



Research Article

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Synergistic flame-retardant effect between lignin and magnesium hydroxide in poly(ethylene-co-vinyl acetate)

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Abstract: In this study, we evaluated the interest of combining magnesium hydroxide (MDH) and lignin for developing complementary flame retardant actions in poly(ethylene-co-vinyl acetate) (EVA). Lignin was selected owing to its char forming ability that was supposed to reinforce the endothermic effect provided by MDH. The effect of lignin chemical modification by ammonium phosphate functions has been also evaluated as a way for enhancing its charring effect. Fire properties and thermal behavior of EVA composites were characterized using cone calorimeter, Pyrolysis Combustion Flow Calorimeter (PCFC) and thermogravimetric analysis (TGA). The effect of the incorporation of lignin alone on EVA composite thermal and fire behavior has been first evaluated. Results evidenced that the incorporation of lignin, whatever its nature, induced important reduction of composite thermal stability during TGA analysis as well as significant reduction of the time to ignition (TTI) in cone calorimeter test. However, a significant reduction of peak of heat release rate (pHRR), higher than that obtained with MDH was observed. The combination of lignin and MDH was led to further reduction of pHRR. Furthermore, it was concluded that the chemical modification of lignin is not required prior obtaining improved flame-retardant properties.

1 Introduction

Poly(ethylene-co-vinyl acetate) is commonly used in cable applications that generally required high flame-retardant properties [1–4]. Metal hydroxides, such as alumina trihydrate (ATH) or magnesium dihydroxide (MDH) are the most effective and low-cost halogen free flame-retardant for this kind of application. However, the flame-retardant action of these additives is effective up to 400°C because they act mainly through endothermic dehydration, that takes place between 180 and 200°C for ATH and 300 and 340°C for MDH [5–8] and that leads to the formation of non-cohesive residues.

Several studies aiming to enhancing the efficiency of the flame-retardant action of hydrated minerals, by partially substituting them with synergistic additives have been conducted. For instance, the partial substitution of ATH or MDH by other flame-retardant additives such as zinc borate [8], ammonium polyphosphate [9], expandable graphite [10] and zinc hydroxystannate [11] presented an interesting way for reducing the peak of heat rate release during cone calorimeter test as well as the generation of cohesive residues. Similar results have been also reported owing to the combination of metallic hydroxides with nanoparticles such as organomodified montmorillonite [12, 13], Multiwalled carbon nanotubes [14], fumed silica [15] and layered double hydroxide [16]. All these systems enable the generation of a thermally stable residue during the combustion, which plays the role of protective layer limiting both heat transfer and diffusion of fuel [17, 18].

More recently, using MDH and calcium hydroxide showed an interesting way for promoting the formation of cohesive mineral residue [19] thanks to the formation of calcium carbonate during the combustion. Moreover, using calcium-based hydrated minerals [20], such as hydrated dolime and semi-hydrated dolime, which contain both magnesium and calcium hydroxides in their structures, enables similar effect.

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Using bio-based product as flame retardant additives for polymeric materials attracted a lot of interest during the last decade [21]. Some biomass constituents, such as lignin [22, 23], cellulose [24], phytic acid [25], are predisposed to form an important quantity of char during their combustion. This char forming ability is particularly useful for reinforcing the condensed phase action of flame-retardant systems.

The aim of this work is thus to investigate the use of bio-based charring compounds, as a part of the flame-retardant systems for EVA in cable applications. Study focused on the effect of combining MDH with lignin, on thermal degradation and flame-retardant behavior of EVA based composites. To the best of our knowledge, the combination of lignin and MDH in EVA has never been reported.

Lignin was selected thanks to its aromatic structure which is responsible for its high thermal stability, as well as for its char forming ability [21]. However, when used alone, lignin induced only slight flame-retardant effect and its combination with other flame-retardant additive is required. Mainly, lignin is used in combination with phosphorus compounds by additive or reactive pathways.

In this study, EVA/MDH/lignin composites were prepared by melt blending and their thermal stability, flammability and fire properties were investigated by thermogravimetric analysis (TGA), pyrolysis combustion flow calorimetry (PCFC) and cone calorimetry. Scanning Electron microscopy (SEM) was used to characterize lignin particles dispersion state in the composites.

2 Experimental

2.1 Materials

EVA is an ethylenevinylacetate copolymer containing 12% vinyl acetate (Escorene FL112, melt flow index = 0.5 g/10 min at 190°C and under 2.16 kg, density = 0.934 g/cm³) was kindly supplied by ExxonMobil. MDH was MAGNIFIN[®] H10 from Albemarle. Kraft lignin with a low sulfonate content (4% of sulfur) was purchased from Sigma Aldrich. Figure 1 shows thermogravimetry analysis (TGA) curves under nitrogen at 20°C/min of the different additives. The chemical modification of lignin is described in a previously work [22] and was performed in two steps (modified lignin named here as “lignin-P”). The first step enabled grafting phosphorus chloride while its conversion into phosphoric acid ester and then into ammonium phosphate groups occurred during the second step [22].

