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Phytic acid–lignin combination: A simple and efficient route for enhancing thermal and flame retardant properties of polylactide

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ABSTRACT

Lignin and phytic acid combinations were used as a simple route for developing bio-based flame retardant systems in PLA.

The composites were prepared by melt blending and their mechanical, thermal and fire properties have been explored. Combining these two additives has been shown to present an interesting way of limiting the negative effect of each of them and for improving the properties of the resulting materials.

On the first hand, the presence of phytic acid enables better dispersion of lignin particles into the matrix, limiting PLA thermal degradation induced by lignin. On the second hand, lignin enables important reduction of the composite hygroscopy induced by the presence of phytic acid.

Moreover, combining lignin and phytic acid leads to significant reduction up to 44% of peak of heat release rate (pHRR) during cone calorimeter test as well as obtaining V-2 classification in UL-94 test. Some positive effects of the binary combinations on the composites mechanical properties have also been evidenced (increase of the elongation at break from 3.1% to 12.6% for one formulation).

1. Introduction

Polymeric materials play a significant role in our daily life owing to their wide range of advantages such as versatile mechanical properties, ease of processing and recycling capability [1]. With the growing concern over the environmental protection, great interest is more and more devoted to improve the sustainability of polymers. Bioplastics issued from renewable resources represent an interesting alternative to reduce carbon footprint instead of using polymers from fossil carbon. These green materials are increasingly used in durable applications instead of short-term applications for which they were initially developed [2]. However, to extend the development of technical and durable applications for these biopolymers, some of their properties such as flame retardancy must be improved.

Among bioplastics, polylactide (PLA) represents one of the most promising technical biopolymer [3,4] thanks to the very efficient use of feedstocks during its production, its relevant mechanical properties such as high stiffness, its high degree of transparency, gas permeability, biocompatibility in addition to relatively low cost and large production volume [5,6].

The flame retardant approaches that have to be developed for PLA must be also sustainable in order to maintain an interesting

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environmental friendly feature as “carbon sequester” bioplastic. The aim of this work is thus to promote the use of bio-based by-products, from bio-refineries or the paper industry, as the main components of the flame retardant systems. Indeed, some widely available biomass compounds would gain to be upgraded since most of these extracted products, such as lignin, are currently used as fuel for energy recovery [7,8]. Indeed, lignin shows some predispositions to be used as flame retardant agent thanks to its aromatic structure which is responsible for its high thermal stability, as well as for its char forming ability [9–17]. The formation of char at the surface of burning material is an effective way to improve flame retardant behavior of polymeric materials [18]. Moreover, the flame retardant effect of lignin could be enhanced by its chemical modification by phosphorus based compounds [19–24] (reactive pathway) or by its combination with phosphorus based flame retardant agents [16,11,15] (additive pathway). The presence of phosphorus contributes to the increase of the char efficiency.

However, as far as PLA is considered, the incorporation of lignin undergoes important polymer thermal degradation during both melt processing and TGA [24]. Lignin chemical modification presents an interesting way to improve its flame retardant effect while limiting its thermo-degradant action [24]. Additive pathway, also presents some benefits since it avoids additional chemical modification process. However, to maintain the good environmental profile of the final composite, lignin must be combined with another bio-based compound. Phytic acid seems to be a good candidate for this purpose. In fact, phytic acid, a saturated cyclic acid, is the principal storage form of phosphorus in plant seeds and contains high phosphorus content (28 wt%) as well as an interesting P/C atomic ratio (=1). Its flame retardant effect has been proved in many applications. It was used in combination with chitosan as part of a flame retarded coating deposited via layer by layer assembly on cotton fabric [25]. Such polyelectrolyte complexes, containing phytic acid combined to nitrogen-based compounds, were employed to enhance the fire performances of ethylene-vinyl acetate [26] and of polypropylene [27,28].

In this paper, a new ecofriendly pathway, allowing significant enhancement of the flame retardant behavior of PLA is proposed. The combination of untreated lignin and phytic acid is studied as novel ecofriendly and fully renewable flame retardant system avoiding additional lignin chemical modification step and significantly limiting its thermo-degradant effect. Two different lignins, i.e. kraft and organosolv, have been used in this study. In fact, lignin structure and properties are greatly affected by their botanical origin as well as the extraction process used. These two different lignins are obtained by different extraction processes, i.e. sulfur based process for kraft lignin and sulfur-free process for organosolv lignin.

2. Experimental

2.1. Materials

PLA resin (3051D) with an average molecular weight of 100,000 g/mol, a dispersity of 2.1 and 4.3% of D-lactide content was purchased from NatureWorks. Phytic acid (Phytic) aqueous solution 50% (w/w) was purchased from Sigma Aldrich. Two lignins were used in this study: a kraft lignin (Kraft), with a low sulfonate content (4% of sulfur), from Sigma Aldrich and an organosolv lignin (Organosolv) from BOC Sciences (USA). These two lignins are separated from cellulose and hemicelluloses by two different extraction processes. Kraft lignin is obtained during the paper making process thanks to a mixture composed of sodium hydroxide and sodium sulfide while organosolv lignin is separated from other plant constituents by selective solubilization in organic solvents. The extraction process impacts significantly lignin structure and composition, especially the number of reactive groups and its molecular weight, resulting in significant variability of the final product properties. Thus, an aqueous titration used to quantify the acidic and phenolic hydroxyl groups of both lignins [24] clearly evidences the highest content in carboxylic functions in organosolv lignin (4.5 mmol/g) in respect to kraft lignin that contains only 1.4 mmol/g (Table 1). The number of phenolic hydroxyl groups remains similar in the two lignins (around 2 mmol/g). The increase of the number of functional groups is due to the organosolv process that induces some depolymerization reactions by ring hydroxylation, oxidative ring opening, cleavage of ether bonds and epoxidation [29]. All these reactions are also responsible for the formation of lignin with reduced molar mass. In fact, the average molar mass of kraft lignin is higher than that of organosolv lignin. It is worth mentioning that the two lignins contain bimodal distribution indicating that both processes generate the formation of shorter lignin fragments.

2.2. Melt processing

PLA and mixtures of lignin and phytic acid, in the appropriate proportions, were first dried in a vacuum oven at 60 °C overnight. PLA composites were prepared in a Brabender internal mixer at 160 °C (7 min mixing at 70 rpm). Plates (100 ∗ 100 ∗ 4 mm^3) for cone calorimeter testing and sheets (100 ∗ 150 ∗ 3 mm^3) for UL-94 specimens were compression molded at 160 °C using an Agila PE20

Table 1
Number of functional groups (phenolic and carboxylic) and average molecular weight of kraft and organosolv lignins.

	Number of functional groups		Average molecular weight (Da)	
	mmol RCOOH/g	mmol phenolic OH/g		
Kraft	1.4 ± 0.1	1.8 ± 0.1	4000	680
Organosolv	4.5 ± 0.1	2.2 ± 0.1	1530	320

Table 2
Formulations of neat PLA and PLA/lignin-phytic acid composites.

Compositions	PLA (wt%)	Phytic acid (wt%)	Kraft lignin (wt%)	Organosolv lignin (wt%)
PLA	100	–	–	–
20 Phytic	80	20	–	–
20 Kraft	80	–	20	–
20 Organosolv	80	–	–	20
15 Phytic/5 Kraft	80	15	5	–
10 Phytic/10 Kraft	80	10	10	–
15 Phytic/5 Organosolv	80	15	–	5
10 Phytic/10 Organosolv	80	10	–	10

hydraulic press and following a precise pressure program: the sample is first deposited for 3 min on the hot part, it is then pressed for 3 min 20 s at 10 bars, followed by 3 degassings, it is then pressed again for 2 min 30 s at 150 bars, and finally the sample is deposited in the cold part where it is pressed for 5 min. Specimens for mechanical testing were prepared by injection molding using DSM Mini Injection Molding apparatus according to the following procedure: 3 min at 170 °C and injection within a mold at 45 °C. The investigated formulations are summarized in Table 2.

2.3. Characterizations

2.3.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out by using TGA Q50 device from TA Instruments. After an isotherm of 10 min at 100 °C for getting rid of any moisture, approximately 10 mg of the sample was submitted to a temperature ramp from 100 to 800 °C at a heating rate of 20 °C/min. All TGA experiments were performed under a gas flow of 60 ml/min (platinum pan). Each sample was tested two times to ensure repeatability of the results.

