

Novel Bio-based Flame Retardant Systems Derived from Tannic Acid

Fouad LAOUTID^{1,*}, Valeriia KARASEVA¹, Lucie COSTES^{1,2}, Sylvain BROHEZ², Rosica MINCHEVA¹ and Philippe DUBOIS¹

¹Laboratory of Polymeric & Composite Materials, Materia Nova Research Center-University of Mons-UMONS, Place du Parc 23, B-7000 Mons (Belgium)

²Service de Génie des Procédés Chimiques; Faculté Polytechnique-University of Mons-UMONS, Place du Parc 23, B-7000 Mons (Belgium)

ABSTRACT: In this study, tannic acid (TA) was investigated as flame retardant agent for PLA. Different strategies to modify its thermal degradation pathway have been explored in order to improve its charring effect. The first one consists in combining TA with organomodified montmorillonite (oMMT), and enables limiting the thermo-oxidative degradation of TA and promoting the formation of an effective char layer. Flame-retardant (FR) behavior of PLA-based composition has been found to be positively impacted by this combination since a reduction of the peak of Heat Release Rate (PHRR), more important than the value recorded when oMMT and tannic acid are used separately, has been obtained. The second strategy, in which tannic acid was associated with a biosourced phosphorous-based compounds, i.e. metallic phytate salt, evidenced another alternative allowing enhancing TA flame retardant effect at 30 wt% loading content. The third and last strategy explored aims to chemically modify TA via a chemical grafting of phosphoric acid groups. This phosphorylated TA was shown to present the most effective flame-retardant (FR) effect. However, an important reduction of PLA molecular weight was observed.

KEYWORDS: Tannic acid, biobased flame retardants, char formation, polylactide, biopolymers

1 INTRODUCTION

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 [1, 2]. However, polymers are also known for their relatively high flammability and improving their flame-retardant (FR) behavior is a major challenge required for many technical applications. Among these bioplastics, polylactide (PLA) represents one of the most promising technical biopolymer thanks to the very efficient use of feedstocks during its production as well as to its relatively low cost and large production volume. The FR approaches that must be used for biobased polymers have also to be sustainable in order to maintain their good environmental profile.

Some biobased compounds, such as cellulose [3], starch [4], β -cyclodextrin [5], DNA [6] or lignin [7], have already attracted research interest in this field and have demonstrated their efficiency as charring agents for polymeric materials. These compounds can be used in combination with other conventional flame retardant additives or after their chemical modification with phosphorous-based compounds.

Amongst all biobased (poly)phenols, that are well adapted for FR application thanks to their aromatic structures, lignin has received much attention in the past decade [8-15]. However, several studies reported that performances are mainly dependent on its botanical origin and the extraction process used [8,11] that are responsible for its high structural diversity, large molecular weight distribution and variability in terms of reactivity and composition.

Another family of phenolic biobased compounds, presenting a certain interest as char-forming agents are tannins [16]. Tannins are important ingredients in the barks of trees since they provide thermal and antimicrobial protection [17,18]. The family of tannins can be classified into two main categories: hydrolysable and non-hydrolysable or condensed tannins [19]. Hydrolysable tannins contain a central core of polyhydric alcohol such as glucose, connected partially or entirely to gallic acid (gallotannins) or hexahydroxydiphenic acid (ellagitannins) through ester

*Corresponding Author: fouad.laoutid@materianova.be

DOI: 10.32604/JRM.2018.00004

linkages. The structures of condensed tannins that are far more complicated than hydrolysable tannins consist of polymerized forms of flavan-3-ols and flavan-3, 4-diols or a mixture of the two [20]. Condensed tannins represent more than 90% of the total production of commercial tannins [21] thanks to their high reactivity towards aldehydes and other reagents rendering them both chemically and economically more interesting for the preparation of adhesives, resins and other applications. In contrast, hydrolysable tannins, because of their low rate of interactions with aldehydes, are not favored for the preparation of resins.

Therefore, it is entirely appropriate to attempt developing new high value applications for hydrolysable tannins. Among the different hydrolysable tannins available commercially, tannic acid has been selected for our study. Different ways for enhancing the flame-retardant effect of tannic acid by improving its char forming ability have been investigated. Two strategies, aiming on improving the charring effect of tannic acid have been explored. The first one concern its combination with nanoclay, that when well dispersed provide a barrier effect that enables the confinement of the degrading materials and thus promotes their recombination to form the char [22]. The second one focused on the increase of the thermal stability of the char through the combination of tannic acid with phosphorus by both additive and reactive routes.

2 EXPERIMENTAL

2.1 Materials

PLA resin (3051D, $\overline{M}_n=100000$ g/mol, $\overline{D}=2.1$ and 4.3% of D-lactide content) was purchased from NatureWorks. Tannic acid (TA), phosphorus chloride (POCl_3 , purity 99%), Kraft lignin and diphenyl chlorophosphite were purchased from Sigma Aldrich. Cloisite 30B, organically modified montmorillonite clay (oMMT) was purchased from BYK Additives. Sodium phytate (Na-Phyt) was purchased from Sigma Aldrich and aluminum phytate (Al-Phyt) was obtained by mixing a 0.1 M aqueous solution of sodium phytate (Na-Phyt) with 0.5 M aqueous solution of aluminum trichloride purchased from Sigma Aldrich. The two solutions were mixed together and the system was refluxed at 100°C under constant mechanical stirring for 1 h. The precipitated metallic phytates were washed by centrifugation with deionized water (five times) and freeze-dried.

2.2 Phosphorylation of Tannic Acid

Grafting phosphoric acid on TA was performed in two steps (Scheme 1). The first step allowed the grafting of

phosphorus chloride while its conversion into phosphoric acid groups occurred during the second step as follows:

Step 1: Production of tannic acid-POCl via grafting of phosphorus chloride:

Tannic acid (100 g) was added to CHCl_3 (400 mL) and heated to 50°C. POCl_3 (85 ml) was added drop by drop to the mixture. The mixture was heated at 60°C for 16 h. The product (tannic acid-POCl) was recovered by filtration and washed with CHCl_3 to remove any ungrafted POCl_3 . Tannic acid-POCl was dried at 60°C in vacuum oven.

Step 2: Hydrolysis of phosphorous chloride:

The hydrolysis of tannic acid-POCl (100 g) into 1.5 L of deionized water (under vigorous agitation for 2 h at room temperature) allowed obtaining TA-POH. After several centrifugations, the residue was collected and dried at 70°C in vacuum.

2.3 Melt Processing

Blending of tannins and oMMT within the molten PLA was carried out in a Brabender internal mixer at 160°C (7 min mixing at 70 rpm). PLA and tannins were previously dried in a vacuum oven at 60°C overnight right before use. Plates (100*100*4 mm³) for cone calorimeter testing were compression-molded at 160°C using an Agila PE20 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. PLA alone and PLA composites containing 20 wt% of each tannin fraction were prepared.

Sample designation and composition are given in Table 1.

