

# A review of flame protection of wooden materials and future potential with nano additives

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## Abstract

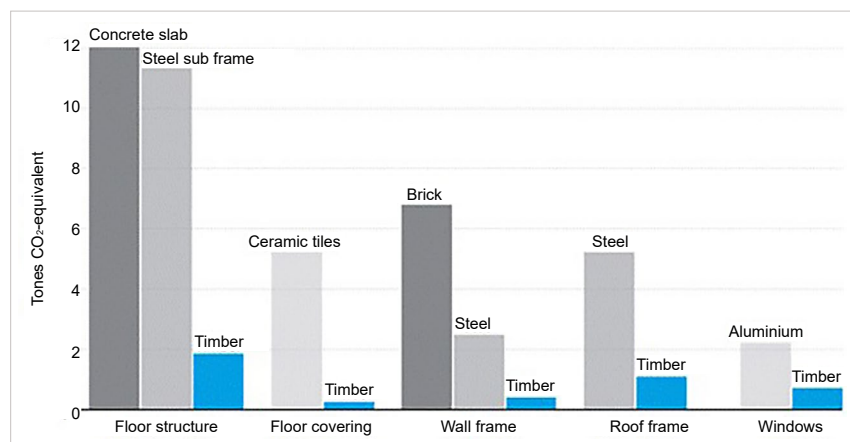
Wood is a highly sustainable material and there is significant interest in its use in the construction industry in terms of modern building construction. However, safety rules and regulations, including fireproof requirements, have become increasingly demanding. In this regard, more effective and eco-friendly approaches for wooden materials treatment related to this topic are subject to research interest in laboratories around the world. The rapid development of nanotechnology offers new materials with unique properties, which will be able to partly substitute or even replace regular chemicals, often toxic to the environment, in the future. This paper overviews traditional fire retarding methods and fire retardants that are applied for the modification of wooden materials. In addition, the potential use of nanomaterials for wood and wooden applications were discussed by extensively literature review.

**Keywords:** wood-based materials; flame retardancy; reaction-to-fire testing; nanomaterials; nano additives

## Introduction

Wood has been a key material in building construction since ancient times. Wood is a renewable, eco-friendly, cost-effective construction material, the use of which could be increased by huge amounts in the near future. For example in the EU, it was assumed that the market share of wood-frame multi-story construction to increase by 30%, and correspondingly 50% increase with light timber frames (Hurmekoski et al. 2023). From an ecological perspective, replacing traditional construction materials with wood will result in a significant reduction of toxic gases emissions related to materials manufacturing, presented in Figure 1 (Horx-Strathern et al. 2017). Several projects related to buildings made from wooden materials are ongoing around the world such as the Canadian government initiated the Green Construction through Wood (GCWood) Program, which is designed to encourage more use of wood in construction projects in Canada (Government of Canada 2019). Another interesting pro-

ject in wood construction is the German Woodcube project, which is the first five-storey glue-free solid wood building, shown in Figure 2a, completed in 2013 (German-Architects 2013). In Finland, the Puukuokka complex, consisting of three eight-storey wooden apartment buildings, available in Figure 2b, was completed in 2018 (NT-Nord Treat 2023).



**Figure 1.** Greenhouse gases emitted in the manufacture of building materials used in a range of construction components for a single-storey house in Sydney, Australia (Modified from: Horx-Strathern et al. 2017)



**Figure 2.** (A) Woodcube, Hamburg, Germany; (B) Apartment building Puukuokka, Jyväskylä, Finland

The use of wood products as a construction material is restricted by fire and environmental safety rules due to its high flammability. In this respect, flame retardancy of wooden materials plays an important role in preventing fire accidents and protecting people from possible fire hazards. Today, numerous flame retarding (FR) systems are applied in different fields. The global flame retardants production was about 2.26 million tons in 2018 and is expected to grow at an annual growth rate of 2.8% during the period 2018–2026 (Ceresana 2022). Aluminium trihydroxide,  $\text{Al}(\text{OH})_3$ , is the most used FR, accounting for about 38% of total FR consumption, followed by halogen-containing FRs, 22%, and phosphorous FR, 17%, as showed in Figure 3a (Flameretardants-Online 2019). Amongst the major markets of halogen-free FR consumers, the building and construction industry is the largest user of FRs, accounting for 28%, followed by the electrical and electronics and transportation industries, available in Figure 3b (Businesswire 2017).

The inherent properties of wood material can be improved by modification, which could be a solution for fire retardancy, but Popescu and Pfriem (2020) have found that the pure wood modification cannot improve the reaction to fire of wood significantly and the combined strategies could provide to the higher protection. Thus, a certain novel flame retardant for wooden applications could be nanomaterials and nano additives. Recent advances in nanomaterials and nanotechnology have attracted remark-

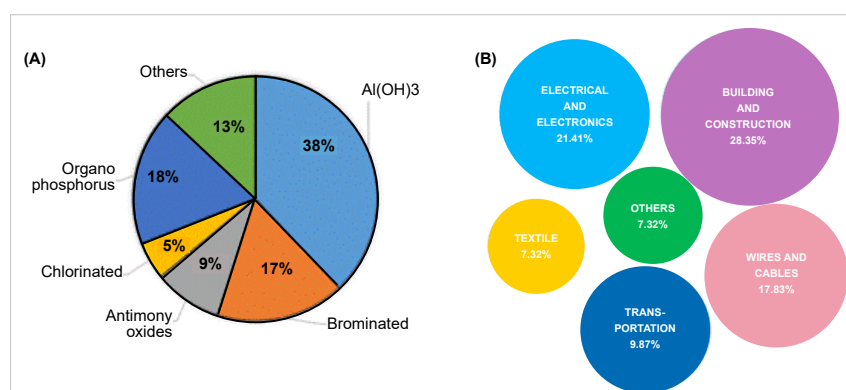
able attention due to the development of innovative materials, with many potential applications. Nanomaterials often demonstrated extraordinary properties and are already used in many commercial applications, including aerospace, civil engineering, and sporting goods applications along with other useful characteristics, their often-superior fireproof properties in polymeric and natural fiber polymeric composites. For example, it was shown in various studies that the optimal nano clay loading amount for better fire performance was 3–5 wt% (Chuang et al. 2011, Bueno et al. 2014, Deka et al. 2014). Nanomaterials and additives, as well as their feasibility for wood-based applications, were presented with more details in sub-chapter *Nanosized additives*.

This paper presents an overview of the commonly used flame retardants in wood and wooden products, and the increasing role of nanomaterials in flameproof is pointed out. The mechanisms of the fire retardant action are also included. This review covers a description of the techniques applied to the flammability of material testing, and the methods for wood material modification with FRs is briefly discussed.

