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A New Direction in Design of Bio-based Flame Retardants for Poly(lactic acid)

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Abstract

A novel bio-based nitrogen-and phosphorus-rich flame retardant (Phyt/PEI-TA) was synthesized and characterized by Fourier transform infrared (FTIR), Inductively Coupled Plasma (ICP) and thermogravimetric analysis (TGA). Thermal degradation and flame retardant properties of poly(lactic acid) (PLA) containing 20 wt.% Phyt/PEI-TA were investigated by TGA, cone calorimetry and microcalorimeter of combustion (PCFC) measurements. TGA results showed that introduction of newly developed Phyt/PEI-TA to PLA significantly improved its thermal stability, as signaled by much more amount of PLA char formed compared to the reference sample. Surprisingly, the use of Phyt/PEI-TA did not decrease the onset degradation temperature of PLA. In agreement with TGA results, the cone calorimetry results approved excellent flame retardancy of PLA upon addition of Phyt/PEI-TA (36% reduction in pHRR compared to that of neat PLA). Based on the analysis performed on the remainder of char after cone calorimeter test as well as analyses on HRR curves, the condensed phase action by promoting the formation of char was identified as principal impact of the Phyt/PEI-TA on flame retardancy of PLA. Finally, the performance of developed bio-based flame retardant was compared with more than 60 flame retardant systems previously reported in the literature.

Keywords: Poly(lactic acid); bio-based flame retardant; flammability

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1. Introduction

Nowadays fire retardancy of polymeric materials has become an important feature of their applications. In this regard, the use of bio-based polymers as substitute for petroleum-based polymers has attracted a great deal of attention. Such green hydrocarbons present much less carbon footprint compared to fossil carbon. Polylactide (PLA) belongs to biopolymer family and can be produced from renewable resources and presents a high stiffness, high degree of transparency in addition to relatively low cost and large production volume.

Flame retardancy is a dynamic research area that has opened new realm of technology to lessen fire risks. When dealing with bio-based flame retardant (FR) systems, sustainability should be considered as an additional requirement. Gas phase FR agents benefit from quenching the flame in the gas phase via formation of radical scavengers, but nowadays they are largely replaced by additives acting in the condensed phase to make possible formation of a protective layer against fire. In contrast to gas-phase-active additives such as halogen-based FR compounds that produce toxics and corrosive smokes, char-forming systems are expected to reduce the amount of harmful volatile compounds released during the combustion.

In the condensed phase, phosphorus-based FRs have particularly appeared effective with polymers containing oxygen [1] because of much less toxic compounds being released compared to halogenated ones [2]. Phosphoric acid produced during thermal decomposition forms into pyrophosphate structures through condensation and generates carbon-carbon double bonds. At higher temperature, crosslinked or carbonized structures are generated via dehydration reaction of the terminal alcohols formed.

Phosphorus based FR additives are usually associated with other synergistic compounds to enhance their efficiency [1]. The use of bio-based char-forming agents, such as lignin [3, 4, 5], starch [6, 7], cellulose [8, 9], β -cyclodextrin [10, 11] or tannic acid [12] has attracted attention of researchers and engineers alike to reduce environmental impact of FR systems whilst enhancing fire performances.

Lignin is a bio-based phenolic compound receiving much attention in the past decade thanks to its aromatic structure. However, due to its high structural diversity, large molecular weight distribution and variability in terms of reactivity and composition, its performances is strongly dependent on its botanical origin and the extraction process used [4,5]. Using natural and non-

polymeric bio-based aromatic compounds could present an interesting pathway for overcoming these limitations.

In this work, a novel flame retardant additive composed of small bio-based molecules, i.e. tannic acid (TA) and phytic acid (Phyt) (Figure 1) was prepared. These two additives could present some interest as flame retardant effects on PLA. Tannic acid, that is a non-polymeric phenolic compound, is a char-forming additive under anaerobic condition that enables for the formation of a char layer when associated with phosphorus [12]. In the other hand, phytic acid, the principal form of storage of phosphorus in many plants, has depicted an interesting flame-retardant effect into PLA owing to its high phosphorus content (28 wt%) and an interesting P/C atomic ratio (=1). However, due to its liquid form, its incorporation into the PLA induces an important increase of the composite hygroscopy [13].

Combining these two compounds for the preparation of a novel bio-flame retardant agent was the aim of this contribution. Tannic acid and phytic acid were coupled together with the use of branched polyethyleneimine (PEI) to enjoy from either its cationic character or high nitrogen content. In fact, nitrogen-based compounds can act in both condensed and gas phases by promoting the formation of thermally stable condensates as well as by diluting oxygen and combustible gases. This novel bio-based flame retardant agent (Phyt/PEI-TA) was synthesized by a two-step process allowing the combination of phosphorus, carbon and nitrogen in the same complex. Phyt/PEI-TA was characterized using thermogravimetric analysis (TGA), Inductively Coupled Plasma analysis (ICP) and Fourier infrared spectroscopy techniques (FTIR). The effect of its incorporation on PLA thermal and flame-retardant properties was investigated using Size Exclusion Chromatography (SEC), TGA analysis, cone calorimeter test. A flame retardant mode of action of Phyt/PEI-TA was also investigated.

2. Experimental

2.1. Materials

PLA resin (3051D) with a number-average molecular weight of 100 000 g/mol, a polydispersity of 2.1 and D-lactide content of 4.3% was purchased from NatureWorks. Branched polyethyleneimine (PEI, 50 wt% in water, M_n : 10 000 g/mol, M_w : 25 000 g/mol, Sigma Aldrich), tannic acid (TA, ACS grade, 97% Aldrich), Potassium carbonate (K_2CO_3) (Merck), 3,3',4,4'-benzophenone tetra carboxylic dianhydride (BTDA)(Merck), and phytic

acid (50% solution, wt% in water, Sigma Aldrich) were used for the preparation of Phytic acid/Polyethyleneimine/Tannic acid complex (Phyt/PEI-TA).

2.2. Synthesis of Phy/PEI-TA complex

First step: synthesis of polyethyleneimine grafted tannic acid (PEI-TA)

In a 250 mL round-bottomed flask fitted with a stirring bar, polyethyleneimine (PEI) (3.0 g) was added to a solution of tannic acid (Ta) (3.0 g) in water (100 mL). K_2CO_3 was then added to the mixture to raise the pH to 11. Stirring was continued at room temperature for 2h. Then, a solution of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) (5.0 g) in DMF (30 mL) was added dropwise and stirring was continued for further 24h at 70 °C. After cooling the mixture down to room temperature, the precipitates were separated by centrifugation and washed using distilled water and ethanol, respectively. The resulting powder was dried at 80 °C to obtain PEI-TA.

Second step: synthesis of Phytic acid / PEI-TA complex (Phyt/PEI-TA)

In a 250 mL round-bottomed flask, PEI-TA powder (2.0 g) was dispersed in ethanol (100 mL). Phytic acid (5 mL) was slowly added and the mixture was stirred for 4 h at room temperature. The obtained solid was separated by centrifugation and dried at 80 °C in vacuum oven.