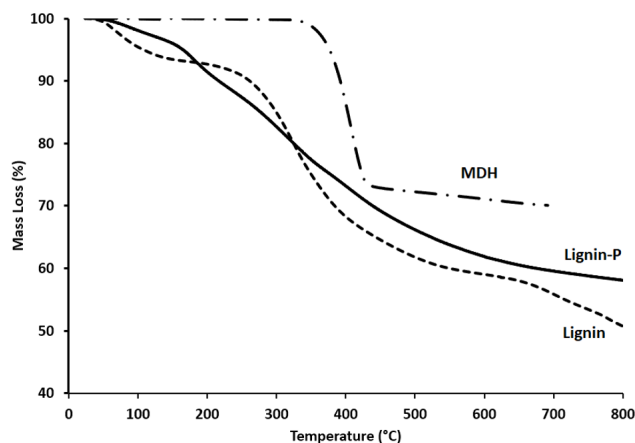


Figure 1: TGA curves of the different flame-retardant additives under nitrogen

These curves evidence the lower thermal stability of lignins in respect to MDH. The thermal degradation of lignin is well described in the literature [26]. After moisture release, the first decomposition step occurs between 230 and 260°C and leads to the formation of low molecular weight products resulted from propanoid side chain cleavage. The main degradation step takes place between 250 and 450°C and corresponds to the cleavage of the main chain. Above 500°C, some rearrangement and condensation reactions of the aromatic structure take place and lead to the formation of char, that decompose above 650°C.

In previous study [22], we reported the chemical modification of lignin by ammonium phosphate groups. The incorporation of ammonium phosphate groups into lignin structure triggers some modifications of its thermogravimetric behavior. Below 200°C, the difference observed between the two curves is simply induced to the presence of more water in the case of untreated lignin. Between 200 and 320°C, modified lignin shows a premature thermal degradation due to the release of ammonia as well as to the degradant action of phosphorous groups which can promote lignin thermal decomposition by inducing dehydration reactions [21, 22]. Above 320°C, the weight loss is reduced for modified lignin (Lignin-P) indicating the formation of thermally stable structures. Indeed, the weight loss between 320°C and 800°C is of about 30wt% in the case of kraft lignin and 22wt% for modified lignin.

Moreover, the chemical modification of lignin by ammonium phosphate groups allows significant reduction of the amount of released CO₂ and phenolic compounds [22]. This reduction was attributed to the formation of a char layer promoted by the reaction between C-OH groups of lignin and grafted P-OH. Therefore, lignin phosphorylation enables the formation of more thermally char layer.

2.2 Melt processing

EVA composites were prepared in a Brabender internal mixer at 180°C (7 min mixing at 70 rpm). Plates (100 × 100 × 3 mm³) for mass loss cone calorimeter testing were prepared by compression molded at 190°C using an Agila PE20hydraulic press and following a precise pressure program: the sample was first deposited for 3 min on the hot part, it was then pressed for 3 min 20 s at 10 bars, followed by 3 degassing processes, it was then pressed again for 2 min 30 s at 150 bars, and finally the sample was deposited in the cold part where it was pressed for 5 min. The investigated formulations are summarized in Table 1.

Table 1: Material designation and composition

Sample code	MDH (wt%)	Lignin (wt%)	Lignin P (wt%)
EVA	-	-	-
20% Lignin	-	20	-
40% Lignin	-	40	-
60% Lignin	-	60	-
60% MDH	60	-	-
60% Lignin-P	60	-	-
50% MDH – 10% Lignin	50	10	-
40% MDH – 20% Lignin	40	20	-
50% MDH – 10% Lignin - P	50	-	10
40% MDH – 20% Lignin - P	40	-	20

2.3 Characterizations

Thermogravimetric analyses (TGA) were carried out under nitrogen on a TGAQ50 device from TA Instruments. The additives and the different composites (10 mg) were submitted to a temperature ramp from 25 to 800°C at a heating rate of 20°C/min. All TGA experiments were performed under a gas flow of 60 ml/min (platinum pan).

The fire behavior was tested by a FTT (fire testing technology) mass loss cone calorimeter on samples according to the ISO 13927 standard. A 100 × 100 × 3 mm³ sheet was exposed to a radiant cone (50 kW/m²) using a forced ignition. Results correspond to mean values obtained from 3 experiments for each formulation, for which a typical variation of 10% was observed.

