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Laurent 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. *Polymer Degradation and Stability*, 2015, 113 (SI), pp.135-143. 10.1016/j.polymdegradstab.2014.12.015 . hal-02914211

HAL Id: hal-02914211

<https://hal.science/hal-02914211>

Submitted on 24 Nov 2020

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Chemical modification of lignin by phosphorus molecules to improve the fire behavior of polybutylene succinate

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A B S T R A C T

Lignin was used as flame retardant for polybutylene succinate (PBS) biopolyester. Lignin was first demonstrated to weakly contribute to material flammability due to a high charring ability and a low heat release when burning. Alkali lignin was proved to be more interesting than organosolv lignin due to the release of sulfur dioxide during decomposition. When incorporated at a 20%wt loading in PBS, alkali lignin significantly reduces pHRR and promotes a thick charring behavior. Alkali lignin was successfully surface modified by grafting molecular or macromolecular phosphorous compounds. When blended with PBS, modified lignin was highlighted to further increase the barrier effect. Char promotion is accelerated and the resulting charred layer exhibits a higher cohesivity. Modified lignin appears as an interesting biobased flame retardant component.

Keywords:

Lignin
Polybutylene succinate
Flame retardancy
Thermal degradation
Grafting
Phosphorus

1. Introduction

Recent years have seen the development of plastics made from renewable resources (bioplastics). These materials represent an interesting alternative to traditional polymers due to their independence towards oil and, in some cases, they offer a different end of life scenario (biodegradation). Ten years ago, bioplastics were essentially used for short life products (packaging for example). Now durable applications can be envisaged. However to penetrate some industrial sectors, a set of functional properties, like mechanical properties, ageing resistance or reaction to fire, have to be improved. Generally, functional properties of plastics are modified by using additives (antioxidant, colorant, flame retardant ...). To get a completely "green" material, these additives should be also bio-based. Until now, this domain has been only poorly studied, particularly with regard to flame retardant additives (flame retardant).

Lignin is an abundant polyphenolic compound that can be extracted from biomass (plant fibers in particular). Lignin exhibits a good thermal stability with a degradation peak temperature around 350 °C in nitrogen atmosphere. Moreover its aromatic chemical structure results in a very high char yield after

decomposition (around 40% at 900 °C) [1]. Thus, advantage could be taken from this char forming ability to use lignin as flame retardant additive [2]. Until now, a limited number of papers have been published on fire behavior of polymers containing lignin. Canetti et al. used lignin in polypropylene (PP) [2] and in polyethylene terephthalate (PET) [3]. They showed an increase in the PP thermal degradation temperature with increasing lignin content. Interactions between PP and lignin lead to a protective surface layer. In the case of PET, lignin influences the overall crystallization of the polymer due a nucleating effect. Lignin was also incorporated in polyhydroxybutyrate (PHB) by Mousavioun et al. [4] and Bertini et al. [5]. It was highlighted that soda lignin decreases the onset of degradation but brings thermal stability on a wider range of temperature. Lignin was observed to be well dispersed in PHB due to interaction between the functional groups of lignin and the carbonyl group of PHB. Song et al. [6] studied the reactive compatibilization of lignin in acrylonitrile butadiene styrene (ABS). They showed that compatibilization can further reduce the flammability of ABS due to an improved char layer.

Lignin has been also used in combination with traditional flame retardant salts. De Chirico et al. [7] used lignin in synergism with aluminum hydroxide, poly(vinyl alcohol), melamine phosphate, monoammonium phosphate and ammonium polyphosphate. They revealed that these flame retardants increase the thermal degradation temperature, the combustion time and the char yield of PP, and decrease the rate of heat release. Réti [8] has utilized lignin as

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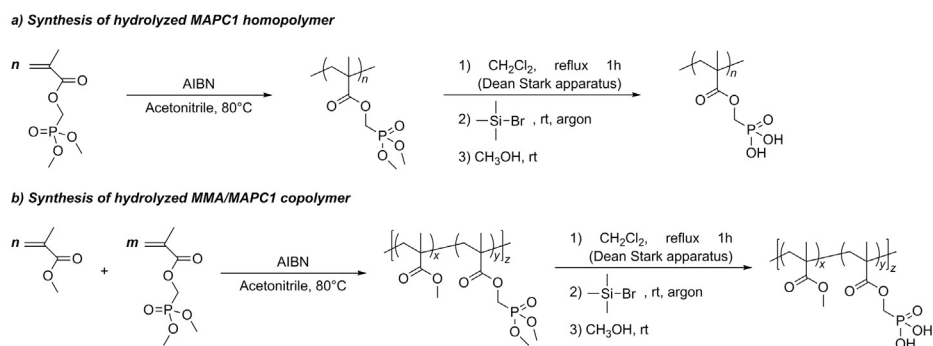


Fig. 1. Synthesis of (a) homopolymer P(MAPC1(OH)₂) and (b) copolymer P(MMA-co-MAPC1(OH)₂).

substituent of the charring source in an intumescent system for PLA. V0 UL94 rating was obtained, however the cone performance was better by using pentaerythritol or starch as charring agent. One recent paper [9] mentions the functionalization of lignin with phosphorus and nitrogen in order to improve thermal stability and flame retardancy of PP. The authors succeeded in increasing the char yield and improving the fire behavior.

In this paper, we tried to improve the fire behavior of a biopolymer, polybutylene succinate (PBS), by grafting of phosphorous compounds onto lignin, to promote a stable char during combustion. A first part is focused on the effect of unmodified lignin on the thermal and fire properties of PBS. A second part is dedicated to the fire behavior of PBS containing the functionalized lignin. Two lignins (alkali and organosolv) obtained from different extraction processes have been compared.