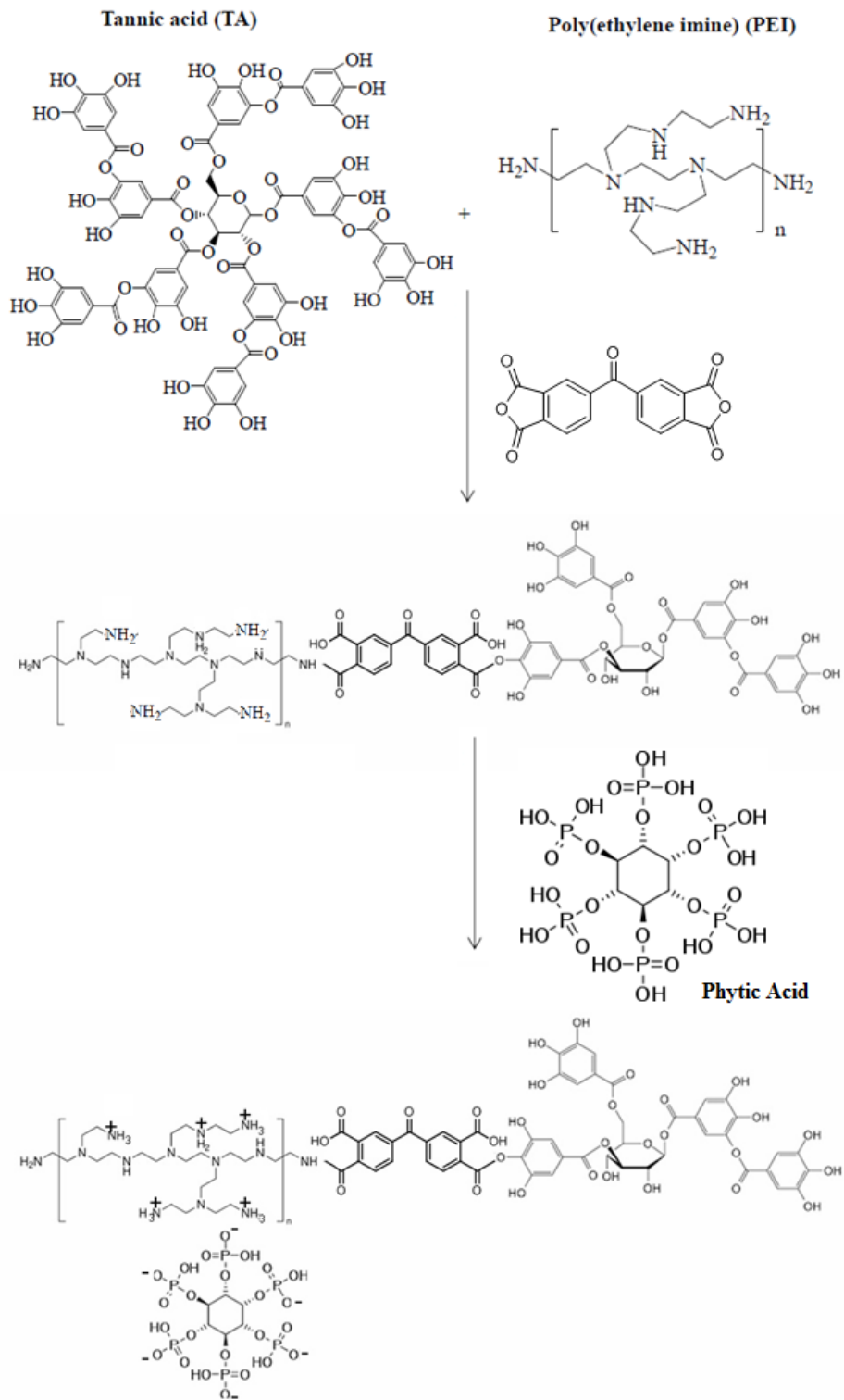


Figure 1: schematic representation of Phyt/PEI-TA structure.

2.3. Melt processing

Blending of Phyt/PEI-TA with the molten PLA was carried out in a Brabender internal mixer at 160 °C (7 min mixing at 70 rpm). Prior to blending, PLA and Phyt/PEI-TA were dried in a vacuum oven at 60 °C overnight. Plates (100*100*4 mm³) for cone calorimeter testing were compression-molded at 160 °C using an Agila PE20 hydraulic press following a precise pressure program: the sample was first deposited for 3 min on the hot part, it was then pressed for 3 min 20 s at 10 bars, followed by 3 degassing, it was then pressed again for 2 min 30 s at 150 bars, and finally the sample was deposited in the cold part and pressed for 5 min. Neat and composite PLA containing 20 wt% of each Phyt/PEI-TA fraction were prepared.

2.4. Characterizations

2.4.1. Fourier transform infrared (FTIR)

Fourier transform infrared (FTIR) spectra were gathered on a Perkin-Elmer RXI spectrometer in the range of 400–4000 cm⁻¹ with a resolution of 2 cm⁻¹ and 32 co-added scans, using attenuated total reflection (ATR) mode.

2.4.2. Inductively Coupled Plasma (ICP)

Inductively Coupled Plasma (ICP) analysis was recorded with an IRIS Intrepid II (Dual view) from Thermo Fisher Scientific. It was used for determination of the amount of phosphorus in the phosphorylated tannic acid. Before ICP analysis, phosphorus-incorporated samples were prepared by the destruction of the organic matrix by a mineralization process with H₂SO₄/HNO₃/H₂O₂ solutions. The amount of phosphorus was determined using a calibration curve obtained from ICP analysis of phosphorus containing standard solutions.

2.4.3. Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) was used to determine the number-average molecular weights of both PLA and PLA/Phyt/PEI-TA blends. The number-average molecular weights and molecular weight distributions were determined in CHCl₃ at 23 °C using an Agilent size exclusion chromatograph equipped with a Knauer 2320 refractometer index detector and two PLGel columns (MIXED-D and 103A). Samples were dissolved in CHCl₃ (5 mg/1 mL), 20 μL of the solutions were injected into the columns using a flow rate of 1 mL/min. Monodisperse polystyrene standards (Polymer Laboratories Ltd.) were used for the primary calibration.

2.4.4. Scanning electron microscopy (SEM)

Morphological investigation was performed to assess the dispersion of Phyt/PEI-TA particles in PLA on a FEI Quanta scanning electron microscopy (SEM) apparatus. PLA composites were cryo-fractured after immersion in liquid nitrogen and then coated with gold sputtering technique to avoid any charging effect during the electron beam scanning.

2.4.5. Thermogravimetric analysis (TGA)

Thermal decomposition behavior of tannic acid, phosphorylated tannic acid, pristine PLA and PLA-based composites were studied by thermogravimetric analysis (TGA) using a TGA Q50 device from TA Instruments. Approximately 10 mg of the sample was submitted to a temperature ramp from 100 to 700 °C at a heating rate of 20 °C/min. Residual weight at 700 °C (Residue) as well as temperature at the peak of mass loss rate (T_{deg}) and corresponding to 20 wt% mass loss ($T_{-20\%}$) were determined.

2.4.6. Cone calorimeter and Pyrolysis Combustion Flow Calorimeter (PCFC)

Fire behavior of compositions has been evaluated using mass loss cone calorimeter test at 35 kW/m². Cone calorimeter is known as the best technique for assessing the flammability of materials at bench scale. The peak of heat release rate (pHRR) as well as time to ignition (TTI), that are considered as two of the most important parameters in this fire test were recorded accordingly. A high pHRR and a low TTI may cause both fast ignition and rapid-fire propagation. Cone calorimeter tests were performed according to ISO 13927 standard procedures with a FTT mass loss cone calorimeter. Samples (100*100*3 mm³) were exposed to an external heat flux of 35 kW/m², corresponding to common heat flux in a mild fire scenario. The flammability was also studied using a Pyrolysis Combustion Flow Calorimeter (PCFC) from Fire Testing Technology (FTT). Heating rate, maximum pyrolysis temperature, combustion temperature were respectively 1 °C/s, 750 °C, 900 °C.

3. Results and discussion

3.1. Structural and thermal properties of Phyt/PEI-TA

FTIR spectra of PEI-TA and Phyt/PEI-TA are compared in Figure 1 with that of tannic acid. FTIR analysis of the intermediate product formed during the first step (PEI-TA) reveals that in addition to the characteristic absorption bands of both tannic acid and PEI, some new peaks are newly appeared. These new bands are attributed to the formation of amide groups (1665 cm⁻¹) and to carboxylic acid OH groups as well as NH₂ functions (2500-3400 cm⁻¹). The

formation of carboxylic acid OH groups is a signature of the opening of the dianhydride group of BTDA that reacts with tannic acid, while the formation of amide functional groups hints at the formation of covalent link between PEI and BTDA.

