# FLAME RETARDANCY OF BIO-BASED THERMOPLASTIC COMPOSITES AND NANOCOMPOSITES

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**Abstract**
*This paper presents several examples of study dealing with the flame retardancy of bio-based composites. Several approaches were followed: the use of intumescent systems, of the "heat sink" concept as well as the nanocomposites approach. It was shown that flame retardant properties of interest can be achieved using those approaches in bio-based composites.*

## 1 Introduction

In recent decades, the development of environmentally friendly materials has led to a particular interest of the scientific community for a certain family of composites: the bio-based thermoplastic composites. Thermoplastic composites are composed of a thermoplastic matrix and of a reinforcing agent. The advantages compared to thermoset-matrix composites are in particular faster production rate or recycling which is of particular interest when dealing with life cycle assessment.

In bio-based composites, either the matrix or the reinforcement could be obtained from natural resources. Natural fibers such as kenaf, hemp or flax could be incorporated in thermoplastic matrices leading to materials exhibiting reductions in weight, cost and carbon dioxide emission, less reliance on foreign oil resources and recyclability [1]. Among the different polymeric matrices, polylactic acid (PLA) appears to be a good candidate; it is produced at large scale, presents properties that are similar to those of conventional polymers [2] and could thus reasonably substitute them in several domains such as packaging, transportation or electrical and electronic equipment. For some of those applications, a high level of flame retardant properties is required. The flame retardant behavior of bio-based composites could be different to that of conventional materials. Indeed, bio-based fibers are mainly organic materials and could thus contribute to the development of the fire whereas mineral fibers (such as glass fibers for example) do not. On the other hand, the flame retardancy of bio-based polymers is poorly reported in the literature since their first applications were designed for disposable or semi-durable materials where there was no really need for flame retardancy [3]. Finally, it is noteworthy that thermoplastic matrices behave differently in presence or not of the fibers and thus the flame retardancy of composites is a complex problem.

In this paper, several examples of bio-based flame retardant composites will be described and compared. First, we will examine the flame retardant properties of structural sandwich composites using an intumescent polylactic acid (PLA) as a matrix and weave flax fabrics as

reinforcement. As a second example, the use of metal hydroxides and intumescent systems to flame retard flax-reinforced polypropylene composites will be examined. Finally, the nanocomposites technology consisting in the use of clay to improve the properties of PLA will be presented as another approach to develop environmentally friendly flame retardant materials.

## 2 Example 1. Structural sandwich composites

*2.1 Materials and testing methods*

The polylactic acid (PLA) was supplied by Cargill Dow (PLA 6200DNatureWorks). The intumescent formulations were composed of ammonium polyphosphate (APP, $(NH_4PO_3)_n$, Exolit AP422 supplied by Clariant) and of pentaerythritol supplied by Acros (PER). Two different flax fabrics were used: a plain weave fabric (flax-Pw) that has an areal weight of 420 g/m² and a twill weave fabric (flax-Tw) that has an area weight of 490 g/m². The FR formulations (PLA/APP/PER 60wt.-%/30wt.-%/10wt.-%) were prepared with a counter-rotating twin screw extruder (L/D=7) (Brabender, Germany) at 180°C (from the feeding zone to the die) at a screw speed of 50 rpm. Films (PLA and PLA/APP/PER) were extruded from pellets using a Rheocord System 40 single screw melt extruder from Haake Buchler Product equipped with a film die with a width of 10 cm. The thickness of the film was adjusted to 250 µm by controlling the take up speed. A film was applied on one side or two sides of the flax structures using a Darragon molding press at 180°C at a pressure of 1 MPa for 5min.

