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Phosphorus and nitrogen derivatization as efficient route for improvement of lignin flame retardant action in PLA

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ABSTRACT

The present study focuses on the use of lignin, which is the second most abundant constituent of the biomass, as sustainable flame retardant additive for polylactide (PLA). Indeed, thanks to its aromatic structure, lignin could be advantageously used, in polymeric matrices, as a char promotor agent that can allow some reduction of the combustion rate. An original and simple approach, based on a two-step phosphorus/nitrogen chemical modification, is proposed to enhance the flame retardant effect of lignin in PLA. This approach has been applied on two different lignins, i.e. kraft and organosolv lignins. The effect of the plant origin, extraction mode of lignin as well as it chemical modification on both its structure and properties was investigated by using several characterization techniques. Fire properties and thermal behavior of PLA composites containing 20 wt% of both untreated and treated lignins were characterized by using cone calorimeter, UL-94 and thermogravimetric analysis (TGA). Results showed that the incorporation of untreated lignins led to a flame retardant action in PLA thanks to the formation of char but also to a significant loss of the thermal stability of PLA and to an important decrease of its time to ignition. In contrast, both phosphorus/nitrogen chemically treated lignins were found to limit PLA thermal degradation during melt processing as well as during TG experiments and also to significantly improve fire retardant properties allowing to reach V0 classification at UL-94. In this paper we also deeply investigated the nature of the gases evolved during thermal decomposition of treated and untreated lignins by using TGA-Mass spectrometer and cone calorimeter – FTIR couplings.

1. Introduction

Polymer materials play a significant role in our daily life thanks to their wide range of advantages such as versatile mechanical properties, ease of processing and possibility of recycling. Great interest is more and more devoted to improve the sustainability of polymers with the growing concern over the environmental protection [1]. Bioplastics issued from renewable resources represent an interesting alternative to reduce carbon footprint instead of using polymers made of fossil carbon. These green materials were initially developed for short-term applications taking advantage of their biodegradability. But recently, more durable and technical applications such as in automotive, electronics and construction industries are considered [2,3].

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However, to extend the development of technical and durable applications for bioplastics, some properties like impact resistance and tensile strength, service temperature, long-term stability, fire retardant behavior need to be improved.

Flame retardancy is an active research subject developing numerous and efficient strategies to endow polymers with good fire-resistant properties [4,5]. Among others, halogenated flame retardant compounds have been widely used to improve fire retardant behavior of polymeric materials. Unfortunately, some of these products have been proved to be linked to cancer, reproductive problems and impaired fetal brain development [6,7]. Even if only 3 halogenated products are currently forbidden (penta- and octa-bromodiphenyl ether as well as hexabromocyclododecane), scientific and industrial communities avoid more and more the use of halogenated flame retardant additives, which are thus gradually forsaken to the benefit of halogen-free flame retardant additives [8–10]. 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 polyesters such as polyethylene terephthalate (PET) and PLA [11–13].

As far as PLA is concerned, the FR approaches that have to be used to improve its fire behavior have also to be sustainable in order to maintain the good environmental profile of this biobased polymer. Actually, biobased compounds have already attracted research interest in the field of polymer fire retardancy. The use of agro-based phosphorous compounds in PLA has been recently studied by some of us [14] and results demonstrated that storage vegetal compounds such as aluminum phytate, among different metallic phytate salts, leads to rapid formation of a char layer that allows significant reduction of pHRR. The use of other biobased char-forming agents, such as starch [15], β-cyclodextrin [16] or lignin [17], has also been studied. Lignin, which is the most abundant renewable aromatic polymer [18,19], exhibits a good thermal stability and a very high char yield after decomposition thanks to its aromatic chemical structure [20].

Reti et al. [15] evaluated the efficiency of intumescent formulations containing ammonium polyphosphate (APP) combined with different carbonization agents such as starch and lignin. They found out that PLA-based composites containing 12% APP and 28% starch reached better fire retardant properties (V0 classification and 32% LOI value) than the traditional ammonium polyphosphate/pentaerythritol-containing system. In order to improve even more the fire behavior of PLA with fire retardant systems containing lignin, Zhang et al. chemically modified the lignin or combined it with synergistic compounds [21–23]. The functionalization of lignin to improve its fire retardant performances proved to be effective. Modified lignin was employed and resulted in better fire behaviors in polyurethane foam [24,25], in polypropylene [26] and in polybutylene succinate [27]. Recently, the use of lignin as flame retardant has been studied in silicone composites [28]. The improved thermal stability and fire behavior was attributed to the formation of char thanks to lignin “repolymerization” in addition to the silica char and the ability of lignin to scavenge free-radicals.

This contribution aims at studying and comparing the flame retardant behavior of PLA containing two lignins, i.e. kraft and organosolv, obtained by two extraction methods. Lignins were chemically modified by using a two-step method allowing phosphorus and nitrogen grafting in order to improve their fire retardant action in PLA. The properties of the different types of unmodified and modified lignins and their effect upon PLA properties when incorporated in this matrix were investigated by original characterization techniques. This work allows to reach a high understanding concerning the relation between the additive structural and physical properties and the effects it induces in a polymer matrix.

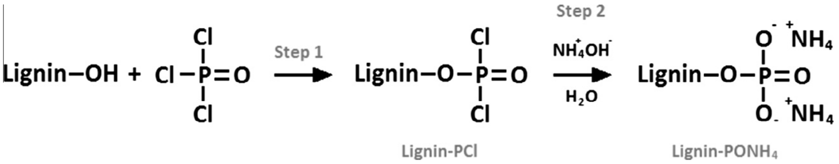
2. Experimental

2.1. Materials

PLA resin (3051D) with a number average molecular weight of 100,000 g/mol, a dispersity of 2.1 and 4.3% of D-lactide content was purchased from NatureWorks. Two lignins were used in this study: a kraft lignin with a low sulfonate content (4% of sulfur), from Sigma Aldrich and an organosolv lignin from BOC Sciences. These two lignins are separated from cellulose and hemicelluloses by two different extraction modes. 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. Phosphorus chloride ($POCl_3$, purity 99%) and ammonium hydroxide solution (NH_4OH, 28–30% NH_3 basis) were purchased from Sigma Aldrich and used as received.

2.2. Lignin treatment

The chemical modification of lignin was performed in two steps (Scheme 1). The first step allowed the grafting of phosphorus chloride while its conversion into phosphoric acid ester and then into ammonium phosphate occurred during the



Scheme 1. Two-step chemical modification of lignin.

second step. In fact, the presence of phosphoric acid groups in lignin may induce some degradations of PLA during melt processing, when the modified lignin is used as additive, and therefore it has been preferred to investigate this phosphorus-nitrogen grafting approach. Practically, $POCl_3$ was grafted onto the lignins in two steps:

- *Step 1:* production of lignin-PCl via grafting of phosphorus chloride:

Lignin (100 g) was added to $CHCl_3$ (500 mL) and heated to 50 °C. $POCl_3$ (65 g) was added drop by drop to the mixture. The mixture was heated at 60 °C for 17 h. The product (lignin-PCl) was recovered by filtration and washed with $CHCl_3$ to remove any ungrafted $POCl_3$. Lignin-PCl was dried at 60 °C in vacuum oven.

- *Step 2:* conversion to ammonium phosphate:

Lignin-PCl (30 g) was added to water (300 mL). NH_4OH (30 mL) was added to the dispersion. The mixture was stirred for 2 h at room temperature. The mixture was filtrated and washed with water. Only the soluble fraction was then used in the study. The insoluble fraction obtained by treatment of kraft lignin contained only 1.7 wt% of P whereas the soluble fraction contained 9.1 wt% of P (P content was determined by ICP analysis, see hereafter). The water soluble fraction (Lignin-$PONH_4$) was precipitated in acetone and recovered by centrifugation in order to remove the excess of NH_4OH (and NaCl which could have formed due to the presence of Na in the studied lignins, see hereafter the analysis of the composition of the lignins, and the released HCl during the conversion of Lignin-PCl). Lignin-$PONH_4$ was then dried in a vacuum oven at 80 °C.

2.3. Melt processing

Blending of lignins within the molten PLA was carried out in a Brabender internal mixer at 160 °C (7 min mixing at 70 rpm). PLA and lignins were previously dried in a vacuum oven at 60 °C overnight right before use. 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 hydraulic press. PLA alone and PLA composites containing 20 wt% of each type of lignin, either unmodified or modified, were prepared.

