

REVIEW PAPER

A Review of Fire Retardant Processes and Chemistry, with Discussion of the Case of Wood-plastic Composites

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Abstract

Wood-plastic composites (WPC) are a relatively new group of materials covering a wide range of applications. Strict safety and quality standards in many industries impose a significant number of technical requirements on wood-plastic composites. One of the main factors limiting the use of WPC in some industrial fields is flammability. This paper presents the main features of the fire retardancy of wood-plastic composites and current approaches to decreasing the combustibility of such composite materials.

Key words: wood-plastic composites, fire resistance, flammability, fire retardancy, retardants

Introduction

Wood-plastic composites (WPC) are a new class of materials that merge the best features of wood and plastic (Li and He 2004, Stark et al. 2010, Najafi et al. 2006). The combination of the favourable properties of wood and plastic provides WPCs with unique advantages. For example, they can be produced in a variety of shapes, colours and sizes (Taylor et al. 2009, Malvar et al. 2001). The addition of cellulose materials to a polymer enhances the strength and stiffness properties of the resultant material (Garcia et al. 2009, Manikandan et al. 2001, Le Bras et al. 2005). Other main benefits of WPCs are resistance against insects and fungi, high moisture resistance, dimensional stability, resistance to decay, and low maintenance costs (Garcia et al. 2009, Anon_a 2002, Kozłowskiy and Władyka-Przybylak 2002). Low cost and considerable weight preservation of material components are advantages of WPCs that make them a viable alternative to glass and carbon fibres. Wood fibre materials are less flexible and are much harder than plastic material, hence the combination of wood fibre and plastic provides a resultant composite with a quite hard strength-to-mass ratio (Kozłowskiy and Władyka-Przybylak 2002, Stark et al. 2009).

Good reaction-to-fire properties are necessary for many possible applications of WPCs. These proper-

ties are important especially for applications in the residential construction (mostly for decking, siding, roof tiles and window frames), transportation and furniture industries. For many applications in these fields, the fire performance of the material has to be known, and in some cases improved (Stark et al. 2010, Kozłowskiy and Władyka-Przybylak 2002, Roth et al. 2007, Stark et al. 2009). Enhancement of the flame resistance properties of WPCs has become a very important area of study in responding to safety requirements (Sain et al. 2004).

Despite the fact that there is significant information in the literature concerning the fire retardancy of wood and plastics separately, the fire performance of wood-plastic composites is poorly studied and understood.

The primary goal of this article is to report fire retardant processes and chemistry with discussion of the case of wood-plastic composites and approaches used to reduce the combustibility of wood-plastic composite materials.

Fire retardant methods and theories of fire retardancy

Fire retardant methods

There are two possible actions for a fire retardant: 1. *Chemical action*. This method is in general targeted at interfering with free radical reactions which

take place during burning (gas phase) and aims to protect internal materials from heating during char creation (solid phase).

2. *Physical action.* This method is based on decreasing the temperature by endothermic reactions, reducing the fire distribution by fluxing oxygen with non-combustible gases, and promoting the formation of a protective impenetrable surface layer (Sain et al. 2004, Troitzsch 1998, Bryson and Craft 2009, Moon et al. 2009, Lu and Hamerton 2002, Hull and Kandola 2009).

Theories of fire retardancy

Approaches to enhancing fire retardancy are based on a number of theories proposed to describe the mechanism of fire retardants.

1. *Barrier theories.* These theories posit the formation of a glassy layer which impedes the liberation of volatile gases, preventing oxygen from reaching the substrate and protecting the material surface from the influence of elevated temperatures (Levan 1984, Sweet 1993, Bryson and Craft 2009, Wang et al. 2004, Hakkarainen et al. 2005). Barrier effects have been noticed as a result of the dispersion in plastic of nanoclay which prevents the diffusion of oxygen and decomposition products (Haurie et al. 2007, Nazare et al. 2006). There are two possible mechanisms for char formation: redirection of the chemical reactions involved in decomposition in favor of reactions yielding carbon rather than CO and CO₂, and formation of a protective char surface layer (Moon and Farris 2009, Lu and Hamerton 2002). A fire retardant can work by means of a mechanism known as intumescence. Intumescent systems swell when subjected to heat or fire and create porous carbonaceous foam, which operates as a barrier and protects from air, heat and pyrolysis products (Levan 1984, Sweet 1993, Moon and Farris 2009, Lu and Hamerton 2002, Zhang and Horrocks 2003, Shen and Schilling 2004, Wang et al. 2008, Chapple and Anandjiwala 2009). Intumescent systems typically consist of three components, that is, a carbonisation agent, an acidic source and a blowing agent. The carbonisation agent is usually a char-creating organic compound (Almeras et al. 2003). Enhancing of fire retardancy of composite materials can be reached by use of fire retardants additives which work by mechanism of char creation, such as zinc borate, ammonium polyphosphate, boric acid and phosphorous compounds (Kozłowski, R. and Władyska-Przybylak, M. 2002, Garcia et al. 2009, Stark et al. 2010, Stark et al. 2009, Suppakarn and Jarukumjorn 2009, Shen et al. 2008).

2. *Thermal theories.* Retardant additives enhance the thermal conductivity of the organic material, which leads to an even distribution of energy in the fuel volume, which in turn prevents ignition of the materi-

al surface. Moreover, the retardants can adsorb energy, since an endothermic reaction is triggered during their thermal decomposition. Aluminium trihydroxide (ATH) and magnesium dihydroxide (MDH) are examples of fire retardancy approaches based on thermal theories (Levan 1984, Sweet 1993, Hakkarainen et al. 2005, Garcia et al. 2009, Klyosov 2007).

