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Metallic phytates as efficient bio-based phosphorous flame retardant additives for poly(lactic acid)

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A B S T R A C T

In this study, we evaluated the potential flame retardant effect of different metallic phytates as bio sourced phosphorous additives for poly(lactic acid) (PLA). Starting from sodium phytate, the sodium cations were replaced by aluminum, iron or lanthanum cations as attested by elemental analysis. PLA metallic phytate composites containing 20 or 30 wt% of additives were produced by melt blending in an internal mixer and their fire properties, thermogravimetric resistance have been characterized as well as the PLA chain degradation occurring during melt processing. The most significant flame retardant effect, observed by cone calorimeter test, was obtained when aluminum phytate was used. Cone calorimeter testing combined with pyrolysis combustion flow calorimetry (PCFC) analysis indicated that the barrier effect was more significant in the case of PLA filled with aluminum phytate. However, aluminum phytate proved to be responsible for PLA chain degradation during melt processing. Combinations of metallic phytate and native sodium phytate overcame this negative effect and allowed for limiting the thermal degradation of PLA during melt processing while preserving good fire performances, i.e. significant pHRR reduction and V 2 classification in UL 94 test.

Keywords:

Metallic phytates

Bio-based flame retardant

Poly(lactic acid)

1. Introduction

In the past two decades, a lot of research activities have increasingly focused on the use of renewable resources due to the growing concern on environmental pollution issued from fossil feedstock. Great interest is more and more devoted to improve the sustainability of polymers owing to their importance in our daily life thanks to their high versatility in terms of properties, processing and recycling capability. Poly(lactic acid) (PLA), that represents one of the most promising biosourced polymers, is mainly used in packaging field and biomedical applications [1,2] taking advantage of relevant mechanical properties such as high stiffness, high degree of transparency, gas permeability and biocompatibility in addition to relatively low cost and large production volume [3,4]. Recently, some more durable applications for PLA, especially in automotive, electronics, and construction industries have emerged

and required PLA grades with improved properties such as higher impact resistance and tensile strength, higher service temperature, i.e., increased head distortion temperature (HDT), long term stability, increased crystallization extent and kinetics as well as flame retardant behavior.

Flame retardancy is an active research subject developing versatile and efficient strategies to endow polymers with good fire resistant properties [5]. More and more, the use of new halogen free flame retardant systems is investigated to reduce health and environmental impact. Flame retardant systems promoting the formation of an insulating char layer during combustion are amongst the most promising strategies to replace halogen flame retardant compounds in PLA. The current trend now relies upon the development of environmentally friendly flame retardant systems [6–8]. With this view, Wang et al. [7] synthesized a phosphorylated pre poly(lactic acid) to be incorporated into PLA. The fire performances of the blend were improved with the increasing amount of phosphorus content. The use of biosourced char forming agents, such as lignin, starch or β cyclodextrin, in PLA has been studied as a way to develop more environmentally friendly materials [9–18]. Reti et al. [14] evaluated the efficiency of intumescent formulations

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containing ammonium polyphosphate (APP) combined with different carbonization agents. They found out that the composite containing 60% PLA, 12% APP and 28% starch reaches better fire properties (VO classification and 32% LOI value) than the traditional ammonium polyphosphate/pentaerythritol system.

Amongst the existing halogen free flame retardants, phosphorus based compounds are the most promising additives in polyesters such as polyethylene terephthalate (PET) and PLA. In order to enhance their flame retardant efficiency, phosphorus based flame retardant additives are usually associated to other synergistic agents such as phenolic resins [19], melamine [20], montmorillonite [21,22], carbon nanotubes [23], expandable graphite [24] and some metallic compounds [25–28]. The use of metallic compounds as synergistic additives for phosphorous based flame retardant systems proved to be very promising owing to the wide range of structures and chemical formulations available. Metal could be associated with phosphorous compounds under various forms such as combination of phosphorous flame retardant agents with metallic oxide nano/micro particles [29–32], phosphinate salts [33], metallic hypophosphite [34] or by grafting phosphorylated compounds onto the surface of metallic nano oxides [35]. The use of metallic compounds helps for improving the thermal stability of the char layer generated during the combustion and makes it stronger and more robust [36].

Some metallic compounds are more effective than others and the reasons for these differences are not always clear. In the case of metallic phosphinates, different works indicated that the salt mostly operates in the gas phase by flame inhibition mechanism and its efficiency is directly related to its availability to evolve from the condensed to the gas phase [37,38]. This evolution could be due to the volatilization of the salt with or without thermal decomposition. The higher volatility of the salt results in the better flame retardant efficiency [39]. Other works attributed the difference of efficiency of the metallic/phosphorus combination to the thermal stability of the metallic/phosphorus crystalline form generated during the combustion [40,41].

The objective of this work is to study the effect of different metallic phytate salts as biosourced phosphorous flame retardant additives for PLA. Few studies reported the use of phytic acid or salts in combination with other flame retardant additives [42–46] but not as a unique FR agent. The literature on this subject is very limited. In our study, starting from sodium phytate, the sodium cations were replaced by three different metallic cations: aluminum, iron and lanthanum. The replacement of sodium by metallic cations has been performed in order to take advantage of the well known flame retardant synergy that occurs between phosphorus and some metallic compounds during combustion (*vide supra*) [31,32]. PLA/phytate composites were prepared by melt blending and their thermal stability and fire properties investigated by TGA, cone calorimetry, UL 94 and pyrolysis combustion flow calorimetry (PCFC). Scanning electron microscopy (SEM) was used to characterize the composite morphology. The effect of the different additives on PLA thermal degradation during melt processing was also investigated by using gel permeation chromatography (GPC).

2. Experimental section

2.1. Materials

PLA resin (3051D) with a molecular weight of 180,000 and 3.3% of D lactide content was purchased from NatureWorks. Sodium phytate, aluminum chloride, iron chloride and lanthanum chloride were purchased from Sigma Aldrich.

2.2. Preparation of metallic phytates

Metallic phytates, aluminum phytate (Al Phyt), iron phytate (Fe Phyt) and lanthanum phytate (La Phyt) were obtained by mixing a 0.1 M aqueous solution of sodium phytate (Na Phyt) with another 0.5 M aqueous solution of metallic trichloride (AlCl_3 , FeCl_3 or LaCl_3). The two solutions were mixed together and the system was refluxed at 100 °C under constant mechanical stirring for one hour. The precipitated metallic phytates were washed by centrifugation with deionized water (five times) and freeze dried.