The flammability was also studied using a Pyrolysis Combustion Flow Calorimeter (PCFC) from Fire Testing Technology (FTT). Heating rate, maximum pyrolysis temperature, combustion temperature were respectively 1°C/s,

750°C, 900°C. Results correspond to mean values obtained from 3 experiments for each formulation, for which a typical variation of 8% was observed.

Morphological investigation was performed to highlight the dispersion of lignin in EVA using a scanning electron microscopy (SEM) Hitachi SU8020 (100 V–30 kV) apparatus. EVA composite 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.

3 Results and discussions

3.1 Fire properties and thermal stability of EVA / lignin compositions

3.2 An unmodified lignin

The flame-retardant effect of lignin has been first evaluated alone in EVA prior to be combined with MDH. Composites containing different lignin contents (20, 40 and 60 wt%) have been prepared and tested using cone calorimeter. Generally, the dispersion of the flame-retardant additives into the polymeric matrix is an important parameter that can strongly affect the fire behavior of the composite [24]. This has been also demonstrated in the case of lignin. In fact, improving lignin dispersion state, by using compatibilizing agent, into acrylonitrile butadiene styrene (ABS) copolymer enables further enhancement of the composite flame-retardant behavior [27] owing to the formation of an intact and almost whole charred layer, with compact microscopic morphology, at the surface of the burning sample.

Prior to the evaluation of the flame-retardant behavior of EVA containing different lignin content, we thus started by the evaluation of the dispersion state of lignin within the composite. SEM pictures of EVA containing 60 wt% lignin (Figure 2) evidence an acceptable lignin particles dispersion state and no agglomerates have been exhibited.

Cone calorimeter is commonly used to evaluate the flammability of materials at bench scale. Samples were exposed to a radiant cone (50 kW/m²) using a forced ignition. Both peak of heat release rate (pHRR) and time to ignition (TTI), that provide important information on the ability of materials to induce and promote fire propagation have been considered. Indeed, a high pHRR and a low TTI may cause both fast ignition and rapid-fire propagation. Curves of cone calorimeter tests are presented in Figure 3 and results summarized in Table 2.

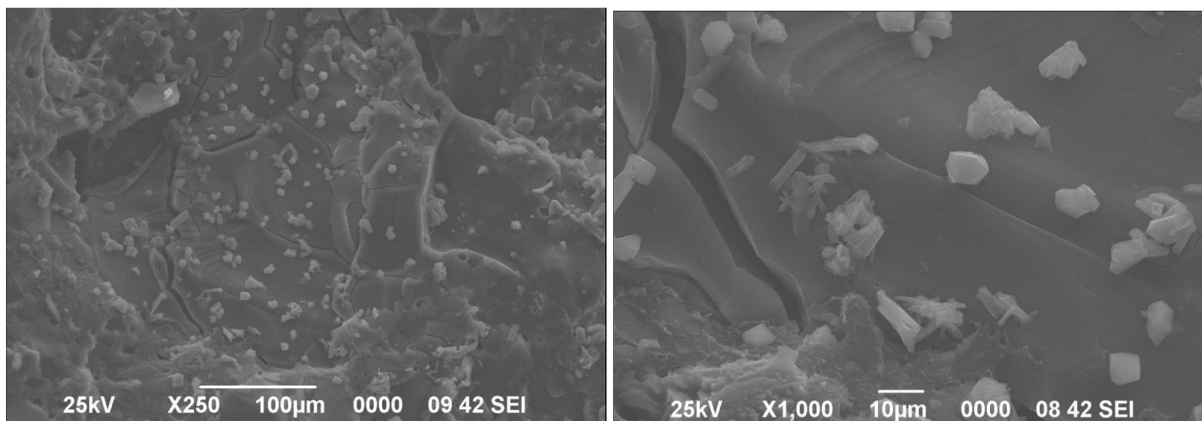


Figure 2: SEM pictures of EVA containing 60 wt% unmodified lignin

Table 2: Cone calorimeter data of neat EVA and flame retarded EVA compositions

	TTI (s)	pHRR (kW/m ²)	pHRR reduction (%)	THR (MJ/m ²)
EVA	30	1400	—	90
20% Lignin	18	630	-55	85
40% Lignin	18	400	-71.4	86
60% Lignin	18	310	-78	87
60% Lignin - P	24	290	-79	60
60% MDH	60	400	-71.4	67
50% MDH – 10% Lignin	36	300	-78.5	70
40% MDH – 20% Lignin	34	250	-82	62
50% MDH – 10% Lignin - P	40	320	-77	53
40% MDH – 20% Lignin - P	38	230	-83.5	54