2.3.2. Differential scanning calorimetry (DSC)

DSC was performed with a MDSC 2920 from TA Instrument to analyse the thermal behavior of PLA composites. Samples were submitted, under a nitrogen flow, to a first heating ramp of 10 °C/min from 0 to 175 °C to get rid of their thermal history. The samples were then cooled down to -50 °C following a ramp of 10 °C/min. Samples were finally subjected to a second heating ramp of 10 °C/min to 175 °C. The values of interest such as glass transition temperature (T_g), melting temperature (T_m), cold crystallization temperature (T_{cc}) or crystallinity index (C_i), were determined from the curve corresponding to the second heating cycle. The degree of crystallinity was calculated by subtracting the enthalpy of cold crystallization (ΔH_c) from the melting enthalpy (ΔH_m) divided by the melting enthalpy of a 100% crystalline PLA which is considered to be 93 J/g.

2.3.3. Size exclusion chromatography (SEC)

The number average molar masses of PLA was determined at 23 °C by using an Agilent size exclusion chromatograph equipped with a Knauer 2320 refractometer index detector and two PL gel columns (MIXED-D and 10^3 A). Samples were dissolved in $CHCl_3$ (5 mg/1 ml) and filtered, 20 µL of the solutions were injected into the columns using a flow rate of 1 mL/min. Monodisperse polystyrene standards (Polymer Laboratories Ltd.) ranging from 200 to 4×10^5 g/mol were used for the primary calibration. Molar masses and molar masses distributions were calculated by reference to a universal calibration curve relative to polystyrene standards.

2.3.4. Scanning electron microscopy (SEM)

Morphological investigation was performed to highlight the dispersion state of the additives in PLA matrix using a scanning electron microscopy (SEM) Hitachi SU8020 (100 V–30 kV) apparatus. PLA composites were cryofractured and coated using a gold sputtering technique to avoid any charging effect during the electron beam scanning.

2.3.5. Evaluation of composites hygroscopy

PLA and PLA containing lignin and phytic acid combinations were weighed and placed at 20 ± 1 °C in a room maintained at a relative humidity of 55 ± 5%. The composites weight was recorded periodically after removing the droplets accumulated at the surface until a constant weight was obtained.

2.3.6. Fire behavior characterizations

2.3.6.1. Cone calorimeter test. Cone calorimeter tests were performed according to ISO 5660 standard procedure with a FTT cone calorimeter. Samples ($100 * 100 * 4$ mm^3) were exposed to an external heat flux of 35 kW/m^2, corresponding to common heat flux in a mild fire scenario. Heat Release Rate (HRR) was measured as function of time from oxygen consumption, and Time To Ignition (TTI), Total Heat Release (THR) and peak of Heat Release Rate (pHRR) were determined.

2.3.6.2. UL-94 burning test. UL-94 vertical burning tests were performed on FIRE apparatus according to ASTM D 3801 standard procedure. Five specimens of $125 * 13 * 3$ mm^3, cut from the $150 * 100 * 3$ mm^3 plates, were subjected to two flame applications

Table 3
UL-94 sample ratings requirements.

Rating	After flame time [s]	Total sum of after flame times [s]	Burning drips	Burn to the clamp
V-0	< 10	< 50	No	No
V-1	< 30	< 250	No	No
V-2	< 30	< 250	Yes	No

(10 s each). The after flame and afterglow times were measured, and the eventual cotton ignition by flaming drops was recorded. UL-94 vertical burning test results in sample classification as V-0, V-1 or V-2 according to specific criteria (Table 3).

2.3.7. Mechanical – thermomechanical characterizations

2.3.7.1. Tensile test. Tensile test was performed by using a Lloyd LR 10 K tensile bench according to ASTM D 638 standard (crosshead speed = 1 mm/min, preload = 5 N and distance between the grips = 58 mm). For each sample, 5 specimens were previously conditioned for 48 h at 20 ± 1 °C under a relative humidity of 55 ± 5%, and the determined values are the average of the 5 specimens.

2.3.7.2. Impact test. Impact strength was measured with a Ray-Ran 2500 pendulum impact tester used in Notched Izod mode following ASTM D256 standard (E = 3.99 J, mass = 0.668 kg and speed = 0.46 m/s). As for tensile test, 5 specimens of each sample were previously conditioned and the results correspond to the average of the 5 specimens.

3. Results and discussion

3.1. Thermal stability of additives and of PLA/lignin/phytic acid compositions

Thermogravimetric analysis was used to investigate the degradation behavior of the additives alone or in combination, as well as their effect on the thermal stability of PLA based composites.

Fig. 1 presents thermo-oxidative decomposition of the different additives and Table 4 gathers TGA results. Lignin thermal degradation is a complex process that has been described and reviewed by several authors [30]. It occurs in several steps and some of them overlap with each other. When we compare TGA curves of the two lignins tested, we observe the formation of a residue even under air. The amount of residue is higher for organosolv lignin. This result is in contradiction with what has already been reported in the literature demonstrating that lignin is a charring material only under pyrolytic conditions [31,23]. The presence of some residual mineral salts, resulting from the extraction process, may explain the amount of the final residue obtained.

At low temperature, the two lignins do not present the same thermal behavior. Organosolv lignin starts to degrade (5 and 20 wt% loss) at lower temperature (238 °C and 327 °C) than kraft lignin (273 and 348 °C). This first degradation step, corresponding to the release of low molecular weight products generated from lignin side chains cleavage takes place at lower temperature in the case of organosolv lignin. This is due to the fact that organosolv process leads to the formation of lignin with low molecular weight and containing a lot of reactive side chains [24]. From 380 °C to 530 °C, the thermal behavior of both lignins, corresponding to the release of methane due to the cleavage of the main chain either by C-C and β-β scission or by aryl-ether cleavage, is similar. Above 530 °C, rearrangements and condensation of the aromatic structure take place and lead to the formation of a char residue.

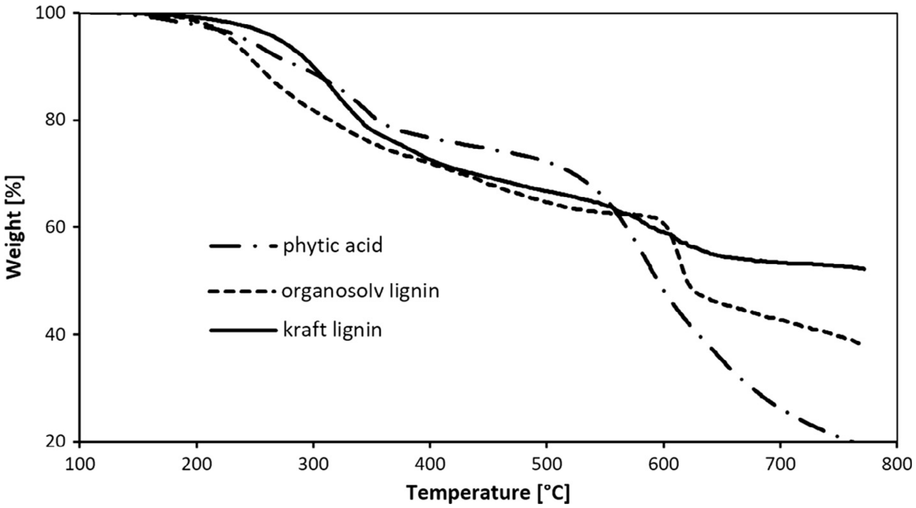


Fig. 1. TGA curves of phytic acid and lignins under air at 20 °C/min.

Table 4
Temperatures corresponding to 5% and 20% weight losses, and residue from TGA of lignins, phytic acid and their blends.

	T 5% (°C)	T 20% (°C)	Residue (%)	Theoretical residue (%)
Kraft lignin	273	348	53	–
Organosolv lignin	238	327	40	–
Phytic acid	255	362	20	–
50% Kraft lignin/50% phytic acid	191	340	48	36.5
50% Organosolv lignin/50% phytic acid	192	300	55	30

Phytic acid decomposes in several degradation steps that have been described and reported in the literature [32] and correspond to dehydration, carbonization and char degradation reactions. It can be observed from Fig. 1 that below 540 °C, only dehydration and carbonization reactions take place. Above 540 °C, thermal decomposition of the char takes place leading to a final char residue of about 20% at 800 °C.

