

## Fire behavior and smoke emission of phosphate-based inorganic fire-retarded polyester resin

M. R. Ricciardi<sup>1</sup>, V. Antonucci<sup>1,2,\*</sup>, M. Zarrelli<sup>1</sup> and M. Giordano<sup>1,2</sup>

<sup>1</sup>IMCB—Institute for Composite and Biomedical Materials CNR, National Research Council, Piazzale Enrico Fermi, 1 Portici, Napoli Italy

<sup>2</sup>IMAST—Technological District on Polymeric and Composite Materials Engineering, P E. Fermi 1, Portici 80055, Italy

### SUMMARY

The fire behavior and the smoke emission of an unsaturated polyester resin modified by the addition of three phosphorus-based fire-retardant materials (ammonium polyphosphate (APP), silane-coated APP, and melamine pyrophosphate) at two concentration levels (20% w/w, 35% w/w) have been investigated. Scanning electron microscopy, Fourier transform infrared spectroscopy and optical microscopy analysis have been performed to verify the dispersion and the action mechanism of additives within the resin. Results from cone calorimetric tests demonstrated that the incorporation of the fire retardants at 35% w/w has a strong effect on flammability and smoke suppressant properties with respect to both the neat resin and the loaded systems at 20% (w/w). In particular, the smoke formation and smoke parameters are reduced by 50% and 80%, respectively, leading to the conclusion that APP can be used single-handedly without combination with specific smoke suppressors. Copyright © 2011 John Wiley & Sons, Ltd.

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KEY WORDS: unsaturated polyester; ammonium polyphosphate; melamine pyrophosphate; fire behavior

### 1. INTRODUCTION

Unsaturated polyester resins are widely used as matrix of composite materials for several industrial applications, such as naval, building, automotive, and transportation because of their low cost, easy processing, low density, and high strength to weight ratio. However, the typical polyester resins are highly inflammable and produce large quantities of smoke and toxic acid when burning, limiting their industrial use [1].

Therefore, to increase and exploit their commercial application, the main need is to produce flame-retardant systems with reduced fire hazard, achieving fire protection [2].

In general, the fire performance of thermoset materials has been improved by modifying the polymer itself and by using the corresponding halogenated resin in place of the traditional resin or adding mineral fillers, like alumina trihydrate (ATH) or proper flame-retardant materials (halogenated additives, ammonium salts, phosphorous materials) and smoke suppressors (zinc compounds, tin oxides, zinc stannates) [3–6]. In most cases, halogenated resins show better behavior in terms of ignition time and heat-release rate [7–9] than the halogen-free resins. Koo *et al.* [7] investigated the effect of fluorine, phosphorus, silicon, and sulfone groups in polymers on the flammability by cone calorimeter, showing that the incorporation of fluorine into the system's backbone increases the fire resistance of polymers. Lay and Gutierrez [8] have studied the fire behavior of halogenated and

\*Correspondence to: Antonucci Vincenzo, Institute for Composite and Biomedical Materials, National Research Council.

†E-mail: vinanton@unina.it

non-halogenated polyester and vinylester glass composites with and without halogen synergist, finding better properties for the halogenated composites especially those with halogen synergy. However, the main disadvantage of this solution is that a fire could create toxic and corrosive smoke. Thus, halogenated resins and halogen flame retardants can be used just for external parts. On the other hand, the introduction of mineral fillers like ATH in a polymer matrix can reduce effectively the fire hazards, but, because of the high load required, processing limitations and a significant decrease of the mechanical performance are observed. In addition, the smoke production is not always reduced. In fact, Scudamore [9] observed that ATH determines a delay of ignition time and heat-release rate of epoxy glass composites but without any effect on smoke production.

Therefore, the most effective and advantageous method to reduce the fire hazard of polymers is the incorporation of proper flame-retardant fillers that act by interfering with the radical flame reaction, changing the solid-state decomposition mechanism of the polymer and producing a barrier layer (char or glass) to the heat feedback [1]. These modifications affect generally the decomposition by interaction at the molecular level. The action of the flame-retardant materials can occur in the condensed or vapor phase or in both phases. For example, Atkinson *et al.* [3, 4] examined the effect of tin inorganic additives as flame retardants and smoke suppressors of halogenated polyester resins, crosslinked with styrene, finding that tin additives act by a combination of condensed and vapor phase mechanism, depending on both the halogen and the resin composition.

In general, phosphorus-based flame retardants influence the polymer behavior, acting in the condensed phase and in the gas phase [10]. Their efficiency depends on the chemical nature of the polymer, being more effective with polymers having high oxygen content, such as polyesters, polyurethanes, and epoxy. The phosphorous flame retardant is converted by thermal decomposition to phosphoric acid and, subsequently, to polyphosphoric acid, which esterifies and dehydrates the polymer with the formation of a carbonaceous layer having a glassy coating. This protective layer shields the polymer from the radiant heat and prevents its decomposition.

The most effective phosphorous flame retardants for unsaturated polyester resin are ammonium polyphosphate (APP) [11] and melamine pyrophosphate (MPP) [12]. These additives have been used alone or in synergy with other fillers. Several authors [10, 11, 13] have studied the degradation mechanisms of APP, which consists mainly of water and ammonia elimination leading to the formation of polyphosphoric acid at temperatures around 250 °C followed by the polyphosphoric acid evaporation and/or dehydration.