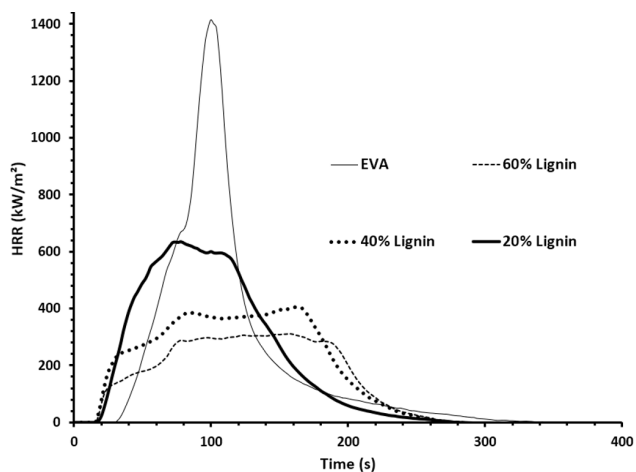


Figure 3: HRR curves of pristine EVA and EVA composites containing 20, 40 and 60 wt% unmodified lignin

The combustion of pristine EVA exhibits an intensive peak, starting after 32 s, consuming all the material with a pHRR of 1400 kW/m². The incorporation of lignin triggers significant modifications of the fire behavior of EVA dur-

ing conecalorimeter test. Time to ignition decreases from 32 s in the case of pristine EVA to around 18 s when lignin is incorporated into EVA, whatever its concentration. The increase of the composites ignitability induced by lignin has been already reported in the literature in many other polymers such as polypropylene [28], acrylonitrile butadiene styrene (ABS) [29], polybutylene succinate (PBS) [30] and PLA [22]. Many factors, such as thermal degradation, emissivity and thermal conductivity of polymer could be affected by the presence of lignin and explain the reduction of time to ignition. The low onset thermal degradation temperature of lignin, that is a combustible product, may also explain the strong decrease of TTI. Moreover, the incorporation of the lignin, which is in black color, into EVA is likely to increase the composites heat absorption and thus earlier degradation and release of combustible products.

The incorporation of lignin also induces significant reduction of the pHRR. This reduction increases with increasing lignin content. The peak of heat release rate decreases from 780 kW/m² for pristine EVA to 630 (-55%),



Figure 4: Picture of the final residue after cone calorimeter test of EVA containing 60 wt% unmodified lignin

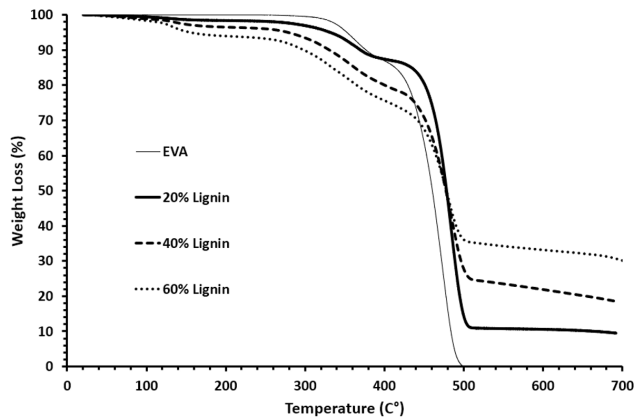


Figure 5: TGA curves of neat EVA and EVA-lignin composites under nitrogen

400 (–71.4%) and 310 kW/m² (–78%) when 20, 40 and 60 wt% lignin are incorporated, respectively. Moreover, increasing lignin content also induces a significant change of the HRR curve shape which is synonym of a thick charring [31]. Indeed, both HRR curves of pristine EVA and EVA containing 20 wt% lignin are characterized by a sharp peak in HRR while curves obtained after the incorporation of 40 and 60 wt% lignin present an initial increase after ignition up to a quasi-static HRR value that decreases only at the end of the test. This change of the HRR curves shape is typical of that induced by the formation of efficient char layer during the combustion. However, it is worth to men-

Table 3: TGA data of neat EVA and the different EVA compositions containing unmodified lignin

TGA	T _{-10%} (°C)	T _{-50%} (°C)	Residue at 700°C (%)
EVA	378	460	0
20% Lignin	368	476	10
40% Lignin	330	476	18
60% Lignin	300	476	30
60% Lignin - P	252	474	27
60% MDH	355	475	42
50% MDH – 10% Lignin	355	474	37
40% MDH – 20% Lignin	356	488	35
50% MDH – 10% Lignin - P	357	476	39
40% MDH – 20% Lignin - P	357	480	35

tion that the thermal stability of the char induced by lignin is not important since no final residue is left at the end of cone calorimeter test (Figure 4). The total decomposition of the whole material explain also why total heat release (THR) is not decreasing and remains slightly similar to that of pristine EVA (around 86 MJ/m²).