2.4. Characterizations

2.4.1. Thermogravimetric analysis (TGA)

Thermal decomposition of the different lignins, pristine PLA and PLA-based composites were studied by thermogravimetric analysis (TGA). 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 after a 10 min isothermal at 100 °C to get rid of any moisture. All TGA experiments were performed under a nitrogen flow of 90 ml/min using a TGA Q50 device from TA Instruments.

TG-MS analysis were performed on lignin samples using TGA Q5000 device from TA Instruments coupled with a mass spectrometer.

2.4.2. Structural characterizations

Fourier transform infrared (FTIR) spectra were recorded using a Bruker IFS 66V/S spectrometer. Spectra were recorded using a spectral width ranging from 600 to 4000 cm^{-1}, with 4 cm^{-1} resolution and an accumulation of 32 scans.

Inductively Coupled Plasma (ICP) analysis were recorded with an IRIS Intrepid II (Dual view) from Thermo Fisher Scientific. It was used for the determination of the amount of phosphorus in the phosphorylated lignins and the char residues of PLA/phosphorylated lignin composites. Before ICP analysis, phosphorus containing samples were prepared by the destruction of the organic matrix by a mineralization process with $H_2SO_4/HNO_3/H_2O_2$ solutions. The amount of phosphorus was determined thanks to a calibration curve obtained from ICP analysis of phosphorus containing standard solutions.

Gel permeation chromatography (GPC) was used to determine the number average molecular weights of both PLA and PLA/lignin blends. The number average molecular weights and molecular weight distributions 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 10^3 A). 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.

Besides, the peak average molecular weights of lignins were evaluated by using a high performance size exclusion chromatography (HPSEC) with UV detection at 280 nm. The HPLC system (Waters 2690) (Waters Inc., Milford, MA, USA) was equipped with a pre-column and two TSKgel GMPWxl columns in series (300 mm × 7.8 mm) with particles sizes of respectively 7 and 6 μm (Tosoh Co. Ltd., Tokyo, Japan), and coupled on-line with UV detection (Waters 996 Photodiode array detector). The eluent solution contained 6.9 g $NaH_2PO_4 \cdot H_2O$ and 3.2 g NaOH in distilled water and the pH was adjusted to 12 with 6M NaOH. Before use, it was filtrated on 0.45 μm and sonicated during 15 min. The calibration was made with a range of poly(4-styrenesulfonic acid) ammonium salts (PSS-Na) with mass average molecular weights from 208 Da to 77.4 kDa. PSS-Na and lignins were dissolved in a volume of eluent, at 1 mg/mL and 3 mg/mL respectively. Before analyses, the lignin solutions were kept under magnetic stirring during 48 h to ensure a complete dissolution and then filtered on a 0.45 μm nylon filter. Elution was carried out at 30 °C, at a flow rate of 0.9 mL/min.

Aqueous potentiometric titration was used to determine the carboxyl and phenolic hydroxyl contents of lignins. To 0.25 g lignin was added 1 ml of deionized water and the pH was brought above 12 with concentrated NaOH. The solution was stirred magnetically until complete sample dissolution. The titration was done with 0.1 N HCl until pH 2, on a Metrohm titrator (model 751 GPD Titrino). Three inflection points were detected using Vesuv software (Metrohm, Swizerland).

Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX) was used to attest for the atomic composition of the untreated and treated lignins.

Morphological investigation was performed to highlight the dispersion of lignin in PLA using a scanning electron microscopy (SEM) Hitachi SU8020 (100 V–30 kV) apparatus. PLA composites were cryo-fractured after immersion in liquid nitrogen and then coated using a gold sputtering technique to avoid any charging effect during the electron beam scanning.

2.4.3. Fire behavior characterization

2.4.3.1. Cone calorimeter coupled with infrared spectroscopy (cone-FTIR). Cone calorimeter tests were performed according to ISO 5660 standard procedures 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 and Time To Ignition (TTI), Total Heat Release (THR) and peak of Heat Release Rate (pHRR) were determined. Cone calorimeter test has been also performed on compacted lignin powder (10 g) under 35 KW/m^2.

A FTIR spectrometer Nicolet 6700 from Thermo Scientific was coupled to the cone calorimeter. The sampling point was located on the drain pipe of the smokes of the cone calorimeter just before the exhaust blower. A filter was positioned after the sampling probe to trap solid particles. The sample was then transported to the gas cell through a transfer line heated at 180 °C. Temperature and pressure conditions in the gas cell were fixed at 180 °C and atmospheric pressure. The determination of the evolution of the gases concentration during the fire test was possible thanks to the identification of the gases and their quantification based on a calibration performed previously [29].

The evolution of the concentration of hydrocarbon compounds present in the smokes released during the fire test was obtained from a flame ionization detector (FID) from JUM Engineering.

2.4.3.2. UL-94 burning tests. UL-94 vertical burning tests were performed on a 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 (10 s each). The after flame and afterglow times were measured, and the eventual cotton ignition by flaming drops was recorded.

3. Results and discussion

3.1. Structural, thermal and fire properties of lignins

The type of lignin appears as a very important parameter that can influence its performance as flame retardant additive. In this study, two untreated lignins and two modified lignins were used to improve the fire behavior of PLA. Kraft and organosolv lignins do not display the same chemical composition and this variability is due to their plant origin and to the extraction method employed to separate the lignin from the other biomass components. Lignin is constituted of a tridimensional network with phenylpropane as a base unit. It is polymerized in the plant from p-coumaryl, synapyl and coniferyl alcohols which differ from each other by the degree of methoxylation of their aromatic rings. These monolignols are subjected to a radical oxidation allowing the radical monomers to create covalent links between each other. After the polymerization, the different monolignols result in p-hydroxyphenyl, guaiacyl and syringyl units. The composition in the different units of the lignin is mainly linked to the plant species [30].

In order to highlight the differences between the lignins used and understand their effects when incorporated into PLA, we investigated the chemical structure and physical properties of unmodified and modified lignins.

3.1.1. Unmodified lignins

3.1.1.1. Lignin chemical composition and functional groups. As it can be observed in Table 1, the atomic composition of the unmodified lignins proved to be very different. Even if both lignins are mainly constituted of carbon, oxygen and sodium

Table 1
Atomic composition of untreated and treated kraft lignin and organosolv lignins determined by SEM/EDX.

Samples	C (wt%)	O (wt%)	N (wt%)	P (wt%)	Na (wt%)	S (wt%)	Cl (wt%)	Si (wt%)	K (wt%)
Kraft lignin	40.2 (±0.3)	41.8 (±0.3)	0	0	11.8 (±0.1)	6.0 (±0.1)	0	0	0
Organosolv lignin	26.2 (±0.3)	44.9 (±0.3)	0	0	20.5 (±0.1)	1.2 (±0.1)	3.2 (±0.1)	1.4 (±0.1)	2.6 (±0.1)
Kraft lignin-$PONH_4$	17.2 (±0.5)	56 (±0.5)	7 (±0.7)	9.1 (±0.2)	8.7 (±0.2)	1.8 (±0.1)	0.2 (±0.1)	0	0
Organosolv lignin-$PONH_4$	14.3 (±0.5)	57.9 (±0.5)	6 (±0.7)	9.4 (±0.2)	11.4 (±0.2)	0.2 (±0.1)	0.1 (±0.1)	0.3 (±0.1)	0.4 (±0.1)

(hydrogen is not detected by this analysis), the proportions between these different elements are not the same. Organosolv lignin has a sodium content higher than kraft lignin. The difference of sodium content in the two lignins cannot be attributed to the extraction/purification steps since organosolv process uses only organic solvents, in contrast to kraft process which takes place in aqueous solution of sodium hydroxide and sodium sulfide [31]. The amount of sodium in organosolv lignin is thus surprising and could be attributed to some lignin neutralization by the addition of NaOH after the extraction process. This hypothesis is supported by the pH value of this lignin that is around 11. However, the use of sodium sulfide during kraft process explains the presence of sulfur in the case of kraft lignin. There is also a small amount of sulfur in organosolv lignin that probably comes from the original composition of the lignin in the plant.