2. Experimental

2.1. Materials

Poly(1,4-butanediol succinate) (PBS film grade 1903 F, from Xinfu Pharm) was used as matrix. Two lignins were used in this study: an alkali lignin (Lig Alk) with a low sulfonate content (4% of sulfur), from Sigma Aldrich and an organosolv lignin (Lig Org) kindly supplied by the Centre de Mise en Forme des Matériaux (CEMEF-Mines ParisTech at Sophia Antipolis, France). Methyl methacrylate (MMA) (Sigma Aldrich, France), dimethyl(methacryloxy)methyl phosphonate (MAPC1) (Specific Polymers, France), 2,2'-azobis(2-methylpropionitrile) at 98% (AIBN) (Sigma Aldrich, France), bromotrimethylsilane (Sigma Aldrich), dihydrogen ammonium phosphate (DHAP) (Prolabo, France) were used as received.

Table 1
Content of PBS, Lig Org or Alk and treatment agent for all samples.

Designation	PBS (wt%)	Lig X ^a (wt%)	DHAP (wt%)	P(MAPC1(OH) ₂) (wt%)	P(MMA-co-MAPC1(OH) ₂) (wt%)
Lig X		100			
Lig X-DHAP		90	10		
Lig X-homoP		90		10	
Lig X- copoP		90			10
PBS-z%Lig X	100-z	z ^b			
PBS-20%Lig X-DHAP (only X = Alk)	80	18	2		
PBS-20%Lig X-homoP (only X = Alk)	80	18		2	
PBS-20%Lig X-copoP	80	18			2

^a X = Org or Alk.

^b z = 5, 10 15 wt%.

2.2. Synthesis of treatment agent

The polymers P(MAPC1(OH)₂) and P(MMA-co-MAPC1(OH)₂) were prepared by a two-step synthesis described in Fig. 1.

2.2.1. Synthesis of P(MMA-co-MAPC1(OH)₂) (75/25 mol%)

The first step consisted in a radical copolymerization of MMA and MAPC1. Into a 100 mL flask with a condenser, 21.6 g (2.16×10^{-2} mol) of MMA, 15 g (7.2×10^{-2} mol) of MAPC1, 0.47 g (2.9×10^{-3} mol) of AIBN and 22 g of acetonitrile were introduced. The mixture was then stirred and heated at 80 °C for 15 h. After reaction the polymer was purified by precipitation in diethylether.

The second step consisted in a hydrolysis of the phosphonate groups of the copolymer obtained from the first step. Into a 100 mL two-necked flask equipped with a Dean Stark apparatus, 10 g of copolymer P(MMA-co-MAPC1) (75/25 mol%) and 40 mL of dichloromethane were introduced, under inert atmosphere. The mixture was then degassed by bubbling argon for 15 min, stirred at dichloromethane reflux for 1 h (water was eliminated by the Dean Stark apparatus). The mixture was then cooled at room temperature and 6.6 g (4.3×10^{-2} mol) of bromotrimethylsilane was added dropwise. After 15 h the solvent was eliminated under vacuum and 80 mL of methanol was then added. Finally, the mixture was stirred for 3 h before precipitation of the copolymer P(MMA-co-MAPC1(OH)₂) in diethylether [10–12].

The same procedure was used to synthesize the homopolymer P(MAPC1(OH)₂).

2.3. Lignin treatment

In a one-necked round-bottom flask (500 mL) equipped with a condenser, 27 g of lignin, 3 g of treatment agent and 250 mL of

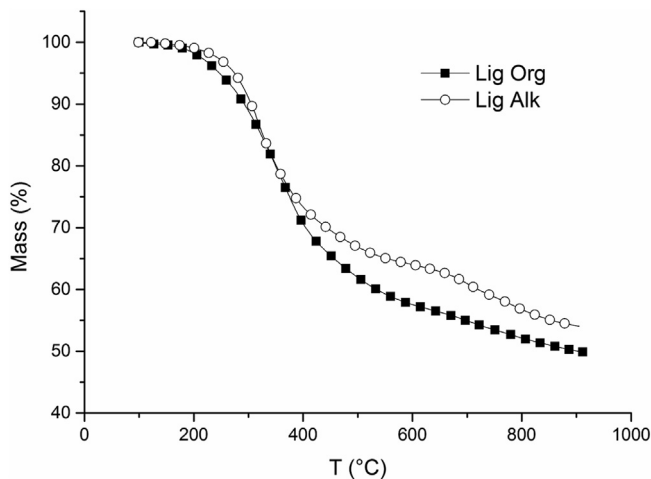


Fig. 2. TGA curves of the two lignins.

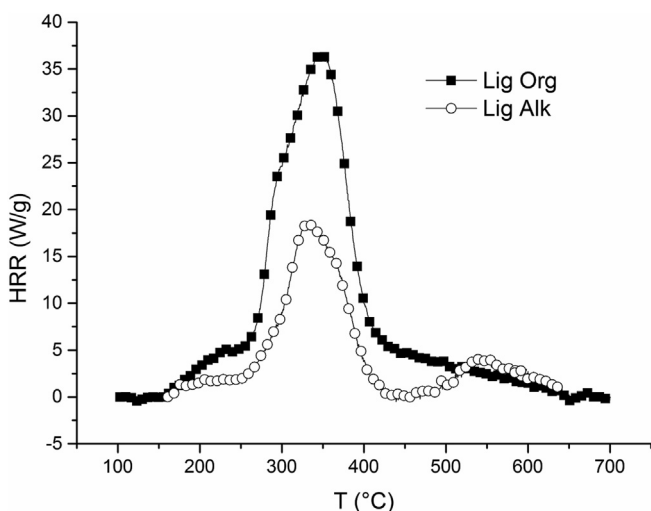


Fig. 3. PCFC curves of the two lignins.

ethanol (96%) were introduced. The mixture was heated under reflux for 5 h with vigorous magnetic stirring. The liquid phase was then eliminated, and the treated lignin was dried at room temperature.