2.4 Characterizations

2.4.1 Inductively Coupled Plasma (ICP)

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 tannic acid. Before ICP analysis, phosphorus containing samples were prepared by the destruction of the organic matrix by a mineralization process with $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}_2$ solutions. The amount of phosphorus was determined thanks to a calibration curve obtained from ICP analysis of phosphorus containing standard solutions.

Table 1 Content (expressed in wt%) of PLA and additives used for the preparation of the different compositions.

Compositions	PLA	oMMT (inorganic content)	Tannic acid	Al-Phytate	Na-Phytate	Tannic acid-POH	Lignin-POH
PLA	100						
20% TA	80		20				
30% TA	70		30				
3% oMMT	95	3	--		--	--	
17% TA-3% oMMT	78	3	--		17	--	
20% Al-Phyt	80			20			
10% TA-10% Al-Phyt	80		10	10			
30 % Na-Phyt	70		--		30	--	
15% TA -15% Na-Phyt	70		15		15	--	
20% TA-POH	80					20	
20% Ligin-POH	80						20

2.4.2 Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) was used to determine the number average molecular weights (M_n) of both PLA and PLA/tannin blends. The 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 103A). 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 calibration.

2.4.3 Infra-Red Spectroscopy (FTIR)

FTIR spectra were recorded in ATR mode with a Bruker Tensor 27 infrared spectrometer using dry powder samples.

2.4.4 Scanning Electron Microscopy (SEM)

Morphological investigation was performed to highlight the dispersion of tannic acid in PLA by 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.

2.4.5 Thermogravimetric Analysis (TGA)

Thermal decomposition of tannic acid, phosphorylated tannic acid, pristine PLA and PLA-based composites were studied by thermogravimetric analysis (TGA) using a TGA Q50 device from TA Instruments. Approximately 10 mg of the sample was submitted to a temperature ramp from 100°C to 600°C at a heating rate of $20^\circ\text{C}/\text{min}$ after a 10 min isothermal at 100°C to get rid of any moisture. Residual weight at 700°C (Residue) as well as temperature at the peak of mass loss rate (T_{max}) and corresponding to 5 wt% and 10% mass loss were determined.

2.4.6 Cone Calorimeter

Fire behavior of the different compositions has been evaluated using cone calorimeter test at $35 \text{ kW}/\text{m}^2$. Cone calorimeter is one of the most used device to assess the flammability of materials at bench scale. The peak of heat release rate (pHRR), time to ignition (TTI), as well as total heat release (THR) that are considered as two of the most important parameters in this fire test, have been considered. A high pHRR and a low TTI may cause both fast ignition and rapid-

fire propagation. Cone calorimeter tests were performed according to ISO 5660 standard procedures with a FTT cone calorimeter. Samples (100*100*4 mm³) were exposed to an external heat flux of 35 kW/m², corresponding to common heat flux in a mild fire scenario. Cone calorimeter tests were also performed on compacted Tannic acid powder (10 g) under 35 kW/m².

3 RESULTS AND DISCUSSION

3.1 Thermal and Combustion Behavior of Tannic Acid

As discussed before, tannic acid (TA, Figure 1), has been here selected as FR for the biobased polyester poly(lactide) (PLA). TA is mainly constituted by decagalloyl glucose but some polygalloyl glucoses, with the number of galloyl moieties per molecule ranging from 2 up to 12, could also be present depending on the plant source.

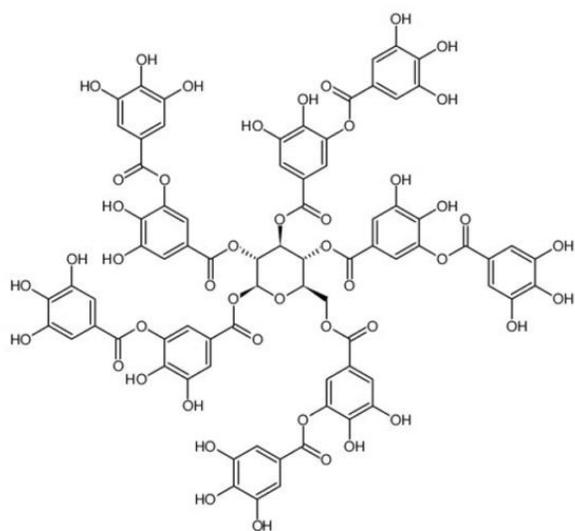


Figure 1 Simplified structure of tannic acid (TA)

Prior to evaluating the effect of tannic acid incorporation on PLA composites properties, the thermo-oxidative and pyrolytic decomposition of TA as well as its fire behavior during cone calorimeter test were investigated. Figure 2 presents TGA curves of TA under air and nitrogen as well as HRR curve

obtained during cone calorimeter test performed on 10 g of tannic acid. TGA curves clearly indicate that the nature of the gas does not affect TA thermal behavior below 400°C. Indeed, between 100°C to 400°C, the two TGA curves are very similar with a weight loss starting at 262°C (T-5%) and resulting in the formation of a residue of around 40%. However, above 400°C, the thermal degradation depends on the nature of the gas used. Under nitrogen, tannic acid exhibited high char yield of 28%, with the formation on intumescent char while no residue was generated under air (Figure 2). This difference has been also evidenced by Xia et al. [16] who reported the mechanism of thermal and thermo-oxidative degradation of tannic acid and established its degradation pathway under both air and nitrogen. Accordingly, below 400°C, tannic acid thermal degradation was shown to be similar whatever the nature of the gas used and corresponds mainly to the release of 1, 2, 3-benzene triol and carbon dioxide from the disintegration of outer layer of gallic acid units. However, under nitrogen, at temperatures above 400°C, the char produced is mainly from the crosslinking of the inner gallic acid units. TA is thus a charring material under pyrolytic conditions.

Cone calorimeter test, performed on tannic acid powder, showed no char formation and a strong combustion starting at 20 s with a combustion peak reaching 350 kW/m². These results also suggested that tannic acid could be used as char forming agent if it is protected and isolated from the action of oxygen during its thermal degradation.

With the view to promote the charring of tannic acid during combustion, two different strategies, aiming the modification of its thermal degradation pathway towards charring thermal decomposition have been tested, i.e. (i) using organoclay (oMMT) and (ii) combination of TA with phosphorus by additive or reactive pathway.

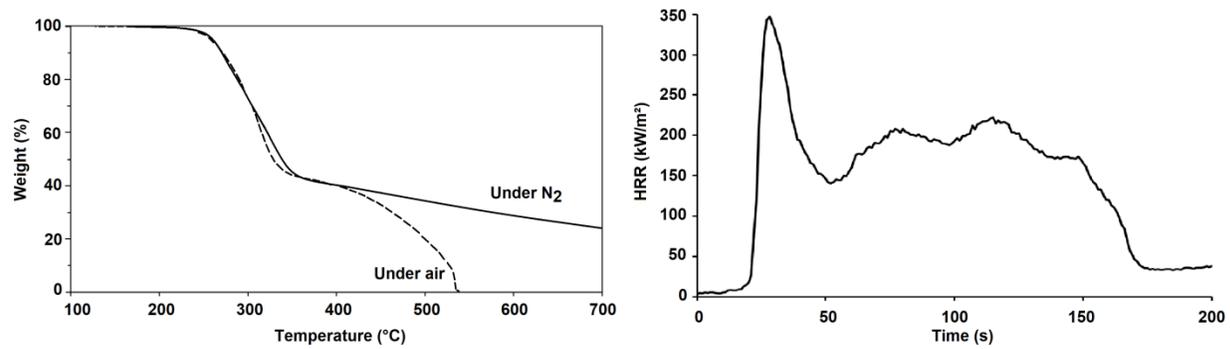


Figure 2 TGA curves of tannic acid under air and nitrogen at 20°C/min (left); HRR curve of tannic acid during cone calorimeter test at 35 kW/m².