The difference in the proportion of C and O between the two lignins has to be pointed out. The amount of carbon in kraft lignin is similar to that of oxygen while there is much more O than C in organosolv lignin. Several reasons could be speculated for this difference in C/O ratio. One of them is related to the composition in *p*-hydroxyphenyl, guaiacyl and syringyl units. Another may concern the effect of the extraction method. Indeed, the organosolv process increases the proportion in O by involving ring hydroxylation, oxidative ring opening, cleavage of ether bonds and epoxidation [32]. The oxidative ring opening of a dihydroxyphenol compound leads to the formation of a quinone and then of a diester derived from the

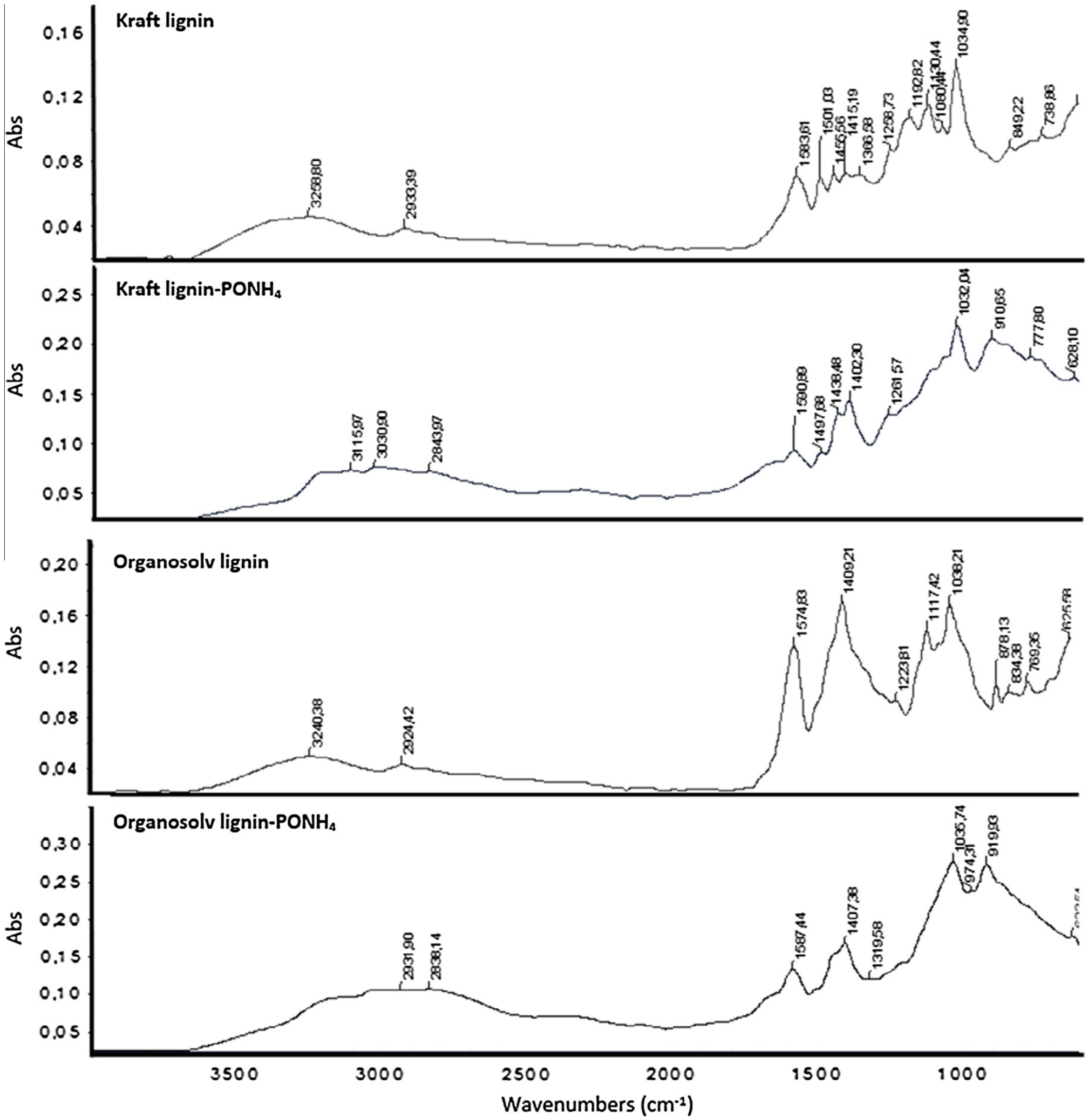


Fig. 1. Infrared spectra of unmodified and modified kraft and organosolv lignins.

initial dihydroxyphenol thanks to the action of an oxidizing agent. Organosolv process leads to the formation of lignin containing a lot of reactive side chains [33].

Infrared analysis was also performed (Fig. 1) in order to investigate the nature of the functional groups of the studied lignins and to determine their amount by using a semi-quantitative approach described by Nada et al. [32]. This approach is based on the determination of the relative absorbance corresponding to the ratio of absorption bands intensity of the functional group to that of aromatic C-C stretches at 1500 cm^{-1} (Table 2).

The use of this semi-quantitative approach proved to be very useful to compare the two lignins. In fact, the relative absorbance of aliphatic C—H stretch around 2930 cm^{-1} which is mainly attributed to the methoxy groups, is higher in kraft lignin than in organosolv lignin. This difference is attributed to the extraction method of organosolv lignin that induces some oxidative demethylation. The relative absorbance of the band at 1035 cm^{-1} which could also correspond to the C—O of methoxy groups confirms this trend. According to the calculated ratio, more organic acid salt (band at 1580 cm^{-1}), more phenolic OH (band at 1360 cm^{-1}) and more C—O of primary or secondary alcohol (1080 cm^{-1}) are found in organosolv lignin than in kraft lignin. It is worth to mention that all these groups are reactive and could induce the thermal degradation at high temperature of a polymer matrix such as PLA when incorporated into this matrix as additive. Moreover, the relative absorbances of bands attributed to syringyl (1260 cm^{-1}) and guaiacyl (1193 cm^{-1}) units indicate that kraft lignin contains both of these units whereas organosolv lignin is mainly constituted of syringyl units [34].

Aqueous titrations were also used to quantify the acidic and phenolic hydroxyl groups of both lignins. The results presented in Table 3 clearly evidence the high content of carboxylic functions in the organosolv lignin (threefold higher than that of kraft lignin), which is perfectly correlated with results obtained from FTIR analysis (Table 2).

3.1.1.2. Lignin molecular weight. Thus it is established that the organosolv lignin used in our study contains higher amount of carboxylic functions than kraft lignin. This is due to the organosolv process that induces some depolymerization reactions by ring hydroxylation, oxidative ring opening, cleavage of ether bonds and epoxidation [32]. All these reactions are also responsible for the formation of lignin with reduced molecular weight as it can be observed in Fig. 2. Indeed, HPSEC results demonstrate that the average molecular weight 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.

3.1.1.3. Thermal degradation behavior. The thermal stability of lignin is mainly dependent on its structure which is strongly affected by both the plant origin and the extraction process used. In fact, the nature of chemical bonds created during the polymerization of lignin depends on the monomer units that constitute the plant. Thus, the thermal stability of lignin depends on the nature and on the amount of the monomers. Furthermore, the extraction method affects the structure of the lignin by breaking some chemical links and modifying others by oxidation for example. The thermal behavior of kraft and organosolv lignins was evaluated by thermogravimetric analysis and the results are shown in Fig. 3. TG curves of both unmodified lignins are very similar and contain several decomposition steps up to 800 °C. The thermal degradation of lignin is relatively well described [35]. After moisture release, the first decomposition step occurs between 230 and 260 °C and

Table 2
Functional groups of the lignins detected by FTIR and semi-quantitative analysis.

