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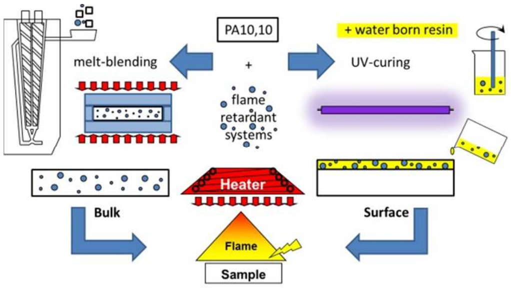


PA 10,10 can be flame retarded either by melt-blending the polymer with intumescent formulations or by coating it with UV-curable mixtures.

Bulk vs. surface flame retardancy of fully bio-based polyamide 10,10

Daniele Battegazzore[1], Jenny Alongi[1*], Gaelle Fontaine[2], Alberto Frache[1], Serge Bourbigot[2], Giulio Malucelli[1]

[1] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino,

sede di Alessandria, Viale Teresa Michel 5, 15121 Alessandria, Italy

[2] Unité Matériaux et Transformations (UMET) - CNRS UMR 8207, R2Fire Group– Ecole Nationale Supérieure de Chimie de Lille CS 90108, F-59652 Villeneuve d'Ascq, France

*Corresponding author: Tel/Fax: +390131229337/+390131229399;

e-mail address: jenny.alongi@polito.it

Abstract

First, polyamide (PA) 10,10-based compounds with enhanced flame retardant properties have been prepared by melt-blending. To this aim, a traditional intumescent formulation consisting of ammonium polyphosphate (APP) and pentaerythritol (PER) derived from oil chemistry has been added to PA 10,10 (30 wt.-% loading) and the resulting morphological, mechanical and flame retardant properties have been investigated. In order to achieve the highest carbon content from bio-source, PER has been replaced by corn starch: thus, it was possible to compare the thermal, mechanical and combustion properties of the compounds containing non-bio additives (APP and PER) with those of the starch-containing counterparts.

Furthermore, the same intumescent ingredients adopted in bulk have been further used for coating PA 10,10 surface, exploiting a UV-curing process.

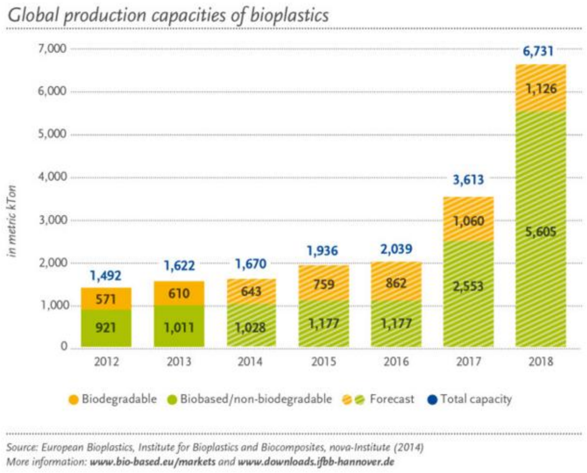
From an overall point of view, cone calorimetry tests have shown that these bulk formulations are able to reduce total heat release and peak of heat release rate - pkHRR - (about 30%), but, contrariwise, they lower time to ignition and increase the smoke production, as well. A similar trend has been found when the flame retardants were added to a UV-curable system coated on PA 10,10 samples, without taking into consideration the effect of specimen mass. Conversely, when the combustion parameters were normalized to the specimen mass, the reduction of pkHRR was significantly higher than that found with the same FR content in bulk (about -65 *vs.* -35%, respectively). As a consequence, the flame retardant results achieved by the surface approach seem to be more promising than those from melt-blending.

Keywords: Polyamide 10,10; flame retardancy; starch; ammonium polyphosphate; thermo-mechanical properties; UV curing.

1. Introduction

Nowadays, the continuous seeking of alternative solutions to crude oil for the recovery/extraction of monomers and oligomers useful for polymer synthesis is one of the most interesting research topics for both industrial and academic researchers. Indeed, due to the growing attention to the environmental impact, new legislations/regulations, and recycling of materials, a lot of work has been carried out for replacing plastics derived from oil chemistry (fossil-based polymers) with others derived from bio-sources. Among them, bio-degradable polymers like PLA (polylactic acid), PHAs (polyhydroxyalkanoates), starch, cellulose, and others, and non-biodegradable products like PE (polyethylene), PET (polyethylene terephthalate), PAs (polyamides), can be considered the most representative.

From an overall consideration, the field of bio-based polymers is continuously evolving, as shown by European Bioplastics (**Figure 1**) [1]. Indeed, their current market is characterized by a yearly growth of about 20-100% that is just 1% of the total worldwide plastics. On the basis of these data, the marketing experts have foreseen an increase of the production capacities from 1.6 to 6.7 million tons within 2018, mainly referring to bio-based non-biodegradable polymers [1].



Source: European Bioplastics, Institute for Bioplastics and Biocomposites, nova-Institute (2014)
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Figure 1. Expected data about the production capacities of bio-based polymers

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Among the bio-based polymers, some aliphatic polyamides were recently revalued by industries for new enduring applications. In particular, PA 6 and PA 6,6 are well known as materials with relatively high strength, high ductility, high flame retardancy, excellent resistance to short term heat exposure and good chemical resistance. Conversely, as PA 10,10 and PA 11 do not exhibit comparable performances, they deserve further investigation, in order to widen their applications. In particular, one of their main drawbacks refers to the low level of flame retardancy. To the best of our knowledge, the open scientific literature lacks of papers reporting flame retardancy enhancements for PA 10,10. In this scenario, the use of specific and suitable flame retardant systems (FRs) can be considered an efficient way for partially overcoming this issue. In particular, it is reasonable to guess promising performances of intumescent FRs for PA 10,10, on the basis of the results already collected for other aliphatic polyamides [2 and references quoted in].