3. *Theory of evolving of noncombustible gases.* In this case, the mechanism works in the vapor phase. The retardant additives decompose and emit nonflammable gases that are mixed with the products of fuel pyrolysis and form a noncombustible mixture of gases. Moreover, the emitted noncombustible gases displace or dilute the air available for oxidative pyrolysis reactions. (Levan 1984, Hakkarainen et al. 2005).

4. *Free radical theories.* Fire retardant additives, for example, halogenated compounds, operate in the vapour phase as inhibitors by interrupting the chain propagation mechanism of flames by releasing free radicals (Sain et al. 2004, Bourbigot and Duquesne 2007). In case of WPCs, antimony trioxide is mostly used as a component of synergetic composition to enhance the efficiency of halogen-containing flame retardants by a stepwise release of radicals that in turn inhibit the vapor-phase exothermic oxidative chain reaction of the flame spread (Garcia et al. 2009, Klyosov 2007).

5. *Theories of simultaneous char increasing and volatile reduction.* These theories are based on the use of fire-retardant chemicals to reduce the temperature required for pyrolysis, the result of which is the production of more char and fewer volatile gases (Levan 1984).

6. *Theories of decreased heat content of combustible volatiles.* Reduction of the heat content takes place when the number of volatiles is decreased and the amount of char is increased. Consequently, the phenomena described in theories 5 and 6 occur at the same time, leading to the creation of more char, and fewer volatiles, as well as lower heat content of combustible volatiles (Levan 1984).

Most fire retardant chemicals generally act via several of the above mechanisms. A synergetic phenomenon emerges when a system of several chemicals is used. The synergy effect is observed when two or more chemicals (also known as miscellaneous) are combined together and the retardancy effect of this mixture is greater than the sum of the individual effects of the separate chemicals. Examples of the most commonly used synergistic systems are the combination of aluminium or magnesium hydroxides with zinc borate, and the combination of ammonium polyphosphate with nanoclays (Levan 1984, Jang et al. 2000, Haurie et al. 2007, Demir et al. 2005).

Fire retardancy of wood

Wood is a natural, renewable material with a complicated structure. Cellulose, hemicelluloses and lignin are the main polymeric components of wood. It is known that hemicelluloses and cellulose contribute to the flammability of wood; with hemicelluloses in particular playing a major role because of their low heat stability. While cellulose and hemicelluloses enhance the flammability of wood, lignin, which is the other polymer included in wood, promotes the fire resistance of wood by charring (Kozłowski and Władysław-Przybylak 2002, Roth et al. 2007, Li et al. 2001, Saheb and Jog 1999). Hemicelluloses decompose at 225–325° C and cellulose at 325–375° C, whereas lignin decomposes over the temperature range of 250–500° C (Di Blasi 2008).

Commonly used lignocellulosic material for wood-plastic composites is wood flour, which can be obtained from industrial residues such as sawdust, planer shavings and wood chips. Wood flour possesses a low length-to-diameter ratio compared with wood fiber, another material used in WPCs. Other lignocellulosic materials used in WPCs are agricultural fibres (such as flax, jute, kenaf, and hemp) and agricultural residues (such as corn stalks, rice hulls, and coconut coir) (White et al. 2011).

Wood as a component containing hydrocarbons burns indirectly as combustion takes place between oxygen and the gases liberated from the material. When wood is exposed to heat, it generates volatile components, which in turn react with oxygen energetically. This leads to the propensity of wood materials to ignition and burning (Hakkarainen et al. 2005).

The ignition and combustion of wood materials are based on the pyrolysis process of cellulose and on interactions between the products of the thermal decomposition of the wood and the surrounding gases (Sweet 1993, Hakkarainen et al. 2005). Depending on the presence or absence of oxygen, the process of the pyrolysis is divided into oxidative pyrolysis and anaerobic pyrolysis, correspondingly (ISO 19706:2007). Various parameters affect the pyrolysis rate, mainly temperature, pressure and heating rate (Di Blasi 2008). Depending on the conditions, the pyrolysis can flow according to two different pathways. The first is a low temperature pathway (temperature below 300° C) in which non-combustible gases (such as H₂O and CO₂) are liberated and char formation promoted. The second is a high temperature pathway (temperature above 300° C) in which tar and combustible gases are created. It should be noted that much tar is created during normal burning of wood, including levoglucosan, and the tar then decomposes into flammable gases under the action of heat (Sweet 1993, Roth et al. 2007, Hakkarainen et al. 2005, Huang and Pan 1975).

Wood possesses some initial or natural fire resistance because of its low thermal conductivity and ability to char formation. The initial fire retardancy of wood varies, depending on the type of tree from which the wood was obtained. For example, it is known that the density, permeability, morphology, moisture content and chemical composition of wood may affect its fire resistance properties (Kozłowski and Władysław-Przybylak 2002, White and Dietsberger 2007, Chapple and Anandjiwala 2009). Wood with a high density has excellent resistance to fire (Giudice and Pereyra 2010, Subyakto et al. 1998). It has also been reported that the fire resistance of wood may have differences within one species. Japanese researchers have found that summer and spring wood has differences in thermal properties. For instance, their results show that the thermal conductivity of summer wood is tenfold that of spring wood. The difference in thermal conductivity determines the differences in the behaviour of the wood during heat exposure. Samples with lower thermal conductivity have better thermo-barrier properties (Hakkarainen et al. 2005). As regards the effect of lignin content on the initial fire resistance, it has been reported that the strong bonds of aromatic rings are thermally destructible only under elevated temperatures, and that the aromatic rings of lignin give good oxidation resistance and correspond to the char layer forming. Thus, wood-plastic composites containing softwood have better thermo-barrier properties than containing hardwood (Kozłowski and Władysław-Przybylak 2002, De Chirico et al. 2003). Also, it has been noticed that fire resistance of wood-plastic composites with and without addition of fire retardant can be considerably improved by enhancement of amount of wood flour (Ayrilmis et al. 2011).