In particular, Hörold [10] has shown that low contents of APP and red phosphorus, in combination with low amount of ATH, improve the fire properties of polyester and epoxy resins for railway applications and guarantee the processability of the loaded polymer matrix. Nazarè *et al.* [14, 15] investigated the flammability properties of unsaturated polyester resins modified by the addition of nanoclay and different condensed-phase flame retardants, such as APP and melamine phosphate. In particular, to determine the nanoclay and flame-retardant content within the resin without processability problems, they performed preliminary cone calorimeter tests on a range samples having different percentages of nanoclays and flame retardants. They found that the clay loading level of 5% was the best concentration to guarantee the polymer curing and processability. In addition, because they observed slight differences in terms of fire behavior between the samples with 20% and 30% of the flame retardant, their studies were concentrated on formulations of 5% clay loading and 20% of flame retardant, finding that APP showed the best results compared with the other flame retardants (MPP and ATH), and the peak heat-release rate (PHRR) of the APP formulation had a reduction of around 70% with respect to the pure resin. In addition, they observed that in well-ventilated fire conditions, the partial replacement of APP with a smoke suppressor like zinc borate causes a slight enhancement of the flammability and smoke suppressing properties with respect to the formulation of 20% APP in an unsaturated polyester resin, concluding that APP itself is a good smoke suppressor.

In this work, a commercial unsaturated polyester resin has been modified by three different phosphorus-based flame retardants: APP, silane-surface-coated APP (S-APP) and MPP. Two concentration levels (20% and 35% by weight with respect to the pure resin) for all additives have been adopted to prepare the hybrid polymer system. The amount of APP and MPP has been selected with the aim of improving simultaneously both the flammability properties and the smoke production

of the polyester resin by just one type of flame-retardant material. Furthermore, because the processability of loaded matrix is a critical issue [16] that needs to be verified, preliminary rheological and calorimetric tests have been performed to measure the viscosity and cure condition variations determined by the incorporation of additives. The dispersion and the action of the fire retardants have been investigated by optical microscopy, scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) analysis. In addition, the flammability behavior and the smoke production of the neat polyester resin and the flame-retarded ones have been investigated by cone calorimeter tests, which enabled to compare the effect of APP and MPP during the burning of the unsaturated polyester resin.

## 2. EXPERIMENTAL

### 2.1. Materials

The investigated commercial resin is the unsaturated low-viscosity prepromoted polyester Arotran Q6530 (Ashland Inc., Milan, Italy), formulated for light resin transfer molding processes (RTM) and transportation applications. It cures at ambient temperature in few hours by adding methyl ethyl ketone peroxide (MEKP) catalyst (1–2%). The resin composition by weight from safety datasheet is 50.0–54.0% for the polymer, 42.7% styrene, 3.4% methyl methacrylate, and 0.2% cobalt compounds.

The flame retardants used in the work were Exolit AP740 by Clariant (Huerth Germany) and FR CROS 486 and BUDIT 311 by Budenheim (Budenheim, Germany). Exolit AP740 (APP) is a non-halogen white powder product based on ammonium polyphosphate, characterized by APP II crystalline phase. It develops its efficiency by the synergy of action of phosphorus and nitrogen. As reported in the datasheet, unlike the chlorine and bromine compounds, it is an intumescent flame retardant that enables the formation of carbon layer char on the surface of a material, which acts as a protective barrier and reduces the heat exchanges and the oxygen access causing a small quantity of smoke.

FR CROS 486 (S-APP) is also an APP-based system but is characterized by a silane-coated surface halogen-free long-chain phase II and a higher content of phosphorus (44%) than the previous APP (18–20%). It appears as a fine white powder and is less soluble in water and insoluble in organic solvents. BUDIT 311 (MPP) is a white powder mainly based on melamine pyrophosphate, which combines the synergistic effect of melamine and phosphorus compound.

Two concentration levels (20% w/w, 35% w/w) of three additives have been adopted. In particular, the fire-retardant resin systems at 20% (35%) have been prepared by mechanical mixing using an homogenizer ULTRA TURRAX 18 basic (IKA, Staufen, Germany) for 15 min (30 min) and then degassing for 15 min (30 min) to eliminate entrapped air. MEKP at 1% w/w was added to the mixture as cure initiator. Cure was performed for 90 min at isothermal temperatures (see Table I). Differential scanning calorimetry (DSC) tests coupled with rheological measurements allowed to assess the processability of the fire-retarded composite matrix. It was found that the incorporation of the additive increases both the resin viscosity and the gelation time. In fact at 30 °C, measured viscosity increases of two magnitude order and gel shift from 15 min to a maximum of 45 min. The higher gel-time value allows the processability of these fire-retarded resins that, hence, can be used to impregnate long fiber reinforcement in liquid infusion processes to manufacture composite systems.

Table I. Cure temperatures.

Sample	Cure temperature (°C)
Neat resin	85
APP (20%) composite	85
APP (35%) composite	95
Coated APP (20%) composite	85
Coated APP (35%) composite	95
MPP (20%) composite	95
MPP (35%) composite	100

APP, ammonium polyphosphate; MPP, melamine pyrophosphate.

The properties of the fire-retarded systems have been analyzed by using different experimental techniques, such as electronic scanning and optical microscopy to take information about the morphology of both additives and fire-retarded systems, FT-IR spectroscopy to outline the action mechanism of the selected flame retardants, and hence, cone calorimeter tests to investigate the fire behavior.