### **Testing methods for thermal stability and flame retardancy**

In many areas of activity, such as public building construction, the use of materials with increased combustibility is prohibited. Materials must pass several standard tests based on which their combustibility class will be determined. By using these tests, a fire retardant efficiency can also be estimated. In general, material flammability is associated primarily with three parameters: ignitability, flame spread and heat release (Morgan and Wilkie 2007). The most common methods used for material flammability and thermal stability include, *inter alia*, the Single Burning Item (SBI) test, cone calorimetry, the flame spread index (FSI), and the limiting oxygen index (LOI).

In the EU countries, a universal system for testing and fire Euro-class rating for construction materials was introduced in 2001 (European Commission 2000): testing standard EN 13501-1, where fire classification is based on reaction-to-fire measurements by using a Single Burning Item (SBI) test, EN 13823, which was specially developed for the Euroclass system. Classification parameters within the SBI test include fire growth rate (FIGRA), lateral flame spread (LFS)



**Figure 3.** (A) The global flame-retardant market by chemistry, 2016; (B) Global halogen-free flame-retardant consumption by industry, 2016

and total heat release (THR), as well as parameters such as smoke growth index (SMOGRA) and total smoke production (TSP) are taken into account for additional classification (Lowden and Hull 2013). The Euroclasses of materials applied in wall and ceiling construction rank from A to F classes. Products that do not contribute or contribute very slightly to the development of fire are rated as Euroclass A; Euroclass E covers materials that can resist ignition from a small flame for a short period; material classified as class F means that this product is not tested or there are no performance requirements (McNally and Pötschke 2011). Generally, it can be stated that untreated wood in this system is rated as class D (FIGRA < 750 W/s), while with FR treatment it is possible to achieve class C (FIGRA < 250 W/s) or even class B (FIGRA < 120 W/s) rating (Lowden and Hull 2013), which is, according to the EU regulations, sufficient for material use on most construction sites except in evacuation routes (B. A. L.; Östman and Mikkola 2006). Four models can be used for the prediction of Euroclass on the basis of the cone calorimeter test: the Trätek model, the Branzfire model, the VTT model and the Rule-of-thumb model (B.; Östman et al. 2006). Cone calorimeter is a universal device for testing the reaction-to-fire of materials and it can define parameters, ignition time (IT), heat release rate (HRR), mass loss rate (MLR), smoke generation, carbon oxide and dioxide release, for example according to the ISO 5660-1. Cone calorimetry method attracts great interest due to a small specimen measuring 100 × 100 mm and with a thickness of up to 50 mm being appropriate for estimating the quality and the Euroclass of fire safety on the material. The rule-of-thumb model, as presented in Table 1, predicts Euroclass based on IT and HRR estimated by the cone calorimetry test at a radiance of 50 kW/m<sup>2</sup>. VTT developed a model for classification, where the measured HRR and the FIGRA index in the SBI test is predicted based on cone calorimetry at an incident heat flux of 50 kW/m<sup>2</sup>, available in Table 2. Another of the most used tests to describe material flammability is Limiting Oxygen Index (LOI), standard ISO 4589 or ASTM D 2863. The testing procedure measures the minimum oxygen concen-

tration required to support candle-like downward flame combustion. In this test, materials with an LOI of below 21% are classified as combustible, whereas materials with an LOI of above 21% are classified as self-extinguishing.

### *Mechanisms of action of FRs in wood and wooden products*

Wood is a highly flammable material and easily burns when exposed to fire. The scenario of wood thermal decomposition is well known. Water loss is observed at 100°C, and subsequently thermo-degradation of hemicelluloses starts at around 290°C, and cellulose decomposes between 320 and 380°C. Lignin has a broad decomposition temperature range of between 200 and 500°C (Kim et al. 2010). During thermal oxidation of the polymeric constituents of wood, a mixture of volatile gases, tar (levoglucosan) and carbonaceous char is produced (Lowden and Hull 2013).

In a fire situation, FRs act to inhibit or suppress the combustion process. Flame retardants, depending on their nature, work either in the vapour phase or the condensed phase through a chemical and/or physical mechanism to interfere with the combustion process, i.e. during heating, ignition, pyrolysis, or flame spread (Lu and Hamerton 2002). In general, several approaches can be used to improve the fire retardancy of materials: changing the pathway of pyrolysis of the wood or chemical mechanism, the formation of the isolating surface layer, absorbing heat and cooling down substrate, and diluting pyrolysis gases (LeVan and Winandy 1990). Thermal degradation of cellulose, the main component of wood, generally takes place through tar (levoglucosan) and flammable gases formation and/or char formation, which also follows carbon oxides and water formation (Östman et al. 2006). Catalytic dehydration reaction, which is found in some types of FR, results in the hydroxyl groups leaving the cellulose polymer, resulting in char development. Char mainly consists of carbon due to H and O atoms escaping in the form of volatile gases during combustion. Char, representing the graphitic structure, is stable even at temperatures above 3000°C, as it has been stated in the traditional publication about the theories of wood combustion decades ago (Browne 1958). Thus, the presence of char can significantly change the decomposition scenario by limiting heat and fuel gases transfer, thereby reducing the spread of flames and can even self-extinguish. Along with cellulose, the decomposition of lignin makes a significant contribution to char yield (Lowden and Hull 2013). Also, the formation of a protective layer that plays the role of a barrier for evaporation of pyrolysis gases and reduces access of oxygen to the burning material. The most effective barrier properties show intumescent coatings, which easily expand at enhanced temperatures and form a porous layer that protects the underlayer material from fire. A third approach is to use additives that decompose endothermically, absorbing heat and cooling down the substrate, thus delaying ignition. This slows down combustion and can even result in the extinguishing of the

**Table 1.** Rule-of-thumb class limits for cone calorimeter tests at 50 kW/m<sup>2</sup>

Euroclass	Time to ignition (s)	Heat release rate maximum* (kW/m <sup>2</sup> )
B	≥ 40	≤ 100
C	≥ 30	≤ 180
D	≥ 15	≤ 250

**Table 2.** FIGRA limits Prediction of EU class based on FIGRA parameter, cone calorimeter at an incident heat flux of 50 kW/m<sup>2</sup>

Euroclass	FIGRA (W/s)
B	≤ 120 W/s
C	120 W/s > FIGRA > 250 W/s
D	250 W/s > FIGRA > 750 W/s
E	> 750 W/s

flame if the temperature decreases below that required for sustaining the combustion process. The next approach is generating many non-combustible gases, ammonia, carbon dioxide and water vapour, thereby diluting combustible gases. Often two or more mechanisms operate simultaneously and can have a synergistic effect. However, to facilitate fire protection, a combination of FRs with different mechanism actions can be used.