Wavenumber (cm^{-1})	Corresponding group	Relative absorbance of lignins	
		Kraft lignin	Organosolv lignin
3250	O—H bonds	0,66	0,54
2930	CH aliphatic	0,57	0,48
1580	(C═O organic acid salt)	1,03	1,51
1360	OH phenolic	1,03	1,42
1260	C—O aromatic ether (syringyl)	1,24	1,07
1193	C—O tertiary alcohol (guaiacyl)	1,53	–
1125	C—O aliphatic ether —O— linkage	1,64	1,64
1080	C—O primary or secondary alcohol	1,44	1,52
1035	C—O primary alcohol or methoxy groups	1,97	1,88
850	CH aromatic	1,27	1,17
750	CH aromatic	1,39	1,2
650	CH deformation	1,64	1,22

Table 3
Results of aqueous titration expressed as mmol of functional groups per g of lignin.

	mmol RCOOH/g	mmol phenolic OH/g
Kraft lignin	1.4 ± 0.1	1.8 ± 0.1
Organosolv lignin	4.5 ± 0.1	2.2 ± 0.1

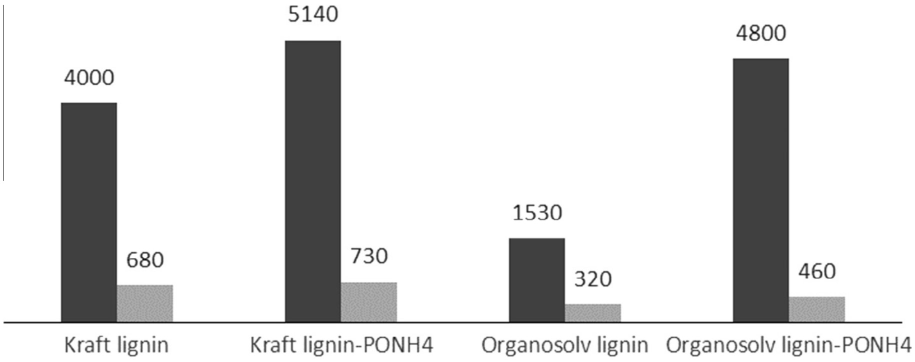


Fig. 2. Average molecular weight (in Da) of unmodified and modified Kraft and Organosolv lignins.

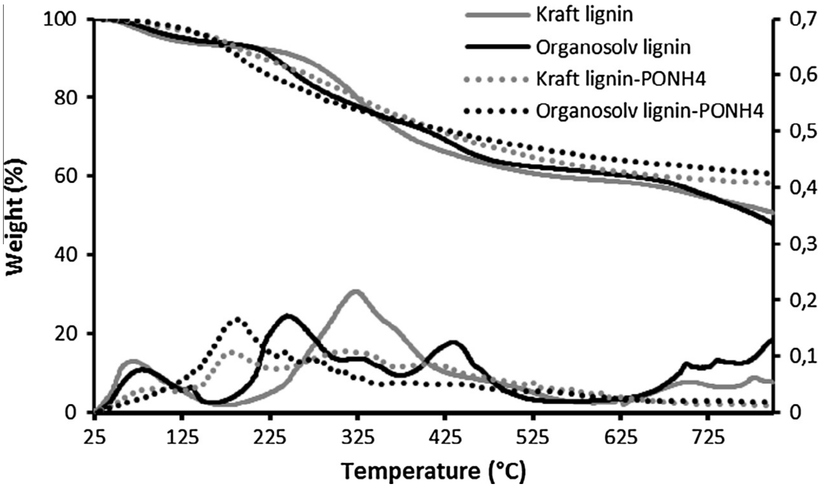


Fig. 3. TG (left axis and upper curves) and DTG (right axis and lower curves) curves of unmodified and modified kraft and organosolv lignins (under N_2, 20 °C/min).

corresponds to propanoid side chain cleavage that leads to the formation of low molecular weight products. This first step is followed by the main degradation (250–450 °C) that leads to the production of a large quantity of methane due to the cleavage of the main chain by either C–C and β-β scission or by aryl-ether cleavage. Above 500 °C, the formation of char takes place thanks to further rearrangements and condensation of the aromatic structure, which thermal decomposition starts at 650 °C.

The amount of residue of kraft lignin at 800 °C is slightly higher than that of organosolv lignin, 50% against 48% (Table 4). It is also important to mention that the maximum of weight loss of organosolv lignin takes place at lower temperature than in the case of kraft lignin, i.e. at 250 °C and 330 °C, respectively. Several reasons could be speculated for this difference of thermal stability; one of them is that kraft lignin contains more guaiacyl units than organosolv lignin, which are more thermally stable than the syringyl ones [36]. Indeed, the fact that guaiacyl units are less substituted allows these units to be more linked to lignin structure. Another reason may be related to the amount of carboxylic groups that could induce some premature thermal degradation of lignin chains.

The gases released during the thermal degradation of the lignins were analyzed by mass spectrometry. At a given temperature, many different gases were released making the distinction between particular compounds difficult. However,

Table 4
Mass of residues of the lignins at different temperatures.

	Residue at 400 °C (wt%)	Residue at 800 °C (wt%)	Weight loss between 400 °C and 800 °C (wt%)
Kraft lignin	68	50	18
Kraft lignin-$PONH_4$	73	58	15
Organosolv lignin	72	48	24
Oraganosolv lignin-$PONH_4$	73	60	13

some masses which are specific of a compound have been selected [36] and their signals according to the temperature are shown in Fig. 4. The release of CO is not analyzed because it is detected at the same mass as N_2 (28 g/mol) in mass spectrometry and this signal was saturated because the analysis was performed under N_2 flux.

Even if the TG curves of the two unmodified lignins display similar profile, their decomposition pathways and the volatile products released are slightly different. The first weight loss, below 150 °C, corresponds to the release of water and some NH_3. Then, the production of CO_2 and acetic acid starts and is followed by the emission of phenolic compounds, such as phenol or guaiacol, and CH_4. The release of these gases takes place during a large temperature range (200–500 °C), starting at lower temperature in the case of organosolv lignin, and could be related to several lignin decomposition steps leading to the maximum weigth loss. The nature of the gases released during this decomposition process (200–500 °C) depends mainly on the composition of the lignin. In fact, more phenolic compounds, furfural and acetic acid are released in the case of

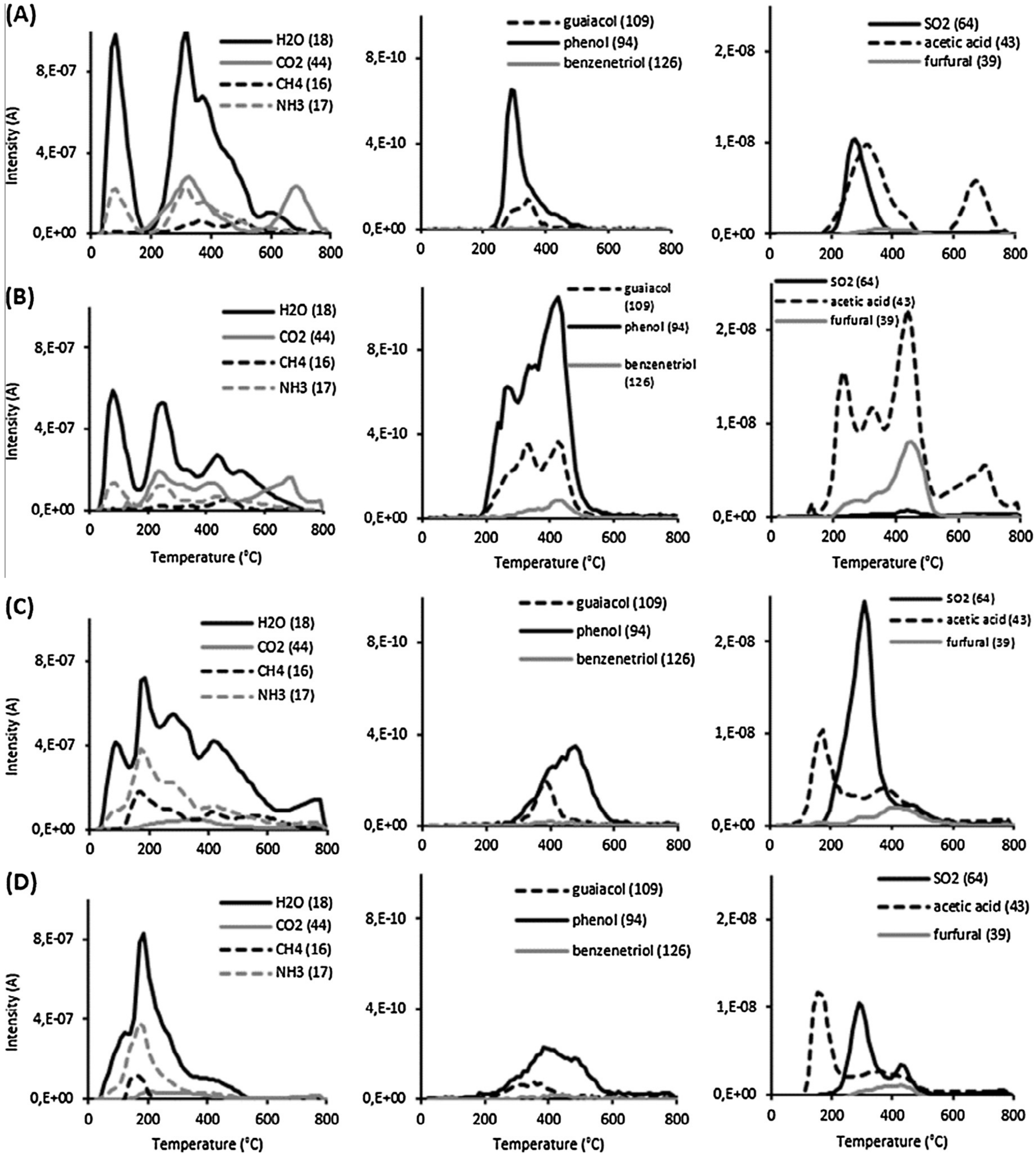


Fig. 4. Gases released during thermal degradation of kraft lignin (A), organosolv lignin (B), kraft lignin-PONH4 (C) and organosolv lignin-PONH4 (D) under N_2.