As it is well known [3], when an intumescent material is exposed to a heat flux, it develops a carbonaceous shield on its surface, commonly called *char*. This protection acts as a physical barrier able to limit the heat, fuel, oxygen and mass transfer between the flame and polymer. Usually, the intumescent formulation consists of three components, namely: i) an acid source (e.g. APP); ii) a carbon source (PER, saccharides and polysaccharides); and iii) a blowing agent (melamine) [3]. Some of these species, such as APP, possess a great advantage in comparison with other chemicals for an industrial application, since they can act both as acid source and blowing agent (e.g. releasing ammonia), at the same time.

As far as aliphatic polyamides are concerned, APP is widely used in fire-retardant coatings formulations because of its ability to catalyze the charring of organic materials and to produce intumescent protective layers [4]. In spite of a relatively low thermal stability, numerous attempts to use APP as a bulk FR additive for PAs are reported in the scientific literature. Levchik and Weil [2] have shown that APP can be incorporated into PA 6,10, PA 11 and PA

12 matrices or even to high-melting PA 6,6 and PA 6 by using a fast compounding process. As a result, APP has proven to be very efficient only at high concentrations (> 10 wt.-% in PA 6,6, >20 wt.-% in PA 11, PA 12 and PA 6,10, and > 30 wt.-% in PA 6) [5]. In order to have a completely intumescent formulation, a carbon source is mandatory: one of the most common carbon sources coupled with APP is PER, usually derived from oil-chemistry [6], although recently new products from bio-source have been commercialized [7].

On the basis of all these considerations, the present paper is addressed to demonstrate that it is possible to confer significant flame retardant features to PA 10,10 first of all through the addition of a traditional intumescent formulation consisting of APP and PER. To the best of our knowledge, up to now, this is the first time, this approach is exploited for conferring flame retardant features to PA 10,10.

Pursuing this strategy, in order to increase the carbon content from bio-source, PER has been replaced with starch (ST), which already has turned out to be an efficient carbon source in flame retarded PLA [8-10]. To this aim, formulations consisting of APP/PER and APP/ST pairs have been melt-blended with polyamide 10,10 in order to obtain materials with enhanced FR properties. The results achieved by using these formulations in bulk have been compared with those obtained coating the same constituents on PA 10,10 surface, by means of a UV-curing process. This latter approach is completely new for the bio-based polymers and in particular for PA 10,10.

In detail, the selected additives have been added to a UV-curable waterborne acrylic resin, thus leading to the obtainment of fully cured coatings in a very fast and efficient way. Indeed, UV-curing exploits some advantages such as high cure rate, reduced energy consumption and absence of Volatile Organic Compounds (VOC) emissions. These features have allowed its rapid growth in a large variety of industrial applications, particularly for the fast drying of varnishes, printing inks and protective coatings on several substrates, including paper, metal, plastic, textile and wood [11].

Finally, a critical comparison between the two proposed approaches (i.e. bulk vs. surface modification of PA) has been carried out on the basis of the achieved thermal, mechanical and combustion properties.

2. Materials and methods

2.1 Materials

PA 10,10 (RADIPOL® DX 45, relative viscosity=2.3 in H_2SO_4 at 25°C, number of amino end groups=45 meq/kg, melting temperature= 203°C) was kindly supplied by Radici Group (Italy). APP (PHOS-CHEK® P30) and PER (Charmor® PM15) were purchased from ICL Performance Products, Inc. and Perstop Holding BA, respectively. The corn starch (CERESTAR® RG 03408, 25-28% of amylose content) used for replacing PER was purchased from Cargill Inc.

A commercially-available UV-curable aliphatic acrylic polyurethane latex, Uceacot®6558 (PUA, solid content: 50 wt.-%), was kindly supplied by Allnex Ltd (USA). In addition, Esacure®DP250, kindly supplied by Lamberti Spa (Italy), was added to the UV-curable mixture as photoinitiator (4 wt.-%, with respect to the solid resin content).

2.2 PA 10,10-based compound preparation by melt blending

First, PA 10,10 was dried at 80°C in a vacuum (-1000 mbar) convection oven for 8 h, reaching 200 ppm of water content as determined by Karl-Fischer titration. Analogously, all the fillers were dried at 80°C, but for 5 h (<400 and 4000 ppm of water content for APP or PER and starch, respectively).

PA 10,10-based compounds were prepared in a co-rotating twin screw micro extruder (DSM Xplore 15 ml Microcompounder), using a residence time of 5 min, heating temperature of 220°C and 100 rpm screw speed. In order to prevent polymer oxidation, the extruder chamber was fluxed with nitrogen (flux: about 50 mL/min). The different formulations, all containing 30 wt.-% of additives, are listed in **Table 1**. APP:PER or APP:ST ratio was fixed at 3:1, according to the previous studies performed on PLA [10]. In addition, two formulations containing PER or ST were prepared as a reference in order to investigate their effect on PA 10,10 mechanical properties.

Table 1. Codes and compositions of melt-blended PA 10,10-based samples.