2.4. Composite preparation

The composites were obtained by mixing PBS pellets and lignin (treated or not) in a Haake Rheomix internal mixer (100 rpm at 110 °C). PBS was firstly introduced in the chamber of the internal mixer and mixed for 2.5 min until a constant torque was obtained. Then the lignin was added progressively during 9 min and mixed

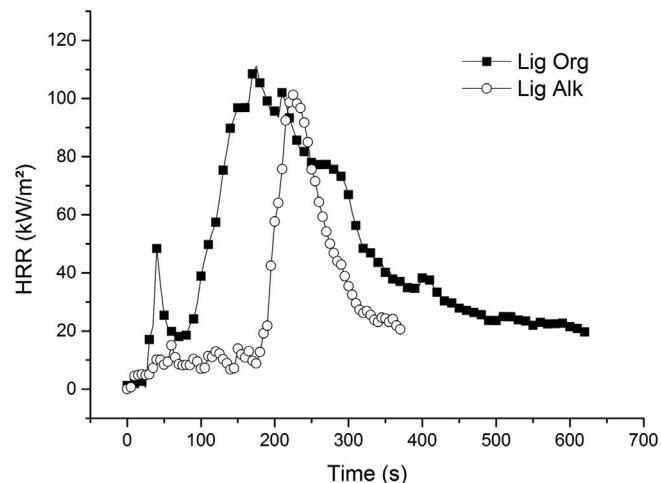


Fig. 4. Cone calorimeter curves of the two lignins.

with the matrix. After the final lignin addition, the mixing was extended for 2 min.

All composites were compression molded at 110 bars into $100 \times 100 \times 4 \text{ mm}^3$ square sheets of around 50 g. Plates of lignin (treated or not) were also manufactured by thermo-compression according to the same protocol. In this latter case, the sample mass was around 20 g.

Sample designation and composition are given Table 1.

2.5. Characterization

2.5.1. Thermogravimetry analysis (TGA)

TGA was performed with a Perkin Elmer Pyros-1 Thermogravimetric analyzer instrument. Sample of weights around 10 mg were heated from 50 to 900 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Residual weight at 750 °C (Res_{exp}) as well as temperature at the peak of mass loss rate (T_{deg}) were determined.

2.5.2. Pyrolysis combustion flow calorimetry

PCFC is a technique developed by Lyon and Walter [13] to investigate fire behavior of sample at microscopic scale. Sample weights of around 2 mg are pyrolyzed at 1 °C/s and the degradation products are transported by inert gas flux. Then, there are mixed with oxygen before entering in a combustor at 900 °C, where the products are completely oxidized. The heat release rate was measured as function of temperature. The value of the peak of heat release (pHRR), the total heat release (THR) which is the integral of the heat release rate between 200 and 750 °C, and the effective heat of combustion (EHC), which correspond to the heat released per gram of mass loss, were determined.

Table 2

TGA and PCFC parameters of unmodified and modified lignins.

Samples	TGA				PCFC		
	T_{deg} (1st) (°C)	T_{deg} (2nd) (°C)	Res_{exp} at 750 °C (%)	Res_{calc} at 750 °C (%)	pHRR (W/g)	THR (kJ/g)	EHC (kJ/g)
Lig Org	349.1	707.1	53.5	—	36.4	4.56	9.84
Lig Alk	320.8	702.1	58.7	—	18.7	2.14	5.19
Lig Alk-homoP	328.8	709.2	53.8	55.6	17.4	2.66	5.77
Lig Alk-copoP	330.0	726.4	53.3	56.7	17.4	3.49	7.47
Lig Alk-DHAP	324.6	—	60.4	55.8	13.9	2.18	5.50

Res_{exp} : experimental residue.

Res_{calc} : residue calculated from the mixing rule applied the residue of the components.

Table 3
Cone calorimeter parameter of the two lignins.

Samples	TTI (s)	pHRR (kW/m ²)	EHC (kJ/g)	Residue (%)
Alkali lignin	189	102	6.4	57.1
Organosolv lignin	25	111	19.9	53.2

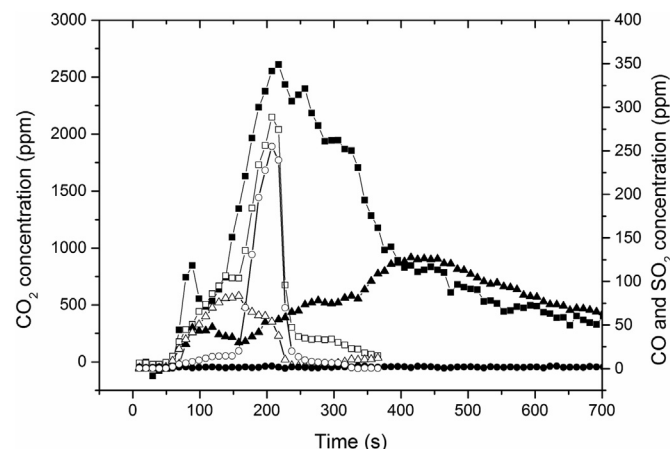


Fig. 5. CO₂ (square), CO (triangle) and SO₂ (circle) release for the organosolv lignin (white symbols) and the alkali lignin (black symbols) during cone calorimeter test.

2.5.3. Cone calorimeter coupled infrared spectroscopy (cone-FTIR)

Cone calorimeter tests were performed using an FTI apparatus test according to ISO 5660 standard. Irradiance was fixed at 35 kW/m². Heat release rate (HRR) was measured as function of time and the time to ignition (TTI), the total heat release (THR), the peak of heat release rate (pHRR), the effective heat of combustion (EHC) and the maximum average of heat emission (MARHE) were determined.

An FTIR spectrometer Antaris IGS from ThermoFisher Scientific was coupled to the cone calorimeter. The sampling point was located on the stack just before the sampling point to oxygen analyzer. Filters were positioned to trap soot particles. A two meters transfer line was heated at 160 °C. Temperature and pressure conditions in the gas cell were fixed at 165 °C and 650 Torr. The evolution of the gases concentration during the fire test was measured using Omnic software from ThermoFisher Scientific.

2.5.4. Scanning electron microscope/(SEM)

The micrographs were obtained using an environmental scanning electron microscope (FEI Quanta SEM) equipped with a scanning transmission electron microscopy detector (STEM). Micrographs were obtained under vacuum at a voltage of 15 kV with a spot size between 3.5 and 5.0 nm and a working distance between 6.8 and 10.8 mm.