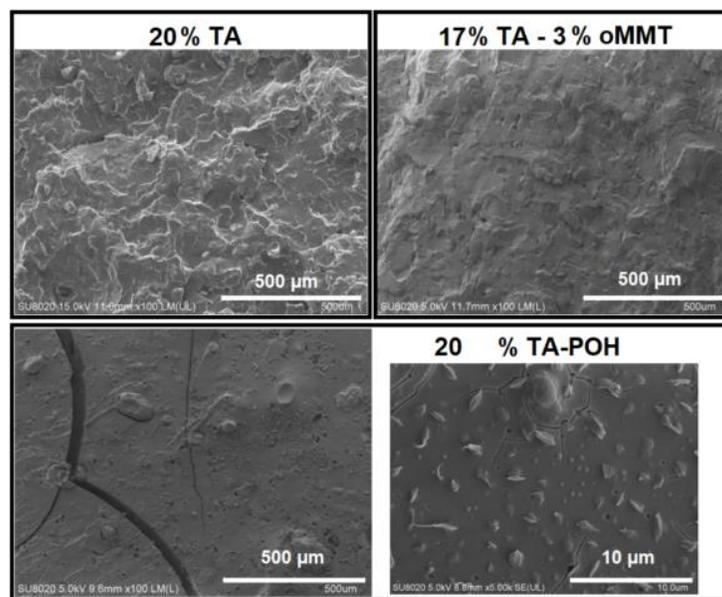


Figure 3 SEM images of PLA containing 20 wt% Tannic acid, 17 wt% Tannic acid+3 wt% oMMT and 20 wt% of TA-POH.

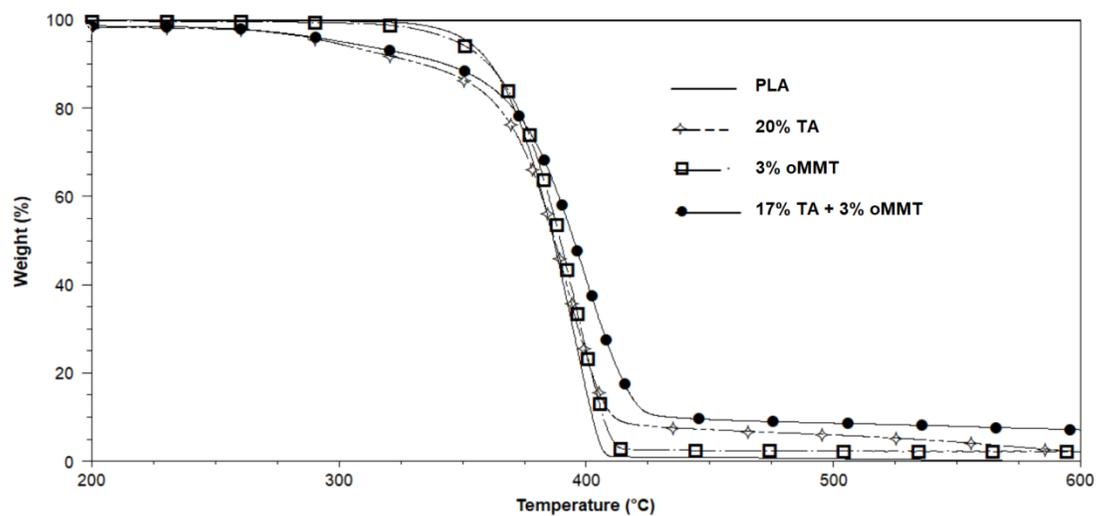


Figure 4 TGA curves of PLA containing tannic acid, nanoclay as well as their combination under nitrogen.

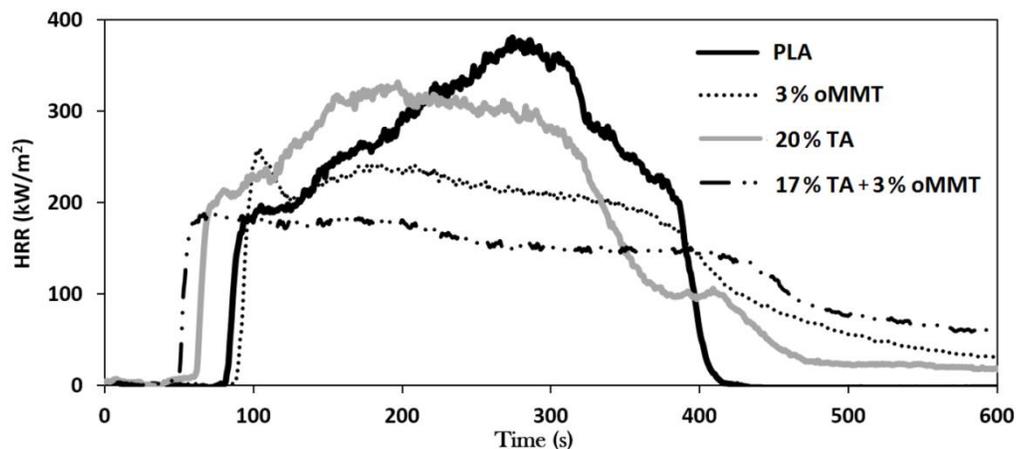


Figure 5 HRR curves obtained during cone calorimeter test at 35 kW/m^2 .

3.2 Thermal and Fire Properties of PLA Containing Tannic Acid-based Compositions

3.2.1 Effect of Tannic Acid Alone

20 wt% TA was incorporated into PLA by melt processing. First, its dispersion state was evaluated by SEM observations. Figure 3 evidences acceptable dispersion TA particles since no big aggregate could be observed. Moreover, no reduction of PLA molar mass was detected by SEC (Table 1), thus suggesting that TA does not induce polyester degradation during processing.

The presence of TA was found to induce some changes in the composite thermal stability during TGA analysis (Figure 4). In fact, some premature thermal degradation of the composite under nitrogen was detected. This thermo-degradant effect is directly related to the fact that TA starts to degrade at lower temperature in respect to pristine PLA. However above 400°C , the composite thermal stability became higher to the unfilled polymer owing to the presence of the char promoted by TA during its thermal decomposition. However, the char formed is not thermally stable and degrades progressively above 500°C .