Sample	PA 10,10 [wt.-%]	APP [wt.-%]	PER [wt.-%]	ST [wt.-%]
PA 10,10	100.0	-	-	-
PA 10,10APP	70.0	30.0	-	-
PA 10,10PER	92.5	-	7.5	-
PA 10,10ST	92.5	-	-	7.5
PA 10,10APP-PER	70.0	22.5	7.5	-
PA 10,10APP-ST	70.0	22.5	-	7.5

2.3 Specimen preparation

All the specimens utilized for mechanical (2x25x0.1 mm^3), dynamic-mechanical (6x25x1 mm^3) and combustion (50x50x1 mm^3) tests were prepared by compression molding (at 220°C for 2 min, under 10 MPa). The same procedure was adopted for obtaining the specimens (50x50x1 mm^3) coated by the UV-curable mixtures.

2.4 PA 10,10 treatment by UV-curing

In a typical experiment, a solution containing the UV-curable aliphatic acrylic polyurethane (PUA) and 4 wt.-% of photoinitiator (PI, with respect to the solid resin content) was manually mixed at room temperature for 5 min. Subsequently, the same intumescent FR formulations used in bulk were added to PUA+PI solution, as detailed in **Table 2**, and coated onto PA 10,10 specimens by using a wire wound applicator (coating thickness=0.6-0.8 mm, measured by micrometer device and further confirmed by SEM performed on specimen cross-section: SEM magnifications are reported in Supporting Information). In doing so, all the samples contain 30 wt.-% intumescent FR (namely, APP, APP+PER or APP+ST) with respect to PA 10,10 amount. Then, these samples were initially thermally-treated at 80°C for 30 min in order to remove water and, subsequently, subjected to the UV-curing process, using a dynamic UV-lamp (F300S from Heraeus Noblelight Fusion UV Inc., USA): to this aim, five exposures of 5 s to UV radiation were employed; the radiation intensity on the surface of the sample was 840 mW/cm^2, as measured by a UV-radiometer (Power Puck, from EIT Inc., USA). These conditions are suitable for achieving the completeness of the UV-curing process of the resin, as previously demonstrated [12].

Table 2. Codes and compositions of PA 10,10 samples subjected to the UV-curing process.

Sample	PA 10,10 [wt.-%]	PUA+PI [wt.-%]	APP [wt.-%]	PER [wt.-%]	ST [wt.-%]
R PA 10,10	81.25	18.75	-	-	-
R PA 10,10 APP	62.5	18.75	18.75	-	-
R PA 10,10APP-PER	62.5	18.75	12.50	6.25	-
R PA10,10 APP-ST	62.5	18.75	12.50	-	6.25

2.5 Characterization techniques

The surface morphology of the prepared compounds was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 20 kV); a X-ray probe (INCA Energy Oxford, Cu-Kα X-ray source, k=1.540562 Å) was used to perform elemental analysis (EDX, energy dispersive X-ray analysis). The samples were obtained by fracturing 1 mm thick films in liquid nitrogen (5x1 mm^2). These pieces were pinned up to conductive adhesive tapes and gold-metallized.

Dynamic-mechanical thermal experiments (DMTA) were performed using a DMA Q800 (TA Instruments) in tensile configuration. The following experimental conditions were adopted: temperature range from 30 to 120 ºC, heating rate of 3 ºC/min, 1 Hz frequency and 0.05% of oscillation amplitude in strain-controlled mode. The storage modulus (E') and tanδ curve were measured; the glass transition temperature (T_g) was calculated as the maximum of tanδ curve. For each formulation, the tests were repeated three times and the experimental error was calculated as standard deviation for all the measured parameters.

In addition, the mechanical properties were further investigated in tensile mode, assessing the stress-strain curves of unloaded and loaded PA 10,10-based samples. To this aim, two tests at 30°C with a strain rate of 1%/min were carried out by using the DMA Q800 equipment (TA Instruments). Maximum stress (σ_{max}) and elongation at break (ε) were measured.

Thermogravimetric analyses (TGA) were carried out both in nitrogen and air, from 50 to 800°C with a heating rate of 10°C/min, using a TA Q500 thermo balance (TA Instruments) (experimental error: ±0.5 wt.-%, ± 1°C). The samples (ca. 10 mg) were placed in open alumina pans and fluxed with nitrogen or air (gas flow: 60 ml/min). $T_{5\%}$ (temperature, at which 5% weight loss occurs), T_{max} (temperature, at which maximum weight loss rate is achieved) and the mass of the final residues at 800°C were evaluated.

The data obtained from TGA were compared with those of a pyrolysis-combustion-flow calorimetry (PCFC, FAA MicroCalorimeter, Fire Testing Technology). This latter was used to assess the flammability of the formulations, according to the ASTM D7309 standard. In detail, the prepared sample (ca. 8 mg) was heated using a linear heating rate (60°C/min) in a stream of nitrogen flowing at 80 mL/min. The thermal degradation products of the sample in nitrogen were mixed with a 20 mL/min stream of oxygen prior to entering the combustion furnace (900°C). The combustion of fuel gases in the mixture of 20% O_2 and 80% N_2 at 750°C for 10 s is a very conservative condition to ensure the complete oxidation of the fuel gases: Total Heat Release (THR), Heat Release Rate peak (pkHRR), corresponding temperature-to-peak (T_{pkHRR}) and final residues were evaluated. For each formulation, the test was repeated three times and the experimental error was ±5%.

