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Effect of aryl phosphates on toxicity of combustion gases of flame-retardant polycarbonate/acrylonitrile butadiene styrene blends according to EN 45545 railway standard

Alberto Sánchez  | Sara Villanueva 

TECNALIA, Basque Research and Technology Alliance (BRTA), Azpeitia (Gipuzkoa), Spain

Correspondence

Alberto Sánchez, TECNALIA, Basque Research and Technology Alliance (BRTA), Área Anardi 5, 20730 Azpeitia (Gipuzkoa), Spain.
Email: alberto.sanchez@tecnalia.com

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Summary

In this study, the toxicity of combustion gases of polycarbonate/acrylonitrile butadiene styrene (ABS) blends that include aryl phosphates as flame-retardants (FRs) was analyzed according to the European railway standard EN 45545-2 (NBS chamber + FTIR). FRs have a significant influence on the evolution of the toxicity of gases generated during the combustion process. In the experiment, the asphyxiant hydrogen cyanide (HCN) was detected at the beginning of combustion (4 min of testing) as a product of ABS degradation. CO was generated throughout the test (8 min) because of the incomplete combustion of both the ABS and PC fractions. The presence of aryl phosphates promoted the inhibition of the flame. The reaction of PO-radicals in the gas phase resulted in OH-scavenging and a higher release of HCN and CO. The results suggest that aryl phosphates act in the first 4 min and do not have an effect later. FRs with lower thermal stability exhibited lower heat release and flame propagation but generated more toxic gases. This effect is attributed to the higher activity of the flame-retardant in the gas phase. Further, additional fire performance parameters, including thermal stability (thermogravimetric analysis), flammability (UL94), and heat and smoke generation (cone calorimeter), were studied. It was found that aryl phosphates reduced the fire hazard, prevented the spread of the flame, reduced heat generation, increased the time to ignition, and, at the same time, promoted the emission of toxic gases that differ in function of the selected flame-retardant.

KEYWORDS

aryl phosphates, EN 45545, flame-retardant PC/ABS, polymer composites, toxicity of gases

1 | INTRODUCTION

Polycarbonate/acrylonitrile butadiene styrene (PC/ABS) blends are engineering thermoplastic compounds widely used in different sectors owing to their excellent features such as ease of processing, low temperature ductility, excellent impact resistance, and good heat stability. Flame-retardant PC/ABS (FR PC/ABS) grades are used

mostly in electrical engineering, automotive, and rail vehicle interiors, where flame retardancy is a key requirement.

Traditionally, halogen-containing FRs were commonly used to protect PC/ABS products.¹ However, certain European Union regulations on the electrical sector (WEEE and RoHS) combined with increasing concerns over the toxicity of generated smoke in case of fire, have progressively led to their replacement by less harmful

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halogen-free systems. Phosphorus-containing FRs are one of the most prominent alternatives,^{2,3} among which organophosphate esters play a major role.⁴⁻⁷ Typically, aryl phosphates provide sufficient flame retardancy, reaching a V-0 rating in the UL94 test at a level of 8–15 wt% of loading in PC/ABS.

Triphenyl phosphate (TPP), resorcinol bis (diphenyl) phosphate (RDP), and bisphenol A bis (diphenyl) phosphate (BDP) are effective FRs in PC/ABS.^{2,3,8} In the combustion process, condensed- and gas-phase modes of action are suggested for these aryl phosphates.^{9,10} The TPP and RDP were studied in polycarbonate by Jang and Wilkie.¹¹ Murashko and Levchik focused on the condensed phase mechanisms of RDP in PC and PC/ABS.¹²⁻¹⁴ More recently, Pawlowski et al. investigated TPP, RDP, and BDP in PC/ABS blends.^{9,15,16} These studies concluded that TPP acts mainly in the gas phase through flame inhibition owing to its high volatility and low decomposition temperature. RDP and BDP act mainly through flame inhibition, together with charring reactions in the condensed phase.

Previous studies have shown that FRs that decompose close to the degradation temperature of PC promote char formation in the pyrolysis zone.^{9,17,18} A higher interaction in the condensed phase can be promoted by matching the degradation temperature of the flame-retardant with that of the PC. This is possible by varying the structure of the bridging unit or the end-group of aryl phosphate oligomers.¹⁷

The vapor-phase fire retardation effect of aryl phosphates is considered to be identical to that of traditional halogen-based FRs. The phosphorus species released in the gas phase interact with the H/OH-radicals in the flame, thereby reducing heat generation (flame poisoning).^{19,20} These vapor-phase reactions affect smoke generation, in addition to a reduction in the generated heat.

Despinasse and Scharrel^{6,21} studied the synergistic effect of two aryl phosphates, BDP and hydroquinone bis (diphenyl) phosphate (HDP), in terms of pyrolysis and fire residues as well as the effective heat of combustion. They attributed the higher thermal stability of the PC/ABS + BDP/HDP blends to the transesterification of oligomeric phosphate, yielding stable intermediate products.

Previous studies have focused on analyzing the main parameters of the combustion process, heat, and smoke release; however, toxicity has not been studied in detail. The toxicity of the generated smoke depends on the amount of material burned, the released species, the individual toxicity of each combustion product, and the duration of exposure. Nowadays, the increasing concern regarding the toxicity of gases generated during a fire event has resulted in extremely restrictive regulations, such as the recently developed EN 45545 railway standard. Within this regulation, the estimation of fire toxicity is limited to toxic products considered most significant in causing incapacitation and death among fire victims. These consist of asphyxiating gases (CO, HCN, and CO₂) and irritants, including acid gases (HBr, HCl, and NO_x).