A laboratory "hybrid" vertical test resulting from the combination of two normalized tests (IN ISO 11925-2 and NF G07-184) was used to measure the flame spread rate of materials. A sample, 150mm × 50 mm × 3 mm, is placed into the sample holder and is exposed to the burner flame with an angle of 45° for 10 s. The flame spread was then recorded.
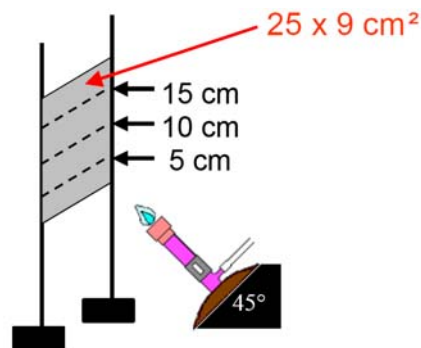


**Figure 1.** Hybrid Flame Spread test

*2.2 Results and discussion*

Figure 2 reports the flame spread of the fabric with and without films in vertical configuration.

First, it is observed that the two fabrics behave differently. Vertical flame spread is higher for the twill weave fabric compare to the plain weave fabric. This result could be explained by the design of the test. Indeed, when measuring the flame spread, the fabric is ignited from one side and the flame propagates. The propagation of the flame is thus clearly linked with the structure of the fabric.

Second, when a PLA film is applied on the fabric, a decrease in the vertical flame spread is observed in the case of the twill weave fabric whereas for the plain weave fabric, the value is closed to that of the virgin fabric. This result is observed when film is applied on one or both sides of the fabrics. It could be explained by the fact that, at the opposite of the virgin fabrics,

the flame propagation is not due only to the fabric but it results from the burning behavior of the polymeric matrix and thus similar results are obtained for the two different fabrics.

Finally, it could be observed that, when an intumescent film is applied on the flax fabrics, the fire performance of the fabrics according to vertical flame spread test is improved. When exposed to a heat source, intumescent materials form an expanded carbonized layer (char) at the surface of the polymer. This layer acts like an insulating barrier reducing heat and fuel transfers between the heat source and the inner part of the polymer [4]. When only one film is applied, the flame spread is decrease up to 10-12cm/min. It is observed that, similarly to the results observed for PLA film, the structure of the textile does not influence the flame propagation. As a consequence, it confirms that the propagation mainly occurs via the polymeric matrix than from the fibers. A very interesting result is obtained when the intumescent PLA film is applied in both sides of the fabric since in that case, the materials auto-extinguish (both the plain and the twill weave fabrics).
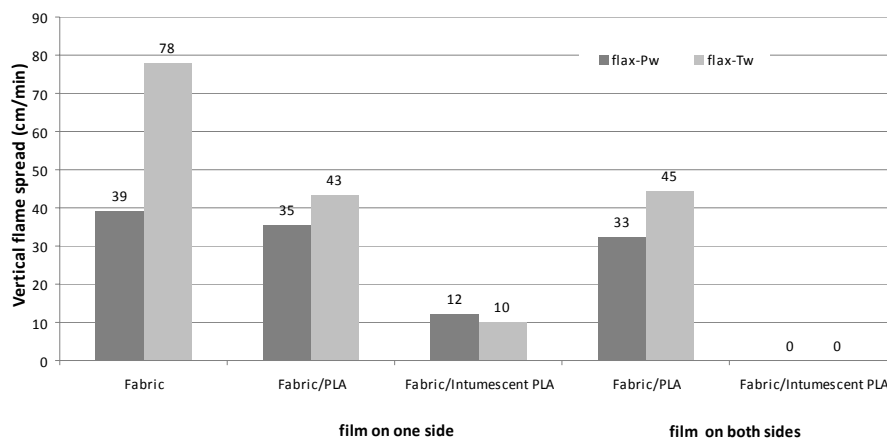


**Figure 2.** Vertical Flame Spread of the Fabric and Composites

*2.3 Conclusion*

This work has shown that intumescent films based on renewable resources can be used to bring flame retardancy to flax fabrics resulting in the formation of a structural sandwich composite. Vertical flame spread measurements have shown no combustion when PLA FR films are coated on both sides of the fabrics thus self-extinguishable materials were obtained. This process is very flexible, easy and quick and could be applied on various kind of substrate (as far as the adhesion does not become an issue). Further studies are currently carried out in the lab in order to investigate the influence of both the film and fabric composition on the flame retardant and mechanical properties of such composites.

