Lignin-based flame retardant systems

Fouad Laoutid[1], Henri Vahabi[2], Mohammad Reza Saeb[2], Philippe Dubois[1]

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

(2) Université de Lorraine, Centrale Supélec, LMOPS, 57000 Metz, France

Abstract

Very recently, China and India as the game changers of the world producing million tons of greenhouse gases have promised to invest up to 35% of their gross domestic product (GDP) on global climate change before 2030. In line with such green policies, but for more than three decades ago, research centers active in the field of materials sciences and engineering and those working on development of flame retardant for polymers have been advised by the governments to switch from halogen-based to sustainable flame retardants. Bio-based flame retardants rapidly proved obvious candidates for this purpose, but to display adequate flame retardancy they require physical and/or chemical modification. Lignin is a versatile biodegradable polymer, which has been widely applied as a part of flame retardant systems in polymers. There is a pletoric number of works on lignin-based flame retardants and flame retardancy of lignin-incorporated polymer systems. This chapter aims at reporting and classifying these works on flame retardancy of unmodified and modified lignin and its “sister”, i.e., nanolignin, as flame retardant additives for polymer systems.

Keywords: Lignin; Flame Retardancy; Nanolignin; Fire Retardant; Biodegradable polymer

1. Introduction

In the second half of the 20th century, polymer materials have become the most commonly used materials and from those times they have been experiencing worldwide progress. Polymers are extremely versatile but highly flammable. The major fire risk of polymers, considering their massive use from commodity to advanced applications, necessitates consideration of their combustible nature in materials design [1,2]. A variety of flame retardants have been developed to minimize fire risk of polymers and meet fire safety requirements. They enable enhancing the resistance to ignition of materials and/or reducing the heat released during their combustion. There are several types of flame retardants, which are grouped into different product families. They are designed to bring the resistance character to polymers against combustion by interfering in the combustion process through different physical or chemical strategies, including minerals, halogenated, phosphorus-based, nitrogen-based and silicon-based compounds [1].

Among such classes, minerals represent the largest segment in the market of flame retardants. This category includes metallic hydroxides, boron-based additives, hydroxycarbonates and even inert fillers. Magnesium and aluminum hydroxides present the most common inorganic flame retardants. They are very efficient owing to their endothermic decomposition, that releases water and absorb heat. However, a large incorporation rate is necessary to achieve significant flame-retardant performances. This can lead to deterioration of other functional properties of the resulting composite including mechanical properties. Halogenated flame retardants act in the vapor phase by releasing halogen radicals that scavenge reactive free radicals and thus stop the combustion. However, their use is more and more avoided and restricted due to environmental and health concerns [3]. Using flame retardant systems capable of promoting the formation of an insulating char layer on the surface of the burning material received more attention among the most promising environmentally friendly strategies for replacing halogenated flame retardants. To address these issues, researchers placed focus on the development of halogen-free flame-retardant systems, such as phosphorus-based derivatives that promote the formation of protective char layer during the combustion.

Among the new emerging solutions, bio-based flame retardants are attracting a lot of attention. Moreover, because of the growing awareness of the environmental issues linked to the reduction of CO_2, the use of fossil feedstock has become less competitive. Lignin is one of the constituents of biomass that is attracting more and more research interest as a flame retardant additive for polymeric materials. Owing to its aromatic structure and thermal behavior, lignin presents great interest for polymer flame-retardant applications. Indeed, its thermal degradation under inert atmosphere leads to the formation of stable charred residues, of 30 to 50 wt.% [4,5] that could be advantageously exploited for the generation of protective char layers during polymer combustion. However, this char residue thermally degrades in the presence of oxygen and its thermal stability must thus be reinforced to enhance its flame-retardant effect. This could be achieved by combining lignin with other flame-retardant additives or by modifying its chemical structure by grafting new chemical functions to increase the thermal stability of the char and/or its quantity.

Besides development of proper materials for flame retardant systems, there is a need for selection and understanding the mechanism of devices analyzing flame retardancy of polymers. Several methods are generally used to evaluate flame retardancy, but two versatile ones were described here: cone calorimetry and UL94. Cone calorimetry is recognized as the best bench-scale test for evaluation of the fire behavior of polymers. It is based on monitoring the oxygen consumption according to Huggett's relation in which 1 kg of consumed oxygen corresponds to 13.1 MJ of released energy [6]. A source of heat in shape of cone is used and irradiates the polymer sample plate (generally with dimensions $100 \times 100 \times 4$ mm^3) at a constant heat flux, Figure 1. The main characteristics measured in this test include the peak of heat release (pHRR; kW/m^2), the total heat release (THR; kJ/m^2), the time to ignition (TTI; s), the quantity of CO and CO_2, and the opacity of the smoke.

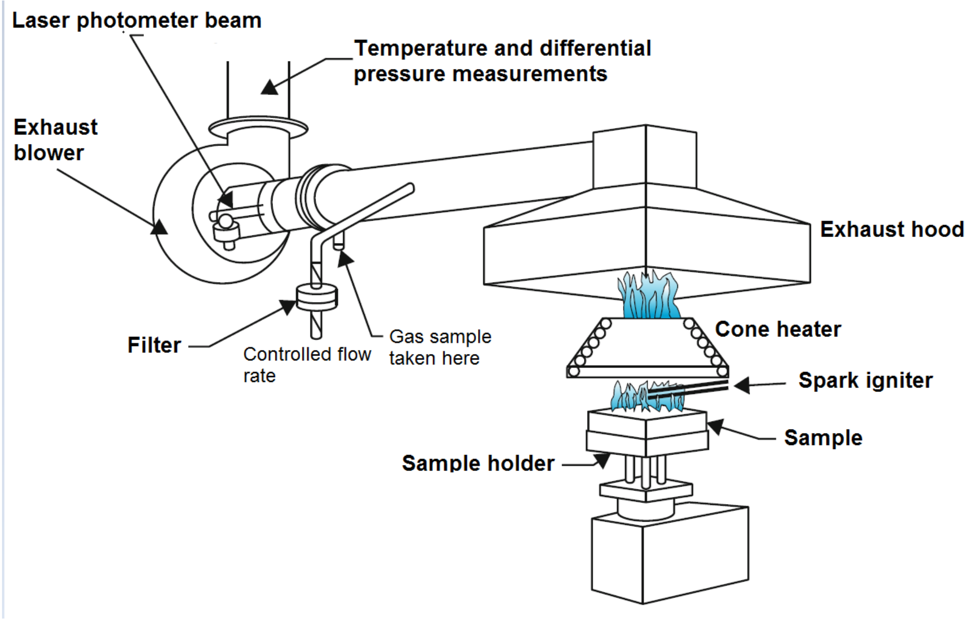

Figure 1: Schematic representation of cone calorimeter apparatus. Different parts of the apparatus are named and specified.

The Underwriters Laboratories of the United States introduced [7] UL94 test. UL94 reveals the aptitude of a material to spread the flame or to extinguish it when the sample is ignited. There are two types of UL94 test including vertical and horizontal tests. Figure 2 shows the schematic representation of vertical UL94 test. The flame is applied to the bottom of the specimen and the top of the burner has to be located at 10 mm from the bottom edge of the specimen. The flame is applied for 10 s and removed. The after-flame time t_1 (the time required for the flame to extinguish) is noted. After extinction, the flame is applied for another 10 s. The after-flame time t_2 is noted, together with the afterglow time t_3 (the time required for the fire glow to disappear). During the application of the flame, the distance between burner and specimen must remain constant. If drops fall, the burner must be tilted through a maximum angle of 45° or slightly isolated from the specimen flame. During the test, the presence of burning drops, causing a piece of cotton located under the sample to ignite, must be noted. The standard specifies that five specimens must be tested. The specimen is classified as V0, V1 or V2 according to the criteria listed in Table 1.

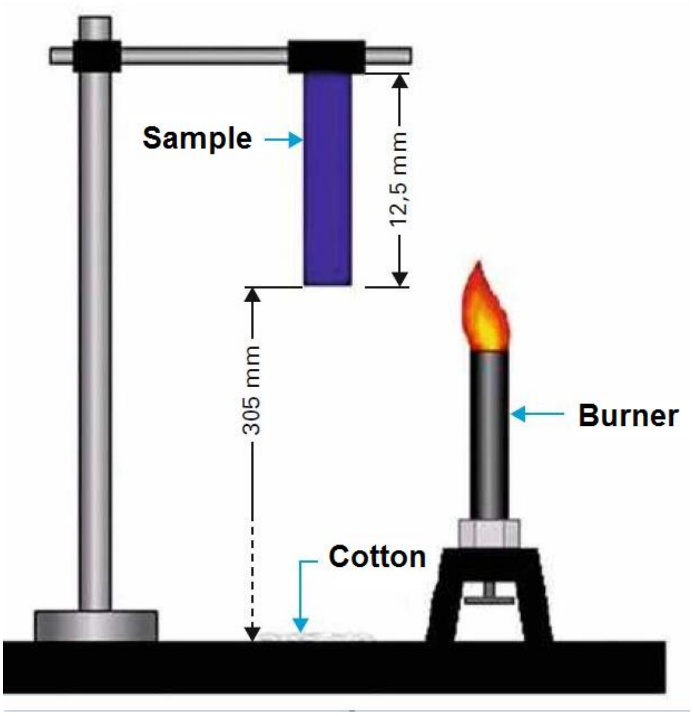

Figure 2: Schematic representation of vertical UL94 test.