These results clearly evidence that lignin could act as flame retardant agent for EVA, allowing significant reduction of pHRR thanks to its charring effect. However, the incorporation of lignin present two important limitations, (i) important increase of the composite ignitability and (ii) the formation of thermally unstable char residue that degrade during the combustion.

Even if no direct correlation could be made between thermal stability during TGA analysis of a material and its flame-retardant behavior during cone calorimeter, the thermal behavior of the different EVA – lignin composites (Figure 5 and Table 3) presents some correlation with cone calorimeter test results. Indeed, the incorporation of lignin induces some premature composite thermal degradation that could be responsible, even partially, for the strong reduction of time to ignition recorded during cone calorimeter test. Temperature corresponding to 10% weight loss (T_{-10%}) decreases from 378°C for neat EVA to 368, 330 and 300°C when 20, 40 and 60 wt% lignin is incorporated, respectively. However, the incorporation of lignin induces an important increase of temperature corresponding to –50% weight loss (T_{-50%}) from 460°C for neat EVA to 476°C for all lignin incorporated composites. Moreover, TGA analysis demonstrate also significant increases of the amount of the char residue at 700°C. The incorporation of 20, 40 and 60% lignin induce the formation of residue of about 10%, 18 and 30% respectively. The formation of such thermally stable char residue when lignin is used is responsi-

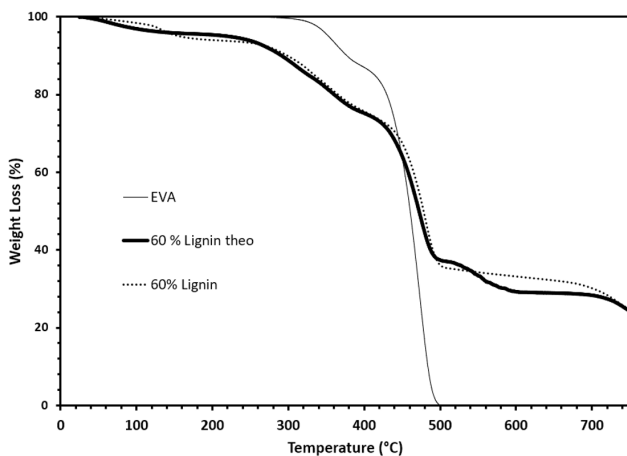


Figure 6: Experimental and theoretical TGA curve of EVA containing 60 wt% unmodified lignin

ble of the significant reduction of pHRR recorded during cone calorimeter tests. Moreover, the comparison of calculated TGA curves (linear addition of the weight loss of components degraded separately under nitrogen) for EVA containing 60 wt% lignin and the experimental curve of the same composition (Figure 6) enables better understanding the origin of the composite premature thermal degradation. Indeed, Figure 6 highlights that below 500°C, calculated and experimental curves are very similar. This result evidences that no interaction between these two additives takes place during their thermal degradation below 500°C. The composite premature weight loss is only due to lignin degradation that takes place earlier than EVA. However, above 500°C, a slight difference could be observed between calculated and experimental curves evidencing some interaction between EVA and lignin. Indeed, calculated curve predicts a decomposition step of the residue at 550°C whereas this step does not take place on the experimental curve. The formation of a char layer owing to the presence of lignin enables for improving the thermal stability of the charred structure formed during EVA thermal decomposition.

The incorporation of lignin into EVA enables significant reduction of the pHRR but this improvement is to the detriment of the ignition time that is strongly reduced.

3.2.1 Phosphorylated lignin (Lignin-P)

Combining lignin and phosphorous has been demonstrated to present an efficient way for enhancing its flame-retardant effect in various polymers [17]. This association could be made by combining lignin with phosphorous based compounds or by its phosphorylation. Both ways en-

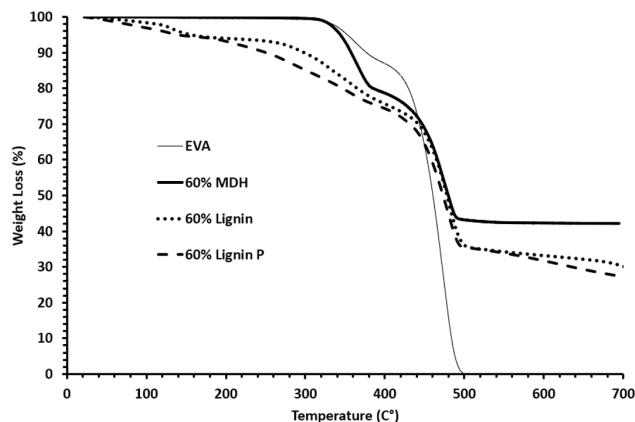


Figure 7: TGA curves of EVA containing 60 wt% MDH, Lignin and phosphorylated lignin

able the enhancement in the amount of char formed as well as its thermal stability.