Cone calorimeter tests (Fire Testing Technology, FTT) were performed according to the ISO 5660 standard [13]. The samples were placed on a holder and irradiated in horizontal configuration under a 35 kW/m^2 heat flux. For each formulation, the test was repeated three times and an experimental error of 5% was calculated as standard deviation for all the measured parameters. Time to Ignition (TTI, s), Total Heat Release (THR, MJ/m^2), and Heat Release Rate peak (pkHRR, kW/m^2), Total Smoke Release (TSR, m^2/m^2), carbon monoxide and dioxide yields (g/s), and final residue (%) were evaluated.

In order to compare the two adopted approaches (bulk vs. surface), THR and pkHRR were normalized to the initial specimen mass: in this case, the measurement units were MJ/m^{2}g and kW/m^{2}g, respectively.

The limitation regarding the amount of available materials led to the use of specimens having a smaller size (50x50x1 mm^3) with respect to the standard size (100x100x6 mm^3) outlined in the ISO 5660 standard.

Prior mechanical and combustion tests, all the samples were conditioned at 23°C and 50% RH, in a climate-controlled chamber Binder BFK240 for 48 h.

3. Results and Discussion

3.1 Morphological characterization of PA 10,10-based composites

The morphological characterization of PA 10,10-based composites has been assessed by SEM. Three magnifications of PA 10,10 APP, PA 10,10 APP-PER and PA 10,10 APP-ST (in back-scattered electrons) are presented in **Figure 2** (**2a**, **2b** and **2c**, respectively). As far as PA 10,10APP is concerned, the presence of filler is well visible from the numerous aggregates homogeneously distributed within the polymer matrix. Although their size ranges from 2 to 40 µm, only few big aggregates are distinguishable. The dispersion level of the additive is however finer as demonstrated by the elemental analysis of phosphorous reported in **Figure 3a** (SEM image on left and P map on right, respectively): indeed, the presence of phosphorous element is visible also in the areas without aggregates.

When APP is partially replaced with PER, the morphology observed by SEM is considerably different, as it is clear comparing **Figures 2a** and **2b**. In this case, the size of aggregates ascribed to APP becomes significantly smaller and better distributed within PA 10,10. It is reasonable to suppose a finer APP dispersion in the presence of PER or ST due to the formation of hydrogen bonds between the two additives, as already observed by Demir et al. in polypropylene compounds loaded with APP and PER [14]. No remarkable differences have been observed when PER is replaced with ST, apart from few APP-based aggregates, as visible comparing the two micrographs in **Figures 2b** and **2c** and the corresponding maps of P element in **Figures 3b** and **3c**.

Comparing the three phosphorous maps reported in **Figure 3**, it is not possible to highlight significant differences among the samples examined. Indeed, as commonly accepted by the scientific community, the elemental analysis performed by SEM-EDX can give only a qualitative information about the distribution and dispersion level of elements. Thus, also in our case, quantitative differences among the samples cannot be highlighted. From a qualitative point of view, however, it seems that where bigger aggregates are present, phosphorous signal is more intense, as well visible in **Figures 3a** and **3c**.

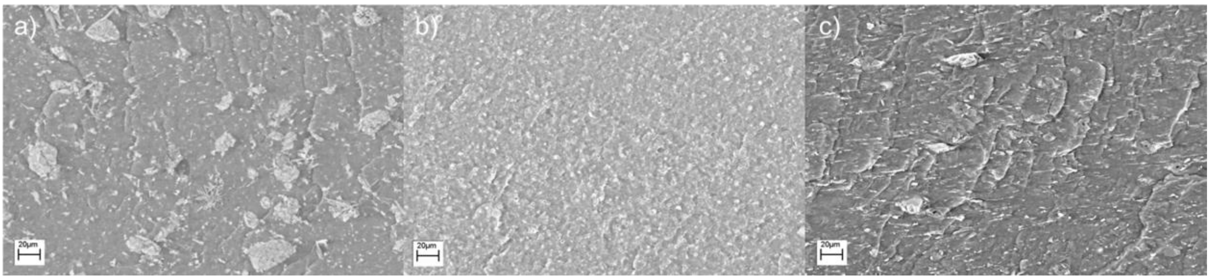

Figure 2. SEM analysis of: a) PA10,10APP, b) PA 10,10APP-PER and c) PA 10,10APP-ST.

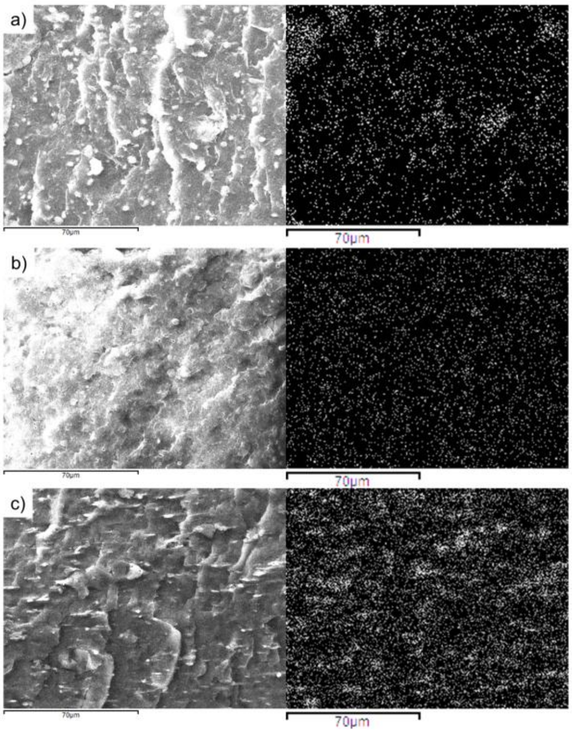

Figure 3. SEM magnifications (left) and P maps (right) of: a) PA 10,10APP b) PA 10,10APP-PER and c) PA 10,10APP-ST.

