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Intumescent formulations based on lignin and phosphinates for the bio-based textiles

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Abstract. This study investigates new intumescent formulations based on lignin and phosphinates to improve the flame retardant properties of Polyamide 11, while preserving the bio-based characteristics of this latter. Lignin has the advantage of being a bio-based compound and can be effectively used as carbon source for the design of intumescent systems in combination with other flame retardant additives. Metal phosphinates belong to a novel class of phosphorus flame retardants. Despite their increasing use, there is lack of scientific understanding as far as their fire retardancy mechanism is considered, especially in char forming polymeric materials. In this context, Polyamide 11 was melt blended with lignin and metal phosphinates. The possibility of melt spinning the prepared blends were assessed through melt flow index (MFI) tests; thermogravimetric (TG) analyses and cone calorimetry tests were exploited for investigating the thermal stability and the combustion behaviour of the obtained products, respectively. MFI results indicate that some formulations are suitable for melt spinning processes to generate flame retardant multifilament. Furthermore, the combination of lignin and phosphinates provides charring properties to polyamide 11. Finally, cone calorimetry data confirmed that the designed intumescent formulations could remarkably reduce PHRR through formation of protective char layer, hence slowing down the combustion process.

1. Introduction

Recently, bio-based polymeric materials are being exploited for various textile applications to address growing environmental concerns due to the shortage of petroleum resources and pollution caused by synthetic polymers. Polyamide 11 (PA11) is one of the bio-based polyamide increasingly used for various applications including manufacturing of textile fibers [1]. However, the low flame retardant properties of PA11 limit its applications in electronics, in the automotive sector and for high performance textiles. Among other halogen-free flame retardant process, intumescence process is one of possible ways to provide PA11 with flame retardancy. In particular, an intumescent formulation based on lignin and phosphinate could be incorporated during the melt spinning process. Recently, lignin has shown great potential as bio-based flame retardant additive because of its high char yield after decomposition ascribable to its aromatic framework. It is well known that the ability to form char during the thermal degradation is a fundamental aspect of flame retardant intumescent systems. Charring properties make lignin an important candidate as a carbon source in combination with other



flame retardant additives in intumescent formulations [2]. Metal phosphinates, namely Zinc phosphinate and Aluminum phosphinates (ZnP/AIP) are used as synergists with low sulfonate (4 wt.%) alkali lignin (LSL) to enhance fire performance of PA. Metal phosphinates are considered very efficient due to their high phosphorus content, thermal stability, low toxicity and low solubility in water and in common organic solvents [3].

This work is aimed at demonstrating the possibility of using lignin/phosphinates combinations for conferring flame retardant features to PA11. More specifically, the proposed new formulations were melt-blended in the polymer, using an extrusion process. MFI results were exploited for assessing the feasibility of melt spinning for producing flame retardant fibers; furthermore, the thermal stability and charring ability of the resulting blends was evaluated by using thermogravimetric analyses. UL94 vertical flame spread tests were utilized for determining flame propagation and total combustion time of the prepared blends. Finally, their combustion behavior was assessed through cone calorimetry tests performed under 35 kW/m² heat flux.

2. Experimental

2.1. Materials

A bio-based Polyamide 11 (Rilsan® BMNO-TLD; $M_n=17,000$ g/mol, MFI=14-20 g/10 min at 235 °C), was supplied by Arkema (France). The alkali lignin (LSL) with low sulfonate content (4% of sulfur) used in this study was purchased from Sigma Aldrich (France). Two different types of phosphinates were used, namely: Zinc phosphinate (Pekoflam SMap, supplied from Archroma, France) and Aluminum phosphinate (Exolit OP 1230, supplied by Clariant).