Table 1: Method of classification in vertical UL94 test.

Classification	
UL94 V0	t_1 and t_2 less than 10 s for each specimen $t_1 + t_2$ less than 50 s for the five specimens $t_2 + t_3$ less than 30 s for each specimen No after flame or afterglow up to the holding clamp No burning drops
UL94 V1	t_1 and t_2 less than 30 s for each specimen $t_1 + t_2$ less than 250 s for the five specimens $t_2 + t_3$ less than 60 s for each specimen No after flame or afterglow up to the holding clamp No burning drops
UL94 V2	t_1 and t_2 less than 30 s for each specimen $t_1 + t_2$ less than 250 s for the five specimens $t_2 + t_3$ less than 60 s for each specimen No after flame or afterglow up to the holding clamp Burning drops allowed

Herein, we focus on the effect of pristine and modified lignin as well as nanolignin on the fire reaction of polymers. The combination of lignin with other conventional flame retardant is also discussed.

2. Flame retardant character of pristine lignin

The incorporation of untreated (pristine) lignin into the non-charring polymers, such as polypropylene (PP), enables significant enhancement of the flame-retardant behavior [8] owing to the generation of a considerable amount of char at the surface of the burning material. This protective layer acts as an insulating barrier against the diffusion of heat and the release of volatile fragments. Lignin has been also shown to enhance flame retardant properties of silicone but only when residual Si-H groups are removed [9]. It has been demonstrated that silicone composites containing untreated lignin are highly flammable, while removing Si-H groups, using NH_3 vapor, enables obtaining V1 rating of the UL94. The flame-retardant action of lignin is based on its ability to generate thermally stable char residue during the combustion. Thermal degradation of lignin and its ability to generate char is a complex mechanism, which can be affected by various parameters. Some of these parameters depend directly on the lignin properties (e.g., its botanical origin and the extraction process used), while some others are induced by external factors (e.g., thermal process, and the presence of other substances). Such a complexity of mechanism makes the flame retardant character evaluation of lignin interesting.

Lignin has a complex structure composed of a cross-linked 3D network based on three monolignols (p-coumaryl, synapyl and coniferyl alcohols). The quantity of the three monolignols and their sequence is mainly related to the plant species [10], which strongly affects the thermal decompostion of lignin [11]. The thermal behavior of lignin also depends on the extraction mode used in its production process. Indeed, each extraction process induces its own modification on the lignin structure (particle size, oxidation, presence of new chemical functions and their relative amount). All these elements induce not only changes in lignin chemical structures and its thermal behavior but also strongly affect their behavior against fire. [11] The combustion of these two different lignins, resulting from unknown botanical origins and different extraction processes, i.e., kraft and solvent pulping processes, has been shown to present different pHRR during cone calorimeter test [12,13], Figure 3.

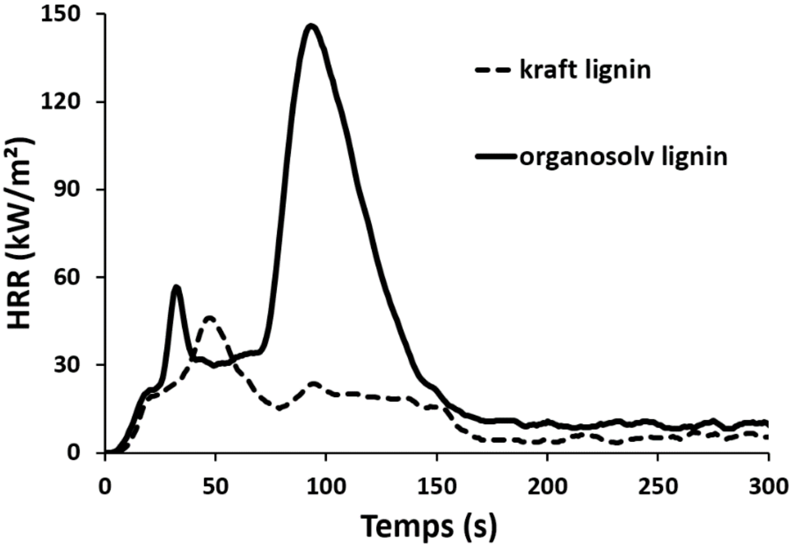

Figure 3 : Heat release rate (HRR) curves obtained from cone calorimeter test of kraft lignin and organosolv lignin (35 kW/m^2). Reproduced from [13] with permission.

Likewise, Ferry et al [12]. reported a lower pHRR during the combustion of a kraft lignin compared to an organosolv lignin. This difference has been attributed by authors to the presence of sulfur in the kraft lignin generating sulfur dioxide during the combustion. Nevertheless, there might be the likelihood of a reverse combustion behavior depending on the polymer matrix into which lignin is incorporated as flame retardant. In other words, several other parameters can determine the flame-retardant character of lignin when incorporated into a polymeric matrix. For instance, the incorporation of 20 wt.% of each of the aforementioned lignins into polylactic acid (PLA) resulted in controversial behavior in flame retardancy. The pHRR reduction was more significant when organosolv lignin was used even if its own combustion leads to a higher pHRR [13], Figure 4. The superior flame retardant effect of organosolv lignin over kraft was attributed to its better dispersion state into the PLA. Moreover, the possible interactions between the PLA carboxylic acid and hydroxyl end-groups with the numerous reactive groups of organosolv lignin likely limits the volatilization of low-molecular-weight fragments. The dispersion state of additives is generally a determining parameter that strongly affects the ultimate properties of composites like mechanical, thermal, and flame retardant properties. When lignin particles are well dispersed into the polymeric matrix, they may avoid the formation of isolated char domains and thus ensures the formation of continuous and homogenous char layer during the combustion. The effect of lignin dispersion within the polymer on flame-retardant performance of the composites has also been evidenced by Song et al. [14] in acrylonitrile-butadiene-styrene copolymer (ABS).

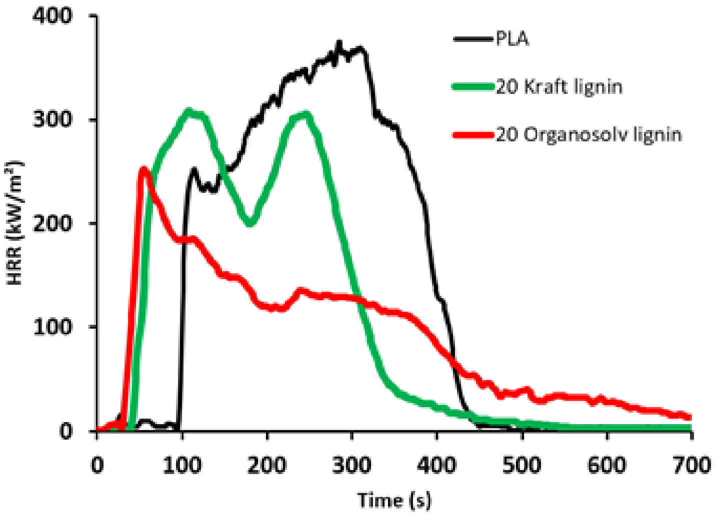

Figure 4 : Comparison between HRR curves of PLA containing 20 wt.% kraft and organosolv lignin. Reproduced from[13] with permission.

In some cases, the presence of lignin can change the degradation behavior of the polymer during melt processing leading to significant reduction in the polymer chain molecular weight [13,15] and also deterioration of the mechanical properties [15]. The thermo-degradant effect of lignin could remain effective even during the combustion, which negatively governs the composite fire behavior, i.e., reduction in the TTI and pHRR, as well as poor char structuration. For instance, the reduction in the TTI is the typical effect of lignin incorporation into polymeric materials as reported in several polymers such as PLA[13], polybutylene succinate (PBS)[12] and ABS[16]. The incorporation of 20 wt.% untreated (pristine) lignin induces a reduction of TTI from 87 s for the neat PLA to 27 s and 40 s for organosolv and kraft lignins, respectively. In PBS, TTI decreased from 72 s to 42s after the incorporation of 20 wt.% kraft lignin. In ABS, the presence of 30 wt.% lignin induces TTI decrease from 80 s for unfilled ABS to 49 s. Such a negative effect of lignin to the resistance to ignition could spring from different causes. It could be directly related to the thermo-degradant effect of lignin that facilitates rapid formation of combustible volatile fragments. The intrinsic ignitability of lignin, however, may change the material heat absorption due to the black coloration of lignin that induces a stronger heating of the decomposition gases. The reality is certainly a combination of all these factors.