**3 Example 2. Thermoplastic PP/Flax composites**

*3.1 Materials and testing methods*

Raw materials were PP (Finapro grade, as pellets supplied by Fina (France); MFI: 12 g/10 min (230°C/2.16 kg)); aluminium tri-hydroxide (Al(OH)$_3$, ATH) and magnesium di-hydroxide (Mg(OH)$_2$, MH) were commercial grade additives (supplied respectively by Alcan and Dead Sea Bromine). The intumescent system was composed of pentaerythritol (PER; Aldrich R.P. grade), melamine (MEL; analytical grade (99%) powder supplied by Avocado Research Chemicals (UK)) and ammonium polyphosphate (APP ((NH$_4$PO$_3$)$_n$, Clariant Exolit 422). Flax "Fibers" are short (mean length about 20 mm), non-textile residue from flax tow obtained from natural tangling after harvesting and natural weathering retting (Fibber,

technilin grade supplied by La Centrale Linière Cauchoise (France), generally used in paper or composites manufacturing). Polymer and additives mixtures (Table 1) were mixed in a Brabender Laboratory Mixer with roller blades monitored by a Brabender Plasticorder PL 2000 data processing torque rheometer system operating at 180°C and 20 rpm. The polymer was first introduced in the heating chamber and, after 3 minutes the additives were introduced into the chamber and mixed for 6 minutes, the total mixing time being of 9 minutes. The obtained mixture was then pressed in a Daragon press at 185°C and 70 bars on a 10 cm x 10 cm plateau in order to obtain 3mm thick sheets, from which all tested specimens were produced.

| | Reference | PP (wt.-%) | Fibre (wt.-%) | Additives (wt.-%) |
|---|---|---|---|---|
| PP | PP | 100 | | |
| PP/Fiber | $PP_f$ | 60 | 40.0 | |
| PP/Fiber/ATH | $PP_f$/ATH | 40 | 26.5 | 33.5 |
| PP/Fiber/MH | $PP_f$/MH | 40 | 26.5 | 33.5 |
| PP/Fiber/APP/PER/MEL | $PP_f$/APP/PER/MEL | 46 | 31.0 | 33.5 |

**Table 1.** Composite composition.

Fire properties have been evaluated according to UL-94 classification obtained on sheets (130 x 12.7 x 3 mm$^3$) according to the conditions of the standard test (ASTM D 3801) i.e. in a vertical position (the bottom of the sample is ignited with a burner). This test provides a qualitative classification of the samples (V0, V1 and V2 labeled samples). Mechanical properties were also evaluated following the three-point bending tests according to ASTM D-790M standard and tensile tests were carried out using an universal mechanical testing machine Instron 4204H0610. For each test and composite a minimum of five samples were tested, at a crosshead speed of 2 mm.min$^{-1}$. The specimens were cut with dimensions 120x12.5x3 mm$^3$ for tensile tests and 60x25x3 mm$^3$ for flexural tests.

*3.2 Results and discussion*

Table 2 compares the mechanical and fire retardant properties of the different PP/Flax composites.

