, Chen, Lin & Ning, 2013; Vasiljević et al., 2013). Different hybrid materials such as graphene, phosphorus, layered silicate, silane-PCL, brucite-polyphosphate-amine based inorganic-organic materials. Messori et al., (2003) prepared organic-inorganic hybrid materials from tetraethoxysilane and α and α,ω-triethoxysilane terminated poly(ε-caprolactone) (PCL-Si) using sol-gel process. PMMA slabs were dip-coated with PCL-Si/silica hybrids and increased flame resistance was reported with respect to neat matrix. This was attributed to a preferential segregation of silica onto the outer surface of the nanocomposites. Bonnet et al., (2012) prepared EVA-based hybrid material containing silicon and phosphorus to improve flame retardancy. Authors found synergistic effect between silicon and phosphorus on the fire properties at 1.3 wt.% silicon and 1.4 wt.% of phosphorus loading. A reduction of 35% in PHRR measured in a cone calorimeter for EVA-hybrid materials compared to pure EVA. This was attributed to the formation of compact charred layer.

2.2.5 Mineral flame retardant

Mineral FRs have been researched and reviewed by numerous investigators (Ahmad Ramazani, Rahimi, Frouchi & Radman, 2008; Cárdenas et al., 2008; Durin France, Ferry, Lopez-Cuesta & Crespy, 2000; Focke, Molefe, Labuschagne & Ramjee, 2009; Haurie et al., 2006, 2007; Hollingbery & Hull, 2010a, 2010b, 2012; Hull, Witkowski & Hollingbery, 2011; Laoutid et al., 2006, 2009; Morgan, Cogen, Opperman & Harris, 2007; Nachtigall, Miotto, Schneider, Mauler & Forte, 2006; Pawlowski, Schartel, Fichera & Jäger, 2010; Qui, Xie, Ding & Qu, 2003; Rothon & Hornsby, 1996; Sain, Park & Suhara, 2004; Tang, Zhou & Liu, 2013; Witkowski, Stec & Hull, 2012). These inorganic fillers can influence the reaction of polymers including inert ones. They reduce the contact of combustible products, modifythe thermal conductivity and all its thermophysical properties, and change the viscosity of the resulting materials. These have indirect incidence on the fire performance of a polymer.

Some minerals (see Table 2) are specifically used as FRs due to their behaviour at high temperatures (Hollingbery & Hull, 2010a, 2010b; Laoutid et al., 2009).

The most commonly used mineral flame retardants are hydrocarbonates (Haurie et al., 2006, 2007; Hollingbery & Hull, 2012; Hull et al., 2011; Laoutid et al., 2006, 2009), metal hydroxide (aluminum and magnesium) (Ahmad Ramazani et al., 2008; Cárdenas et al., 2008; Durin France et al., 2000; Grexa & Lübke, 2001; Haurie et al., 2007; Hollingbery & Hull, 2010a, 2010b; Laoutid et al., 2009; Nachtigall et al., 2006; Qui et al., 2003; Rothon & Hornsby, 1996; Sain et al., 2004; Witkowski et al., 2012) and borates (Durin France et al., 2000; Grexa & Lübke, 2001; Laoutid et al., 2009; Pawlowski et al., 2010; Sain et al., 2004). Inorganic fillers have a physical flame retardant action. As the temperature of the system rises, fillers decompose endothermically and consequently absorb energy. Furthermore, they release non flammable molecules such as H_2O and CO_2. These molecules serve to dilute combustible gases and can also promote the formation of a protective ceramic or vitreous layer due to their release which leaves behind such a layer (Hollingbery & Hull, 2010a, 2010b; Laoutid et al., 2006, 2009).

Table 2. Physical properties of potential fire retardant mineral fillers. Reprinted from Hull et al. (2011), Copyright 2011, with permission from Elsevier.

Filler	**Formula**	**T_{decomp}/ °C**	**ΔH_{decomp}/kJ g^{-1}**
Aluminium hydroxide	$Al_2O_3 \cdot 3H_2O$	180-200	1300
Magnesium hydroxide	$Mg(OH)_2$	300-320	1450
Calcium hydroxide	$Ca(OH)_2$	430-450	1150
Nesquehonite	$MgCO_3 \cdot 3H_2O$	70-100	1750
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	220-240	1300
Huntite	$Mg_3Ca(CO_3)_4$	400	980
Ultracarb	Hydromagnesite/Huntite	220-400	1172
Boehmite	60/40 AlO(OH)	340-350	560

2.2.5.1 Hydroxycarbonates

All carbonates release CO_2 at high temperatures, except for magnesium and calcium carbonates releasing it below 1000 °C. Magnesium carbonate seems to be the one releasing carbon dioxide at the lowest temperature of about 550 °C (Haurie et al., 2007). In comparison with other conventional flame retardants, hydrocarbonates are less widely used but remain an alternative to metal hydroxides. Natural magnesium carbonate (magnesite) and synthetic magnesium hydrocarbonate (hydromagnesite) release water, break down endothermically and liberate CO_2 at high temperature. The thermal decomposition of hydromagnesite ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ or $5MgO \cdot 4CO_2 \cdot 5H_2O$) in air can be described as (Haurie et al., 2006, 2007; Hollingbery & Hull, 2012; Hull et al., 2011; Laoutid et al., 2006, 2009):

$$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O \rightarrow 4MgCO_3 \cdot Mg(OH)_2 + 4H_2O$$

$$4MgCO_3 \cdot Mg(OH)_2 \rightarrow 4MgCO_3 \cdot MgO + H_2O$$

$$4MgCO_3 \cdot MgO \rightarrow 5MgO + 4CO_2 \qquad (800kJ/kg)$$

Hydromagnesite releases water and carbon dioxide over a wider temperature range than aluminum trihydroxide (ATH) and magnesium dihydroxide (MDH) (also called magnesium hydroxide, MH) (see section 2.2.5.2). It has been used as flame retardant in polypropylene (PP), ethylene vinyl acetate (EVA) (Haurie et al., 2006) and low density polyethylene (LDPE)/ethylene vinyl acetate (EVA) blends (Haurie et al., 2006, 2007). It releases both water and carbon dioxide between 200 and 550 °C in comparison with ATH (180 to 200 °C) and MDH (300 to 340 °C) suggesting that it may have similar or even better flame retardancy effectiveness than ATH and MDH (Laoutid et al., 2009).

Some studies have been conducted on magnesium carbonate (Focke et al., 2009) and hydromagnesite (Haurie et al., 2006, 2007; Hollingbery & Hull, 2012; Hull et al., 2011; Laoutid et al., 2006). Haurie et al. (2006, 2007) investigated the flammability and thermal stability of hydromagnesite alone in polyethylene (Haurie et al., 2006) and combined with aluminum hydroxide, magnesium hydroxide and montmorillonite mixtures in polyethylene/ethylene vinyl acetate blends (Haurie et al., 2007). Laoutid et al. (2006) compared the flame retardancy of a combination of hydromagnesite/organomodified montmorillonite (MMT) with a magnesium hydroxide (MH and/or MDH)/MMT flame retardant system. In all these studies, improved fire resistance (i.e. reduced peak heat release rate, auto extinguishability, and increased time to ignition) was generally reported. The conclusions made were, namely, reduction in mineral filler content as well as improved mechanical properties due to the presence of nanoclays.

2.2.5.2 Metal hydroxide

Metal hydroxides are the largest group of mineral fire retardants. They act as flame retardants for polymers by releasing water vapour through endothermic decomposition and leave a thermally stable inorganic residue. This has to occur at temperatures higher than the polymer processing temperature range and around the polymer decomposition temperature. Aluminum trihydroxide, $Al(OH)_3$ (ATH) and magnesium dihydroxide, $Mg(OH)_2$ (MDH) are the most commonly used metal hydroxides. They are both used as smoke suppressants and have been incorporated in wood products as flame retardants (Grexa & Lübke, 2001; Hollingbery & Hull, 2010a, 2010b; Laoutid et al., 2009).

The endothermic decomposition of ATH occurs between 180 and 200 °C, depending on particle size and physical form, leading to the release of water and formation of alumina:

$$2Al(OH)_{3(s)} \rightarrow Al_2O_{3(s)} + 3H_2O_{(g)} \qquad (1050\ \text{kJ/kg})$$

The decomposition reaction of ATH has several effects on the combustion of a polymer, namely it absorbs 1050 kJ/kg of energy, and then cools down the polymer material, the formed solid alumina (Al_2O_3) provides a thermally insulating protective coating, and the released water vapour dilutes the combustible gases and forms a protective gas layer. The use of ATH lowers fire growth in cone calorimetry and markedly reduces smoke production. However, the fire properties of ATH filled polymers are only of interest at high loading levels i.e. 60wt.%. Such high loadings have a negative effect on the mechanical properties of the composites. This limits the application of mineral flame retardants. Due to its low processing temperature, ATH is limited to polymers with low processing temperatures such as EVA and LDPE (Cárdenas et al., 2008; Haurie et al., 2007; Hollingbery & Hull, 2010a, 2010b; Laoutid et al., 2009; Witkowski et al., 2012).

The use of ATH as a flame retardant was explored in different studies (Ahmad Ramazani et al., 2008; Cárdenas et al., 2008; Haurie et al., 2007; Nachtigall et al., 2006; Witkowski et al., 2012) where it was used in combination with other additives. Haurie et al. (2007) used hydromagnesite, MDH, ATH and montmorillonite in LDPE/EVA blends, Cárdenas et al.

(2008) and Witkowski et al. (2012) investigated the influence of ATH (different particle sizes and surface treatments) and both ATH and MDH, respectively, on the fire retardant properties of EVA/nanoclay composites. As a way to minimize the negative effects of high loads of metallic hydroxides, Nachtigall et al. (2006) incorporated interfacial coupling agents for polypropylene (PP)/ATH composites. The effect of a combination of ATH and zinc borate on a PP matrix was investigated by Ahmad Ramazani et al. (2008). In all these investigations, it was generally concluded that there is synergy between the ATH and other additives (i.e. nanoclays, MDH and zinc borate) resulting in improved fire retardancy and mechanical properties.

Magnesium dihydroxide (MDH) acts the same way as ATH except that its endothermic decomposition occurs at temperatures above 300 °C. This makes MDH an interesting additive with respect to extrusion and injection moulding processes of some polymers (Laoutid et al., 2009; Rothon & Hornsby, 1996).

$$2Mg(OH)_{2(s)} \rightarrow 2MgO_{(s)} + 2H_2O_{(g)} \qquad \text{(1300 kJ/kg)}$$

Its flame retardant action is effective up to 400 °C. Beyond this point, the exothermic character of degradation predominates. On decomposition, MDH may have a catalytic effect on the carbonized residues produced by combustion. This leads to an after glow effect, which could be cancelled by incorporating additional additives to acquire effective barrier formation (Focke et al., 2009; Laoutid et al., 2009).

Various polymer matrices such as PP (Sain et al., 2004), EVA (Durin France et al., 2000; Laoutid et al., 2006; Qui et al., 2003; Ye et al., 2009) and unsaturated polyester resins (Tang, H. et al., 2013) have been compounded with MDH filler and their flammability and mechanical properties were investigated. Sain et al. (2004) studied the flammability of sawdust and rice husk filled PP with magnesium hydroxide combined with boric acid and zinc borate as flame retardant systems. MDH (25 wt.%) lowered the burning rate (using a horizontal burning test) of the composites by 50% relative to the untreated ones. It was further reported that there was no flame resistance synergy observed between MDH and other additives. Grexa and Lübke (2001) investigated the effect of magnesium hydroxide (type A) on the flammability properties of wood particle boards.This was compared to combinations of monoammonium phosphate with ATH (type B) and monoammonium phosphate with boric acid (type C). The group reported decreased peak values of HRR (using a cone calorimeter) as a function of MDH content (see Figure 2, where A1, A2 and A3 = 8, 15 and 24 wt.%, respectively) showing the possibilityof improving the overall fire performance of wood particleboard using this flame retardant.

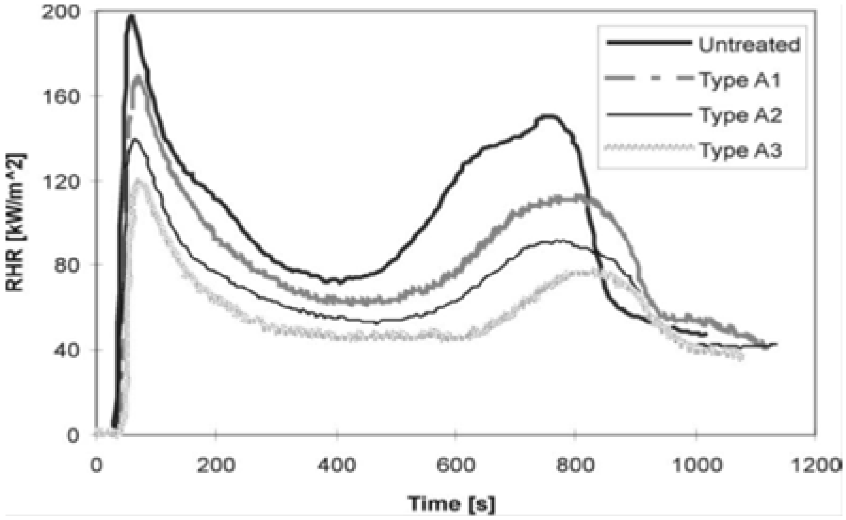

Figure 2. HRR as a function of time for untreated and FR treated particleboard with the use of magnesium hydroxide. Reprinted from Grexa and Lübke (2001), Copyright 2001, with permission from Elsevier.

MDH nanoparticles have also been considered as flame retardant agents (Qui et al., 2003). They can be obtained by several methods including a solgel technique followed by a hypercritical drying procedure, hydrothermal reaction using various precursors and solvents, or precipitation of magnesium salts with alkaline solution. This last method allows for the control of nanoparticles morphology by fine tuning of experimental parameters such as the chemical nature of a base used as precipitant, type of counterion, temperature as well as hydrothermal treatment. The use of nanometric MDH led to good fire performance at lower loading levels (Laoutid et al., 2009). This was also shown by Qui et al. (2003) who prepared and characterized MDH nanoparticles as flame retardant for EVA nanocomposites. They attributed this to good dispersion of the nanoparticles resulting in the formation of more compact and cohesive char during combustion tests (i.e. limiting oxygen index, LOI).

2.2.5.3 Borates

Borates are another family of inorganic additives with flame retardance properties. The most frequently used borate is zinc borate ($2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$). It undergoes endothermic decomposition (503 kJ/kg) between 290 and 450 °C and liberates water (H_2O), boric acid (H_3BO_3) and boron oxide (B_2O_3). Boron oxide softens at 350 °C and flows above 500 °C, leading to the formation of a protective vitreous layer. In the case of polymers with oxygen atoms, the presence of boric acid causes dehydration, leading to the formation of a carbonized layer. This layer protects the polymer from heat and oxygen thus reducing the amount of released combustible gases (Durin France et al., 2000; Grexa and Lübke, 2001; Laoutid et al., 2009; Pawlowski et al., 2010; Sain et al., 2004).

3. Flammability testing techniques

Flammability of polymers can be characterized by the ignitability, flame spread rate and heat release. A number of small, intermediate and/or full scale flammability tests are used in industrial and/or academic laboratories. They are used for either screening materials during production or testing manufactured products. This section discusses commonly used flammability testing techniques such as cone calorimetry, pyrolysis combustion flow calorimetry (PCFC), limiting oxygen index (LOI), underwriters' laboratories (UL 94), and Ohio state university (OSU) heat release rate (Carvel et al., 2011; Horrocks, 2011; Price et al., 2001).