Based on these results, the three additives start to decompose above 200 °C and thus they could be used as additives into PLA that is processed at 160 °C. Moreover, thanks to their char forming ability, both lignins and phytic acid are expected to induce improvement of PLA fire behavior. Moreover, the combination of lignin and phytic acid is expected to result in better properties thanks to the presence of phosphorus that is well known to promote char formation via condensation reactions. In order to evaluate the interest of these combinations, we studied the thermal behavior of phytic acid/lignin blends by TGA under oxidant gas (Fig. 2 and Table 4).

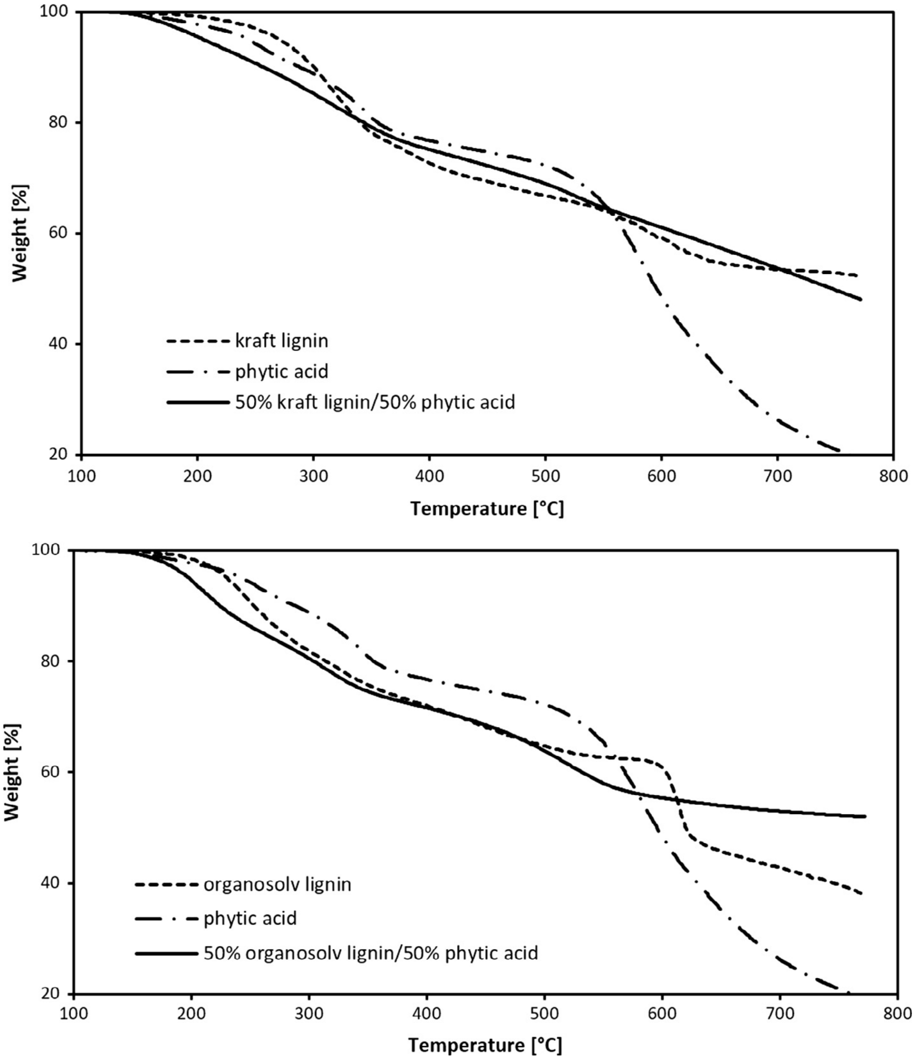


Fig. 2. TGA curves of lignin/phytic acid blends performed at 20 °C/min under air.

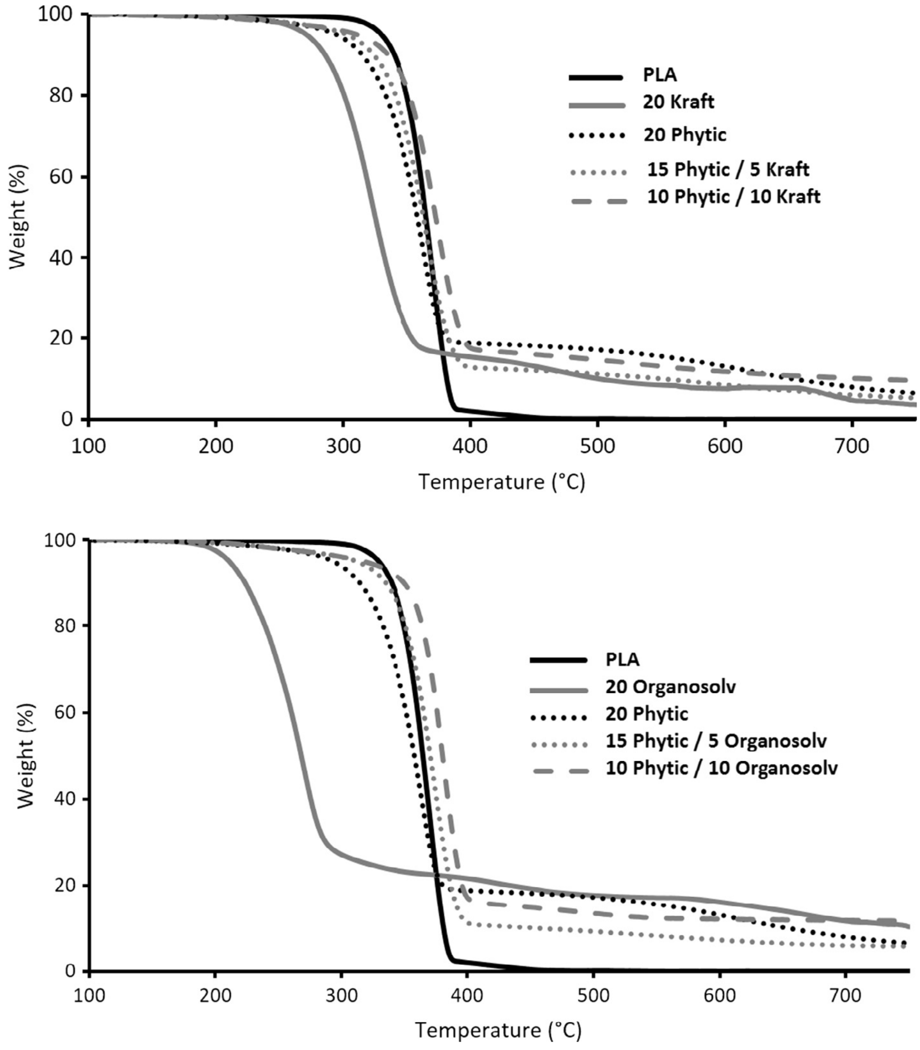


Fig. 3. TGA curves of PLA/lignin/phytic acid compositions performed at 20 °C/min under air.

Surprisingly, combining the two additives induces a premature decomposition since the blend starts to decompose earlier than the individual components. This decrease of the decomposition temperature takes place whatever the nature of lignin used (5% weight loss at 190 °C for both lignins and 20% weight loss at 340 and 300 °C in the presence of kraft and organosolv lignin respectively). This behavior highlights the presence of some interactions between lignin and phytic acid that induce a release of volatile products. In the literature, it has been reported that phosphoric acid-based molecules can induce, at low temperature, dehydration reactions of bio-based products such as starch [16]. This kind of reaction has also been reported to be responsible for the decrease of the thermal degradation temperature of phosphorylated lignin [23]. The occurrence of this modification of lignin thermal behavior demonstrates good affinity between the two additives. Indeed, we also observed that after drying lignin/phytic acid blends at 60 °C, the collected powder became hard and their grinding was required prior to their incorporation into PLA. No phase separation or presence of gel/liquid phase, characteristic of phytic acid was observed.

At high temperature, lignin/phytic acid combination enables for the formation of important amount of final residue. In fact, the thermal degradation of phytic acid is strongly limited and the experimental residue formed has been shown to be more important than the theoretical one (table 4).

Even if a premature weight loss occurs when lignin is combined with phytic acid, the amount of the final residue has been shown to be higher than that obtained with phytic acid alone. The improvement of the char thermal stability at high temperature compensates the weight loss occurring at low temperature.