First, it is observed that the addition of fibers leads to a very low value of the elongation and to a high tensile modulus. Similar results were already reported in the literature [5],[6]. Fiber addition also leads to a slight increase of the flexural modulus of composites. However, it is noteworthy that relatively high values of flexural modulus standard deviation. This is a proof of the low homogeneity of materials, i.e. local accumulation of fiber in the composite as experimentally evidenced by us.

| Materiasl | PP | $PP_f$ | $PP_f$/ATH | $PP_f$/MH | $PP_f$/APP/PER/MEL |
|---|---|---|---|---|---|
| Tensile modulus, GPa | 1.5 | 3.2 | 4.1 | 5.4 | 5.4 |
| Elongation at break, % | 5 | 0.6 | 0.35 | 0.23 | 0.23 |
| Flexural modulus, E; GPa | 2.0 | 2.6 | 4.8 | 4.9 | 3.7 |
| E standard deviation, % | 3.3 | 16 | 12 | 9.2 | 13.6 |
| UL94 rating (3mm thick) | NC | NC | NC | NC | V0 |

**Table 2.** Composite composition.

The addition of the flame retardant additives in the PP/Flax composite increases significantly the flexural modulus. This is particularly the case when metal hydroxides are used. However, it has to be underlined that in that case, higher additives/fiber content was used. It has to be

noticed that, in that case, standard deviation is also important and thus, low homogeneity of materials is suspected.

Mechanical properties of these materials are significantly influenced by the interfacial interactions, which depend on the size of the interface and the strength of the interaction [7]. As a consequence, optimized mechanical properties should be obtained via the optimization of the particle sizes [8], the use of coupling agents [9] or chemical treatments (such as maleic anhydride or vinyl trimethoxy silane treatments [8] which may affect the hydrophilic nature the fibers [10]).

UL-94 testing shows dripping and very rapid combustion of virgin PP and of PP$_f$ and they are thus non-classified according to UL94 test.

When metal hydroxides are incorporated in the PP$_f$, formation of a ceramic like structure is observed (Figure 3). Metal hydroxides are widely used to flame retard polymer. As the temperature rises, these fillers decompose endothermically and therefore absorb energy. Furthermore, they release non-flammable molecules ($H_2O$, $CO_2$), which dilute combustible gases, and can also promote the formation of a protective ceramic or vitreous layer. The endothermic decomposition of aluminium tri-hydroxide ($Al(OH)_3$) occurs between 180 and 200°C whereas that of magnesium di-hydroxide (MDH) occurs at a higher temperature (>300°C). The PP$_f$ composites including ATH or MDH are however non-classified at UL94 since the protective effect is not enough to stop the fire. This rating shows that addition of hydroxides is not enough to obtain a correct fire retardant classification.
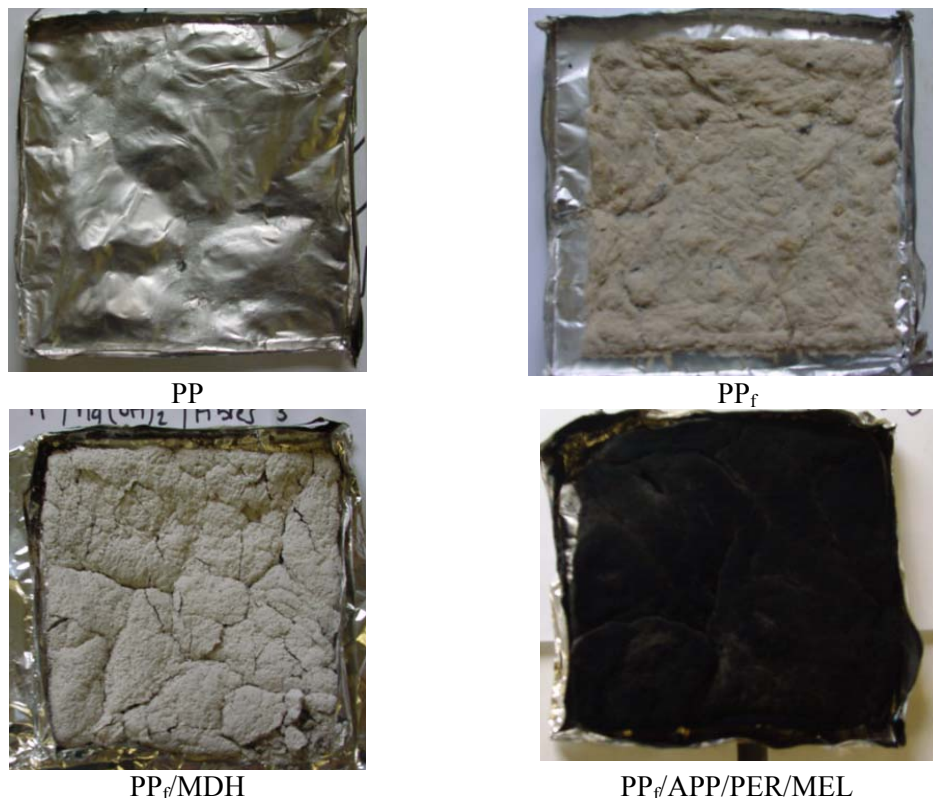