3.1 Cone calorimetry

Cone calorimetry is a technique used to quantify the flammability of materials by determining various flammability parameters. It was first reported on by the National Bureau of Standards (NBS), now known as the National Institute of Standards and Technology (NIST), in 1982. This came after several attempts to design a reliable bench scale engineering device for measuring heat release rate (HRR). Although there were such tools already built for this purpose in the late 1970's and early 1980's by NBS and other institutions, none was appropriate for normal engineering laboratory use. It was during this time when the concept of oxygen consumption was developing and becoming familiar. From this concept, the successful bench scale heat release rate (HRR) apparatus was developed and the method was termed cone calorimetry. There were numerous improvements made on the cone calorimeter since its introduction. However, its basic principle has remained unchanged. The greatest changes were introduced in 1987 with the inclusion of systems for measuring smoke optically and soot yield gravimetrically. Most other changes involved parts redesign for ease of use and reliability of operation (Babrauskas, 1993; Lindholm, Brink & Hupa, 2009; Wichman, 2003). Figure 3 shows a picture of a cone calorimeter apparatus.

Figure 3. Cone calorimeter apparatus (from the Council for Scientific and Industrial Research (CSIR) fire testing laboratory).
(*Intended for colour on the Web and black-and-white in print*)

Cone calorimetry is one of the most effective medium sized fire behaviour tests used to study the rate of heat released by materials exposed to radiant heat flux. Its principle is based on the measurement of decreasing oxygen concentration in the combustion gases of the sample that is subjected to a given heat flux (10 to 100 kW m^{-2}). It has been standardized in the United States (ASTM E 1354) and now in an international standard (ISO 5660) (Carvel et al., 2011; Guillaume et al., 2012; Laoutid et al., 2009; Wichman, 2003).

Figure 4 shows an experimental schematic representation of a cone calorimeter. A sample of 100 mm x 100 mm dimensions is horizontally (occasionally vertically) placed in a sample holder on a load cell for evaluation of the mass loss during the experiment. The sample is aluminum foil wrapped on the sides and at the bottom. It is put in a retainer frame over low density ceramic wool and the retainer frame is secured to the specimen holder. A conical radiant electrical heater uniformly irradiates the sample from above, and combustion is triggered by an electrical spark. The combustion gases that are produced pass through the cone and are removed by means of an exhaust duct system with a centrifugal fan and an extraction hood. The centrifugal fan is situated in the combustion gas line to set the flow rate of combustion products. Along the combustion gas line there is a gas sampling ring positioned before the fan. The gas sampled in the ring is first passed through two filters to remove particles. It is then passed through a cold trap and a drying agent to remove possible water. Finally it reaches the gas analyzers. Between the gas sampling ring and the fan there is also a smoke measurement system. This system determines the amount of smoke produced using a laser photometric beam (Carvel et al., 2011; Guillaume et al., 2012; Laoutid et al., 2009; Lindholm et al., 2009; Wichman, 2003).

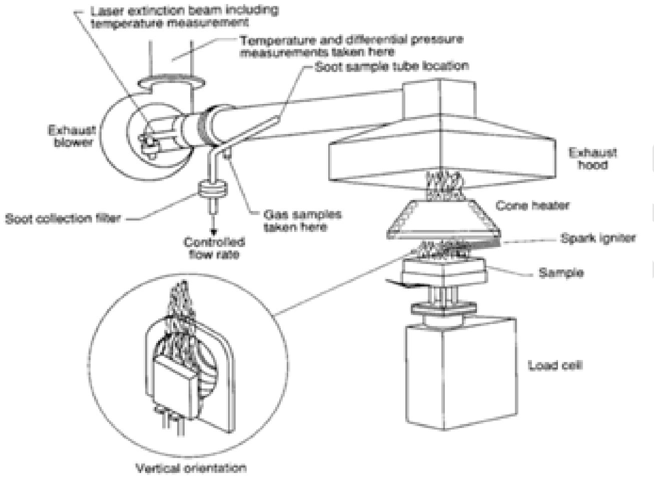

Figure 4. Schematic representation of an experimental set-up in a cone calorimeter. Reprinted from Babrauskas and Peacock (1992), Copyright 1992, with permission from Elsevier.

To perform the basic cone calorimeter experiments, only an oxygen analyser is required. Furthermore, to better understand the burning process and minimize the uncertainties in the results, additional analyzers are usually fitted. These may be CO and CO_2 analyzers. To further analyse combustion products and gaseous species, a Fourier transform infrared (FTIR) spectrometer can be coupled through a heated line (Lindholm et al., 2009).

The measurements of gas flow and oxygen concentration are used to calculate the quantity of heat released per unit of time and surface area (heat release rate, HRR) expressed in kW m^{-2}. Development of HRR over time i.e. the value of its peak maximum (PHRR) or HRR maximum is considered in order to assess the fire properties of materials. The calculation of

HRR is based on Huggett's observation in a study of the estimation of HRR via oxygen consumption measurements (Huggett, 1980). Huggett observed that most organic materials release an amount of heat that is practically proportional to the amount of oxygen consumed while burning. The proportionality factor is constant from one material to another and is equal to13.1 kJ g^{-1} consumed oxygen, with an accuracy of approximately 5%. Integration of the heat release rate (HRR) versus time curve gives the total heat release (THR) expressed in MJ m^{-2} (Carvel et al., 2011; Guillaume et al., 2012; Laoutid et al., 2009; Wichman, 2003).

Cone calorimetry, in addition to the aforementioned parameters, also enables the characterization of time to ignition (TTI), time to flame out (TFO), mass loss rate, levels of oxygen, carbon monoxide and carbon dioxide, and total smoke released (TSR). Furthermore, it provides more detailed fire characteristics, with HRR being the most widely used parameter for evaluating the fire properties. Some conditions, such as ignition and flammability of weakly reacting materials, conditions of low or fluctuating oxygen concentration, and variable material thickness and composition, pose difficulty for proper examination of samples (Carvel et al., 2011; Guillaume et al., 2012; Laoutid et al., 2009;Wichman, 2003). However, cone calorimetry is regarded as the most versatile medium sized fire testing method ever invented.

3.2 Pyrolysis combustion flow calorimetry (PCFC)

Pyrolysis combustion flow calorimetry (PCFC) is a fire test method for evaluating the combustibility of milligram sized samples. It is also known as microscale combustion calorimetry (MCC). This was originally developed by the Federal Aviation Administration (FAA) in the United States. The intent was to identify inherently fire resistant polymers for use in commercial air flights. Later on the FAA adopted the method to screen new polymers for heat release rate in flaming combustion. Recently, PCFC has been used to assess the flammability of flame retarded polymers. It is now a standardized technique classified as ASTM D7309-07 (Lyon & Walters, 2002, 2004; Lyon, Walters & Stoliarov, 2007a; Morgan & Galaska, 2008; Morgan, Wolf, Guliants, Shiral Fernando & Lewis, 2009; Schartel, Pawlowski & Lyon, 2007).

PCFC simulates the burning of a polymer solid. It separately reproduces the solid state and gas phase processes of flaming combustion in a nonflaming test. This is achieved by controlled pyrolysis of the sample in an inert gas stream followed by high temperature oxidation of the volatile pyrolysis products. The heat of combustion of the pyrolysis products is measured by the use of oxygen consumption calorimetry. This method combines the constant heating rate and flow characteristics of thermal analysis (i.e. thermogravimetry) with the ability to determine the heat of combustion typical of oxygen bomb calorimetry. Nonetheless, PCFC determines the heat release and heat release rate using an oxygen consumption method. Consequently, PCFC is more of a fire calorimetry parallel rather than a thermal analysis (Lyon & Walters, 2004; Schartel et al., 2007).

The PCFC technique attempts to improve upon laboratory pyrolysis combustion methods by providing a dynamic capability for solids without the need to measure mass loss rate during the test. It helps in measuring the maximum specific heat release rate Q_{max} (HRR, W g^{-1}) at a heating rate β, the total amount of heat release for complete combustion h_c^0 (THR, J g^{-1}), and the temperature at maximum pyrolysis rate T_{max} (°C) of polymers using only milligram samples. For polymeric materials that thermally decompose to fuel gases and possibly forming char in a single step, the pyrolysis temperature interval ΔT_p is given by equation 1:

$$\Delta T_p(°C) = eRT_{max}^2/E_a \qquad (1)$$

where E_a (J mol^{-1}) is the global activation energy for pyrolysis, e is the natural number and R is the gas constant. These combustion parameters help define a heat release capacity η_c (HRC, J g^{-1} K^{-1}) given by equation 2:

$$\eta_c = Q_{max}/\beta = h_c^0/\Delta T_p \qquad (2)$$

The heat release capacity is the maximum potential of the material to release combustion heat in a fire. From the above derivation, the heat release capacity(η_c) is a combination of material properties, consequently, is itself a material property as measured in PCFC (Lyon & Walters, 2005; Lyon et al., 2007a, b; Schartel et al., 2007). According to Schartel et al. (2007) the use of HRC as a measure of fire risk is based on the assumption that the maximum specific heat release rate at the decomposition temperature reached at constant heating rate correlates with the mass loss rate during pyrolysis in a fire characterized by a transient temperature gradient.

The apparatus construction and calibration method are well described by Lyon and Walters (2002, 2004) and its schematic representation is shown in Figure 5a. PCFC is based on linear programmed heating of milligram samples in an inert atmosphere to separate the solid and gas phase processes of flaming combustion as would normally be the case in a fire situation (Morgan et al., 2009).

The principles of this technique are as follows: A solid sample is subjected to heating at a constant rate (β) of temperature rise under an inert (N_2) gas flow. The heating goes to a maximum temperature (T_{max}) and the sample is held at this maximum temperature for between 10 and 120 s in order to stimulate pyrolysis. The volatile pyrolysis products generated during the temperature rise are removed from the pyrolyser by the nitrogen purge gas, and O_2 gas is added to the pyrolyzate/nitrogen gas stream at the inlet to the combustor. Combustion products such as carbon dioxide, water, and acid gases that exit the combustor are removed by the scrubbers, and the dry nitrogen and the residual oxygen pass through the flow meter and oxygen analyser. Deconvolution of the oxygen consumption signal is performed numerically during the test and the heat release rate, heat release capacity, and total heat of combustion are calculated and displayed. To determine the residual mass of the sample, the quartz tube is weighed after the test. Figure 5b shows the experimental setup of the PCFC in comparison with the flaming combustion of a polymer. This figure illustrates how the condensed phase (pyrolysis) and gas phase (combustion) processes of flaming combustion are separately reproduced in a nonflaming combustion test using the flaming polymer combustion as a reference (Lyon et al., 2007b; Lyon & Walters, 2002, 2004, 2005; Morgan et al., 2009; Schartel et al., 2007).

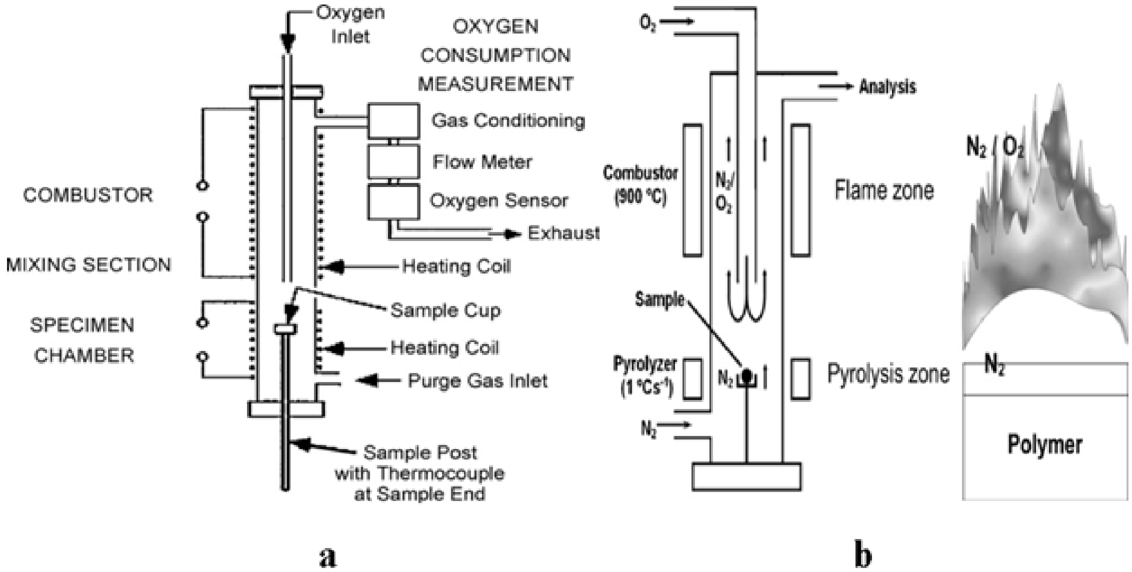

Figure 5 (a, b). Schematic representation of pyrolysis combustion flow calorimetry (PCFC):
(a) basic section of the apparatus. Reprinted from Morgan et al. (2009), Copyright 2009, with permission from Elsevier.
(b) Experimental set-up of the PCFC (left) in comparison with the flaming combustion of a polymer (right). Reprinted from Schartel et al. (2007), Copyright 2007, with permission from Elsevier.

The total heat of combustion of the solid, as opposed to just the pyrolysis gases, can be measured by switching the purge gas from nitrogen to air after the temperature ramp, or by using air as the purge gas during the ramp and hold cycles. Thus, selective thermooxidative degradation of the solid or char can be accomplished and the oxygen consumption can be measured to determine the heat of complete combustion since any residual organic material will be oxidized in air at a maximum temperature (T_{max}) (Lyon & Walters, 2004).

The pyrolysis combustion flow calorimetry method has some advantages. This technique requires small sample size of 5 to 50 mg, ideal for research work giving small product yields during synthesis. When a sample is reacted in an air atmosphere, it can separate oxide forming reactions from nitride forming reactions. PCFC has the capability of separately measuring the combustion of volatile and nonvolatile components (Lyon & Walters, 2004).

3.3 Limiting oxygen index (LOI)

Limiting oxygen index (LOI) is the minimum concentration of oxygen in a mixture of oxygen and nitrogen that is needed to support the flaming combustion of a material. It is expressed in volume percent (vol%). It was first introduced in 1966 by Fenimore and Martin (Lyon et al., 2007a; White, 1979). It is used to indicate the relative flammability of materials. It is standardized in the United States (ASTM D 2863) and in France (NF T 51-071), as well as internationally (ISO 4589). The principle of the method is that a sample is placed vertically within a controlled atmosphere and its top inflamed with a burner. LOI, the minimum concentration of oxygen in a mixture of oxygen and nitrogen that either maintains flame combustion of a material for 3 minutes or consumes a length of 5 cm of a sample, is expressed as:

$$LOI = 100 \times [O_2]/([O_2] + [N_2]) \qquad (3)$$

where $[O_2]$ and $[N_2]$ are the concentrations of oxygen and nitrogen gases, respectively. According to ISO 4589, LOI is measured on specimen (dimensions: 80 x 10 x 4 mm) vertically placed at the centre of a glass chimney as illustrated in Figure 6. A mixture of gases flows upstream via this chimney and is homogenized by passing through layers of glass beads. After 30 s purge of the column, the top of a specimen is ignited like a candle (Kandola, 2012; Laoutid et al., 2009; Wichman, 2003).

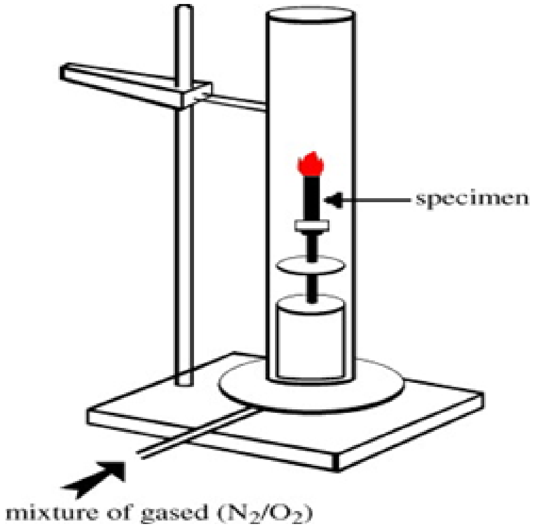

Figure 6. Schematic representation of a limiting oxygen index (LOI) test setup. Reprinted from Laoutid et al. (2009), Copyright 2009, with permission from Elsevier.