The lower composite and char thermal stability impacts also negatively the material fire behavior. In fact, cone calorimeter test curve of PLA containing 20 wt% TA (Figure 5) shows an important increase of the composite ignitability without any significant effect on the pHRR. 20 wt% TA induces a significant decrease of the time to ignition (TTI) from 80 s to 60 s. The lower tannic acid thermal stability, evidenced by TGA analysis as well as its low resistance to inflammation (TTI=20 s) are responsible for this reduction through two possible mechanisms. The first one concerns the combustion of volatile compounds produced during

TA thermal degradation while the second one is due to the premature PLA thermal decomposition induced by TA or its degradation products. Additionally, the pHRR level is not significantly reduced by the presence of tannic acid. Indeed, the incorporation of non-charring and flammable tannic acid into non-charring and flammable PLA does not induce any char formation during cone calorimeter test.

It is thus clear that TA alone does not present any flame-retardant effect into PLA. Moreover, its introduction induces both premature thermal degradation step and significant increase of composite ignitability without any reduction of the pHRR. Therefore, various strategies aiming at enhancing tannic acid char forming ability have been investigated.

3.2.2 Effect of Tannic Acid/OMMT Combination

The first improvement pathway explored in this work consists in the combination of TA with nanoclays. In fact, clay nanoplatelets, when well dispersed, enable for the formation of an insulating barrier layer [22, 23]. The formation of such layer was expected to improve PLA flame retardancy through two possible mechanisms. The first one, concern its action during the pre-ignition period by reducing the amount of combustible volatile products released and thus allowing some enhancement of the composite ignitability. The second mechanism concerns the ability of this layer to promote a change of TA thermal degradation pathway towards charring thermal decomposition thanks to the confinement of degradation products that promotes charring by recombination reactions. This latter action aims at limiting pHRR during cone calorimeter test.

Table 2 TGA parameters of PLA composites.

	T ₅ (°C)	T ₁₀ (°C)	T _{MAX} (°C)	MLR (%/°C)	Residue at 600 °C
PLA	312	325	372	2.1	0
3% oMMT	347.7	360.5	397	2.4	2.5
20% TA	296	334	391	2.1	2
17% TA+3% oMMT	300	343	400	1.1	7.2
20% TA-POH	286	317	350	2.7	6

Table 3 Cone calorimeter parameters of PLA based composites.

	TTI (s)	PHRR (KW/m ²)	PHRR reduction (%)	THR (MJ/m ²)	THR Reduction (%)	Residue (%)	Mn (g/mol)
PLA	80	380		85	---	0	85000
20% TA	60	320	-15.7	90	+ 4.7	0.6	94000
3% oMMT	86	260	-31.6	84.5	- 0.7	8.5	78670
17% TA-3% oMMT	52	190	-50	77	-9.4	14.7	88630
20% Al-Phyt	77	217	-43	70	- 16.5	15	24200
10% TA + 10% Al-Phyt	65	317	-16.6	77	- 9.4	9	40500
30% TA	52	310	-18.4	87.7	+ 3	2.2	77100
30% Na-Phyt	92	252	-34.2	71	- 16.5	23	94700
15% TA+15% Na-Phyt	53	180	-52.6	71.5	-15.8	13.4	93100
20% TA-POH	75	160	-58	71.5	-15.8	6.75	15700

Tannic acid and oMMT alone or in combination have been incorporated within PLA by melt mixing. The presence of nanoclays is not disturbing the dispersion state of tannic acid since no large aggregated are evidenced by SEM observations (Figure 3). The dispersion state of nanoclay could not be evaluated by using SEM but seems to be dispersed at nanometric scale if we consider cone calorimeter test result of the PLA nanocomposite presented in Figure 5 and will be discussed later.

In order to evaluate if the presence of nanoclays induces the formation of a protective barrier as it was expected, we first investigated the thermal stability of PLA containing both TA and organomodified clay using TGA under nitrogen. Figure 4 shows that the composite premature thermal degradation, induced by the presence of tannic acid is not reduced when both TA and nanoclay are combined. In fact, this

composition starts to degrade (T_{5%}) at 300°C while this temperature is recorded at 296°C for PLA/20 wt% TA composition (Table 2). However, the positive effect of this combination is more marked at higher temperature. In fact, above 400°C, the weight loss became lower when TA and nanoclay are combined owing to the formation of the char layer that reduces the volatilization of degradation product. The MLR decreases from 2.4%/°C for PLA containing nanoclay up to 1.1%/°C for PLA containing 17% TA and 3% oMMT.

These results clearly indicate that the presence of nanoclay enables for modifying the thermal degradation pathway of tannic acid from non-charring to charring process. This assumption is confirmed by the increase of the amount of residue formed at 600°C. In fact, the residual weight at 600°C formed when TA and nanoparticles are combined (Residue: 7.2%) is

significantly higher to 2% and 2.5% obtained during thermal decomposition of PLA containing TA and nanoclay separately.

The beneficial effect of combining tannic acid and nanoclays has been also evidenced during cone calorimeter test. HRR curves, presented in Figure 5, show that using 17% TA and 3% oMMT enables for further pHRR reduction (-50%), higher to that obtained when only nanoparticles are used (-31.6%) (Table 3). Total heat release is also positively affected by this combination since it decreases up to 77 kW/m² in respect to 89 kW/m² and 84.4 kW/m² obtained respectively when both TA and nanoclays are used separately.

These results demonstrate that tannic acid contributes to the char formation thanks to the presence of nanoclays that promotes its charring effect. In fact, the amount of the final residue increased from 0.6% and 8.5% when TA and nanoclays are used respectively up to 14.7% when both additives are combined (Figure 6 and Table 3).

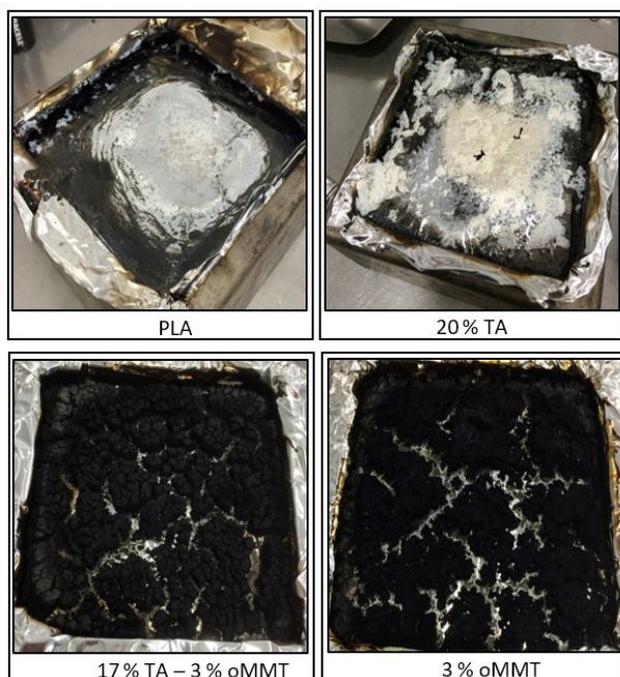


Figure 6 Cone calorimeter test residues.