## 2.2. Methods

Scanning electron micrographs of neat resin, additive powder, 35% w/w fire-retarded composites, and after-burning residuals were taken by an E-SEM Quanta 200 microscope (FEI, Hillsboro, OR, USA). Furthermore, the morphology of the additives was studied through optical microscopy by using the polarized light optical Olympus BX51 Instruments equipped with a hotplate (Linkam, model THMS 600, Tadworth Surrey, UK). In particular, the powder of the three flame retardants was placed between two glass supports and heated at 10 °C/min up to 300 °C in order to analyze the microstructure evolution as function of temperature.

Fourier transform infrared analysis was performed by FT-IR Nexus (Nicolet; Thermo Scientific, Waltham, MA, USA) equipment at different temperature levels.

Thermogravimetric analysis (TGA) was carried out by TA-Q5000 (TA Instruments Ltd, West Sussex, UK) equipment at 10 °C/min up to 800 °C in air. The cone calorimeter measurements were performed by using a Fire Testing Technology Ltd. equipment according to the American Society for Testing and Materials E1354-04 procedure. Samples, with nominal dimensions of 100 × 100 × 3 mm<sup>3</sup>, were tested horizontally under an incident flux of 50 kW/m<sup>2</sup>. This level was chosen as it corresponds to the evolved heat during a medium-scale fire [13, 14]. Three samples were tested and results averaged.

## 3. RESULTS AND DISCUSSION

### 3.1. Optical and scanning electron microscopy

The morphology changes of the three additives due to temperature variations have been examined by optical microscope analysis from environmental temperature to 300 °C. Figures 1(a), (b), and (c) show the micrographs of the APP material at 25 °C, 200 °C, and 300 °C, which evidence a fine powder at ambient temperature: a more opened and expanded system at 200 °C indicated by the presence of white zones and the formation of bubbles at 300 °C indicative of the additive decomposition. This behavior has been confirmed by the DSC analysis that was performed at 10 °C/min from 10 °C to 280 °C. Figure 2 reports the DSC thermogram of the three additives where it is possible to observe some endothermic peaks. In particular, in the case of the APP, the first endothermic peak starts at 177 °C and is characterized by a peak area of 61.56 J/g. On the other hand, S-APP and MPP begin to melt at higher temperature values, absorbing lower heat (see Figure 2) than APP. Further, similar microscopy analysis on the silane-coated APP material and MPP system did not exhibit relevant morphological changes with increasing temperature. These results outline the higher effect of APP as flame retardant. In fact, the endothermic nature should decrease the temperature burning by enhancing the combustion-retarding effect as the area of the endothermic peak is larger [17].

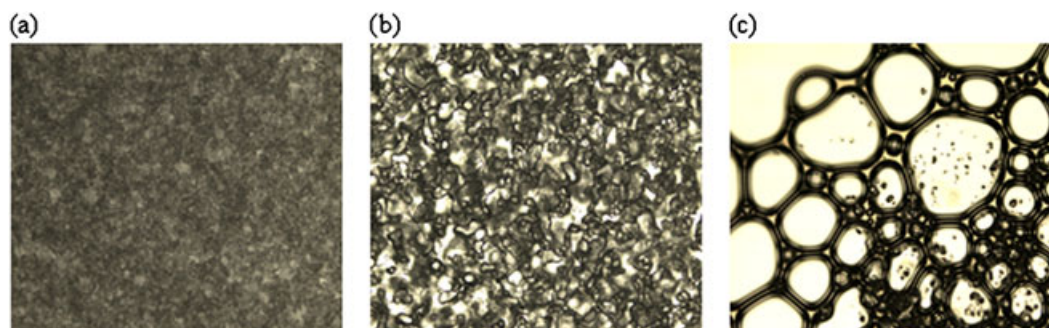


Figure 1. Micrographs of ammonium polyphosphate material: (a) at 25 °C, (b) 200 °C, and (c) 300 °C.

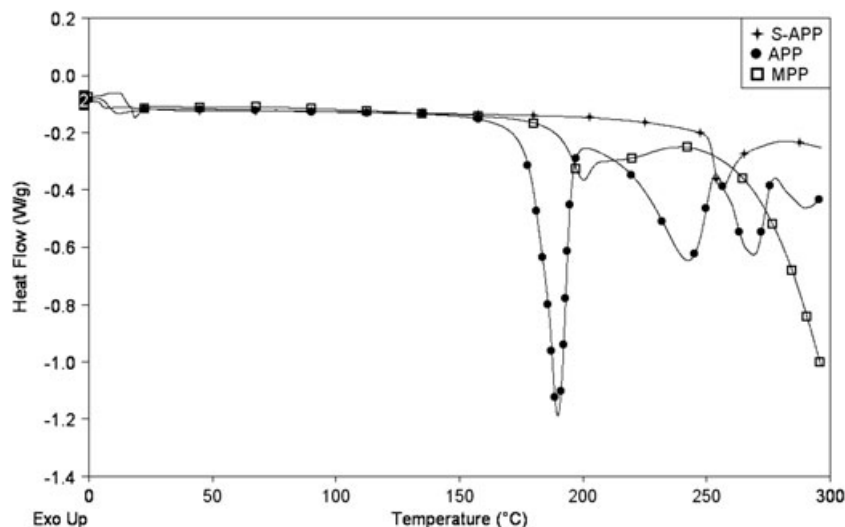


Figure 2. Differential scanning calorimetry thermogram of ammonium polyphosphate (APP), silane-coated APP (S-APP), and melamine pyrophosphate (MPP) material.