Along with FR effectivity, the effects of FRs for wood durability and on the environment, i.e., the ecological concern, are also considered. Today the most applied FRs in timber are phosphorous- and boron-containing as well as metal- and nitrogen-containing. Toxic compounds containing FRs, e.g. halogens, are prohibited due to their negative impact on the environment (Regulation (EU) No 305/2011, 2013, REACH Regulation (EC) No 1907/2006, 2006). Boric acid is a candidate for the REACH list, being a Substance of Very High Concern (SVHC) due to its negative impact on reproduction (Lowden and Hull 2013). Wood durability might be negatively influenced by hygroscopic FR that increases the hygroscopicity of the wooden end-product. In this context, a new Nordic system with Durability of Reaction to Fire (DRF) performance classes for fire retarded wood products has been developed (Östman et al. 2006). This new method for durability testing of FR wooden materials and classification should also be transferred to a European method within CEN. In the developed for FR wood end-product requirements, the moisture content and retained reaction-to-fire parameters for interior and exterior wood-based products are recorded in accordance with NT Fire 054. For materials for interior use, usually only hygroscopic properties are studied, NT Build 504. For outdoor applications, the accelerated ageing test is used, NT Fire 053. In practice, water-insoluble leach-resistance systems have been developed:

- i) resins polymerized after impregnation into wood (includes mixtures of urea, melamine, dicyandiamide, phosphoric acid and formaldehyde);
- ii) graft polymer fire retardants attached directly to cellulose (Russell et al. 2004).

Wooden products can be usually modified with FRs using two methods: impregnation with chemical agents (pressure-less and high-pressure) and surface treatment or coating (Bednarek and Kaliszuk-Wietecka 2007, Seo et al. 2016). Wooden materials, such as particleboard or plywood, can be modified by loading FRs into the adhesive system. In the case of natural fiber composites/wood-plastic composites, fire retardants are usually mixed with other components during compounding procedures before extrusion, molding or pressing procedures (Turku and Kärki 2014). Impregnation, in comparison to coating or dipping, provides deep chemical penetration into a wood structure. For example, in pressure-impregnated pine, the whole sapwood is usually thoroughly impregnated, whereas in surface-treated samples, the depth of FR penetration is 1 mm or less (Hakkarainen et al. 2005). Impregnation with

inorganic salts due to their small size and high solubility in water is mostly applied for flame retardancy of wood and wooden products at a commercial level. Salts, such as mono- and diammonium phosphate, ammonium sulphate, borax, boric acid, zinc chloride, guanlyl urea phosphate and sodium tetraborate, are mostly used (White and Dietsberger 2010). However, a few negative aspects can be risen with FR impregnation, such as damaged wood strength, accelerated corrosion and toxic gases (Russell et al. 2004, Bednarek and Kaliszuk-Wietecka 2007). The effectiveness of impregnation with micro-/nano-sized particles depends on the wood type, e.g. the anatomy of wood and the size of openings in the wood structure, which allows chemicals to penetrate the wood. Wood incising (Islam et al. 2013, Civardi et al. 2016) or pretreatment with steam (Ishikawa et al. 2005, Islam et al. 2013) can improve the penetration and retention of chemicals.

In order to facilitate the impregnation procedure, Ishikawa et al. (Ishikawa et al. 2005) pretreated wood with steam by using a heating-type drying pressurizer. This procedure allowed the destruction of open pits, thereby opening the pathway for fire retardant solution ingress inside the wood. Several FRs, namely borax/boric acid, triphenyl phosphate, bisphenol A bis(cresyl) phosphate, aluminium oxide, magnesium hydroxide and perfluoro butane sulphonic acid potassium salt, were tested. In the example of boron-containing FR, it was observed that the rate of impregnation with FR increased significantly when the pretreatment temperature was increased up to 120°C. Cone calorimetry results showed that pretreatment had a significant impact on wood flammability. Thus, treatment of sapwood with borax/boric acid without pretreatment resulted in a decrease of pHRR from 182 kW/m<sup>2</sup> to 106 kW/m<sup>2</sup>, and total heat release (THR) from 91.2 MJ/m<sup>2</sup> to 55.4 MJ/m<sup>2</sup>, for the neat and FR-containing samples, respectively. The pretreatment of wood at 120°C allowed for a decrease of pHRR to 23.5 kW/m<sup>2</sup> and THR to 7.3 MJ/m<sup>2</sup>. The combustion test of UL showed that ignition time for samples after pressure-treatment was extended significantly, and high temperature pretreated samples did not ignite. Among other studied FRs, one remarkable effect showed fluorocarbon acid salt and organic phosphate. Plasma impregnation of wood with FRs was studied by Pabelina et al. (2012). It is argued that this method is more ecofriendly than direct chemical treatment. Pabelina et al. (2012) compared three different methods: painting, pressure impregnation and plasma impregnation of plywood. As fire retardants, the researchers used 10% boric acid solution, 85% phosphoric acid (PA), and some commercially available flame retardants. It was determined that the material after phosphoric acid plasma treatment was more thermally stable, having the highest onset temperature, degradation temperature and char residue compared to other samples tested under similar conditions (Pabelina et al., 2012). Also, plasma-impregnated PA material had a higher thermal stability than PA painted or vapour impregnated specimens.



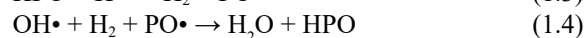
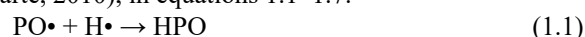
In comparison to the impregnation method, the coating is simpler and more cost effective. Fire retarding coatings do not involve the chemical modification of a substrate, but rather the formation of a protective layer that delays ignition time and can inhibit thermal degradation (Mariappan 2017). As a drawback of coating, the leaching of FRs from a substrate in an outdoor application, physical damage or inaccessible aesthetics of some treatments can limit the application of FR coatings in some cases. There are two types of coatings available to reduce surface flammability: intumescent and non-intumescent. Intumescent coatings swell when a critical temperature is reached, typically at temperatures around 200°C, to form a low-density charred layer, i.e. a combination of charring and foaming processes. This layer usually protects the substrate from the flame spread and plays the role of a physical barrier for heat and mass transfer from and to a substrate. The intumescent system is a combination of a (1) dehydrating agent or acid donor, (2) char-forming ingredients, and (3) a blowing/spumific agent (Serge Bourbigot et al. 2004). The intumescent system action can be described as follows: an acid-generating catalyst, commonly ammonium polyphosphate (APP), reacts with a char former (starch, glucose, di/tripentaerythritol, cellulose powders) to initiate its dehydration and following cross-linking, and a blowing agent, e.g. urea, melamine or some other additive, generate gas in the molten mass to create foam, which solidifies to form a barrier layer (Wladyka-Przybylak and Kozłowski 1999).