For this purpose, we used a phosphorylated lignin containing ammonium phosphate groups (9.1 wt% of P and 7 wt% of N) that we developed in previous study [18] and demonstrated important flame-retardant effect in PLA. Grafting ammonium phosphate groups enable improving the char thermal stability produced during TGA analysis as it can be evidenced by TGA analysis (Figure 1).

However, in respect to EVA composite containing unmodified lignin, the incorporation of 60 wt% phosphorylated lignin (Lignin-P) does not induce significant change of the shape of the TGA curve. In fact, Figure 7 shows that both composites start to degrade at lower temperatures than EVA but using phosphorylated lignin induce more severe thermo-degradant effect since $T_{-10\%}$ is further reduced to 250°C in respect to 300°C obtained with untreated lignin and 378°C for neat EVA. $T_{-50\%}$ remains similar whatever the nature of lignin used. Both untreated and phosphorylated lignins lead to the formation of similar amount of final char residue. It is worth to mention that using this phosphorylated lignin does not prevent the premature composite degradation.

The flammability of the gases released during anaerobic thermal decomposition of EVA and the different composites has been investigated using Pyrolysis Combustion Flow Calorimeter (PCFC) test. Figure 8 displays HRR curves of EVA and EVA containing 60 wt% untreated lignin, phosphorylated lignin or MDH. Results are summarized in Table 4.

HRR curves obtained during PCFC tests showed that both EVA and the different composite exhibit one heat release rate peak. Moreover, the incorporation of lignin, whatever its nature, was beneficial since pHRR is strongly reduced. This result is interesting and indicates that lignin,

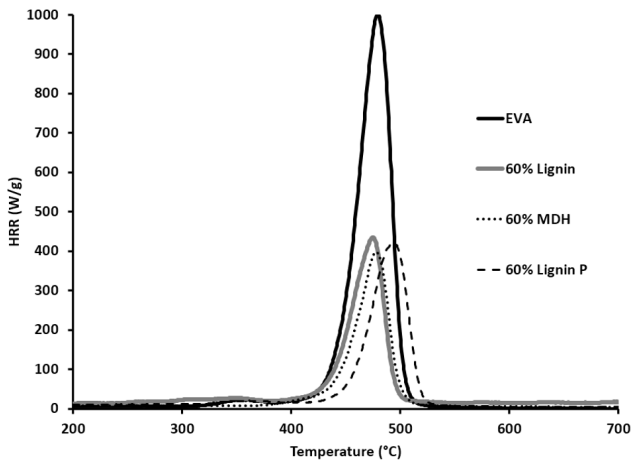


Figure 8: HRR curves of neat EVA and EVA composites containing 60 wt% MDH, Lignin and phosphorylated lignin

Table 4: PCFC data of neat EVA and flame retarded compositions

PCFC	Time of pHRR(t_{pHRR}) (°C)	pHRR (W/g)	THR (kJ/g)
EVA	480	994	37.7
60% MDH	480	394	15.4
60% Lignin	475	434	17.2
60% Lignin - P	492	420	16
40% MDH – 20% Lignin	466	383	16
40% MDH – 20% Lignin - P	472	375	16

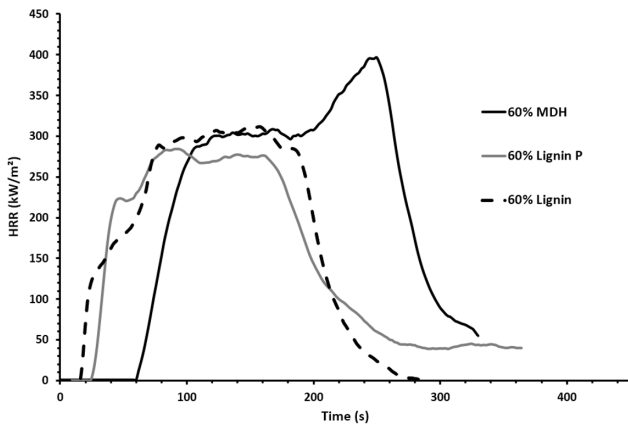


Figure 9: HRR curves of EVA composites containing 60 wt% MDH, 60 wt% untreated lignin and 60 wt% phosphorylated lignin

even unmodified one, does not induce any further release of flammable gases. In fact, THR obtained with both lignin is only slightly higher to the value obtained when same amount of MDH is incorporated (17.2 J/g with untreated lignin, 16 J/g with phosphorylated lignin and 15.4 J/g with MDH). 15.08 J/g is the theoretical value corresponding to