Further, the size morphology of the three additives within the resin has been verified by SEM that has been performed at first on the additive powder and then on the fire-retarded resin systems. Figures 3(a), (b), and (c) show the micrographs of APP, S-APP, and MPP, respectively. One should observe that the S-APP powder is characterized by more circular microspheres than APP, and MPP has a more compact structure, which is common for salts.

Figures 4(a), (b), and (c) report the micrographs of the loaded composites at 35% w/w of APP, S-APP, and MPP, respectively. For all analyzed samples, the additives show a uniform distribution within the hosting polyester resin and a particle diameter of about 20  $\mu\text{m}$ .

### 3.2. Thermogravimetric and Fourier transform infrared analyses

Thermogravimetric analysis scans were performed in air on the neat resin and on the 35% w/w fire-retarded composite samples. Figure 5 shows the derivative of thermogravimetric signals as function of temperature. It is possible to observe that the APP composite is characterized by more degradation steps than the neat resin and the other two composite systems related to the thermal decomposition of the APP material. In particular, an additional peak is noticed at 260  $^{\circ}\text{C}$  for the APP-based composite system, which is not evident for the neat resin and for the other fire-retarded resin systems. This first peak can be related to the APP decomposition by the production of phosphoric acid that converts to polyphosphoric acid, which enhances the cross-linking of polymer fragments to form a stable char [18]. Further, because the adopted APP is an intumescent fire retardant and its intumescence action is exhibited at temperatures lower than the degradation temperature of the resin, it should be more efficient than the other two fire-retardant additives in the foaming and swelling of the soft polymer and the subsequent formation of a char layer that insulates and protects the underlying composite material [19]. FT-IR analysis has been performed to identify the action mechanism of the selected fire-retardant materials. It is carried out on the neat resin, on the additive powder, and on the fire-retarded resin systems at environmental temperature and on the heat-treated materials at higher temperatures. In particular, the neat resin and the fire-retarded resin systems have been partially consumed by thermogravimetric tests in air and then analyzed by FT-IR at 200  $^{\circ}\text{C}$ , 300  $^{\circ}\text{C}$ , 350  $^{\circ}\text{C}$ , and 400  $^{\circ}\text{C}$ , whereas for the additives, the same analysis has been performed until 350  $^{\circ}\text{C}$ .

Table II reports the main peaks and the corresponding band of the FT-IR spectra obtained for the neat resin at environmental temperature and 350  $^{\circ}\text{C}$ . No peak changes have been observed as a function of temperature. At 400  $^{\circ}\text{C}$ , the resin sample was totally consumed, and hence, no significant peaks were observed in the FT-IR spectra.

The results relative to the FT-IR analysis for the APP additive are reported in Table III, where it is possible to notice a double peak at environmental temperature at 1382 and 1250  $\text{cm}^{-1}$  and a single

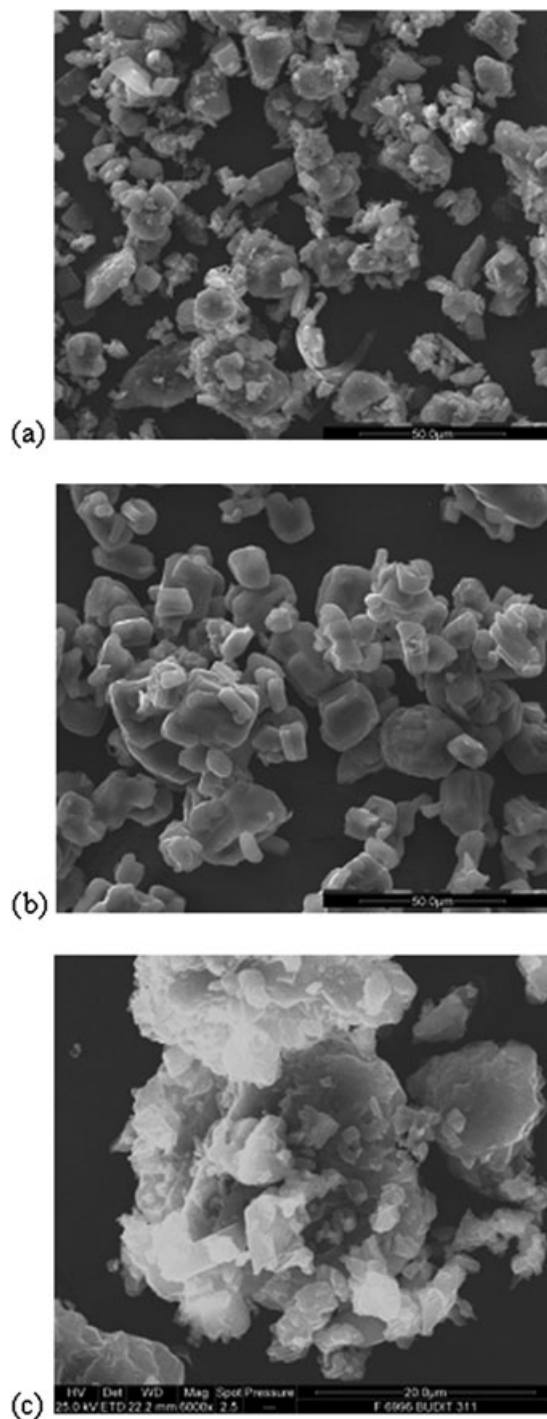


Figure 3. Scanning electron micrographs of the additive powder: (a) ammonium polyphosphate (APP), (b) silane-coated APP, and (c) melamine pyrophosphate.

peak at 300 °C at  $1250\text{ cm}^{-1}$ . In all cases, these peaks are relative to P=O bonds. However, the peak at  $1382\text{ cm}^{-1}$  includes ammonia  $\text{NH}_4^+$  that, because of the thermal decomposition, for temperatures greater than 250 °C, is eliminated together with water [10, 11, 13].