In this study, smoke toxicity evaluation of FR PC/ABS blends, including aryl phosphates, was carried out based on Fourier-transform infrared spectroscopy (FTIR) measurements of selected fire effluents (NBS-FTIR, EN 45545-2 Annex C). In addition, a complete characterization of flammability (UL94), combustion process (heat release related parameters using the cone calorimeter method, according to

ISO 5660-1), and smoke opacity analysis (based on the single-chamber smoke test according to ISO 5659-2; NBS chamber) was carried out. Finally, other key properties, such as mechanical performance and thermal stability, were evaluated.

2 | EXPERIMENTAL

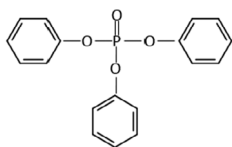
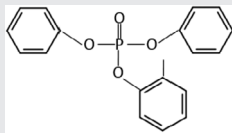
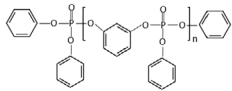
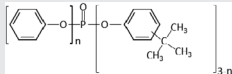
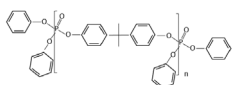
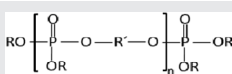
2.1 | Materials

Six aryl phosphates were evaluated in FR PC/ABS formulations (FR PC/ABS) in a proportion of 10 wt%. The influence of the presence of an antidripping agent, polytetrafluoroethylene (PTFE), was also investigated because of the potential toxicity of the evolved gases. The chemical structures of the different FRs are listed in Table 1. The PC/ABS ratio was held constant at 8:1 for all blends. The ABS employed was MA 221 from LG and the PC was Lexan 105 from Sabic. The FRs were TPP from polymer additives; RDP, butylated triphenyl phosphate (BTPP), and fyroflex Sol-DP aryl phosphate (Sol-DP) from ICL-IP; BDP from Adeka Palmarole; and cresyl diPhenyl phosphate (CDP) from Lanxess.

2.2 | Test specimen preparation and characterization

Polymers and additives were compounded and granulated using a twin-screw corotating extruder machine (APV: 19 mm; L/D: 25), with a throughput of 5 kg/h at a temperature profile of 230-250-250-250-210°C and a rotation speed of 80–100 rpm.

TABLE 1 Chemical structure of studied aryl phosphates

Reference	Form	Formulation
TPP	Flakes	
CDP	Liquid	
RDP	Liquid	
BTPP	Liquid	
BDP	Viscous liquid	
Sol-DP	Solid	

Prior to being introduced into the extruder, polymers were dried for 4 h at 120°C for PC and at 80°C for ABS.

Test specimens of PC/ABS compounds were obtained via injection molding using a Battlefield Plus 35 (diameter: 18 mm; L/D: 21) using barrel temperature of 230°C, mold temperature of 80°C, and speed of 240 mm/s.

Fire propagation tests were carried out according to the standard UL94 specifications (Underwriters Laboratories Inc.), which are now harmonized with IEC 60707, 60 695-11-10, 60 695-11-20, and ISO 9772 and 9773. The test specimens were 1.6 mm thick, 125 mm long, and 13 mm wide.

An NBS smoke density chamber (FTT, UK) coupled with FTIR was used to analyze smoke density (ISO 5659-2: plastics—smoke generation—Part 2: determination of optical density by a single-chamber test) and toxicity (EN 45545-2, railway applications—fire protection on railway vehicles—Part 2: requirements for fire behavior of materials and components). Eight different critical gases were analyzed during the combustion process: CO₂, CO, HCN, HF, HCl, HBr, SO₂, and NO_x.

The analysis of the collected spectrum during the test determined the concentration of gases.

The reference limits of the dangerous concentrations of each gas are provided in Table 8. These reference values are based on the immediately dangerous to life and health (IDLH) values, recognized as a limit for personal exposure to the gas component by the National Institute for Occupational Safety and Health (NIOSH).

For each gas listed in the table, the concentration values present in the smoke chamber at 240 and 480 s were calculated. The toxicity of smoke is defined in terms of the conventional index of toxicity (CIT).

$$\text{CIT}_G = 0.0805 \times \sum_{i=1}^{i=8} \frac{C_i}{C_i}$$

where, the first term (0.0805) is the precursor and defines a burning model, a scaling factor that includes the burning area and enclosure volume from the smoke chamber to a fire in a train compartment,

C_i is the concentration measured in mg/m³ of gas i in the smoke chamber,

C_i is the reference concentration (threshold) measured in mg/m³ of gas i .

Test specimens measuring 75 × 75 × 1.5 mm³ were prepared. These specimens were subjected to a heat flux of 50 kW/m² for 10 min without a pilot flame, following the most extreme conditions to which samples can be subjected in this test according to the standard. The test was carried out by triplicate, and the registered result is the average value.

To characterize the forced-flaming behavior, a cone calorimeter (FTT, UK) was used (ISO 5660-1 standard). The applied external heat flux was 50 kW/m², and the samples (100 × 100 × 3 mm³) were tested horizontally in a frame. Each specimen was wrapped in aluminum foil and exposed to an external flux. The test was carried out by triplicate, and the registered result is the average value.

A thermogravimetric analysis apparatus (TGA) from TA instruments were used to investigate the thermal decomposition of both the

FR additives and FR PC/ABS compounds. All measurements were performed under air and nitrogen conditions at a heating rate of 10°C/min.

Vicat softening temperatures were obtained according to ISO 306 using an Öko Vicat/HDT-tester from COESFELD. The applied method was according to the VST/B50 standard.