| | |
|---|---|
| PP | PP$_f$ |
| PP$_f$/MDH | PP$_f$/APP/PER/MEL |

**Figure 3.** Residue of combustion of PP and PP$_f$ composites

On the other hand, PP$_f$/APP/PER/MEL shows the formation of a stable intumescent char (Figure 3) with no polymer dripping and instantaneous complete extinction after the 2nd flame exposure (i.e. V0 rating). This result shows that char forming fibers need an intumescent composite structure maintaining coherence of the protective shield and thermal barrier properties, to give a high level of flame resistance to the material.

*3.3 Conclusion*

The effects of hydroxides and intumescent flame retardant additives on the flammability and mechanical properties of the flax filled polypropylene composites were compared. The hydroxides have been proved to be reinforcing fillers for polypropylene on the basis of increases in the tensile and flexural strength whereas it was shown that better fire performances were obtained for the intumescent system.

## 4 Example 3. PLA nanocomposites

*4.1 Materials and testing methods*

PLA (number average molar mass = 74,500 g/mol, residual monomer content = 0.18%, D-isomer content = 4.3%, melt flow index (190°C, 2.16 kg) = 6.61 g/10 min and density: 1.25 g/cm3) was supplied by NatureWorks and dried overnight at 110°C before use. MMT originated from Southern Clay Products, Inc. (Gonzales, TX – USA). The starting material, sodium-MMT, was commercially modified using methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride (Cloisite 30B). PLA was melt-mixed with the clay using a micro-extruder (from DSM Xplore) at 185°C and 25 rpm. The clay loading (Cloisite 30B) was 4 wt.% organoclay.

All samples were ultra-microtomed with a diamond knife on a Leica Ultracut UCT microtome to give sections with a nominal thickness of 70 nm. The sections were transferred from water (room temperature) to Cu grids of 400 mesh. Bright-field TEM images of nanocomposites were obtained at 120 kV under low-dose conditions with a Philips 400T electron microscope, using Kodak SO-163 film. The materials were sampled by taking several images of various magnifications over 2–3 sections per grid to ensure that analysis was based on a representative region of the sample.

Fire retardant properties of the nanocomposites were evaluated using a FTT (Fire Testing Technology) Mass Loss Calorimeter following the procedure defined in ASTM E 906. External heat flux of 35 kW/m² was used for running the experiments on samples ($10 \times 10 \times 0.3 cm^3$). This test was used to determine the heat release rate (HRR).

*4.2 Results and discussion*

Nanometric particles (nanoclays, carbon nanotube…) when properly dispersed in polymer matrices are known to contribute to the enhancement of properties such thermal, mechanical or fire resistance [11],[12]. They enable a considerable reduction of the loading at which an acceptable efficiency is observed since the interfacial area between the polymer and the nanofiller is greatly increased. Indeed, we have previously shown that flame retardant additives content are usually higher than 20wt.-% for intumescent system and than 50wt.-% for hydroxides to achieve interesting properties resulting in a decrease in the mechanical properties. In the case of nanocomposites, both improvements in mechanical and fire retardant properties could be achieved at low loading. Improvement of the fire performances of polymers including nanoparticles is mostly associated to a decrease of the heat release rate (pHRR) evaluated by cone calorimetry. This effect is usually due to the formation, during thermal decomposition, of a protective barrier on the polymer surface (due to accumulation of inorganic at the surface) that limits heat transfer into the material, volatilization of combustible degradation products and diffusion of oxygen into the material.