The incorporation of two different lignins, i.e., kraft lignin and sulfonated lignin, into polyamide 11 resulted in dissimilar thermal and flame retardant behaviors [17]. Owing to the presence of sulfonate groups, sulfonated lignins have been found to generate higher amount of char residue and also revealed higher thermal stability than with respect to the kraft lignins. The higher amount of char has been also induced by the larger content of p-hydroxyphenyl units in sulfonated lignin and guaiacyl units in kraft lignins. Notably, p-hydroxyphenyl units favor the formation of char during thermal degradation, while guaiacyl units induce the formation of more volatile compounds. As a result, polyamide filled with sulfonated lignin present lower pHRR and THR than the one containing kraft lignin, Figure 5. All these details highlight that the functional properties of polymers filled with lignin could change depending on lignin functionality, reactivity, heterogeneity, and molecular weight distribution.

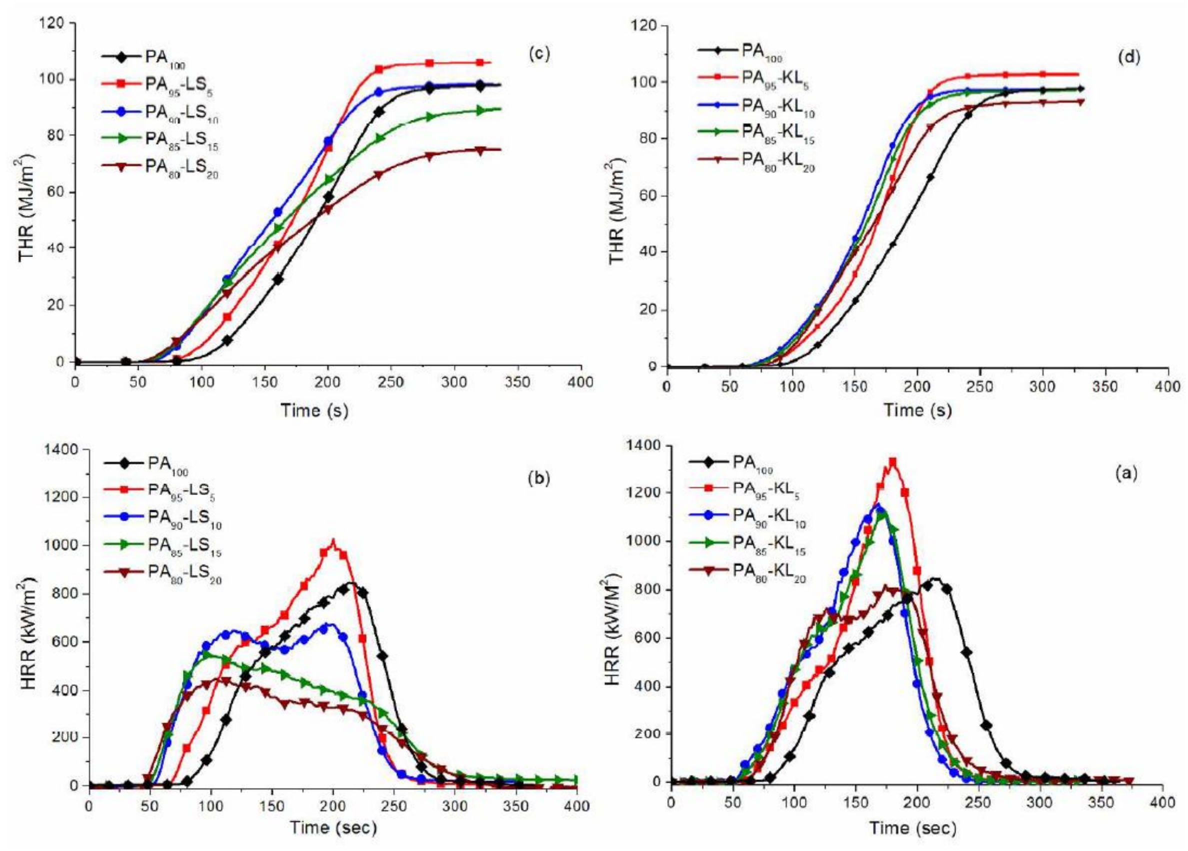

Figure 5 : HRR (a & b) and THR (c & d) curves obtained from cone calorimeter test of polyamide (PA) filled with sulphonated lignin (SL) and kraft lignin (KL). Reproduced from [17] with permission.

The variability of lignin in terms of size, reactivity and composition could be reduced through the fractionation of lignin into specific fractions. The macromolecular weight of lignin chain could vary from some hundreds to a few thousands g/mol within the same specimen. This could be achieved mainly by differential precipitation through variation of the solution pH, by using selective solvents extraction or by membrane technology. The fractionation of a kraft lignin has been shown to present a real benefit for enhancing thermal stability and flame-retardant effect of lignin. Laoutid et al. [18] reported flame retardant properties of PLA containing two lignin fractions, obtained using ultrafiltration membranes method having different molecular weights. The high-molecular-weight fraction (HMW) has been shown to allow obtaining PLA composites with superior thermal stability and flame-retardant behavior, Figure 6. It has been shown that the low-molecular-weight fraction (LMW) contains small oxidized fragments that induce PLA premature thermal degradation and higher pHRR during cone calorimeter test, Figure 7. A noteworthy achievement was that these two fractions displayed different thermal stability and combustion behaviors. Lignin fraction with HMW presented superior thermal stability and lower pHRR in thermogravimetric analysis (TGA) and cone calorimeter.

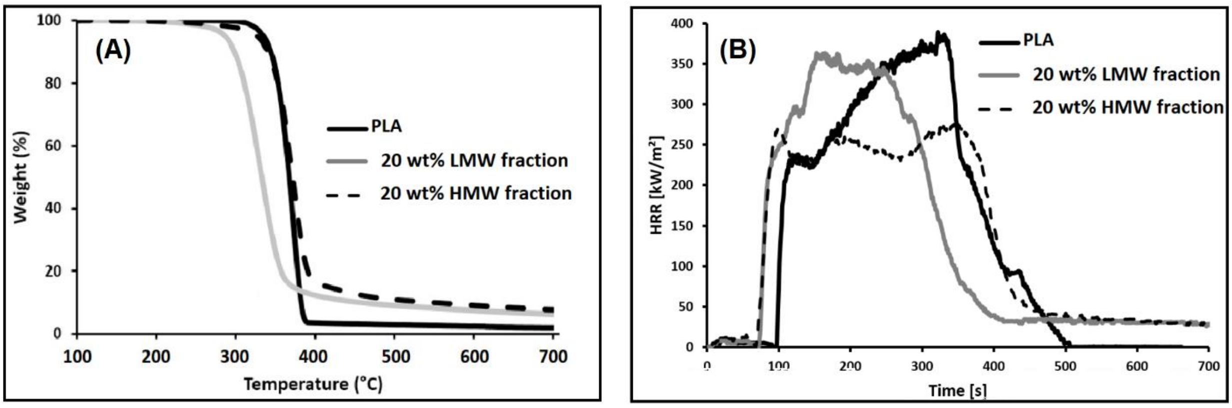

Figure 6 : TGA curves (under nitrogen, 20 °C/min) and HRR curves (35 kW/m^2) of PLA containing LMW and HMW lignin fractions. Adapted from [19].

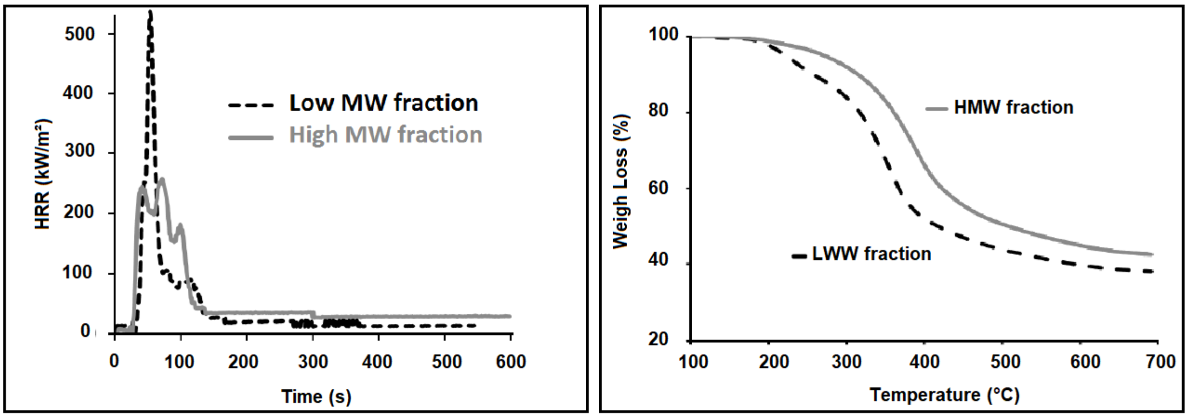

Figure 7 : HRR curves obtained from cone calorimeter test (left) and TGA curves under nitrogen (right) of high (HMW) and low (LMW) molecular weight fractions. Adapted from [19].