In FTIR spectrum of the final complex (Phyt/PEI-TA), the presence of phytic acid has been confirmed by the presence of the absorption band at 998 cm^{-1} corresponding to P–O bond.

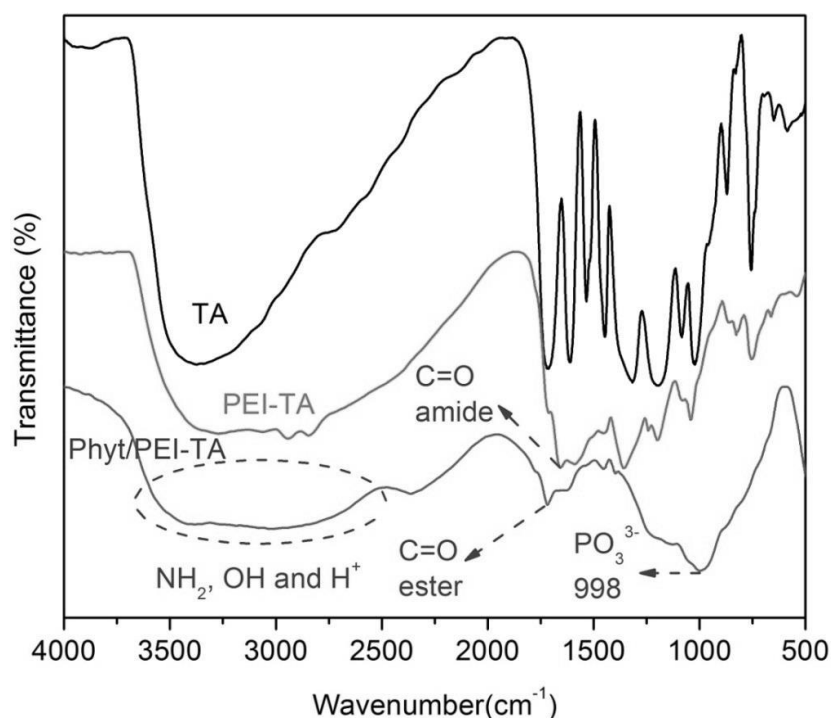


Figure 2: FTIR spectra of TA, PEI-TA and Phyt/PEI-TA.

The structure of Phyt/PEI-TA has been further investigated by determining its chemical composition. ICP analysis was used to quantify its phosphorus, nitrogen and carbon content. The results presented in Table 1 make evident that the synthesis method applied in this work enables for developing a compound predominantly composed of carbon (26.4 wt%) and contains a high phosphorus and nitrogen content, i.e. 14 wt% and 4.9 wt% respectively. Moreover, Phyt/PEI-TA presents an interesting C/P/N ratio.

	P (wt%)	N (wt%)	C (wt%)
Phyt/PEI-TA	14	4.9	26.4
Residue after combustion	13.1	2.4	39.2

Table 1: phosphorus, nitrogen and carbon content determined by ICP analysis.

The thermal stability of Phyt/PEI-TA has been first investigated to test whether the product could be melt processed with PLA at 160 °C. Fig. 3 presents thermo-oxidative and anaerobic decomposition of the product. According to the curves, no important thermal degradation took place below 200 °C and only a small weight loss of about 5 wt%, probably due to some water release, is recorded at 160 °C. The product must therefore be dried prior melt processing. TGA analysis has further been used to investigate the thermal behavior of produced additive and its char forming ability. Results suggest that thermal decomposition of the product takes place over a large temperature range signifying several decomposition steps. No clear separation between these steps can be distinguished since several of them overlap with each other. The comparison of TGA curve under air of Phy/PEI-TA with those of tannic and phytic acid gives some interesting information. First, we can observe that below 550 °C, TGA curve of Phyt/PEI-TA is very similar to that of the more thermally stable compound, i.e. phytic acid. Moreover, the presence of tannic acid, which undergoes important mass loss between 250 and 350 °C did not affect Phyt/PEI-TA thermal stability. The presence of TA in combination with phytic acid and PEI enables avoiding its thermal degradation. Another advantage of combining phytic acid and tannic acid lies to the increase of the amount of char formed at 700 °C. In fact, at the end of TGA analysis, the amount of char is of about 53% in the case of Phyt/PEI-TA (53%) and is higher to that obtained with phytic acid (25 %). Tannic acid decomposes totally and any residue is left at the end of the analysis.

Moreover, TGA curves of Phy/PEI-TA, under air and nitrogen (Fig. 3b) evidence that its thermal behavior is not affected by the nature of gas used below 600 °C. Above 600 °C, some thermo-oxidative degradation of the char occurs but it does not significantly affect its amount at 700 °C, which is an important feature that remains almost high, i.e. 53% under air and 60% under N₂. It is worth mentioning that at the end to TGA analysis, an intumescent and porous char layer is left (Fig. 4). Phyt/PEI-TA can thus be considered to be a charring additive under both oxidant and anaerobic conditions. The high phosphorus content of Phyt/PEI-TA together

with the presence of tannic acid into its structure are mainly responsible for its high char forming ability. The combination of phosphorous and tannic acid enabled for the generation of important char residue during thermal decomposition [12].

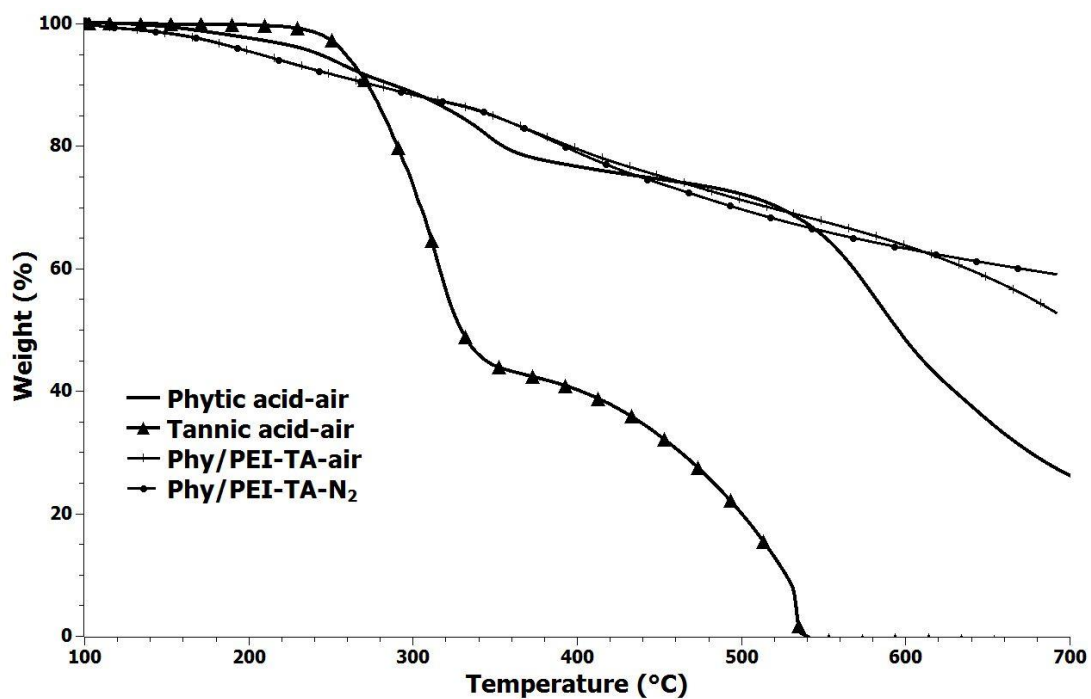


Figure 3: TGA curves of Phytic and tannic acid, under air, and Phyt/PEI-TA compound under both air and N₂ atmosphere (20 °C/min).



Figure 4: images of the char formed during TGA analysis (under air) of Phyt/PEI-TA.