It is also worth mentioning that the presence of tannic acid still induces faster ignition even in combination with nanoclay. Several assumptions might explain this observation. First, clay nanoplatelets have been already reported to increase nanocomposite ignitability by reducing thermal diffusion into the sample. Thus, the temperature at the surface of the nanocomposite rises more rapidly than with unfilled

polymer [24]. Fast increase of the temperature at the surface of the materials promotes earlier release of combustible decomposition products. Moreover, TGA analysis indicated that combining TA with nanoclays does not totally suppress the premature thermal degradation of the composite but only limited it.

In conclusion, combining TA and nanoclay presents an interesting way for taking advantage of TA char forming ability. In fact, the presence of nanoclay enables the modification of TA thermo-degradation pathway through charring thermal decomposition. This induces further improvement of the composite flame retardant behavior by reducing the pHRR but unfortunately does not positively affect the composite ignitability that remains high.

3.2.3 Effect of Phosphorus/Tannic Acid Association

Phosphorous flame retardant additives are well known to promote char formation via condensation reactions [23]. With this view, combining tannic acid and phosphorus-based chemical compounds, through additive and reactive pathway, is expected to result in better flame retardant properties.

A Additive Pathway

To maintain the good environmental profile of the investigated composites due to the biobased origin of the different components used, phytate salts have been selected as phosphorous based co-additive. Phytate salts seem to be a good candidate for this purpose as the incorporation of phytic acid, a liquid compound that contains high phosphorus content (28 wt%) as well as an interesting P/C atomic ratio (=1), into PLA recently proved to induce an important increase of the composite hygroscopy [25]. Using its salts form enables for limiting this negative effect.

With this view, tannic acid was combined with aluminum phytate salt (Al-Phyt, also known to promote the formation of an effective char layer during the combustion [26]). Figure 7 presents HRR curves obtained with this combination in comparison with that obtained with 20 wt% Al-Phyt alone. As seen, using only Al-Phyt enables for an important reduction of the pHRR down to 200 kW/m², and to the generation of a residue of 16.5%. Results showed that PLA/10 wt% TA/10 wt% Al-Phyt exhibits a strong combustion, similar to that of pristine PLA and no synergistic effect is reached. Moreover, an important increase of the composite ignitability is obtained when both additives are combined.

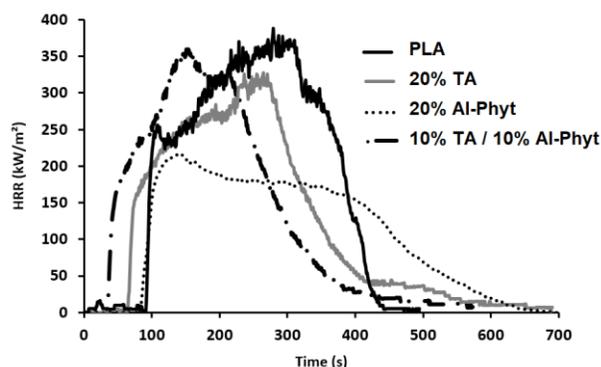


Figure 7 HRR versus time curves from cone calorimeter test at 35 kW/m^2 .

Combining 10 wt% TA with 10 wt% Al-Phyt is thus not efficient FR system probably because of the low phosphorus content in the blend that do not enable for the formation of continuous char layer. Increasing Al-Phyt content in the blend may help for enhancing the efficiency of the char layer. However, in previous study [26], we demonstrated that aluminum phytate, when used at higher content (20 wt%) induces an important PLA degradation during melt processing. This point is also to be taken into consideration for the selection of adapted FR systems. In contrast, sodium phytate (Na-Phyt) has been found to enable for lower pHRR reduction than aluminum salt but presented the advantage of not affecting PLA thermal stability during melt processing. For this reason, we selected Na-Phyt to investigate the effect of increasing phosphorous content in the blend. Since adding 20 wt% Na-Phytate has been demonstrated to only present limited efficient flame retardant effect [26], its incorporation content has been increased up to 30 wt%. Cone calorimeter test curves of PLA containing 30 wt% Na-Phyt, 30 wt% TA and their 15wt%/15wt% combination are presented in Figure 8, results are summarized in Table 3 and residue pictures are presented in Figure 9. Increasing TA content up to 30 wt% did not induce any change of the composite flammability, which remains high with an inflammation occurring after only 52 s, a pHRR of about 310 kW/m^2 , a total heat release similar to that of pristine PLA (87.7 MJ/m^2) and without generation of any residue at the end of the test. In contrast, 30 wt% Na-Phytate leads to a reduction of pHRR of about 34%. However, the best performance is obtained when both additives are combined. In fact, using 15 wt% TA and 15 wt% Na-Phyt enables a reduction of both pHRR and THR of by 52.6% and 15.8%, respectively. THR obtained with 15 wt% TA/15 wt% Na-Phyt are combined is similar to that obtained with 30 wt% Na-Phyt. This is due to the fact that combustion takes place during larger range

of time when both additives are combined. This explains also why the residue content is higher with 30 wt% Na-Phyt (Table 3 and Figure 8). Moreover, HRR curve shape changes from a non-charring to a thick charring behavior according to the classification of Schartel and Hull [27]. It is worth mentioning that the combination of TA with Na-Phyt does not enable any enhancement of the resistance to ignition of the composite. TTI remains lower to that of pristine PLA and similar to that obtained when only TA is used (53 s).

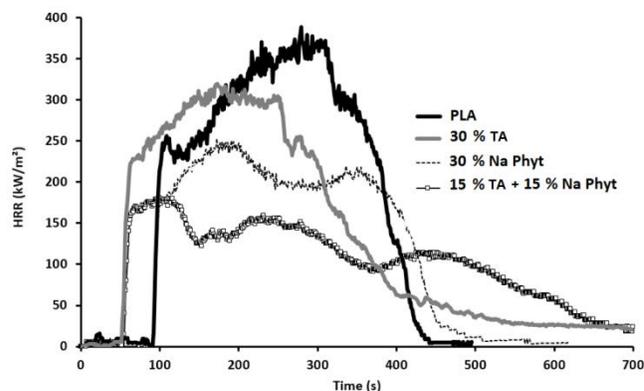


Figure 8 HRR versus time curves from cone calorimeter test at 35 kW/m^2 .

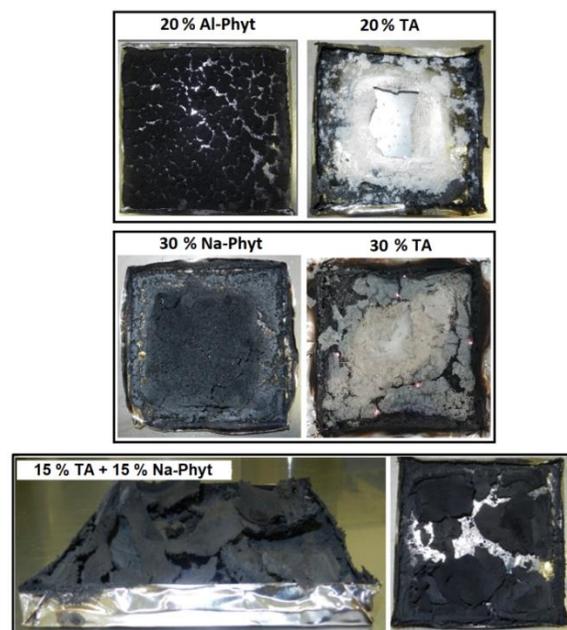


Figure 9 Images of the final residues formed during cone calorimeter test.