3 | RESULTS

3.1 | Vicat temperature

The introduction of different FRs and antidripping agent in the PC/ABS formulations have an influence on the softening of the material, as can be observed in the Vicat temperature of all the studied compounds. The results are shown in Figure 1. The addition of the antidripping agent, PTFE, caused a slight decrease in the softening temperature of the PC/ABS mixture. However, when FRs were added to the PC/ABS + PTFE blend, the Vicat temperature decreased significantly. This effect is more remarkable with TPP and CDP (FRs of lower molecular weight) but less remarkable with BDP and Sol-DP. Both, antidripping agent and FRs, have a “plasticizing” capacity, which is more remarkable in the case of FRs

3.2 | TGA analysis

The TGA curves (Figures 2 and 3) show that the degradation/volatilization of phosphorous compounds is unimodal, within a narrow range of temperatures; details of the TGA results are summarized in Tables 2 and 3. FRs can be divided into two groups. Those with greater thermal stability (RDP, BDP, and Sol-DP) and those with lower thermal stability (CDP, TPP, and BTPP). The thermogravimetric curves did not undergo significant variation when the heating ramp was carried out in nitrogen or air. The results showed no significant differences in the thermal stability when the antidripping agent, PTFE, was added to the PC/ABS polymer. Instead, when different FRs were added to the PC/ABS + PTFE formulation, significant differences were observed. Formulations that contain TPP and BTPP showed lower thermal stability, while those containing BDP and RDP were more thermally stable. These results suggest that TPP, CDP, and BTPP could act mainly in the gas phase through flame inhibition, owing to their high volatility and low decomposition temperature. RDP, BDP, and Sol-DP could act through flame inhibition, but they also could promote some charring effect in the condensed phase by overlapping the degradation temperature of FRs and neat PC/ABS.¹⁷

3.3 | Fire behavior—combustion

The fire spread and flammability of neat PC/ABS and FR PC/ABS compounds were examined using UL94 tests, and the results are listed in Table 4. PC/ABS blends without FRs reached the V2 classification. When an antidripping agent, PTFE, was added to the plain PC/ABS

blend, the formulation burned up to the clamp; thus, the antidripping agent fulfilled its function by reducing the polymer dripping. This effect is responsible for the inferior performance compared to the neat PC/ABS; therefore, UL94 rating was not obtained. At a FR loading of 10 wt%, all the samples achieved a V0 rating, except for the one filled with CDP. This sample displayed dripping behavior during the second flame application, and it ignited the absorbent cotton; consequently, a V2 rating was reached. This effect is attributed to the lower phosphorous content (CDP: 9.1%) than in other FRs (TPP: 9.5%; RDP: 10.7%) and also to the plasticizing effect shown in the Vicat temperature analysis, which can promote dripping of the melted polymer (Figure 1).

A cone calorimeter (FTT, UK) was used to characterize the forced-flaming behavior according to ISO 5660-1.

The results of the cone calorimeter experiments related to heat generation are shown in Table 5 and plotted in Figure 4. Generally, the time to ignition (TTI) increases when FRs are added to plain

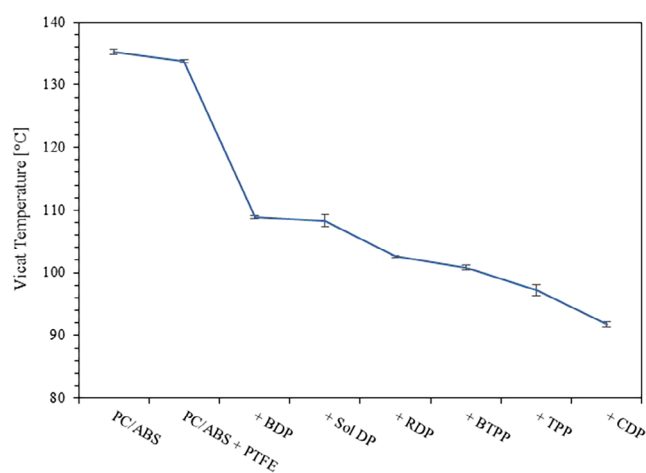


FIGURE 1 Evolution of the Vicat softening temperature of FR PC/ABS blends in function of the flame-retardant

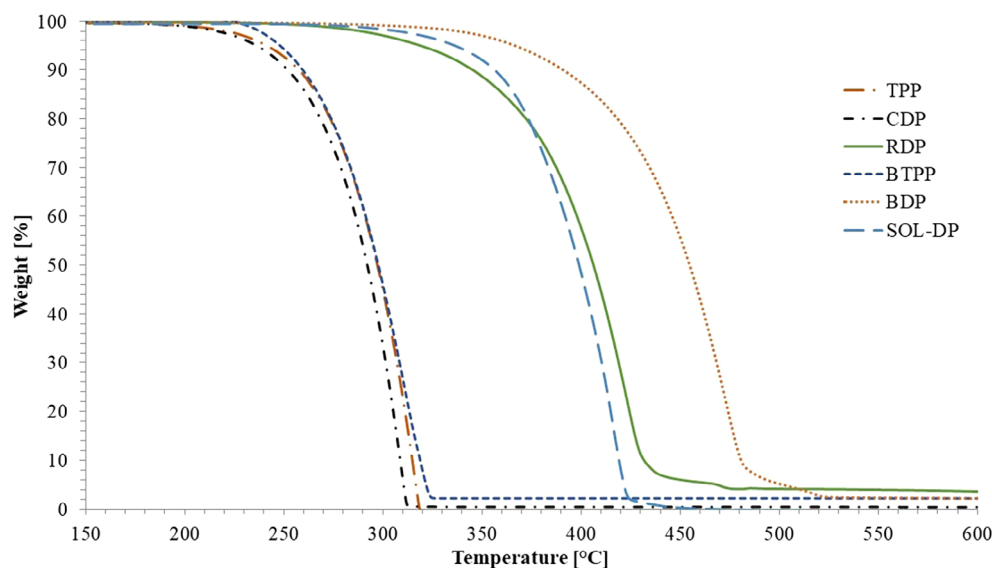


FIGURE 2 TGA thermogram of the different flame-retardants measured under air conditions at 10 °C/min