A number of theories describe the mechanisms of wood fire retardancy.

1. *Reduction of the flow of heat which promotes further combustion.* This theory states that fire retardant additive may operate by creating a glassy protective skin or foam, which in turn works as an isolator. An example of this approach is an intumescent coating of the wood surface (Sweet 1993). Intumescent flame retardant coating (IFRC) is an effective and low cost method to protect a material from fire. A typical composition of the IFRC is a carbon agent, an acid source and a blowing agent. During exposure to the heat source the IFRCs swell and their volume is increased 50-200 fold, creating a protective char layer on the material surface (Chou et al. 2009, Władysław-Przybylak and Kozłowski 1999). Some of the additives can enhance the thermal conductivity of the wood to a level at which the adsorbed heat energy is removed and uniformly distributed in the wood volume, which

decreases the ignition potential. Another branch of this theory is that during thermal decomposition some flame retardant additives adsorb a lot of heat energy and support the endothermic reaction of the destruction of the retardant additives (Sweet 1993).

2. *Extinguishment of the flame.* The flame extinguishing theory states that flame retardant additives evolve radicals at elevated temperatures which trap the hydrogen and hydroxyl radicals of the vapour phase and thus inhibit the flaming combustion (Sweet 1993).

3. *Changes to the thermal degradation process.* The mechanism of thermal degradation proposes that the thermal degradation of wood may be changed by the creation of a physical barrier. This barrier covers the wood surface, prevents contacts with the oxygen of the surrounding atmosphere and blocks the evolution of combustible volatile gases from the wood. The mechanism of thermal degradation may be changed by different approaches. Fire retardant additives may reduce the pyrolytic temperatures, directing the combustion process to a low temperature pathway, which in turn enhances char formation and reduces the amount of volatile gases. The decreased amount of flammable volatile gases leads to a reduction of the effective heat of the material, which in turn leads to reduced fire propagation (Sweet 1993).

The chemicals providing the fire-retardant phenomena listed above include phosphates, some nitrogen compounds, some borates, silicates and amino-resins (Levan 1984, Levan and Winandy 1990). All these chemicals are known to increase the fire resistance properties of wood; they however have some unfavourable features. For example, it has been observed that the addition of fire retardants leads to decreased strength properties of wood (Levan and Winandy 1990). Moreover, introducing fire retardant additives affects the durability, machinability, toxicity, gluability and paintability of wood (Levan 1984). Fire retardants can be introduced into wood in two ways: impregnation of an additive into the wood; and by surface treatment (Levan 1984, Hakkarainen et al. 2005).

Fire retardancy of plastics

Depending on their thermal behaviour, plastics are divided into two groups; thermosets (aminiresins, phenolic resins, epoxy resins, etc.) and thermoplastics (polyolefins, styrenics, polyamides, etc.). Thermoplastics are subjected to deformation at temperatures which are not enough to produce chemical decomposition, and they commonly include long non cross-linked chains. Thermosets, however, undergo chemical changes at elevated temperatures that lead to non melting products with strong cross-linked chains (Horrocks and Price 2006). The cross-linked structure of

thermosets makes them more thermostable. This factor determines the principle difference in the approaches used to improve the fire retardancy of thermoplastics and thermosets. Thermosets usually require the application of fire retardants with more elevated operating temperatures than thermoplastics (Troitzsch 2004, Weil et al. 2006). Furthermore, the production features of thermosets are very suitable for flame retardation using a reactive strategy (Horrocks and Price 2006, Josepha and Tretsiakova-Mcnally 2011).

Polyethylene (high and low density), polypropylene and polyvinylchloride are the plastics generally used for the production of wood-plastic composites (Najafi et al. 2006, Chapple and Anandjiwala 2009). The most commonly used plastic is polypropylene (PP), which has applications in many fields, for example, buildings, wire, cars, electric and electronic industry and many others. Since PP is a strongly flammable material, improvement of flame retardancy is required in many cases (Lv et al. 2005). The ways in which fire retardants are applied for plastics and wood-plastic composites differ greatly from the ways for wood. Wood is usually saturated with solutions of fire retardants, but the fire retardants for plastics and WPCs are introduced in solid form straight into the material (Klyosov 2007, Ayrlmis et al. 2011).

There are several ways to achieve flame retardancy in polypropylene:

1. Creation of a carbonaceous char by means of modification of the pyrolysis reactions. This char obstructs the transfer of the heat and therefore decreases the formation of volatiles, thus preventing subsequent oxidation.

2. Addition of reagents which form a char barrier, mainly additives with an intumescent property.

3. Prevention of the formation of initiating radicals in the flame and preflame areas.

4. Addition of hydrated inorganic additives which decay endothermically with water liberation and therefore adsorb the heat from the surface of the material and attenuate the combustible volatiles.

5. Modification of the polymer chemical structure in order to modify its decomposition process or improve its compatibility with other fire retardants (Zhang and Horrocks 2003, Jang and Lee 2001).

The fire retardancy of polymers can be achieved by two different strategies: an "additive" approach and a "reactive" approach. Fire retardants of additive type are widely used and are introduced into polymeric material through physical forces such as van der Waals interactions. This method is the most economical and rapid way to improve the fire retardancy of polymers. However, drawbacks such as a decrease of mechanical properties, leaching and weak compatibility reduce the

attractiveness of the additive approach. Fire retardants of reactive type are introduced into polymeric material by chemical reaction through covalent bonding and can be used for the creation of a new fire retardant polymer or for the adaptation of an existing polymer by means of copolymerisation with a fire retarding component either in the chain or as a pendent group (Lu and Hamerton 2002, Troitzsch 2004).