3.2. Effect of Phyt/PEI-TA on thermal stability and flame-retardant behavior of PLA

Based on TGA results, Phyt/PEI-TA could be advantageously used for enhancing PLA flame retardant behavior thanks to its high char forming ability. Having this in mind, 20 wt% of this novel additive was incorporated into PLA by melt processing. It is worth mentioning that the incorporation of Phyt/PEI-TA does not induce any significant degradation of PLA during melt processing; In fact, SEC analysis (Table 2) shows that the number-average molecular weight of PLA decreased only from 99000 g/mol to 79000 g/mol in the presence of 20 wt% Phyt/PEI-TA. SEM images taken from composite sample (Fig. 5) show that the Phyt/PEI-TA complex is constituted of small spherical micro-sized particles (1 to 20 μm) that are very well dispersed in PLA.

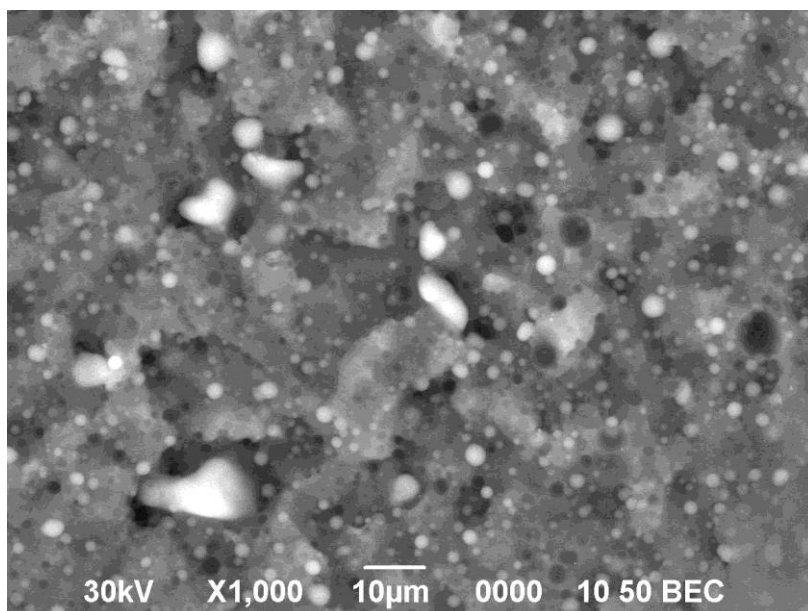


Figure 5: SEM image of the composite morphology.

3.2.2. Thermal behavior

The effect of the addition of Phyt/PEI-TA particles on PLA thermal stability has been investigated using TGA analysis under both oxidant and anaerobic condition (Fig. 6). The temperatures at 20 % weight loss ($T_{20\%}$) and at the maximum weight loss rate (T_{max}) as well as the char yield at 700 °C were determined from TGA and DTG curves, and the values are summarized in Table 2.

Thermal and thermo-oxidative degradations of PLA are single stage processes, starting at 320 °C under nitrogen and 300 °C under air, without formation of any residue at 700 °C.

The initial decomposition temperature of PLA under inert atmosphere (320 °C) is higher to that obtained under oxidizing conditions (300 °C), evidencing that the onset bond scission is sensitive to thermal-oxidation.

The incorporation of Phyt/PEI-TA into PLA was found to induce important changes in the composite thermal stability. Regardless of the testing atmosphere, the incorporation of Phyt/PEI-TA shifts TGA curves toward higher temperatures, since 300 °C and 320 °C under air and nitrogen atmosphere respectively. In contrast to unfilled PLA, the composite thermal stability is not affected by the presence of oxygen since $T_{-5\%}$, $T_{-20\%}$ and T_{max} recorded for the composite under air (360 °C, 390 °C and 412 °C) are very close to those under inert atmosphere (366 °C, 395 °C and 417 °C).

The calculated TGA curves (linear addition of the weight loss of the components degraded separately under air and nitrogen atmosphere) for PLA containing 20 wt% Phyt/PEI-TA was compared to the experimental curves in order to evaluate the interaction between PLA and Phyt/PEI-TA during the degradation, Figure 7. When PLA and Phyt/PEI-TA are separately degraded without interaction, it could be expected that the calculated TGA curve might be similar to that of experimental one. Interestingly, the comparison of calculated and experimental curves is revealed a significant difference. The calculated curves, in both N₂ and air atmospheres, showed less thermal stability than experimental curves which evidences the presence of some interactions between PLA and Phyt/PEI-TA during the degradation. However, the obtained char quantity is similar in calculated and experimental curves.

Thus, the use of Phyt/PEI-TA enables enhancing PLA thermal stability as well as modifying its thermal decomposition pathway from non-charring to char forming degradation. Its use strongly limits the composite thermal-oxidation owing to its char forming ability that limits oxygen diffusion through the material. At 700 °C, a final residue of about 10% is left under oxygen and 12.5% under nitrogen. A small difference between the residue yield formed under anaerobic and oxidant conditions evidence the important resistance of the residue against oxidation.

In conclusion, the incorporation of Phyt/PEI-TA enables for significant improvement of PLA thermal stability and to the formation of thermally stable char residue whatever the testing atmosphere. Thanks to these positive effects, it is expected that the incorporation of Phyt/PEI-TA into PLA enables for obtaining a material with improved flame retardant behavior.

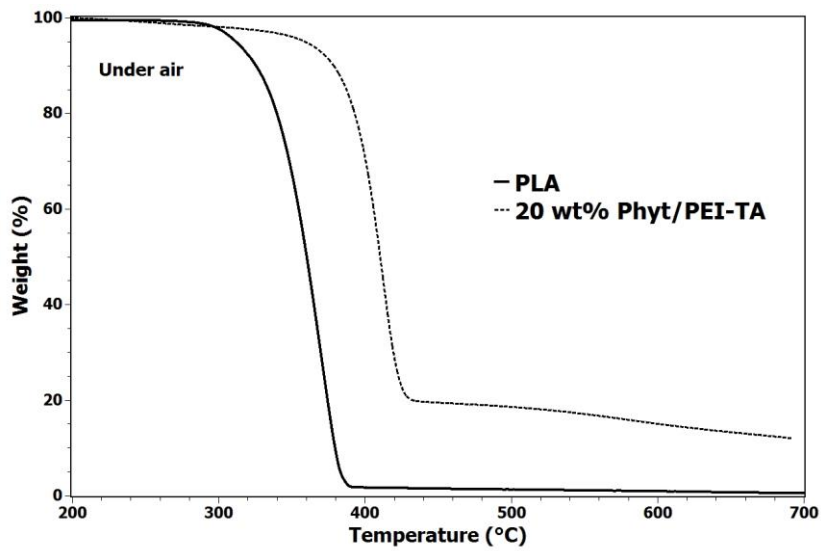
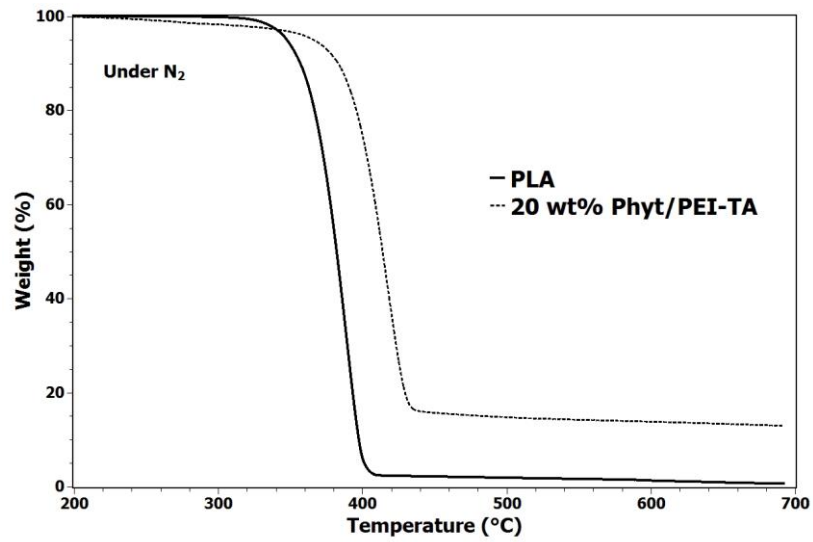


Figure 6: TGA curves of PLA and PLA containing 20 wt% Phyt/PEI-TA under nitrogen and air atmospheres (20 °C/min).