3. Functions of lignin in flame-retardant systems

Even though the incorporation of lignin in some polymers can provide flame retardant effect as evidenced in calorimetric cone tests, it does not provide any acceptable UL94 ratings. Therefore, the flame-retardant effect of lignin must be enhanced either by combining it as a synergistic agent with other existing flame-retardant systems (additive pathway), or by its chemical modification (reactive pathway). In fact, the char forming ability of lignin as well as thermal resistance of this char could be enhanced through the combination of lignin with other flame retardant agents [20–22], such as metallic hydroxides and phosphorus-based compounds. Such combinations generally enable further reduction in pHRR and prevent the decrease of TTI. Similar effect could also be obtained through the chemical modification of lignin, mainly through phosphorylation.

3.1. Additive pathway

Using lignin in combination with other flame retardants can be motivated by several reasons. For example, it can be used as a substitute for a petrochemical additive while maintaining the same functionality. For example, this is the case when lignin is used in replacement of pentaerythritol (PER) as carbonizing agent in intumescent formulations [23,24]. In such systems, lignin is combined with phosphorus-based flame retardants to increase the bio-based fraction of the composite while maintaining at least similar flame-retardant properties. In the presence of phosphorus compounds, such as orthophosphoric acid, ammonium polyphosphate and ammonium dihydrogen phosphate, the amount of char as well as its thermal stability are enhanced. This positive effect can be explained by the formation of a highly conjugated and cross-linked system, resulting from lignin dehydration and the cleavage of its C-O linkage induced by these phosphorus-based additives [25,26].

Lignin could also be advantageously combined with bio-based phosphorus compounds, such as phytic acid, for developing fully bio-based flame retardant systems. Blending lignin and phytic acid has been found to present an interesting way of enhancing the properties of PLA with limiting the negative effect of each additive [15]. The incorporation of 20 wt.% lignin or phytic acid separately improves the fire behavior of PLA, but negatively affects some other thermo-mechanical properties of the composite. When used alone, lignin induces rapid degradation of the polymer during melt processing, reflected in reduction in PLA chain molecular weight. This effect also results in premature thermal decomposition of the composite in TGA and a decrease in ignition time in cone calorimeter tests. On the other hand, phytic acid could not be used alone in PLA because it induces a significant increase in the material hygroscopy. When combined with lignin, the presence of phytic acid in the blend improves the dispersion of lignin in the polymer and limiting its thermo-degradant action, while the presence of lignin significantly decreases the material hygroscopy. Moreover, the combination of 15 wt.% phytic acid and 5 wt.% organosolv lignin leads to the formation of a material exhibiting improved elongation at break (12% instead of 3% for pristine PLA and the other composites), low pHRR (250 kW/m^2) and a V2 classification at UL94 test.

Lignin has also been combined with magnesium hydroxide (MDH) to develop complementary flame-retardant system in which the char formation induced by lignin reinforced the endothermic effect of MDH [21]. The cone calorimeter test results evidenced the efficiency of this combination that enables significant reduction in pHRR, higher than what observed when MDH or lignin used separately. Moreover, the decrease in the resistance to ignition that is induced by lignin when used alone was limited owing to the combination with MDH. Lignin could be advantageously combined with nanoparticles for developing efficient flame-retardant coating. Song et al [27] prepared lightweight, highly flexible, and self-extinguished cellulosic paper with increased gas impermeability by applying a coating based on combination of lignin, carbon nanotubes and graphene nanoplatelets, Figure 8. Papers coated with this combination presented superior thermal stability and fire retardancy than samples treated with each component separately. Combining the three components enabled reaching superior performances owing to the formation, at the paper surface, of a more uniform and compact protective layer presenting lower air permeability and a higher amount of thermally conductive pathways.

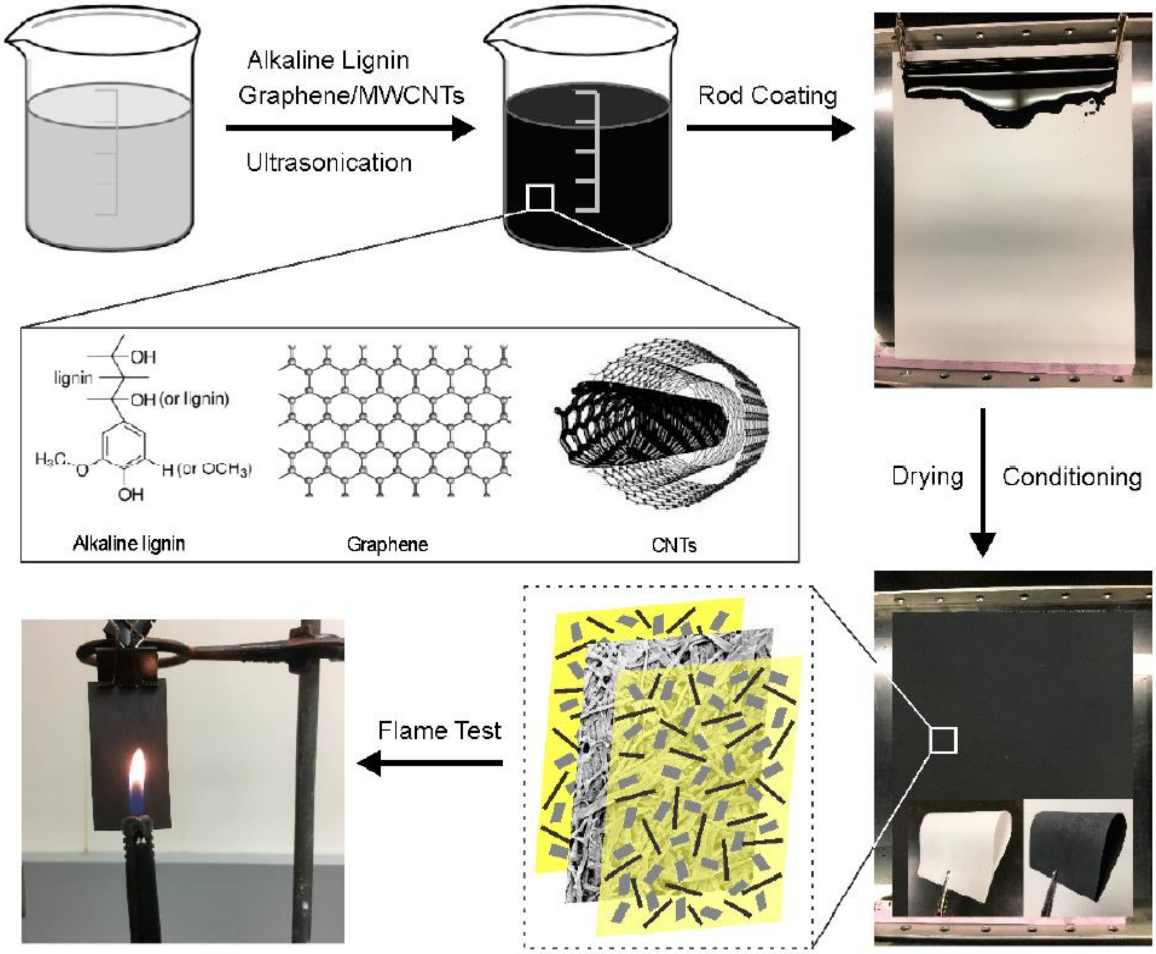

Figure 8 : Schematic presentation of the fabrication process and fire test of the paper coated with lignin, carbon nanotubes and graphene combination. Reproduced from [27] with permission.

Zhang et al [28] investigated the effect of combining different organic-modified montmorillonites (OMMT) with microencapsulated ammonium polyphosphate and lignin on PLA flame retardant properties. Results highlighted that the OMMT induced less flammable gas release during TGA enabling the formation of much more compact and continuous char.

As a result, superior flame retardant properties, i.e., lower pHRR, higher limiting oxygen index (LOI) value and UL94 V0, were achieved.

3.2 Reactive pathway

Chemical modification of lignin represents the second way for enhancing its flame retardant effect [20]. It opens diversity of possibilities for designing flame retardant systems owing to the wide range of functional groups contained in its chemical structure [29], i.e., (i) lignin fragmentation, (ii) creation of new functional groups and (iii) functionalization of native hydroxyl groups. The main reactions employed in the synthesis of new chemical active sites on lignin are halogenation, sulfomethylation, amination, hydroxy-alkylation, alkylation/dealkylation, and nitration.

Lignin phosphorylation is being increasingly utilized for improving its flame retardant properties by enhancing its char forming potential [12,13,16,20]. During thermal degradation, the presence of phosphorus-based groups leads to the formation of phosphoric acid that induces dehydration and condensation reactions, responsible for the formation of charred structures1. Different phosphorylation reactions have been used for the preparation of phosphorylated lignin, mainly modification by using phosphoric acid [30,31], phosphonate [32] and through Williamson reaction using chloro-phosphorus compounds [33,34]. A recent contribution [35] reported a large overview on the synthesis of phosphorus-, nitrogen-, and phosphorus-nitrogen- modified lignin, Figure 9, and their flame retardancy in several polymers. This subject has also been reported in other reviews and book chapters discussing bio-based flame retardant additives for polymeric materials [20,35–37].