In addition to satisfying obligatory fire requirements and regulations, an efficient fire retardant has to have the following features:

- It must have thermal stability at the usual polymer processing temperature (for polypropylene this temperature is 260°C).
- The retardant should have compatibility with the polymer and no leaching should occur.
- The additive has to conserve its fire retardant properties when exposed to fire action.
- The retardant has to decrease the creation of toxic gases and smoke during combustion.
- The amount of required additive to achieve flame retardancy should be at a low level (usually not more than 10% w/w) to reduce costs and its effect on the mechanical properties of the material.
- The retardant has to be easy to introduce into the polymer mass.
- The retardant has to be easily removed from the polymer during recycling.
- The additive must have no harmful environmental properties nor be harmful to health.
- The additive should be commercially available and cost efficient.
- The retardant must not provoke corrosion. (Moon et al. 2009, Zhang and Horrocks 2003, Anon^c 2009)

Examples of commonly used flame retardants in different plastics are presented in Table 1.

Fire retardancy of wood-plastic composites

It has been noted that addition of lignocellulosic fibres to polypropylene (PP) reduces the heat release rate peak essentially. Characteristics such as heat released in combustion and mass loss rate are also reduced. However, criteria such as time to ignition and production of smoke deteriorate in comparison with pure polypropylene (Borysiak et al. 2006). The flammability of WPCs depends on several factors: type of raw material, structure, density, thermal conductivity, humidity, and the nature of composite (Kozłowskiy and Władka-Przybylak 2002, Chapple and Anandjiwala 2009).

Fire retardants can be introduced into composites by two methods:

1. Mass treatment: The addition of fire retardants to the mass during the production process
2. Surface protection: The addition of fire retard-

Table 1. Typical fire retardants used depending on plastics' application (Innes and Innes 2004, Dufton 2003, Döring et al. 2010, Troitzsch 2004)

Fire retardant application	Product examples	Polymer	Fire retardant additive
Electrical/electronics	Components/parts in appliances (ovens, refrigerators, dishwashers) office/home automation products (computer monitors, keyboards, telephones) wire/cable products (telephone and computer communication cable, electric cable)	Polyvinyl chloride, ethylene-propylene rubber (EPR), polyethylenes, unsaturated polyesters, polyamides (PA), elastomers, thermoplastic elastomers (TPE), polypropylene (PP), ethylene-vinyl acetate copolymers	Aluminium tri-hydroxide (ATH), magnesium di-hydroxide (MDH), zinc borate as synergistic agents with ATH and MDH, phosphorus flame retardants, phosphate esters, intumescent products based on ammonium polyphosphates (APP), antimony trioxide, melamine phosphate red phosphorus
Building/construction	Roofing, pipe and conduit, decking, structural products, carpet backing, other products like blown film and extruded shapes for window applications, wall coverings	Polyvinyl chloride, ethylene-propylene rubber (EPR), polyethylenes, unsaturated polyesters, acrylics, epoxy resins, phenolics	Aluminium tri-hydroxide (ATH), magnesium di-hydroxide (MDH), antimony oxides, zinc borate
Transportation	Automotive components under-the-bonnet and passenger compartment, mass transit air ducts and seating, marine floor coverings and furniture, aviation seating, toilet components, and waste containers	Polyvinyl chloride, polyolefins, epoxy resins, phenolic resins, urethane elastomers, polyamide	Aluminium tri-hydroxide (ATH), magnesium di-hydroxide (MDH), zinc borate, ammonium polyphosphate (APP), melamine borate, phosphate esters
Furnishings	Public institution furniture like plastic stacking chairs, thermoset laminates for countertops, walls and floors	Polypropylene, polyvinyl chloride (PVC), polyesters	Antimony oxide, hindered amines, aluminium tri-hydroxide (ATH), melamine
Fibre/textiles	Draperies, carpets, heavy duty apparel, automotive interior fabrics	Polyester, polyamide, polypropelene	Aluminium-tri-hydroxide (ATH), aluminium phosphinate, melamine, ammonium sulphate, zinc borate

ants onto the surface of the composite in the final stage of production (Kozłowskiy and Władka-Przybylak 2002, Bourbigot and Duquesne 2007).

The flame retardancy of WPCs can be enhanced by several methods:

1. Insertion of lignocellulosic natural fibers together with flame retardants before the production process by impregnation in an autoclave.
2. Addition of fire retardants in liquid or solid form during the production of the composites.
3. Use of nonflammable polymers and resins.
4. Addition of nanoparticles to the composites.
5. Insulation of the composites to prevent penetration of heat flux (intumescent coatings and fire barriers). (Kozłowskiy and Władka-Przybylak 2002, Hakkarainen et al. 2005)

The above methods can be used together or separately. The current ecological situation dictates the new tendency of use halogen-free fire retardants. Nowadays, halogen containing fire retardants are replacing by intumescent fire retardants because the last one have low smoke production, high resistance to corrodibility and low generation of toxic gases (Ayrilm-

is et al. 2011). Commonly used fire retardant compounds for wood-plastic composites are magnesium hydroxide, boric acid, ammonium phosphates and borates, ammonium sulphate and chloride, zinc chloride and borate, phosphoric acid, dicyanodiamide, sodium borate and antimony oxide. These additives are generally introduced in a powder form and the quantity used is generally within the range 5 to 10% of dry mass. The dimensions of the fire retardant particles affect their effectiveness and the amount added, especially for the fire retardation of polymers (Stark et al. 2010, Kozłowski and Władysław-Przybylak 2002, Sain et al. 2004). Commonly used inert fillers for composite materials are silica, calcium carbonate, talc, glass fiber and other. They improve the fire retardancy and decrease smoke yield by mechanism of fuel dilution in the solid phase (Klyosov 2007, Mouritz and Gibson 2006).