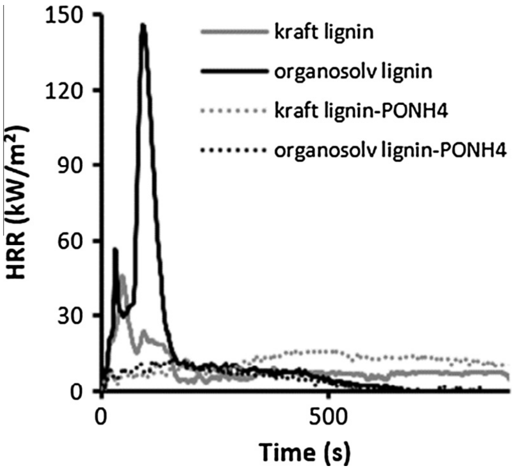


Fig. 5. HRR curves of untreated and treated kraft and organosolv lignins.

organosolv lignin. Furthermore, benzenetriol is detected only in the decomposition gases of organosolv lignin. The studied organosolv lignin is mainly constituted of syringyl units while kraft lignin contains both syringyl and guaiacyl units. Syringyl units are the most substituted units which results in their weaker binding to lignin structure and their easier release as phenolic compounds during decomposition. The extraction process of lignin also affects the nature of the gases released. Indeed, SO_2, that is generated from sulfur grafted on lignin during kraft process, is much more emitted in the case of kraft lignin. Above 600 °C, the weight loss corresponding to the degradation of the char structures produces CO_2 and acetic acid.

3.1.1.4. Fire behavior. The fire behavior of lignins during cone calorimeter test was evaluated (Fig. 5) since it could allow to better understand their contribution when incorporated as fire retardant in PLA. 10 g of each compacted lignin powder was deposited into the cone calorimeter pan and were submitted to the cone calorimeter test following the same parameters as for cone calorimeter test performed on composite sample (35 kW/m^2). Comparison of the HRR curves obtained indicates that the two unmodified lignins exhibit different behaviors. Kraft lignin has both a lower pHRR value (45 kW/m^2) and a shorter time to ignition (40 s) with respect to organosolv lignin (150 kW/m^2 and 70 s). It is worth to mention that the shortest time to ignition observed in the case of kraft lignin is due to its swelling that occured before the ignition and that the flame lasted only for a very short time (a few seconds). While in the case of organosolv lignin, the flaming combustion lasted for approximately one minute. Furthermore, the char content is higher after the fire test of kraft lignin (Fig. 6).

To further investigate the origin of these different fire behaviors between the lignins, the evolution of the concentration of CO_2, CO, NH_3, NO, HCN, CH_4, CH_2O and SO_2 were followed during the cone calorimeter test (Fig. 7). The measurents were performed by the FTIR-cone calorimeter coupling. For both untreated lignins, CO_2 curves follow the same trend than HRR curves. For kraft lignin, a little amount of NH_3 as a primary product of pyrolysis is measured during all the test. No release of NO is observed since flaming combustion occurred during only a few seconds at 40 s. On the other hand, for organosolv lignin, a little amount of NH_3 is measured until ignition. Then, a release of NO is observed which is due to the oxidation chemistry of NH_3 during flaming combustion. Releases of CO, CH_4 and CH_2O are also measured for both lignins but with a less extent for the organosolv one since a longer flaming period was observed for this lignin.

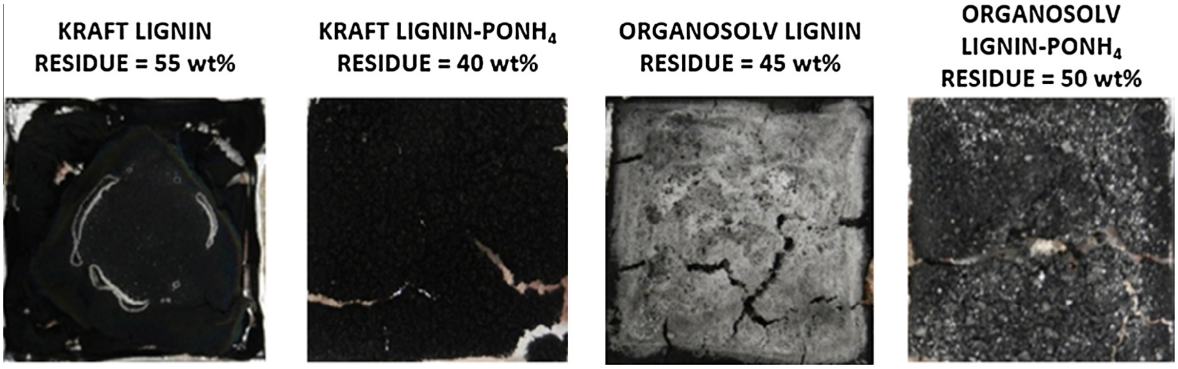


Fig. 6. Pictures of the residues obtained after cone calorimeter test.