Table IV reports the FT-IR data for the other two additives, S-APP and MPP, which did not show any change in the analyzed temperature range and did not display relevant peaks at 350 °C. One should notice that the FT-IR spectra of S-APP did not exhibit the peak at environmental temperature at

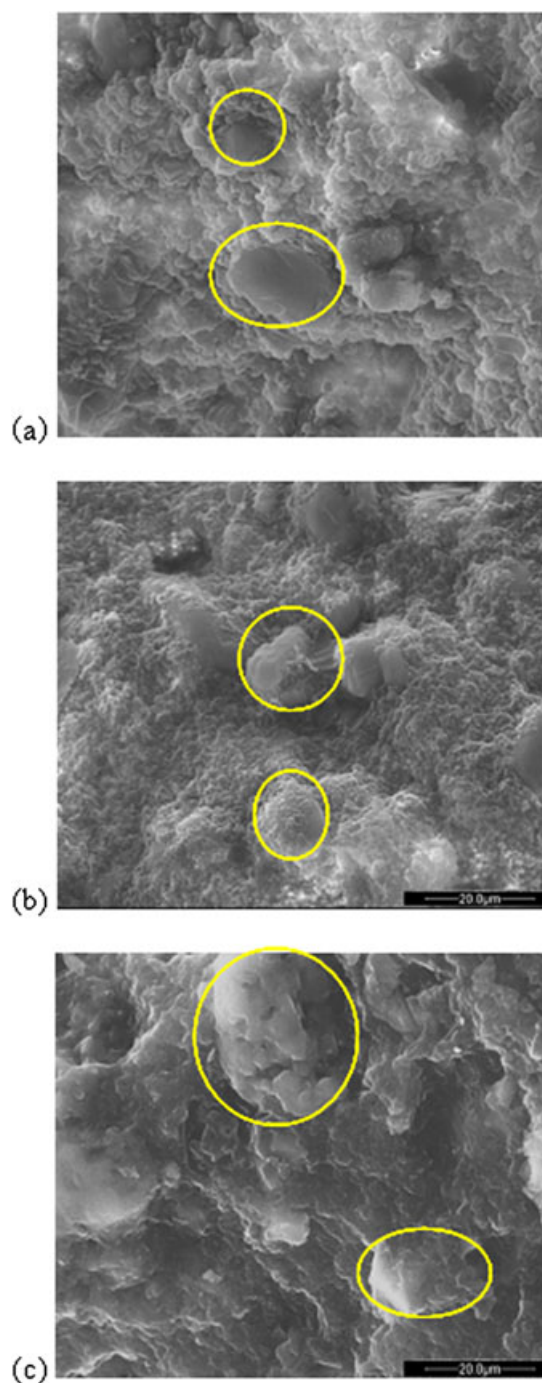


Figure 4. Scanning electron micrographs of fire-retarded composites at 35% w/w: (a) ammonium polyphosphate (APP), (b) silane-coated APP, and (c) melamine pyrophosphate.

$1382\text{ cm}^{-1}$  as observed for the APP additive, indicating a higher thermal stability for the S-APP and a different composition of the two commercial investigated ammonium polyphosphate additives, APP and S-APP.

The FT-IR spectra on the fire-retarded composite materials showed that the different amount of additive concentration (20, 35% w/w) did not affect the peaks position, just their intensity. Thus, the analysis here is reported for the composites with 35% w/w additives.

Table V reports the results of the FT-IR for the fire-retarded composite materials with APP and S-APP, whereas Table VI shows the results of the FT-IR for MPP composites at environmental

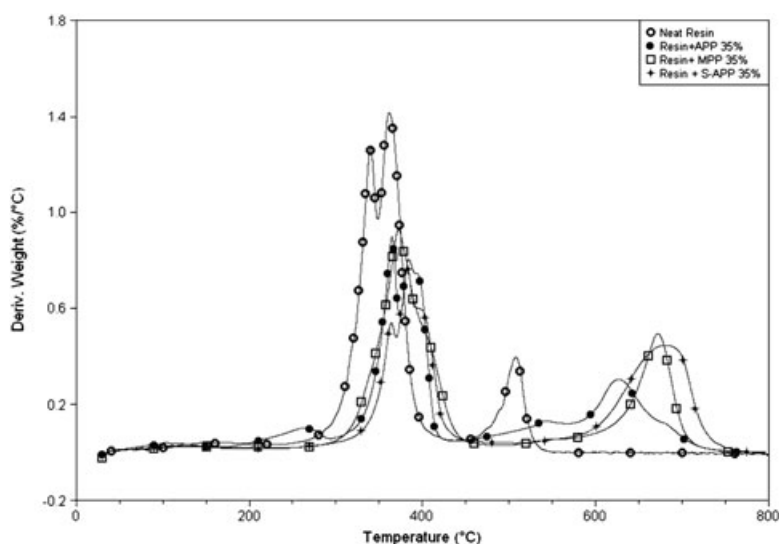


Figure 5. Derivative of thermogravimetric signals of neat resin and fire-retarded composites at 35% w/w.