3. Results and discussion

3.1. Thermal and fire properties of lignin

3.1.1. Unmodified lignin

The thermogravimetric curves of alkali and organosolv lignin are presented in Fig. 2. It can be seen that lignin decomposes in several steps up to 900 °C. These steps are relatively well described in the literature, especially in the review of Brebu et al [14]. In a first step (230–260 °C), low molecular weight products resulting from the propanoid side chain cleavage are released. Then the main degradation step (275–450 °C) corresponds to the cleavage of the main chain either by C–C and β–β scission or by aryl-ether cleavage. In this step a large quantity of methane is evolved. Above 500 °C, further rearrangements and condensation of the aromatic structure take place leading to the formation of an important char and the release of dihydrogen in the gas phase. At high temperature (650–850 °C) a small part of the char can decompose. It can be observed that the behaviors of the two lignins are very similar. However the residue of alkali lignin is slightly higher than that of organosolv, 58.7% against 53.5% at 750 °C. The difference in residue is even more pronounced in the range 500–650 °C, but a larger part of alkali lignin char decomposes around 700 °C.

Combustion properties were investigated by pyrolysis combustion flow calorimetry (PCFC). HRR curves presented in Fig. 3 reveal the same decomposition steps than those observed on the derivative thermogravimetric curves (Fig. 2).

The experimental values of effective heat of combustion (EHC) are respectively 5.19 and 9.84 kJ/g for the alkali lignin and the organosolv lignin (Table 2). These values can be compared to the theoretical values calculated from thermochemistry. In the case of complete combustion, a chemical compound containing carbon, hydrogen and oxygen undergoes oxidation that leads to CO₂ and H₂O release according to Equation (1) [15,16]. According to Huggett's relation, the heat released by the combustion is 13.1 kJ per gram of consumed oxygen. Thus, theoretical EHC of organic compounds can be calculated.

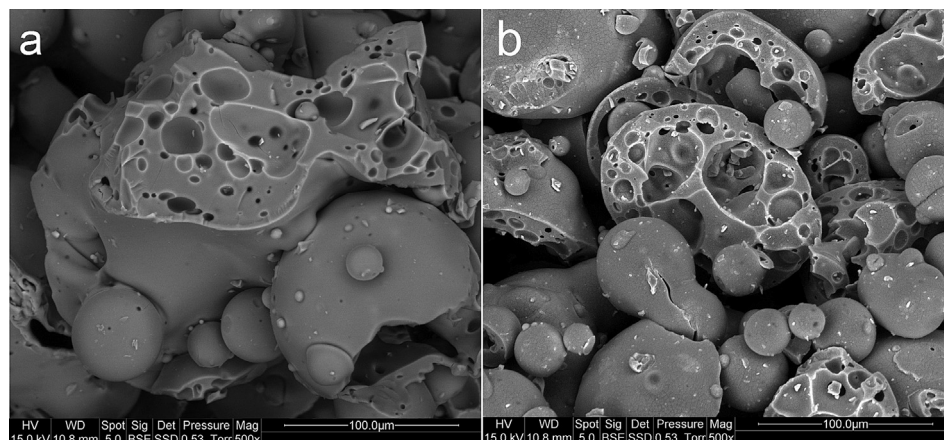
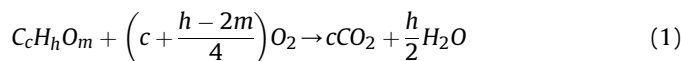


Fig. 6. SEM images of (a) alkali lignin particles and (b) alkali lignin combustion residue after the cone calorimeter test.

Table 4
Elemental composition of alkali lignin residue determined by EDX.

Element	Content (wt%)
Carbon	48.9–49.2
Oxygen	34.1–34.9
Sodium	12.3–12.5
Sulfur	3.8–4.1



Lignins have a complex macromolecular structure consisted mainly of phenylpropane units, originating from three aromatic alcohol precursors (monolignols), p-coumaryl, coniferyl and sinapyl alcohols [17]. Depending on the constituting unit (p-coumaryl C₉H₁₀O₅, coniferyl C₁₀H₁₂O₃ and sinapyl C₁₁H₁₄O₄), EHC calculated from equation (1) should be between 19.1 and 26.8 kJ/g (cf appendix). These values are much higher than the experimental ones. However, this calculation does not take into account the large char residue of lignin. Considering that the residue is mainly composed of carbon and that this carbon does not participate to the combustion reaction, stoichiometry of burning lignin can be estimated and EHC re-calculated. Theoretical EHC including char formation decreases between 0.77 and 17.4 kJ/g. These values are more consistent with the experimental data. Moreover, it can be remarked that pHRR and EHC of alkali lignin were much lower than those of organosolv lignin. As indicated in the materials section, the alkali lignin used in this study is a low sulfonate content alkali lignin with a 4 wt% sulfur content. It may be assumed that these sulfur containing moieties will decompose during lignin pyrolysis by releasing sulfur dioxide thus limiting the release of heat [18]. SO₂ emission will be confirmed in the following by using the cone calorimeter/FTIR coupling.

Plates of lignin have been prepared by thermocompression of lignin particles and tested by cone calorimetry under 35 kW/m² heat flux. It can be observed on Fig. 4 that the two lignins exhibit different behaviors. Organosolv lignin has a short time to ignition (25 s) while the time to ignition of alkali lignin is very long (189 s). pHRR are almost equivalent (Table 3). But the total heat release (THR) and thus the effective heat of combustion are very different. Once again, alkali lignin exhibits a very low EHC. Fig. 5 shows the evolution of CO₂, CO and SO₂ during the cone calorimeter test as