2.2. Preparation and characterization of the flame retardant blends

The pellets and additives were dried for 12 hrs at 80 °C before extrusion. Different PA/LSL/(ZnP/AIP) formulations were prepared using co-rotating twin-screw extruder (ThermoHaake, screw diameter 16 mm and L/D 25), within 170 and 220 °C; the rotation speed was fixed to 100 rpm. The obtained monofilaments were pelletized before use. Different analytical tools were employed for evaluating thermal stability and flame retardancy. The fluidity of the different blends was measured by Melt Flow Index (MFI) tests, performed at 220 °C with 2.16 kg weight, using ThermoHaake apparatus. Thermal stability of blends was studied by thermogravimetric (TG) analyses in N₂ at heating rate 10 °C/min from room temperature to 700 °C. The flammability properties were assessed by vertical flame test method according to IEC 60695-11-10 is well known as UL 94 flammability test. Fire retardant properties were evaluated by using cone calorimetry test according to ISO 5660 standard procedure.

Table 1. Formulations of the blends investigated.

Sample Code	Polyamide 11 (Wt.%)	Low sulfonate lignin (Wt.%)	Al-Phosphinate (Wt.%)	Zn-Phosphinate (Wt.%)
PA11	100	-	-	-
PA90-LSL10	90	10	-	-
PA80-LSL20	80	20	-	-
PA90-AIP10	90	-	10	-
PA90-ZnP10	90	-	-	10
PA80-LSL10-ZnP10	80	10	-	10
PA80-LSL10-AIP10	80	10	10	-

3. Result and Discussion

3.1. Fluidity and Melt spinnability

The fluidity and melt flow viscosity of the different blends were measured by MFI tests. The MFI values have significant impact on determining spinnability conditions and possibility of melt spinning. As shown in Fig. 1, the addition of lignin in PA11 progressively decreases the fluidity of the polymer blend. This reduction in MFI could be attributed due to extensive cross-linking and strong intermolecular interactions taking place in between the polymer chains and lignin. However, the formation of lignin aggregates could also justify the increase in viscosity [4]. The same MFI trend is observed when AIP is blended alone with PA. Nevertheless, the incorporation of phosphinates in the PA11-LSL systems (i.e. PA11/LSL/(AIP/ZnP) samples) turns out to increase the fluidity and MFI values; furthermore, the interactions between phosphinate and lignin may contribute to achieve a good filler distribution and to an enhanced miscibility. The fluidity increase observed for PA11/LSL/(AIP/ZnP) systems make these blends compatible with the spinning process.

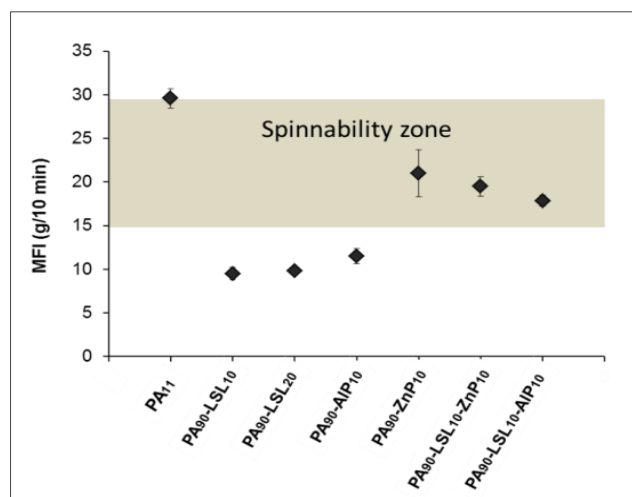


Figure 1. MFI values for PA11 blends.

3.2. Thermal decomposition

The thermal decomposition of PA11, lignin, phosphinates and of the resulting blends in N_2 was evaluated by thermogravimetric analyses: the typical TG curves are shown in **Fig. 2**. PA11 exhibits a single decomposition step, which takes place in between 400 and 450 °C without generating any char residue.

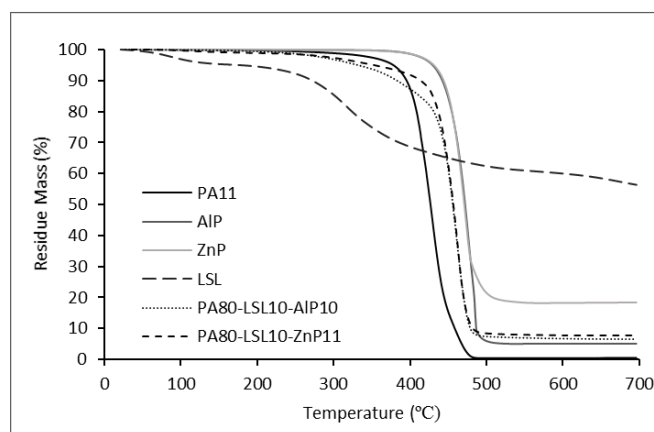


Figure 2. TG thermograms in nitrogen for the different systems investigated.