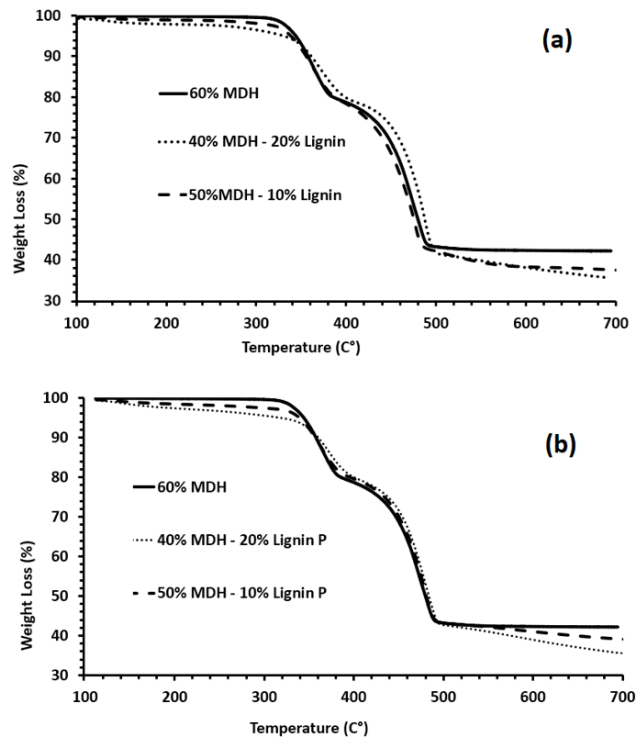


Figure 10: TGA curves of EVA composites containing 60 wt% MDH and combinations of lignin, phosphorylated lignin with MDH

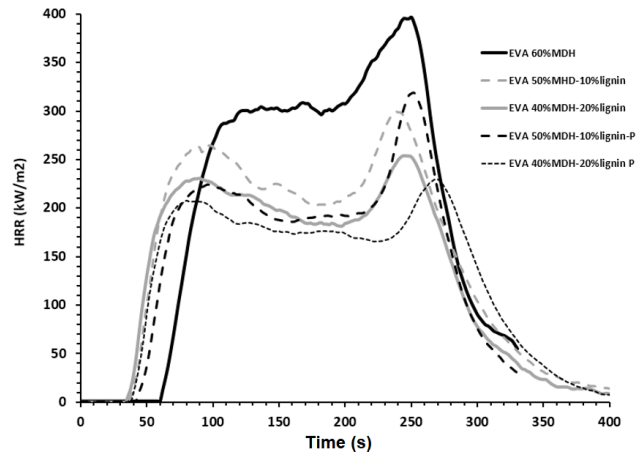


Figure 11: HRR curves of EVA composites containing combination of MDH and both lignin particles at different content

the reduction of EVA content, from 100 wt% to 40 wt%. From these results, we can estimate lignin contribution to the total heat release to be equal to only 2.12 J/g for untreated lignin and 0.92 J/g for phosphorylated lignin). Moreover, time to pHRR is affected by the nature of lignin used. In fact, the incorporation of phosphorylated lignin induces an increase of t_{pHRR} from 480°C for neat EVA to 492°C. This result is not in good accordance with TGA results that evidenced that the incorporation of lignin, in

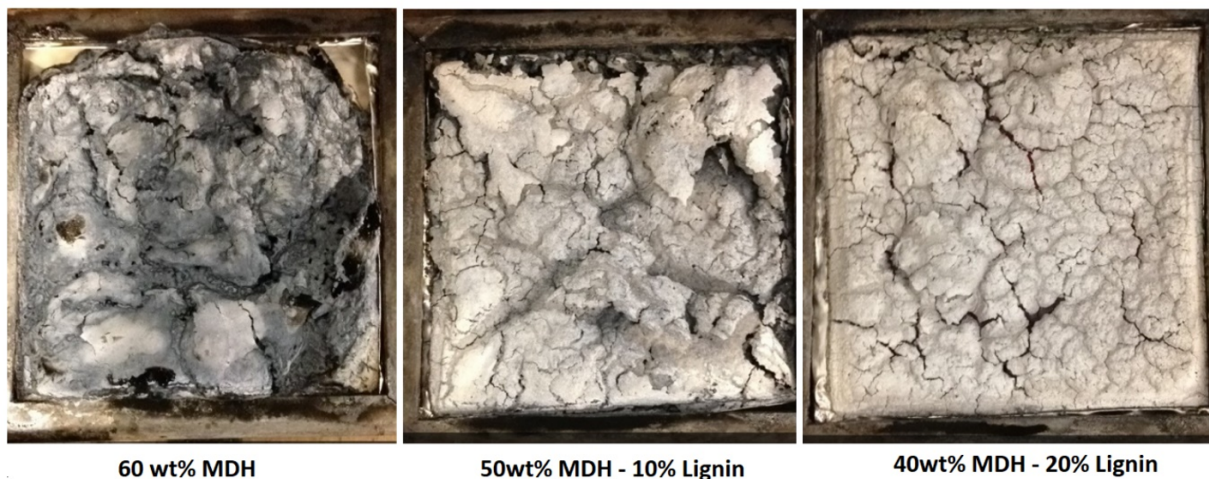


Figure 12: Char residue formed during cone calorimeter test (50 kW/m^2)