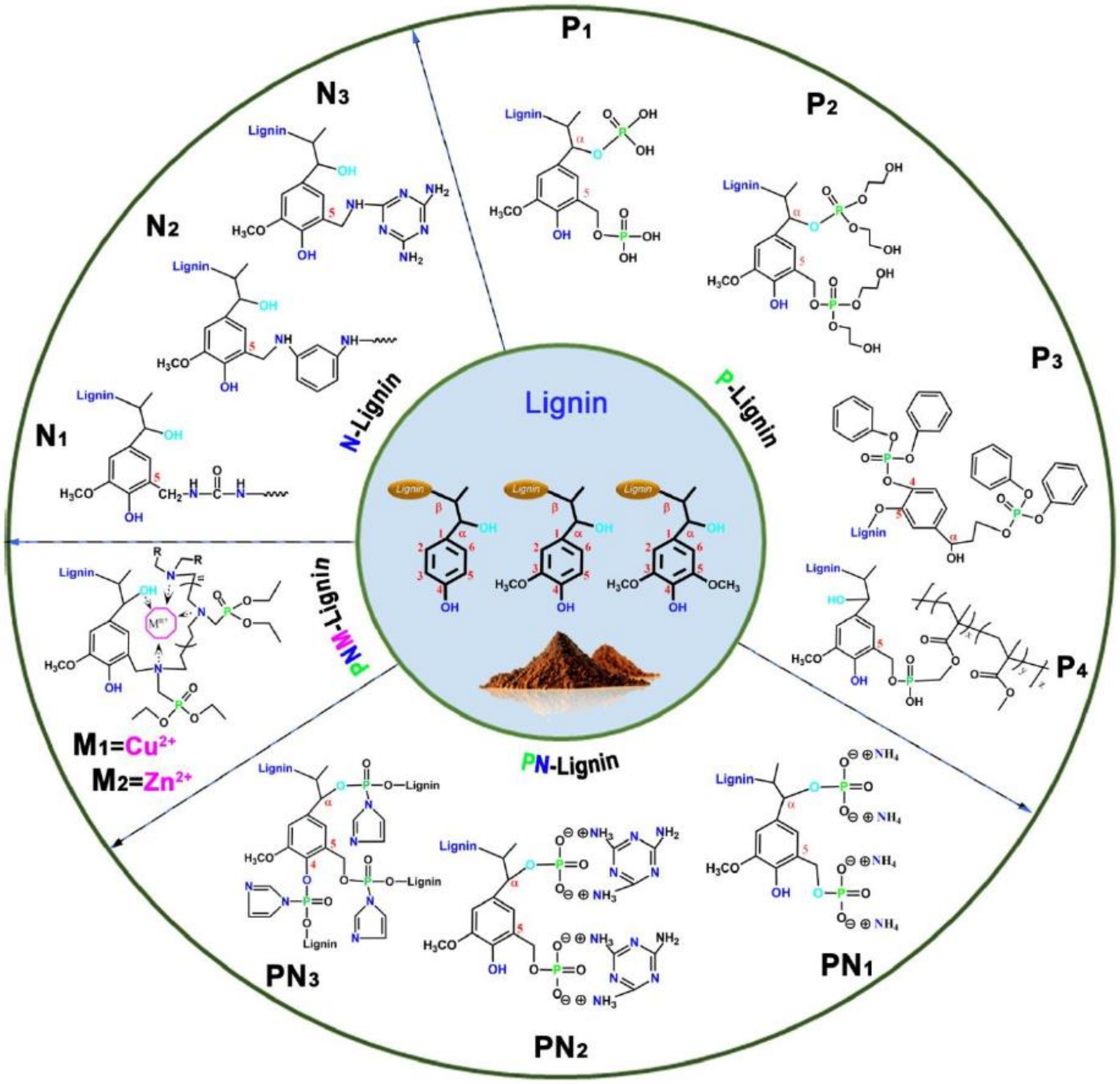

Figure 9 : The main representative chemical modification reactions for developing lignin-derived flame-retardants. Reproduced from [35] with permission.

The amount of phosphorous in the modified lignin greatly affects its char forming ability and thus, its flame-retardant effect. This amount could be increased by using highly functionalized raw lignin, via selecting the right chemical modification process or increasing the amount of lignin functional groups prior phosphorylation reaction. The pretreatment of lignin by formaldehyde, for example, enabled Yu et al. to prepare modified lignin (PN-lignin) containing 8.1 wt.% phosphorus and 7.2 wt.% nitrogen [38]. Authors first prepared hydroxymethylated lignin by reacting HCHO on the washed lignin. The resulting product has been phosphorylated by $POCl_3$ using a two-step reaction. The incorporation of 20 wt.% PN-lignin into PP allowed for the formation of a compact char residue and superior flame retardant effect than what obtained using 30 wt.% pristine lignin. Lignin formaldehyde pre-treatment has also been used by Xing et al [39] for the preparation of hydroxypropyl lignin prior phosphorylation reaction. The partial substitution of polyether polyol by phosphorylated lignin (Lignin-POH) has been used for the preparation of polyurethane foams filled with phenolic encapsulated ammonium polyphosphate (PFAPP). The combination of phosphorylated lignin and PFAPP led to polyurethane foam presenting superior flame retardant effect, more uniform morphology, smaller cells, and higher mechanical properties with respect to the polyurethane foam containing only PFAPP.

In addition to the improvement of the fire behavior, the chemical modification of lignin proved to bring other advantages. Costes et al [13] prepared modified kraft lignin using a two-step phosphorus nitrogen grafting approach, Figure 10.

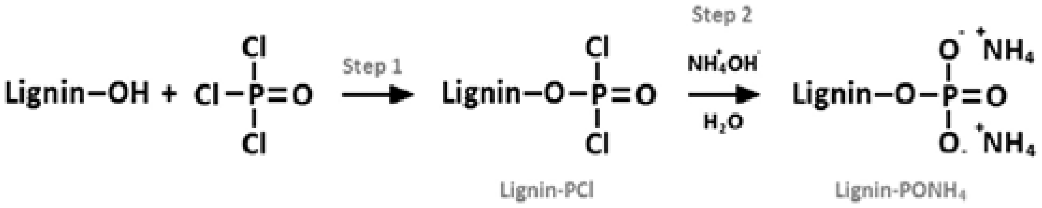

Figure 10 : The proposed two-step mechanism through which kraft lignin is modified with phosphorus nitrogen grafting. Reproduced from [13] with permission.

The incorporation of this ammonium phosphate modified kraft lignin into PLA enables significant enhancement of the composite flame retardancy (V0 classification at UL94 and 40% decrease in pHRR), Figure 11, but also significantly reduced the PLA degradation during melt processing, as evidenced by size-exclusion chromatography (SEC) analysis. The transformation of raw lignin hydroxyl functions into ammonium groups also present a positive effect on the resistance of composite to ignition. When modified lignin is used, TTI remains almost unchanged with a value close to that of the pristine PLA (87 s), while the incorporation of the same amount of raw lignin is responsible for a strong reduction in the TTI up to 40 s. The flame-retardant effect of lignin is very dependent on its intrinsic properties, even when it is chemically modified. Costes et al [13] applied the same phosphorus nitrogen grafting approach on organosolv lignin, but their results were not promising. Unlike modified kraft lignin, the incorporation of modified organosolv lignin did not end in significant flame retardant effects.

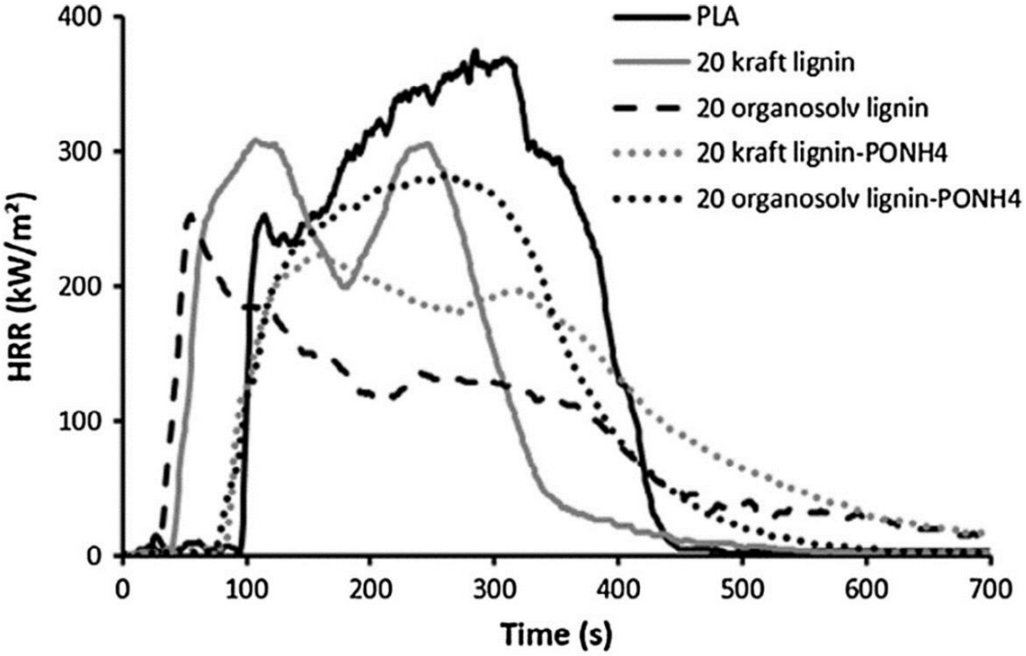

Figure 11 : HRR curves of the neat PLA and PLA containing 20 wt.% untreated and modified kraft and organosolv lignins. Reproduced from [13] with permission.