Fire safety regulations usually differ from country to country, and in many cases these differences are essential. Thus, some composites may satisfy the fire safety requirements in one country but not satisfy in other countries (Mouritz and Gibson 2006). The most cited regulatory test and standards are ASTM E 84, which is the main regulatory fire test for interior finish in the U.S., ASTM D7031-11 and ASTM D7032. These standards contain the following standard requirements for WPC fire performance properties:

- Flame spread shall be determined using Test Method E 84.
- Criterion-Materials shall have a flame-spread index no greater than 200 when tested in accordance with Test Method E 84.
- Other test procedures may be permitted for determining a flame-spread rating for the material. Depending upon material formulation, other fire performance tests may be required.
- Other fire performance properties may be determined using Test Methods E 1354 or D 1929, as appropriate. These test methods provide an assessment of one or more of the following properties: smoke release rate, mass loss rate, heat release rate, and ignition temperatures. (ASTM D7031-11 Section 5.13, ASTM D7032 Section 4.9 and Note 5)

Fire retardant chemicals

The mechanisms of chemical reactions, the chemical structure and the range of applications of the major fire retardant chemicals are described in this chapter.

From the chemical point of view, fire retardants are divided into five main classes:

- Inorganic compounds, which are divided into “active” and “passive”. “Active” fire retardants operate by releasing water at elevated temperature and therefore adsorb the heat from the surface of the ma-

terial. “Passive” fire retardants work by removing fuel for flame spread and by charring (“active”: aluminium trihydroxide and magnesium dihydroxide; “passive”: ammonium polyphosphate, zinc borate, antimony trioxide)

- Silicon-containing additives (silicon dioxide, silsesquioxanes, nanoparticles, nanofillers, natural clays)

- Organic phosphorous compounds (phosphate esters such as triphenylphosphate, halogenated phosphorus compounds, ammonium polyphosphate)

- Halogenated organic compounds (brominated, chlorinated compounds and fluorinated compounds)

- Nitrogen based compounds (melamines)

Zinc chloride, expandable graphite, ammonium borates, sulphates and chlorides, boric acid, sodium borate, and dicyanodiamide have also been used as flame retardant additives (Klyosov 2007, Kozłowski and Władysław-Przybylak 2002, Sain et al. 2004, Bryson and Craft 2009, Jang and Lee 2001).

Inorganic compounds

Aluminium trihydroxide $\text{Al}(\text{OH})_3$ (ATH) and magnesium dihydroxide $\text{Mg}(\text{OH})_2$ (MDH) Aluminium trihydroxide and magnesium dihydroxide are widely used as flame retardants. The main feature of these chemicals is that under the effect of heat (when the temperature is raised to 200° C for ATH and to 300° C for MDH) these chemicals are decomposed as the result of an endothermic reaction in which heat energy is consumed (see Formulas 1 and 2). In addition, water is released during dehydration and as a consequence the fuel is diluted. The concentrations of oxygen and flammable gases in the gas phase are reduced, as are the temperatures of the material and gas phase. The oxides of metals derived as a product of decomposition create a nonflammable protective layer on the surface of the material (Garcia et al. 2009, Klyosov 2007, Zhang and Horrocks 2003, Jang and Lee 2001, Haurie et al. 2006, Chen and Wang 2010, Weil et al. 2006, Hollingbery and Hull 2010).

The main difference between aluminium trihydroxide and magnesium dihydroxide in the sense of retardancy is that magnesium dihydroxide can be used at higher processing temperatures than the dehydration temperature of ATH. In addition to the fact that magnesium hydroxide is more thermo-stable than ATH, it has also been reported that magnesium dihydroxide prevents smoke creation (Weil et al. 2006).

Metal hydroxides are interesting from the point of view of flame retardancy because of their low cost, low toxicity and good anticorrosion properties. They have some serious drawbacks, however, such as poor thermal stability, low efficiency (loading up to 50-65%

from the mass of material) and a decrease in the strength properties of the material (Klyosov 2007, Levan 1984, Chen and Wang 2010, Bourbigot and Duquesne 2007).

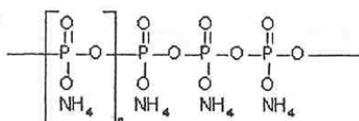
A combination of magnesium dihydroxide and ATH can be used as a synergetic system to increase the protection time or temperature limits (Weil et al. 2006). The question of enhancing the efficiency of metal hydroxide as a fire retardant has been discussed in many publications (Haurie et al. 2006, Chen and Wang 2010, Weil et al. 2006, Hollingbery and Hull 2010). For example, it has been reported that the addition of nanocomposites to the system with metal hydroxide shows a synergetic effect that allows a decrease in the loading of the system with metal hydroxides (Bourbigot and Duquesne 2007).

$2 \text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad \Delta H = 298 \text{ KJ/mol (71.2 kcal/mol)}$ (1)
 $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O} \quad \Delta H = 380 \text{ KJ/mol (90.8 kcal/mol)}$ (2)
 (Sain 2004)

Ammonium polyphosphate (APP)

Ammonium polyphosphate is the ammonium salt of polyphosphoric acid – a water-insoluble, nonmelting solid with high phosphorus content (see Figure 1) (Childs 2003).

Figure 1. Chemical structure of ammonium polyphosphate (Childs 2003)



Under the heating action APP is decomposed to give polyphosphoric acid and ammonia that in turn create an intumescent protection layer which prevents the oxidation of the material and improves the function of charring. It has also been reported that APP reduces smoke production and provides resistance to flame spread (Stark et al. 2010, Stark et al. 2009). It has been suggested that APP can be effectively used as a retardant for polypropylene, wood and cellulose materials, especially in miscellaneous mixtures with nitrogen containing compounds and zeolite (for these combinations synergism has been observed) (Li and He 2004, Demir et al. 2005, Scharitel et al. 2003, Li et al. 2001, Matko et al. 2005).