## Fire retardant categories

### Phosphorus and nitrogen-based

Phosphorus-based FRs are most used for the flame protection of wooden products. Among phosphorus-based FRs, elemental red-phosphorus, inorganic-phosphorus and organic-phosphorus are the most applied (Morgan and Wilkie 2007). FRs containing phosphorus are mostly reactive in oxygen-containing polymers, such as cellulose, polyesters, polyamides, etc. (Laoutid et al. 2009). Working in the condensed phase, they facilitate the charring process, thereby protecting the material from burning. In terms of wood, phosphoric acid, which is liberated during the thermal decomposition of FRs, catalyses the dehydration reaction of cellulose, reacting with OH groups of cellulose. Dehydration of the polymer induces cyclisation, cross-linking, and aromatization/graphitization, where phosphorus compounds or their decomposition products act as cross-linkers (Scharte 2010). Upon further heating, phosphorylated cellulose undergoes thermal decomposition and a significant amount of char is formed at the expense of combustible volatile products, which would be produced by virgin cellulose (Lewin and Weil 2001). Also, char formation is often accomplished by the release of water, thereby diluting the mixture of flammable gases (Laoutid et al. 2009). Along with its effect on facilitating

char residue, phosphorous FRs may coat the char and thus create additional protection of the surface from fire (Lewin and Weil 2001). Along with working in the condensed phase, P-containing FR can act in the gas phase by trapping free radicals involved in combustions (Laoutid et al. 2009, Morgan and Wilkie 2007). Volatile phosphorus compounds are among the most effective inhibitors of combustion. It was shown that phosphorous FRs are five times more effective than bromide and ten times more effective than chloride. The most abundant phosphorus radicals in the flame are  $\text{HPO}_2\cdot$ ,  $\text{PO}\cdot$  and  $\text{PO}_2\cdot$ . Some examples of radical scavenging are shown below (Morgan and Wilkie 2007, Scharte, 2010), in equations 1.1–1.7.



Another mode of action in which phosphorus is important as a char former is in intumescent fire-retardant paints. These typically have a phosphorus compound such as ammonium polyphosphate and a char-forming polyol such as pentaerythritol, along with a blowing agent such as melamine (Lewin and Weil 2001).

The most important reactive type of nitrogen containing FRs is melamine and its derivatives. Often nitrogen-based FRs are used in combination with phosphorus-containing FRs exhibiting the synergistic effect. Melamine, with its high thermal stability, does not melt, but it sublimates at about 350°C. Upon sublimation, significant energy is absorbed that decreases the surface temperature of the polymer (Morgan and Wilkie 2007). Melamine does not sublime completely in fire; a portion of unsublimated melamine undergoes self-sublimation with the forming residue consisting of thermally stable melamine derivatives, *melam*, *melem* and *melon* compounds, and condensation of melamine is accomplished by evaporation of ammonia, which dilutes a mixture of flammable gases in a gas phase (Morgan and Wilkie 2007, Lowden and Hull 2013). Melamine condensates and phosphoric acid react at a temperature above 600°C, where triazine rings of melamine derivatives are opened and cross-linked, resulting in phosphorus oxynitride formation, a very thermally stable compound that can contribute to the condensed-phase mechanism (Morgan and Wilkie 2007).

The melamine derivatives as a FR for wood were investigated in various studies. Jiang et al. (2010) studied the influence of three FRs, obtained by the polymerization reaction of phosphoric acid with pentaerythritol, and then urea or triethanolamine were added. As a result, only phosphorus-containing FR and two nitrogen-phosphorus (N-P) containing intumescence FRs were synthesized. The individual phosphorus-based FR pentaerythritol phosphonate

**Table 3.** Fire performance of NFC with 10 wt% of the flame retardance (Arao et al. 2014)

Sample	IT (s)	Peak HRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	Average HRR (tot) (kW/m <sup>2</sup> )	Average burning rate (mm/min)	UL-94
PP	31.6	1395	117	434	27.4	HB
NFC (WF : 50 wt%)	21.4	563	93.4	336	32.4	HB
NFC + APP	19.6	312	78.9	136	Self-extinguish	V0
NFC + MPP	20.4	352	98.6	83.7	Self-extinguish	HB
NFC + Al(OH) <sub>3</sub>	24.8	467	99	96.5	20.9	HB
NFC (WF : 30 wt%) + APP	-	-	-	-	21.2	HB

sample increased LOI from 18% for pure wood to 36% while both N-P containing FRs were more effective, increasing LOI up to 43 and 58% for triethanolamine- and urea-containing FRs, respectively, showing intumescence and synergistic N-P action. TGA analysis under air conditions showed that the residual char increased from 23% to 46–51% for untreated and FR samples. Xiao et al. (2018) studied fire retarding properties of poplar veneers made of plywood with intumescent varnish coating, containing melamine urea-formaldehyde (MUF), 15%, which played the role of binder and blowing agent and pentaerythritol (PER), 10%, as a carbon donor, and FR guanyl urea phosphate (GUP), 0–20%. Because varnish with 20% GUP became opaque, only 0–12% GUP containing samples were examined. Cone calorimetry testing showed that coated plywood samples exhibited intumescence with a thickness of 120 (0% GUP) to 140 (4–12% GUP) times that of the initial thickness. This carbonized layer acted as a barrier for O<sub>2</sub> and thermal energy, thereby protecting the under-layer wood from burning. A further incorporation of GUP, 4–12%, resulted in significantly improved reaction-to-fire parameters. GUP is known to accelerate dehydration and decarbonisation of PER, and to stabilize the porous carbon layer, resulting in a thicker intumescent layer and improved barrier properties. Arao et al. (2014) compared the influence of APP, melamine polyphosphate (MPP) and aluminium trihydrate (ATH) on the polypropylene/wood fibres composite, and the results are shown in Table 3. As has been seen, all studied FRs were effective, leading even to self-extinguishing in the case of N-P containing FRs. The mechanism action of ATH is endothermal decomposition and release of water, thereby diluting fuel gases and absorbing heat. However, a 10% loading amount was not enough for significant changes in composite fire performance. APP and MPP mechanism action were related to char formation, where wood flour (WF)/cellulose was the charring agent. The char layer prevented the absorption of heat and also blocked the flammable gases produced during polymer/wood decomposition. Accelerated charring by APP was also the reason for shortened ignition time, whereas ATH delayed the starting time of char forming. Interestingly, reducing the WF amount from 50 wt% to 30 wt% resulted in the deterioration of the flame retardancy rating, showing a correlation between APP and WF content and the synergistic effect.

### Boron containing

Boron-based flame retardants, boric acid, sodium borate (borax), and salts of boric acid, are also widely used as commercial flame retardants for wooden products. In general, the mechanism action of boron based FRs can be described as follows: chemicals decompose endothermically evolving water and form a glassy melt on the surface of the substrate. In addition, water-soluble borates, boric acid, and sodium borate (borax) esterify the hydroxyl groups of cellulose generating carbonaceous char formation (Ishikawa et al. 2005, Morgan and Wilkie 2007).