Phosphorus-nitrogen functionalization of lignin has been also explored by Haibin et al [40] for the preparation of flame retardant polyurethane foams. Authors first prepared lignin-based phosphate melamine compound (LPMC) using polyphosphoric acid and melamine via a liquefaction–esterification–salification process. The free hydroxyl groups remaining in the modified lignin have been used to substitute parts of polyols and; therefore, produced lignin-modified polyurethane foam by reacting with isocyanate compounds. The resulting foam presented several superior properties. In one hand, compression strength has been significantly increased owing to the rigid aromatic structure of lignin and its covalent linkage with the matrix. In the other hand, the presence of modified lignin enabled the formation of compact and dense intumescent layer at the surface as well as the release of large amount of non-flammable gases during thermal degradation. As a result, significant enhancement of the foam self-extinguishment, melt-dripping inhibition as well as reduction in smoke production were achieved.

Lignin chemical modification by phosphorus, nitrogen and zinc (II) ions (PNZn-lignin) has been shown to present an effective way for enhancing its flame retardant effect in PBS [41]. Alkali lignin was first purified (O-lignin) and functionalized with polyethylenimine (PEI) to produce amino-modified lignin (A-lignin). The obtained lignin has been modified by formaldehyde (HCOH), diethyl phosphite (DEP) and zinc acetate ($Zn(Ac)_2$), Figure 12.

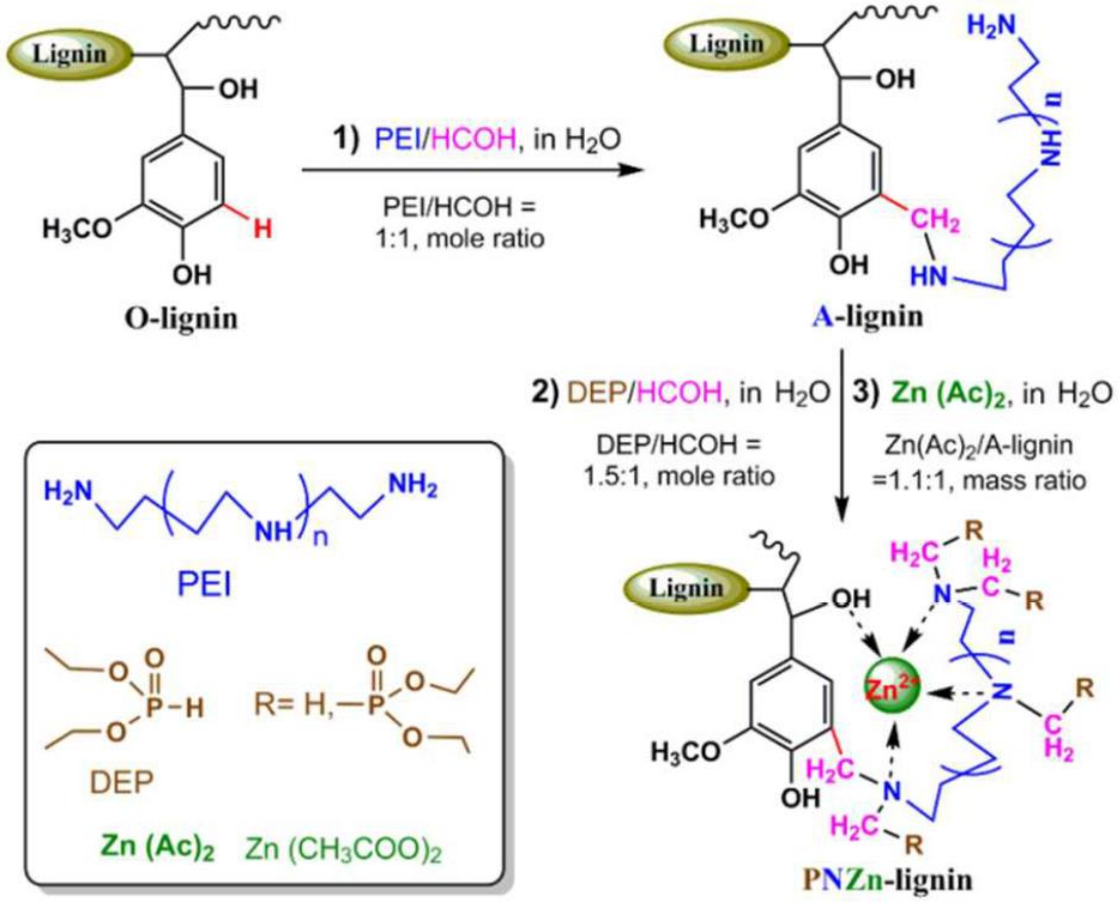

Figure 12 : Schematic representation for the synthetic route to the functionalized PNZn-lignin. Reproduced from [41] with permission.

The incorporation of PNZn-lignin into PBS significantly enhances flame-retardant properties, even at relatively low content, Figure 13. In respect of pristine PBS, the incorporation of only 10 wt.% PNZn-lignin enables significant reduction in the pHRR and THR, Figure 13, as well as smoke production in cone calorimeter test, by 50%, 67% and 50%, respectively, owing to the formation of a compact and thick char layer.

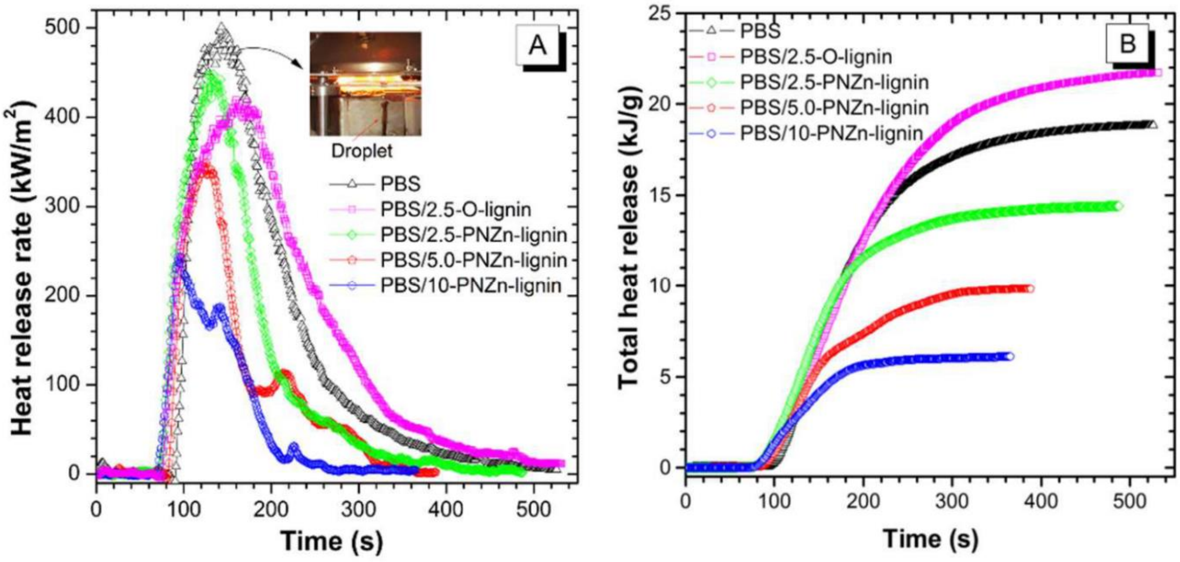

Figure 13 : THR curves and pHRR shifts during cone calorimeter test. Reproduced from [41] with permission.

Lignin phosphorylation can limitedly improve the flame-retardant behavior of the final composite. Ferry at al [12] developed two phosphorylated lignins modified with phosphorylated PMMA-based homopolymer and copolymer. Results showed that using phosphorylated lignins enables only slight flame retardant improvement of PBS-based composites even if microscopic observations revealed some enhancement of char cohesion. Lignin and phosphorylated lignin mainly act in the condensed phase by favoring the formation of protective char layer. However, depending on the grafted phosphorous group, some gas phase action could also take place. Prieur et al. [16] highlighted that the lignin chemically modified with P_2O_5 incorporated into ABS presented, in addition to the condensed phase action, some gas phase flame retardant effect owing to the release of phosphorus radicals that scavenge free radicals from the flame.

The chemical modification of lignin by something other than phosphorus-based molecules may also be of interest, especially when such a modified lignin is associated with a phosphorus flame retardant. This is the case for example of urea-modified lignin, Figure 14, that was prepared by Mannich reaction (14.45 wt.% nitrogen) and used in combination with ammonium polyphosphate (APP) in PLA [42]. The incorporation of 18.4 wt.% APP and 4.6 wt.% urea modified lignin enables reaching V0 classification at UL-94 test, a LOI value as high as 34.5 and a pHRR of 105 kW.m^{-2}. On the other hand, using untreated lignin in the same composition led to UL-94 V2 classification, a LOI of about 33 and pHRR equal to 150 kW.m^{-2}. The superior flame retardant effect of the system containing modified urea was attributed to the better charring effect of modified lignin.