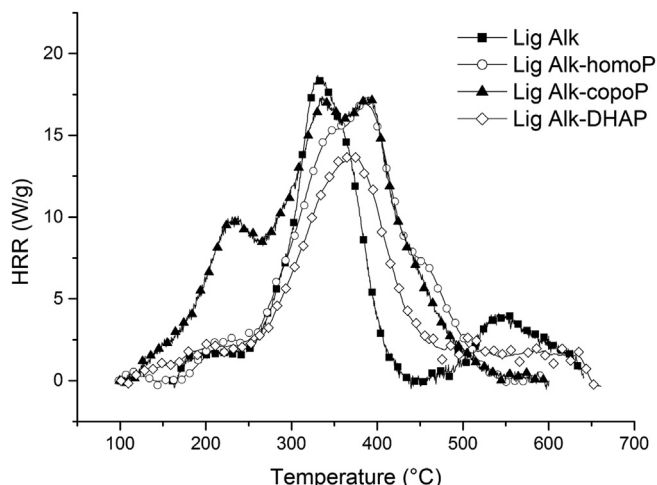


Fig. 7. PCFC curves of grafted lignin.

measured by the FTIR-Cone calorimeter coupling. In the case of organosolv lignin, the evolution of CO₂ follows the same trend than HRR does while CO release increases in the second part of the experiment. These results indicate that the combustion of decomposition products is almost complete in the first 300 s and become incomplete as a protective char residue is formed. Since organosolv lignin does not contain sulfur, SO₂ concentration remains null.

In the case of alkali lignin, CO₂ as well as CO are released in large amount before ignition. This reveals that, in a first step, lignin undergoes an aerobic pyrolysis with incomplete oxidation. The temperature is probably not high enough to obtain flaming combustion. It should be noted that SO₂ is released all along the experiment but the ratio SO₂/CO₂ increases drastically after ignition meaning that C–S bond cleavage is favored at high temperature. This result confirms the hypothesis that SO₂ release can act as heat sink, thus limiting EHC of alkali lignin.

Fig. 6b shows the combustion residue of alkali lignin after the cone calorimeter test. It can be observed by comparison with Fig. 6a that the lignin particles are not very affected by combustion. They keep their shape and the residue is not cohesive. It is noteworthy from Table 4 that despite SO₂ release, a large part of sulfur stays in the residue.

Considering that alkali lignin exhibits a lower EHC and a longer time to ignition compared to organosolv lignin, it was decided to select alkali lignin for the following of the work, i.e. surface modification and incorporation in PBS.

3.1.2. Modified lignin

In a previous paper [19], we have highlighted that the phosphonic acid moiety could react with hydroxyl groups of lignin leading to the creation of covalent P–O–C bonds and enabling the surface modification of lignin by octadecyl phosphonic acid. Based on these results, lignin particles have been surface treated using three phosphorous compounds containing P–OH moieties: dihydrogen ammonium phosphate (DHAP), a homopolymer of (methacryloyloxy) methyl phosphonic acid (HomoP) and a copolymer of (methacryloyloxy) methyl phosphonic acid and methyl methacrylate (CopoP). Grafting was performed according to the protocol described in the experimental part.

Treated alkali lignin was characterized by TGA. Results are summarized in Table 2. It was observed that the thermal stability of

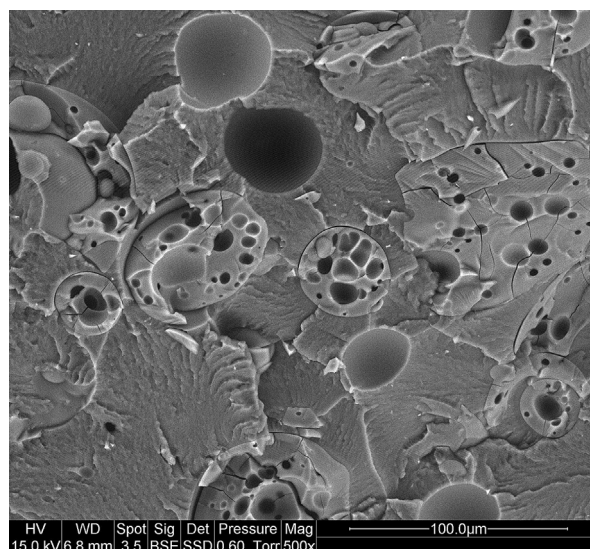


Fig. 8. SEM image of the dispersivity of the alkali lignin into PBS matrix.

alkali lignin is not strongly affected by surface modification. The two main decomposition steps occur at temperatures close to those of untreated alkali lignin. Char yields are consistent with those calculated from the mixing rule except for DHAP treatment. DHAP surface modification seems to confer a higher thermal stability to the char residue as proved by the disappearance of the second decomposition step in the range 650–850 °C.

PCFC enables to better highlight differences between the various graftings (Fig. 7). When the phosphonated copolymer is grafted onto lignin, two additional HRR peaks are evidenced: a first one in the range 200–250 °C corresponding to the release of MMA units and a second one in the range 375–450 °C corresponding to the degradation the phosphonated units and the subsequent combustion of the resulting char [11]. On the whole, THR is increased due to the high heat of combustion of MMA units. Grafting with the phosphonated homopolymer leads to the presence of an additional HRR peak in the range 400–500 °C corresponding to the decomposition of phosphonated units and the corresponding char.

Finally the better result is obtained with DHAP grafting since the main decomposition step of lignin is slightly shifted towards high temperature and its intensity decreases. Moreover, the high temperature HRR peak corresponding to the partial combustion of char disappears, indicating the promotion of a thermally stable residue.

3.2. Thermal degradation and fire behavior of PBS/lignin biocomposites

Lignin particles have been incorporated in PBS by melt mixing. After incorporation, it can be observed on Fig. 8 that lignin particles are relatively well dispersed in the polymer matrix. However some decohesion can be observed, indicating that compatibility between lignin and PBS should be improved.

3.2.1. Influence of the alkali lignin content

In a first step, the effect of unmodified alkali lignin on the thermal and fire behavior of PBS was investigated. For that purpose, various quantities of lignin ranging from 0 to 20 wt% were incorporated in the polymer matrix. The thermal decomposition of the various blends was studied by TGA between 20 and 900 °C under inert atmosphere. The main characteristics are presented in Table 5. The measurements indicate that the thermal stability of PBS is not really affected by the presence of lignin since the main decomposition step occurs always at the same temperature (395 °C) whatever the lignin content. However, in the presence of lignin a slight weight loss can be observed from 200 °C. This corresponds to the decomposition of lignin as described on Fig. 2. Furthermore, the char yield increases with increasing lignin content. Experimental char yields are slightly higher than the theoretical ones calculated

Table 5
Data from TGA and PCFC for PBS-Alkali lignin blends.