The next step consists in the incorporation of phytic acid, lignins (kraft and organosolv) as well as their combinations into PLA and the evaluation of their effects on the composites thermal, fire and mechanical properties. TGA curves of thermo-oxidative degradation of PLA containing organosolv lignin, kraft lignin and phytic acid separately or in combinations are presented in Fig. 3, and the results are summarized in Table 5. Pristine PLA decomposition takes place in one step from 315 to 405 °C with a maximum weight loss observed at 371 °C. The incorporation of 20 wt% lignin, whatever its nature, induces significant reduction of PLA thermal

Table 5
Temperatures corresponding to 5% and maximum weight losses, and residue from TGA of PLA and PLA/lignin/phytic acid compositions.

	T 5% (°C)	T max (°C)	Residue (%)
PLA	315	371	0
20 Kraft lignin	276	332	5
20 Organosolv lignin	210	271	11
20 Phytic acid	295	364	8
15 Phytic/5 Kraft	304	366	6
10 Phytic/10 Kraft	313	374	10
15 Phytic/5 Organosolv	314	374	6
10 Phytic/10 Organosolv	319	381	11

stability since TGA curves are shifted to lower temperature. This premature decomposition is more important when organosolv lignin, that contains more functional groups (Table 1), is used. The composite starts to decompose ($T_{-5\%}$) at 210 °C and 271 °C when organosolv lignin and kraft lignin are used respectively. The incorporation of 20 wt% phytic acid also induces some premature PLA thermal degradation that remains however limited. It is worth to mention that despite the premature degradation of PLA, the three additives enable obtaining residue at the end of the test. Surprisingly, the combination of lignin and phytic acid enables important limitation of the thermo-degradant effect of lignin. In fact, TGA curves become closer to that of pristine PLA ($T_{-5\%}$ between 304 and 319 °C). This effect was not expected because TGA performed on lignin/phytic acid blends (Fig. 2) displayed significant reduction of the blend thermal stability, lower than that of the additives when analyzed separately. The reduction of PLA thermal degradation when both additives are combined means that lignin reactive groups are no longer available to induce PLA chain scission thanks to the good affinity between lignin and phytic acid. This effect has also been reported in the case of phosphorylated lignin that induces less thermo-degradant effect than untreated lignin [24]. Carboxylic and phenolic functions are not anymore inducing PLA thermal degradation because they have already reacted. This protective effect is also evidenced during melt processing since PLA chain molecular weight reduction is less important when lignin and phytic acid are combined (Table 6) except for PLA containing 5 wt% kraft lignin. For all the other compositions, PLA chain molecular weights, are higher than those obtained when lignins and phytic acid are used separately.

At high temperature, no synergistic effect concerning the amount of char residue is noticed. Lignin/phytic acid combinations do not enable the formation of more char content than that obtained when only lignin is used.

In conclusion, using lignin alone induces an important thermal degradation of PLA noticeable during both TGA and SEC analyses. However, its combination with phytic acid proves to be interesting to overcome this negative effect since lignin/phytic acid blends result in the limitation of PLAchain molecular weight reduction, as well as in the formation of PLA composites displaying a significantly enhanced thermal stability.

3.2. Fire behavior

3.2.1. Cone calorimeter test

Cone calorimeter is one of the most used device to assess the flammability of materials at bench scale. Samples have been tested with a heat flux of 35 kW/m^2, corresponding to common heat flux in a mild fire scenario. 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, have been considered. In fact, a high pHRR and a low TTI may cause both fast ignition and rapid fire propagation. Curves of cone calorimeter test are presented Fig. 4 and results summarized in Table 7.

Pristine PLA exhibits a strong combustion, starting after 87 s, consuming all the material and releasing a total heat of about 90 MJ/m^2 with a pHRR of 390 kW/m^2.

The effect of lignin and phytic acid incorporated separately has been first evaluated. Addition of 20 wt% lignin, whatever its nature, leads to an important increase of PLA ignitability since TTI decreases from 87 s to 37 s and 26 s for kraft and organosolv lignins respectively.

Table 6
Number average molecular weight of processed PLA and PLA/lignin/phytic acid composites.

Compositions	M_n (g/mol)
PLA	87600
20 Phytic	44500
20 Kraft	37700
20 Organosolv	15100
15 Phytic/5 Kraft	30900
10 Phytic/10 Kraft	52500
15 Phytic/5 Organosolv	54700
10 Phytic/10 Organosolv	65200

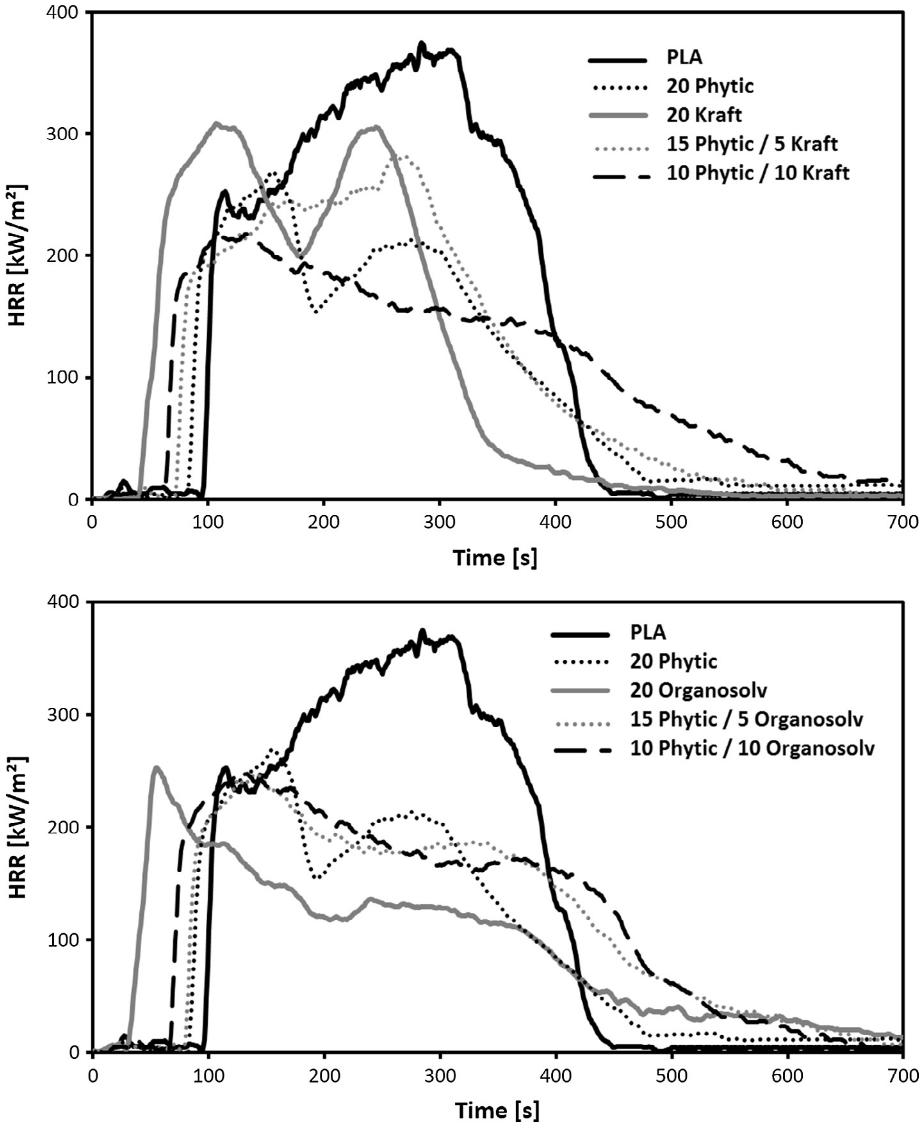
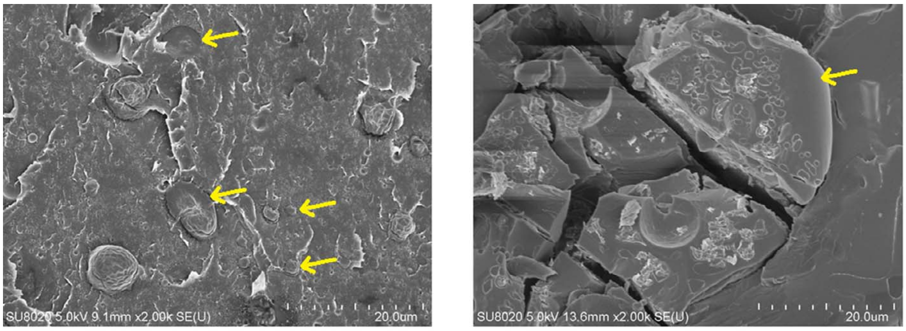


Fig. 4. HRR curves of PLA/lignin/phytic acid compositions.