PC/ABS. The heat release rate (HRR) curves are typical of char-forming polymers such as PC, with an increase in the HRR at the beginning of burning.²²⁻²⁴ The char then forms and acts as a barrier, protecting the underlying material from heat. Mass transfer from the pyrolysis zone to the flame was also hindered by the char barrier. Therefore, a reduction in HRR was induced. The peak of HRR (PHRR) determines fire propagation. It represents the maximum rate of heat released by the flaming combustion of the material. The addition of the FRs in PC/ABS clearly reduced the PHRR compared to neat PC/ABS and PC/ABS+PTFE, which was independent of the FR composition. A reduction of approximately 50% was observed with TPP, BTPP, and BDP. The fire hazard of a material is determined by a combination of factors, among which the most important are its ignitability and the amount (and rate) of heat released when it burns.²⁵ The fire performance index (FPI) is frequently used to evaluate the fire safety performance of materials and has been shown to be a reasonable first-order indicator of the propensity to flashover, that is, near-simultaneous ignition of most of the directly exposed combustible material in an enclosed area. FPI is obtained as the proportion of TTI to PHRR. The higher the FPI value, the higher is the safety performance of the materials. All the PC/ABS samples with FR additives possessed higher FPI values than those of the control sample, that is, plain PC/ABS. Among them, the FPI value of PC/ABS+TPP + PTFE was the highest, followed by PC/ABS+BTPP+PTFE, PC/ABS+BDP + PTFE, and finally Sol-DP and RDP-based compounds. The lower thermal stability of TPP could justify the faster and more effective reaction of the phosphorous radical in the gas phase.

The total heat released (THR) was reduced by approximately 13–25% with the addition of different FRs to the PC/ABS blend. THR/ML is related to the effective heat of combustion of volatiles in the gas phase, where ML indicates the mass loss. The reduction in THR/ML is an indicator of the gas-phase action of the flame-retardant. For all the flame-retarded blends, THR/ML reduced by 22–27% compared to

FIGURE 3 TGA thermogram of PC/ABS compounds including different flame-retardants in the formulation. Thermogram measured under air conditions at 10°C/min

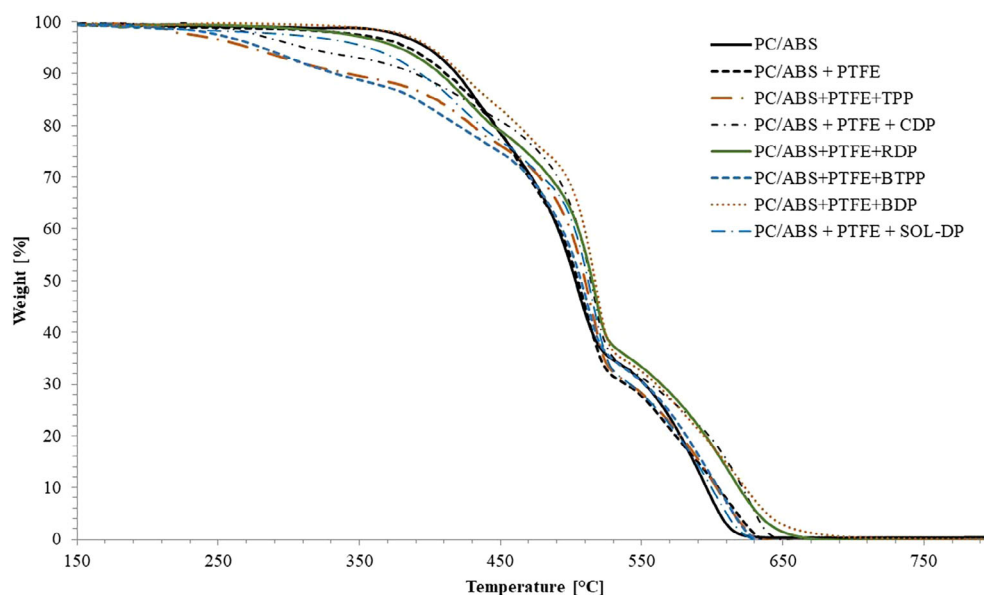


TABLE 2 Thermal performance parameters (TGA) of different aryl phosphates

Sample	Nitrogen				Air			
	Residue at 600°C (%)	T _{2%} (°C)	T _{5%} (°C)	T _{max} (°C)	Residue at 600°C (%)	T _{2%} (°C)	T _{5%} (°C)	T _{max} (°C)
TPP	0.5	212	235	310	0	212	221	314
CDP	0	230	250	316	0.2	215	236	307
RDP	1.8	275	312	409	1.8	288	319	422
BTPP	2	220	241	318	2.1	237	248	311
BDP	1.7	329	373	457	1.3	337	367	473
Sol-DP	0.33	298	335	422	0	307	336	416

TABLE 3 Thermal performance parameters (TGA) of plain PC/ABS and FR PC/ABS compounds

Sample	Air			
	Residue at 600°C (%)	T _{2%} (°C)	T _{5%} (°C)	T _{max} (°C)
PC/ABS	0.3	371	398	507
PC/ABS + PTFE	0.0	332	384	513
+ TPP	0.0	218	273	514
+ CDP	0.0	270	312	516
+ RDP	0.0	331	378	518
+ BTPP	0.0	241	282	512
+ BDP	0.3	375	400	518
+ Sol-DP	0.0	272	357	515

that of PC/ABS (Table 5). The combustion in the flame was inhibited because the FRs acted through flame poisoning in the gas phase. Released phosphates can form several types of radicals, where PO· is believed to play a major role.²⁶ These radicals react with highly reactive H· or OH· radicals during combustion.^{19,27}