Zinc borates (ZBs) has long been known as an additive in wooden materials manufacturing and along with fire retardancy function, the ZBs are used as an antifungal preservative for wood (Klyosov, 2007). Zinc borates, upon heating, dehydrate endothermically and vaporized water absorbs heat and dilutes a mixture of flammable gaseous components, which can melt at a sufficiently high heat, producing a glassy insulating layer and changes the decomposition route of some flammable substances, inhibiting the formation of flammable gases. Zinc borates, showing synergism with halogen-containing FR, improve the surface barrier by creating glassy residue in a condensed phase. The ZBs can enhance the action of Al trihydroxide (ATH) or bauxite and Mg hydroxide (MDH) in polymers by improving formed char performance, creating a ceramic-like residue, thus lowering peak heat release. In addition, ZB works as a smoke and afterglow suppressant (Shen et al. 2008, Weil and Levchik 2008).

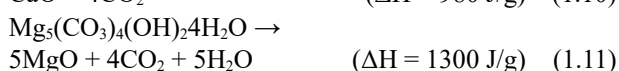
Di Blasi et al. (2007) studied the pyrolysis of wood impregnated with boric acid, 0–5.4%. The authors reported that yields of char and non-flammable gases continuously increase as acid concentration increases, whereas the amount of organic liquid products is reduced. The largest changes happened under boric acid concentration below 2%. LeVan and Tran (1990) studied the flame retardancy of wood material, pressure impregnated with a mixture of borax and boric acid (BX/BA) (some commercial product), with 1–20 wt% loadings. It was shown that HRR decreased rapidly with an increasing loading level of borax-boric acid, whereas char residue increased from approx. 22% to 45% for clear wood and 20 wt% add-on of borax-boric acid. It was showed that 7.5 wt% of BX/BA was enough

for achieving the highest class of fire safety of the material. Borax tends to reduce flame spread but can promote smouldering or glowing. Therefore, these compounds are normally used together (LeVan and Tran 1990). Baysal et al. (2007) have studied the effect of BA and BX mixture as well as natural extractives on the fire performance of Douglas fir wood species. The flameproof effect of BX/BA (3/7 weight ratio) was observed over untreated and treated wood samples with natural extracts. It was also shown that Douglas fir wood treated with BX/BA (3/7 weight ratio) had a better flame-retarding effect than when solely BA or BX were applied (Baysal et al. 2007, Tomak and Cavdar 2013). The LOI of pine impregnated with BX/BA mixture (1.5–25 kg/m<sup>3</sup> retention) increased from 25 (control) to 28–43.5% depending on the degree of retention but after a leaching procedure LOI dropped to 26–28% (Tomak and Cavdar 2013).

As mentioned above, mixtures of FRs with different mechanism actions are often used to facilitate the fire retardancy of a product. Grexa and Lübke (2001) studied the flammability of wood particleboard, where wood particles were treated with Mg(OH)<sub>2</sub> or monoammonium phosphate (MAP) combined with boric acid or Al(OH)<sub>3</sub>. The total number of FRs loaded was 24–25 wt%. Cone calorimeter testing showed that the strongest FR effect was in the case of a MAP/boric acid system. A sample with MAP/boric acid had the shortest burning time, leaving 83% residue, whereas 72% of the original weight of untreated particleboard was burned at the end of the experiment. Also, the pHRR was significantly lower without formation on the second peak of HRR, unlike other tested samples. The study of Winandy et al. (Winandy et al. 2008) showed that the pHRR, time to ignition and heat release decreased with the mixture of guanylurea phosphate and boric acid as the FR loading amount increased from approx. 5 to 14 wt% at an increased residual mass fraction. Using a modelling procedure, the authors predicted that it is possible to achieve Euroclass B in the flame-spread classification at FR levels of ≤ 8% to 10% and even better ratings can be achieved at higher FR loadings.

### Mineral fillers

Endothermic or mineral additives, usually inorganic hydrates or carbonates, are thermally unstable and decompose upon heating, releasing carbon dioxide and water vapour in the first step, diluting fuel gases and cooling down the substrate, and in the second step they form a protective ceramic around the charred fibres, as presented in Equations 1.8–1.11 (Bourbigot 2008).



Metal-containing hydroxides, Al trihydroxide or bauxite (ATH), and Mg dihydroxide (MDH), are known to be non-toxic, abundant, and cheap. ATH is identified as the most used FR, as presented in Figure 3a. The onset temperature of decomposition for ATH is about 180–200°C, whereas MDH decomposes at about 300–320°C (Hull et al. 2011), available in Equations 1.8 and 1.9. They release approximately the same amount of water, about 35 wt% and 31 wt%, for ATH and MDH, respectively. Yet, both hydroxides act as smoke suppressants during polymer combustion (Hollingbery 2011). In plastic manufacturing, ATH is more often used than MDH because ATH starts to decompose at a temperature below the temperature degradation of most polymers. A small amount of catalyst, Ni or ZB, can enhance the action of ATH and MDH (Weil and Levchik 2008). The synergistic action of MDH and layered silicates in EVA polymer fireproofing is also observed (Laoutid et al. 2006).

The FRs containing carbonate minerals, e.g. huntite and hydro magnesite, are rarely used for wooden materials, while as a fire-retardant additive in polymers they have been in use for many years. Both minerals endothermically decompose, hydromagnesite starting from 220–240°C, releasing water and carbon dioxide, and huntite decomposes starting from 400°C, releasing carbon dioxide, as shown in Equations 1.10 and 1.11 (Hull et al. 2011). The final weight loss is 54% for both minerals (Laoutid et al. 2006).

In recent years, different FR coatings consisting of mineral additives have attracted attention. Thus, carbonate minerals, hydromagnesite and huntite, as an alternative to long-term FRs, are proposed to avoid a toxic effect on the environment (Liodakis et al. 2008, 2010, 2013). Liodakis et al. (2010) studied the fire retardancy effect of hydromagnesite/huntite mixture as well as long-term FRs usually used for forest protection, viz. diammonium phosphate (DAP), monoammonium phosphate (MAP) and ammonium sulphate (AS), on pine and rockrose samples. The samples were studied with the use of TGA, and the flame spread test and results showed that these minerals have an FR effect on the forest sample; however, they were less effective than conventional long-term ones (DAP, MAP and AS). Despite that, it was concluded that their commercial application might be preferred to common use FRs due to their availability, low cost, and absence of toxic effect. Thermal analysis showed that better fire performance had the wood samples treated with a mixture of sodium polyacrylate and both minerals. It was suggested that the possible synergistic effect between gel and minerals facilitated the formation of char and suppression of a flammable gases release.