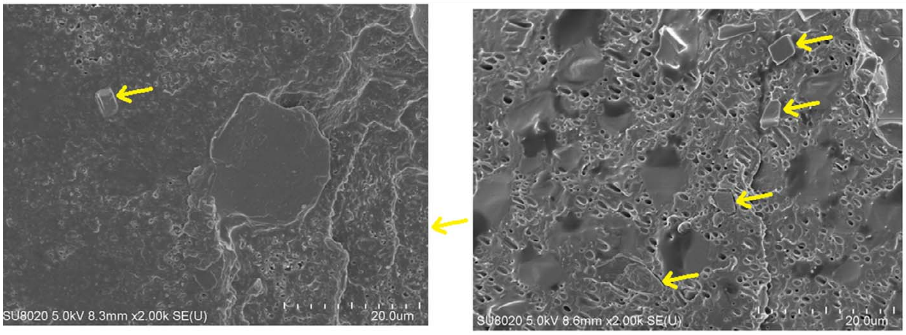
Table 7
Cone calorimeter data and UL 94 ratings of neat PLA and flame retarded PLA compositions.

	TTI (s)	pHRR (kW/m^2)	% Reduction	THR (MJ/m^2)	% Reduction	Residue (%)	UL-94 rating
PLA	87	390	–	90	–	0	NC
20 Phytic	71	270	31	74	18	13	V-2
20 Kraft	37	310	21	71	21	17	NC
20 Organosolv	26	260	33	67	26	19	NC
15 phytic/5 Kraft	77	285	27	74	18	13	V-2
10 Phytic/10 Kraft	43	220	44	74	18	12	V-2
15 Phytic/5 Organosolv	61	250	36	78	13	13	V-2
10 Phytic/10 Organosolv	46	250	36	65	28	13	V-2

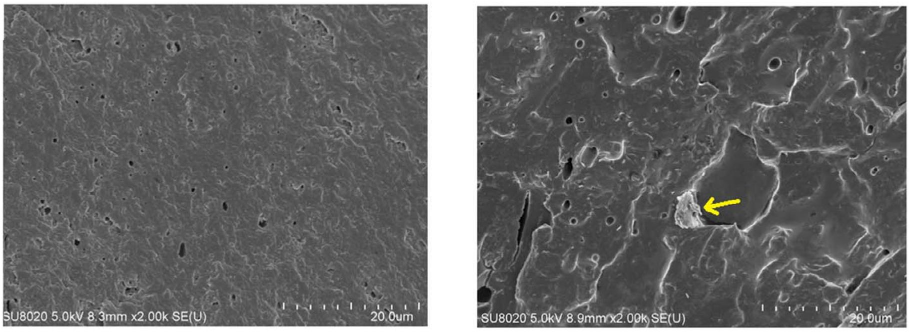
Similar effect of lignin has been reported in PBS [22] and ABS [23]. Among several factors (thermal degradation, emissivity and thermal conductivity changes), Prieur et al. [23] attributed the reduction of TTI induced by lignin to the modification of the heat absorption coupled with earlier release of combustible products. An increase of the heat absorption of the material, due to its coloration, was suggested to promote the ignition by inducing a stronger heating of the decomposition gases. The same scenario occurs in our case. In fact, TGA indicated that lignin is responsible for significant premature PLA thermal degradation that led to earlier release of volatile products. Moreover, the incorporation of lignin induces modification of the sample color: the transparent



20 Organosolv **20 Kraft**



10 Phytic / 10 Organosolv **10 Phytic / 10 Kraft**



15 Phytic / 5 Organosolv **15 Phytic / 5 Kraft**

Fig. 5. SEM pictures of PLA/lignin/phytic acid based compositions.

pristine PLA becomes black with lignin. This leads to an increase of its heat absorption, also contributing to the earlier production of volatile gases and to the release of more thermal energy during its decomposition.

The incorporation of lignin also enables significant reduction of both pHRR and THR. This reduction is more important when organosolv lignin is used. Moreover, a significant change of the HRR curve shape is noticed and depends on the nature of lignin used. HRR curve of PLA/organosolv blend is characteristic of a thick charring behavior while that of PLA/kraft lignin contains a second HRR peak (around 240 s) corresponding to the char cracking and to the release of further combustible products. The higher flame retardancy effectiveness of organosolv lignin is due to its better dispersion state as it is evidenced by SEM images. As shown in Fig. 5, large aggregates, higher than 20 μm are present in the case of PLA/20 Kraft composite.

In contrast, phytic acid seems to be more interesting as flame retardant additive for PLA since its effect on PLA ignitability is not as drastic as that of lignin (TTI is only slightly reduced from 87 s to 71 s). Moreover, its presence induces similar pHRR and THR reduction to that obtained with organosolv lignin. The limited reduction of TTI may be directly related to the fact that phytic acid induces only a slight premature PLA thermal degradation and a white sample coloration. Both lignins and phytic acid act in condensed phase by promoting the formation of charred structures during the combustion. The amount of residue is lower when phytic acid is used (13%). However, using phytic acid alone, as flame retardant additive for PLA, is not suitable since it is susceptible to migrate onto polymer surface during storage owing to its liquid form, and to be responsible for increasing the hygroscopic behavior of the material. In fact, some drops have been observed on the surface of samples after some days of storage. This phenomenon is further studied in the following.

Combining lignin and phosphorus based compounds has been shown to be efficient for improving its flame retardant effect in different polymers [16,11,15]. When lignin is combined with phytic acid, TTI increases up to 50–60 s. As it was shown by TGA, the presence of phytic acid restricts the thermo-degradant effect of lignin since no premature thermal degradation was observed. This attests for the link between the ignitability of the composite and the earlier release of combustible products, coupled with the modification of the material heat absorption.

The combination of lignin and phytic acid also results in some modification of the heat release rate. Kraft lignin/phytic acid combinations allow significant reduction of the combustion peak, higher than that obtained when the two additives are used separately. The partial substitution of phytic acid by only 5 wt% kraft lignin is not enough to induce significant reduction of the pHRR. Only a change of HRR curve shape is observed from a two HRR peaks to an “Intermediate thick non-charring” according to Shartel and Hull classification [33]. The presence of so low fraction of kraft lignin seems disturbing the char formation since the first peak, that has been observed only when phytic acid is used, desappears. It is worth to mention that the pHRR of this combination is similar to that obtained with 20 wt% phytic acid (285 and 270 kW/m^2 respectively) but takes place 114 s later (at 156 and 270 s respectively).

Increasing the amount of kraft lignin in the blend up to 10 wt% enables to obtain lower pHRR and improvement of the material ignitability. A change of the HRR curve to a “Thick charring” corresponding to a burning behavior with an initial increase in HRR until the formation of an efficient char layer is also noticed. In contrast and since pHRR level reached with 20 wt% organosolv lignin was relatively low (260 kW/m^2), no further reduction of pHRR has been recorded when combined with phytic acid.

In addition, the presence of phytic acid allows for better dispersion of lignin particles within PLA (Fig. 5). This effect is more obvious in the case of kraft lignin that displayed poor dispersion when used alone. In fact, the large lignin aggregates disappear and only some isolated particles are present. However, SEM observations also evidenced the presence of debonding that clearly indicates a poor adhesion between PLA and lignin particles. Better dispersion state of lignin particles may ensure the formation of more homogenous char during the combustion and avoid the formation of isolated char domains. This effect has been evidenced by Song et al. [34] into ABS/lignin compositions. However, in our study, no correlation could be made between lignin dispersion state and final char structure (Fig. 6). In fact, in addition to the dispersion state of lignin, other parameters such as the molten viscosity and the kinetic of the char formation affect the cohesion of the final char layer. For example, a char that is formed too late will not ensure any