3.2 DMTA of PA 10,10-based compounds

One of the main drawbacks of any fire-retarded material refers to the poor mechanical properties due to the presence of FR additives [15]. For this reason, also in the present work, this issue has been thoroughly investigated. With this purpose, DMT analyses were carried out for assessing the effect of the used FRs on PA 10,10 glass transition temperature (T_g) and storage modulus (E') that can be referred to the material's stiffness. **Table 3** summarizes the collected data.

First of all, the presence of APP slightly affects the glass transition temperature of PA 10,10 which increases from 66 to 70°C, while PER (or ST) decreases it (62°C). Employing APP/PER-based formulation, a higher PA 10,10 T_g has been found (75°C). In addition, the replacement of PER with starch shows a significant T_g increase, from 66 to 79°C. Furthermore, with the only exception of PA 10,10APP-PER, all the prepared compounds become stiffer with respect to the neat polymer, as demonstrated by E' trend.

Although the results presented up to now are worthy, in order to have a more complete mechanical characterization, stress-strain tests have been carried out. To this aim, maximum stress (σ_{max}) and elongation at break (ε) were measured: the collected data reported in **Table 3** demonstrate that all the investigated formulations showed a significant reduction of σ_{max} and ε (about -30 and -70%, respectively). This finding may be ascribed to the low adhesion between polymer matrix and additives: indeed, the σ_{max} value of all compounds is reduced as much as the additive concentration, namely 30 wt.-%. In addition, during processing, at 220°C, APP may partially degrade, releasing ammonia and water. This latter can affect PA 10,10 elongation at break.

As a reference, compounds containing only PER or ST were also tested (**Table 3**). In this case, due to the lower additive content (namely, 7.5 vs. 30 wt.-%), the reductions of these parameters were not so relevant as in the case of the flame retardant formulations under investigation.

Table 3. Dynamic mechanical properties for the samples under investigation.

Sample	T_g [°C]	E' at 30°C [MPa]	σ_{max} [MPa]	ε [%]
PA 10,10	66 ± 1	1650 ± 116	50±2	55±5
PA 10,10APP	70 ± 1	2100 ± 147	36±2	16±2
PA 10,10PER	62± 1	1725± 121	42±2	43±4
PA 10,10ST	62± 1	1700± 119	39±2	36±3
PA 10,10APP-PER	75 ± 1	1930 ± 135	34±2	17±2
PA 10,10APP-ST	79 ± 1	2160 ± 151	37±2	16±2

3.3 Thermogravimetry and pyrolysis-combustion flow calorimetry of PA 10,10 compounds

The thermal and thermo-oxidative stabilities of the samples under investigation have been assessed by thermogravimetry in nitrogen and air, respectively. The obtained data are collected in **Table 4** and plotted in **Figures 4** and **5**.

Usually, in nitrogen PA 10,10 degrades through a single step (T_{max1} centered at 468°C) without leaving any residue (**Figure 4**). The presence of APP strongly sensitizes the polymer matrix decomposition, as evidenced by the $T_{5\%}$ value (332 vs. 425°C for PA 10,10APP and PA 10,10, respectively). However, the released phosphoric acid favors the formation of a thermally stable char that further decomposes at higher temperatures, leaving a significant residue (16 wt.-%) [16]. The same trend already found for APP is observed by adding a carbon source (independently of its origin): indeed, $T_{5\%}$ and T_{max} values are significantly lowered and the final residue increases with respect to unfilled polyamide. The only considerable difference between APP and APP/PER or APP/ST pairs regards the higher reduction of $T_{5\%}$ value due to the carbon source (**Figure 4a** and **Table 4**); indeed, as already reported in the literature, the presence of hydroxylated groups catalyzes the degradation of polyamides [17].

In order to complete the information about the effect of the FR formulations under investigation on PA 10,10 thermal behavior, PCFC measurements were carried out. Indeed, very recently, our group has demonstrated that these two techniques can be combined for describing the thermal behavior of a polymer in a more detailed manner with respect to thermogravimetry only [18]. Although these measurements are performed at different heating rates (namely, 10 and 60°C/min for TGA and PCFC, respectively), the TG, dTG and HRR curves can be overlapped for better describing what occurs when a polymer degrades, as clearly observable in **Figure 4**.

Usually, PCFC measurements point out the effect of a FR on polymer combustion, showing that its presence is able to significantly reduce its THR, HRR and corresponding peak (pkHRR). This finding has been observed also in the present work (**Table 4**, last three columns). As expected, APP, APP/PER and APP/ST pairs significantly reduce PA 10,10 THR (-17%, -37% and -32%, respectively). A slight decrease of pkHRR has been registered for PA 10,10APP-PER and PA 10,10APP-ST, as well (-11% and -15%, respectively).

On the other hand, dTG and HRR curves (**Figures 4b** and **4c**) are perfectly superimposed and T_{max} and T_{pkHRR} values are almost comparable. These findings can be ascribed to the phenomena that are correctly observed in PCFC. Indeed, in these tests, the registered pkHRR reports only the combustion kinetics of the volatile species produced during polymer pyrolysis operated in the first step of this measurement: therefore, the two techniques describe the same phenomena. Thus, it is noteworthy that when TGA reveals the formation of a thermally stable residue for the presence of FR (regardless of its composition), PCFC detects the formation of a lower amount of volatile species produced by the same polymer. Indeed, the THR values of PA 10,10-based compounds are lower than that of unfilled PA 10,10.