The combination of tannic acid with phosphorous-based flame retardant agent (Na-Phyt) presents an effective way to promote its charring and thus improving the flame retardant behavior of the corresponding composite. However, in this configuration, using at least

30 wt% loading is required prior to obtain significant effect. Moreover, combining TA and Na-Phyt does not allow for enhancing the composite ignitability. In fact, even if tannic acid is used in combination with Na-Phyt, its presence induces an important reduction of the time to ignition that remains similar to that obtained when only tannic acid is used (53 s). The thermo-degradant effect of TA is thus not limited at the pre-ignition period.

With the view of limiting this negative effect, we investigated the effect of the phosphorylation of tannic acid as a possible way for enhancing its charring effect and limiting its negative effect on the time-to-ignition of the composite.

b- reactive pathway

Chemical modification, especially by phosphorous-based derivatives, presents an efficient way to promote the charring effect of compounds such as flax [22], lignin [11] and cellulose [3]. In fact, phosphorous is able to act in condensed phase by promoting the formation of charred structures during the combustion through an acid-catalysed cross-linking action [22]. With this view, grafting phosphoric acid on tannic acid (TA-POH) has been performed in two steps (Scheme 1) allowing for grafting 1.74 wt% phosphorus. The incorporation of phosphoric acid groups in the structure of tannic acid triggers some modifications of its thermogravimetric behavior (Figure 10 and Table 4), i.e. (i) premature thermal degradation ($T_{-5\%}$ decreases from 260°C to 206°C), (ii) reduction of its degradation rate (from 0.6%/°C to 0.15 %/°C) and (iii) enhancement of its char forming ability (the amount of the final char increases from 24% to 45%). The premature TA thermal degradation could be attributed to the action of phosphoric acid groups, which are able to induce dehydration reactions able to catalyze its thermal degradation. This behavior has already been observed when lignin and cellulose was associated to phosphorous compounds [3, 15, 11, 28]. The reduction of the degradation rate and the increase of the amount char residue result from the condensation reactions induced by the presence of phosphorus.

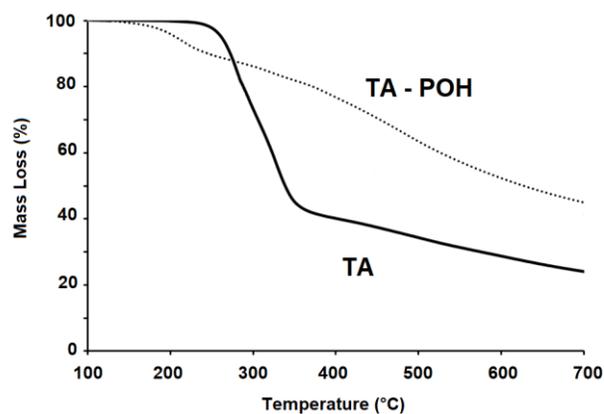


Figure 10 TGA curves of untreated and phosphorylated tannic acid under nitrogen.

Table 4 TGA parameters of TA and TA-POH (under N₂) as well as the P content determined by ICP analysis.

	T-5% (°C)	T _{degradation} (°C)	Residue (%)	P content (%)
TA	260	296	23	----
TA-POH	206	220, 320, 480	44	1.75

The premature thermal degradation of TA induced by the presence of phosphoric acid groups affects also the thermal stability of the composite. In fact, the incorporation of 20 wt% phosphorylated tannic acid induced an important reduction of the composite thermal stability since both $T_{-5\%}$ and $T_{-10\%}$ are respectively reduced from 312°C and 325°C recorded for pristine PLA to 286°C and 317°C in the presence of phosphorylated tannic acid (Figure 11 and Table 2). Thermo-degradant effect of TA-POH has been also found to take place during melt processing. In fact, PLA molecular weight loss recorded in the presence of phosphorylated tannic acid is very low (15 700 g/mol). It is worth mentioning that even if TA-POH is responsible for the reduction of PLA thermal stability, its use enables the generation of some char during TGA analysis of about 5.6% in contrast to untreated tannic acid.

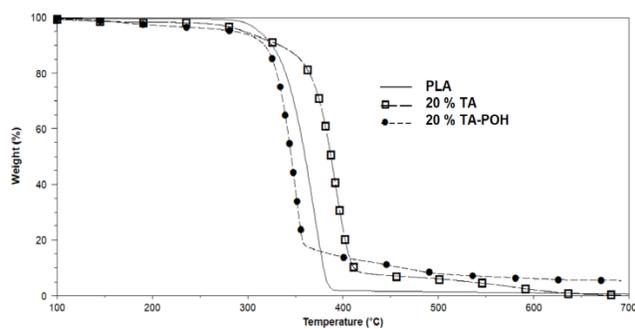


Figure 11 TGA curves of PLA containing 20 wt% TA and TA-POH under N₂. Under N₂.

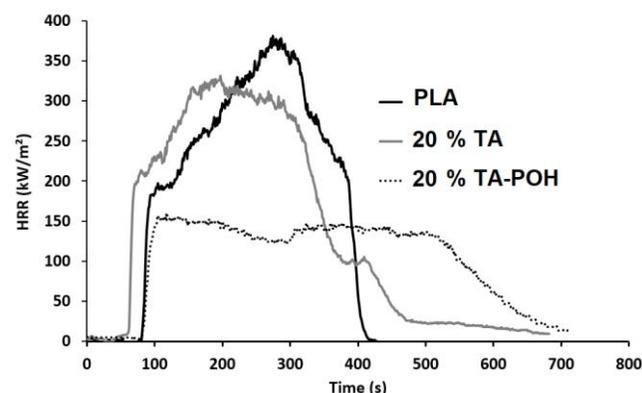


Figure 12 HRR curves of PLA containing 20 wt% TA and TA-POH.

Surprisingly, even though phosphorylated tannic acid induces important PLA thermal degradation, cone calorimeter test reveals its high flame retardant effect since its presence enables for an important pHRR reduction of about 58% (Figure 12 and Table 3) thanks to the formation of a homogenous char residue (Figure 13). It is worth mentioning that the presence of phosphorylated tannic acid does not affect the composite ignitability. Phosphorylated tannic acid presents thus an antagonist effect that promotes in the meanwhile an important enhancement of the composite flame retardant properties but affects its thermal stability during both melt processing and TGA analysis. It is worth mentioning that the phosphorylation of tannic acid induces important change of its dispersion state in the blend. In fact, SEM observations reveal the presence of TA-POH microparticles that are likely formed due to the condensation reaction of phosphoric acid groups. This kind of reaction has been also observed in the case of lignin and was found to induce an important increase of lignin molecular weight [11].