temperature and 350 °C. The MPP-based composites were characterized by the same behavior in the whole temperature range (Table VI). On the other hand, the spectra of APP and S-APP composites at 350 °C resulted similar by displaying a peak at 992  $\text{cm}^{-1}$  relative to the P–O bond, which results from the polyphosphoric acid evaporation and/or dehydration to  $\text{P}_4\text{O}_{10}$  [11]. In addition, for both APP and S-APP composites, an additional peak in the range 1600–1460  $\text{cm}^{-1}$  relative to  $\text{NH}^+$  deformation vibration is visible.

Collected data indicate that S-APP and MPP are more stable thermally than APP. However, the TGA results reveal that APP has a greater interaction with the polyester resin by its intumescence behavior and higher reactivity by the ammonia elimination and the polyphosphoric acid formation. In fact, because of the silane coating, S-APP is characterized by both a lower water solubility and, on the other hand, a reduced reactivity as the temperature increases, behaving as an inert additive.

### 3.3. Cone calorimeter tests

The flammability behavior of the polyester resin with various flame-retardant formulations has been investigated by cone calorimeter tests. Figure 6 shows the heat-release rate versus time for the neat resin and the fire-retarded composites incorporating the flame retardant at 35% (w/w) level. The derived data from the cone calorimeter tests on the neat resin and the fire-retarded composites incorporating the flame retardant at 20% (w/w) and 35% (w/w) level are given in Table VII.

Addition of the flame retardants at 20% (w/w) reduces the PHRR of unsaturated polyester resin by 32% with S-APP and up to 52% with APP. A significant decrease of PHRR is observed for the fire-retardant composition of 35% (w/w). In particular, the greatest effect is found by the use of APP: APP and S-APP lower the PHRR of the polyester resin from 773  $\text{kW/m}^2$  to 225  $\text{kW/m}^2$  and 263  $\text{kW/m}^2$ , respectively. Further, the S-APP composites are characterized by the highest time to ignition (TTI) and residual mass (residue) because of the external surface layer that delays the material combustion by the

Table II. Fourier transform infrared spectroscopy data for the neat resin.

Band ( $\text{cm}^{-1}$ )	Assignment (25 °C, 350 °C)
4000–3000	Formation carboxylic acid
3500–2500	Stretching C–H and O–H
1734	C=O
1602	Stretching C=C conjugated with C=O
1495–1455	Deformation C–H to $\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)$
762–700	Polyester groups



Table III. Fourier transform infrared spectroscopy data for the ammonium polyphosphate additive.

Band (cm <sup>-1</sup> )	Assignment (25 °C)	Assignment (300 °C)
3500–3000	Bending vibration O–H and N–H	Stretching NH
1700–1450	Stretching NH	Stretching NH
1250	Double peak P=O	Single peak P=O
1110–930	P–O	P–O
815	P–O–P	P–O–P

Table IV. Fourier transform infrared spectroscopy data for the silane-coated ammonium polyphosphate (S-APP) and melamine pyrophosphate (MPP) additives.

S-APP		MPP	
Band (cm <sup>-1</sup> )	Assignment (25 °C, 300 °C)	Band (cm <sup>-1</sup> )	Assignment (25 °C, 300 °C)
3500–3000	Ammine group	3500–3000	Presence of melamine with NH <sub>2</sub> and NH <sub>3</sub> stretching
2892	Stretching PO–H	1689	Bending NH <sub>2</sub>
2500	P–H	1676	Stretching C=C
1700	Stretching P–OH	1520	Bending NH <sub>3</sub>
1434	Bending N–H	1200	P=O
1200	P=O		
1015	P–O bond		
884–800	Bending P–H		

Table V. Fourier transform infrared spectroscopy data for the ammonium polyphosphate (APP) and silane-coated APP (S-APP) composite.

Band (cm <sup>-1</sup> )	Assignment (25 °C)	Assignment ( <i>T</i> = 350 °C)
3200–2800	Ammine group	Ammine group
1733	C=O	C=O
1600–1460		NH <sup>+</sup> deformation vibration
1455	Bending Ammine group	Bending ammine group
1250	P=O	P=O
992		P–O
700	Polyester group	Polyester group

Table VI. Fourier transform infrared spectroscopy data for the melamine pyrophosphate composite.

Band (cm <sup>-1</sup> )	Assignment ( <i>T</i> amb, 350 °C)
3500–3000	Ammine
1728	C=O carbonyl group
1520	Ammonium salts
1246	P–O
1165	C–N
700	Polyester group

emission of non-combustible gasses, which form a blanketing gas layer and prevent the access of oxygen to the substrate. Moreover, the fire growth rate index, which is defined as the ratio of PHRR and the time at which PHRR occurs (TTP), is significantly reduced for the APP composites from 4.55 kW/m<sup>2</sup> s to 2.14 kW/m<sup>2</sup> s (at 35% w/w of APP content).