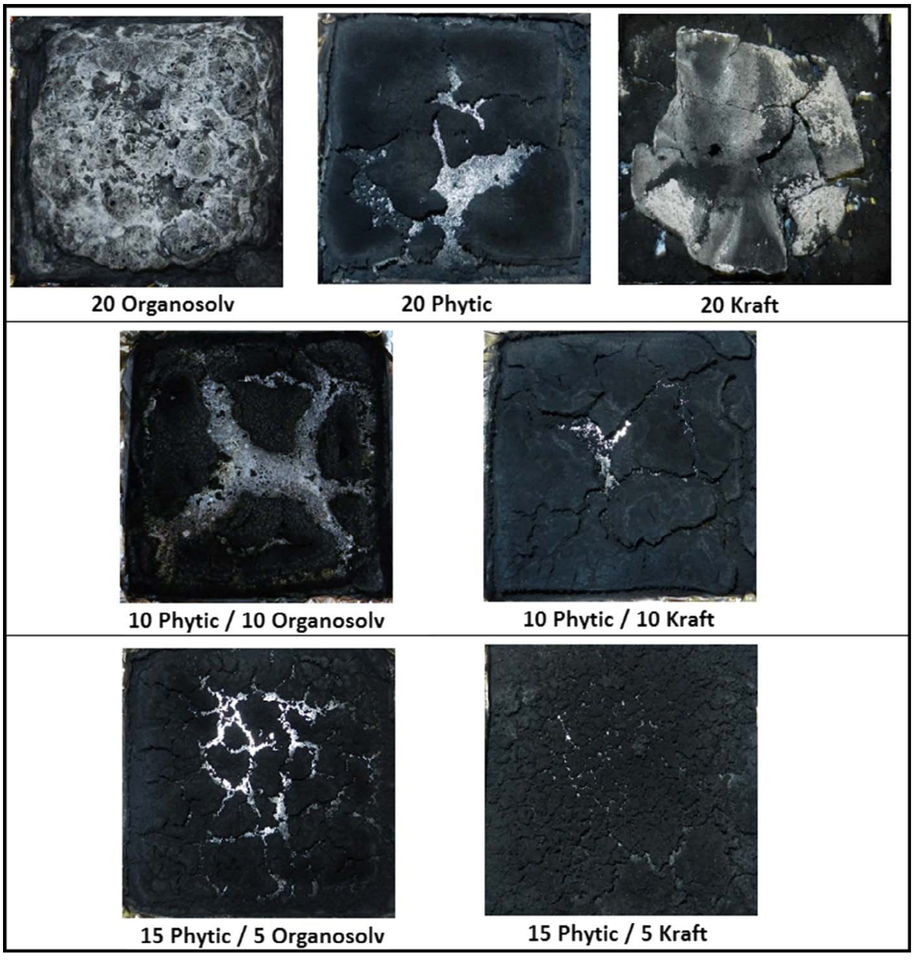


Fig. 6. Pictures of the char formed during cone calorimeter test of PLA containing lignin, phytic acid and their combinations.

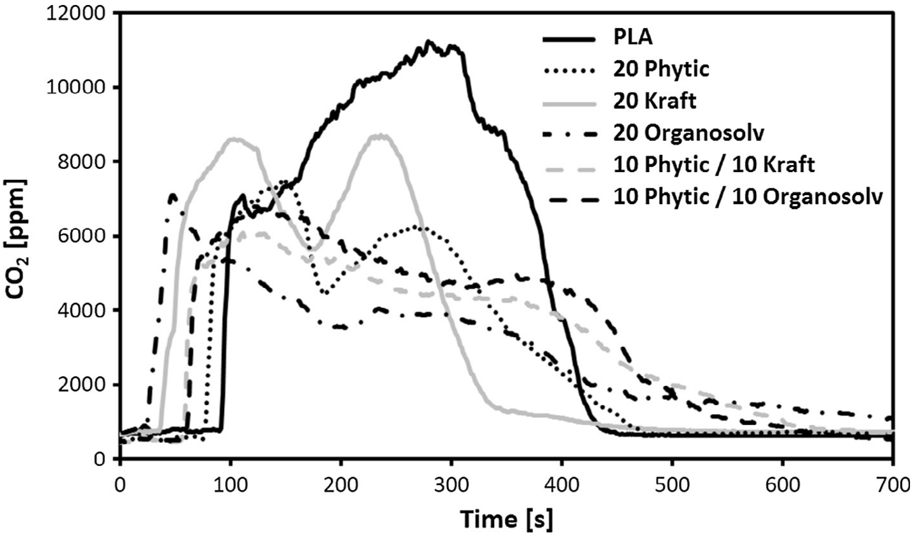


Fig. 7. Evolution of CO_2 production during cone calorimeter test.

efficient protection of the material even if it is cohesive. On the contrary, an effective char that is early formed may protect appropriately the material and decompose at the end of the test since it will be subjected to more longer thermal stress.

The combustion of PLA is complete under well-ventilated fire conditions, releasing mainly CO_2 and water without any residue. As expected, similar curves are obtained for the HRR and the CO_2 concentration for all the compositions (Fig. 7). Indeed, the HRR is calculated from the oxygen consumption but it can also be estimated from the carbon oxides generation thanks to the Hess Law [35,36]. Figs. 8 and 9 evidence some traces of CO and unburned hydrocarbons as indicated by the presence of peaks at the ignition of the sample.

Addition of 20 wt% kraft lignin induces an important increase of the amount of unburned hydrocarbons. In fact, threepeaks with intensities of about 60 ppm are observed before 400 s. Phytic acid also induces increase of the amount of unburned hydrocarbons but to a less extent than kraft lignin. In the case of PLA/kraft lignin composition, thegeneration of such unburned species is due to the aromatic structure of kraft lignin. In fact, during the combustion, lignin decomposes and produces aromatic structures that burn less easily than aliphatic compounds and that are responsible for smoke production. In the case of phytic acid, the formation of unburned hydrocarbons is due to the presence of phosphorus that is unfortunately well known to increase the amount of smoke emission during the combustion. Phosphorus may act through two mechanisms. The first one concerns its flame inhibition action in the gas phase that limits oxidations reactions and generates incomplete combustion. The second one is attributed to the char forming ability of phosphorus based compounds in condensed phase that promotes the generation of aromatic structures. Some of them are thermally degraded and volatilized.

In the case of PLA/organosolv lignin composition, the amounts of unburned hydrocarbons and CO are very low owing to the formation of efficient char layer during the combustion owing to the better lignin dispersion state. The degradation of this char occurs at the end of the test and generates an important release of unburned hydrocarbons.

The combination of lignin, whatever its nature, and phytic acid induces significant changes of both CO and unburned hydrocarbons releases, especially around the end of the combustion. In fact, the amount of unburned hydrocarbons released during char degradation is significantly reduced while the production of CO is increased. The absence of unburned hydrocarbons indicates that combining phytic acid and lignin enables the formation of very thermally stable char residue.

3.2.2. UL-94 test

The cone calorimeter remains one of the most useful bench-scale tests for fire safety assessment, allowing the determination of the fire behavior of material during its combustion. However, due to the horizontal position of the sample during the test, the information thus obtained does not consider the effect of polymer dripping. Dripping of flaming polymer should be considered since it can strongly affect the fire scenario and can be either a benefit or a drawback during a fire. In fact, the formation of flaming polymer drops can take the fire away from the surface of the specimen, causing its extinction, or it can on the other hand provide an additional ignition source to other materials increasing fire spreading.

In our case, all the investigated compositions have been tested at both cone calorimeter and UL-94 tests. UL-94 test provides useful information about horizontal burning behavior of our compositions. Using 20 wt% of lignin does not allow any classification in contrast to phytic acid that leads to V-2 rating (Table 7). Combining lignin and phytic acid enables conserving the V-2 classification.