In order to investigate the contribution of phosphoric acid groups on the thermal stability and

fire performance of PLA, we performed the same chemical modification on another biobased aromatic compound, i.e. lignin. This modification enables for grafting similar phosphorus content (as determined by ICP analysis) than with tannic acid, i.e. 1.8% for lignin-POH and 1.75% for TA-POH.

Unexpectedly and even if the phosphorus content is similar in the two products, the average molecular weight of PLA is less affected by phosphorylated lignin (Table 5). This result seems indicating that phosphoric acid groups are not the only ones responsible for TA-POH thermo-degradant effect.

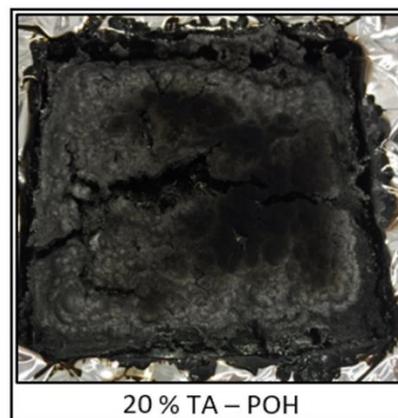


Figure 13 Residue after cone calorimeter test of PLA containing 20 wt% TA-POH.

Table 5 Effect of the incorporation of phosphorylated lignin (Lig-POH) on PLA average molecular weight.

	\bar{M}_n (g/mol)
PLA	98 400
20% TA	94 000
20% TA-POH	15 690
20% Lignin Kraft -POH	40 400

A modification of tannic acid structure, induced by the phosphorylation reaction, could explain its more important degrading effect. In order to investigate this hypothesis, we analyzed TA-POH by FTIR and compare its spectrum with that of untreated tannic acid. ATR-FTIR spectra were recorded in the wavelength range 4000 cm⁻¹ and 600 cm⁻¹ however, as both compounds present a strong band between 3600 cm⁻¹ and 3400 cm⁻¹ due to OH stretching vibration, analysis of the two samples spectra was performed in the fingerprint

region between 1800 and 700 cm^{-1} (Figure 14). As expected, the five common bands of tannins are present: 1609–1605 cm^{-1} and 1445–1441 cm^{-1} (aromatic ring stretching vibration), 1206–1175 cm^{-1} and 1078–1024 cm^{-1} (C-O bond stretching vibration) and 1533–1526 cm^{-1} (skeletal vibration of aromatic rings) [29–33].

ATR-FTIR spectrum of TA-POH clearly showed the appearance of new bands at 1088 cm^{-1} (symmetric P-O vibrations), 1026 cm^{-1} (PO_2 vibrations), 955 cm^{-1} (symmetric P-O vibrations) and 901 cm^{-1} (asymmetric P-OH vibrations), thus confirming successful phosphorylation. Interestingly, a shift of the TA band at 1701 cm^{-1} (C=O stretching vibration of ester linkages) towards the lower value of 1651 cm^{-1} (characteristic of doubly conjugated ketone carbonyl) was observed.

This shift evidences that the phosphorylation procedure used induces significant hydrolysis of gallic acid ester linkages. Gallic acid thus formed may react with ester functions of PLA and trigger the polymer chain breakage.

4 CONCLUSION

The effect of using tannic acid as flame-retardant additive for PLA was investigated taking advantages of its char forming ability under pyrolytic conditions. Alone, TA does not display any FR effect and its combination with additional compounds is required. When combined with nanoclays, TA thermal degradation pathway changes towards charring thermal decomposition. In this condition, the amount of the char formed during the combustion increases and a further reduction of the pHRR is reached (around -50%).

Combining tannic acid with phosphorus-based chemical functions/derivatives was investigated as a second strategy aiming to improve its charring effect. Phosphorus was either grafted on TA surface or added into the matrix as phytate salt. In both cases, improved flame retardant behavior was reached but the two pathways lead to different effects. The additive pathway required at least 30 wt% loading content to reach significant pHRR reduction (-52.6% for 15% TA +15% Na-Phyt composition) and does not allow any improvement of the composite resistance to ignition. In contrast, reactive pathway was shown to be more efficient since using only 20 wt% enables for strong pHRR reduction (-58%) without effecting the time-to-ignition that remains similar to that of pristine PLA. However, using phosphorylated TA induces important PLA thermal degradation during both melt processing and TGA analysis. This degradant effect has been found to be induced by the hydrolysis of tannic acid during its phosphorylation. Development of novel phosphorylation reactions avoiding tannic acid hydrolysis is a promising path for developing efficient biobased flame retardant additive for PLA.

ACKNOWLEDGMENTS

This work was supported by the European Commission and Région Wallonne FEDER program (Materia Nova), by the Interuniversity Attraction Pole program of the Belgian Federal Science Policy Office (PAI 7/05) and by FNRS-FRFC.

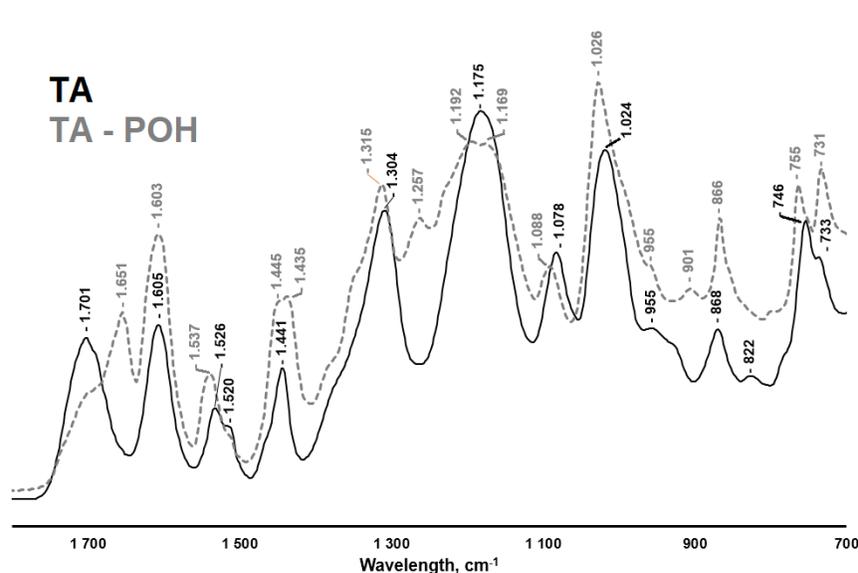


Figure 14 ATR-FTIR spectra of TA (black line) and of TA-POH (grey dotted line) in the fingerprint region of 1800-700 cm^{-1} .