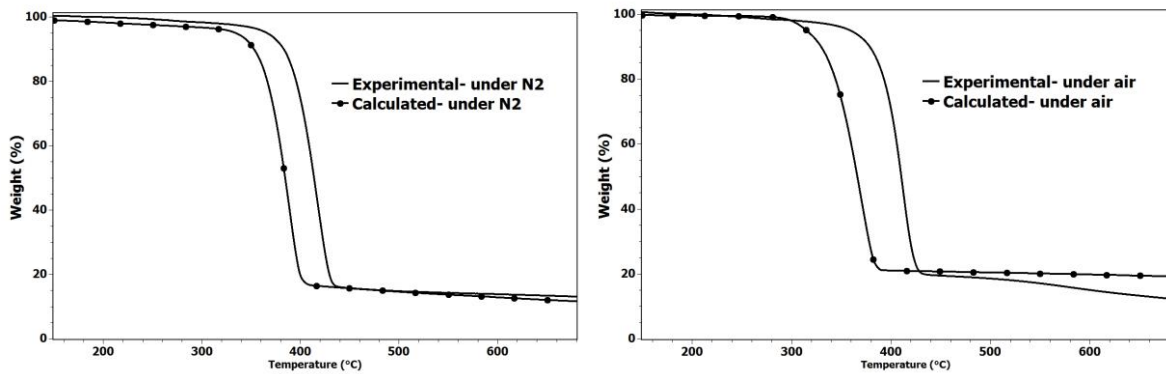


Figure 7: Calculated and experimental TGA curves for PLA containing 20 wt% Phyt/PEI-TA.

	TGA (under N ₂)				TGA (under air)				SEC
	T _{.5%} (°C)	T _{.20%} (°C)	T _{max} (°C)	Residue (%)	T _{.5%} (°C)	T _{.20%} (°C)	T _{max} (°C)	Residue (%)	M _n (g/mol)
PLA	347	366	390	0	313	340	370	0	99000
20 wt% Phyt/PEI-TA	366	395	417	12.5	360	390	412	10	79000

Table 2: TGA and SEC data of pristine PLA and composite containing 20 wt% Phyt/PEI-TA.

3.2.3. Fire behavior

Figures 8A and 8B show the heat release rate curves of PLA and PLA containing 20 wt% Phyt/PEI-TA. Pristine PLA exhibits a strong combustion, starting after 34 s, consuming all the material and releasing a total heat of about 66.7 MJ/m² with a pHRR of 670 kW/m². In the presence of Phyt/PEI-TA, curves and Table 3, an important decrease in both pHRR (-36 %) and THR (-13 %). The incorporation of Phyt/PEI-TA did not induce any improvement of the composite resistance to ignition. In fact, only a slight change of the time to ignition from 34 s to 26 s has been observed. This result does not support the improvement of the thermal stability observed during TGA analysis and demonstrate that no correlation could be done between thermal stability during TGA analysis and time to ignition during cone calorimeter test. In fact, several factors such as sample shape and weight, thermal conductivity and diffusivity are dependent on the type of the analysis. A significant change in the shape of HRR curve is noticed from unimodal to bimodal curve. HRR curve of PLA/Phyt/PEI-TA blend is characteristic of a thermally thick charring material while that of unfilled PLA is characteristic of thermally thin samples according to the classification of Scharrel and Hull [13]. In fact, HRR curve of pristine PLA presents a sharp HRR peak, indicating that the whole sample is pyrolyzed at the same time while a second HRR peak, corresponding to the char cracking and to the release of further combustible compounds, is recorded for the composite.

The pHRR reduction is due to the presence of Phyt/PEI-TA that induced the formation of a char residue during the combustion. A residue of about 19.4% is left at the end of the combustion (Table 3). Macroscopic scale observation shows the formation of a cohesive char layer (Fig. 9) while microscopic scale analysis confirms that its structure is not porous but very compact (Fig. 10).

These results clearly evidence that the presence of phosphorus in the FR additive structure greatly enhances the FR properties of the composite. It is worth remembering that thanks to its high phosphorus content (14 wt%), the incorporation of Phyt/PEI-TA, even at only 20 wt%, enables reaching an interesting phosphorus content in the composite, i.e. 2.8 wt%. Tannic acid, that is also another constituent of Phyt/PEI-TA complex, similarly assisted in promoting char formation during the combustion. Tannic acid has been reported to act in the condensed phase through the formation of an effective char layer, especially when combined with phosphorus [12].

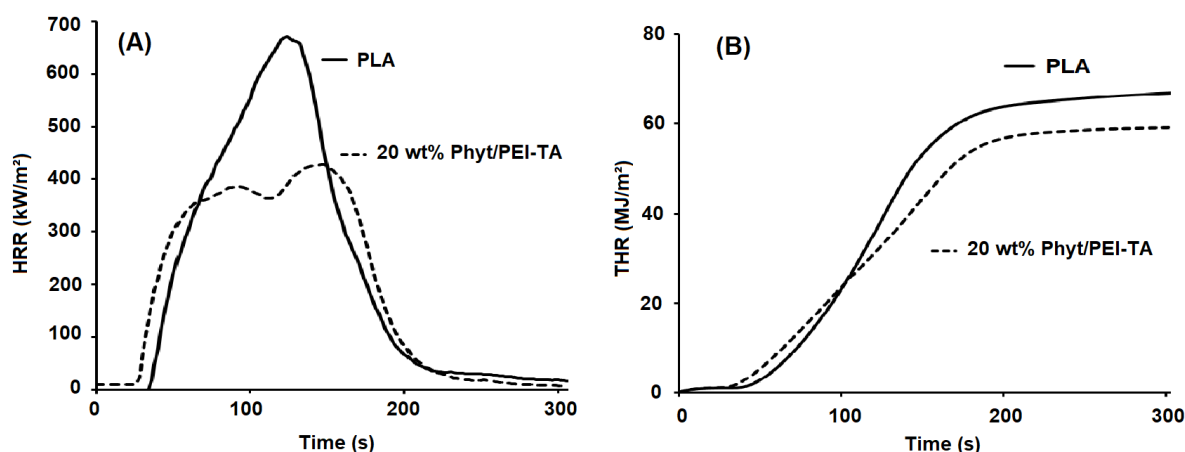


Figure 8: (A) Heat release rate and (B) total heat release of PLA and PLA containing 20wt% Phyt/PEI-TA from cone calorimeter test (irradiance: 35 kW/m²).

	TTI (s)	pHRR (kW/m ²)	pHRR reduction (%)	THR (Mj/m ²)	THR reduction (%)	Residue (%)
PLA	34	670	-	67	-	0
20 wt% Phyt/PEI-TA	26	428	-36	58	-13	19.4

Table 3: Cone calorimeter results (35 kW/m²)

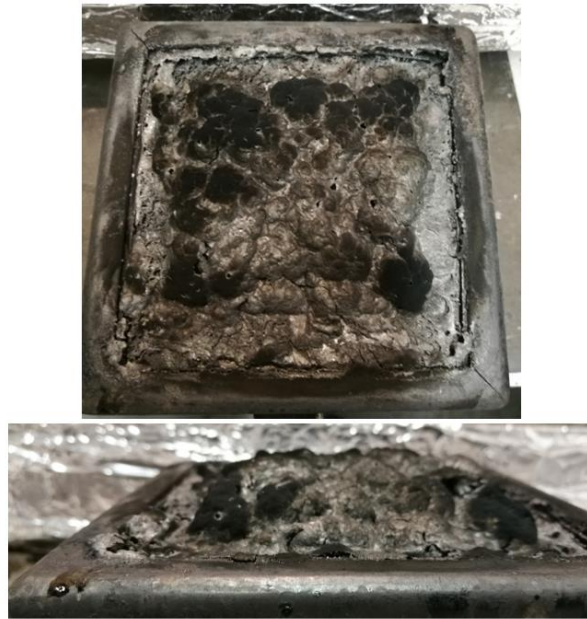


Figure 9: photographs of the residues remaining after the cone calorimeter test.