As air contains 21% of oxygen, materials with LOI values less than this are classified as combustible, but those with LOI greater than 21 are classed as self extinguishing since their combustion cannot be sustained at ambient temperature without an external energy contribution. It therefore means that high LOI value materials generally exhibit a better flame retardant property. This method remains one of the most important screening and quality control tools in the plastics industry to characterize both the ignitability and flammability resistance. However, LOI measurements are taken at room temperature and LOI values decrease as temperature increases. This means that self extinguishing cannot be considered a fast rule since materials with high LOI values at room temperature may burn without self extinguishing under intense fire conditions. It should be noted that melting and dripping of a polymer during the LOI test may cause a specimen to extinguish and thus give misleading high LOI values. In addition, LOI has a limitation as a test for nanocomposites in that organomodified nanoclay reinforced polymer nanocomposites exhibit decreased LOI values due to an increased flame spread rate over the surface of the specimen, while inside the material nanoclays form a barrier layer that limits the propagation of fire (Chapple & Anandjiwala, 2010; Kandola, 2001; Laoutid et al., 2009; Wichman, 2003).

The advantages of LOI are that it provides a convenient, reproducible means of determining a numerical measure of flammability. Furthermore, the test equipment is inexpensive and only a small sample size is required for testing (Nelson, 2001).

3.4 UnderwritersLaboratories 94 (UL94)

UL 94 is a set of tests approved by Underwriters Laboratories Inc. as flame tests for plastics materials for parts in devices and appliances. It includes a range of tests such as small and large flame vertical (V) tests, horizontal (H) tests for bulk and foamed materials, as well as radiant panel flame spread test. The commonly used test is UL 94 V in terms of practice and usage. It measures ignitability and flame spread of vertical bulk materials exposed to small flame. It is equivalent to international standard IEC 60695-11-10 (Test method B) for small flames (50W) and ASTM D3801-10 (Laoutid et al., 2009; Patel, Hull & Moffatt, 2012; Wang, Y., Zhang, Chen & Zhang, 2010).

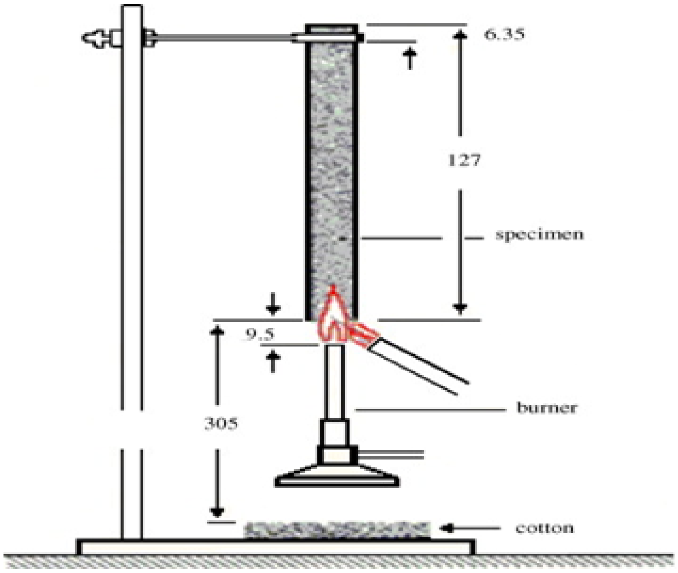

Figure 7. Schematic representation of UL 94 vertical test. Reprinted from Laoutid et al. (2009), Copyright 2009, with permission from Elsevier.

As shown in Figure 7, the burner is adjusted to produce a blue flame with 20 mm high central cone and a power of 50W. The flame is applied to the bottom of a specimen with the top of the burner located approximately 10 mm from the bottom edge of the specimen. The flame is applied for 10 s and removed, and the time required for flaming combustion to cease (after flame time) is noted as t_1. After flaming combustion has ceased, the flame is applied for another 10 s and after flame t_2 is noted together with afterglow time t_3. The distance between the burner and specimen must remain constant during flame application. If some drops fall from the specimen, the burner is tilted to a maximum angle of 45° and slightly removed from the edge of the specimen. During the test, the presence of burning drops and any ignition of a piece of cotton placed under the specimen must be noted. The standard specification is that at least 5 specimens must be tested. The classification is made via V-0, V-1 and V-2 rating and criteria as shown in Table 3(Laoutid et al., 2009; Patel et al., 2012; Wang, Y., et al., 2010).

Table 3. UL-94 V ratings and criteria. Reprinted from Patel et al. (2012), Copyright 2011, with permission from John Wiley and Sons.

Sample classified to the following criteria	**V-0**	**V-1**	**V-2**
After flame time for each individual specimen t_1 or t_2	≤10 s	≤30 s	≤30 s
Total after flame for any set (t_1 plus t_2 for five specimens)	≤50 s	≤250 s	≤250 s
After flame/glow time for each specimen after second application ($t_1 + t_3$)	≤30 s	≤60 s	≤60 s
After flame glow of any specimen up to clamp	No	No	No
Cotton indicator ignited by flaming drips	No	No	Yes

s stands for seconds

The UL 94 test is widely used both in industry and academic research centres. It is intended to meet industrial requirements as well as classify polymeric materials hierarchically. The information obtained remains limited due to its basic and unrefined character. For specimens that flow, the test seems less appropriate than for more cohesive materials (Laoutid et al., 2009; Patel et al., 2012; Wang, Y., et al., 2010).

3.5 Ohio State University heat release apparatus (OSU)

The OSU is a technique developed to describe how a material burns. It is a quantitative method of analysis that was available in its basic form in the early 1970's. The technique is used to measure the rate of heat release (RHR) of materials and products in a forced flaming combustion. Originally RHR is determined by measuring the temperature change (ΔT) of a constant mass flow of air (m_a) through the apparatus caused by the heat released from the burning sample. The change in enthalpy of the air is calculated using the usual relation:

$$\Delta H = m_a c_p \Delta T \qquad (4)$$

where c_p is the heat capacity of air (Smith, 1996).

The fundamental principles of the OSU heat release apparatus are outlined in the Federal Aviation Administration (FAA), FAR 25.853 (ASTM E906/E906M-10, 2010) and American Society of Testing and Materials (ASTM), ASTM E906 (http://www.flightsimaviation.com/data/FARS/part_25-appF4.html ; http://www.astm.org/Standards/E906.htm) test methods.This apparatus is used in two configurations A and B. Configuration A is used by FAA under the designation FAR 25.853 as a regulatory tool in determining the fire properties of aircraft interior cabin materials. The FAA requirements are exclusively based on heat release. In order for a material to satisfy the requirements it must have an average maximum heat release of < 65 kW m^{-2}, during 5 minutes of the test and an average total heat release of < 65 kW min m^{-2} within the first 2 min of the test, when the incident heat flux is set at 35 kW m^{-2} (Hirschler, 2000; http://www.fire.tc.faa.gov/pdf/handbook/00-12_ch5-0909.pdf). Configuration B, under the designation ASTM E906, is intended for use in research and development and not as a basis for rating, regulatory, or code purposes. Figure 8 shows the OSU rate of heat release apparatus (http://www.fire-testing.com/astm-e-906-osu).

In the standard method (ASTM E906, configuration B), the OSU determines the rate of heat release (RHR) (also heat release rate, HRR) of a material from the sensible enthalpy (temperature) rise of the air. The specimen is injected into an environmental chamber through which a constant flow of air passes. The specimen'sorientation varies from vertical (configuration B) to horizontal (configuration A). The air flows past a 150 mm x 150 mm specimen with maximum thickness of 45 mm. The OSU monitors the temperature difference between the air entering and exiting the environmental chamber by a thermopile. The specimens of materials or products are exposed to different levels of radiant heat at incident fluxes up to 100 kW mm^{-2}. Combustion is initiated by piloted ignition. The combustion products leaving the chamber are monitored and the change in temperature (enthalpy) due to theseis used to calculate the rate of heat release(Hirschler, 2000; http://www.fire.tc.faa.gov/pdf/handbook/00-12_ch5-0909.pdf;http://www.fire-testing.com/astm-e-906-osu).

Numerous modifications had been proposed to the OSU technique (Tran, 1988, 1990; Tran & White, 1992). This was because the standard thermal mode had some errors caused by the heat losses that were not accounted for, as well as the fact that the mass flow rate is controlled (White & Dietenberger, 1999). Consequently the oxygen consumption mode was put in place in addition to the standard thermal mode within the OSU apparatus. For example, Tran and White (1992) modified OSU with the aim to improve its accuracy during the investigation of the burning characteristics of wood. They used four ways in this regard: a) addition of oxygen consumption calorimetry, b) addition of an auxiliary heat flux meter, c) gas phase piloted ignition of the sample, and d) a mass loss determining system using an injection shaft as a lever. According to Tran (1990), the common finding was that the HRR measurements obtained by the OSU standard thermal mode are lower than those obtained by the OSU oxygen consumption method in the same apparatus, despite some differences in the way gas samples are taken. The oxygen consumption mode is based on the fact that the quantity of net heat released by complete combustion per unit of oxygen consumed is almost constant over a wide range of materials (i.e. 13.1 kJ/g) (Huggett, 1980; Tran, 1988). It is through measuring the quantity of oxygen consumed that the amount of heat release is calculated. The heat release rate (HRR) measured through OSU and cone calorimeter were investigated and compared in some studies (Filipczak, Crowley & Lyon, 2005; Tran, 1990). The general conclusion made by Tran (1990) was that there is some agreement of the HRR results from these two different test methods when a modified OSU was used. However, the HRR results from these two test methods did not agree in most cases according to Filipczak et al. (2005), who used single ply fibre glass reinforced epoxy thin composite materials.

Figure 8. Ohio State University heat release (OSU) apparatus. Reprinted from http://www.fire-testing.com/astm-e-906-osu , with permission from Fire Testing Technology Limited.
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The other modification is that of determining the smoke release rate. This is done by an optical method, with a white light source and a photo detector fitted above the exhaust stack close to the thermopile (Hirschler, 2000). Both heat and smoke release are measured from the moment the specimen is injected into a controlled exposure chamber. Measurements are continued during the period of ignition and to such a time that the test is terminated.

Although the OSU heat release apparatus is a good tool for flammability testing, there are known limitations of this test method (Hirschler, 2000; ASTM E906/E906M-10, 2010):

- The heat and smoke release depend on several factors such as formation of surface char, formation of adherent ash, sample thickness, and method of mounting.
- Heat release values are a function of the exposed tested area of the specimen.
- The test method is restricted to the specified specimen size of materials, products or assemblies. In the case of products, the test specimen (i.e. prototype) is representative of the product in actual size.
- At very high specimen heat release rates, flaming above the stack is possible making the test invalid.

- There is no established general relationship between heat release rate values obtained from horizontally and vertically oriented specimens. Specimens that melt and drip in a vertical position are tested horizontally.
- Vertical testing remains a problem for testing thermoplastic materials in the OSU. Moreover, the reflector used for horizontal testing leads to serious reproducibility errors in the heat flux input to the horizontal sample.

Other analytical techniques including thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are useful in broadening the understanding of the response of different materials under fire circumstances. Furthermore, TGA coupled with FTIR is also a useful tool for identifying gases being emitted during the thermal decomposition process. For example, TGA provides valuable information on char residue that remains after thermal degradation of a material, which helps clarify some flame retardancy mechanisms that are based on the formation of a protective char and/or vitreous layer by different materials (i.e. intumescent flame retardants). DTA aids at giving the amount of heat liberated or absorbed by materials during any physical transition or chemical reaction. Consequently, it is useful in measuring heat capacity, provides kinetic data, and gives transition temperatures. Similarly, DSC provides information on enthalpies of various transitions and chemical reactions (Rowell & Dietenberger, 2013).

4. Flammability of biofibres and biocomposites

The properties of biofibre (natural fibre) reinforced biocomposites have been reviewed by numerous authors. This section is divided into three subsections, namely, flammability studies on biofibres, biopolymers and biofibre reinforced biopolymer composites (Bourbigot & Fontaine, 2010; Chapple & Anandjiwala, 2010; Kandola, 2012; Kozlowski &Wladyka-Przybylak, 2008; Price et al., 2001).

4.1 Biofibres (natural fibres)

Biofibres are natural lignocellulosic composites composed of highly crystalline spirally wound cellulose fibrils embedded in an amorphous hemicellulose, lignin, pectin and wax matrix (Kandola, 2012). They have rounded and elongated structures with hollow cross sections spread over the whole plant (Zavareze & Dias, 2012). Generally, their composition consists of cellulose, lignin, hemicellulose, pectin and wax. Depending on their origin, they may be classified as plant, animal, and minerals based. The minerals based fibres (e.g. asbestos) are scarcely used due to their negative effects on health. The examples of animal based fibres are wool, hair and silk. Table 4 gives the list of examples of important plant based natural fibres, which may be classified according to the anatomical origin such as stem, leaf, wood and fruit. There is plenty of published literature on natural fibres and its composites based either on thermoplastics, thermosets or biopolymers as composites matrices (Faruk et al., 2012; John & Thomas, 2008; Sahari & Sapuan, 2011; Satyanarayana et al., 2009; Zavareze & Dias, 2012).

Biofibres offer numerous advantages such as energy efficiency, low cost, low density, high toughness, appreciable specific strength and biodegradability. However, they are hydrophilic in nature and have poor fire resistance. These disadvantages limit their application in outdoor panels (i.e. construction) and in areas that pose fire hazard to humans (i.e. aerospace and marine) (Grexa, Poutch, Manikova, Martvonova, & Bartekova, 2003).

Biofibres are non-thermoplastic materials and their thermal degradation temperature is less than their glass transition (T_g) and/or melting (T_m) temperatures. When natural fibres are exposed to fire or a high intensity heat source, they are subject to thermal decomposition and combustion depending on prevailing conditions. Conditions such as direct contact with air and physical, chemical and microbiological stimuli associated with heat release can make the combustion of natural fibres possible. In addition, the intensity of heat stimulus, oxygen concentration and circulation around the combustion area, as well as the intensity of the combustion process, influence the time to ignition (TTI) of natural fibres. The thermal degradation of plant fibres involves a number of processes: a) dehydration of adsorbed water molecules; b) depolymerisation and decarboxylation of cellulose chains with evolution of water to form dehydrocellulose; c) decomposition of formed dehydrocellulose to yield char and volatiles; d) formation of levoglucosan (an intermediate nonvolatile liquid product); and e) decomposition of the levoglucosan to yield lower molecular weight and highly flammable volatiles as well as nonflammable volatiles and gases, tar and char (Chapple & Anandjiwala, 2010; Kandola, 2012).

Table 4. List of important biofibres. Reprinted from John and Thomas (2008), Copyright 2008, with permission from Elsevier.