2.3. Melt processing

Blending of metallic phytates within the molten PLA was carried out in a Brabender internal mixer at 160 °C (7 min mixing at 70 rpm). PLA and metallic phytates were previously dried in a vacuum oven at 60 °C overnight before use. Plates (100*100*4 mm³) for cone calorimeter testing and sheets (100*150*3 mm³) for UL 94 specimens were compression molded at 160 °C using an Agila PE20 hydraulic press. The investigated formulations are summarized in Table 1.

2.4. Characterizations

Gel permeation chromatography (GPC) was used to determine the number average molecular weights of PLA. The number average molecular weights and molecular weight distributions of the polymers were determined in CHCl_3 at 23 °C using an Agilent size exclusion chromatograph equipped with a Knauer 2320 refractometer index detector and two PLGel columns (MIXED D and 10³ Å). Samples were dissolved in CHCl_3 (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.

Scanning electronic microscopy (SEM) was used to attest for the dispersion state of the different metallic phytates in PLA matrix. Observations were performed on the surface of samples previously cryo fractured at liquid nitrogen temperature, and by using a SEM Philips XL at an accelerated voltage up to 30 kV and various magnitudes.

Inductively Coupled Plasma (ICP) analysis was used for the determination of the amount of phosphorus as well as sodium, aluminum and lanthanum in the different phytate salts and the different char residues. The total Organic Carbon (TOC) in these salts and these residues has been determined by using Vario TOC from Elementar.

Thermogravimetric analysis (TGA) was used to assess the thermal degradation of metallic phytates, the effect of their incorporation on both thermo oxidative decomposition of PLA and thermal stability of the char generated during cone calorimeter test. Approximately 10 mg of the sample was submitted to a temperature ramp from 25 to 600 °C at a heating rate of 20 °C/min. All the TGA experiments were performed under a flow of 90 ml/min of air using a TGA Q50 device from TA Instruments.

The cone calorimeter tests were performed according to ISO 5660 standard procedure. Samples were exposed to an external heat flux of 35 kW/m². For each formulation, at least, two samples were tested. The heat release rate (HRR) was measured from both oxygen consumption calorimetry and carbon oxides generation calorimetry [47]. Results from both calorimetric methods were in good agreement and thus confirmed the good quality of these measurements.

The pyrolysis combustion flow calorimetry (PCFC) analysis were performed using an FTT apparatus. 2–3 mg samples were heated to 750 °C at a heating rate of 1 K/sec in a stream of nitrogen. The

Table 1

Formulations of flame retarded PLA composites.

Sample	PLA (wt %)	Na-Phyt (wt %)	Al-Phyt (wt %)	Fe-Phyt (wt %)	La-Phyt (wt %)
PLA	100				
20 Na-Phyt	80	20			
30 Na-Phyt	70	30			
20 Al-Phyt	80		20		
30 Al-Phyt	70		30		
20 Fe-Phyt	80			20	
20 La-Phyt	80				20
10 Na-Phyt/10 Al-Phyt	80	10	10		
10 Na-Phyt/10 Fe-Phyt	80	10		10	
10 Na-Phyt/10 La-Phyt	80	10			10
15 Na-Phyt/5 Al-Phyt	80	15	5		
15 Na-Phyt/5 Fe-Phyt	80	15		5	
15 Na-Phyt/5 La-Phyt	80	15			5

combustor temperature was fixed at 900 °C, and the oxygen/nitrogen ratio was 20/80.

UL 94 vertical burning tests were performed according to ISO 7629 0082 2 standard procedure. Five specimens of 125*13*3 mm³ were subjected to two flame applications of 10 s each. The afterflame times and afterglow time were measured, and the eventual cotton ignition by flaming particles drops was recorded. UL 94 vertical burning test results in sample classification as V 0, V 1 or V 2.

3. Results and discussion

3.1. Characterization of metallic phytates

Table 2 shows the atomic composition determined in weight % of dry powder of the four metallic phytates prepared. These results indicate that the investigated chemical modification method allows replacement of sodium by aluminum, iron or lanthanum cations. Indeed, the modified metallic phytates contain only traces of sodium. The chemical formula of each metallic phytate is C₆H₁₈-xP₆O₂₄M_x.yH₂O with x indicating the proportion of metallic cations and y the proportion of water. The proportion of metallic cations in each metallic phytate has been calculated from the mass percentages and is indicated in Table 2.

The replacement of sodium by the other metallic cations leads to some differences in the thermal behavior of phytate salts as shown on TGA curves (Fig. 1). Sodium phytate and iron phytate are those allowing the formation of a smaller amount of char during their thermal degradation. In contrast, the replacement of sodium by aluminum or lanthanum cations leads to the formation of higher amounts of char. The amount of absorbed water is also varying depending on the metallic cation of the phytate. Fe Phyt and Al Phyt are the most hygroscopic salts.

3.2. PLA/metallic phytate properties

3.2.1. Dispersion state of metallic phytates

SEM observations (Fig. 2) of PLA containing 20 wt% of the different metallic phytates do not show any phytate salt

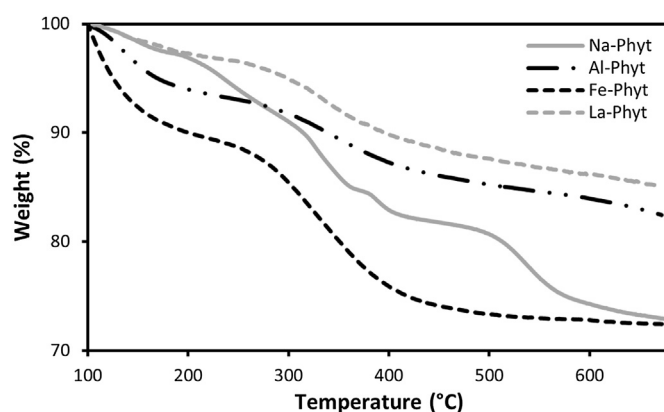


Fig. 1. Effect of the metallic cation on the thermal decomposition of phytate salts (20 °C/min) under air.

aggregation but demonstrate the presence of well dispersed submicronic domains spread in the continuous PLA phase. The formation of such morphology highlights good affinity between the metallic phytates and PLA.