Neat Lignin shows a slow rate of weight loss from 60 to 300 °C, leading to the formation of a higher residue (~60 wt.%) at 600 °C. Phosphinates (AIP/ZnP) are also characterized by a sharp single degradation step occurring between 450 and 500 °C; in particular, ZnP shows a higher char residue (~20 wt.%) with respect to AIP (~7 wt.%) at 600 °C [5]. In the presence of lignin and phosphinates, the degradation of PA11 is shifted towards higher temperatures by about 50°C; furthermore, the char residue approaches about 10 wt.% at 600 °C.

3.3. Fire retardancy

Cone calorimetry tests were exploited for assessing the combustion behaviour of PA11 and its blends. The HRR curves as function of time, using a heat flux of 35 and 25 kW/m² are shown for varied materials in **Figs. 3a** and **3b**, respectively. The data concerning time to ignition (TTI), peak to heat release rate (PHRR) and total heat release (THR) are collected in Table 2a and 2b.

Table 2a. Cone calorimeter data for the characterized blends (35 kW/m²).

Samples	TTI (s)	PHRR (kW/m ²)	PHRR reduction (%)	THR (MJ/m ²)	THR reduction (%)	Residue (wt.%)
PA11	71	988.4	-	103.5	-	0.5
PA90-LSL10	45	687.8	30.4	98.8	4.6	3.4
PA90-LSL20	36	451.0	54.4	75.1	27.4	8.7
PA90-ZnP10	84	610.6	38.4	92.6	7.5	2.1
PA80-LSL10-ZnP10	58	485.6	50.9	88.5	14.5	7.0

Table 2b. Cone calorimeter data for the characterized blends (25 kW/m²).

Samples	TTI (s)	PHRR (kW/m ²)	PHRR reduction (%)	THR (MJ/m ²)	THR reduction (%)	Residue (wt.%)
PA11	208	847.2	-	100.1	-	0.8
PA90-LSL10	156	509.8	39.8	96.0	4.1	4.4
PA90-LSL20	86	337.7	60.1	84.2	16.0	12.3
PA90-AIP10	144	767.0	9.5	90.7	9.4	2.5
PA80-LSL10-AIP10	134	395.8	53.0	84.5	15.6	8.1

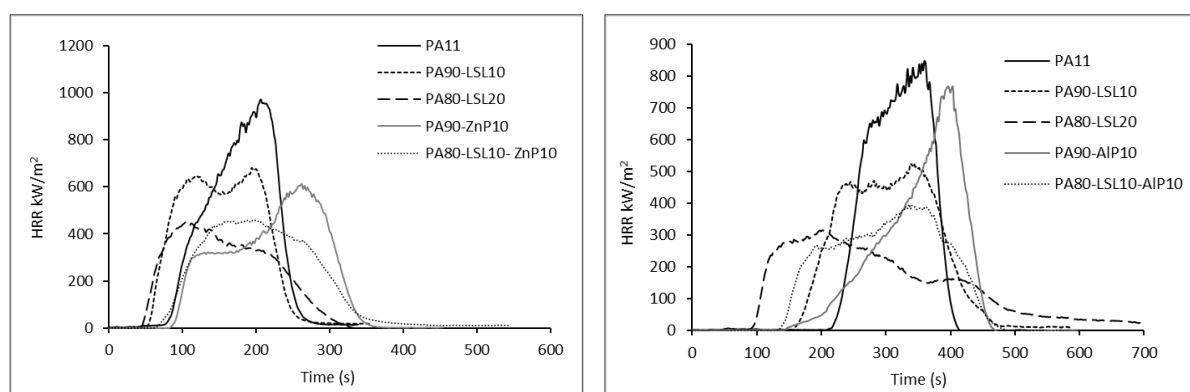


Figure 3. HRR vs. time curves at 35 (a) and 25 (b) kW/m² for PA11 and its blends.