Fibre source	Species	Origin
Abaca	*Musa textilis*	Leaf
Bagasse	–	Grass
Bamboo	(*>1250 species*)	Grass
Banana	*Musa indica*	Leaf
Broom root	*Muhlenbergia macroura*	Root
Cantala	*Agave cantala*	Leaf
Caroa	*Neoglaziovia variegata*	Leaf
China jute	*Abutilon theophrasti*	Stem
Coir	*Cocos nucifera*	Fruit
Cotton	*Gossypium sp.*	Seed
Curaua	*Ananas erectifolius*	Leaf
Date palm	*Phoenix Dactylifera*	Leaf
Flax	*Linum usitatissimum*	Stem
Hemp	*Cannabis sativa*	Stem
Henequen	*Agave fourcroydes*	Leaf
Isora	*Helicteres isora*	Stem
Istle	*Samuela carnerosana*	Leaf
Jute	*Corchorus capsularis*	Stem
Kapok	*Ceiba pentranda*	Fruit
Kenaf	*Hibiscus cannabinus*	Stem
Kudzu	*Pueraria thunbergiana*	Stem
Mauritius hemp	*Furcraea gigantea*	Leaf
Nettle	*Urtica dioica*	Stem
Oil palm	*Elaeis guineensis*	Fruit
Piassava	*Attalea funifera*	Leaf
Pineapple	*Ananus comosus*	Leaf
Phormium	*Phormiumtenas*	Leaf
Roselle	*Hibiscus sabdariffa*	Stem
Ramie	*Boehmeria nivea*	Stem
Sansevieria (Bowstring hemp)	*Sansevieria*	Leaf
Sisal	*Agave sisilana*	Leaf
Sponge gourd	*Luffa cylinderica*	Fruit
Straw (Cereal)	–	Stalk
Sun hemp	*Crorolaria juncea*	Stem
Cadillo/urena	*Urena lobata*	Stem
Wood	(*>10,000 species*)	Stem

These processes occur during the course of the three stages of heat action on natural fibres and natural polymers as detailed by Kozlowski and Wladyka-Przybylak (2001), i.e. *preliminary flameless stage*, followed *by main flame stage* and then the *final flameless stage*. Generally, these stages may be briefly described as follows:

Preliminary stage involves dehydration (up to 105 °C) and release of liquid and volatiles, and further heating of natural fibre leads to their decomposition temperature. At this stage, reactions are slow and endothermic. Above 105 °C, the fibre components begin to decompose with gaseous products being released within the temperature range of 150 to 200 °C. The bonds between natural fibre components become weak.

The *main flame stage* includes ignition of thermal decomposition products, flame spread by combustible gases and increase in heat release and mass loss rates. This is an active process of decomposition occurring in the temperature range of 260 to 450 °C.

The *final flameless stage* includes the slow burning of residue and the formation of ash from the remaining matter, which occurs above 500 °C.

The mechanism of thermal degradation of plant fibres may be similar from a thermogravimetric analysis point of view. However, the flammability behaviour of plant fibres is different. This is motivated by factors such as chemical composition, fine structure, degree of polymerization and fibrillar orientation. The decomposition of the major constituents (cellulose, hemicellulose and lignin) making up the natural fibre may be described as follows:

Lignin: begins to decompose in the temperature range of 160 to 400 °C. At lower temperatures, relatively weak bonds break, whereas at higher temperatures phenols result from cleavage of ether and carbon-carbon linkages. This results into more char than in the case of either cellulose or hemicellulose. Lower lignin content in natural fibre contributes to higher decomposition temperatures but lower resistance to oxidation which would be provided by the aromatic structure of lignin.

Hemicellulose: decomposition of these low molecular weight polysaccharides begins at 180 °C releasing more incombustible gases and fewer tar substances. Released gases usually contain 70% of incombustible CO_2 and about 30% of combustible CO. Depending on the availability of oxygen, subsequent reactions may be exothermic or endothermic. Between 200 and 260 °C, exothermic reactions start and are characterized by increased emission of gaseous products of decomposition, release of tar substances and the appearance of local ignition areas of hydrocarbons with low boiling points. No spontaneous ignition at these temperatures may occur, but under favourable conditions ignition can start from a pilot flame.

Cellulose: decomposes in the temperature range of 260 to 350 °C, primarily yielding flammable volatiles and gases, noncombustible gases, tars as well as some char. The thermal degradation of cellulose can be catalysed in the presence of water, acids and oxygen. Consequently, natural fibres turn brown and a carbonaceous char (pyrophoric carbon) is formed. The reaction below 260 °C is still low. High contents of cellulose are likely to increase flammability of a fibre whereas high contents of lignin are likely to reduce it (Chapple & Anandjiwala, 2010; Kandola, 2012; Kozlowski and Wladyka-Przybylak, 2001).

The fine structure of the fibre also plays a role in influencing the flammability characteristics of a fibre. Fibres rich in cellulose have high levels of crystallinity. This results in high levels of levoglucosan during pyrolysis leading to increased flammability. Additionally, this increased level of crystallinity requires more activation energy (E_a) of the pyrolysis of cellulose to decompose the crystalline structure, consequently leading to higher ignition temperatures (Chapple & Anandjiwala, 2010; Lewin, 2005).

The degree of polymerization and fibrillar orientation also dictate the fibre flammability. Increased degree of polymerization and orientation results in decreased pyrolysis. Fibrillar orientation controls the quantity of oxygen that can penetrate into the fibre, thus the higher the orientation, the lower the permeability of the fibre to oxygen (Chapple & Anandjiwala, 2010; Lewin, 2005). In their review on the flammability of natural fibre reinforced composites and strategies for fire retardancy, Chapple and Anandjiwala (2010) made an important conclusion that, from a flammability perspective, natural fibres with low crystallinity, high degree of polymerization and high fibrillar orientation would be the best choice to use as reinforcement in composite materials.

The flammability properties of natural fibres were reported (Chai, Bickerton, Bhattacharyya & Das, 2012; Grexa & Lübke, 2001; Grexa et al., 2003; Hapuarachchi & Peijs, 2010; Jang et al., 2012; Kandola & Horrocks, 2000; Lazko et al., 2013; Reti et al., 2009; Sain et al., 2004), and mostly the biofibres were compounded with different polymer matrices [i.e. poly(lactic acid) (PLA), polypropylene (PP) and epoxy resin] in the presence of flame retardants. In some studies, fibres alone were treated with flame retardants and characterized. The different flame retardant additives used for lignocellulosic materials include ammonium salts of phosphoric acid (i.e. melamine phosphate, ammonium polyphosphate), boric acid, zinc chloride, zinc borate, salts of sulphuric acid, vermiculite, magnesium hydroxide, aluminumhydroxide, expandable graphite and pentaerythritol (as the carbon source for intumescent systems) (Durin France et al., 2000; Grexa & Lübke, 2001; Grexa et al., 2003; Kandola & Horrocks, 2000; Lazko et al., 2013; Reti et al., 2009). The preparation of flame retardant treated natural fibres is achieved in different ways including a) impregnation of fibres with a solution of the flame retardant, b) incorporation of the flame retardant into the adhesive system, c) surface treatment of the fibres, and d) mixing of the fibres with the flame retardant before the addition of an adhesive (e.g. melamine urea formaldehyde condensate, pea protein) (Grexa & Lübke, 2001; Grexa et al., 2003; Lazko et al., 2013).

Grexa and Lübke (2001) and Grexa et al. (2003) reported on the flammability of lignocellulosic particleboard using a cone calorimeter. In both studies, samples were conditioned to equilibrium at 55% relative humidity (RH) and 23 °C prior to testing. In the first study (Grexa & Lübke, 2001), the authors looked at the effect of magnesium hydroxide loading and that of other flame retardants (i.e. monoammonium phosphate (MAP), aluminum hydroxide and boric acid), whereas in the second study (Grexa et al., 2003) they dealt with an intumescent system for wood based panels. The RHR (see Figure 2, section 2.2.5.2), average specific extinction area of smokeand the rate of smoke release (Figure 9) were generally improved with increasing amount of magnesium hydroxide flame retardant (type A) [where A1, A2 and A3 are 8, 15 and 24 wt.% respectively]. In addition to smoke production improvement, carbon monoxide yield was also improved due to this flame retardant (Grexa & Lübke, 2001).

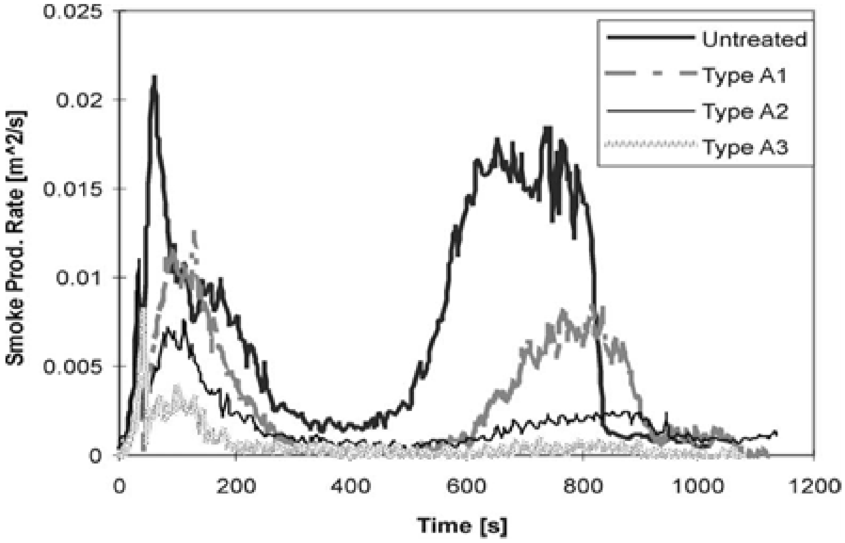

Figure 9. Smoke production rate versus time for non-treated and magnesium hydroxide-treated particleboard. Reprinted from Grexa and Lübke (2001), Copyright 2001, with permission from Elsevier.

Furthermore, when different flame retardant combinations [i.e. monoammonium phosphate (MAP) 17wt.% + aluminium hydroxide 8wt.% (type B), and MAP 20wt.% + boric acid 5wt.% (type C)] were used and compared, the authors concluded that the combination of MAP/boric acid (type C) was the most effective system. As seen in Figure 10, the type C flame retardant system did not only lower the RHR, but also eliminated the second peak and shortened the time of burning with respect to other modifications including magnesium hydroxide. The mass loss was reduced for the flame retardant treated systems, especially type C (i.e. from 72% to 17%), but the mass loss rate was almost the same for all the studied materials. In this study, the authors distinguished between the yield of CO and the production of CO, and they concluded that the stronger retardant effect may give better results on the total CO production than the weaker retardant effect, even though the CO yield per burned portion of the pure material increased (Grexa & Lübke, 2001).

In the second study (Grexa et al., 2003) ammonium phosphate and expandable graphite intumescent flame retardant systems formed a protective char layer on the surface of wood. Similar to the previous study (Grexa & Lübke, 2001), the RHR was reduced to about 55-66% of the untreated material. The time to ignition (TTI) remained unchanged with the presence of the flame retardant, and authors concluded that the flammable particles of wood on the surface were not directly protected. The intumescent flame retardant system based on expandable graphite showed better flammability performance at low loadings than the phosphate based systems, which required high contents (i.e. 30 wt.%). This was explained in terms of the difference in the presence of the expanding charring foam layer on the pyrolysis surface. The other important aspect is that CO emissions increased for expandable graphite at the lowest loadings, and increased noticeably for the phosphate based system at 13 wt.% and higher.

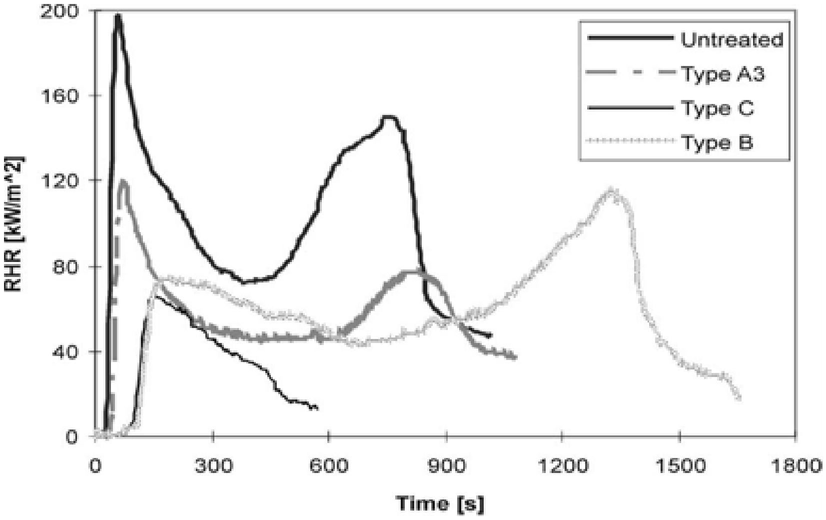

Figure 10. HRR versus time for untreated and flame retardant treated particle board with the use of different flame retardant combinations. Reprinted from Grexa and Lübke (2001), Copyright 2001, with permission from Elsevier.

The flammability properties of flax fibres were investigated by Lazko et al. (2013). They used a wet process to prepare the flame retarded insulating agro materials made of flax short fibres with a pea protein binder. It was reported that the incorporation of different flame retardants [i.e. aluminum hydroxide (ATH), zinc borate (ZB), melamine phosphate (MMP) and melamine borate (MMB)] did not interfere with the expanded structure and the open porosity of the lignocellulosic matrix. This was shown by macroscopic and SEM results (see Figure 11). Two conclusions arose from these: a) the appropriate choice of process parameters allowed a coherent set of materials with comparable morphologies and densities, and b) the use of a pea protein binder permitted all flame retardants to be fixed firmly and permanently onto the flax fibre matrix. The presence of FRs lowered the flexural strength by 50% and the flexural modulus by 65% (see Table 5), except for ATH, for which the properties remained at the same levels as the reference. Different flax fibre flame retardant treatments led to lowered peak and total HRR (especially for ZB, MMP and MMB) relative to the untreated flax short fibres. Similar to studies by Grexa et al. (2003), the TTI remained unchanged including the resistance to ignition.

Table 5. Density and flexural properties of non FR treated flax short fibres with pea protein binder (i.e. reference) and FR treated materials. Reprinted from Lazko et al. (2013), Copyright 2013, with permission from Elsevier.

Composition	**Density [g/cm^3]**	**Flexural strength [MPa]**	**Flexural modulus [MPa]**
Reference	0.07 ± 0.01	0.34 ± 0.02	14.4 ± 2.5
ATH 20%	0.09 ± 0.01	0.39 ± 0.03	15.8 ± 6.6
ZB 20%	0.07 ± 0.01	0.18 ± 0.04	5.3 ± 1.9
MMP 20%	0.08 ± 0.01	0.21 ± 0.03	5.8 ± 2.6
MMB 20%	0.07 ± 0.01	0.15 ± 0.03	4.2 ± 1.4

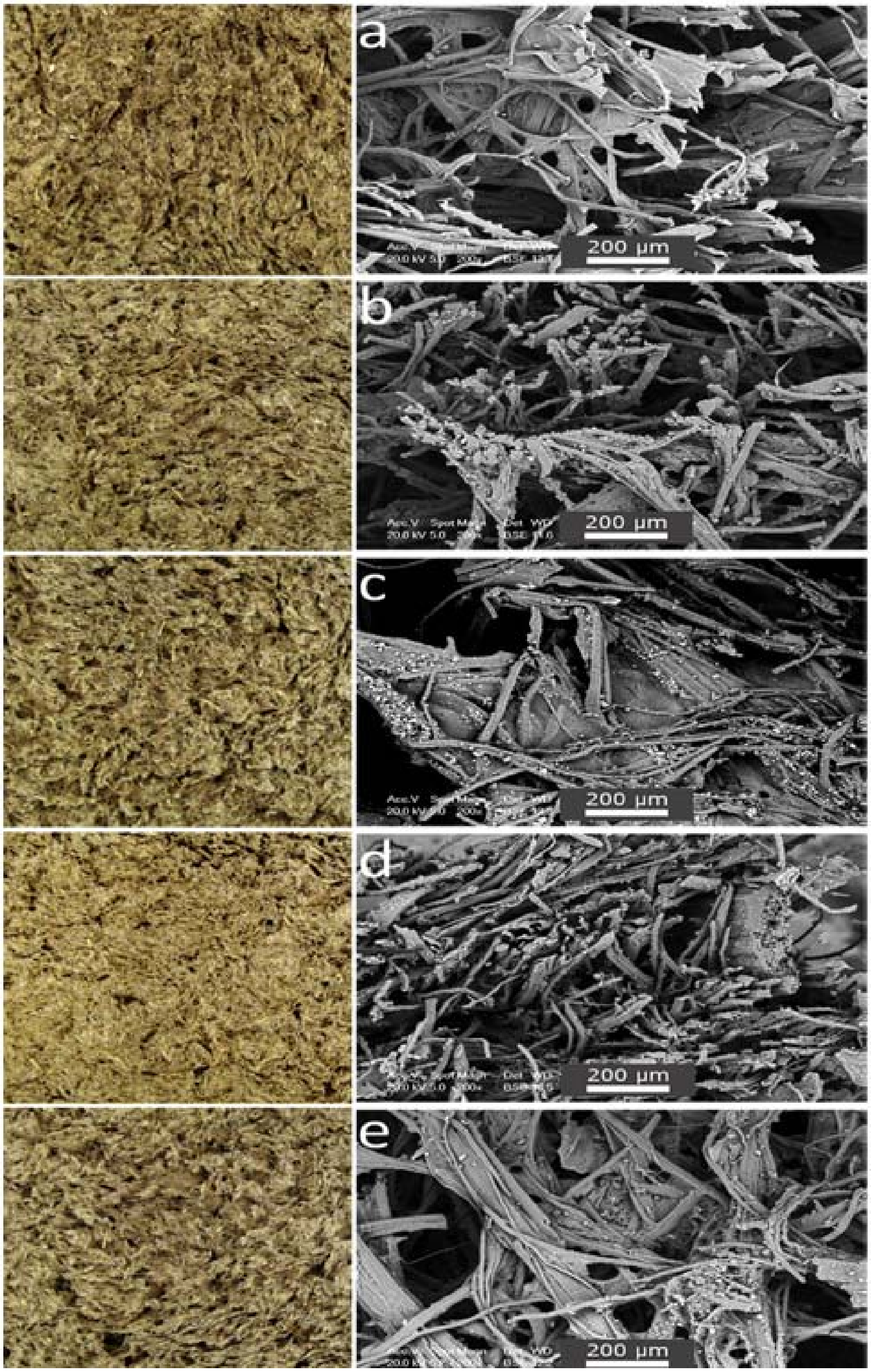

Figure 11. Macroscopic and SEM pictures (x200) of a) reference (untreated flax fibre), and flame retardant treated flax (fibre and pea protein binder) containing 20 wt.% of b) ATH, c) ZB, d) MMP and e) MMB. Reprinted from Lazko et al. (2013), Copyright 2013, with permission from Elsevier.