In air, PA 10,10 decomposes through two degradation steps: the first is located between 457 and 471°C and can be related to the maximum weight loss (about 90 wt.-%); the second step, during which the just formed residue (about 9 wt.-%) is further oxidized at higher temperatures to CO and CO_2. In spite of this char-former feature of neat PA 10,10, the formed residue is not thermally stable and disappears, so that it is not found at 800°C. In the presence of APP, PA 10,10 thermal stability significantly decreases in air as this additive starts to decompose releasing phosphoric acid; however, at the same time, it promotes the formation of a thermally stable residue, according to the same mechanism mentioned above in nitrogen. In this case, the residue is about 30 wt.-% and decomposes beyond 600°C only; at higher temperatures, it further lowers up to 8 wt.-%, giving rise to CO and CO_2 (**Figure 5a**). In doing so, the $T_{5\%}$ and T_{max1} values of PA 10,10 are remarkably reduced, as evidenced in **Table 4** and **Figure 5b**. Conversely, T_{max2} is shifted toward higher temperatures. In the presence of PER or ST, PA 10,10 thermal behavior is the same already observed in the presence of APP only: indeed, once again, the presence of the FR system favors the formation of a higher thermally stable char at lower temperatures, reducing PA 10,10 $T_{5\%}$ and T_{max1} and increasing T_{max2} values (**Table 4**). From an overall consideration, all the samples have shown a higher final residue with respect to neat PA 10,10.

Table 4. Thermogravimetric and pyrolysis-combustion flow calorimetry data of PA 10,10-based compounds.

	TGA							PCFC		
Sample	Nitrogen			Air						
	$T_{5\%}$ [°C]	T_{max} [°C]	Residue [%]	$T_{5\%}$ [°C]	T_{max1} [°C]	T_{max2} [°C]	Residue [%]	THR [kJ/g]	pkHRR [W/g]	T_{pkHRR} [°C]
PA 10,10	425	468	0	410	457-471	539	0	32.6	720	467
PA 10,10APP	322	388	16	328	395	618	8	26.9	710	392
PA 10,10APP-PER	283	385	18	302	386	719	9	20.6	640	388
PA 10,10APP-ST	279	383	17	266	392	696	7	22.0	612	389

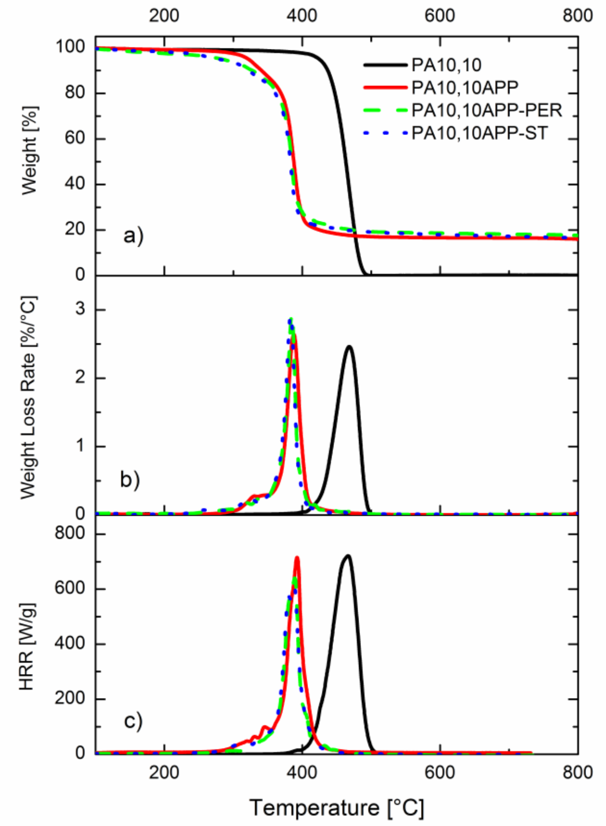

Figure 4. TG, dTG and HRR curves of PA 10,10-based composites in nitrogen.

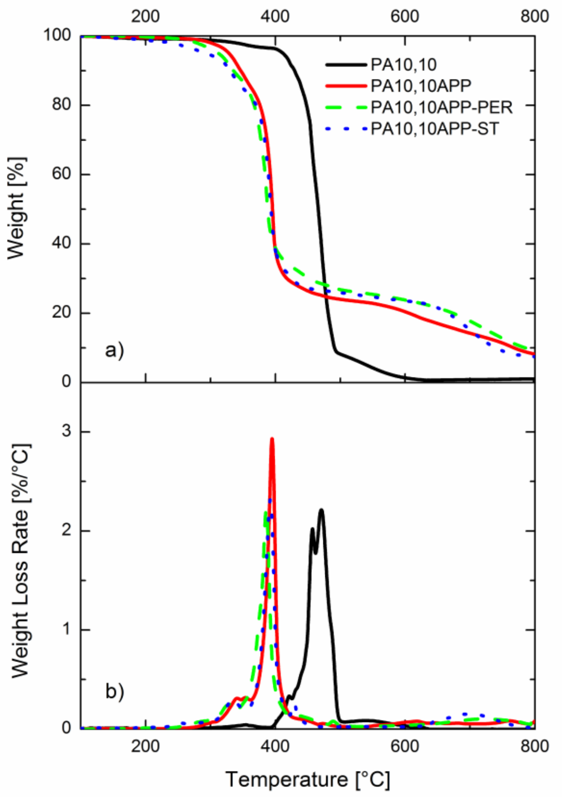

Figure 5. TG, dTG curves of PA 10,10-based composites in air.