Samples	TGA			PCFC		
	T _{deg} (°C)	Res _{exp} at 750 °C (%)	Res _{calc} at 750 °C (%)	pHRR (W/g)	THR _{exp} (kJ/g)	THR _{calc} (kJ/g)
PBS	398.1	0.7	0.7	394	21.6	21.6
PBS-5%Lig Alk	398.7	5.3	3.6	383	18.1	20.6
PBS-10%Lig Alk	395.0	5.7	6.5	361	17.1	19.6
PBS-15%Lig Alk	394.3	11.1	9.4	340	16.1	18.7
PBS-20%Lig Alk	398.0	14.4	12.3	319	15.1	17.7
PBS-20%Lig Alk homoP	398.2	13.6	11.3	326	15.0	17.8
PBS-20%Lig Alk copoP	380.6	12.9	11.2	336	15.7	18.0
PBS-20%Lig Alk DHAP	391.8	14.8	12.6	363	17.0	17.7

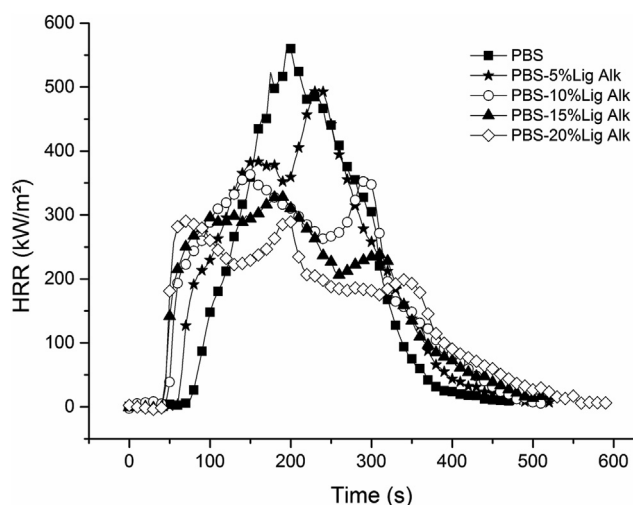


Fig. 9. HRR versus time curves from cone calorimeter test at 35 kW/m² for the various PBS-alkali lignin blends.

from the respective char yields of lignin and PBS using the mixing rule (Table 5). This indicates interaction between the two constituents during thermal decomposition, promoting residue formation.

PCFC measurements reveal a decrease of pHRR and THR with increasing lignin content (Table 5). pHRR decrease is quasi proportional to the lignin content. The pHRR occurs at 410 °C and it can be assigned to the decomposition of the PBS matrix. In this range of temperature, the decomposition of lignin is almost complete as highlighted by Fig. 3. Therefore, lignin can be considered as inert filler whose degradation does not contribute to HRR. Experimental THR decrease was higher than that expected from the mixing rule. This could be attributed to enhanced char residue as evidenced by TGA.

Fig. 9 shows the HRR curves obtained in cone calorimeter tests. It is noteworthy that lignin increases ignitability of PBS since time to ignition decreases from 72 s for pure PBS to 42 s at 20 wt% lignin loading (Table 6). This decrease was not really explained since it must be reminded that pure lignin has a long time to ignition (189 s). It can be observed that pHRR decreases with increasing lignin content. Moreover there is a modification in the curve shape that changes from a non-charring behavior to a thick charring behavior according to the classification of Scharrel and Hull [20]. At 15 and 20 wt% of lignin content, there is an initial increase of HRR until an efficient char layer is formed. Then the HRR slowly decreases due to the barrier effect of the char layer. However it should be underlined that HRR is not completely under control since small peaks can be observed in the steady state region. It may be assumed that the protective layer undergoes cracking, enabling the sporadic

Table 6
Data of cone calorimeter tests for the various PBS- alkali lignin blends.

Sample	Residue (%)	TTI (s)	pHRR (kW/m ²)	THR (kJ/g)	MAHRE (kW/m ²)
PBS	5.7	72	562	22.1	270
PBS-5% Lig Alk	6.4	61	497	20.7	265
PBS-10% Lig Alk	9.5	51	363	20.0	247
PBS-15% Lig Alk	12.5	44	329	19.7	225
PBS-20% Lig Alk	17.0	42	290	19.0	197
PBS-20%Lig Alk homoP	13.7	37	276	20.0	183
PBS-20%Lig Alk copoP	14.8	40	270	20.4	206
PBS-20%Lig Alk DHAP	11.9	41	295	19.7	203