3.2.2. Thermal degradation

The incorporation of the different metallic phytates affects the thermal stability of PLA based composites. In fact, as seen on Fig. 3, below 375 °C, the incorporation of the different metallic phytates decreases the thermal stability of PLA, especially in cases of Al Phyt and Fe Phyt. Above 375 °C, the rate of mass loss decreases owing to the formation of a char layer during the thermal decomposition. At the end of the thermal decomposition, a char residue of about 15 wt % is generated.

3.2.3. Effect of processing on molecular weight of PLA

The thermal degradation of PLA, triggered by the presence of the different phytates, occurs also during melt processing as observed on Fig. 4. In fact, the incorporation of Al Phyt and Fe Phyt strongly reduces PLA molecular weight in contrast with Na Phyt and La

Table 2

Atomic composition of metallic phytates.

	C		P		Na		Al		Fe		La	
	Wt%	Atom nb	Wt%	Atom nb	Wt%	Atom nb	Wt%	Atom nb	Wt%	Atom nb	Wt%	Atom nb
Na-Phyt	8.201	6	18.1	6	13.9	6						
Al-Phyt	6.523	6	19.3	6	0.033		8.95	3				
Fe-Phyt	6.144	6	14.6	6	0.054				16.0	4		
La-Phyt	5.691	6	13.5	6	0.096						29.5	3

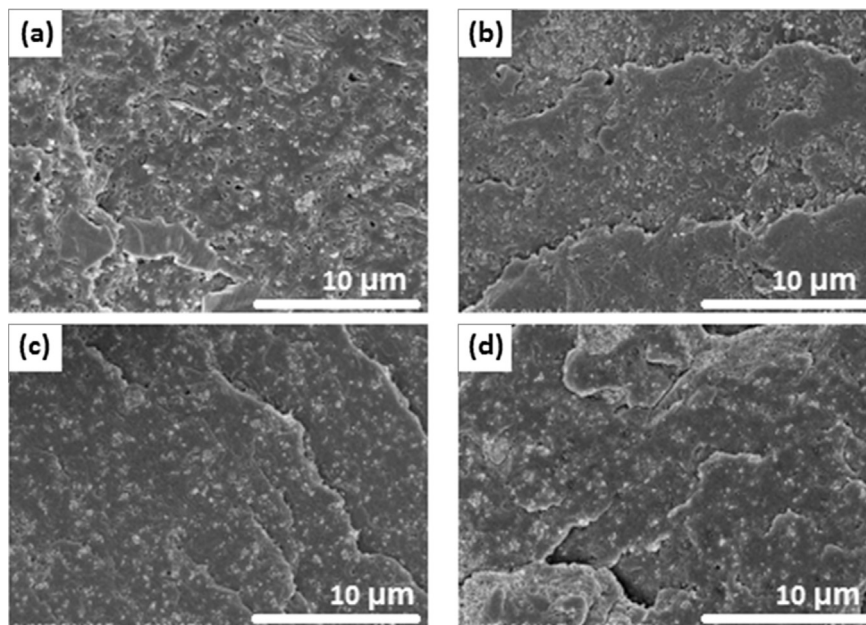


Fig. 2. SEM pictures of (a) PLA/20 Na-Phyt, (b) PLA/20 Al-Phyt, (c) PLA/20 Fe-Phyt and (d) PLA/20 La-Phyt.

Phyt, which trigger a limited degradation of PLA during melt processing. These observations are in good accordance with previously discussed TGA results that highlighted the degrading effect of both Al Phyt and Fe Phyt.

3.2.4. Cone calorimetry

The cone calorimeter is the most significant bench scale instrument to evaluate flame retardancy of materials. It provides key information about flame retardant properties of composites such as heat release rate (HRR), total heat release (THR) and time to ignition (TTI).

The results of cone calorimeter tests of PLA and PLA/metallic phytate composites are summarized in Table 3 and Figs. 5 and 6. Pristine PLA burns very fast after ignition and no residue is left at the end of the combustion. The efficiency of sodium phytate as phosphorous flame retardant agent for PLA is weak. Indeed, the use of 20 wt% and even 30 wt% of Na Phyt allows a pHRR reduction of only 23% and 36% respectively. The effective heat of combustion (EHC) is almost not reduced in respect with the EHC of pristine PLA.

In order to enhance the flame retardant efficiency of phytates, sodium cations were replaced by aluminum, iron or lanthanum cations with the view to develop synergistic effects between these

compounds.

Cone calorimeter results showed that only the replacement of sodium by aluminum cations allows for significant improvement of PLA fire behavior. Indeed, Fig. 5 and Table 3 show that the use of 20 wt% of Al Phyt leads to a strong reduction of pHRR (44%) and this reduction is higher than that obtained with 30 wt% of Na Phyt. Moreover, the use of Al Phyt leads to the lowest weight loss rate. The fire behavior of PLA filled with 20 wt% of Fe Phyt or La Phyt is similar to that obtained with Na Phyt. The chelation of phytate with aluminum cations improves its flame retardant efficiency but this positive effect is noticeable only on pHRR reduction and weight loss rate but no significant impact on total heat release (THR) reduction is observed. THR of PLA/Phytate composites are lower than that of unfilled PLA. Incorporation of 20 wt% of Al Phyt is sufficient to reach low pHRR since the increase of its content up to 30 wt% does not allow any additional significant reduction of pHRR as it can be seen on Table 3 and Fig. 6. We can also observe that the composite containing 20 wt% of Al Phyt leads to the lowest weight loss between 200 and 450 s. However, this composition does not generate higher final residual mass (15%) in comparison to that formed when

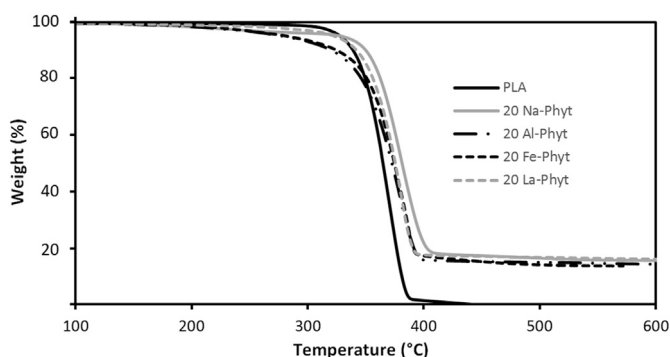


Fig. 3. TG curves of PLA and PLA/20% metallic phytate composites (20 °C/min) under air.