Kumar et al. (2015) used an inorganic-inorganic clay-sodium silicate composite coating for red pine. Samples were tested using a cone calorimeter, and the parameters for selected samples are displayed in Table 4. As can be seen, FR coatings had a significant effect on material flammability. The protective action of sodium silicate,

**Table 4.** Selected parameters of cone calorimeter analysis data (Kumar et al. 2015)

Sample	IT (s)	pHRR (kW/m <sup>2</sup> )	AHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	Weight of coating (g/m <sup>2</sup> )
Neat wood	17	179	83	98	-
Vermiculite (V)	20	166	78	93	8.56
Sodium Silicate (SS)	54	134	68	78	143.4
VSS	66	120	57	64	151.5
VSS2	101	106	46	50	290.46
5VSS	60	144	59	63	123.63

which is known to be an intumescent inorganic material, is related to its ability to form a solid foamy layer when burned. This expanded layer delays the ignition time and protects the substrate from burning. In addition, sodium silicate releases water, up to 30 wt%, cooling down under layered material. Vermiculite, which releases about 5 wt% of waters, had less of an effect than sodium silicate. The best results showed samples coated with both vermiculite and sodium silicate, brushed as separate layers (VSS and VSS2) and as composite (5VSS). Vermiculite reinforces sodium silicate foamed structure, making it thinner and denser, i.e. less permeable for heat and mass transfer, thus improving barrier properties. Yet, as seen, double layer vermiculate-sodium silicate coating (VSS2) was more effective in comparison to the singular one (VSS).

Kozłowski et al. (1999) used expanded vermiculite with urea-formaldehyde resin as a binder for fire protection of lignocellulosic particleboard. The incorporation of minerals significantly improved the fire performance of the material. Kazmina et al. (2018) studied a mixture of water-soluble silicate (liquid glass) with magnesium-containing minerals, Mg(OH)<sub>2</sub>, magnesite, MgCO<sub>3</sub>, and hydromagnesite as possible FR additives in paints. Silicates themselves show FR properties because they decompose endothermically and release water at enhanced temperatures. Among the tested coatings, a hydromagnesite-containing mixture had the highest intumescence, 151%. At the same time, this type of coating showed the highest mass loss due to water loss and incombustible CO<sub>2</sub> evolution. Plotnikova et al. (2003) studied the effect of the composition of urea-formaldehyde resin (UFR) filled with natural minerals, mica, mineral wool, basalt fibres and graphite in different combinations, in the presence of diammonium hydrogen phosphate, on the flame retardancy efficiency of coatings on wooden material. It was reported that the incorporation of the fillers had a significant effect on material flammability in terms of mass of residue and thermal conductivity. The better result was seen in coating where 16% graphite, 16% mica, 3% basalt fibres and 12% of diammonium hydrogen phosphate were applied (Plotnikova et al. 2003). Ozkaya et al. (2007) compared the influence of three different FRs, potassium carbonate, wolmanit and borax, applied by brushing or dipping, on the ignition time and burning period of strand board. Potassium carbonate was most effective in terms of ignition time delay. Concerning the burning period, borax and potassium carbonate

were more suitable for reducing burning and embers after turning off the flame than wolmanit. The dipping method was more effective in terms of prolonging the ignition time and reducing the burning period of flames and embers.

### *Nanosized additives*

Among the numerous different types of nanoparticles available, in the flame retardancy field mostly layered silicates (LSs), metal oxides, namely SiO<sub>2</sub>, ZnO, TiO<sub>2</sub>, carbon-based, such as carbon nanotube (CNT), graphite, expandable graphite and recently graphite are considered. They mostly work in a solid phase, facilitating char formation and thereby improving the barrier properties of the composite. Often the synergistic effect between different types of nanoparticles or nanoparticles and conventional FRs is observed (Laoutid et al. 2006, Hassan et al. 2008). It is also important to highlight that nano additives often show multifunctionality, improving the mechanical and physical properties of the material simultaneously.

### *Layered silicates*

Layered silicates (clays, LSs) are the most applied nano-additives in composites manufacturing. Numerous research studies have demonstrated that the layered silicates improve mechanical performance, thermal stability, and fire retardancy of polymer-based nanocomposites (Zanetti et al. 2000, Kashiwagi et al. 2004, Kiliaris and Paspapyrides 2010). A layered structure, high surface-to-volume ratio along with availability and low cost make the LSs suitable additives for composites manufacturing that can also be modified by surfactants. The main disadvantage of the LSs is their poor dispersion in a polymer matrix due to their stacked structure. Surfactants not only exfoliate clay layers, but they also change the nature of clay to a less hydrophilic, making them more miscible with the hydrophobic polymeric matrix. An exfoliated nanocomposite structure, where nano clay layers are fully dispersed through the substrate, is considered the most effective one compared to intercalated or conventional types (Gilman et al. 2000, Kashiwagi et al. 2004). In general, the flame retarding mechanism of the LS nanocomposites involves the formation of high-performance carbonaceous-silicate char during burning, which insulates the underlying material and slows the mass loss rate of decomposition products (Gilman et al. 2000). Additionally, the layered structure increases the tortuosity pathway, thereby delaying the diffusion of the volatile products (Deka et al. 2014).



In the wood industry, the LSs are not so popular as they are in polymer manufacturing. However, their application, along with other mineral based FRs, can be increased because they are good candidates for replacing the traditional FRs. Several interesting research papers have demonstrated a positive effect of the LSs on the flameproof property of wood and wooden products. According to Fu et al. (2017), wood impregnated with nano clay resulted in an improved flame retardancy compared to pure wood. The formed unique wood/clay nanostructure dramatically increased thermal stability because of thermal insulation, oxygen depletion and catalytic charring effects. Often nano additives, including the LSs, are used as reinforcing agents for conventional FR action ( Hassan et al. 2008, Chuang et al. 2011). Several research works described the positive influence of the LSs on wood plastic composites (WPC). Guo et al. (2007a) demonstrated that the use of a small amount of modified Cloisite 20A, 0.1–0.5 wt%, can significantly improve the flame retarding properties of high-density polyethylene (HDPE) composites containing wood fibre (WF). Exfoliated nanocomposites demonstrated better flame retarding properties than intercalated or conventional ones did. As the clay content increased, the flame retarding properties were enhanced (Guo et al. 2007a). The same authors in another paper showed that nano clay, 5 wt%, improved charring and thereby reduced the burning and prevented the fire from spreading in WPC (Guo et al. 2007b). The influence of the degree of nanoparticles dispersion on the WF/HDPE nanocomposite properties, including flameproof, was studied by Lee et al. (2010). Their research has shown that the LSs, 1–5 wt%, improved the flame retardancy of the composite compared to an unfilled one, and maximum protection was achieved at 5 wt% LS loadings. It was also shown that exfoliated type of the composite had better performance than the intercalated one; the burning rate of the exfoliated sample decreased by 27% whereas intercalated ones by 16% over the base material (Lee et al. 2010). Several other research works demonstrated that the LSs positively influenced the thermal and flameproof parameters of natural fibres composites by decreasing a coefficient of thermal expansion ( Zhong et al. 2007, Meng et al. 2011), increasing thermal decomposition temperature (Kumar and Singh 2007, Lee and Kim 2008, Meng et al. 2011), decreasing the burning rate and extending the ignition time, as well as decreasing smoke production (Kord, 2012).