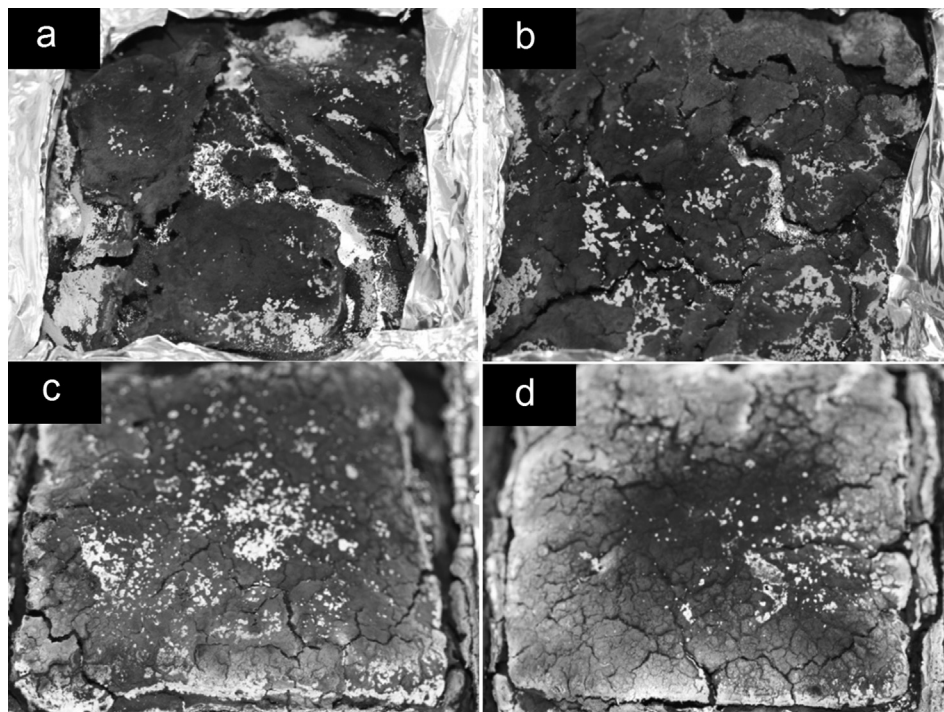


Fig. 10. Residues after cone calorimeter test of: (a) PBS-5%Lig Alk, (b) PBS-10% Lig Alk, (c) PBS-15% Lig Alk and (d) PBS-20% Lig Alk.

release of fuel. The amounts of residue are consistent with those measured by TGA (Table 5).

At macroscopic scale (Fig. 10), the observations of residues confirm that, as lignin content increases, a protective layer is progressively formed at the sample surface. However, it can be noticed that residues are crumbly. This detail advocates for possible fuel breakout after layer formation and observation of corresponding small HRR peak.

At microscopic scale, lignin particles are still visible in the residue (Fig. 11a). They seem to be bound together. However the structure of particles is modified and a very tortuous and porous structure is created at the surface particle (Fig. 11b) similarly to what was observed by Sharma et al. after lignin pyrolysis [21].

In the following, an attempt will be made to improve the cohesion of residue by using phosphorus modified lignin.

3.2.2. Influence of phosphorous grafting onto lignin

PBS-phosphorus modified lignin blends were characterized by TGA under nitrogen atmosphere. The results are presented in Table 5. As already mentioned with unmodified lignin, the main degradation step of blends corresponding to the decomposition of PBS was not impacted by modified lignin. Blends start to decompose earlier due the degradation of lignin which generates a slight weight loss between 200 and 350 °C. The char yields are quasi equivalent whatever the phosphorous compound used for the surface modification of lignin. Thus, it can be concluded that phosphorus treatment does not induce any additional charring, consistently with what was obtained by Li et al. in the case of larch lignin treated with dihydrogen ammonium phosphate [22]. Similar conclusions can be drawn from PCFC test on the same samples (see Table 5).

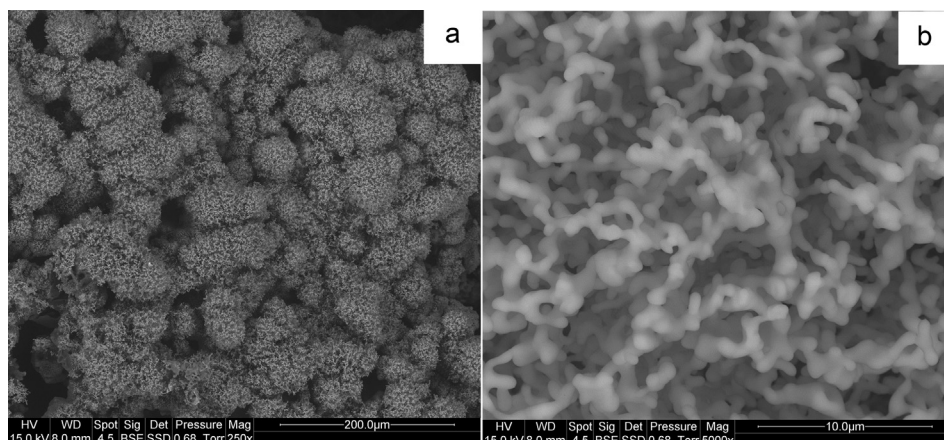


Fig. 11. SEM images of residue of PBS-20%Lign Alk, (a)×250 magnification, (b)×5000 magnification.

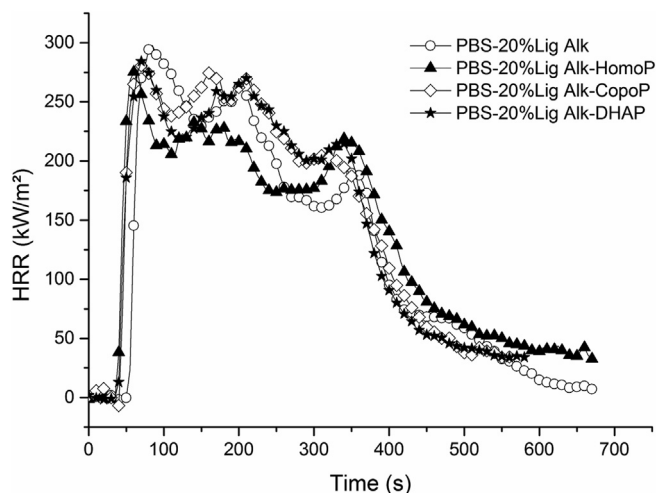


Fig. 12. HRR curves of PBS-phosphorus modified alkali lignin blends.

Fig. 12 shows the HRR curves recorded during cone calorimeter test for the various PBS- modified lignin blends at 20 wt% loading. On the whole, the grafting of phosphorous compound onto lignin surface does not drastically modify the fire behavior of PBS-lignin composite. However, it can be noticed that the pHRR slightly decreases in the presence of phosphorus. Moreover, just after ignition, the HRR decrease is more rapid when using modified lignin. This result indicates that phosphorus helps in the rapid promotion of a char layer at the sample surface. The best result is obtained with the phosphonated homopolymer treatment that leads to a well-controlled HRR in the period from 100 to 350 s. In this case, a decrease of 5% of pHRR and 7% of MAHRE is observed (Table 6). But, it must be conceded that calorimetric parameters are only slightly reduced.