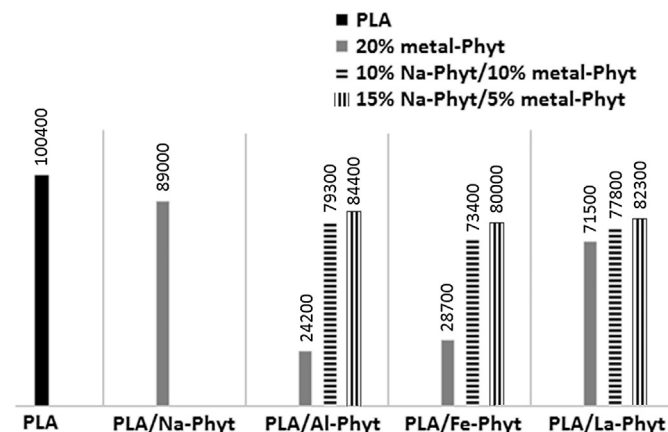


Fig. 4. Effect of the composition on the number average molecular weight of PLA.

Table 3

Cone calorimeter test results of PLA and flame retarded PLA-based composites.

Sample	TTI (s)	pHRR (kW/m ²)	% reduction	THR (MJ/m ²)	% reduction	Residual mass (%)	EHC KJ/g
PLA	86	388		92		0	19
20 Na-Phyt	84	297	23	76	17	18	18.5
30 Na-Phyt	86	250	36	71	23	23	18.6
20 Al-Phyt	77	217	44	73	21	15	17.8
30 Al-Phyt	86	184	53	65	29	22	17.2
20 Fe-Phyt	72	295	24	69	25	18	17.3
20 La-Phyt	70	252	35	73	21	19	18

La Phyt and Fe Phyt are used (around 18%). Thus, it came out that Al Phyt leads to a rapid char formation without improving its thermal stability.

As it can be seen on Fig. 7, the char residue at the end of the combustion is not thick neither cohesive. It is composed of isolated domains of carbonaceous char. The observation of the final char residue, generated during the combustion, does not allow any correlation between the cohesion of the char and the evolution of HRR during cone calorimeter test.

In order to further investigate the origin of the superior effect of aluminum phytate, PCFC analyses have been carried out.

3.2.5. Pyrolysis combustion flow calorimeter analysis (PCFC)

The heat release rate (HRR) curves versus temperature of PLA and PLA composites containing 20 wt% of metallic phytate are shown in Fig. 8. Table 4 summarizes the values of pHRR (W/g), maximum degradation temperature (T_{max}) and THR (kJ/g). Pristine PLA and PLA composites exhibit one heat release rate peak around 380 °C, which corresponds to the polymer degradation.

Combining cone calorimetry and PCFC results is an interesting

way to evaluate the barrier effect of flame retardant additives since PCFC is non sensitive to physical effects whereas both chemical and physical actions are effective in cone calorimetry. Hence, the pHRR of a flame retarded composite compared to the pHRR of the pristine polymer should be more decreased (or equal to) in cone calorimeter test than in PCFC.

To determine the main mode of action of the different metallic phytates, an evaluation was carried out by combining the results obtained with the cone calorimeter and the PCFC. This method was reported by Sonnier et al. [48]. Fig. 9 shows the evolution of R1 (Y axis) versus R2 (X axis) where R1 is the ratio between Heat Release Capacity (HRC) in PCFC of the flame retarded polymer and HRC in PCFC of the pristine polymer and R2 is the ratio of pHRR in cone calorimeter of the flame retarded polymer and the pHRR in cone calorimeter of the pristine polymer. Heat release capacity is equal to the pHRR divided by the heating rate (1 K/s).

As observed in Fig. 9, PLA composites filled with Al Phyt and La Phyt are above the straight line R1 = R2 (corresponding to similar decrease of pHRR in cone calorimeter and of HRC in PCFC). This result indicates that the pHRR reduction in cone calorimeter is

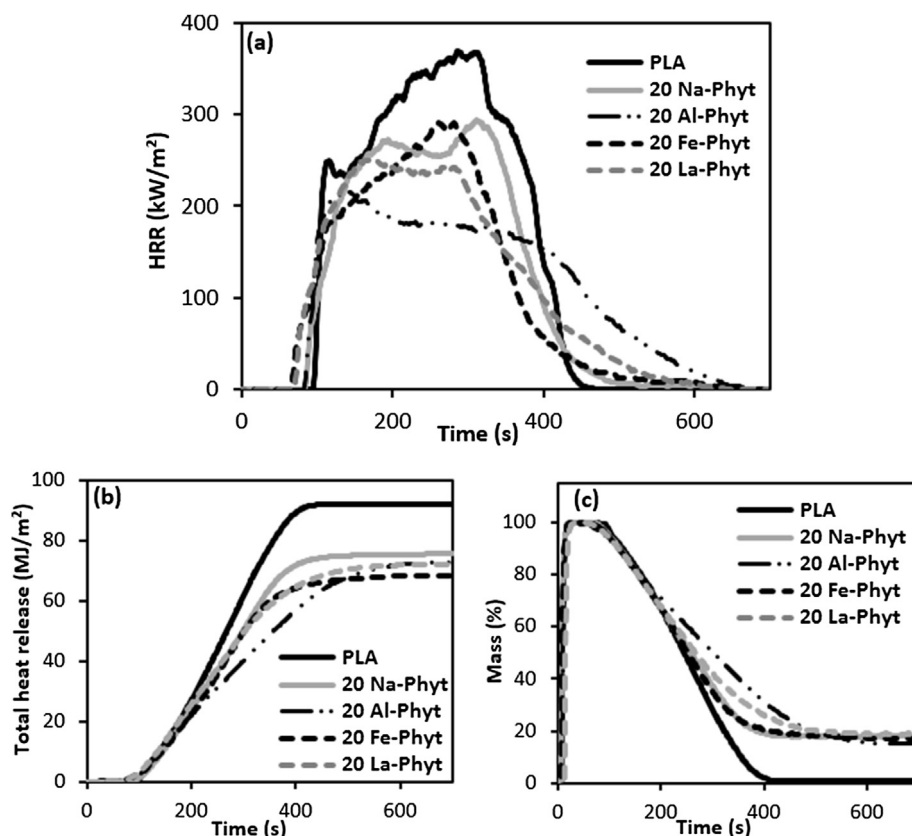


Fig. 5. (a) HRR curves, (b) THR curves and (c) Mass loss rate curves of PLA and PLA/20% metallic phytate composites.