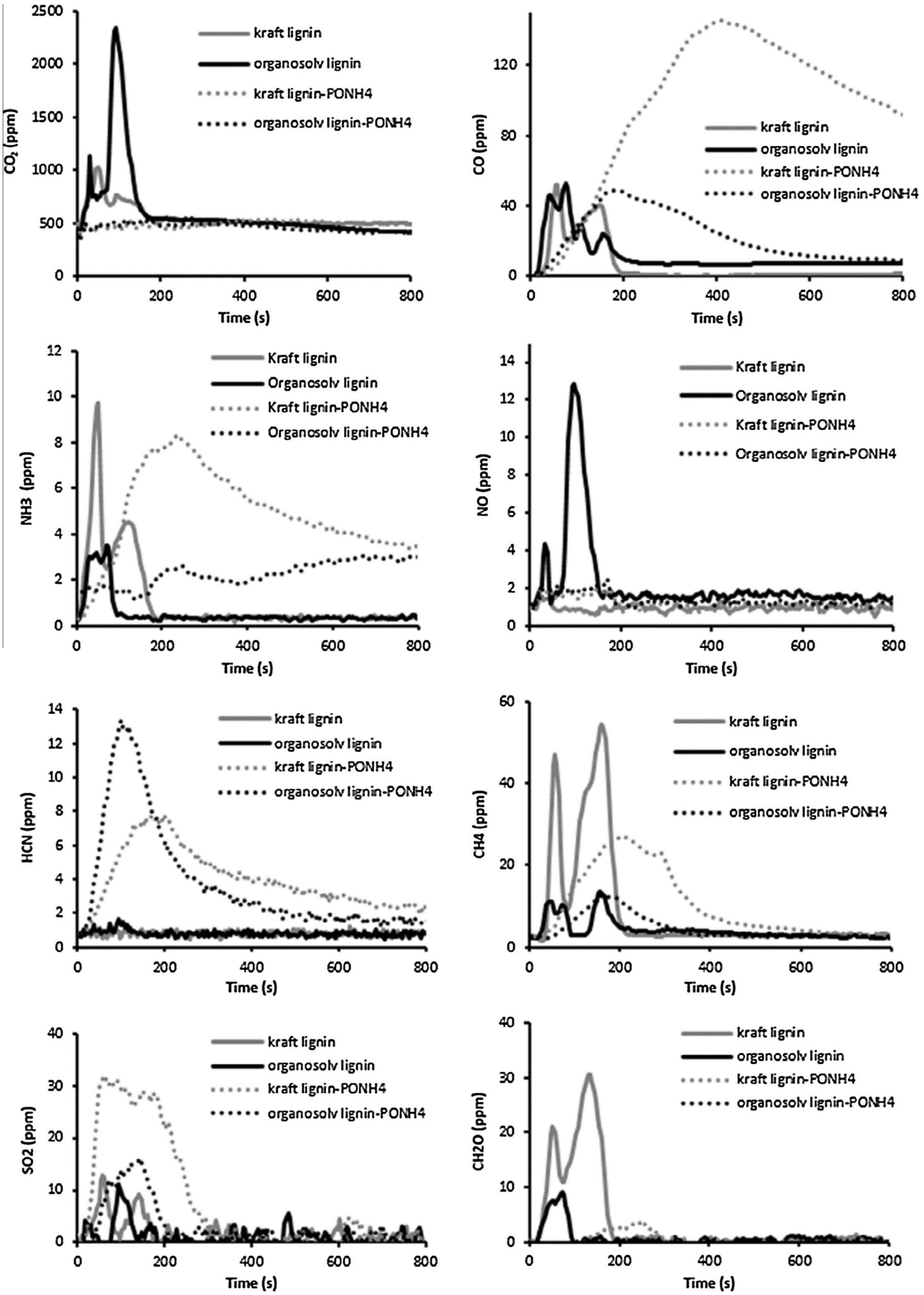


Fig. 7. Composition of the smokes in CO_2, CO, NH_3, NO, HCN, CH_4, CH_2O and SO_2 of kraft and organosolv lignins (untreated and treated).

3.1.2. Chemically modified lignins

3.1.2.1. Structure and functional groups of modified lignins. ICP analysis was performed on both treated lignins in order to determine the amount of phosphorus grafted. Results indicate that both treated lignins contain similar phosphorus content (9.1 wt% in kraft lignin and 10.4 wt% in organosolv lignin). This result is very similar to that determined by SEM/EDX and demonstrates that the nature of lignin does not affect the yield of grafting reaction. SEM/EDX results (Table 1) show also that the amount of nitrogen is similar in both modified lignins and is slightly lower than that of phosphorus. This result supports the hypothesis that ammonium reacts with phosphoric acid groups. Furthermore, it is worth mentioning the presence of very low chlorine contents in both modified lignins that attests for the (quasi) total hydrolysis of chlorophosphate functions and the entire replacement of chlorine by ammonium hydroxide groups in the second step of the reaction. The low chlorine content demonstrates also that the washing protocol used is efficient to remove the chlorine released.

Infrared analysis of modified lignins were performed to determine whether the chemical grafting of phosphorus and nitrogen was successfully operated. Results presented in Fig. 1 and Table 5 show the appearance of new peaks characteristic of P—O—C bonds (915 cm^{-1}) and of N-H from ammonium ions (2840–3200 cm^{-1}). The presence of these bonds attests for the effective chemical modification of the two lignins by the grafting of ammonium phosphate groups. Semi-quantitative evaluation however proved to be more complex in this case because of the detection of broader peaks which could mask other ones.

3.1.2.2. Lignin molecular weight. As it is observed in the case of unmodified lignins, the modified lignins contain also bimodal distribution (Fig. 2) with average molecular weight values higher than that of the corresponding unmodified lignins. This result seems to indicate that some phosphorous groups have condensed or reacted with other lignin fragments. During the chemical modification bridges between two lignins could be created allowing the formation of higher molecular weight lignins.

3.1.2.3. Thermal properties. The incorporation of phosphorous groups into lignin structure triggers some modifications of its thermogravimetric behavior. Without taking into account the water released in the case of untreated lignin, Fig. 3 shows clearly that the chemical modification of lignins leads to its premature thermal degradation. It could be attributed to the action of phosphorous groups grafted on the lignin which can induce a dehydration reaction that can catalyze its thermal degradation. This behavior has already been observed when lignin was associated to phosphorous compounds such as phosphinates or phosphates [26,37]. The maximum weight loss of both modified lignins takes place at lower temperature (190 °C) than that of untreated lignins. During the degradation step corresponding to the maximum weight loss, mainly water, NH_3, CH_4 and acetic acid are released (Fig. 4). It is worth mentioning that the chemical modification of both lignins allows significant reduction of the amount of CO_2 produced. This result could be due to the formation of a char layer promoted by the reaction between C—OH groups of lignin and grafted P—OH. The emission of phenolic compounds is also less important in the case of treated lignins. Furthermore, the release of CO_2 and acetic acid above 600 °C is not anymore observed. The char formed in the case of modified lignins is slightly more thermally stable at high temperature than that obtained with unmodified lignins (Table 4). Above 400 °C, the weight loss is reduced indicating the formation of thermally stable structures. Indeed, the weight loss between 400 °C and 800 °C is of about 18 and 24 wt% in the cases of kraft lignin and organosolv lignin respectively while this difference decreases up to 14 wt% in the cases of modified lignins.

3.1.2.4. Effect of the phosphorus/nitrogen modification on fire properties of lignins. Cone calorimeter tests (Fig. 5) of the chemically modified lignins reveal an interesting modification of the fire behavior of lignins. Indeed, a charring effect is developed and no ignition occurs. In addition to NH_3 releases, HCN which is an intermediate compound in the formation of both NO and N_2 is also released (Fig. 7) certainly due to the char formation which leads to a barrier effect for the oxygen transfer [38]. This

Table 5
Functional groups of the modified lignins as determined by FTIR and semi-quantitative analysis.

Wavenumber (cm^{-1})	Corresponding group	Relative absorbance of lignins	
		Kraft lignin-$PONH_4$	Organosolv lignin-$PONH_4$
3200–2840	N—H ammonium ion	0,83	0,99
1670	C=O conjugated acid	0,87	0,92
1590	C=O organic acid salt	1,03	1,26
1360	OH phenolic	–	–
1260	C—O aromatic ether (syringyl)	1,42	1,21
1193	C—O phenol or tertiary alcohol (guaiacyl)	–	–
1125	C—O aliphatic ether —O— linkage	1,90	–
1080	C—O primary or secondary alcohol	2,07	–
1035	C—O primary alcohol or methoxy groups	2,41	2,60
915	P—OR	2,26	2,57
860	CH aromatic	2,20	2,30
770	CH aromatic	2,05	2,04
630	CH deformation	1,82	1,67

is confirmed by the fact that no release of NO is observed for the modified lignins. Furthermore, it seems that the modification leads to the more important release of SO_2 while the sulfur was mainly remaining in the condensed phase or released in another form in the cases of untreated lignins. Thus, instead of burning, these lignins are slowly thermally degraded. However, the final amount of char formed at the end of cone calorimeter test is lower in the case of modified kraft lignin (40 wt%) in comparison to 55 wt% left after the combustion of unmodified kraft lignin (Fig. 6). This behavior is quite surprising since modified kraft lignin does not undergo combustion. In the case of organosolv lignin, results proved to be different since the chemical modification of this lignin allows increasing the amount of char residue. Nevertheless, these results have to take into account that the combustion of unmodified kraft lignin leads to low pHRR value (45 kW/m^2) and to the formation of a film at the surface of the burning material limiting heat and oxygen transfers through it. This film results in the reduction of kraft lignin thermal degradation and the decrease of the amount of volatile combustible products. On the contrary, the combustion of organosolv lignin is more intense and the pHRR value is higher (150 kW/m^2), which may have entertained the combustion and induced further thermal decomposition of the material.

The investigations performed on lignins reveal several differences concerning their chemical composition and physical properties between them, i.e. (i) differences between the native lignins; (ii) differences when the lignins are modified. All these differences could influence the thermal and fire behavior of PLA composites when incorporated as additive in this polymer matrix.

3.2. Influence of lignins on thermal degradation and fire behavior of PLA

Lignin could be advantageously used to improve the char formation during the combustion of polymeric matrices [17]. In the present study, 20 wt% of each lignin, were incorporated into PLA and their dispersion in the matrix as well as their effect on thermal and fire behavior of the corresponding compositions were studied.