(*Intended for colour on the Web and black-and-white in print*)

In their study of sawdust and rice husk filled polypropylene (PP) composites, Sain et al. (2004) used magnesium hydroxide, boric acid and zinc borate as flame retardant agents. The composites were melt blended and then injection moulded in the presence of a maleated PP coupling agent. It was reported that magnesium hydroxide (i.e. 25 wt.%) effectively reduced the flammability of natural fibre/PP composites by 50% when tested using horizontal burning and LOI tests. The partial replacement of magnesium hydroxide with either boric acid or zinc borate (i.e. 5 wt.%) did not show synergy, but rather the retarding effect of different flame retardants. A marginal decrease in the mechanical properties of flame retarded natural fibre composites compared to non-flame retarded composites was reported. This was attributed to the poor compatibility of the flame retardants with the polymer. However, better mechanical properties were observed for these composites with respect to neat PP.

A large number of studies focused on the FR properties of natural fibre based fabrics (Abou-Okeil, El-Sawy & Abdel-Mohdy, 2013; Alongi & Malucelli, 2012; Alongi, Brancatelli & Rosace, 2012b; Alongi, Ciobanu & Malucelli 2011, 2012a; Alongi et al., 2013; Bosco et al., 2013; Chai et al., 2012; Didane, Giraud & Devaux, 2012; Flambard et al., 2005; Kandola & Horrocks, 2000; Laufer, Kirkland, Morgan & Grunlan, 2012; Nguyen, Chang, Condon, Uchimiya & Fortier, 2012; Šimkovic, 2012; Wang, L., Zhang, Yan, Peng & Fang, 2013; Yang, Wang, Lei, Fei & Xin, 2012;). Chai et al. (2012) used flax based fabrics reinforced epoxy resin and compared them with glass fibre reinforced epoxy composites of similar fabric architecture. These composite panels were prepared by a resin transfer moulding (RTM) process without any FR. The group reported, from cone calorimetry, horizontal and vertical burning tests, that the flax fibre samples ignited earlier, released more heat overall, had an increased time to extinguish and increased smoke production rate (SPR) when compared to their glass fibre counterparts. This was attributed to a number of reasons, amongst others that flax fibres are themselves susceptible to ignition and combustion, that they provided additional fuel at a lower HRR, that fibres combusted exothermically, and that they burned more vigorously during combustion.

Additionally, flax fibre samples showed deformation during combustion while glass fibre samples kept their integrity. It was postulated that the bulging and delamination effect of the flax fibre composites (see Figure 12) may be due to internal or external forces applied to the fibres, causing buckling. The authors, therefore, suggested further investigations to understand the mechanisms and behaviour that govern the combustion of natural fibre reinforced composites.

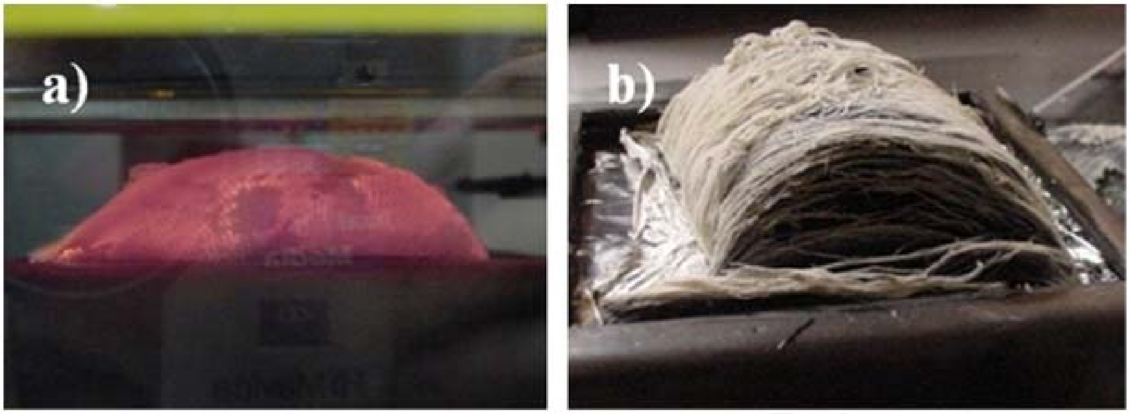

Figure 12. Images of (a) flax twill weave in a cone calorimeter, and (b) a burnt flax unidirectional fabric sample. Reprinted from Chai et al. (2012), Copyright 2012, with permission from Elsevier.
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Kandola and Horrocks (2000) looked at the nonwoven cores of flame retardant cellulose/regenerated cellulose (viscose and cotton fibres) with intumescent melamine and phosphate based chemicals. They investigated the mass loss and thermal barrier properties of these systems. A large quantity of char formation was observed above 500 °C. This was resistant to oxidation and had better thermal insulative properties. The presence of intumescent FR led to increased activation energy (E_a) values for the full char development stage of FR/cellulosic fibre composites, and reduced thermal conductivity values. According to the authors, this revealed the existence of an interaction between different FRs and the fibre substrate, and improved thermal barrier properties. Flambard et al. (2005) used wool, flax and blends made of poly(p-phenylenediamineterephthalamide) (PPTA) with wool in textile materials for use in public transportation (i.e. buses). They studied the flame retardancy properties of these materials. The group concluded that these natural fibres could be used to manufacture fabrics that are acceptable for use in seats for transportation when they are combined with a specific flame retardant treatment or in combination with high performance fibres (wool/PPTA). The advantages offered by these materials included good flammability and mechanical properties (abrasion and cutting resistance), dyeability and ultraviolet (UV) resistance, biodegradability and no technological problems during manufacture.

In some studies,fabric materials were generally surface coated with either commercial or laboratory synthesized flame retardants (AbouOkeil et al., 2013; Didane et al., 2012; Laufer et al., 2012; Nguyen et al., 2012; Šimkovic, 2012; Wang, L. et al., 2013; Yang et al., 2012).

Abou-Okeil et al. (2013), Nguyen et al. (2012) and Yang et al. (2012) developed environmental friendly halogen free and formaldehyde free FRs which were subsequently applied onto cotton fabrics and evaluated for flammability performance. These were methacryloyloxyethylorthophosphorotetraethyl diamidate (MPD) (Abou-Okeil et al., 2013), novel halogen and formaldehyde free flame retardants (NeoFR) (Yang et al., 2012) and phosphorus-nitrogen bond (diethyl 4-methylpiperazin-1-ylphosphoramidate) (CN-3) (Nguyen et al., 2012) FR compounds. In the first two studies (Abou-Okeil et al., 2013; Yang et al., 2012), the performance of the novel FRs was compared with that of a commercial flame retardant (Pyrovatex), and it was concluded that the novel FRs were performing better in terms of flammability and durability than the latter. NeoFR was said to have played the role of an intumescence on the flame retarding mechanism of cotton. This was due to its ability to form char. Higher tensile strength and elongation were also reported (Yang et al., 2012). Similarly, better flame retardant properties were observed by Nguyen et al. (2012) when print-on and twill fabrics were treated with a CN-3 flame retardant. At certain loadings the char lengths of the FR treated fabrics were less than 50% of the original fabric with no after-flame and after-glow times. The LOI values increased from 12 vol.% (print cloth) and 18 vol.% (twill) to 28 vol.% and 29-31 vol.% respectively. In general, the improvement of flammability properties of cotton fabrics emphasized the role played by char formation for treated samples which prevented them from being completely burnt.

Extensive work on developing novel systems based on a sol-gel process for cotton based fabrics was done by Alongi and co-workers (Alongi et al., 2011, 2012a, b, 2013; Alongi & Malucelli, 2012; Bosco et al., 2013). These flame retardant finishing systems were developed in the presence of different FR compounds. The FRs were phosphorus based compounds (Alongi et al., 2011), metal alkoxide precursors (e.g. tetraethylorthosilicate, titanate, zirconate, and aluminium isopropylate) (Alongi et al., 2012a), polyhedral oligomeric silsesquioxane (POSS) and bohemite nanoparticles (Alongi et al., 2012b), and compounds with smoke suppressant features (e.g. zinc oxide, zinc borate) or flame retardant properties (e.g. 9-oxa-10-phosphaphenanthrene10-oxide) (Alongi & Malucelli, 2012). The fabric exhibited improved flammability and thermooxidative stability. This was attributed to several factors including the homogeneous distribution and dispersion of FR additives on and in between the cotton fibres (Alongi et al., 2011), the morphology of the inorganic coatings on the fabric surface, the water content in the treated textiles (Alongi et al., 2012a) and the ability of the nanoparticles to release water at high temperatures, forming a ceramic barrier that was able to delay the cellulose ignition and lower the heat release and corresponding rate (Alongi et al., 2012b). The homogeneous distribution and fine dispersion of POSS at nanometric level (Alongi et al., 2012b) is said to have modified the degradation profile of cotton by playing a protective role on the thermo-oxidation of fabrics. During thermal decomposition in the presence of POSS nanoparticles, a carbonization mechanism was favoured and the final char residue increased which slowed down the overall thermo-oxidation kinetics and hence improved the properties. The TTI was increased and the HRR was reduced up to 40%. Based on LOI and cone calorimetry test results, nanoparticles show better performance in the flammability of cotton than the other flame retardant used. On the other hand, the major observation from the cone calorimetry tests was that in the presence of zinc based smoke suppressants, the release of CO and CO_2 was remarkably reduced relative to fabrics treated with silica alone (Alongi & Malucelli, 2012). It was found that the combination of ZnO and silica showed a joint effect in reducing the release of these gases when compared to combinations of silica with phosphorus or boron based flame retardants.

The current published work by Alongi and co workers looked at using whey protein (folded and unfolded structures) (Bosco et al., 2013) and deoxyribonucleic acid (DNA) powder from herring sperm (Alongi et al., 2013) on cotton fabrics. This was achieved by deposition of whey protein on cotton fabrics and impregnation whereby cotton fabrics were dipped in a DNA solution for some time, according to respective studies. The treated samples were assessed for their thermo-oxidative stability and flammability characteristics. It was found that the presence of protein coating (Bosco et al., 2013) significantly sensitized the cotton degradation, but led to very high final residues. These protein treated cotton materials were shown to have increased the total burning time as well as reducing the burning rate. The authors concluded that the system may represent a novel and promising eco-friendly finishing treatment for cellulosic substrates. Additionally, only a minimum of 10 wt.% DNA (Alongi et al., 2013) loading on cotton was necessary to reach the flame out of cotton when a methane flame was applied, and that 19 wt.% DNA was able to show resistance to an irradiation heat flux of 35 kW m^{-2}. In general, this cotton/DNA sample did not burn at increased loadings, but pyrolysed due to the presence of DNA molecules that absorbed heat and released inert gases. It was concluded that although these materials displayed promising flame retardant and suppressant properties, the design of DNA based FR needs some careful consideration and further investigation. This was due to the poor durability and resistance to washing treatments of materials according to the ISO 6330 standard.

4.2 Biopolymers

Biodegradable polymer matrices are those materials with an ability to decompose into biomass, carbon dioxide, inorganic compounds, methane or water due to enzymatic action by micro-organisms when disposed-off into landfills (Chapple & Anandjiwala, 2010; Jang et al., 2012; Kandola, 2012). The classification of biodegradable polymers is illustrated in Figure13. They are broadly classified as natural or synthetic depending on their origin. Furthermore, they are sub-classified into those from renewable resource, the chemically synthesized, microbial synthesized as well as blends systems (John & Thomas, 2008; Satyanarayana et al., 2009). The class of chemically synthesized biodegradable polymers may be further subdivided into those that are from biotechnology (i.e. polyacids, e.g. PLA) and the ones from petrochemical products (i.e. polycaprolactone, PCL, aliphatic and aliphaticaromatic polyesters, polyesteramides) (Chapple & Anandjiwala, 2010; Jang et al., 2012; John & Thomas, 2008; Kandola, 2012; Satyanarayana et al., 2009). These biopolymers are hydrophilic polyesters that absorb moisture. They are characterized by higher cost and lower performance than conventional plastics. Their application is mainly in the packaging industry and other applications that need lower strength. Of these biopolymers, PLA is currently the most studied, both in blends and biocomposites reinforced with natural fibres (Frone, Berlioz, Chailan & Panaitescu, 2013; Gallo, Schartel, Acierno, Cimino & Russo, 2013; Sahari & Sapuan, 2011).

Different biopolymers have been used as matrices in the investigation of various composite materials. These were compounded with additives, fillers or reinforcements. The broader goal of this was to improve their performance compared to conventional polymeric materials, to lower the market cost of their final products and to broaden their range of applications to high performance polymer sectors (including aerospace, marine and electronics). The studied biopolymers include poly(lactic acid) (PLA), polycaprolactone (PCL), starch, cellulose, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly(butylene adipate-co-terephthalate) (PBAT), poly(trimethylene terephthalate) (PTT) and polyetherblockamide polymers. Different properties of biopolymers such as mechanical, thermal, biodegradability and flammability performance were studied (Cheng et al., 2012; Das, Ray, Chapple & Wesley Smith, 2013; Frone et al., 2013; Gallo et al., 2013; Tang, G., et al., 2012).