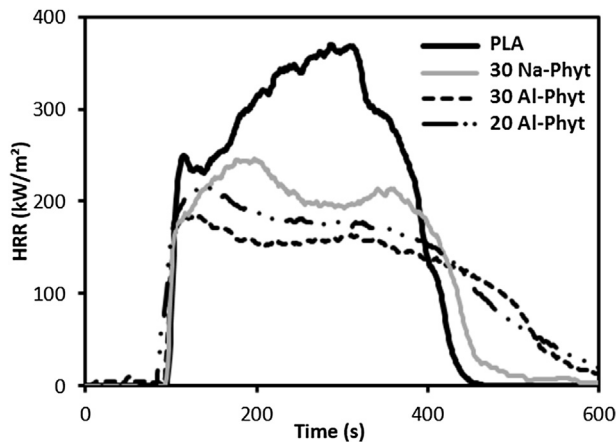


Fig. 6. Effect of Al-Phyt content on HRR curves of PLA composites.

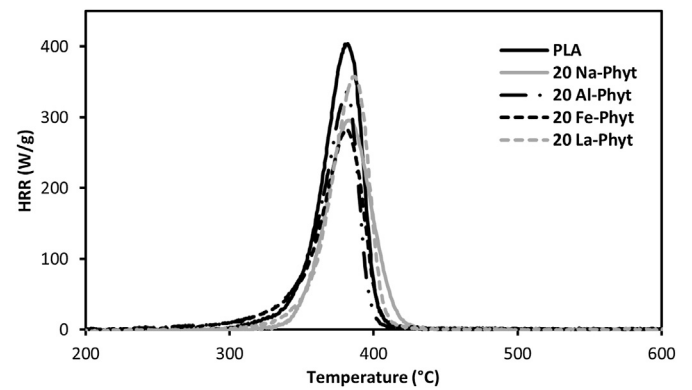


Fig. 8. PCFC heat release rate curves of PLA and PLA/20% metallic phytate composites.

Table 4

PCFC results of PLA and PLA/20% metallic phytate composites.

	T_{max} (°C)	pHRR (W/g)	% reduction	THR (KJ/g)	% reduction
PLA	380	405		14.3	
20 Na-Phyt	378	296	27	11.3	21
20 Al-Phyt	382	336	17	11.4	20
20 Fe-Phyt	377	285	30	11	23
20 La-Phyt	387	357	12	11.6	19

pHRR level, shows the most homogeneous and cohesive char layer. We can also observe that this composition contains the highest amount of char residues.

In addition, we also performed some ICP and TOC analysis on the residual char of PLA filled with 20 wt% of the different metallic phytates. Results are summarized in Table 5 and show that the char residues of the different composites are mainly composed of carbon, oxygen, phosphorus and the corresponding metal. The most carbon rich char is formed when Al Phyt is used. This result

higher than the decrease of HRC in PCFC. This tendency indicates that the main mode of action of Al Phyt and La Phyt is a physical barrier effect. The most efficient barrier effect corresponds to formulations that are the most distant from the line R1–R2. The most efficient barrier effect is obtained in presence of Al Phyt. It is worth pointing out that the point corresponding to 20 Fe Phyt composition is just below the line R1–R2. This unexpected result is generally attributed to uncertainty of data since the point should be plotted above the R1–R2 straight line. However, in our case, TGA analysis performed on the different cone calorimeter residues let suggest another explanation (see below).

The barrier effect efficiency could also be investigated by analyzing the char formed during and at the end of cone calorimeter test. With this view, the cone calorimeter test has been stopped at 250 s, which corresponds to the time of half combustion of the composites, and the surfaces of the samples have been observed. As seen in Fig. 10, PLA/20 Al Phyt, which allows for reaching a lower

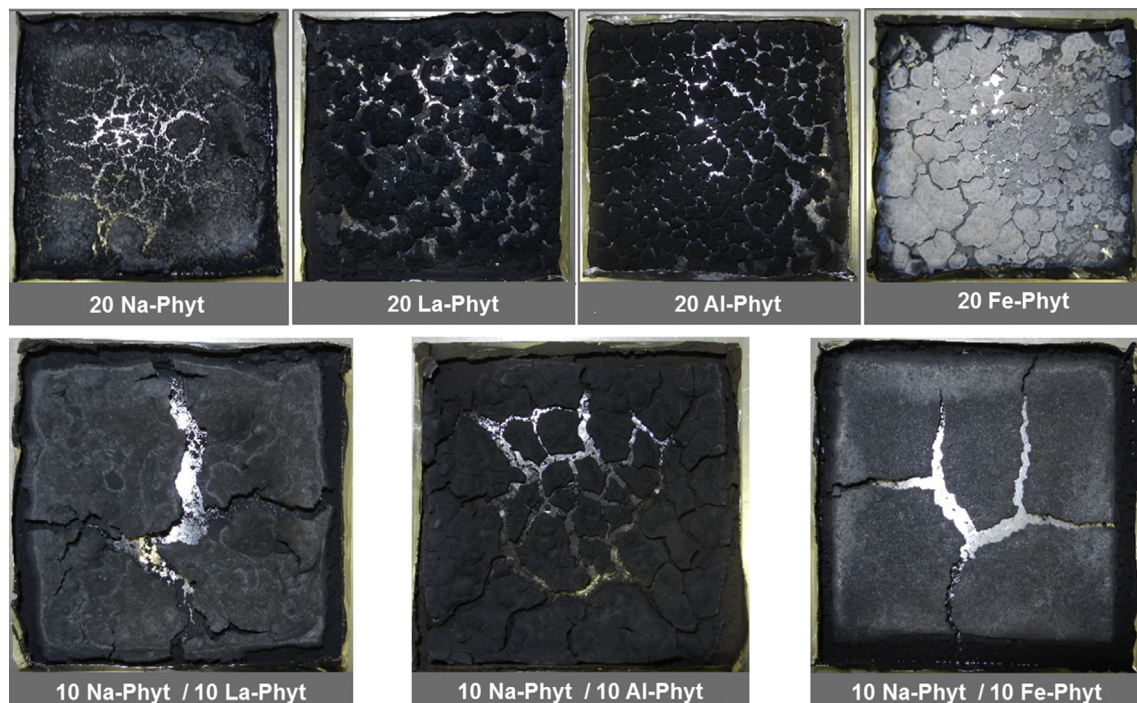


Fig. 7. Char residues generated at the end of the combustion during cone calorimeter test.