Antimony trioxide (ATO)

Antimony trioxide is an amphoteric oxide with the chemical formula Sb_2O_3 (Sb_4O_6) (see Figure 2). Antimony trioxide is mostly used as a component of synergetic composition to enhance the efficiency of halogen-containing flame retardants by a stepwise release of radicals that in turn inhibit the vapor-phase exothermic

oxidative chain reaction of the flame spread. ATO is applicable as a retardant additive for plastics, paints, rubbers, papers and many others areas (Garcia et al. 2009, Klyosov 2007, Zhang and Horrocks 2003).

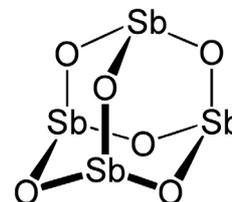


Figure 2. Chemical structure of antimony trioxide (Anon^d)

Zinc borate (ZB)

Zinc borate is an inorganic compound with the chemical formula $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$. It is a white crystalline or amorphous powder, colorless, odorless and insoluble in water (Klyosov 2007, Zhang and Horrocks 2003). The heat decomposition of zinc borate leads to the creation of a glassy protection layer, which acts as a barrier for polymer chain oxidation (Suppakarn and Jarukumjorn 2009, Shen et al. 2008). Zinc borate shows the best synergetic effect in combinations with aluminium and magnesium hydroxides, and good synergism has also been observed in combination with antimony trioxide (Haurie et al. 2007, Chen and Wang 2010, Anon_e 1996, Shen et al. 2008). In addition to fire retardancy properties, borates have other advantages: good smoke suppressant properties, protection from fungi and insects, low cost, environment friendliness, low mammalian toxicity, and low volatility (Baysal et al. 2007, Anon_f 1995, Shen et al. 2008).

Expandable graphite

Expandable graphite (EG) is a porous, sulphuric acid-containing compound that is insoluble in water, and which has been found to be an efficient fire retardant (Schartel et al. 2003, Chen et al. 2010, Shih et al. 2004). When EG is subjected to a high temperature (over 220°C) it expands and creates a protective layer which increases the fire resistance of the graphite containing a polymeric compound (Chen et al. 2010, Shih et al. 2004, Higginbotham et al. 2009). As a result of its porous structure, EG can accumulate volatile liquids and gas (Shih et al. 2004). Moreover, EG has been found to be an efficient smoke suppressant (Schartel et al. 2003). It has been reported that EG can be used in a synergetic system with some non-halogenated compounds, such as APP, phosphorus-containing compounds and zinc borate (Xie and Qu 2001). Furthermore, an intumescent system can be created in combination with APP in the role of the acid source and melamine as the blowing agent (Shih et al. 2004).

Silicon and aluminium oxides

Significant research has been done to study the fire retardancy properties of silicon compounds. It has been shown that silicates can improve the flame retardancy of materials considerably. Silicates as retardants operate by the mechanisms of forming a char layer in the condensed phase and trapping active radicals in the vapour phase (Lu and Hamerton 2002, Zhang and Horrocks 2003, Chen and Wang 2010). As a result of their low surface energy, silicates are usually concentrated on the material surface. The product of heat destruction of silica compounds is silica carbon with high thermal stability, but this residue is structurally very weak and fragile (Li et al. 2005, Hanu et al. 2004). During the combustion process, silica carbon may create a protective barrier which prevents the material from undergoing further heat destruction (Li et al. 2005). Silicone and aluminium oxides based retardants are a large group of chemicals including clay, kaolin, silsesquioxanes, silicon dioxide (SiO_2) and aluminium oxides. The main advantages of silicates are low cost, affinity with the environment, high thermal stability, low non-corrosive smoke evolution, and comparably high dielectric strength (Lu and Hamerton 2002, Zhang and Horrocks 2003, Chen and Wang 2010).

Silsesquioxanes

POSS (preceramic compound) reagents are a huge class of three-dimensional oligomeric organosilicon compounds of the general formula $(\text{RSiO}_{1.5})_n$, where n is an even number and R can be any of a large number of groups (typically methyl, halogen, vinyl or phenyl), see Figure 3 (Lu and Hamerton 2002, Chen and Wang 2010, Bourbigot et al. 2009, Pyun et al. 2010). During the combustion of POSS-containing composites, POSS acts as precursor which forms nonflammable, thermally stable ceramic materials that in turn affect the fire performance (by reducing the quantity of heat release during combustion), and dimensional and thermal stability. The presence of POSS increases the oxygen permeability and glass transition temperature and reduces the heat evolution of polymeric materials (Lu and Hamerton 2002, Chen and Wang 2010).

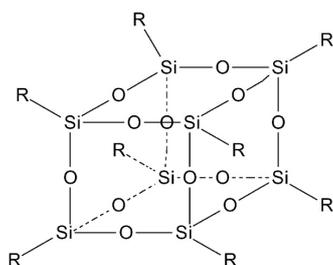


Figure 3. Chemical structure of silsesquioxanes (Lu and Hamerton 2002)