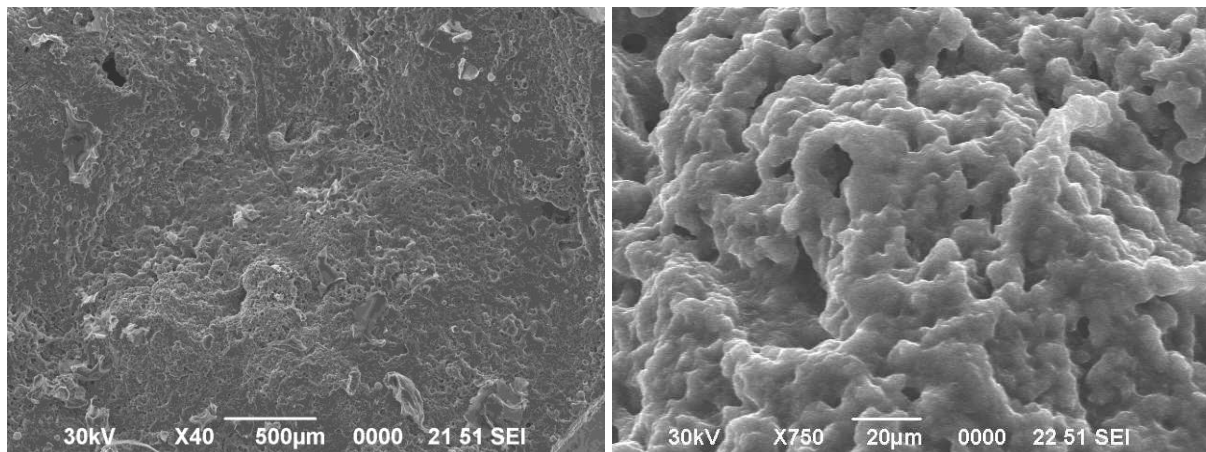


Figure 10: SEM images of the char residue obtained after the cone calorimeter.

The residue of cone calorimeter test was analyzed by Inductively Coupled Plasma (ICP) analysis to determine its phosphorus, nitrogen and carbon content. Table 1 presents the results and evidences that using Phyt/PEI-TA FR additive enables for the formation of a carbon-rich char composed by 39 wt% carbon. Moreover, it was possible to compare the evolution of P and N amount before and after the combustion (Fig. 11). It was found that the phosphorus mainly (more than 90 wt.%) remains in the condensed phase demonstrating that the presence of Phyt/PEI-TA induces mainly a condensed phase action with a barrier effect. This result is not surprising since both tannic and phytic acid based flame retardant agents have been found to act in the condensed phase by promoting the formation of char layer [12, 14]. However, some gas phase action is not excluded since some nitrogen is lost during the combustion.

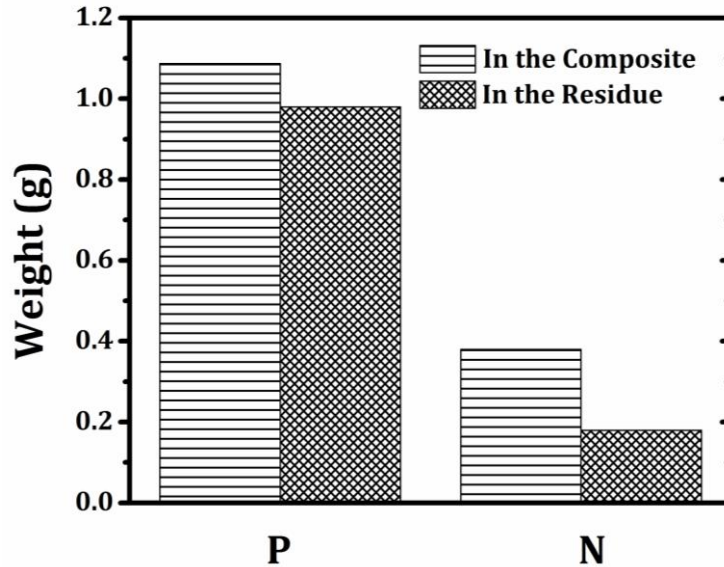


Figure 11: mass of phosphorus and nitrogen in the composite before the combustion and after the combustion in the residue.

The flammability was also investigated using Pyrolysis Combustion Flow Calorimeter (PCFC) test. Figure 12 displays HRR curves of PLA and PLA containing 20 wt% Phyt/PEI-TA. It is worth mentioning that samples used during PCFC analysis (few mg) were very smaller than those used during cone calorimeter test (around 40 g). This makes the comparison between PCFC and cone calorimeter results very difficult. However, PCFC test results can provide precious information on the flammability of the released gases that could reveal any changes of the chemical nature of the degradation product.

HRR curves obtained during PCFC tests showed that both PLA and the composite exhibit one heat release rate. Moreover, the incorporation of Phyt/PEI-TA into the PLA was really beneficial and had two important impacts on PLA flammability. First, the peak of HRR and Total Heat Release (THR) were decreased from 550 to 330 W/g (-40%) and from 17 to 13.8 kJ/g respectively. Second, and in accordance with TGA measurements, the temperature of pHRR was shifted from 362 to 376 °C owing to the enhancement of the composite thermal stability. The decrease in both pHRR and THR recorded in the presence of Phyt/PEI-TA is due to its ability to form a char even during anaerobic composite decomposition (Figure 6). As a consequence, the amount of gases decreases since a part of both polymer and additive remains in the condensed phase.

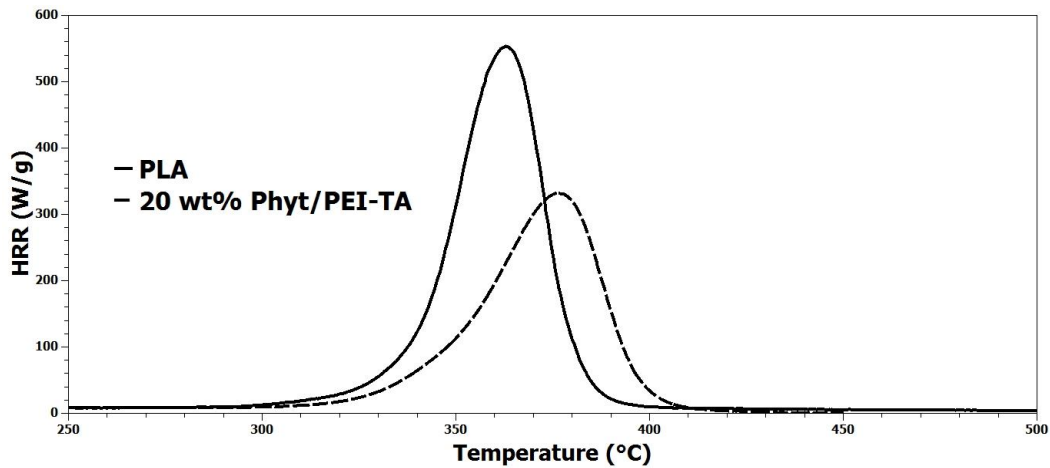


Figure 12: Heat Release Rate (HRR) curves obtained from PCFC tests.