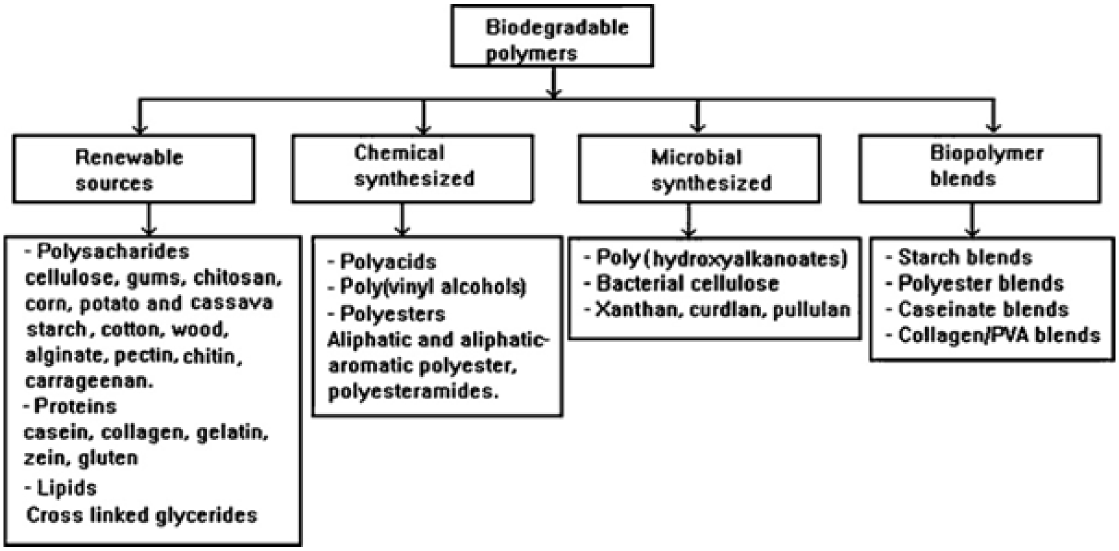

Figure 13. Classification of biodegradable polymers and their nomenclature. Reprinted from Satyanarayana et al. (2009), Copyright 2009, with permission from Elsevier.

A wide range of additives or reinforcements are used to fill biopolymers. The additives or reinforcements may be inorganic, organic, synthetic or natural in nature. These may include natural fibres (i.e. kenaf, flax, hemp, wool, cellulose, coconut fibre, rice husk and kraft lignin), clays, silica, metal oxides and hydroxides, phosphate compounds and graphite. The preparation of reinforced biopolymer composites and/or blends is achieved through different methods. They include melt blending, extrusion, compression moulding and injection moulding. Of all the investigated properties of the filled biopolymer composites, flammability performance is of recent research interest (Das et al., 2013; Ke et al., 2010; Tang, G., et al., 2012; Zhan, Song, Nie & Hu, 2009; Zhu et al., 2011).

Flame retardant treated PLA composites have been investigated more than those of other biopolymers (Das et al., 2013; Ke et al., 2010; Tang, G., et al., 2012; Zhan, Song, Nie & Hu, 2009; Zhu et al., 2011). Ke et al. (2010), Zhan et al. (2009) and Zhu et al. (2011) prepared PLA/flame retardant composites by a melt blending/mixing method. In these studies, ammonium polyphosphate (APP) (Ke et al., 2010; Zhu et al., 2011), hyperbranched polyamine charring agent (HPCA) (Ke et al., 2010), expandable graphite (EG) (Zhu et al., 2011) and spirocyclic pentaerythritol bisphosphorate disphosphoryl melamine (SPDPM) (Zhan et al., 2009) were used to formulate different flame retarded systems with PLA. Both HPCA and SPDPM were synthesized and characterized by the authors before incorporation into the PLA composites. Techniques that include UL94, LOI, TGA, MCC (PCFC), SEM and cone calorimetry were employed, amongst others, for various tests on the composites.

All these studies reported that the intumescent flame retardant (IFR)/PLA showed improved flame retardancy and anti-dripping performance. It was found that different combinations of APP/HPCA (3:2) at 30 wt.% (Ke et al., 2010), APP/EG (1:3) at 15 wt.% (Zhu et al., 2011) and SPDPM at 25 wt.% (Zhan et al., 2009) exhibited LOI values of 36.5 (Ke et al., 2010; Zhu et al., 2011) and 38 (Zhan et al., 2009) vol.%, as well as UL94 V0 rating (see Table 6). Additionally, Zhu et al. (2011) indicated that APP/EG (1:3) showed better performance than APP and EG alone. As shown in Figure 14 for specimens after an LOI test, the presence of different IFR additives led to the formation of charred layers. Pure PLA does not form any char and decomposes almost completely.

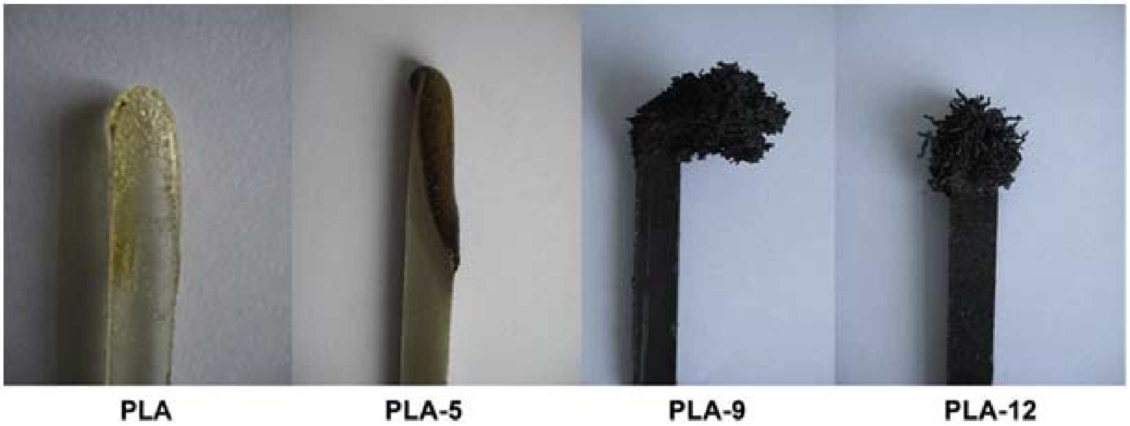

Figure 14. Photographs of PLA specimens after LOI tests. Reprinted from Zhu et al. (2011), Copyright 2011, with permission from Elsevier.
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Table 6. Composition of the samples and the flame retardancy of the composites. Reprinted from Ke et al. (2010), Copyright 2010, with permission from Elsevier.

Sample	**PLA**	**APP**	**HPCA**	**t1 + t2[a] (s)**	**LOI vol.%**	**UL-94 rating**	**Flaming dripping**
PLA-1	100	–	–	–	21	Fail	Yes
PLA-2	70	30	–	10 + 5	33	V-2	Yes
PLA-3	70	20	10	0 + 1	34	V-0	No
PLA-4	70	18	12	0 + 1	36.5	V-0	No
PLA-5	70	15	15	0 + 2	28	V-0	No
PLA-6	70	12	18	0 + 13	27.5	V-1	No
PLA-7	70	10	20	1 + 14	26.5	V-1	No
PLA-8	70	–	30	–	22	Fail	Yes
PLA-9	75	15	10	0 +1	28.5	V-0	No
PLA-10	80	12	8	0 + 1	26.8	V-0	No
PLA-11	85	9	6	0 + 1	26.2	V-0	No
PLA-12	90	6	4	0 +3	25.2	V-2	Yes

[a] t1: the burning time after first ignition, t2: the burning time after second ignition.

This phenomenon of charred layer formation is further emphasized by the char residue as seen from TGA results (see Figure 15). Furthermore, both the cone calorimetry and microscale combustion calorimetry results were indicative of the improved fire retardancy of PLA in the presence of FR agents. This was concluded from the reduction in time to ignition (TTI), heat release rate (HRR), peak HRR, average HRR, total heat release (THR) and mass loss rate (MLR) (Ke et al., 2010; Zhu et al., 2011) (see Table 7), as well as reduction in heat release capacity (η_c) (HRC), total heat release (h_c) and the temperature at maximum pyrolysis rate ($T_{\max}$) (Zhan et al., 2009) (see Figure 16). From all the studies, the key conclusion made by the authors is based on the efficiency and synergistic effect between different intumescent flame retardant agents. This effect led to the formation of an intumescent protective charred layer and a change in the degradation process of PLA as concluded by Zhan et al. (2009). On the other hand, Ke et al. (2010) made the conclusion that PLA/APP/HPCA can form a char layer containing a P – O – C structure. This layer may have possibly hindered the transfer of heat and combustible gas resulting in good flame retardancy without melt dripping.

Table 7. Part data recorded in cone calorimeter experiments. Reprinted from Ke et al. (2010), Copyright 2010, with permission from Elsevier.

Sample	**TTI (s)**	**Av-HRR (kW/m^2)**	**PHRR (kW/m^2)**	**TTPH (s)**	**Av-MLR (g/s)**	**THR (MJ/m^2)**
PLA	60	161	272	203	0.098	65.1
PLA-2	81	125	228	146	0.072	48.6
PLA-4	65	65	153	98	0.038	35.6

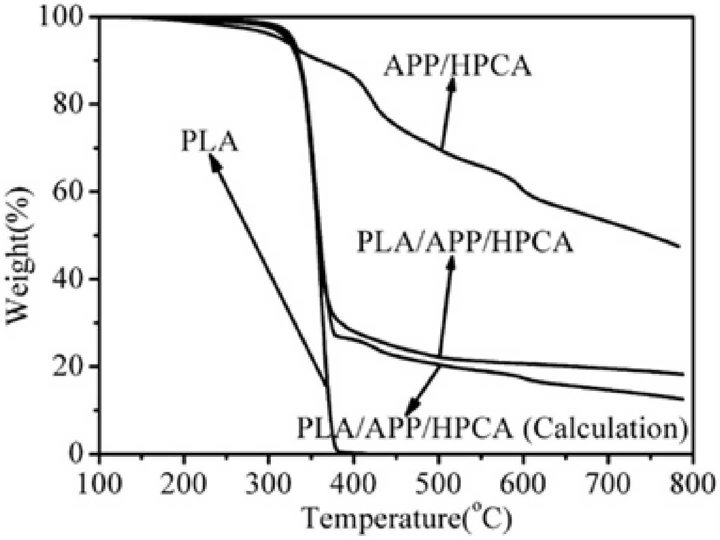

Figure 15. TGA curves of PLA, APP/HPCA, PLA/APP/HPCA, PLA/APP/HPCA (Calculation). Reprinted from Ke et al. (2010), Copyright 2010, with permission from Elsevier.

Zhu et al. (2011) proposed a possible flame retardancy mechanism of PLA/APP/EG composites in which the synergism between APP and EG is explained. Figure 17 illustrates the phenomenon. This is explained in that EG expands and migrates with the flow of

PLA/APP. This is followed by the decomposition of APP which produces polyphosphoric and ultraphosphoric acids. These compounds catalyse PLA to form char residue. During the decomposition of EG and APP, incombustible gases such as SO_2, CO_2, NH_3, and H_2O are released, which diluted the fuels that originate from the degradation fragments. The flow of PLA/APP degradation products (i.e. polyphosphate) provides adhesion between the graphite flakes, consequently leading to continuous, dense and sealed char layers. It is these layers that inhibit the further degradation of PLA, APP and EG, and slow down the volatilization of polyphosphoric and ultraphosphoric acids at high temperatures.

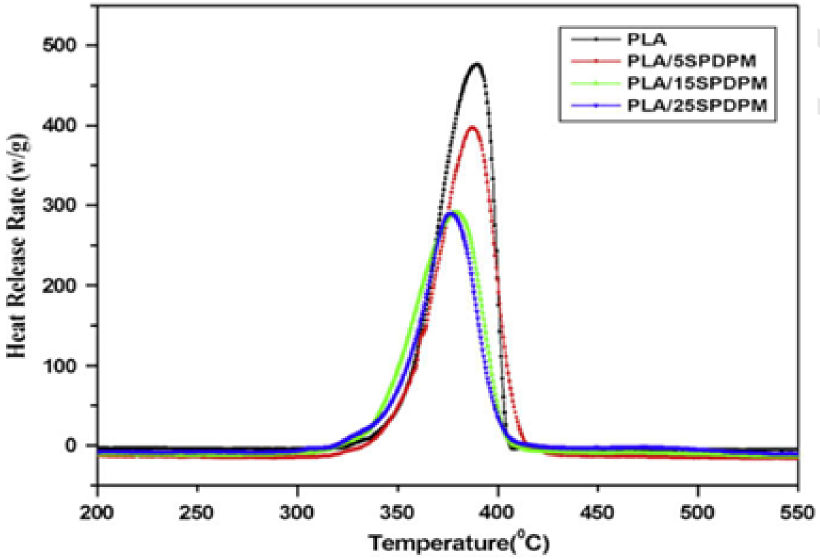

Figure 16. The HRR curves of PLA and its composites at 1 K/s heating rate. Reprinted from Zhan et al. (2009), Copyright 2009, with permission from Elsevier. (*Intended for colour on the Web and black-and-white in print*)

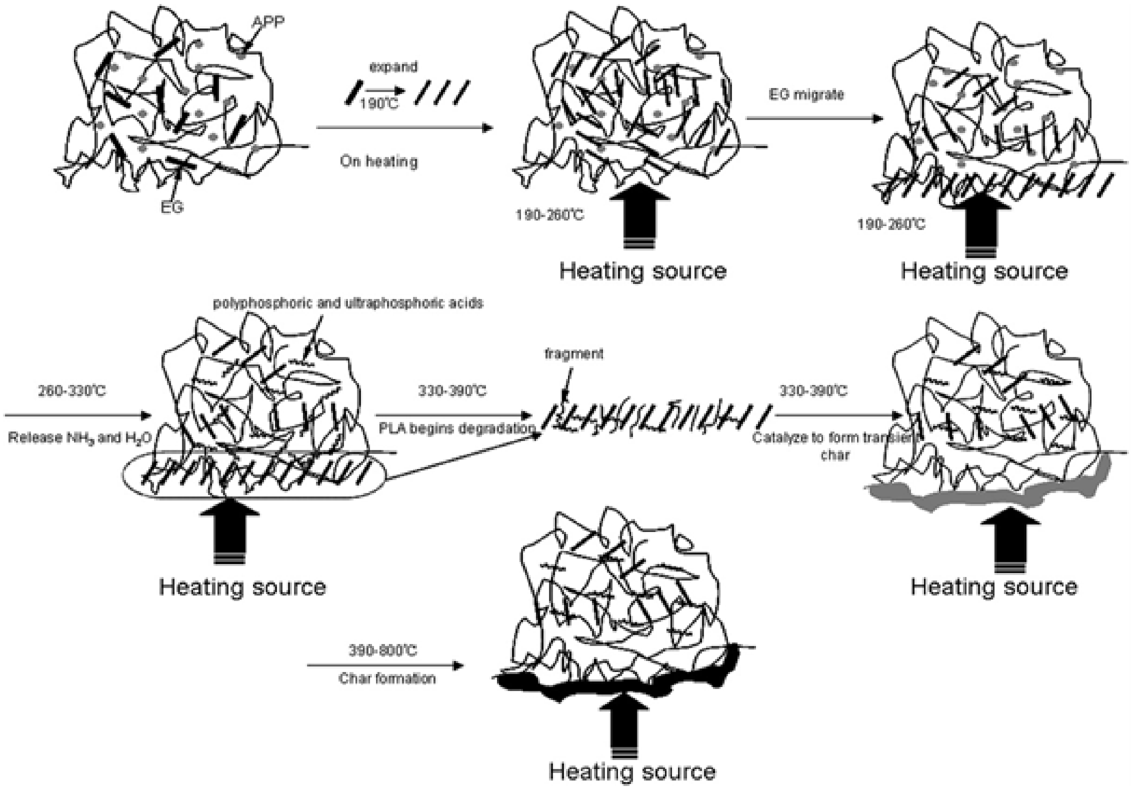

Figure 17. Possible flame retardant mechanism of PLA/APP/EG composite. Reprinted from Zhu et al. (2011), Copyright 2011, with permission from Elsevier.

In another study, the flame retarded biopolymers containing aluminium based compounds, melamine (MA) and organoclays were investigated for their thermal, mechanical and flammability performances. These biocomposites were prepared by melt compounding and extrusion methods. The matrices used were PLA (Cheng et al., 2012; Das et al., 2013; Tang, G., et al., 2012) and polyetherblockamide (PEBAX) (Hoffendahl, Fontaine & Bourbigot, 2013) biopolymers. In all these studies, it was reported that the incorporation of flame retardant additives such as ammonium hypophosphite (AHP) at 30 wt.% (Tang, G., et al., 2012), boehmite alumina at 5 wt.% (Das et al., 2013), ATH and organoclay at 50 wt.% and 5 wt.% respectively (Cheng et al., 2012), and a maximum loading of 30 wt.% MA and 6 wt.% organoclay (Hoffendahl et al., 2013) promoted carbonization of the biopolymers. This was supported by the increased char residues of the composites as seen in TGA studies (Figure 18). An additional contribution to carbonization due to the presence of organoclays was also reported (Cheng et al., 2012; Hoffendahl et al., 2013). Consequently, this contributed to improved fire resistance performance of filled biopolymers as reported from LOI, UL94, cone calorimetry and MCC tests used in these studies.