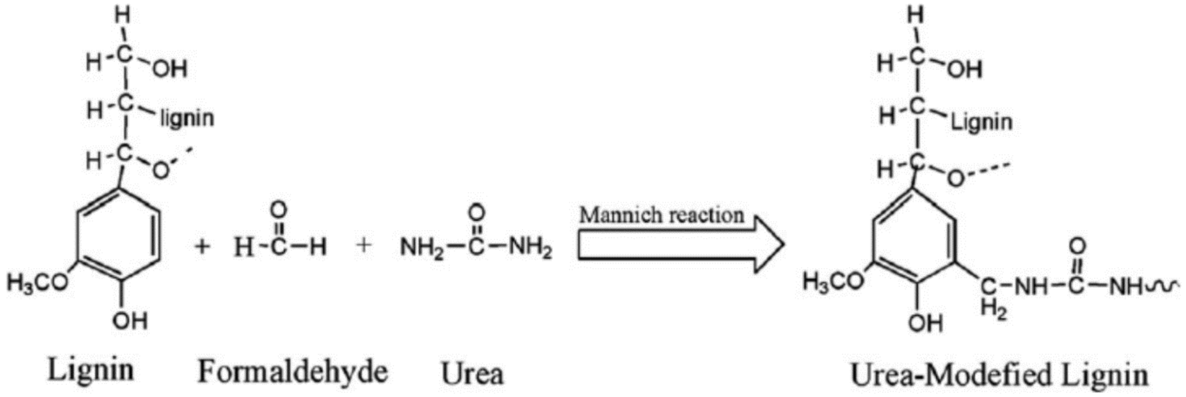

Figure 14 : Schematic representation of Mannich reaction used for the preparation of urea modified lignin. Reproduced from [42] with permission.

Similar flame retardant effect has been observed when silica-modified lignin was combined with APP in PLA[43]. Combining 15 wt.% APP with silica-modified lignin enabled reaching UL-94 V0 classification, a LOI value of 34, pHRR of about 145 kW/m² and a THR equal to 38 MJ/m²). In contrast, combining APP with untreated lignin, in the same proportion led to only a UL94 V2 classification, a LOI value of 32.5, a pHRR of 180 kW/m² and THR of 44 MJ/m².

4- Nanolignin as flame retardant for polymers

Lignin has thus been used as carbon source in flame retardant polymer systems. It mainly contributes to flame retardancy in the condensed phase because it is highly char forming.

Nanolognin is a nanostructured derivative of lignin able to act similarly in the condensed phase. Having nano-scale size, nanolignin can be much more finely dispersed in the polymer matrix, through which it appears more efficient as a flame retardant with respect to the lignin. Cholet et al. [44] studied the effect of lignin nanoparticles (LNP) obtained from kraft lignin microparticles (LMP) via dissolution-precipitation, and modified LNP with diethyl chlorophosphate and diethyl (2-(triethoxysilyl)ethyl) phosphonate (SiP). As shown in Figure 15, they prepared PLA composites based on 5 wt.% and 10 wt.% of the resulting additive. The flame retardancy behavoir of samples containing unmodified and modified LNPs was investigated and compared. Cone calorimeter highlighted that both neat LNP and LMP had no obvious effect of flame retardancy of PLA at the aforementioned loading levels, Figure 15, and even flame behaviour was worsened with bith an increase in the pHRR and a decline in the TTI values.

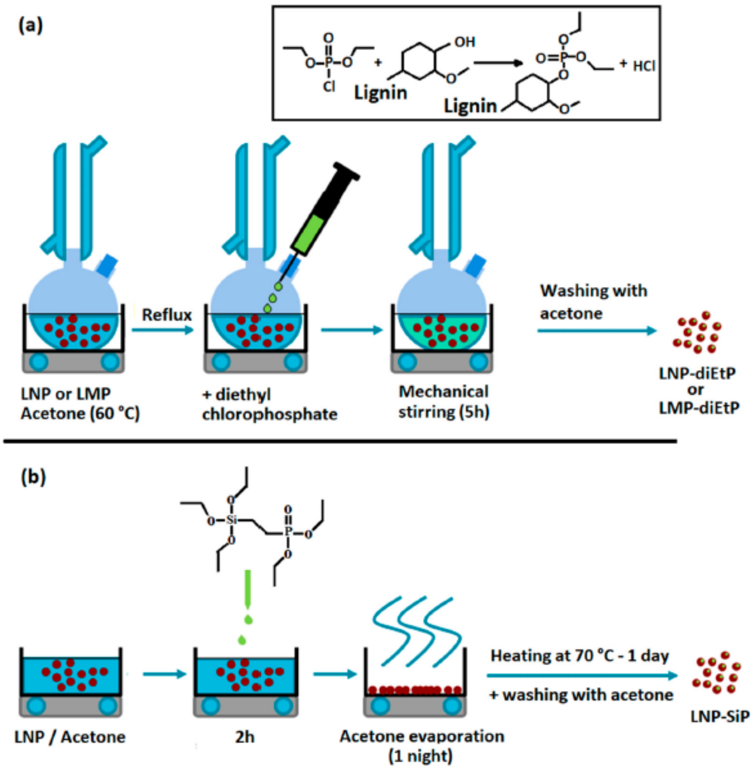

Figure 15 : Schematic representation of chemical modification of micro and nano-lignin by a) diethyl chlorophosphate, and b) diethyl (2-(triethoxysilyl)ethyl) phosphonate. Reproduced from [44] with permission.

Interestingly, once LNP was modified with SiP, the pHRR and TTI decreased and increased, respectively, Figure 16. The pHRR of PLA decreased by 11 and 18% for the PLA containing 5 wt.% and 10 wt.% of the modified nanolignin, respectively. By contrast, the TTI of PLA decreased from 68 s to ca. 20 s regardless of the loading level. Unsurprisingly, the modification of LNP and LMP with diethyl chlorophosphate did not improve the flame retardancy of PLA.

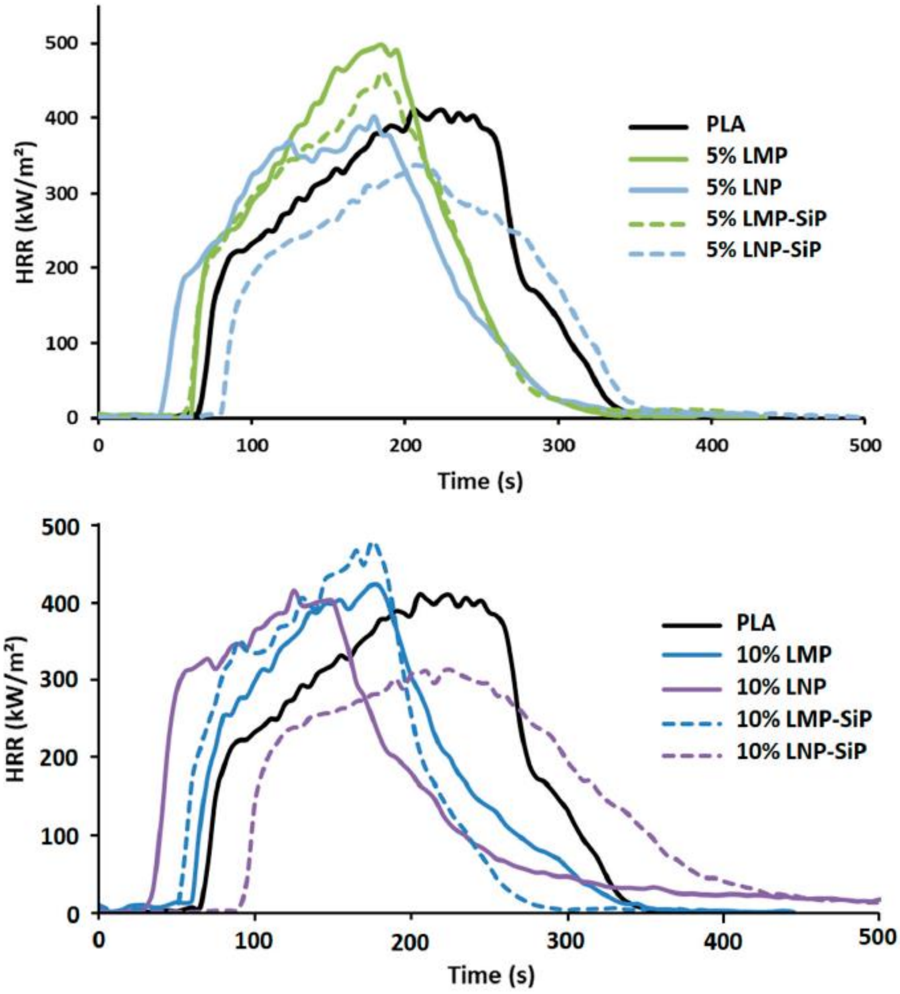

Figure 16. Curves of HRR as a function of time for PLA and PLA composites containing micro (LMP) and nano-lignin (LNP) and modified (with diethyl (2-(triethoxysilyl)ethyl) phosphonate (SiP)) micro and nano-lignin particles, obtained in cone calorimeter test. Reproduced from [44] with permission.