The performance of new bio-based flame retardant (Phyt/PEI-TA) in PLA was compared to different flame retardant for PLA (bio and non-biobased FR) through a detailed review of the literature, Fig.13 and Annexe 1. The comparison was performed by a focus on more than 60 flame retardant systems. Two important values were extracted from the literatures which are flame retardant content and reduction in pHRR, Annexe1. The reduction in pHRR was then plotted as a function of flame retardant content (wt%), Fig.13. It must be noted that even if some parameters such as heat flux and PLA grade in different works, however we compared only “the reduction in pHRR”. First, we can observe that flame retardants used in PLA are not mostly bio-based (black points, Fig.13). Secondly, our flame retardant (Phyt/PEI-TA), with 36% reduction in pHRR, offers a relatively acceptable performance compared to other bio-based flame retardants.

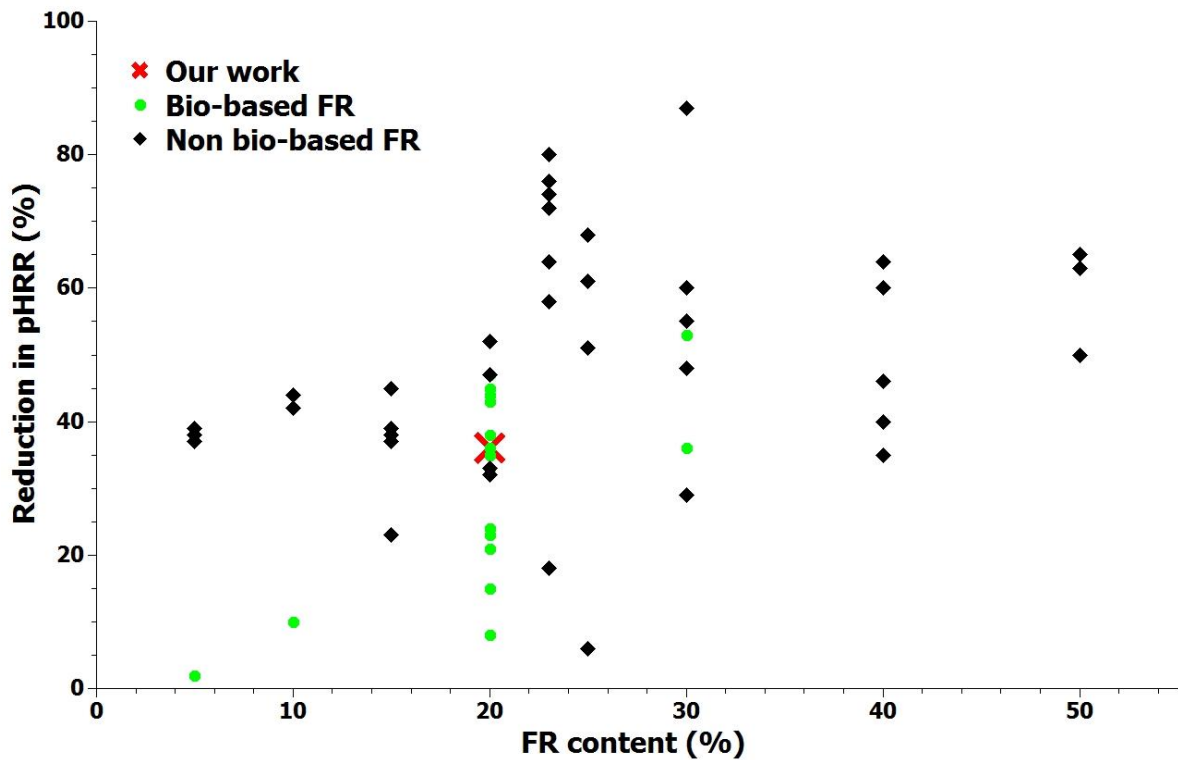


Figure 13: Reduction in pHRR as a function of flame retardant content for PLA systems (bio-based FR and non-bio-based flame retardant points were collected from the literature).

This performance would be of higher importance considering the effect of the FR additive on PLA thermal degradation during melt processing (Table 2). In the presence of newly developed bio-based flame retardant (Phyt/PEI-TA), PLA underwent limited thermal degradation and its molar mass decreased from 99000 to 79000 g/mol (-20.3%). This result was compared to the reduction of PLA molar mass obtained with other bio-based flame retardant from the literature as well as the reduction in pHRR of each system. Figure 14 displays this investigation and shows that only one bio-based flame retardant induces lower PLA thermal degradation but without leading to any significant pHRR reduction.

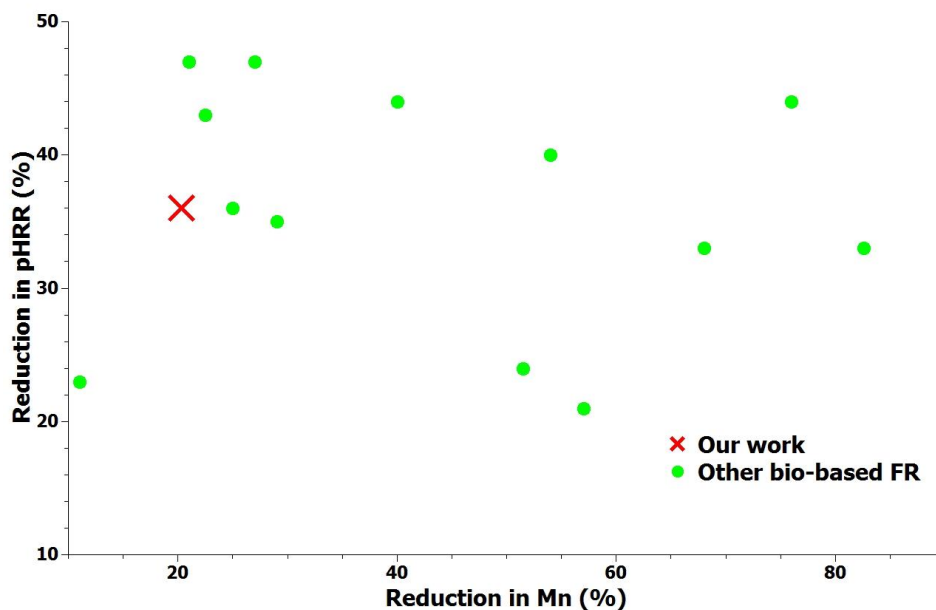


Figure 14: Reduction in pHRR as a function of reduction in molar mass (Mn) (other bio-based FR points were collected from the literature).

4. Conclusion

This paper reports on the synthesis and the flame retardant action of a novel bio-based Phosphorus-Nitrogen containing flame retardant additive (Phyt/PEI-TA) for PLA. Phyt/PEI-TA was prepared by coupling two bio-based compounds together, i.e. tannic acid and phytic acid. These two molecules were successfully linked thanks to the action of cationic branched polyethyleneimine (PEI) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride. The resulting FR agent was characterized using several techniques (FTIR, TGA and ICP). TGA data show that Phyt/PEI-TA thermal degradation enables for obtained char residue under both anaerobic and oxidant conditions owing to its composition (13% of phosphorus, 2.4% of nitrogen and 39% of carbon). The thermal stability as well as fire retardancy performance of PLA containing 20 wt% Phyt/PEI-TA were then examined. SEM observations showed well dispersed Phyt/PEI-TA microparticles into the PLA. TGA analysis evidenced significant enhancement of the composite thermal stability in comparison with pristine PLA. Furthermore, the presence of Phyt/PEI-TA in PLA did not affect the onset of degradation. Moreover, the distinct difference between the calculated and experimental TGA results indicated a strong interaction between Phyt/PEI-TA and PLA during the degradation. Composite containing 20 wt% Phyt/PEI-TA exhibited improved flame retardant properties during cone calorimeter test since both pHRR and THR were reduced by 36 % and 13 %,

respectively. However, a slight decrease in TTI was to deplore. In addition to cone calorimetry results, the investigation of char residue revealed that the principal action of Phyt/PEI-TA was in the condensed phase by promoting the formation of char and providing the flame retardancy by barrier effect. Finally, the comparison of obtained results in this study and those of the literature revealed the properness of our new bio-based flame retardant.