Nanocomposites

Nanocomposites are a new class of flame retardant additives for polymeric composite materials. From the chemical point of view, a nanocomposite is a plastic containing nanoparticles, usually in the range 2-10% (w/w). Nanocomposites used to increase the fire retardancy of polymers include montmorillonite clays, TiO_2 , Sb_2O_3 , aluminosilicates, vermiculite, perlite, boroxosiloxanes and organoclays (Kozłowski and Władysław-Przybylak 2002, Klyosov 2007, Zhang and Horrocks 2003). Of these compounds, sodium cation exchanged montmorillonite is the most popular retardant because of its low price (Zhang and Horrocks 2003, Patra et al. 2005). Following the addition of montmorillonite to the polymer material, the following modifications have been observed: improvement of thermal stability, reduction of the rate of heat release in a fire, improvement of mechanical properties, improved gas barrier performance, enhancement of char formation, and inhibition of mass loss rate of decomposition products (Haurie et al. 2007, Nazare et al. 2006, Zhang et al. 2009, Morgan 2006, Gilman 2009). These changes can be explained by the existence of a barrier effect which occurs by exfoliation of the dispersed lamella of clay in the polymer matrix and this barrier prevents the diffusion of oxygen and decomposition products. The exfoliated clay layers firstly collapse into an intercalated structure, which is altered into a laminated carbonaceous-carbonate structure. The carbonaceous char develops on the surface during combustion and protects the underlying materials (Haurie et al. 2007, Nazare et al. 2006, Ratna 2005). Nanoretardant additives have very high efficiency compared to traditional flame retardants, for example, it has been reported that the addition of 3-5% of nanoparticles shows a better or the same fire resistance as polymer materials loaded up to 30-50% with a traditional flame retardant. A synergetic phenomenon of organoclays and common flame retardants (for example brominated compounds) has also been observed (Klyosov 2007). Other factors promoting the use of nanoclays are low cost, easy availability of nanoclays, and in some cases, improvement in the strength properties of plastic materials in comparison with general fire retardants which usually reduce these properties (Nazare et al. 2006, Zhang et al. 2009, Morgan 2006).

Organic phosphorous compounds

Phosphorous-containing compounds, which are one of the most effective flame retardant additives, are widely used (Chen and Wang 2010, Li et al. 2005). The availability of the full range of phosphorous chemicals is explained by the existence of phosphorus in several oxidation states. The most commonly used phosphorous flame retardants are phosphines, phosphine oxides,

phosphonium compounds, phosphonates, phosphites, and phosphate (Lu and Hamerton 2002, Zhang and Horrocks 2003). Organophosphorus flame retardants can be divided into three classes based on differences in the active groups and differences in the morphology of the chemical compounds: simple reactive phosphate monomers, linear polyphosphazenes, and aromatic cyclic phosphazenes (Zhang and Horrocks 2003). Phosphorus-containing compounds have a beneficial feature in that they are able to decompose at a low temperature, lower even than the destruction temperature of basic polymers. In other words, the added phosphorous retardant is decomposed with heat adsorption and the polymer matrix stays unaffected. This behaviour of phosphorous compounds is explained by the existence of weak phosphorate bonds which are thermally destructible (Li et al. 2005). Phosphorous fire retardants can direct the chemical reaction of combustion in the desired direction – enhancing the amount of carbonaceous residue rather than CO and CO₂. On combustion, they build a protective surface film which retards access to oxygen (Stark et al. 2010, Garcia et al. 2009, Stark et al. 2009, Moon et al. 2009, Jang et al. 2000, Jang and Lee 2001, Li et al. 2005).

A combination of phosphorus and nitrogen-containing compounds is usually used as a synergetic retardance composition (Stark et al 2009). The efficiency of such composition is that improving the fire retardant properties of the flaming material can be achieved with a small amount of added chemicals. The combination of phosphorus and nitrogen-containing compounds creates a very efficient catalyst for dehydration, owing to enhancement of the extent of char formation, and increases the amount of retained phosphorous in the char. For example, when wood is loaded with this synergetic combination, the retention of phosphorous in the char is caused by cross-linking of the cellulose during the process of pyrolysis by esterification with the dehydrating agents. In addition, the amino groups which are contained in this synergetic mixture induce retention of the phosphorous as a nonvolatile compound (amino salt). Another possible mechanism improving the fire retardancy is that addition of nitrogen compounds to phosphorus-containing compounds stimulates the polycondensation of phosphoric acid to polyphosphoric acid. Polyphosphoric acid in turn can act as a thermal and oxygen barrier limiting access to the material surface because it creates a viscous fluid coating (Rakotomalala et al. 2010, Levan 1984, Chen and Wang 2010, Li et al. 2005).

Phosphate esters

Phosphate esters are a large class of artificial organic compounds. The mechanisms of flame retar-

dancy depend on the chemical morphology of the esters, but generically they act in the vapour phase by inhibiting the combustion of pyrolysis products. The inhibiting action occurs by means of chemical reactions, the result of which is a change in the nature of the decomposition gases (Anon⁵ 2009). A good example of phosphate esters used as fire retardants is triphenylphosphate (TPP), which is the ester (triester) of phosphoric acid and phenol. TPP is a colourless crystalline solid with the empirical formula (C₆H₅O)₃PO (see Figure 4). It has low solubility in water but can be soluble in benzene, chloroform, ether and acetone (Anon_n).

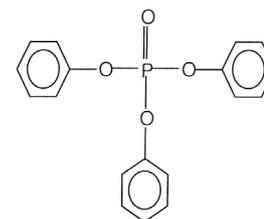


Figure 4. Chemical structure of triphenylphosphate (Jang and Lee 2001)

Aromatic esters (compounds which contain benzene rings), an example of which is TPP, are usually more thermally stable than aliphatic esters (compounds which do not contain benzene rings), and for this reason they are more prevalent during polymer processing. The presence of aromatic groups in the body of a retardant additive enhances the chemical affinity of this substance to polymers, the matrix of which also includes aromatic groups. For instance, it is known that aromatic phosphates are used to improve the fire resistance properties of aromatic polycondensates (such polymers as polyethylene terephthalate) (Chen and Wang 2010). Along with their advantages, aromatic phosphates, particularly TPP, have a major drawback; their low hydrolytic stability which in turn leads to loss of clarity when mixed into a polymer matrix (Rakotomalala et al. 2010).

Nitrogen based compounds

Nitrogen compounds in the role of fire retardants are not dangerous for the surrounding environment since they have low toxicity and, nitrogen containing polymers do not have extraneous impurities. The products of their combustion do not contain harmful dioxin and halogen acids, and the burning takes place with little smoke creation. However, nitrogen based compounds could release HCN and/or NO_x during fires, depending on combustion conditions (Anon₆ 2007, Lu and Hamerton 2002).