TEM pictures (Figure 4) reveals that clay is evenly dispersed in PLA. Many individual MMT platelets are observed associated with few small tactoids of 2–3 layers in size. It demonstrates that an exfoliated nanocomposites structure is achieved.
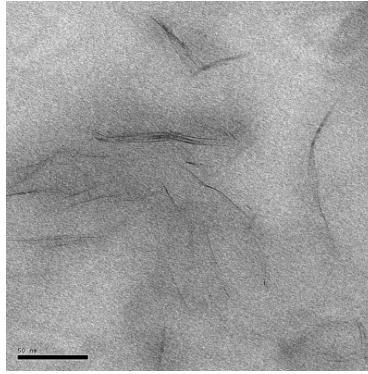
**Figure 4.** TEM images of PLA/ MMT nanocomposites

Adding a small amount of clay has been shown to reduce peak of HRR (PHRR) for polymer nanocomposites such as polystyrene [13], styrene-acrylonitrile [14] or polyamide-6 [15] (Figure 5). Indeed, a significant reduction in PHRR in PLA when dispersing at the nano-scale MMT platelet in the matrix. PHRR is decreased by 40%.
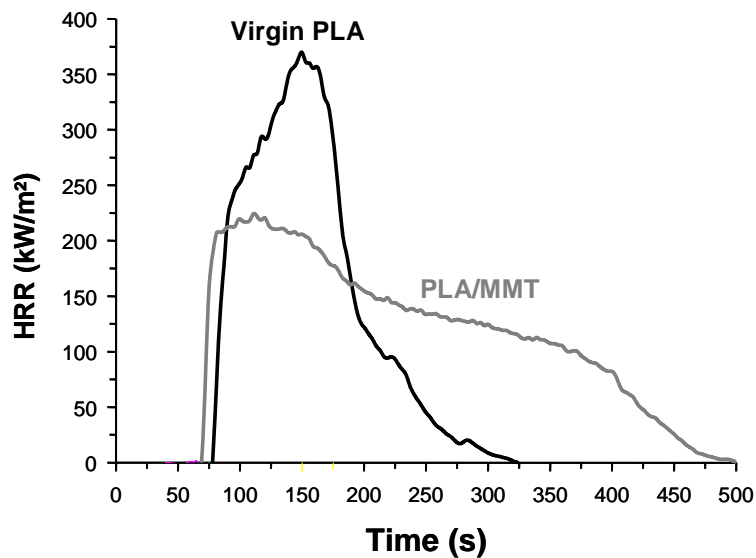


**Figure 5.** HRR as a function of time of PLA and PLA/clay nanocomposites (external heat flux = 35 kW/m$^2$)

The suggested mechanism by which clay nanocomposites function involves the formation of a char that serves as a potential barrier to both mass and energy transport [13]. Visually a smooth char layer is formed at the surface of the nanocomposites leaving a black char residue at the end of the experiment (Figure 6). In the case of pure PLA, vigorous bubbling is observed when the polymer is burning and there is no residue left at the end of the experiment.



**Figure 6.** PLA/clay nanocomposites residue obtained after cone calorimeter experiment

*4.3 Conclusion*

This work has characterized the dispersion of montmorillonite clay in PLA and evaluated the reaction to fire of PLA/MMT nanocomposites. The nanodispersion has been evaluated qualitatively by TEM and it was shown that MMT platelets are evenly dispersed in PLA. The presence of clay in PLA (exfoliated morphology) leads to a significant decrease of peak of heat release rate measured by cone calorimetry by oxygen consumption.

**Acknowledgments**

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