#### *Nano / metal oxides*

Another important group of nano-fillers that can be applied as FRs is nano oxides. Interest in using the na-

no-oxides, such as  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZnO}$ , is growing because they are cheap, easily available, non-toxic, and thermally stable. Miyafuji and Saka (1997) used the sol-gel technique for the modification of wood with  $\text{TiO}_2$  nanoparticles to improve mechanical and flame retardancy properties. They reported that the thermal and dimensional stability of wood/ $\text{TiO}_2$  hybrid were enhanced. Sol-gel treatment of wood with silica resulted in an increased degradation temperature (Mahltig et al. 2008). It was assumed that  $\text{TiO}_2$  and  $\text{SiO}_2$  gels act as chemicals that melt at enhanced temperature and coat the wood cell wall components with a layer, preventing flammable gases from escaping as well as contact with oxygen. Also, a combination of  $\text{SiO}_2$ - $\text{B}_2\text{O}_3$  resulted in improved thermostability, but the combination of  $\text{SiO}_2$ - $\text{P}_2\text{O}_5$  leads to decreased fire-resistance properties. The incorporation of  $\text{SiO}_2$ , 0.1% aqueous solution, did not improve reaction-to-fire of pine and birch wood samples (Jaskolowski et al. 2013). Bueno et al. (2014) studied the influence of  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  nanoparticles on the fire behaviour of pine veneers. The samples were immersed into a 3 wt% aqueous solution of each type of nano oxide for 30 seconds. Testing of samples on thermal and fire properties changes showed that all three oxides resulted in improved fireproof characteristics, where  $\text{SiO}_2$  had a stronger impact.

Silica,  $\text{SiO}_2$ , was found to improve the action of ammonium polyphosphate (APP) in WPC. Cone calorimeter and LOI test results are displayed in Table 5. During sample burning, silica particles tended to accumulate on top of the sample and form a charred layer by combining with APP. It was also detected that silica prevented cracking of the sample surface (Zhang et al. 2012). Habibzade et al. (2016) used pressure impregnation of poplar wood with nanosized  $\text{ZnO}$  particles, 0.5–1.5%, which were previously dispersed in the polymer in order to prevent particle agglomeration during the impregnation process. Ignition time for the untreated and  $\text{ZnO}$ -treated samples increased from 15 s to 20 s, respectively. However, glowing time and the carbonized area increased significantly in the nanocomposites. This was because of the flammable nature of styrene, one of the components of polymer, which was used for the nanoparticle dispersion. The treated samples showed better mechanical performance, tensile, flexural and compression properties, as well as better dimensional stability. Nanosized wollastonite ( $\text{CaSiO}_3$ ) was found to be an effective FR for wood (Poshtiri et al. 2014) because it acts as an impenetrable physical barrier, preventing the spread of flames into the wooden structure. Nanosized wollastonite is also effective for medium-density fiberboard (MDF) fire pro-

**Table 5.** Effect of silica 10 phr on cone calorimeter and LOI results of wood fibre (WF)/polypropylene (PP)/APP composite (Zhang et al. 2012)

Sample/parameter	IT (s)	pHRR (kW/m <sup>2</sup> )	Average HRR (kW/m <sup>2</sup> )	MLR (g/s)	LOI
PP/WF	12	701	301	0.175	21.4
PP/WF/APP(30)	18	505	199	0.124	27.4
PP/WF/APP(20)/silica(10)	32	428	156	0.11	28.9

tection (Taghiyari et al. 2013) and especially, the surface treatment was more effective compared to the resin modification with wollastonite nanoparticles.

#### *Carbon-based agents*

The multifunctionality of carbon-based (C-based) nanomaterials, which is characterized by electronic, thermal, optical, and unique mechanical properties for some types of C-based nanoparticles, have attracted interest in many applications, including nanocomposites manufacturing. In terms of flame retardancy, most research works are focused on several types of C allotropes: carbon nanotubes, graphite/expandable graphite, carbon black and graphene. Graphene was the last C-based nanomaterial to be discovered/synthesized at the beginning of the current century (Novoselov et al. 2004). The increasing interest in utilizing graphene in different fields is due to its unique properties, including its high strength/density ratio, high thermal stability, and reactivity, among others and for example, its derivatives have been to be potential agents in the flame retardancy of plastics (Dittrich et al. 2013). Dittrich et al. (2013) compared the flammability and thermal stability of PP nanocomposite filled with different types of carbon-based nanomaterial, carbon black (CB), multiwall nanotubes (MWNT), expanded graphite (EG) and graphene, 5 wt% for each. The decomposition temperature of nanocomposites filled with uniformly dispersed particles, CB, MWNT, and graphene, increased by 25–30 degrees, whereas EG, being poorly dispersed, did not show any influence on the thermal stability of the nanocomposite. Graphene showed the highest efficiency in reaction-to-fire, reducing pHRR by up to 74%. The mechanism action of graphene can be attributed to the formation of a network in a matrix and a dense continuous char layer during thermal decomposition, which will play the role of a barrier for heat and mass transfer between condensed and gas phases. The layered structure of graphene can additionally decrease a permeability of the material due to tortuosity of the pathway, similarly to nano clay. Related to wooden materials, there are interesting results concerning wood impregnation with graphene nanoparticles (GNP) (Goodman et al. 2018). It was stated that the vacuum method for impregnation was able to pull the GNP into the whole 29 mm length and 6 mm thickness of a wood piece. The fixation of graphene nanoparticles to wood cells was stable due to the affinity of aromatic rings of graphene and cellulose through  $\pi$ - $\pi$  stacking. Scan electron microscopy showed that nanoparticles deposited on the wood vessel sidewalls. Irreversible

adsorption of GNP was confirmed by multiple regenerations of the spent wooden filter.

Graphite, mostly expandable graphite, is often used as an intumescence. Seo et al. (2016) studied the influence of different types of graphite, viz. natural graphite (NG), expandable graphite (EG) and exfoliated graphite nanoparticles (xGnP) and CNT, incorporated into MDF protective coating and the results are shown in Table 6. According to the study of Seo et al. (2016), EG or xGnP containing coatings exhibited the most effective protection. Endothermic reactions inside EG pores resulted in the lowest values of pHRR; however, the stability of the protective layer formed by xGnP was better than that formed by EG/MDF. The lowest mass loss rate for EG/MDF was attributed to the fact that EG treated with acid has a high surface area and lacks a high negative surface charge, the factors responsible for the good heat capacity of EG. The total heat release was the lowest for EG/MDF, showing unique thermal stability of EG, whereas NG-loaded samples displayed similar THR to the reference, i.e. the sample without coating. The low degree of dispersion of NG in the coating resulted in the rapid removal of this coating during burning. The EG/MDF composite also had the lowest smoke production rate (SPR) among the studied samples.