The fire hazard, which is related to the smoke and CO evolution, is another important parameter that was evaluated from the cone calorimeter results and further examined in the NBS + FTIR test. Table 6

and Figure 5 show the smoke emission behavior in all formulations at an incident heat flux of 50 kW/m² in the cone calorimeter. The presence of FRs increases the smoke production rate (SPR) and total smoke production (TSP). The smoke extinction area (SEA), defined as the smoke produced per unit mass of volatiles, indicates the smoke generation potential of a material. The six FRs resulted in a significant increase in average SEA. In addition, released CO and CO₂ gases were measured using a cone calorimeter. It was found that compared with

TABLE 4 UL94 results of plain PC/ABS and FR PC/ABS compounds

Composition	t_1/t_2^a (s)	Dripping	Rating	Ignite the cotton
PC/ABS	4/1.8	Yes	V2	Yes
PC/ABS + PTFE	- ^b	Yes	N.R. ^c	Yes
+ TPP	1.2/6.4	No	V0	No
+ CDP	0/7.8	No/Yes ^d	V2	Yes
+ RDP	0.8/3.8	No	V0	No
+ BTTP	0.2/5.2	No	V0	No
+ BDP	6.2/6.6	No	V0	No
+ Fyroflex Sol-DP	3/3.6	No	V0	No

^a t_1/t_2 , represents the after-flame time for first and second 10 s flame applications, respectively.

^bThe specimen burns completely.

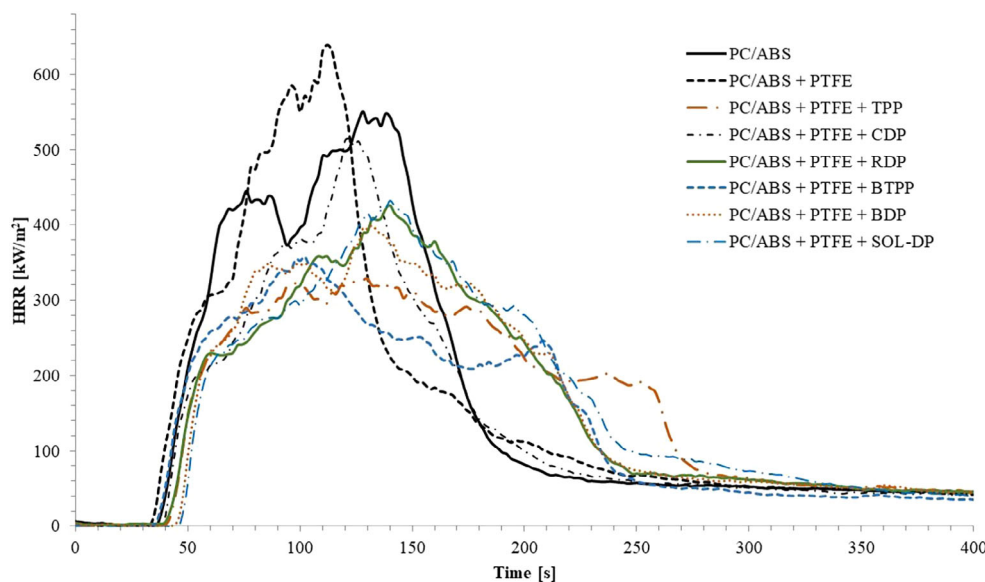
^cN.R. represents no rating.

^dNo/yes corresponds to the first/second flame application.

TABLE 5 Cone calorimeter data of plain PC/ABS and FR PC/ABS compounds at 50 kW/m²

Composition	TTI (s)	t_{peak} (s)	PHRR (kW/m ²)	THR (MJ/m ²)	FPI (10 ⁻²) (s m ² /kW)	THR/ML (MJ/g .10 ⁻²)	ML (g/m ²)
PC/ABS	39	128	551.0	82.6	7.1	2.4	3367
PC/ABS + PTFE	36	112	638.4	79.9	5.6	2.7	2937.6
+ TPP	43	139	349.7	70.8	12.3	2.0	3529.5
+ CDP	39	110	457.7	60.1	8.5	2.0	3047.5
+ RDP	43	133	418.4	70.5	10.3	2.1	3380.1
+ BTTP	39	102	335.5	61.2	11.6	2.0	3102.7
+ BDP	44.5	158	384.0	68.8	11.6	2.0	3395
+ Fyroflex Sol-DP	45	115	401.1	68.5	11.2	2.0	3465.6

Note: TTI, time to ignition, ± 2 s; t_{peak} , time to reach the peak HRR, ± 2 s; PHRR, peak heat release rate, ± 15 kW/m²; THR, total heat release, ± 0.5 MJ/m²; FPI, fire performance index, is defined as the proportion of TTI and PHRR; ML, mass loss, ± 10 g/m².

**FIGURE 4** Heat release rate (HRR) of different PC/ABS blends measured using the cone calorimeter at an irradiance of 50 kW/m²