3.2.1. Dispersion of lignins in PLA matrix

The dispersion of the fire retardant additive into the matrix is an important parameter which can affect the fire behavior of the composite. Lignin is constituted of micron-size particles which tend to agglomerate when incorporated into PLA highlighting poor affinity between PLA and lignin. Indeed, the SEM pictures of PLA/20 unmodified lignin sample (Fig. 8) exhibit large

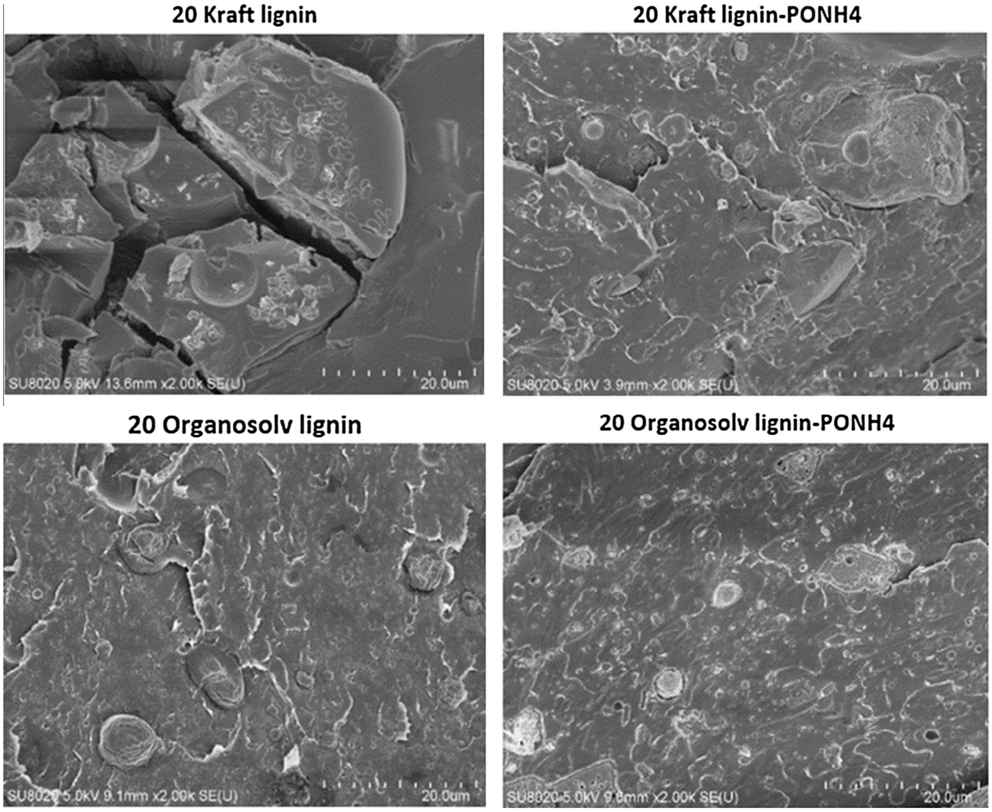


Fig. 8. SEM pictures of PLA/20 lignin composites. Effect of the lignin type (kraft or organosolv) and chemical functionalization via ammonium phosphate grafting reaction.

particle agglomerates with some cracks and poor interfacial compatibility, particularly in the case of PLA/20 kraft lignin composition. The grafting of phosphorus and nitrogen to lignin seems to improve its dispersion ability in PLA and to reduce the size and number of agglomerates. The modification may increase the affinity between the polymer matrix and lignin particles.

3.2.2. Thermal behavior

The addition of untreated lignin, whatever its nature, leads to similar thermal behavior in TGA (Fig. 9), i.e. a decrease in thermal stability of PLA. However, the thermal stability is more affected in the presence of organosolv lignin. Indeed, the temperature corresponding to 10% weight loss ($T_{-10wt\%}$) is around 225 °C and 275 °C for PLA/20 organosolv lignin and PLA/20 kraft lignin, respectively, whereas it is recorded at about 330 °C for pristine PLA. This thermo-degradant effect also takes place at lower temperature during melt processing (160 °C). In fact, GPC analysis (Table 6) performed on processed PLA and PLA-based composites shows that the average molecular weight is strongly decreased when lignin is used. Once again, organosolv lignin induces the most important thermal degradation and leads to much higher reduction of PLA number average molecular weight with respect to those of pristine PLA and PLA/20 kraft lignin composition. First it was thought that the important thermo-degradant effect induced by untreated lignin incorporation is mainly due to the content in sulfur groups. However, it is not the case since the amount of sulfur is lower in organosolv lignin that causes the higher thermal decomposition. The thermo-degradant effect of organosolv lignin is thus most likely attributable to its content in carboxylic acid functions which is significantly higher than that of kraft lignin.

It is worth mentioning that the presence of 20 wt% of lignin allows the formation of thermally stable char residue (around 15%) at 600 °C. For sake of comparison, pristine PLA degrades entirely without formation of any residue.

The incorporation of 20 wt% of the chemically treated lignins into PLA allows significant reduction of the thermo-degradant effect observed with untreated lignins. PLA/20 modified lignin composites present similar thermal stability to that of pristine PLA (Fig. 9). Furthermore, the incorporation of treated lignins allows the creation of significant amount of char residue (around 13 wt% at 600 °C). The first thermal degradation step of PLA containing modified lignins remains higher than that of PLA composites containing unmodified lignins but starts at lower temperature than that of neat PLA. This thermal behavior shape is usually observed in the case of polymers containing phosphorous flame retardant additives. Under the influence of heat, the phosphorous groups are cleaved and catalyze the early degradation of PLA before promoting the formation of char. Furthermore, using modified lignins allows to increase the thermal stability of PLA during TGA by delaying the release of volatile compounds, and to limit the thermal degradation during melt processing since the number average molecular weight of PLA/20 modified lignin composites is decreased with respect to neat PLA but remains at the level of

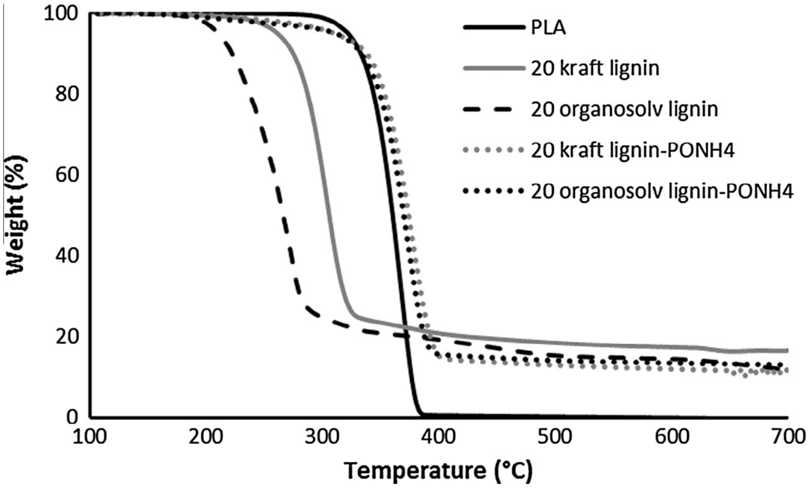


Fig. 9. TG curves of PLA/20 lignin composites compared to the thermal behavior of neat PLA (under N_2, 20 °C/min after 10 min of isothermal at 100 °C).

Table 6
Results of GPC analysis on neat PLA and related composites recorded after melt processing.

	Mn	Mw	Mw/Mn
PLA (processed)	87,600	168,300	1,9
20 kraft lignin	37,700	74,300	2,0
20 kraft lignin-PONH$_4$	40,000	74,700	1,9
20 organosolv	15,100	35,400	2,3
20 organosolv lignin-PONH$_4$	27,600	67,100	2,4

the degradation induced by the incorporation of conventional flame retardant system in PLA such as melamine/ammonium polyphosphate system [39] (Table 6).