both natures, induce a premature composite thermal decomposition. However, the heating rate ramp used during PCFC analysis was $60^\circ\text{C}/\text{min}$ while it is only about $20^\circ\text{C}/\text{min}$ during TGA analysis. The difference of heating ramp could explain this difference. Moreover, it seems that the contribution of released gases at the beginning of combustion is not important. Increasing t_{pHRR} as well as the slight reduction of THR seems indicating that some char is formed during PCFC analysis when phosphorylated lignin is used.

However, in cone calorimeter test, using phosphorylated lignin, instead of untreated lignin, does not induce any further enhancement of EVA flame retardant behavior. In fact, $pHRR$ reduction remains similar and only a slight increase of the composite time to ignition is obtained but remains lower to that of neat EVA. In comparison with untreated lignin, using phosphorylated lignin do not enables any further enhancement of the flame-retardant properties of EVA-based composites. However, in respect to EVA composite filled with 60 wt% magnesium hydroxide, using lignin, whatever if modified or not, enables more important $pHRR$ reduction. In fact, the incorporation of 60 wt% MDH enables reaching 400 kW/m^2 in $pHRR$ while the same content of lignin leads to 310 kW/m^2 .

Combining both MDH and lignin seems presenting an interesting way for developing synergistic flame-retardant system. MDH will ensure improved resistance to ignition while the char formed thanks to lignin is expected to enable reaching lower $pHRR$ level.

3.3 MDH – lignin combinations

TGA curves of EVA containing different combinations of MDH and lignin (untreated and phosphorylated) are presented in Figure 10. All composites present two steps decompositions and the first one is slightly reduced because of the presence of the less thermally stable lignin fraction that is also responsible for the reduction of composites time to ignition. The second decomposition step is not affected since EVA/lignin composite demonstrated higher thermal stability in respect to EVA/MDH composite above 450°C (Figure 5). The final residue is higher when only MDH is used. However, in this case, the residue contains only non-cohesive white MgO powder while in the presence of lignin, a dark char, presenting higher cohesion, is left at the end of the thermal decomposition. The amount of the char residue is not responsible for the further enhancement of the flame-retardant behavior of MDH-lignin based composites but more likely its cohesion.

Combining lignin and MDH induces some changes of flame-retardant behavior of EVA-based composites. In fact, as it can be seen in Figure 11, combining MDH with both lignin particles enables further reduction of $pHRR$ during cone calorimeter test. Partial substitution of 10 wt% MDH by lignin, whatever its nature, enables $pHRR$ reduction up to 300 kW/m^2 while the substitution of 20 wt% MDH by lignin enables reduction up to 230 kW/m^2 . This strong $pHRR$ reduction evidence the synergistic effect obtained when lignin charring effect is combined with MDH's endothermic action. Figure 12 highlights an increase of the cohesion of the residue formed during cone calorimeter test. This cohesion is not further enhanced when phosphorylated lignin is used (images not presented). MDH and lignin actions are complementary and thus enables

the development of a more effective flame-retardant system. Using phosphorylated lignin instead to untreated one does not enable any significant effect. Combining both additives enables for limiting the reduction of the composite time to ignition but without reaching higher resistance to ignition than that of EVA containing 60 wt% MDH (Table 2).

4 Conclusion

The thermal stability and flame-retardant properties of EVA containing two lignins, *i.e.* untreated and phosphorylated, alone and in combination with magnesium hydroxide were investigated.

Results demonstrated that thanks to their charring effect, both untreated and phosphorylated lignins enable significant reduction of pHRR, more effective than that induced by MDH when they are incorporated at 60 wt% loading. However, because of the lower thermal stability of lignins, their presence affects the thermal stability of the corresponding composites and induces a premature weight loss during TGA analysis. The lower lignin thermal stability is also responsible for the reduction of the composite time to ignition (TTI) in cone calorimeter test.

Combining lignin charring effect and endothermic effect of magnesium hydroxide creates interesting complementary flame-retardant system that allows for further reduction of pHRR and some enhancement of the composite resistance to ignition. Results showed that lignin chemical modification is not required prior to obtaining improved flame-retardant properties.

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