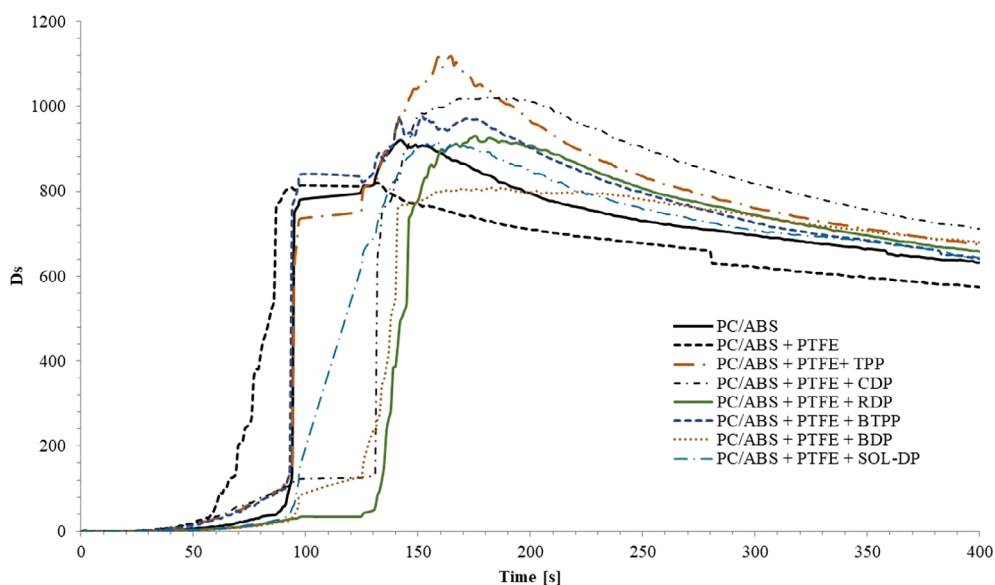
the control sample, aryl phosphates promoted CO production and reduced the generated CO₂.

Smoke production and toxicity are especially important if polymer blends are used for indoor applications or mass transportation, where rapid escape can be hindered by the loss of

visibility due to high smoke release. Therefore, smoke opacity and toxicity were studied in detail in this work. For this purpose, the transport standard (the most restrictive regulation in toxicity field), EN 45545-2: *Railway applications—Fire protection on railway vehicles—Part 2: Requirements for fire behavior of*

TABLE 6 Cone calorimeter smoke emission data of PC/ABS and FR PC/ABS compounds under 50 kW/m²

Composition	SPR _{average} (m ² /s)	SEA _{average} (m ² /kg)	TSP (m ²)	CO _{average} (kg/kg)	CO _{2average} (kg/kg)
PC/ABS	0.025	960.5	28.6	0.092	1.64
PC/ABS + PTFE	0.020	939.7	24.4	0.102	1.65
+ TPP	0.062	1103.3	34.7	0.133	1.33
+ CDP	0.055	1148.6	31.0	0.145	1.31
+ RDP	0.054	1000.2	30.0	0.151	1.38
+ BTPP	0.056	1145.0	31.6	0.132	1.28
+ BDP	0.056	1047.4	31.4	0.137	1.35
+ Fyroxflex Sol-DP	0.055	1001.4	30.7	0.148	1.31

FIGURE 5 Specific Optic Density of different PC/ABS blends measured using the smoke density chamber at an irradiance of 50 kW/m²**TABLE 7** Smoke opacity results of plain PC/ABS and FR PC/ABS compounds

Reference	VOF ₄ (min)	DS _{máx}	t _{DSmáx} (s)
PC/ABS	1469.2	919.8	143
PC/ABS + PTFE	1933.6	819.4	133
+ TPP	1832.0	1117.6	166
+ CDP	—	—	—
+ RDP	1774.5	931.1	167
+ BTPP	1673.2	976.9	153
+ BDP	1728.6	809.1	183
+ Fyroxflex Sol-DP	1554.9	917.6	158

materials and components, was chosen. A smoke density chamber (NBS, ISO 5659-2) was used to measure the amount of smoke in terms of its capacity to obscure the transmission of light. An FTIR spectrometer was coupled to this chamber to determine the nature of the gases emitted during the combustion process.

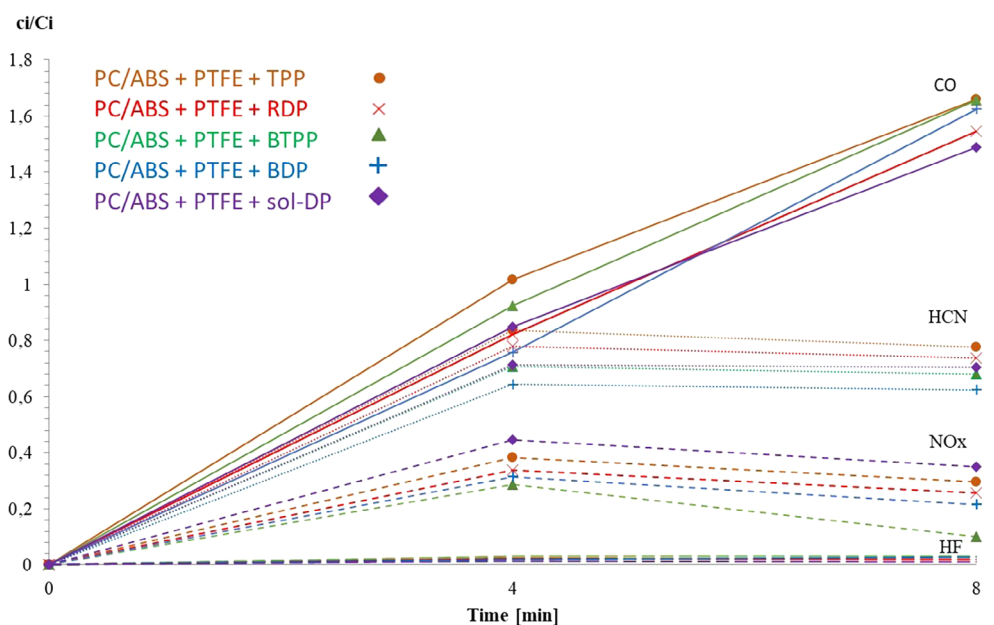
Table 7 shows smoke darkness represented by VOF₄. It is the cumulative value of specific optical densities in the first 4 min of the test. It also includes DS_{máx} (a reference for the visible smoke intensity), the maximum optical density in the chamber along the test, and t_{DSmáx}, (the time at which the maximum optical density is reached). Results show that at the beginning of the combustion process, fumes are darker (↑VOF₄) when PTFE is present in the formulation; however, the maximum specific density reached is lower (↓DS_{máx}). When different FRs are included in the PC/ABS + PTFE blend, fumes emitted at the beginning of the test are also darker than those for neat PC/ABS, and they keep getting darker with the time (increasing the DS_{máx}). In addition, the presence of FRs delays the time at which DS_{máx} occurs. TPP is the flame-retardant that has a higher negative contribution in the darkening of the fumes, (highest DS_{máx}). The contribution of BDP flame-retardant is positive, decreasing the DS_{máx} and t_{DSmáx}. RDP and BDP could partially act in the condensed phase, reducing the generated smoke, compared with the FRs exclusively acting in the gas phase such as TPP.