3.4 Combustion tests of PA 10,10-based compounds

The combustion behavior of the samples under investigation has been assessed in terms of resistance to a heat flux of 35 kW/m^2 by using a cone calorimeter. **Table 5** presents the collected data.

As already discussed for TGA, the presence of APP, APP/PER or APP/ST affects the thermo-oxidation of PA 10,10, strongly reducing its $T_{5\%,}$ but promoting the formation of a thermally stable residue. The same trend has been observed during the pre-ignition phase and, as a consequence, on PA 10,10 TTI. Furthermore, analogously to what found in PCFC measurements, the presence of these FR additives significantly reduces PA 10,10 THR and increase the final residue. More specifically, APP has proven to be efficient as FR for PA 10,10 with this purpose, but at the same time seems to be responsible of a considerable increase of TSR (+62%) and CO yield (+69%). The addition of PER as carbon source does not enhance the performances of APP; conversely, it seems to worse them, as evidenced by the pkHRR value (833 vs. 735 kW/m^2 for PA 10,10APP-PER and PA 10,10APP, respectively). On the contrary, ST jointly cooperates with APP, further slightly reducing PA 10,10 pkHRR (712 vs. 1101 kW/m^2 for PA 10,10APP-ST and PA 10,10, respectively).

From an overall consideration, taking into account the experimental error, CO_2 yield is practically constant for all the investigated formulations. On the contrary, either APP alone or jointly combined with PER or ST drastically affects the total smoke release (TSR, **Table 5**) and CO yield. This trend is in agreement with what already observed in PA6 [17].

However, it is important to assess the ratio between CO_2 and CO yields as it represents an indicator of combustion efficiency: indeed, high ratios point out an efficient combustion while low ratios refer to inefficient combustion. Thus, as the CO_2/CO ratio is considerably lower for the compounds with respect to unfilled PA 10,10 (**Table 5**), this indicates that the FR formulations proposed here are efficient in hindering the combustion of the polymer, favoring the formation of thermally stable chars and reducing the amount of combustible volatiles released during combustion. This latter finding is in agreement with the results collected by TGA and PCFC and discussed above.

Furthermore, the effect of these additives on the residue at the end of tests (**Figure 6**) is worthy to comment: APP leaves a thin but dense residue, while its combination with PER or ST generates a more coherent and expanded swollen char.

Table 5. Cone calorimetry data of PA 10,10-based composites.

Sample	TTI	THR	pkHRR	ΔpkHRR	TSR	CO yield*	CO_2 yield*	CO_2/CO	Residue
	[s]	[MJ/m^2]	[kW/m^2]	[%]	[m^2/m^2]	[g/s]	[g/s]		[%]
PA 10,10	43±2	30±3	1101±55	-	226±11	0.00016	0.027	169	0
PA 10,10APP	21±2	22±2	735±37	-33	367±18	0.00027	0.023	85	18±1
PA 10,10APP-PER	27±2	23±2	833±40	-24	360±20	0.00034	0.018	53	17±1
PA 10,10APP-ST	22±2	23±2	712±36	-35	409±20	0.00043	0.022	51	18±1

* standard deviation=±5%

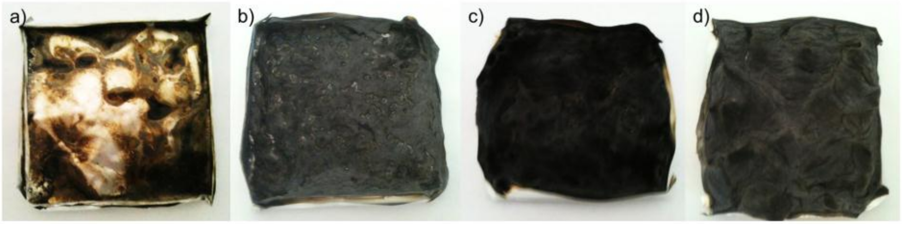

Figure 6. Pictures of cone calorimetry tests for PA 10,10 (a), PA 10,10APP (b), PA 10,10APP-PER (c) and PA 10,10APP-ST (d).

3.5 Combustion tests of PA 10,10 treated with UV-curable FR formulations

As already mentioned in the Introduction, the same intumescent constituents used in bulk have been further exploited for designing a new formulation to apply on PA 10,10 surface only, exploiting a UV-curing method. To this aim, these species have been mixed with a UV-curable waterborne acrylic resin (**Table 2**). Our purpose was to compare their performances when used in bulk or applied on the surface as a coating in order to fulfill a possible industrial exploitation.

Once again, the formulations applied on PA 10,10 surface have been tested under a 35 kW/m^2 heat flux by using cone calorimetry; the collected data are summarized in **Table 6**.

First of all, it is important to highlight the effect of the only UV-cured resin coating on PA 10,10 combustion. Indeed, it is responsible of PA 10,10 combustion anticipation (TTI decrease) and slowing down (pkHRR reduction), as well as of a high smoke production (TSR and CO yield increase). When the resin is partially mixed with APP, a further reduction of PA 10,10 pkHRR and higher final residues have been observed, but, at the same time, a strong increase of TSR and CO yield ascribed to APP only was attained. This finding is in agreement with what already observed in bulk. However, once again, CO_2/CO ratio of the coated samples, regardless of ingredient types, has proven to be lower than that of PA 10,10.