Unfilled PA11 shows which shows TTI of 71 s; after ignition HRR increases quickly, reaches PHRR (988 kW/m²) and then decreases, with total heat release of 101 MJ/m². The presence of 10

wt.% lignin in PA11 slightly modifies the combustion behaviour of this latter, as HRR drops by 30%; furthermore, a two-step combustion process, which is generally accepted [6], occurs. More specifically, the first peak (635 kW/m^2) can be attributed to formation of char layer and is followed by plateau, whereas the second peak (675 kW/m^2) corresponds to destruction of the char layer. Further increasing the lignin content (up to 20 wt.%) reduces the TTI (36 s) drastically. In addition, PHRR decreases with increasing the lignin content. Moreover, there is a modification in shape of the curve that changes from a two-step process to a single step combustion; this leads to the maximum reduction in PHRR (~54%) due to barrier effect.

As shown in **Fig. 3b**, HRR curves at 25 kW/m^2 for AIP alone in PA11 and AIP with LSL in PA11 are discussed. HRR curves for PA-LSL systems are already discussed before and not repeated, since the nature of curves are same. It is worth noticing that AIP alone does not enhance the combustion behaviour of PA11. Intumescent formulation of PA11/LSL/AIP shows steady increase of HRR and substantial reduction in PHRR (~53 %) and THR (~16 %) observed due to protective char layer formation and flame retardant property increases.

3.4. Flammability test

UL94 vertical flame tests were exploited for evaluating the flame propagation and total combustion time of varied blends. This test is a small-scale laboratory screening procedure for comparing the relative burning behaviour of vertically oriented specimens which are classified in to non-flammable (V-0), less flammable (V-1), flammable (V-2) and highly flammable (Non-classified) rating. The data regarding combustion time, weight loss, burn length and their respective rating are reported in Table 3.

Table 3. UL94 vertical flame test for PA11 and composites.

Samples	T1 ^a (sec)	T2 ^b (sec)	Total time (sec)	Cotton ignition	Weight loss (%)	Burn length (cm)	Rating
PA11	13.3	10.6	23.9	T1	28.0	3.5	V2
PA90-LSL10	25.8	16.6	42.4	T1	42.6	4.7	NC
PA80-LSL20	27.3	57.5	84.8	T2	62.7	7.0	NC
PA90-ZnP10	14.6	8.5	23.0	T2	20.0	2.5	V2
PA90-AIP10	18.0	10.7	28.7	T1	37.3	4.7	V2
PA80-LSL10-ZnP10	6.8	6.0	12.8	Not burn	20.0	2.5	V1
PA80-LSL10-AIP10	14.3	5.6	20.0	Not burn	25.3	3.2	V1

^a Sample burning time after first flame application.

^b Sample burning time after second flame application.

Pure PA11 shows longer combustion time which results high flammability properties of material. The addition of lignin alone increases total burning time and weight loss and material is not classified. This behavior could be attributed due to degradation of lignin at lower temperature. However, presence of ZnP/AIP in PA11 does not lead any flame retardant properties as compare to PA11. Nevertheless, combination of LSL and ZnP/AIP decreases total combustion time, mass loss, burn length and thus material classification upgraded to V2. It is worth noticing that intumescent formulation seems to be effective in case of PA11-LSL-(ZnP/AIP) blends which enhanced flame retardant properties of blends.

4. Conclusion

In this work, lignin, a bio-based compound, was utilized as an effective carbon source in combination with phosphinates for providing PA11 with flame retardant properties. In particular, these two additives were able to confer an intumescent behaviour to the polymer, favouring the formation of a

protective char layer. Furthermore, MFI results demonstrated that it is possible to melt spin blends of PA11 with the design intumescent formulation, hence generating to multifilament fibres suitable for developing fire retardant fabric structures.

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