Grexa et al. (2003) compared the fire retardancy actions of intumescent expandable graphite and ammonium polyphosphate (APP) for the protection of wood particleboard. Fire retardants in amounts from 5 wt% to 25 wt% were mixed with the glue or, at high concentrations, wood particles were also treated, and results showed that EG with an intumescent effect were effective. The first pHRR was significantly reduced and the second peak was almost eliminated, even at low EG concentrations. Thus, at 5 wt% the first pHRR of EG containing particleboard was reduced from 87 kW/m<sup>2</sup> to 44 kW/m<sup>2</sup> for untreated and EG-treated particleboard, respectively. At 25 wt% of EG loading, the pHRR was reduced to 27 kW/m<sup>2</sup>. Scharrel et al. (2003) have compared the efficiency of an APP-based commercial FR and expandable graphite for flux/PP composite protection. Both FRs significantly improved the composite fire performance, but the best result was achieved with EG. The incorporation of EG resulted in reduced pHRR up to 73%, but an expansion of the sample during burning caused sample cracking, thereby destroying the thermal barrier and flame-retardant effect. The combination of EG with red phosphorus (RP) or APP prevented cracking of the residue due to its crosslinking. Yu et al. (2017) showed

**Table 6.** Cone calorimetry parameters of carbon-based fire retardant (10 wt%) coatings (Seo et al. 2016)

Sample/parameter	pHRR (kW/m <sup>2</sup> )	tpHRR (s)	MLR (%)	THR (KW/m <sup>2</sup> ) at 300 s
Reference	213.97	75	77.23	24.48
CNT/MDF	143.28	65	34.00	~ 17.99
xGnP/MDF	122.89	100	33.61	17.99
NG/MDF	128.09	65	29.25	~ 24
EG/MDF	77.95	30	7.97	~ 10

a synergistic effect of APP and EG in wood flour/PP/carbon black composite. Yin et al. (2019) reported that both EG- and APP-based FR in WPC formed expanded porous layers during heating, resulting in a significant decrease of pHRR and increased residue. Residue formation was due to the action of sulphuric acid (in EG) and phosphoric acid, which reacts with the hydroxyl group of wood components (Yin et al. 2019).

The use of carbon nanotubes in composites has received wide attention due to their extraordinary physical and mechanical properties. In addition, their high aspect ratio, length-to-diameter ratio, and large surface area make them very suitable for reinforcement purposes in composites manufacturing. In the field of fire retardancy, adding CNT to a polymeric matrix leads to decreased flammability in terms of changes in the pHRR and MLR. Thus, loading only 0.2 wt% of single walled carbon nanotube (SWCNT) in a blend of poly(methyl methacrylate) PMMA resulted in a decrease of pHRR by 25% (Kashiwagi et al. 2005). The main mechanism action for CNT is attributed to the formation of a continuous protective layer consisting of a network of nanoparticles, and the layer appears to act as a heat shield and a barrier for flammable gases escaping to the flame as well as oxygen penetration inside the burning sample (Morgan and Wilkie 2007). Obviously, the continuous network is formed in the case of the presence of an optimal number of nanoparticles and their homogeneous dispersion in the matrix (Kashiwagi et al. 2005, Bourbigot and Duquesne 2007). When the dispersion of nanoparticles is good enough, they form networks during burning instead of their localized accumulations. The effect of the degree of dispersion of CNTs on the fire performance of wood flour/PP nanocomposite was studied by Fu et al. (2010). It was shown that the incorporation of hydroxylated CNT, CNT-OH, resulted in better dispersion and a stronger effect on the reaction-to-fire parameters (Table 7). The degree of dispersion is usually monitored by optical techniques, i.e. TEM and SEM, and X-ray diffraction spectroscopy. Yet, due to the direct relationship between heat release rate and a storage modulus, the viscoelastic parameter of the matrix can be measured at a stage of composite manufacturing (Morgan and Wilkie 2007).

A synergistic effect between CNTs and layered silicates was confirmed in several research works (Peeterbroeck et al. 2004, Gao et al. 2005, Ma et al. 2007). The study of Peeterbroeck et al. (2004) found that nanofillers showed thermo-oxidation barrier properties, but their combination

had a better effect. Similar results were observed by Gao et al. (2005). Flame retardancy was attributed to reinforced char residue, which was much less cracked than in the case of binary systems. A combination of CNTs and nano clay resulted in the promotion of graphitization of the char structure, giving better protection from oxidation at high temperatures. Yet, CNTs act as a sealing agent connecting clay layers, thereby reducing cracks in chars. It was shown that CNTs have a reinforcing effect in the case of conventional FR use. Also, it was demonstrated that CNTs had a synergistic effect when combined with the intumescent FR system. Interesting results published by Huang et al. (2014) in the study of PP nanocomposite flammability, where standard intumescent flame retardant (IFR) (MPP, a dehydration catalyst and blowing agent) and pentaerythritol, char former), CNTs and graphene oxide (GO) solely or in combination, which were used as flame retardants. It was shown that the PP filled with 18 wt% IFR, 1 wt% CNTs and 1 wt% GO achieved the LOI value of 31.4% and, the pHRR was reduced by about 83%, and the time of ignition was delayed by 40 s compared to neat PP. The flame retardancy mechanism was attributed to a barrier action of the intumescence layer, which was reinforced with CNTs and graphene nanosheets. In fact, IFR exhibits a good flame protective effect, but its stability at high temperatures needs to be improved.

## Conclusions

As is generally accepted, wood is sensitive to fire and for its wider application in the construction industry, more effective and environmentally friendly methods for their flame retardancy treatment are needed. Despite knowledge about the toxicity of halogenated FRs and the fact that they are banned from use in the developed countries, the consumption of halogenated FRs remains high (Flamere-tardants-Online 2019). In this regard, introducing novel flame-retarding methods, e.g. described by Geoffroy et al. (2019), and materials, which are at least equal to halogenated FRs in their cost/performance ratio, are of great interest to scientists, manufacturers and consumers. Nanotechnology is being rapidly developed and nowadays life without products made using different nanomaterials is difficult to imagine. Nanosized materials are a promising alternative or addition to conventional flame retardants. Nevertheless, relatively few applications of nanomaterials in the flame protection field are really in use commercially, and this is a subject that requires more study in the near future. It is also felt that nanomaterials and nanotechnology can provide significant progress in flame retardancy. The achievements in nanotechnology are also of great interest in the field of flame retardancy. As a rule, novel technologies are more focused on the environmental aspects that enhance the sustainability of the end-products, along with the improved fire safety of consumers. Currently, FR nanomaterials are mostly applied in plastic manufacturing and efforts to ex-

**Table 7.** Cone calorimeter data of wood fibre WF/PP nanocomposite; heat flux 35 kW/m<sup>2</sup> (Fu et al. 2010)

Sample/Parameter	IT (s)	pHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )
WF/PP	26	383	77
WF/PP	25	375	75
WF/PP/CNT (1%)	23	318	65
WF/PP/CNT-OH (1%)	23	285	56



pand nanomaterial application to wooden materials are reflected in the increasing number of publications in this field during the last decade.

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