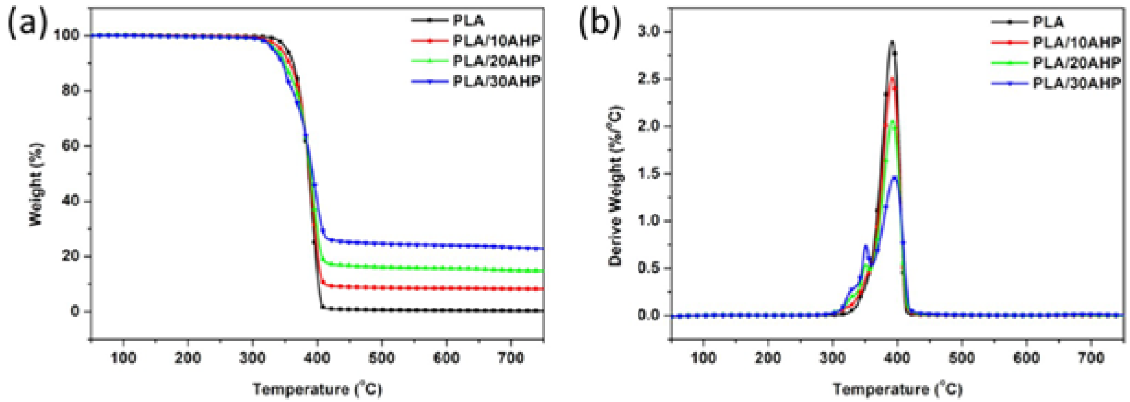

Figure 18. TGA and DTG curves of PLA and FR-PLA composites under nitrogen condition. Reprinted from Tang, G., et al. (2012), Copyright 2012, with permission from American Chemical Society.
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According to Cheng et al. (2012), the addition of organoclay into a PLA/ATH system led to further thermo-oxidative stability, and the presence of both organoclay and ATH increased the degradation activation energy of the composites. The authors proposed that during the UL94 test, both the layered silicates and a high content of ATH in PLA were integrated to form a compact insulator on the burning surface, thus lowering the melt dripping. It was further reported that at high loadings of the conventional flame retardant ATH (i.e. 50 wt.%), the PLA composites were brittle, but improved with the addition of organoclay. On the other hand, after a series of tests based on solid state nuclear magnetic resonance (NMR) (^{13}C and ^{27}Al) and TGA-FTIR, Hoffendahl et al. (2013) established the possible flame retardancy mechanisms of PEBAX/MA with and without organoclay. They concluded that MA acted by a gas phase mechanism through different routes including fuel dilution, a cooling effect due to endothermic processes, and the formation of free radicals that interacted with the flame. The incorporation of organoclay into PEBAX/MA resulted in the formation of a char layer, adding a condensed phase mechanism to the flame retardancy mechanisms.

The mechanical properties of these flame retarded PLA biocomposites were also reported. Tang, G. et al. (2012) reported a decreased tensile strength and elongation at break with the incorporation of ammonium hypophosphite (AHP) from 10 to 30 wt.% (Figure 19). This reduction was attributed to the rigid nature of the AHP particles, especially on the elongation at break. On the other hand, Das et al. (2013) reported improved mechanical properties of the PLA/Boehmite alumina (BAl) (with a maximum loading of 5 wt.%) composites as seen from Table 8. This observation was explained as being due to an optimum uniform dispersion of Bal in the PLA matrix, good filler/matrix interaction and the high aspect ratio of the filler. Consequently, this led to increased rigidity and effective stress transfer between the matrix and the filler. The increased rigidity was further emphasized in the dynamic mechanical analysis (DMA) results where storage modulus increased inconsistently with BAl loading. The explanation was that the high D content of the neat PLA made it less rigid and inconsistently increased the modulus.

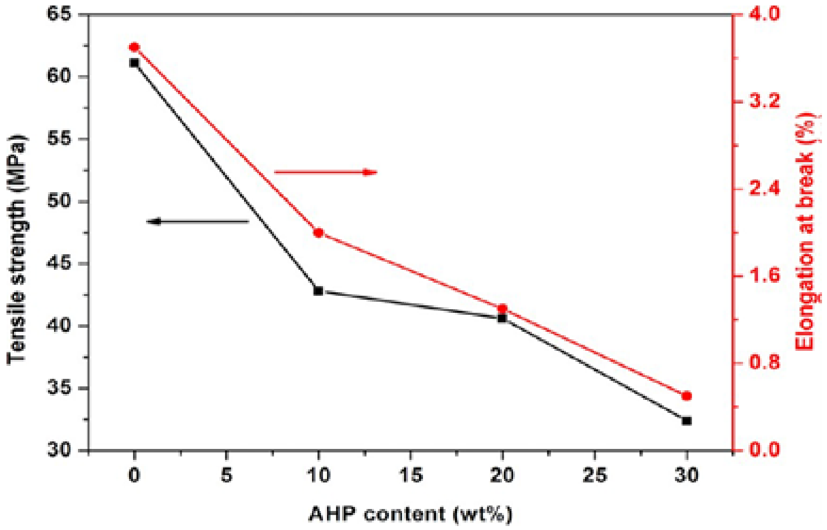

Figure 19. Effect of AHP loading on the mechanical properties of FR/PLA composites. Reprinted from Tang, G. et al. (2012), Copyright 2012, with permission from American Chemical Society.

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Table 8. Mechanical properties of the PLA/BAl composites. Reprinted from Das et al. (2013), Copyright 2013, with permission from American Chemical Society.

Sample identification	Tensile strength (MPa)	Standard deviation	Tensile modulus (GPa)	Standard deviation	Elongation at break (%)	Standard deviation
PLA BAl 0	74.4	3.2	3.0	0.2	6.3	0.2
PLA BAl 1	84.4	2.6	3.3	0.06	5.5	0.1
PLA BAl 2	97.5	5.3	3.2	0.09	5.4	0.7
PLA BAl 3	116.4	7.8	3.1	0.1	6.1	0.5
PLA BAl 4	113.4	4.4	3.4	0.04	5.2	0.3
PLA BAl 5	107.9	8.2	3.3	0.1	4.8	0.2

Hapuarachchi and Peijs (2010) developed a flame retarded system based on PLA, multiwalled nanotubes (MWNTs), sepiolite organoclays and hemp fibres. These were prepared by an extrusion followed by film stacking method in the case of hemp fibre reinforced biocomposites. The separate introduction of MWNTs and sepiolite nanoclays resulted in decreased onset temperatures of degradation and thermal stabilityof the PLA. It was attributed to a percolation threshold causing a network of MWNTs that acted as a conducting pathway causing early onset of decomposition. The addition of sepiolite nanoclays resulted in a catalytic effect on the pyrolysis of PLA. The flame retarded biocomposites exhibited improved flammability performance with a reduction of 58% in PHRR. This was attributed to the presence of nanofillers that increased the melt viscosity of the system and eliminatedthe bubbling of neat PLA.

PLA based materials were used in developing flame resistant housings for notebook computers as reported by Kimura and Horikoshi (2005). Flame retarded PLA biocomposites were prepared by an extrusion method with the incorporation of different flame retardants including aromatic silicon resin, polydimethylsiloxane and aluminum hydroxide, amongst others. Due to the low rigidity of PLA, the authors used several resin additives (e.g. polystyrene, polyethylene and polypropylene) to improve its physical properties. The developed PLA based materials showed optimal physical and flammability properties that qualified them for the purpose.

In an attempt to address the environmental concerns, Feng, Su and Zhu (2011) investigated the use of β cyclodextrin (β CD) as carbon agent in an intumescent flame retardant (IFR) system based on PLA/APP/melamine (MA). This β CD is a bio product mainly from starch.

It contains many hydroxyl groups that aid at forming char during burning. It is said to decompose in one major step in an inert atmosphere leaving a char that is thermally stable and decomposes at a low rate at high temperatures. The gaseous products such as CO_2, CO and H_2O are released during its decomposition. The IFR complex system was prepared by mechanical grinding, whereas the IFR/PLA composites were melt blended and then hot/melt pressed.

The authors reported that the combination of β CD/APP resulted in more char formation due to the presence of APP. Both β CD and APP contributed to the release of gaseous products such as NH_3 and H_2O from APP in addition to those mentioned in the case of β CD. Furthermore, phosphoric and polyphosphoric acids were also formed as products from APP degradation. Melamine (MA) was reported to promote β CD char formation too. On heating, both intramolecular and intermolecular dehydration were involved in β CD degradation. The char formation during decomposition of β CD followed several complex pathways and is elaborated by the authors. In the case of IFR/PLA composites, it was concluded that β CD is an efficient green carbon agent when coupled with APP and MA at appropriate weight ratios. This was due to improved LOI values and UL94 rating tests. However, it was noted that MA containing systems formed unstable char and had some degradation effect on PLA due to the basic NH_3 it produced during burning.

Gallos, Fontaine and Bourbigot (2013) investigated the effect of an IFR from APP, MA and nanoclays on poly L, D lactide (PDLLA). The stereocomplexed PLA was synthesised by reactive extrusion in a two step polymerization of L lactide and D lactide to yield PDLLA multiblocks, and then the IFR system was incorporated to form the PDLLA/IFR nanocomposites. The group reported improved flame retardancy as observed from cone calorimetry test results, namely a decrease of 83% in the HRR peak for nanocomposites relative to neat PDLLA. A THR of 2 MJ m^{-2} was also reported for the nanocomposites and related to a 95% drop with respect to the matrix (i.e.THR of 45 MJ m^{-2}). Consequently, the authors suggested the mechanism of flame retardancy to be the decomposition of APP into acids that reacted with melamine and PLA. Such a reaction led to the formation of protective intumescent char. Additionally, APP reacted with nanoclays to produce alumino phosphates, which limited the formation of large cracks at the surface of the coating and provided an efficient protection.

Similar to Feng et al. (2011),Wang, X. et al. (2011) reported on the flame retardancy and thermal degradation of PLA/starch biocomposites where starch was used as the carbonizing agent. Starch is a polyol that is inexpensive, biocompatible, biodegradable and renewable, and could be utilized as a natural carbon source. In this study, microencapsulated ammonium polyphosphate (MCAPP) and melamine (MA) were used to formulate a MCAPP/MA/starch IFR system. The group reported improved flammability of the PLA based biocomposites with an LOI value of 41.0 vol.% and a UL94 V0 rating when 30 wt.% IFR was incorporated. This was related to the effectiveness of starch as a carbonizing agent. In the MCC tests, biocomposites exhibited reduced PHRR and THR. This was explained as being due to IFR catalysing the degradation of PLA with the release of less flammable gaseous products. Improved char yields and thermal stability from TGA tests were also reported, and the char was said to be made up of pyrophosphoric acid and/or polyphosphate compounds. It was due to this formed char layer that the inner polymer degradation was retarded and PLA fire resistance was improved.

Recently, Lin et al. (2013) synthesized flame retardant poly(1,2-propanediol-2-carboxyethyl phenyl phosphinates) (PCPP) and developed PLA based blends by melt blending. It was reported, using DMA and scanning electron microscopy (SEM) results, that PCPP/PLA blends were immiscible with LOI values higher than 26 vol.% as well as at a UL94 V0 rating as low as 3 wt.% PCPP loading. The presence of PCPP was found to have simultaneously enhanced both the rheology (i.e. reducing PLA brittleness and improving processability) and mechanical properties of the PLA based blends. Finally, from both the morphology of the residual material and phosphorus content measurements, it was concluded that both condensed phase and gas phase flame retardant mechanisms existed during burning.

4.3 Biofibre reinforced biopolymer composites

This section deals with flammability studies of composites made of biopolymer matrices reinforced with biofibres. Various additives/agents may be incorporated in biocomposites which may include coupling, processing, dispersion and fire retardant agents. It is the latter that forms the focus point of this study (Chapple & Anandjiwala, 2010; John & Thomas, 2008; Kandola, 2012; Tang, G., et al., 2012; Zavareze & Dias, 2012).

FR additives, as discussed earlier, have the ability to alter the flammability character of the composite material. The properties, including flammability, of the biocomposites are governed by various factors such as a) the structure of the composite, b) adhesion between matrix and reinforcement, c) type of natural fibre and d) type of biodegradable polymer matrix (Chapple & Anandjiwala, 2010; John & Thomas, 2008; Kandola, 2012; Tang, G., et al., 2012; Zavareze & Dias, 2012).

Several studies were carried out for natural fibre reinforced biopolymer composites and their thermal, morphological, mechanical and flame retardancy properties were reported (Biswal, Mohanty & Nayak, 2012; Fox, Lee, Citro & Novy, 2012; Gallo et al., 2013; Hapuarachchi &Peijs, 2010; Jang et al., 2012). Gallo et al. (2013) investigated the performance of a multi component laminate composite based on a biodegradable commercial blend E-PHBV reinforced with kenaf fibres. The E-PHBV consists of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(butylene adipate-co-terephthalate) (PBAT). Furthermore, a phosphate based additive and a metal oxide (Sb_2O_3) were incorporated to formulate the flame retarded biocomposites. The biocomposites were prepared by an extrusion method followed by compression moulding. Their laminate structure and thickness were as shown in Figure 20.

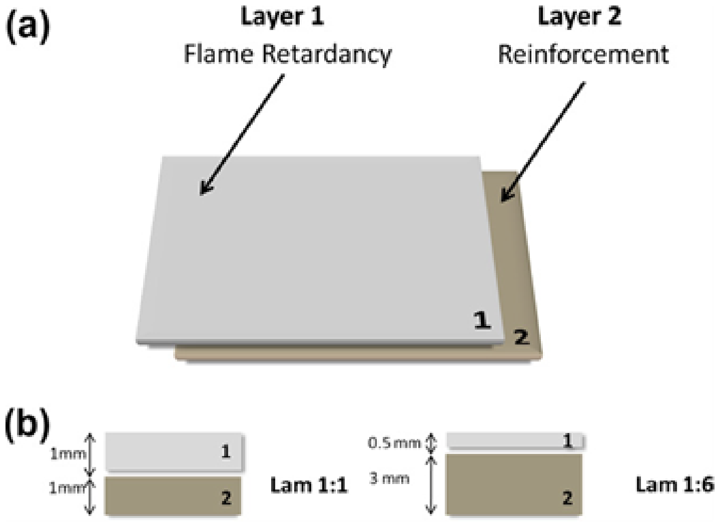

Figure 20. Structure (a) and laminate thickness (b) of the investigated materials. Reprinted from Gallo et al. (2013), Copyright 2013, with permission from Elsevier.

(*Intended for colour on the Web and black-and-white in print*)

Table 9. Mechanical properties.Reprinted from Gallo et al. (2013), Copyright 2013, with permission from Elsevier.

	Flexural strength (σ_f) (MPa)	**Flexural modulus (E_f) (MPa)**	***R* (KJ m^{-2})**
E-PHBV	7.5 ± 0.4	233 ± 3	4.3 ± 0.7
Layer 1	7.0 ± 0.2	215 ± 5	2.5 ± 0.4
Layer 2	19.8 ± 1.1	804 ± 26	6.8 ± 0.8
Lam 1:1	10.7 ± 0.3	450 ± 35	4.8 ± 0.4
Lam 1:6	13.4 ± 1.5	488 ± 5	6.1 ± 1.1

This multi component structure approach was reported as a successful way to balance the mechanical and fire retardancy performance in biopolymer composites. It was reported that the presence of both the flame retardant and antimony oxide nanoparticles did not significantly change the flexural properties of the matrix, but reduced its resilience in comparison to the blend. On the other hand, addition of kenaf fibres was reported to have improved all the mechanical parameters of the matrix (see Table 9). The different ratios of used samples (E-PHBV/Kenaf/AlPi/Sb_2O_3) were: 100/0/0/0 (E-PHBV), 90/0/8/2 (Layer 1), 70/30/0/0 (Layer 2), Layer 1/layer 2 (Lam 1:1), Layer 2/layer 1 (Lam 1:6).