REFERENCES

1. C.L. Cheung, A. Kurtz, H. Park, C.M. Lieber, Diameter-controlled synthesis of carbon nanotubes. *J. Phys. Chem. B* **106**, 2429 (2012).
2. J. Kuczynski, D.J. Boday, Bio-based materials for high-end electronics applications. *Int. J. Sustain. Dev. World Ecol.* **19**, 557 (2012).
3. J.T. Wertz, T.C. Mauldin, D.J. Boday, Polylactic acid with improved heat deflection temperatures and self-healing properties for durable goods applications. *ACS Appl. Mater. Interfaces.* **6**, 18511 (2014).
4. L. Costes, F. Laoutid, F. Khelifa, G. Rose, S. Brohez, C. Delvosalle, P. Dubois, Cellulose/phosphorus combinations for sustainable fire retarded polylactide. *European Polymer Journal* **74**, 218 (2016).
5. C. Reti, M. Casetta, S. Duquesne, S. Bourbigot, R. Delobel, Flammability properties of intumescent PLA including starch and lignin. *Polym. Adv. Technol.* **19**, 628 (2008).
6. J.X. Feng, S.P. Su, J. Zhu, An intumescent flame retardant system using β -cyclodextrin as a carbon source in polylactic acid (PLA). *Polym. Adv. Technol.* **22**, 1115 (2011).
7. J. Alongi, F. Cuttica, A. Di Blasio, F. Carosio, G. Malucelli, Intumescent features of nucleic acids and proteins. *Thermochim. Acta* **591**, 31 (2014).
8. A. De Chirico, M. Armanini, P. Chini, G. Cioccolo, F. Provasoli, G. Audisio, Flame retardants for polypropylene based on lignin. *Polym. Degrad. Stab.* **79**, 139 (2003).
9. L. Ferry, G. Dorez, A. Taguet, B. Otazaghine, J.M. Lopez-Cuesta, Chemical modification of lignin by phosphorus molecules to improve the fire behavior of polybutylene succinate. *Polym. Degrad. Stab.* **113**, 135 (2015).
10. B. Prieur, M. Meub, M. Wittemann, R. Klein, S. Bellayer, G. Fontaine, S. Bourbigot, Phosphorylation of lignin to flame retard acrylonitrile butadiene styrene (ABS). *Polym. Degrad. Stab.* **127**, 32 (2016).
11. J. Zhang, E. Fleury, Y. Chen, M.A. Brook, Flame retardant lignin-based silicone composites, *RSC Adv.* **5**, 103907 (2015).
12. L. Costes, F. Laoutid, M. Aguedo, A. Richel, S. Brohez, C. Delvosalle, Ph. Dubois, Phosphorus and nitrogen derivatization as efficient route for improvement of lignin flame retardant action in PLA. *European Polymer Journal* **84**, 652 (2016).
13. A. A. Alalykin, R. L. Vesnin, and D. A. Kozulin, Preparation of modified hydrolysis lignin and its use for filling epoxy polymers and enhancing their flame resistance. *Russian Journal of Applied Chemistry* **84**, 1616 (2011).
14. A. Cayla, F. Rault, S. Giraud, F. Salaün, V. Fierro, A. Celzard, PLA with intumescent system containing lignin and ammonium polyphosphate for flame retardant textile. *Polymers* **8**, 331 (2016).
15. R. Zhang, X. Xiao, Q. Tai, H. Huang, Y. Hu, Modification of lignin and its application as char agent in intumescent flame-retardant poly(lactic acid). *Polymer Engineering and Science* **52**, 2620 (2012).
16. Y. Yu, S. Fu, P. Song, X. Luo, Y. Jin, F. Lu, Q. Wu, J. Ye, Functionalized lignin by grafting phosphorus-nitrogen improves the thermal stability and flame retardancy of polypropylene. *Polymer Degradation and Stability* **97**, 541 (2012).
17. Z. Xia, A. Singh, W. Kiratitanavit, R. Mosurkal, J. Kumar, R. Nagarajan, Unraveling the mechanism of thermal and thermo-oxidative degradation of tannic acid. *Thermochimica Acta.* **605**, 77 (2015).
18. H. Tributsch, S. Fiechter, The material strategy of fire-resistant tree barks. *WIT Trans. Built Env.* **97**, 43 (2008).
19. M. Cowan, Plant products as antimicrobial agents. *Clin. Microbiol. Rev.* **12**, 564 (1999).
20. K. Freudenberg, *Die Chemie der Natürlichen Gerbstoffe*, Springer-Verlag, Berlin (1920)
21. K.T. Chung, T.Y. Wong, C.I. Wei, Y.W. Huang, Y. Lin, Tannins and human health: A review. *Crit. Rev. Food Sci. Nutr.* **38**, 421 (1998).
22. N. Brosse, A. Pizzi, Bio-based Wood Adhesives: Preparation, Characterization, and Testing, Chap 8: *Tannins for Wood, Adhesives, Foams and Composites*, Zhongqi He (Eitor), CRC Press Taylor & Francis Group, February **14**, 2017.
23. B.N. Jang, M. Costache, C.A. Wilkie, The relationship between thermal degradation behavior of polymer and the fire retardancy of polymer/clay nanocomposites. *Polym.* **46**, 10678 (2005).
24. F. Laoutid, L. Bonnaud, M. Alexandre, J.M. Lopez-Cuesta, P. Dubois, New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Mater. Sci. Eng.* **63**, 100 (2009).
25. S. Bourbigot, S. Duquesne, Fire retardant polymers: recent developments and opportunities. *J. Mater. Chem.* **22**, 2283 (2007).
26. L. Costes, F. Laoutid, S. Brohez, Ch. Delvosalle, Ph. Dubois, Phytic acid-lignin combination: A simple and efficient route for enhancing thermal and flame retardant properties of polylactide. *European Polymer Journal* **94**, 270 (2017).

27. L. Costes, F. Laoutid, L. Dumazert, J-M. Lopez-Cuesta, S. Brohez, C. Delvosalle, P. Dubois, Metallic phytates as efficient bio-based phosphorous flame retardant additives for poly(lactic acid). *Polymer Degradation and Stability* **119**, 217 (2015).
28. B. Schartel, T. R. Hull, Development of fire-retarded materials-Interpretation of cone calorimeter data. *Fire Mater.* **31**, 327 (2007).
29. G. Dorez, A. Taguet, L. Ferry, J-M. Lopez Cuesta, Phosphorous compounds as flame retardants for polybutylene succinate/flax biocomposite: Additive versus reactive route. *Polym. Degrad. Stab.* **102**, 152 (2014).
30. J. Li, B. Li, X. Zhang, R. Su, The study of flame retardants on thermal degradation and charring process of manchurian ash lignin in the condensed phase. *Polym. Degrad. Stab.* **72**, 493 (2001).
31. L. Falcão, M.E.M. Araújo, J. Cult. Tannins characterization in historic leathers by complementary analytical techniques ATR-FTIR, UV-Vis and chemical tests. *Herit.* **14**, 499 (2013).
32. K. Nakagawa, M. Sugita, Spectroscopic characterisation and molecular weight of vegetable tannin. *J. Soc. Leather Technol. Chem.* **83**, 261 (1999).
33. A. Edlmann, B. Lendl, Toward the optical tongue: flow-through sensing of tannin-protein interactions based on FTIR spectroscopy. *J. Am. Chem. Soc.* **124**, 14741 (2002).
34. K. Fernández, E. Agosin, Quantitative analysis of red wine tannins using Fourier-transform mid-infrared spectrometry. *J. Agric. Food Chem.* **55**, 7294 (2007).