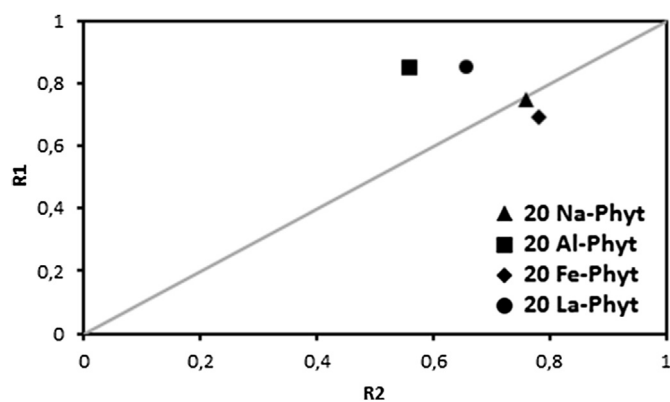


Fig. 9. R1 versus R2 for PLA/20% metallic phytate composites.

indicates that Al Phyt is the most efficient char promoter, which is in good accordance with the conclusions drawn from both cone calorimetry and PCFC results.

Results of ICP analysis, performed on the char formed during the combustion show also that metallic phytate salts act in the condensed phase. In fact, the comparison of the phosphorus as well as the metal contents in the composite, before and after fire testing (Figs. 11 and 12) indicates that only a small fraction of phosphorus and metal is lost during the combustion. In addition, the decrease of phosphorus is similar whatever the nature of the metallic phytate used. This result clearly indicates that metallic phytates act mainly in the condensed phase. The thermal stability of the char formed during the combustion is strongly affected by the nature of the metallic cations as evidenced by TGA analysis (Fig. 13). TGA curve of

Table 5

Atomic composition of residues of PLA/20% metallic phytate composites.

Sample residues	C (wt%)	P (wt%)	Na (wt%)	Al (wt%)	Fe (wt%)	La (wt%)
20 Na-Phyt	4.5	23.1	18.1			
20 Al-Phyt	6.2	22.7		10.6		
20 Fe-Phyt	0.2	18.9	2.52		27.6	
20 La-Phyt	5.6	15.3				32.6

the char resulting from the combustion of 20 Al Phyt composite is distinguished from the other TGA curves by the presence of two consecutive decomposition steps, while the other char residues undergo only one decomposition step. The first decomposition step takes place between 100 and 200 °C and seems to correspond to water adsorbed during residue sample storage. The higher hygroscopic behavior of this residue could be attributed to the formation of some aluminum oxide form during the combustion, which is water absorbent. DRX analysis (results not presented here) of the char residue of 20 Al Phyt composite does not allow determining the nature of this aluminum oxide because of the presence of amorphous carbon char. The second decomposition step, that is present also in the cases of La Phyt and Na Phyt based residues, corresponds to a thermal degradation of the carbonaceous part of the char residues. This second decomposition step is more important in the case of Al Phyt based residue. Finally, TGA analysis carried out on the char formed during the combustion of PLA/Fe Phyt composition shows a weight increase above 600 °C. This weight change corresponds to the oxidation of iron that has been previously reduced during the combustion. Similar oxidative action was already reported in the case of red phosphorus/iron oxide combination in PET [38]. This may explain the pronounced reduction of pHRR observed during PCFC test. Indeed, during PCFC test, a

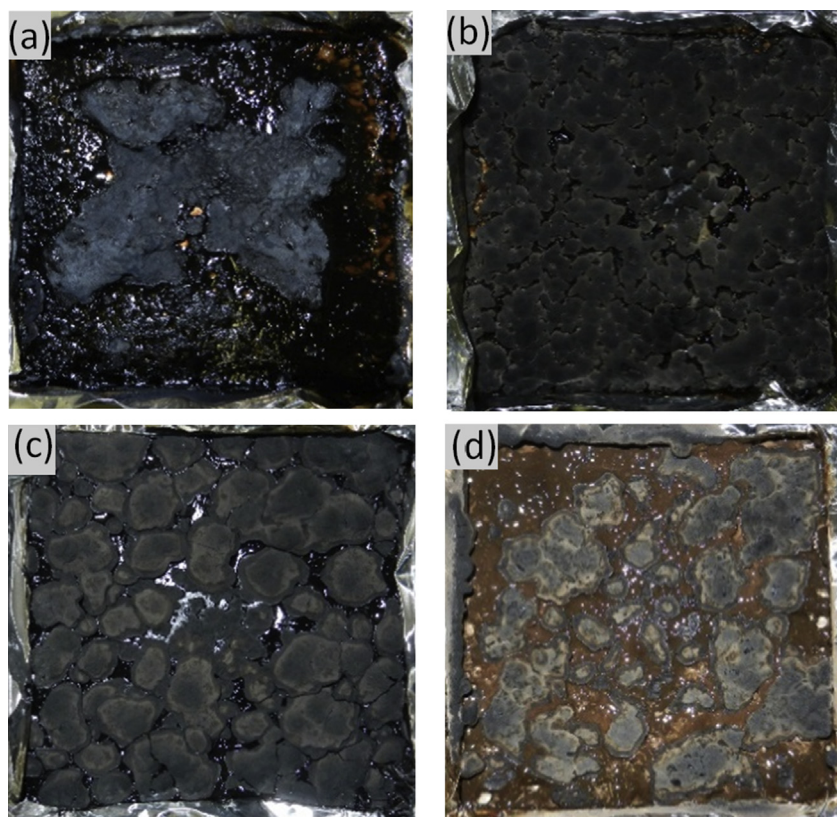


Fig. 10. Pictures of (a) 20 Na-Phyt, (b) 20 Al-Phyt, (c) 20 Fe-Phyt and (d) 20 La-Phyt after 250s of combustion.