3.3. Mechanical properties

When developing a flame retardant system for polymeric materials, it is necessary to evaluate the effect of these additives on the

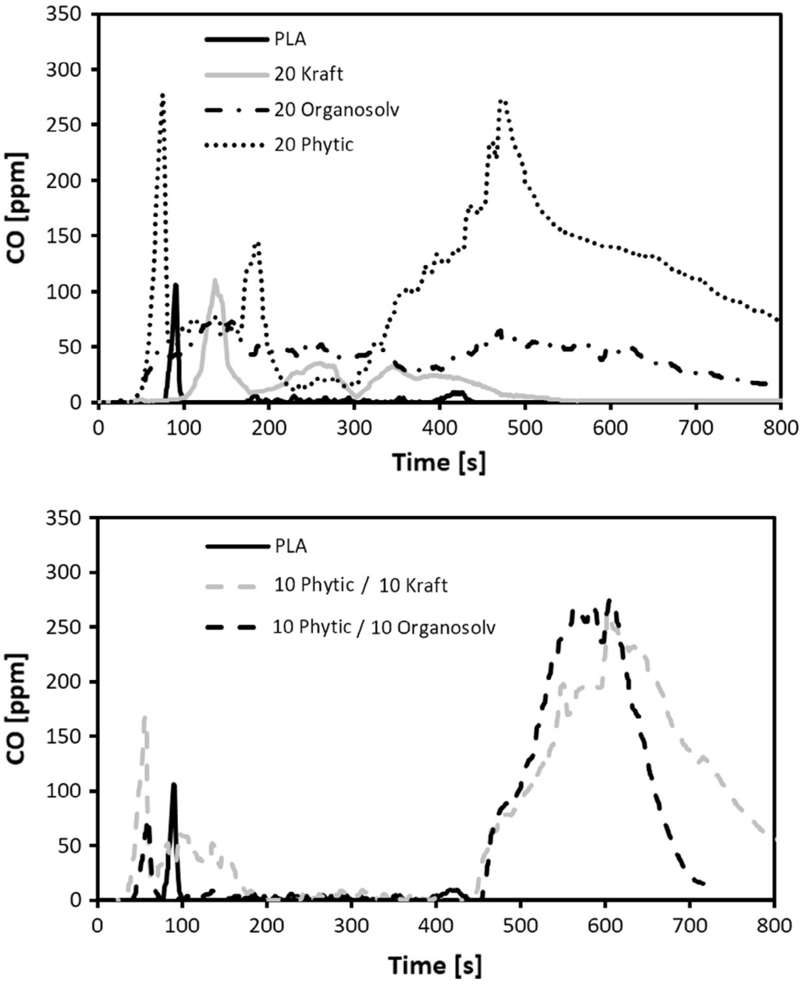


Fig. 8. Evolution of CO production during cone calorimeter test.

other functional properties of the final material such as mechanical properties.

As it can be shown in Table 8 and Fig. 10, pristine PLA presents a high rigidity (3200 MPa), a high tensile strength (70.3 MPa) and a low elongation at break (3%). The incorporation of lignin or phytic acid separately induces considerable deterioration of PLA mechanical properties, and especially its elongation at break, stress at yield, and impact resistance. This poor mechanical behavior results from the low PLA chain molecular weight. It is also important to mention that mechanical properties of PLA containing 20 wt% organosolv lignin was not determined since this composite was so brittle that it was impossible to obtain specimens for mechanical testing.

Limiting PLA degradation during melt processing owing to the combination of lignin and phytic acid enables some enhancement of composites mechanical properties. Impact resistance and tensile strength are improved, with the former up to the level of unfilled PLA.

A surprising change of the mechanical behavior of PLA is obtained for the combination containing 5 wt% organosolv lignin and 15 wt% phytic acid. The curve shape changes from that of a brittle material to a ductile one, with an elongation at break that increases from 3.1% for unfilled PLA to 12.6%. This improvement could not be explained by the good dispersion of lignin in this blend or by the limitation of PLA chain molecular weight reduction since the elongation at break reached is higher than that of pristine material. Some plasticization effect of phytic acid or modification of PLA crystallization are assumed to be responsible for this improvement.

In order to understand the origin of the improvement of mechanical properties of PLA containing 5 wt% organosolv lignin and 15 wt% phytic acid, we performed DSC analysis on the compositions containing organosolv lignin.

3.4. DSC analysis

The incorporation of 20 wt% lignin or phytic acid induces considerable modifications of PLA thermal behavior during DSC analysis (Fig. 11 and Table 9). In fact, Fig. 11 evidences the presence of cold crystallization and melting peaks for all the composites

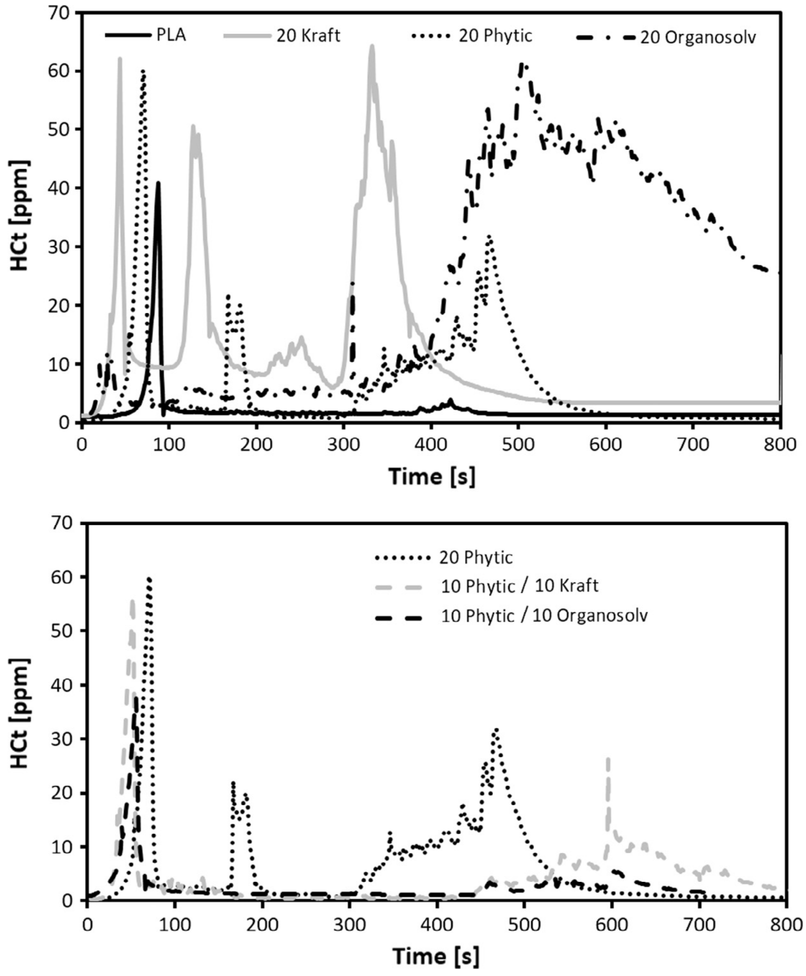


Fig. 9. Evolution of unburned hydrocarbons during cone calorimeter test.

Table 8
Young's modulus, tensile strength, elongation at break from tensile test, and impact resistance of PLA and PLA/lignin/phytic acid composites.

	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Impact resistance (kJ/m^2)
PLA	3.2	70.3	3.1	2.8
20 Phytic	2.5	27.7	2.3	1.4
20 Kraft	3.7	16.9	0.6	1.4
15 Phytic/5 Kraft	2.4	35.8	3.0	2.8
10 Phytic/10 Kraft	3.0	38.6	2.3	2.9
15 Phytic/5 Organosolv	2.6	45.1	12.6	2.9
10 Phytic/10 Organosolv	2.9	57.3	3.9	3

except for pristine PLA. No effect on PLA glass transition temperature has been observed. The appearance of the cold crystallization peaks clearly evidences the nucleant effect of lignin particles while it is attributed to a plastificization effect in the case of phytic acid. However, phytic acid acts as poor plasticizer since the presence of a heat flow variation around 20 °C on DSC curve of PLA/20 wt% phytic acid composition, attributed to the melting of phytic acid, highlights that most phytic acid is located in an interfacial zone and is not well mixed with PLA chains. During DSC heating, phytic acid may diffuse into PLA chains and support their cold crystallization.

For the PLA containing lignin/phytic acid blends, DSC curves show the disappearance of the melting peak of phytic acid, indicating that phytic acid is not anymore segregated into a separate phase. This result clearly evidences the good affinity between lignin and phytic acid. Moreover, the cold cristallization is more pronounced when 5 wt% organosolv lignin is combined with phytic acid. In fact, temperature of cold crystallization peak of this composition is lower (111.4 °C) than that of PLA containing 20 wt% phytic acid (124.6 °C), 20 wt% organosolv lignin (129.4 °C) or their combination (10/10 wt%/wt%) (126.4 °C).

The combination of 5 wt% organosolv lignin and 15 wt% phytic acid enables thus for increasing PLA cold crystallization owing to lignin nucleant effect combined with its good dispersion state.