Annex 1: collected data from the literature on “Flame retardancy of PLA”.

N°	Name(s) of Flame retardant(s), incorporated into PLA	Wt.% FR	Reduction in pHRR (%)	Ref.
1	Melamine/APP	30	87	16
2	APP/PER	40	64	17
3	APP/LIG	40	46	17
4	APP/starch	40	40	17
5	MCAPP/lignin	23	58	18
6	MCAPP/Lignin/octadecyl trimethylammonium and cetyltrimethylammonium	23	76	18
7	MCAPP/Lignin/methyl tallow bis(2-hydroxyethyl) ammonium	23	80	18
8	MCAPP/Lignin/dioctadecyl dimethyl ammonium bromide	23	72	18
9	Melamine/APP	30	29	19
10	Melamine/APP/MMT	30	60	19
11	APP	23	18	20
12	APP/ modified lignin	23	74	20
13	APP/lignin	23	64	20
14	APP	15	23	21
15	APP/expandable graphite	15	39	21
16	APP/PER	15	37	22
17	PP/nanofibrillated cellulose	15	38	22
18	PP/POSS-modified nanofibrillated cellulose	15	45	22
19	MPP	20	33	22
20	OP1311	25	6	22
21	APP	25	51	23
22	Tris(2-hydroxyethyl) isocyanurate polyphosphate melamine (TPM)	25	61	23
23	APP/TPM	25	68	23
24	APP	5	38	24
25	Lignin	5	2	24
26	APP/Lignin	20	32	24
27	ATH	30	29	25
28	ATH/MMT	30	48	25
29	ATH/MMT	30	55	25
30	ATH	40	35	25
31	ATH/MMT	40	60	25
32	ATH/MMT	40	60	25
33	ATH	50	50	25
34	ATH/MMT	50	63	25
35	ATH/MMT	50	65	25
36	Functionalized α -zirconium phosphate	5	37	26
37	Functionalized α -zirconium phosphate	10	42	26
38	Functionalized α -zirconium phosphate	20	52	26
39	α -zirconium phosphate	5	39	26
40	α -zirconium phosphate	10	44	26
41	α -zirconium phosphate	20	47	26
42	kraft lignin	20	21	5
43	Organosolv lignin	20	33	5
44	Na- Phytate	20	23	15

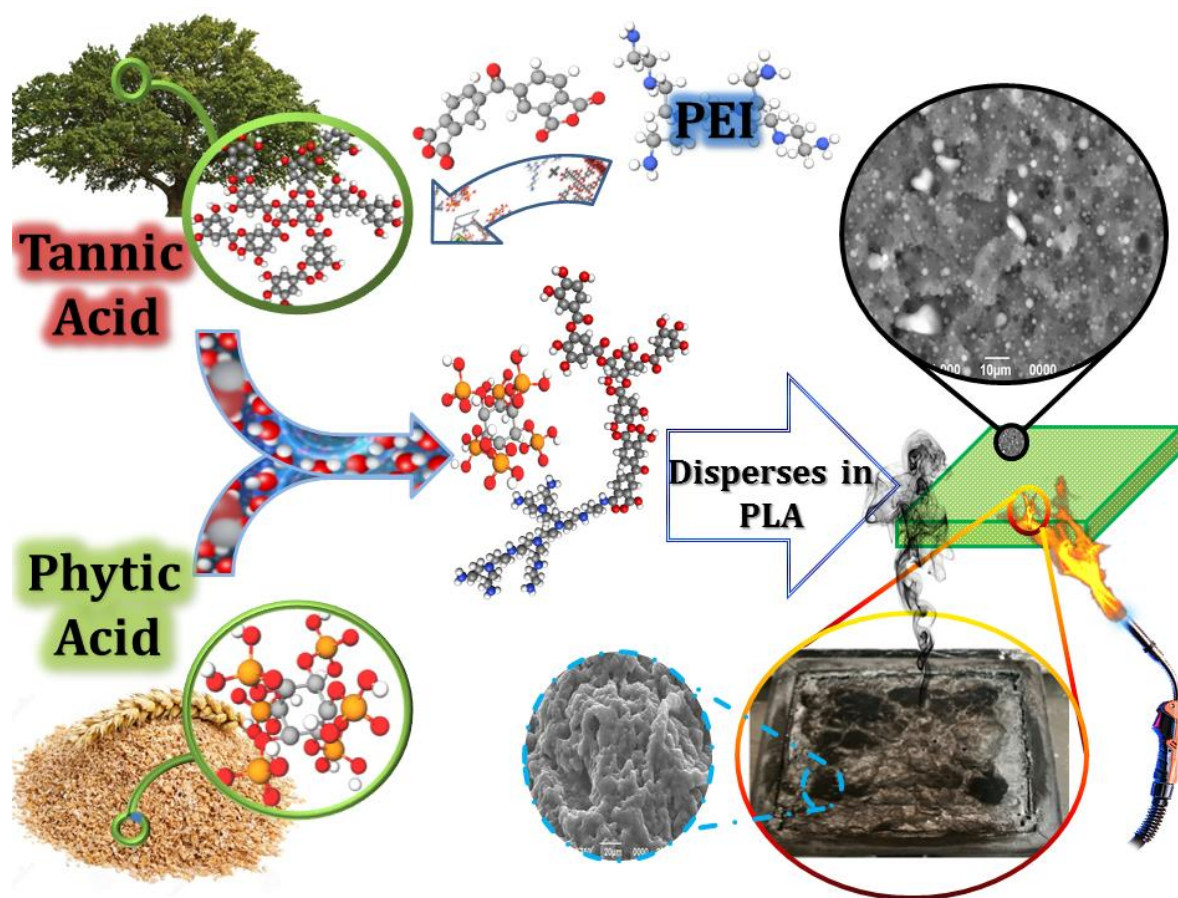
45	Na- Phytate	30	36	15
46	Al- Phytate	20	44	15
47	Al- Phytate	30	53	15
48	Fe- Phytate	20	24	15
49	La- Phytate	20	35	15
50	Na- Phytate /Al- Phytate	20	47	15
51	Na- Phytate /Fe- Phytate	20	47	15
52	Na- Phytate /La-Phytic acid	20	43	15
53	Na- Phytate /Al-P Phytate	20	45	15
54	Na- Phytate /Fe- Phytate	20	36	15
55	Na- Phytate /La- Phytate	20	36	15
56	MicroCrystalline Cellulose	20	8	8
57	NanoCrystalline Cellulose	20	35	8
58	Al-Phytate	10	10	8
59	Al-Phytate	20	44	8
60	Al- Phytate /MicroCrystalline Cellulose	20	15	8
61	Al- Phytate /NanoCrystalline Cellulose	20	38	8
62	phosphorylated MicroCrystalline Cellulose	20	15	8
63	Al- Phytate /phosphorylated MicroCrystalline Cellulose	20	33	8
64	Al- Phytate /phosphorylated MicroCrystalline Cellulose	20	38	8

Annex 2: collected data from the literature on “Flame retardancy and mass molar of Flame retarded-PLA”.

N°	Name(s) of Flame retardant(s), incorporated into PLA	Reduction in pHRR (%)	*Reduction in molar mass (%)	Ref.
1	Phytate Na	23	11	15
2	Phytate Fe	24	51.5	15
3	Phytate La	35	29	15
4	Phytate Al	44	76	15
5	phyt Al/ phyt Na	47	21	15
6	phyt Fe / phyt Na	47	27	15
7	phyt La/ phyt Na	43	22.5	15
8	organosolv lignin	33	82.6	5
9	kraft lignin	21	57	5
10	organosolv lignin phosphorus	33	68	5
11	kraft lignin phosphorus	40	54	5
12	kraft /phytic	44	40	13
13	organosolv / phytic	36	25	13

*Molar mass of all PLA used in these studies was around 100000 g/mol.

Graphical Abstract



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