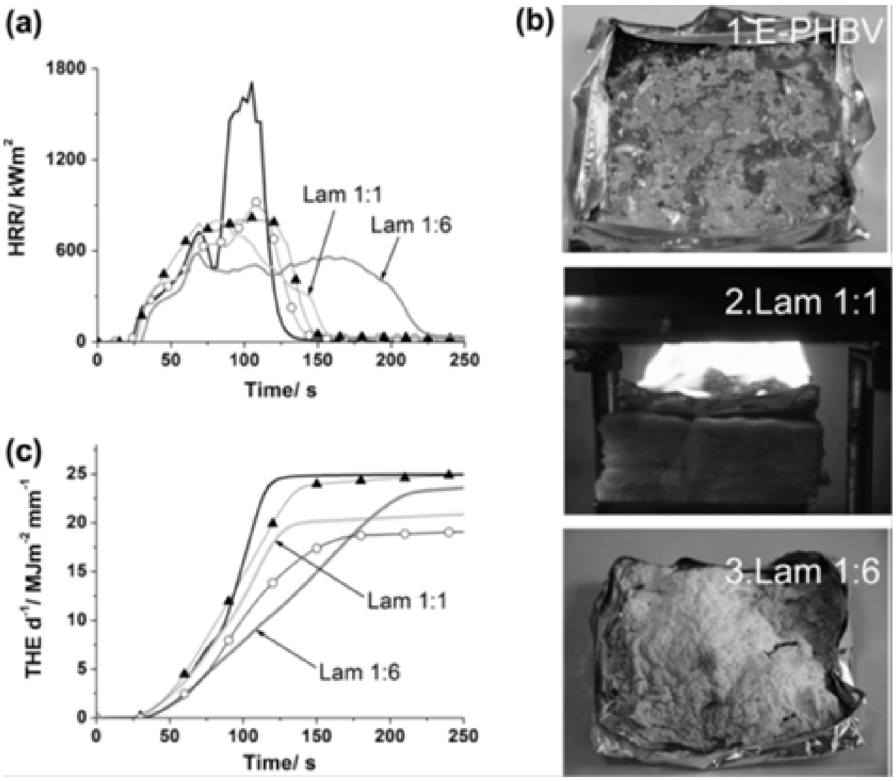

Figure 21. Heat release rate for E-PHBV (solid line), Layer 1 (open circles), Layer 2 (solid triangles) and laminate structures (a); fire residue after cone calorimeter test for E-PHBV (b.1), barrier formation during burning (Lam 1:1) (b.2) and fire residue for Lam 1:6 (b.3); total heat evolved (c). Reprinted from Gallo et al. (2013), Copyright 2013, with permission from Elsevier.

A reduction in the PHRR, HRR, and fire spread indices from the cone calorimetry test were reported as shown in Figure 21. This was explained as being due to a combination of both gas and condensed phase mechanisms from phosphorus and natural fibre. The kenaf fibres were said to have contributed by promoting the formation of an additional stable char layer during combustion. It is reported that kenaf fibres achieved this through intermolecular crosslinking and by inducing oxidation of phosphorus in the solid phase. Consequently, this prevented heat and flammable volatiles from penetrating the flame zone.

The char residue obtained after cone calorimetry tests were studied by SEM as seen in Figure 22, and the relationship between the microstructure of the residue and the flame retardancy mechanism was established. It was concluded that the dense, porous structure in the residue proved that hydroxyl rich kenaf fibres acted as a carbonization agent by forming a network of holes and cavities that affected the release of pyrolysis gases. However, the authors noted that there is a need to refine the coupling between the skin and core layer for improved interaction at the interphase.

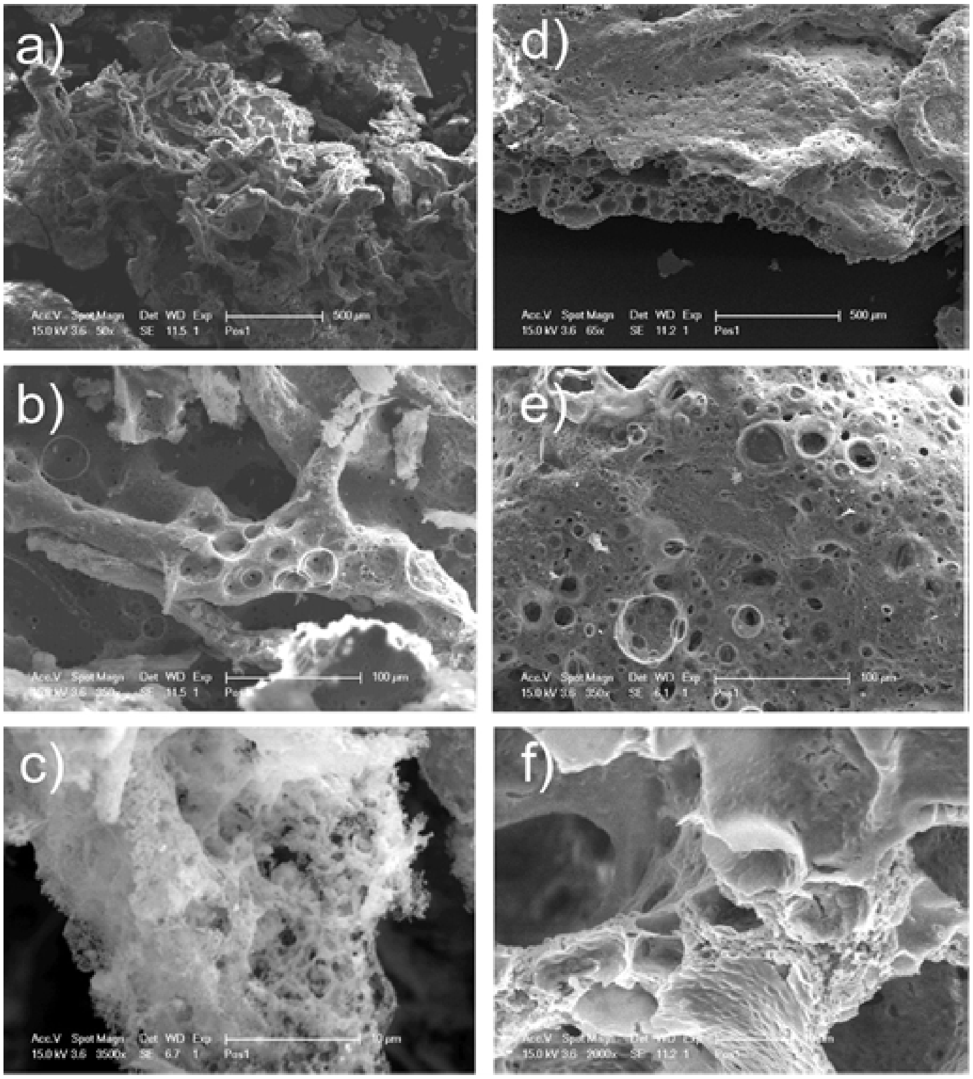

Figure 22. SEM micrograph of Layer 2 (a–c) and Lam 1:6 (d–f) at different magnifications. Reprinted from Gallo et al. (2013), Copyright 2013, with permission from Elsevier.

In the study discussed previously, Hapuarachchi and Peijs (2010) reinforced the flame retarded ternary system based on PLA/MWNTs/organoclays with nonwoven needle punched hemp fibre mat (800g m^{-2}). The authors reported that these hemp fibres reduced the HRR relative to pure PLA, but increased the THR. It was attributed to natural fibres causing the composites to burn for longer. The flame retardant effect of hemp fibres was thought to be due to fibres charring and protecting the underlying polymer.

Furthermore, it was reported that introducing hemp fibres lowered the HRR when compared to the non reinforced ternary system. In general, the authors proposed that the main flame retardant mechanism was due to silicate char surface layer that acted as a barrier for heat and mass transportation. The group concluded by suggesting that the use of short fibre compounds may be more suitable for these composites. This was to avoid thick layered structures that delaminated during cone calorimetry tests and exposed the underlying materials.

Similar results were reported by Biswal et al. (2012) where banana fibre was used to reinforce polypropylene nanoclay composites in the presence of a maleic anhydride grafted polypropylene (MA-*g*-PP) compatibilizer. The nanocomposites were prepared by melt intercalation and the fibre reinforced nanocomposites by melt blending, followed by compression moulding. The group reported that both the tensile and flexural strengths showed a linear increase as a function of clay content. This was explained as being due to the insertion of the polymer chains inside the silicate clay layers, which led to an increase in the surface area of interaction between the clay and the polymer matrix. Furthermore, MA-*g*-PP facilitated expansion of the gallery space of the nanoclay by the inclusion of polar groups to intercalate between the clay layers through hydrogen bonding with the oxygen groups of the tetrahedral clay. No considerable increase in the impact strength was observed and this was due to the presence of clay agglomerates resulting in non uniform dispersion within the polymer matrix. It was concluded that the better system was based on PP/clay/MA-*g*-PP (92/3/5 w/w), and it was termed optimized polypropylene (OPP).

As far as the flammability properties of these nanocomposites are concerned (Table 10), the incorporation of nanoclay showed a remarkable reduction in the HRR. This was attributed to i) nanoclay changing the degradation path of the polymer matrix, thus acting as a barrier by creating a roundabout path for migration, and ii) the change in thermal properties or an increase in the radiation absorptivity due to the high aspect ratio of the nanoclay. The group reported that the compatibilized banana fibre/PP/clay nanocomposites indicated a variation in reaction to fire parameters and exhibited an earlier ignition time relative to neat PP. However, the combustion process proceeded at lower HRR and mass loss rate (MLR) due to improved interfacial adhesion, but increased as a function of fibre in the nanocomposites. This was attributed to the typical characteristics of lignocellulosic fibres. Higher thermal stability was also reported and it was attributed to the presence of nanoclays. Finally, it was concluded that the banana fibre had some nucleating ability on the PP during crystallization which was due to strong interaction between the polymer matrix, fibres and nanoclays.

Table 10. Cone calorimetric parameters for the PP, OPP and banana fibre-PP (BRPP) nanocomposites. Reprinted from Biswal et al. (2012), Copyright 2012, with permission from John Wiley and Sons.

Description	**PP**	**OPP**	**BRPP-10**	**BRPP-20**	**BRPP-30**
Time to ignition (s)	30	36	28	27	26
Time of flameout (s)	561	855	719	648	615
Total heat release (MJ/m^2)	100.5	107.3	121.7	137.4	141.5
Mass lost (g)	30.8	31	32.5	32.2	32.6
HRR (kW/m^2)	2498.2	748.3	926.4	1136.77	1256.2
Total smoke release (m^2/m^2)	1298.8	1164.5	1581.9	1746.5	1612.7
SEA (m^2/kg)	445.87	519.61	304.1	322.24	360.42

Jang et al. (2012) looked at the mechanical and flammability performance of plasma treated (without any FR) coconut fibre reinforced PLA composites prepared by the comingled yarn method. The mechanical properties were determined and flammability tests were carried out using the LOI method. It was reported that the tensile strength and Young's modulus increased with the introduction of the natural fibres, but no improvement was observed for the elongation at break. The group reported that although there was no obvious distinction between the LOI values for the coconut fibres/PLA composites, they were above 20 vol.%, indicating a non flammability character.

Fox et al. (2013) investigated the flame retarding properties of PLA using POSS modified nanofibrillated cellulose as a carbon source in IFR systems. Improved flammability was reported for both the APP/cellulose and the APP/PER (pentaerythritol) systems. POSS modified cellulose showed an additional benefit by slightly lowering the PHRR and reducing the smoke. Furthermore, the use of POSS modified cellulose in IFRs proved effective at lowering flammability while simultaneously inhibiting APP induced PLA degradation, increased thermal oxidative resistance and increased composite stiffness.

Recently the researchers at CSIR have been involved in a project in collaboration with AIRBUS focussing on the development of natural fibre reinforced thermoset panels for use in aircraft. The research work involved the development of aqueous based flame retardant treatments for flax fabric to ensure that the composite panels comply with Federal Aviation Airworthiness (FAA) regulations. In addition to primary flame retardant, the composite contained non fibrous natural silicate fire resistant material as well. The composite material was reported to exhibit superior flammability, smoke and toxicity properties for the aforementioned purpose (Anandjiwala et al., 2013).

5. Summary

The flammability of biofibre (natural fibre) reinforced biopolymer composites as well as that of the biopolymer blends was reviewed in this work. Different flame retardants ranging from phosphorus, halogen, silicon, nanometric particles and minerals were discussed. Their different flame retarding mechanisms, advantages and uses, disadvantages and limitations were elaborated on. The fire testing techniques such as cone calorimetry, pyrolysis combustion flow calorimetry, limiting oxygen index, UL94 and Ohio State University rate of heat release apparatus were also discussed. From this work, it could be seen that not only these testing technologies are needed to help define and come up with flame retardancy mechanisms, but other methods do play a role too. These may include burning tests, horizontal and vertical, thermal and thermomechanical methods of analysis (i.e. TGA, DSC), microscopic methods [i.e. SEM, transmission electron microscopy (TEM)], spectroscopic methods [i.e. FTIR and X ray diffraction (XRD)] and TGA-FTIR coupled systems.

Based on the reviewed work, a number of conclusions on the flammability of biofibre (natural fibre), biopolymers and biofibre reinforced biopolymer composites can be made:

- Natural fibres (NFs) alone are a source of fuel. Thus, they are highly flammable, susceptible to ignition and combustion, combust exothermically and are burned vigorously during combustion.
- The range of studied NFs from the flammability perspective is narrow since thus far it includes wood (saw dust, particle board), flax, rice husk, regenerated cellulose (viscose), wool and mainly cotton fabric materials. There is therefore a need to investigate other often used NFs including bamboo, coir, hemp, jute, kenaf, ramie and sisal.
- In general, the treatment of NF with various FR compounds does indeed result in improved flame resistance.

- The flammability of biofibres is mainly dependent on their immediate environment: the nature of the polymer matrix and other FRs present, the presence or absence of coupling agents and the method of manufacturing natural fibre reinforced biocomposites. The main flammability mechanism favoured by FR treatment of NFs is carbonization followed by increased char formation.
- Depending on the system, the mechanical properties may improve or show marginal decrease due to treatment.
- Current research has mainly focused on PLA as the preferred biopolymer matrix for the development of biofibre reinforced biocomposites. As a result, there is a need to begin exploring the use of other biopolymers {e.g.polycaprolactone(PCL), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly(tetraethylene terephthalate) PTT, poly(ether ether ketone) (PEEK), polybutylene succinate (PBS)} in this field.
- The current interest in using biobased materials such as nanoclays, β CD, pea binder, starch, whey protein and DNA as participants in developing flame retardant systems (FRs) could lead to discoveries of “all green”FRs that may aid to addressing the environmental concerns. However, the important point on such systems may be two phased: the successful development of “all green” FRs on one hand, and the performance and fulfilment of the required standards for the market on the other. This poses a challenge to the scientific arena on fire retardancy.
- Finally, further studies need to be conducted to develop flame retarded biofibre reinforced biopolymer composite systems that simultaneously possess good flammability, thermal, mechanical, morphological and thermo mechanical properties for practical engineering applications.

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Highlights

Discusses types of flame retardants and their mechanisms in biocomposites

Covers the principles and methodology of various flammability testing techniques

Reviews literature on flammability of biofibres, biopolymers and their biocomposites

Successful use of flame retardants on biopolymers like PBS, PCL and PHBV still need to be explored.