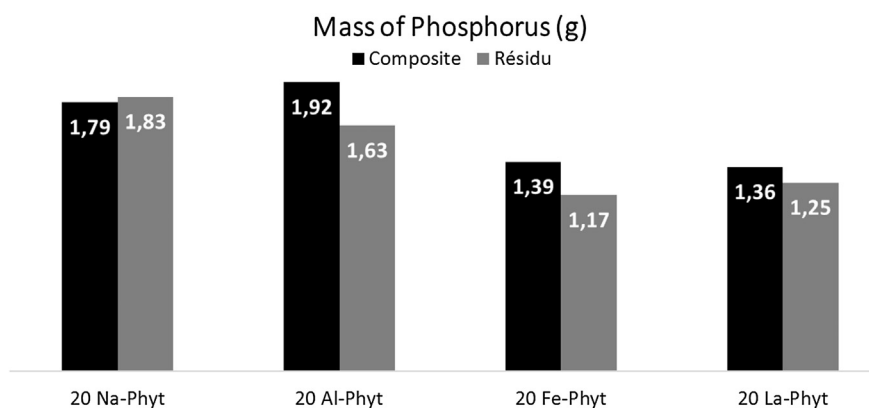


Fig. 11. Mass of phosphorus in PLA/20% metallic phytate salt composites before and after combustion.

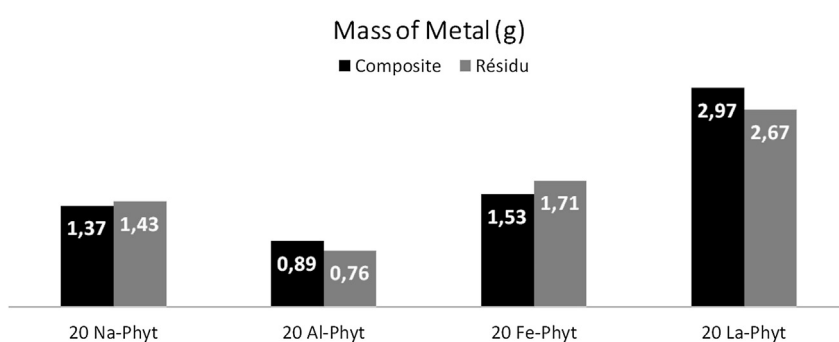


Fig. 12. Mass of metal in PLA/20% metallic phytate salt composites before and after combustion.

part of phosphorous compound that has been degraded during the pyrolysis step may be partially oxidized by the action of iron. The generation of partially oxidized compounds may lead to less oxygen consumption during combustion. As a consequence, reduced oxygen consumption means lower heat release rate according to Huggett's relation (1 kg of consumed O_2 corresponds to 13.1 MJ of released energy).

3.3. PLA/Na phytate and Al, Fe or La phytate combinations

The replacement of sodium cations by aluminum ones allows PLA composites to reach better flame retardant properties. Indeed, with respect to unfilled PLA, the addition of 20 wt% of Al phyt results in a pHRR and THR reduction of around 45% and 20%, respectively, and to the decrease of the burning rate. Furthermore, the flame retardant effect obtained with 20 wt% of Al Phyt is higher

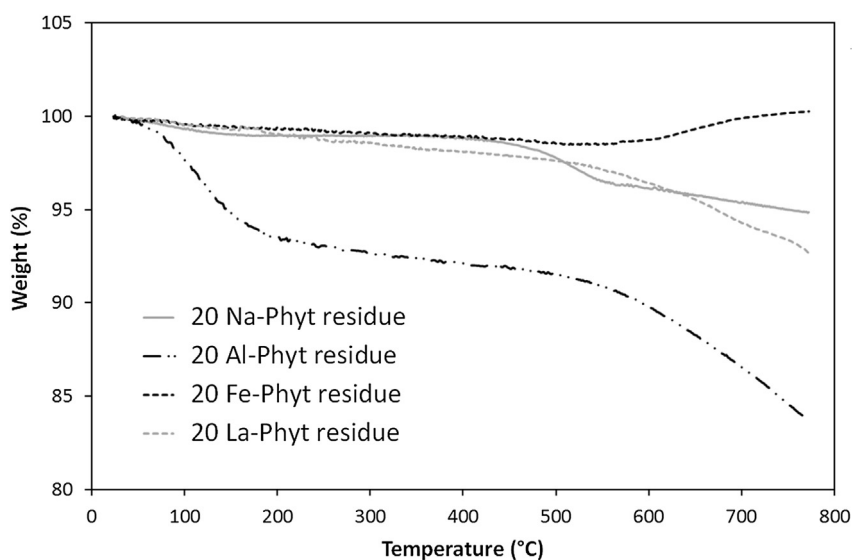


Fig. 13. TG curves of residues of PLA/20% metallic phytate composites (20 °C/min) under air.

Table 6
Cone calorimeter test results of PLA and flame retarded PLA/metallic phytate combinations.

Sample	TTI (s)	pHRR (kW/m ²)	% reduction	THR (MJ/m ²)	% reduction	Residual mass (%)	EHC KJ/g
PLA	86	388		92		0	19
10 Na-Phyt/10 Al-Phyt	63	205	47	76	17	16	17.9
10 Na-Phyt/10 Fe-Phyt	68	205	47	74	20	16	17.4
10 Na-Phyt/10 La-Phyt	68	220	43	74	20	16	17.5
15 Na-Phyt/5 Al-Phyt	69	212	45	74	20	15	17.5
15 Na-Phyt/5 Fe-Phyt	70	250	36	74	20	16	17.5
15 Na-Phyt/5 La-Phyt	75	250	36	74	20	16	17.6

than that obtained with 30 wt% of Na Phyt. However, the use of Al Phyt leads to a dramatic degradation of PLA during melt processing in contrast with Na Phyt that induces only a slight decrease of PLA chain molecular weight. Based on these PLA fire properties and the impact of the different phytates on PLA thermal degradation during melt processing, the co addition of Na Phyt with either Al Phyt, Fe Phyt or La Phyt seems to be a good compromise. With this view, we prepared different PLA composites in which 10 wt% and 15 wt% of the metallic phytate have been replaced by Na Phyt.