3.2.3. Fire behavior

3.2.3.1. Cone calorimeter. The incorporation of lignin triggers some modifications of the fire behavior of PLA during cone calorimeter test (Fig. 10). In fact, both untreated lignins induce important reduction of the resistance to ignition of PLA since time to ignition decreases from 87 s in the case of pristine PLA to 27 s and 40 s for PLA containing 20 wt% of organosolv and kraft lignin, respectively. This effect could be directly related to the thermo-degradant effect of lignins previously observed by TG and GPC analyses. In addition, the presence of unmodified lignin leads to some improvement of the fire behavior of these composites and allows reducing both peak of heat release rate (pHRR) and total heat release (THR) thanks to the formation of a char layer at the surface of the burning material. This fire retardant behavior was already observed by Ferry et al. [27] in another aliphatic polyester, i.e. polybutylene succinate (PBS). They showed that the incorporation of 20 wt% of kraft lignin into PBS reduced its TTI from 72 s to 42 s and induced a reduction of about 45% of the pHRR thanks to the apparition a thick charring behavior. In this study, the pHRR and the THR decrease of about 21% and 23% respectively for PLA/20 kraft lignin and of about 33% and 30% respectively for PLA/20 organosolv lignin. The reduction is more pronounced when organosolv lignin is used. This result seems surprising since organosolv lignin induces important thermal degradation of PLA according to TGA and GPC. It is worth pointing out that PLA/20 organosolv lignin composition behaves like a brittle composite as a result of the very low PLA molecular weight, i.e. Mn at ca. 15,000 (Table 6). Such low molecular weight of PLA results from chain cleavage most likely triggered by thermally induced hydrolysis of the aliphatic ester functions reaction leading to the formation of hydroxyl and carboxylic acid end-groups. Accordingly, the higher pHRR reduction observed when organosolv lignin is used could be related to the *in situ* formation of ester bonds between the carboxylic acid functions at the extremities of the PLA chains and the numerous phenolic groups of the lignin counterpart. Indeed, this esterification reaction is expected to limit/refrain the volatilization of low molecular weight PLA volatile fragments and hence reduce the pHRR during the combustion.

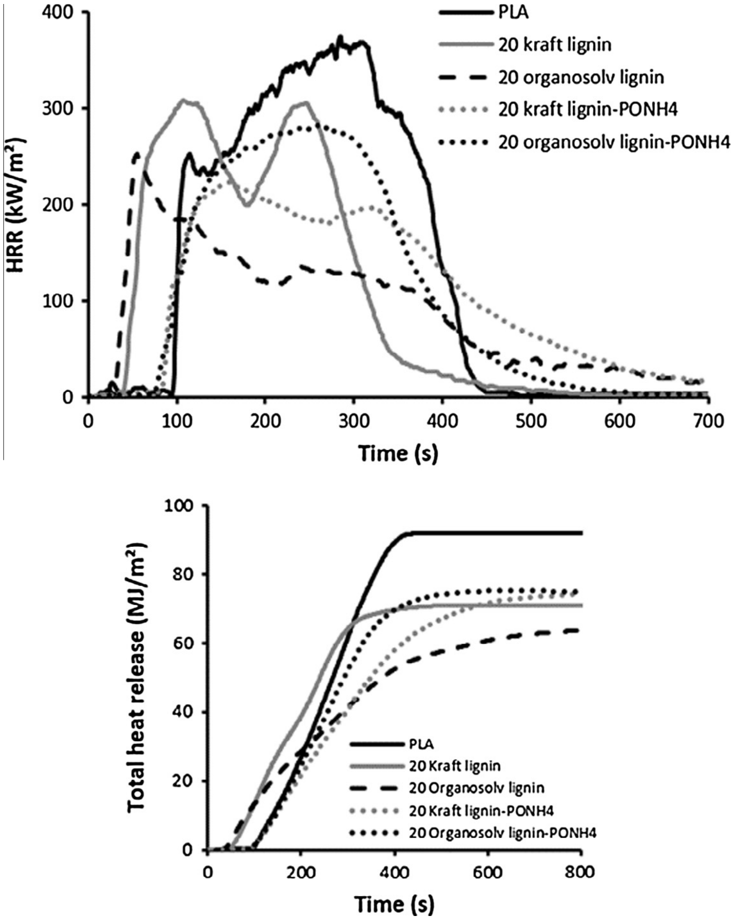


Fig. 10. HRR and THR curves of neat PLA and PLA/20 lignin composites.

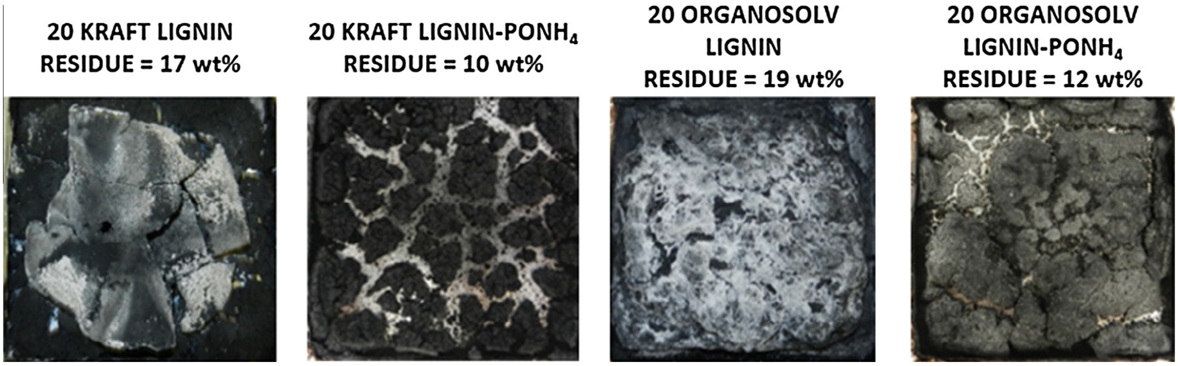


Fig. 11. Pictures of the residues of combustion of PLA/20 lignin composites.

The incorporation of treated lignins results in some interesting modifications of the fire behavior of PLA composites; i.e. significant increase of time to ignition up to that of pristine PLA for both treated lignins and significant reduction of pHRR but only when modified kraft lignin is used (Fig. 10). Indeed, TTI increases from around 35 s in the case of untreated lignins to around 85 s when modified lignins are used. This improvement of the resistance to ignition is due to the presence of ammonium functions that could allow to dilute the gas phase, to the lower thermo-degradant effect of modified lignins and to the presence of phosphorous groups that allows char layer formation before ignition.

As far as kraft lignin is considered, the incorporation of the chemically modified version instead of unmodified one allows to obtain further reduction of the pHRR, of about 40% regarding pristine PLA and of about 25% in comparison with unmodified kraft lignin. However, at the end of the combustion, the amount of char recovered is less important than for the PLA/20 kraft lignin (Fig. 11) and the THR is slightly higher.

In contrast, using 20 wt% of treated organosolv lignin does not allow further decrease of pHRR value in comparison with PLA containing 20 wt% of untreated organosolv lignin. It is worth pointing out that pHRR obtained when untreated organosolv lignin is used is already low (around 250 kW/m^2). In this case, the pHRR is decreased of about 30% with respect to that of pristine PLA.

3.2.3.2. UL-94 test. PLA/20 untreated lignin composites were also tested in UL-94 fire test and the results demonstrate that these compositions do not allow to reach a classification at UL-94 fire test since the samples burn completely after the second flame application.

The chemical treatment of the lignins improves their fire retardant properties by reducing their flammability. The use of phosphorus/nitrogen modified lignins in PLA provides it with auto-extinguishment ability. Indeed, the incorporation of 20 wt% of the treated lignins allows to reach V0 classification at UL-94 fire test.

4. Conclusion

This study compared the use of organosolv and kraft lignins as flame retardant for PLA and highlighted the dependence of the composite properties on the type of lignin employed, since both had different compositions and structures due to their extraction method and their botanical origin. When compared to kraft lignin, organosolv lignin was less thermally stable and contained more carboxylic acid functions and phenolic OH, which were responsible for higher PLA degradation during melt processing.

The use of these lignins as flame retardant for PLA proved to reduce the heat released along the combustion owing to the formation of an insulating char layer at the surface of the burning sample. Those lignins improved the fire retardant behavior of PLA by decreasing the pHRR and the THR, however they also decreased drastically the TTI and the thermal stability of PLA.

In order to address this problem, both lignins were chemically modified by grafting phosphorus and nitrogen. The efficiency of the grafting was established and the flame retardant effect of the modified lignins was then evaluated. The so-modified lignins proved to be highly effective to reduce the flammability of PLA composites. PLA/modified lignin composites were V0 at UL-94. The TTI and thermal stability of PLA were also maintained. Once modified, the effect of both lignins became similar and neither the plant origin nor the extraction process of the lignins were affecting the properties of the PLA composites.

Acknowledgments

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