The toxicity of the gases emitted during the combustion process was evaluated using FTIR coupled to the smoke chamber.

TABLE 8 Concentration of evolved toxic gases at 4 and 8 min, ISO 5659-2 test, for neat PC/ABS and FR PC/ABS compounds

Reference Time	CO ₂ (mg/m ³)		CO (mg/m ³)		HCN (mg/m ³)		NO _x (mg/m ³)		HF (mg/m ³)	
	4 min	8 min	4 min	8 min	4 min	8 min	4 min	8 min	4 min	8 min
PC/ABS	14 230	20 372	1049	1922	26.9	27.4	8.4	4.5	0.5	0.7
PC/ABS + PTFE	19 871	23 143	756	1380	18.0	18.8	28.6	24.9	1.0	0.7
+ TPP	15 645	21 705	1403	2291	46.0	42.7	14.5	11.3	0.7	0.5
+ CDP	–	–	–	–	–	–	–	–	–	–
+ RDP	8904	11 823	1134	2134	42.8	40.6	12.8	9.8	0.5	0.5
+ BTPP	7937	13 112	1276	2288	38.9	37.4	10.9	3.8	0.8	0.8
+ BDP	10 048	12 488	1045	2241	35.4	34.3	12.0	8.2	0.5	0.7
+ Sol-DP	8540	13 591	1172	2053	39.3	38.7	16.9	13.2	0.3	0.2
Threshold	72 000		1380		55		38		25	

Reference	CO/HCN (4 min)	CO/HCN (8 min)	CIT _G (4 min)	CIT _G (8 min)
PC/ABS	39.0	70.1	0.138	0.189
PC/ABS + PTFE	42.0	73.4	0.159	0.191
+ TPP	30.4	53.6	0.200	0.247
+ CDP	–	–	–	–
+ RDP	26.4	52.5	0.169	0.221
+ BTPP	32.8	61.1	0.169	0.216
+ BDP	29.5	65.3	0.155	0.218
+ Sol-DP	29.8	53.0	0.174	0.223

TABLE 9 CO/HCN ratio and conventional index of toxicity (CIT) at 4 and 8 min at ISO 5659-2 test, for plain PC/ABS and FR PC/ABS compounds**FIGURE 6** ISO 5659-2 test. Contribution to CIT factor of CO, HCN, NO_x, and HF at 4 and 8 min for different FR PC/ABS compounds

The CIT (at 4 and 8 min [EN ISO 5659-2]) for the evaluated formulations are shown in Table 9. Plain PC/ABS shows the lowest toxicity index due to the absence of additives. The presence

of the antidripping agent (PTFE) and phosphorus-based FRs is responsible for the increase in the toxicity of the evolved smoke.

FIGURE 7 ISO 5659-2 test. Contribution to CIT factor of CO, HCN, and NOx at 4 and 8 min for neat PC/ABS and TPP FR PC/ABS

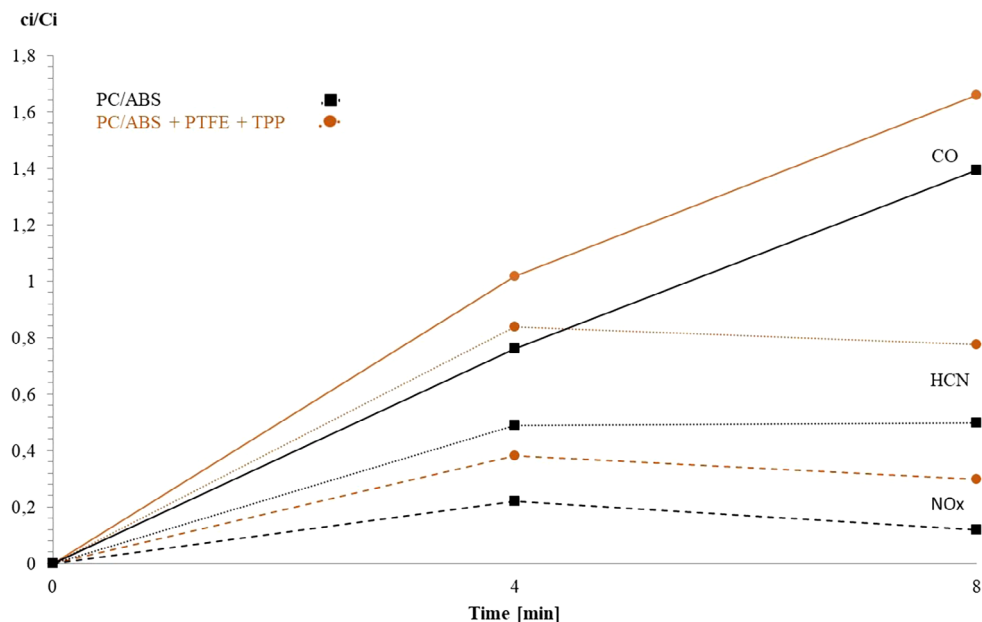


Figure 6 shows individual contributions to CIT of relevant toxics (C_i/C_i : [CO, HCN, NOx, HF]) recorded during the NBS test at 4 and 8 min. The toxicity index increases mainly owing to the increase in the CO, HCN and NOx emissions (Table 8). By contrast, the presence of fluorine does not have a relevant contribution. No significant differences in performance are observed among the different FRs. Formulations with BTPP and BDP are the ones with lower CIT, and the formulation containing TPP reaches higher values. Apparently, different thermal stability values, such as the ones for TPP and BTPP vs RDP, BDP and Sol-DP (TGA, Figure 2), do not modify the degradation path of FR PC/ABS compounds.