Cone calorimeter tests results of PLA filled with these different binary combinations of metallic phytates are summarized in Table 6 and Fig. 14. The combinations of metallic phytates with Na Phyt allow important reduction of pHRR whatever the nature of the metallic cations. The two compositions of PLA containing 10 wt% of Al Phyt and Fe Phyt in combination with 10 wt% of Na Phyt proved to be characterized by the lowest recorded pHRR, corresponding to a pHRR reduction close to 50% in comparison to the one measured for pristine PLA. In addition, the combinations of the different metallic phytates with Na Phyt reduce significantly the thermal degradation of PLA during the melt processing. As far as PLA containing Al Phyt or Fe Phyt are concerned, the PLA chain molecular weight increases from 24200 and 28700, to 79300 and 73400 respectively, when 10 wt% of these additives are replaced by Na Phyt. Furthermore, the combination of only 5 wt% of Al Phyt with 15 wt% of Na Phyt clearly overcomes the problem of PLA thermal degradation during melt processing while keeping the same pHRR reduction than that obtained with 20 wt% of Al Phyt. The reduction of PLA thermal degradation has a positive impact on the char structuration and consequently the material fire behavior. In fact, the recovered chars proved to be more homogeneous when PLA was filled with metallic phytates binary combinations with respect

to that formed when individual phytates were used (Fig. 7). The reason of that behavior could be directly related to the viscosity of the molten polymer. A lower viscosity, resulting from lower molecular weight, will lead to unstable char, mainly composed of isolated “island in sea” morphology while a higher viscosity, resulting from higher molecular weight, will promote the formation of interconnected “island in sea” structure, which will generate more homogeneous and cohesive char.

The composites containing binary combinations, as well as composites containing 20 wt% of Na Phyt and Al Phyt, have been tested at UL 94 vertical burning test. For each sample, a set of 5 specimens were tested. The results are summarized in Table 7.

UL 94 test allows determining the relative flammability of plastic materials and their dripping behavior. Table 7 presents UL 94 rating of PLA containing different metallic phytate compositions. In contrast to cone calorimeter test, using 20 wt% of Al Phyt leads to the poorest fire properties since this composition is not classified at the vertical UL 94 test. Indeed, the sample completely burns and forms flaming drops. Surprisingly, PLA/20 Na Phyt composition leads to V 2 classification whereas this blend presents low flame retardant properties in cone calorimeter test. UL 94 seems to be molecular weight dependent. Indeed, the molecular weight of PLA chain is higher in the case of PLA/20 Na Phyt composition (89000) than in the case of PLA/20 Al Phyt composition (24000).

The effect of PLA molecular weight decrease is more pronounced in vertical UL 94 test than in horizontal cone calorimeter test.

Controlling PLA chain degradation during melt processing by combining Na Phyt and the other metallic phytates impacts positively UL 94 results, except in the case of PLA/10 Na phyt/10 Al

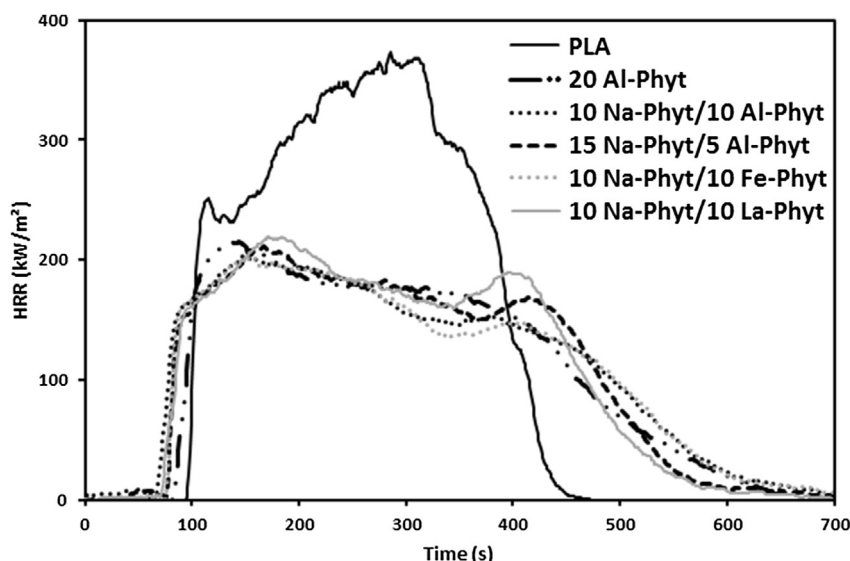


Fig. 14. HRR curves of PLA and PLA/metallic phytate combinations.

Table 7UL-94 vertical burning test results; (t₁ time of combustion after the first flame application, t₂ time of combustion after the second flame application).

Sample	T ₁ (s)	T ₂ (s)	Cotton ignition	Entirely burned	Classification
20 Na-Phyt	14	1	Yes	No	V-2
20 Al-Phyt	60		Yes	Yes	NC
10 Na-Phyt/10 Al-Phyt	15	60	Yes	Yes	NC
10 Na-Phyt/10 Fe-Phyt	10	2	Yes	No	V-2
10 Na-Phyt/10 La-Phyt	12	1	Yes	No	V-2
15 Na-Phyt/5 Al-Phyt	13	4	Yes	No	V-2

Phyt combination. In fact, the binary combinations of metallic phytates allow reaching a V 2 rating except for PLA/10 Na Phyt/10 Al Phyt which burns completely after the second flame application. For sake of comparison, V 2 rating is the classification obtained for PLA fire proofed with 23 wt% of APP [16] or with 40 wt% of the classical intumescent system APP/PER (3:1) [10].

4. Conclusion

This paper reports the preparation and the flame retardant effect of several metallic phytates in polylactide (PLA). The study focused on the understanding of the effect of the nature of the metallic cations on PLA fire properties. Aluminum phytate exhibits greater flame retardant properties in comparison to sodium, iron and lanthanum phytates by promoting significant reduction in pHRR values. The combination of both PCFC and cone calorimeter analyses has highlighted that this significant improvement is related to a physical barrier effect. Furthermore, the observation of the char formed at 250 s (half combustion) clearly shows that this effective barrier effect is attributed to the fast formation of a homogeneous char layer at the surface of the burning sample. However, the use of Al Phyt proved to be responsible for the PLA thermal degradation during melt processing, i.e. sharp reduction of the polyester molecular weight. To overcome this negative effect, the co addition of Al Phyt and Na Phyt represents a very efficient approach. Indeed, this combination allows for reaching a pHRR reduction similar to that obtained with 20 wt% of Al Phyt while limiting the PLA chain degradation. This synergistic effect was also observed in presence of either Fe Phyt or La Phyt that allows obtaining a V 2 classification in UL 94 test.

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