Yu et al. [45] studied flame retardant effect of LNP and acylated LNP deposited on a commercially available melamine-formaldehyde (MF) sponge foams, Figure 17. The acylation of LNP was carried out in acetic acid + acetyl bromide mixture at 55 °C for 3 h. Afterwards, a solution of LNP and also another solution containing acylated LNP containing 100 mL THF/H_2O (80:20, vol.%) was prepared. An amount of 1 mL of MF sponges was conditioned by immersion in the solution prepared in previous step for 20 min. The removal of THF followed by drying led to having samples for flame retardancy assessment. Flame tests was simply conducted by examining the ignitability of samples by an alcohol lamp via weighing the remaining fraction of combustion reaction. For MF modified with two types of LNP, a small flame was seen up to 3 s, and 90% of the initial mass was remained in the test dish, and some evidence for the hydrophobicity of treated MF.

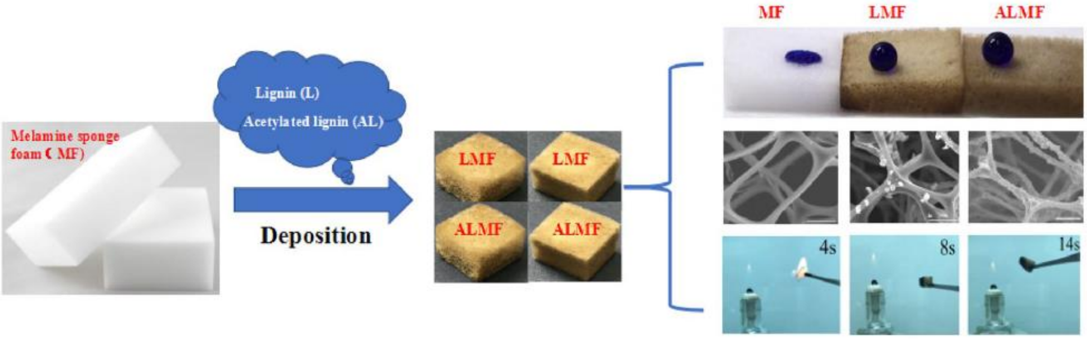

Figure 17 : Deposition of nanolignin (L) and acylated nanolignin (AL) particles on melamine-formaldehyde (MF) sponge foams and detecting their flame retardant actions (LMF: lignin modified MF, ALMF: acylated nanolignin modified MF). Reproduced from [45] with permission

Wang et al. [46] used LNP to reinforce and to bring flame retardancy to a boron nitride (BN)-OH/polyvinyl alcohol (PVA) composite film. The preparation of composite was carried out in several steps, starting with synthesis of BN-OH, PVA containing hydroxyl groups and LNPs with phenol hydroxyl groups. The crosslinking of the aforementioned reactive agents has been performed using glutaraldehyde (GA), Figure 18. Using a simple flame test applying a lighter, authors concluded that 2.5 % vol. LNP was able to improve the flame retardancy properties, Figure 19. However, no more test and explanation have been presented.

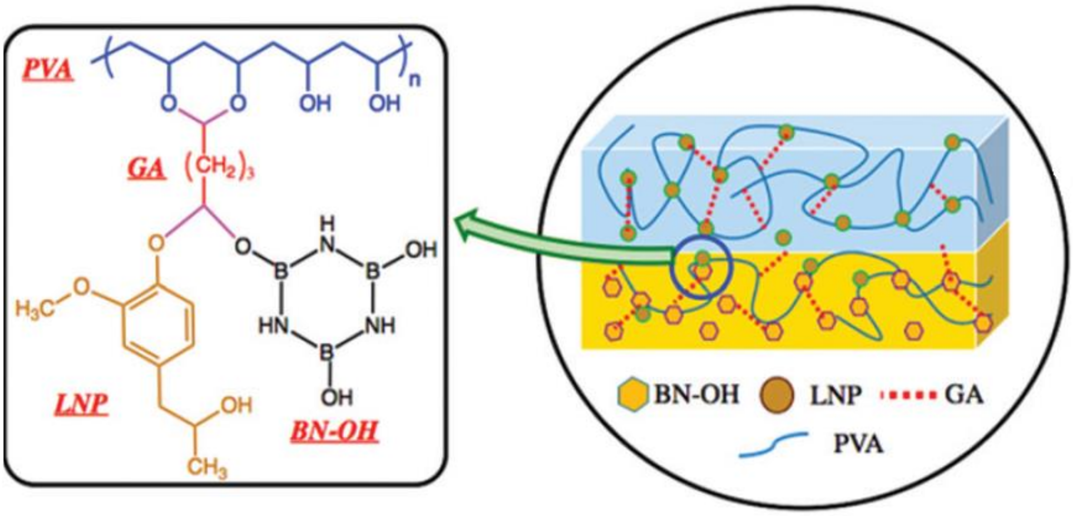

Figure 18 : Schematic representation of BN-OH/PVA/LNP composite (PVA: polyvinyl alcohol, LNP: lignin nanoparticle, BN-OH: boron nitride-OH, GA: glutaraldehyde). Reproduced from [46] with permission.

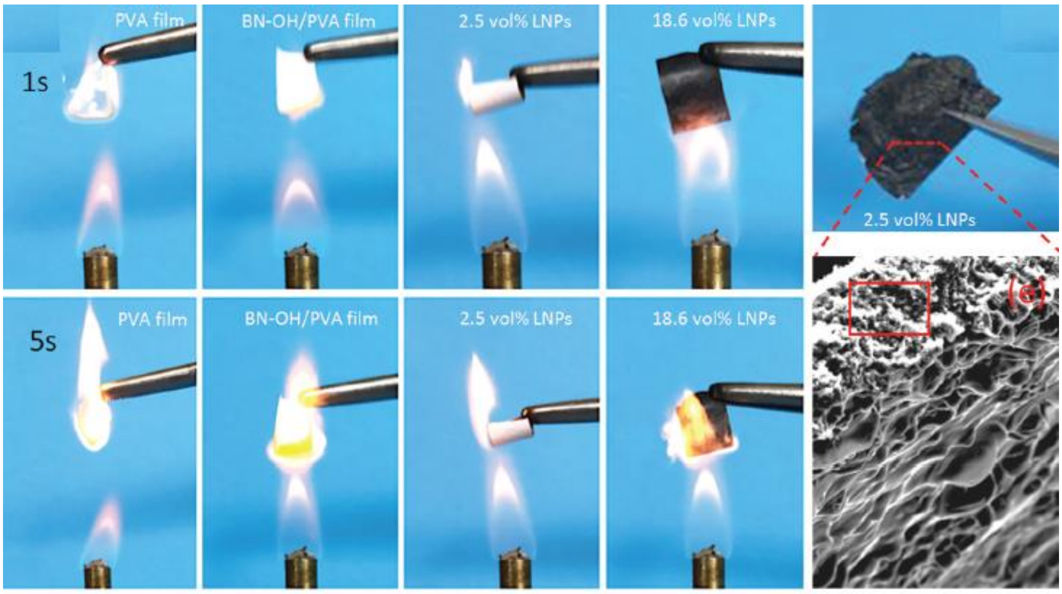

Figure 19 : Flame test applied on PVA and PVA containing lignin nanoparticles, showing the flame behavior of these samples. Reproduced from [46] with permission.

5. Conclusions

The development of sustainable bio-based flame-retardant systems is attracting a lot of attention. Among this new class of products, lignin is one of the most studied compounds owing to its abundance in the nature and its ability to generate char residue during its thermal degradation. However, except in some limited cases during cone calorimeter test, lignin alone does not provide an acceptable level of flame retardancy, especially in flame propagation tests such as UL94. It is therefore required to enhance flame retardant effect of lignin through either chemical modification or by its use as synergist additive with conventional flame retardants. The state of dispersion of lignin in the polymeric matrix is an important factor that needs to be properly addressed. Nevertheless, there are some more parameters affecting the flame-retardant performance of the final polymer composite materials. For instance, the nature of lignin (botanical origin and extraction process) proved to greatly affect its physicochemical properties. In this regard, the mean particle size, average macromolecular weight, the nature of reactive functions and their relative content are found to be among the main influencial factors. Investigations show that these parameters will affect the lignin thermal stability and its flame-retardant effect. Thus, careful selection of the raw lignin, is of vital importance in achieving acceptable flame retardancy. The use of nano-lignin attract recent interest for its unique ability to get finely dispersed in the polymers. Today, the inherent variability of lignin properties represents one of the main points limiting the design and production of lignin-based flame retardant formulations. Additional research and innovation are therefore required to finely tune and tailor the physicochemical characteristics of nano-lignin allowing it for finding definitive applications as flame retardant additives.

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