The burning of nitrogen-containing substances causes ammonia liberation, which dilutes the combustible gases of the flame-surrounding atmosphere, mak-

ing them nonflammable. In the condensed phase, melamine under the influence of external heat is modified into a cross-linked structure which is favorable for char forming. Another distinctive feature of nitrogen-containing retardants is that they are recyclable after their service life (Anon_b 2007, Lu and Hamerton 2002).

Synergism effects have been noticed when nitrogen has been used in combination with phosphorous compounds. It has been reported that nitrogen increases the affinity of the phosphorus to the polymer matrix. The mechanisms of fire retardancy of a nitrogen phosphorus miscellaneous combination are similar to those discussed above. Only the fact that the retained phosphorus creates a barrier to the heat and gases distinguishes the mechanism of the fire retardancy of the nitrogen – phosphorus synergetic mixture (Anon_b 2007, Li et al. 2005, Anon_c 2009).

Melamine

The most widely used nitrogen-containing reagents in fire retardancy are melamine and its derivatives (salts with organic or inorganic acids such as boric acid, cyanuric acid, phosphoric acid or pyro/poly-phosphoric acid, and melamine homologues such as melam, melem and melon), see Figure 5 (Anon_b 2007, Lu and Hamerton 2002, Chen and Wang 2010, Troitzsch 2004).

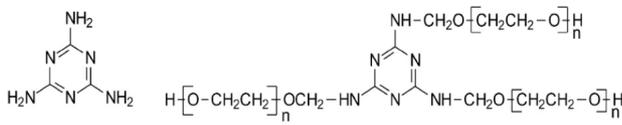


Figure 5. Melamine and derivatives (Anon_b 2007, Lu and Hamerton 2002)

Melamine and its derivatives, as other nitrogen containing compounds, tend to build synergism with phosphorous when compounded with phosphates (Stark et al. 2010, Stark et al. 2009, Lu and Hamerton 2002). Concerning the mechanisms of retardancy of melamine, it has to be noted that under heat action this compound is decomposed endothermically, which promotes the escape of energy from the system. Furthermore, the products of the decomposing melamine interrupt the chain of free radical reactions in the gas phase by trapping the free radicals. Additionally, the products of the decomposing melamine, mainly nitrogen and ammonia, dilute the fuel gases. Melamine also assists the formation of char (Stark et al. 2010, Garcia et al. 2009, Stark et al. 2009).

Melamine polyphosphate (MPP, Figure 6) is quite broadly used in a mixture with phosphates, metal phosphinates and metal hydroxides. These combinations are characterized by good thermostability. Melamine decomposition is accompanied by the formation of phosphoric

acid, which favours the creation of a protective layer on the polymer surface (Rakotomalala et al. 2010).

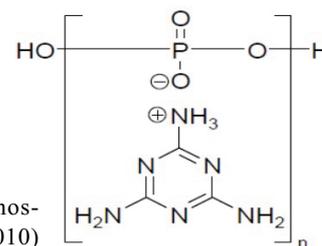


Figure 6. Melamine polyphosphate (Rakotomalala et al. 2010)

Summary

The fire retardant properties of composites depend mainly on the structure of the material. Accordingly, characterization of the flammability of a material should be done by analyzing independently the properties of the matter constituting the composite, in the case under consideration, wood and plastic. It is known that cellulose and hemicelluloses enhance the flammability of wood, but lignin, which is the other polymer included in wood, promotes the fire behaviour of wood by charring. The literature review showed that the most effective and widely used fire retardant chemicals for wood are phosphates, nitrogen compounds, borates and silicates. Typical fire retardants used in plastics include aluminium trihydrate, chlorinated compounds, organophosphorus compounds, brominated compounds and antimony oxides. Commonly used fire retardant compounds for wood-plastic composites are magnesium hydroxide, boric acid, ammonium phosphates and borates, ammonium sulphate and chloride, zinc chloride and borate, phosphoric acid, dicyanodiamide, sodium borate and antimony oxide. It has been reported that fire retardant chemicals mainly work by the mechanism of forming a char layer in the condensed phase and the trapping of active radicals in the vapour phase.

As shown in this literature review, many efforts have in recent years been devoted to the problem of reducing the loading of WPC's with metal hydroxides as traditional fire retardants. With the aim of reducing the total loading of metal hydroxides, a great number of researchers are working on the development of synergetic co-additives. For example, it has been reported that the addition of nanocomposites based on layered silicates and carbon nanotubes to a system with metal hydroxide shows a synergetic effect that allows a decrease in the loading of the system with metal hydroxides. The combination of metal hydroxide with inorganic clay also gives sufficiently good synergetic results. In spite of all these favourable findings, there are still many open questions and much additional research is required regarding modifications

to synergetic agents already used and the development of new agents improving the fire resistance of wood-plastic composites.

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МЕТОДЫ ПОВЫШЕНИЯ ОГНЕЗАЩИТЫ ДРЕВЕСНО-ПОЛИМЕРНЫХ КОМПОЗИТОВ

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Резюме

В данной работе рассмотрены основные принципы горения, его химических и физических аспектов. Детально разобраны сценарии и стадии протекания процесса горения органических веществ, как на примере древесины, так и синтетических полимерных веществ – компонентов древесно-полимерных композитов. Также изложены методы и теории огнезащиты полимерных материалов, в частности на примере пластиков, древесины и древесно-полимерных композитов. Приведен широкий спектр ретарданционных добавок – антипиренов. Разобраны их свойства, механизмы действия, синергизм, дозировки и возможные побочные действия на обработанный материал.

Ключевые слова: древесно-полимерные композиты, огнестойкость, антипирен, ретардант, химическая огнезащита, поверхностная огнезащита, огнезащитное вещество, огнезащитное изделие