The cone calorimeter measurement provides information on the smoke generation of analyzed samples in well-ventilated conditions. Table VIII reports the main smoke-emission data that can be

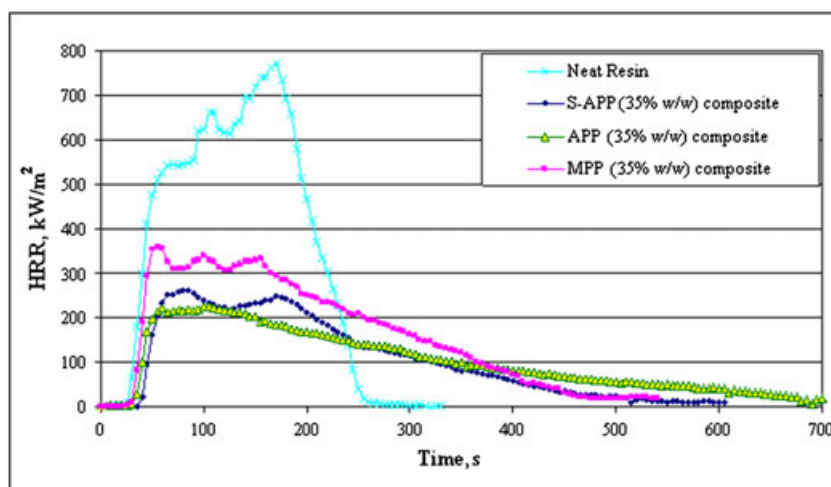


Figure 6. Heat-release rate (HRR) versus time for the neat resin and the fire-retarded composites at 35% w/w.

derived by a cone calorimeter test: the specific extinction area (SEA,  $\text{m}^2/\text{kg}$ ), the total smoke released (TSR), the smoke parameter (SP), and the smoke factor (SF).

The SEA is defined as the total obscuration area per unit mass of sample consumed in the fire and is generally expressed as Avg. SEA over time. It is a measure of the smoke amount being produced per unit mass of specimen burnt. The cone calorimeter expresses smoke production rates as the smoke obscuration produced per unit area of sample ( $\text{m}^2/\text{m}^2$ ). TSR is the cumulative smoke yield over the sustained flaming time. SP is the product of the PHRR and the SEA, whereas SF is the product of PHRR and TSR. From the analysis of the above parameters, it can be observed that the formulation with 20% (w/w) of APP shows slight reduction in TSR value compared with the pure resin, whereas significant reductions in SP and SF values are found. Regarding the composites with MPP, it can be noted that, except for the SP, no significant improvements are attained by increasing the additive content from 20% (w/w) to 35% (w/w). However, superior smoke suppressant properties are generally shown from all formulations at 35% w/w, especially for the APP composite.

Finally, SEM observations have been performed on the final residual samples including the additives at 35% (w/w). Figures 7(a), (b), and (c) show the scanning electron micrographs of the composite materials incorporating APP, S-APP, and MPP, respectively. The APP-based material is characterized by an evident char layer that covers a non-porous lamellar structure. Conversely, the topography of the silane-coated APP composite is quite different being slightly porous and simultaneously compact. Lastly, large pores distinguish the morphology of the MPP-based material residual. Therefore, the morphology analysis of the burned samples indicates that the APP-based composite is characterized by a better quality of char responsible of the good combustion behavior.

Table VII. Cone calorimeter results.

Sample	TTI	PHRR	TTP	THR	FIGRA	Residue
	s	$\text{kW}/\text{m}^2$	s	$\text{MJ}/\text{m}^2$	$\text{kW}/\text{s}$	%
Neat resin	11	773	170	113.2	4.55	1
APP (20%) composite	20	372	95	84.4	3.92	16
APP (35%) composite	29	225	105	70.7	2.14	27
Coated APP (20%) composite	28	521	140	84.0	3.72	19
Coated APP (35%) composite	37	263	80	64.6	3.29	38
MPP (20%) composite	28	424	115	85.1	3.69	14
MPP (35%) composite	26	360	55	87.3	6.54	15

APP, ammonium polyphosphate; FIGRA, fire growth rate index; MPP, melamine pyrophosphate; PHRR, peak heat-release rate; TTI, time to ignition; TTP, time at which PHRR occurs; THR, total heat released.

Furthermore, because significant differences have been found between the samples with 20% and 35% of the flame retardant in terms of fire behavior and smoke production, the addition of APP at 35% (w/w) should be adopted both as flame retardant and smoke suppressant for the analyzed unsaturated polyester resin.

#### 4. CONCLUSION

The fire behavior of an unsaturated commercial polyester resin modified by the incorporation of three different phosphorus-based fire-retardant materials at two different concentrations (20% and 35% w/w) has been investigated experimentally. These content levels have been selected after preliminary DSC and rheological tests, which demonstrated the processability of fire-retarded hybrid resins. The dispersion of the three fire retardants, APP, S-APP, and MPP, has been verified by SEM observations. FT-IR analysis on the neat resin, the flame retardants and the hybrid composite evidenced a higher thermal stability for S-APP and MPP additive powders than for APP. Conversely, APP seems to be more reactive and have more interaction with the polyester resin. In fact, the TGA tests showed that the APP composite is characterized by more degradation steps than the neat resin and the other two composite systems, which can be related to the thermal decomposition and intumescence behavior of the APP material occurring at temperature levels below the degradation temperature of the neat resin. Further, the optical microscopy analysis at high temperature on the additive powders has evidenced a melting phenomenon for the APP material associated to the bubbles formation. This behavior has been confirmed by the DSC analysis that displayed larger endothermic peaks for the APP at lower temperature values than the endothermic peaks of S-APP and MPP. From these experimental results, it is possible to conclude that APP has a higher effect as flame retardant for the investigated polyester resin because of its decomposition mechanism, intumescences, and endothermic nature that should provide better capability to reduce the composite temperature burning and to efficiently form a good-quality char.