The emissions of CO₂, CO and SO₂ have been measured during the cone calorimeter test using the FTIR coupling. The release of CO₂ and SO₂ follow the same trend as heat release rate. Their emission factors are almost constant whatever the surface

treatment of lignin with values of 1.7 g/g and 7 mg/g for CO₂ and SO₂ respectively. Contrarily, CO is released in two steps with an emission factor of about 20 mg/g. A first emission is observed during the steady state of combustion and reaches its maximum after ca. 200 s. A second emission is observed at the end of the test above 500 s. Interestingly the first CO emission is significantly reduced in the case where lignin is modified by the phosphonated homopolymer. This may indicate that char oxidation is limited during the flame phase and postponed to the end of the test.

The main difference between the various samples concerns the residue aspect. It can be remarked that the cohesion of residues seems to be improved with grafted lignin. Namely with unmodified lignin (Fig. 10d), the layer exhibits lot of cracks whereas with grafted lignin the layer is more homogenous and cohesive (Fig. 13a,b,c).

At microscale, the structure of residue is also changed. When using phosphonated polymers (HomoP or CopoP) as grafting agent, the surface of residue is more regular and the layer seems to be more compact (Fig. 13d). It may be assumed that those polymers being themselves char former [11]. They are likely to promote a thin carbonaceous layer that covers the lignin particles and sticks them together. But this change in the residue morphology does not strongly affect the macroscopic behavior.

4. Conclusion

The thermal degradation and flammability of alkali and organosolv lignin were compared. It was highlighted that the two lignins degrade in the same temperature range and exhibit a high residue. However alkali lignin shows a lower effective heat of combustion that was attributed to the release of sulfur dioxide. Alkali lignin was successfully modified using various phosphorous compounds. The modification with DHAP results in an increase of the main degradation step and a decrease of peak of heat release. The incorporation of unmodified lignin in PBS leads to a change in fire behavior with on one hand a reduced time-to-ignition but on the other hand a decrease of heat release rate associated with a thick charring behavior. When modified lignin was incorporated in

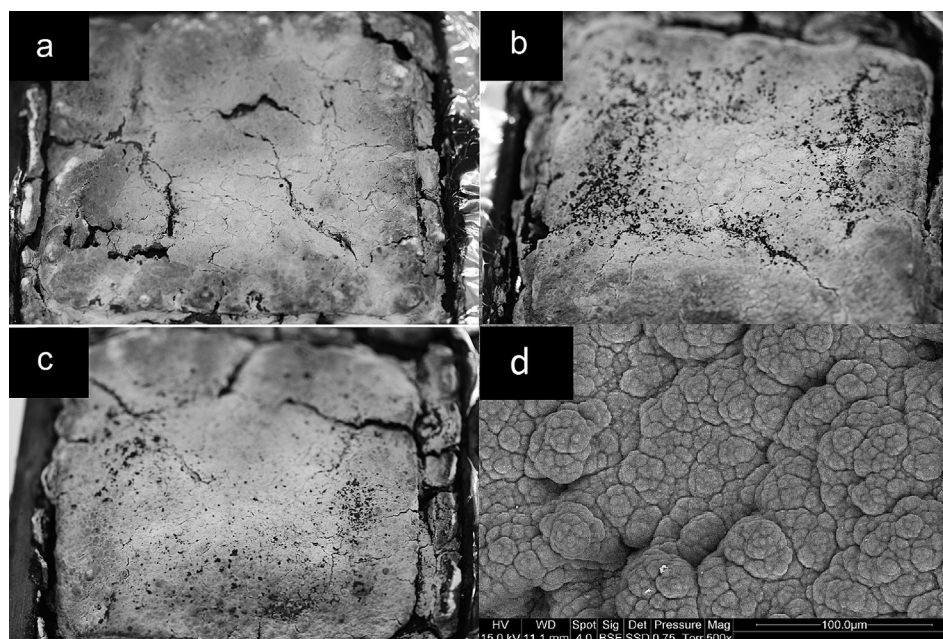


Fig. 13. Residues of cone calorimeter tests (a) PBS-20%Lig Alk-HomoP, (b) PBS-20%Lig-Alk CopoP, (c) PBS-20%Lig Alk-DHAP, (d) SEM images of residue of PBS-20%Lign Alk-CopoP.

PBS, flammability parameters were only slightly improved. However microscopic observations reveal that the barrier effect was further strengthened with enhancement of char cohesion.

Acknowledgments

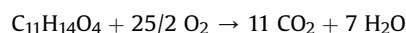
The authors want to acknowledge Ms. Lea Floch for her contribution to this work.

Appendix

Calculation of theoretical heat of combustion: example considering that lignin is composed only with synapyl units $C_{11}H_{14}O_4$.

- Case of complete pyrolysis and combustion (no charring)

According to the Equation (1):



So 400 g of O_2 ($12.5 \times 16 \times 2$) is consumed for 210 g of lignin ($11 \times 12 + 14 \times 1 + 4 \times 16$).

The heat of combustion is equal to:

$$EHC_{theo} = \frac{400 \times 13.1}{210} = 24.9 \text{ kJ/g}$$

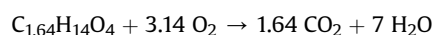
- Case of incomplete pyrolysis (charring) followed by complete combustion.

Lignin exhibits 53.5%wt of residue composed of carbon (char). So the amount of lignin concerned by the complete combustion is not 210 g but. $210 \times (1 - 0.535) = 97.65$.

To find the quantity of carbon atoms subjected to the complete combustion

$$x \times 12 + 14 \times 1 + 4 \times 16 = 97.65$$

$x = 1.64$ and the theoretical chemical formula of lignin subjected to combustion is $C_{1.64}H_{14}O_4$.



In this case the heat of combustion is equal to

$$EHC_{theo}^{char} = \frac{(3.14 \times 16 \times 2) \times 13.1}{1.64 \times 12 + 14 \times 1 + 4 \times 16} = 13.5 \text{ kJ/g}$$

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