On the other hand, the presence of PER or ST has promoted the highest reduction of PA 10,10 pkHRR (458 and 451 vs. 1101 kW/m^2).

Table 6. Cone calorimetry data of PA 10,10 treated with UV-curable FR formulations.

Sample	TTI [s]	THR [MJ/m^2]	pkHRR [kW/m^2]	ΔpkHRR* [%]	TSR [m^2/m^2]	CO yield** [g/s]	CO_2 yield** [g/s]	CO_2/CO	Residue [%]
PA 10,10	43±2	30±3	1101±55	-	226±11	0.00016	0.027	169	0
R PA 10,10	27±2	37±3	695±35	-37	415±21	0.00019	0.030	158	2±1
R PA 10,10 APP	35±2	32±3	634±32	-42	734±37	0.00046	0.025	54	17±1
R PA 10,10APP-PER	39±2	30±3	458±23	-58	780±39	0.00041	0.024	58	17±1
R PA10,10 APP-ST	29±2	30±3	451±23	-59	765±38	0.00042	0.024	57	17±1

*Calculated with respect to PA 10,10
** standard deviation=±5%

As far as the THR trend is concerned, no significant differences have been found, although pkHRR was strongly reduced. Two main reasons can be suggested: first, the coating deposited on PA 10,10 surface is only able to slow down its combustion kinetics and not capable of protecting it. Second, these two parameters usually employed to describe the combustion of a polymer in cone calorimetry are not suitable in the present case. In our opinion, it is necessary to normalize THR and pkHRR parameters with respect to the mass of the tested specimens. Indeed, the presence of the resin with the other additives on PA 10,10 surface strongly increases the same specimen mass: thus, the compared data refer to two different amounts of combustible mass that can burn. The collected data reported in **Table 7** show how the mass can actually affect the THR and pkHRR values in cone calorimetry. The presence of the resin only reduces PA10,10 THR and pkHRR of 22 and 57%, respectively. Further reductions (31 and 60%, respectively) have been observed by partially replacing the resin with APP (**Table 2**); a certain joint effect between resin and APP is demonstrated by the values of ΔTHR/mass calculated with respect to PA 10,10. However, the best performances have been achieved providing the formulation with a carbon source (36 and 72% reductions of THR and pkHRR for both R PA 10,10APP-PER and R PA 10,10APP-ST samples). No differences have been observed between PER and ST: however, starch represents the optimal solution when a higher carbon content from bio-source in a FR formulation is desired.

In order to compare the performances of the two approaches investigated in the present study, THR and pkHRR values have been recalculated for the formulations used in bulk (last three rows of **Table 7**). Also in this case, the THR reductions have proven to be around 35% as in the case of the formulations applied on the polymer surface, but the pkHRR reductions were considerably lower.

Table 7. Main combustion parameters normalized to mass and comparison between bulk and surface approaches

Sample	THR/mass [MJ/m^{2}g]	ΔTHR/mass with respect to PA 10,10 [%]	ΔTHR/mass with respect to R PA 10,10 [%]	pkHRR/mass [kW/m^{2}g]	ΔpkHRR/mass [%]	ΔpkHRR/mass with respect to R PA 10,10 [%]
PA 10,10	15.1±0.8	-	-	520±26	-	-
R PA 10,10	11.7±0.6	-22	-	221±11	-57	-
R PA 10,10APP	10.4±0.5	-31	-11	205±10	-60	-7
R PA 10,10APP-PER	9.6±0.5	-36	-18	145±7	-72	-34
R PA 10,10APP-ST	9.7±0.5	-36	-17	148±8	-72	-33
PA 10,10 APP	10.0±0.5	-34	-	340±17	-35	-
PA 10,10 APP-PER	9.9±0.5	-34	-	363±20	-30	-
PA 10,10 APP-ST	9.5±0.5	-37	-	299±15	-42	-

4. Conclusions

The present work has clearly demonstrated that it is possible to provide flame retardant features to PA 10,10 either by melt-blending the polymer with intumescent FR formulations (consisting of ammonium polyphosphate, ammonium polyphosphate and pentaerythritol or ammonium polyphosphate and starch), or by coating the polymer with UV-curable mixtures containing the same additives. Starch has been further combined with ammonium polyphosphate in order to increase the carbon content from bio-sources.

From an overall point of view, the presence of all the three intumescent FR formulations within PA 10,10 has promoted a strong sensitization of the polymer degradation, as assessed by TGA, significantly increasing, at the same time, the residues at high temperatures. PCFC and cone calorimetry tests have shown that the FR formulations are able to reduce THR and pkHRR, but, conversely, they lower TTI and increase the smoke production (namely, TSR and CO yield). However, their CO_2/CO ratios are significantly lower than that of PA 10,10. Finally, a similar trend of the main combustion parameters (assessed by cone calorimetry, without taking in consideration the effect of specimen mass), has been found when the FR additives were embedded in a UV-curable formulation coated on PA 10,10. On the contrary, by normalizing the combustion parameters to the specimen mass, the surface approach has clearly demonstrated a higher FR potential than melt-blending. Indeed, notwithstanding a similar THR decrease, the reduction of pkHRR promoted by the presence of the coating was more considerable than that found with the same formulations in bulk (about -65 *vs.* -35%, respectively).

Acknowledgements

The authors wish to thank Ms. Aline Massy, Mr. Fabio Cuttica (for cone calorimetry tests), Mr. Andrea Messina (for PCFC tests), Mr. Alessandro Di Blasio (for SEM analyses) and RadiciGroup (for supplying PA 10,10).

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