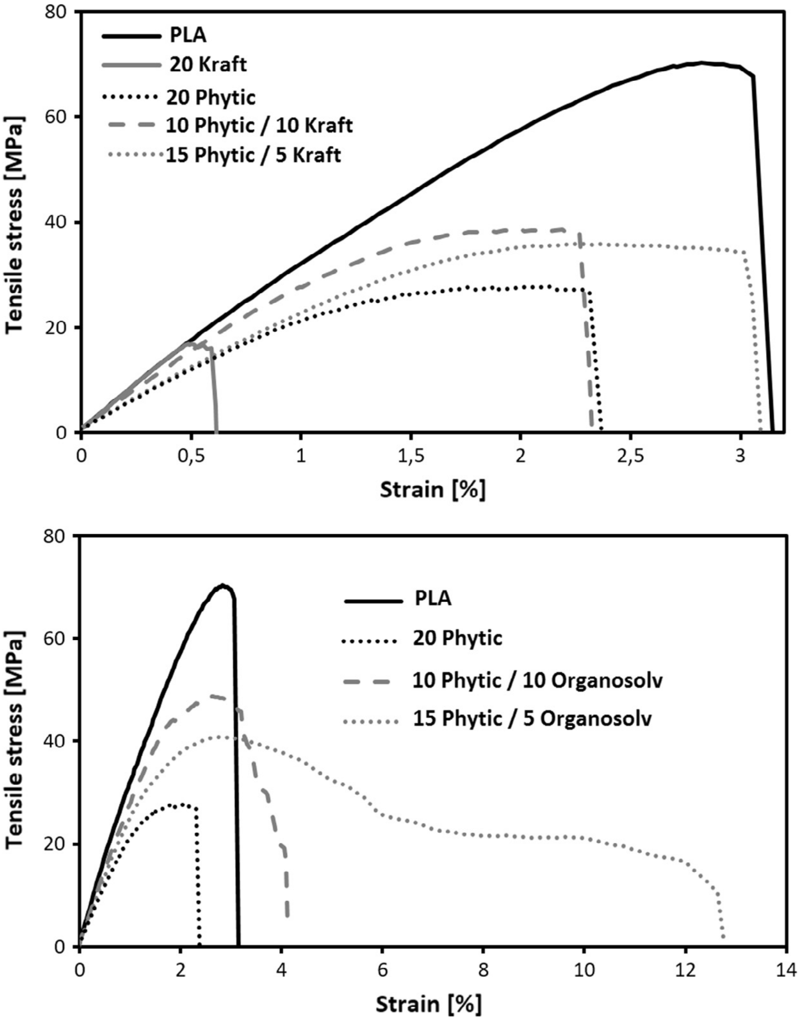


Fig. 10. Stress/strain curves of neat PLA and PLA/lignin/phytic acid composites from tensile test.

Table 9
Glass transition (T_g), cold crystallization (T_{CC}) and melting (T_m) temperatures, and crystallinity index (C_i) values of PLA and PLA/lignin/phytic acid composites.

	T_g (°C)	T_{cc} (°C)	T_m (°C)	C_i (%)
PLA 3051D	61.5	–	–	–
20 Phytic	58.0	124.6	150.4	4.7
20 Organosolv	58.0	129.4	150.7	3.5
15 Phytic/5 organosolv	57.8	111.4	153.4	4.8
10 Phytic/10 organosolv	57.5	126.4	151.9	5.9

3.5. Hygroscopic behavior

In comparison to lignin, phytic acid seems to be more efficient as flame retardant additive for PLA. Its incorporation at 20 wt% results in significant reduction of pHRR (Fig. 4), V-2 rating at UL-94 (Table 7) and does not induce substantial decrease of PLA thermal stability as observed on TG curve (Fig. 3). However, phytic acid presents an important drawback that hinders its use as fire retardant for PLA. We observed that in the presence of 20 wt% phytic acid, some droplets are formed at the surface of the material during its storage. Due to its water uptake ability [37], the incorporation of 20 wt% phytic acid induces an important increase of PLA composite hygroscopy. The weight of PLA sample, containing 20 wt% phytic acid and maintained at a relative humidity of 55%, increases rapidly and a plateau corresponding to 6% weight increase is reached after 600 h (Fig. 12). Whereas, neat PLA in the same conditions does not present any weight change.

The association of lignin and phytic acid allows significant limitation of the weightincrease. Moreover, the weight increase is directly related to the content in phytic acid. The less phytic acid in the blend, the lower is the hygroscopy of the composite. Using

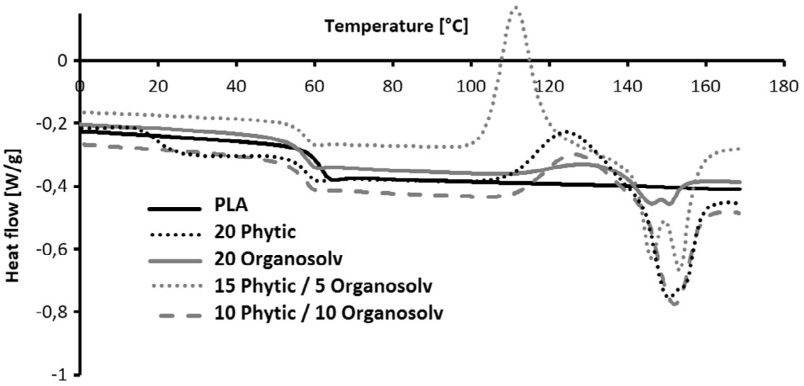


Fig. 11. DSC curves of PLA and PLA/lignin/phytic acid composites.

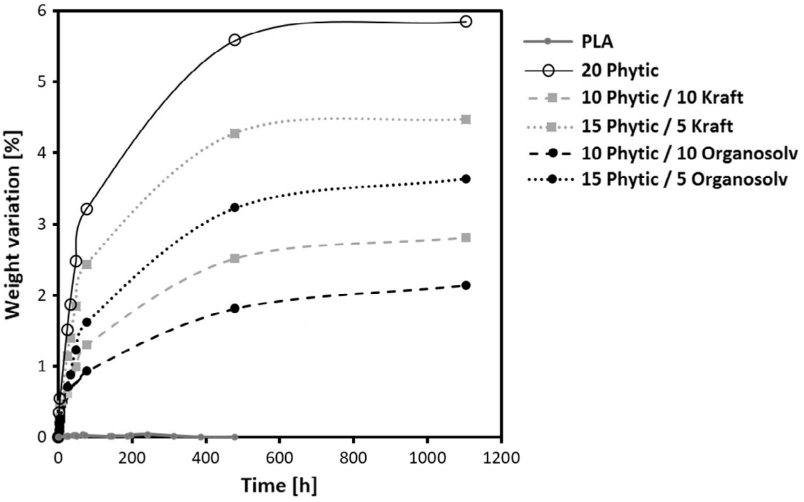


Fig. 12. Evolution of the weight vs. time of PLA/lignin/phytic acid compositions.

organosolv lignin results in the most important reduction of the hygroscopic behavior of the blend. The partial substitution of 5 wt% phytic acid by organosolv lignin enables reducing the weight gain from 6% to 3% only. This demonstrates that the preferential interaction between the two additives reduces phytic acid water uptake ability.

4. Conclusion

The interest of using phytic acid and lignin blends on the flame retardant properties of PLA has been investigated. Results show that the combination of these two additives is an interesting way for taking advantage of both while limiting their negative effect. In fact, the use of 20 wt% of lignin alone or 20 wt% of phytic acid alone improves the fire behavior of PLA thanks to their effect leading to the formation of an insulating barrier of char during the combustion. However, using lignin alone induces significant PLA thermal degradation due to its numerous functional groups, during both melt processing and TGA, while the incorporation of phytic acid only is not adapted for PLA because it increases the composite hygroscopic behavior.

The incorporation of phytic acid/lignin blend into PLA limits the negative effects induced by each, in addition to significantly improving the fire behavior of PLA. PLA/phytic acid/lignin composites exhibit very promising FR performances since pHRR was significantly reduced as well as the composite ignitability. Thanks to the favorable interaction between the two additives, phytic acid enables better dispersion state of lignin and makes its functional groups less reactive causing less PLA thermal degradation. The thermal stability of the material was enhanced and the reduction of PLA chain molecular weight significantly limited. The improvement of thermal stability is partly responsible for the reduction of the ignitability of the material. The limitation of the reduction of PLA chain molecular weight is also essential to restrict the degradation of mechanical properties which is a considerable disadvantage of the use of lignin alone. Moreover, this association results in the reduction of PLA hygroscopy: the weight gain is decreased from 6% to 3% when 5 wt% of phytic acid is substituted by organosolv lignin. This blend also exhibits important elongation at break (12%), low pHRR (250 kW/m^2) and a V-2 classification at UL-94 test.

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