The combustion properties and the smoke emission of the neat resin and the hybrid materials have been studied by cone calorimeter, which provides useful information on the material behavior during a real fire scenario under well-ventilated conditions. Cone calorimeter results evidence slight differences between hybrid composites incorporating the MPP additive at 20% and 35%. Conversely, the composites based on the APP additives at 35% (w/w) have superior performances in terms of both flammability behavior and smoke emissions with respect to the neat resin and composites at 20% (w/w). In fact, the formulation incorporating the S-APP at 35% (w/w) showed the lowest values of TTI, THR (Total heat released), and residual mass. On the other hand, the composites with the non-coated APP at 35% (w/w) were characterized by the highest reductions of PHRR (70%) and smoke-release parameters: TSR (50%), SP (78%), and SF (85%). Thus, it can be concluded that APP can be adopted without combination with specific smoke suppressor materials. Finally, SEM observations on the burned samples confirmed that the APP-based composite is characterized by a better quality of char that is responsible for the good combustion behavior.

Table VIII. Smoke emission data.

Sample	Avg. SEA	TSR	SP	SF
	m <sup>2</sup> /kg	m <sup>2</sup> /m <sup>2</sup>	MW/kg	MW/m <sup>2</sup>
Neat resin	773 ± 43	3941 ± 210	597.53 ± 41	3046.39 ± 180
APP (20%) composite	809 ± 48	3715 ± 150	300.95 ± 37	1381.98 ± 85
APP (35%) composite	577 ± 35	1965 ± 108	129.83 ± 27	442.13 ± 54
Coated APP (20%) composite	765 ± 41	3215 ± 142	398.57 ± 39	1675.02 ± 92
Coated APP (35%) composite	690 ± 40	2130 ± 133	181.47 ± 29	560.19 ± 78
MPP (20%) composite	729 ± 42	3321 ± 184	308.95 ± 36	1407.44 ± 91
MPP (35%) composite	512 ± 34	3300 ± 181	184.29 ± 27	1187.73 ± 82

APP, ammonium polyphosphate; MPP, melamine pyrophosphate; SEA, specific extinction area; SF, smoke factor; SP, smoke parameter; TSR, total smoke released.

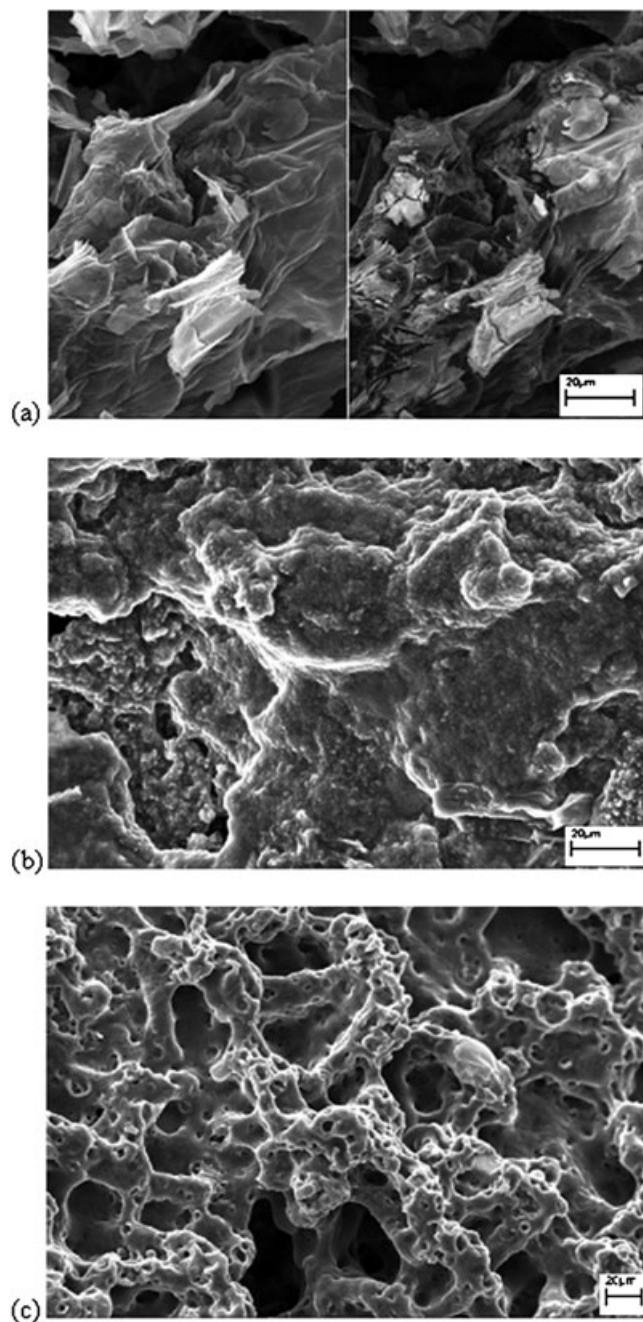


Figure 7. Scanning electron micrographs of fire-retarded (35% w/w) composite residual: (a) ammonium polyphosphate (APP), (b) silane-coated APP, and (c) melamine pyrophosphate.

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