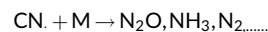
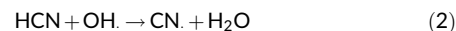
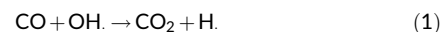
Figure 7 compares the evolved gases during the tests of plain PC/ABS and FR PC/ABS, including PTFE and TPP. The evolution of CO is well understood; the higher level attained in the FR PC/ABS is associated with an incomplete combustion due to the action of the flame-retardant in the gas phase. At the same time, the generation of nitrogen-containing toxic gases such as HCN and NOx is promoted, and this group of toxins has a larger contribution to the increase in the CIT_G factor (Table 8). The CO/HCN ratio is not constant and increases with time in neat PC/ABS and FR PC/ABS, but is higher in non-FR compounds. The NBS chamber test is not steady; therefore, it can be assumed that the combustion of polymer blends such as PC/ABS begins with the decomposition of the less stable polymer, in this case, the ABS fraction (TGA, Figure 3). Thus, the initial release of HCN could be related to the degradation of the nitrile group in ABS, which is observed in the results obtained at 4 min and does not increase subsequently. The higher CO concentration above 4 min is associated with the combustion of PC and the remaining non-nitrogen parts of ABS. The nature of the degradation stages is not affected by the presence of FRs. However, they modify the ratio of gases generated during the test

It is supposed that FR additives volatilize in relation to their thermal stability (TGA, Figure 2); thus, the FR action is considered to occur

in the first few minutes of the combustion process. In this stage, when the degradation of ABS occurs, the presence of phosphorous active species promotes the generation of incomplete combustion gases, CO, HCN, and NOx. Once the flame-retardant has exhausted in the FR PC/ABS blends, its effect on the combustion process is complete, showing a similar evolution of combustion gases as plain PC/ABS over 4 min (Figures 6 and 7). Table 9 shows the ratio between CO/HCN at 4 and 8 min, which has proven to be dependent not only on the composition of materials but also on time.

Finally, the results show that less stable FRs such as TPP (containing 9.5% P) render more toxic, incomplete combustion gases (CO, HCN) than more stable aryl phosphates such as RDP (containing 10.7% P). This indicates higher effectiveness of TPP in flame poisoning in the gas phase.

It is well known that gas-phase FRs interfere with the free radical reactions responsible for flaming combustion.^{28,29} The efficiency of P in the gas phase is reported to be similar or even superior to that of hydrogen halides such as HBr.³⁰ The scavenging of these highly reactive radicals influences the combustion process, resulting in the generation of incomplete combustion products. Equations (1) and (2) show the main combustion reactions that are affected by the release of OH-radicals during the combustion of PC/ABS blends.



Recent studies have reported that organophosphorus FRs, which act predominantly in the gas phase, increase the CO and HCN yields in nitrogen-containing polymers, such as polyamides.³¹ Several authors have shown that, for a specific material under different fire

conditions, the HCN yield increases in proportion to the CO yield.³²⁻³⁴ Galea³³ established empirical relationships to estimate HCN concentrations from the CO concentrations (or vice-versa), which are functions of the elemental composition of burning materials. Our work shows that the HCN/CO ratio is also time-dependent in the combustion process of PC/ABS blends.

4 | CONCLUSIONS

The FPI, which is used to evaluate the fire safety performance of materials, was found to be higher in PC/ABS compounds when aryl phosphates were included as FRs. However, other key parameters, such as the opacity and toxicity of combustion gases, worsened when these additives were used. The concentration of toxic gases generated in the combustion process, measured according to the standard EN 45545-2, was shown to be a function of time and depended on the materials included in the compound. ABS degraded at a lower temperature than PC, which promoted the early generation of HCN. The concentration of this asphyxiant gas was maximized by the presence of FRs, which also decomposed at the beginning of the fire test. Less thermally stable FRs contributed to a higher generation of HCN. For example, FR PC/ABS compounds, including TPP as a flame-retardant, achieved the best FPI value, while simultaneously obtaining the highest opacity and toxicity of smoke. This observed performance was attributed to the interference of FRs in the free radical reactions responsible for flaming combustion in the gas phase. This radical scavenging process resulted in the incomplete oxidation of vapor-phase fuel molecules, leading to higher yields of all products of incomplete combustion (CO, HCN, NO_x, etc.). These gases are more toxic than the cleaner products of complete combustion (CO₂ and H₂O).

The presence of FRs increased smoke and toxicity of evolved gases, but the level reached cannot be considered dangerous for human beings, in the scenario of the specific fire size and ventilation rate in an actual fire according to EN 45545-2. Considering this specific model, CIT_G values in all the FR compounds were found to be far from what is considered a risk to human health (CIT_G ~ 1) and fulfilled even the most demanding requirements in the railway sector (CIT_G < 0.75). Thus, it was found that the addition of the studied FRs provides benefits in terms of reaction to fire, generation, and propagation parameters, but increased toxicity in case of combustion.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Alberto Sánchez  <https://orcid.org/0000-0002-2169-6217>

Sara Villanueva  <https://orcid.org/0000-0002-6152-7610>

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